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GLASS
IONOMER
CEMENTS
—
STRENGTH
FILM
THICKNESS
AND SEM
INVESTIGATION

T.C.C.
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M.D.Sc.

1983

STATEMENT OF AUTHORSHIP

The work submitted for examination in this thesis is the original work of the candidate alone. The original research was conducted in the Department of Operative Dentistry and in the Electron Microscope Unit of the University of Sydney between the period 1981 and 1983 (inclusive), during candidature within the Department of Operative Dentistry, University of Sydney. No portion of this work has been submitted by the candidate to this or any other university, either in part or in full, for the award of any other degree.

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to my supervisor, Dr. R.W. Bryant, for his invaluable encouragement, advice and assistance. Thanks are due to Associate Professor G. Wing, the Head of the Department in which the M.D.Sc degree is being undertaken, and Mr. M.C. Kafalias, the Director of the M.D.Sc programme.

I also wish to express my appreciation to Dr. D.J.H. Cockayne and the staff of the Electron Microscope Unit in which the SEM work was conducted. In particular, I would like to thank Dianne Hughes for her untiring assistance.

Last but not least, my heartfelt thanks to Gary for his unfailing support and encouragement.

ABSTRACT

The strength (compressive and tensile), film thickness, surface obtained with various clinical finishing techniques, and the particle size of seven commercial glass ionomer cements were investigated. Three restorative cements and four luting cements were examined. Three aspects of the experimental method were also investigated : the dispensing of the powder and liquid, specimen preparation for scanning electron microscopy (SEM), and the technique for examining the glass particle size of the cements in the SEM.

The current literature on glass ionomer cements were reviewed and, where applicable, comparison was made with the findings of this investigation.

The more important conclusions of this investigation were summarized and, where appropriate, recommendations were made concerning the clinical use of these cements.

PREFACE

The aims of this investigation were to examine the strength (compressive and tensile), film thickness, surface obtained with various finishing techniques, and the particle size of commercial glass ionomer cements. Several aspects of the experimental method were also investigated, namely, the dispensing of the powder and liquid, the specimen preparation for scanning electron microscope (SEM) examination, and the technique for examining the glass particle size of the cements in the SEM.

The first part of the thesis (Chapters 1 - 4) is a *review of the literature*. Chapter 1 traces the development and marketing of glass ionomer cements. The constituents of the powder and liquid, and the setting reaction are discussed in Chapter 2. The properties associated with the clinical performance of glass ionomer cements are discussed in Chapter 3. Chapter 4 is a review of the recommended uses and clinical studies on glass ionomer cements.

The second part of the thesis describes the *original research*. The method used in the investigation is discussed in Chapter 5. The findings are presented and discussed in Chapters 6, 7, 8 and 9. The more important conclusions are reviewed in Chapter 10. The *bibliography* is found at the back of the thesis.

Tables and *figures* are placed together in a chronological order at the end of the chapter in which they are first mentioned. The lists of tables and figures detail the page number on which a particular table or figure (identified by number) is found. The numbering of the tables and figures identifies first the chapter in which the table or figure is found and, secondly, the chronological order in which it occurs within that chapter (for example, Table 6.1 and Table 6.2; Fig. 6.1 and Fig. 6.2).

Sections of the text are identified by a standardized numerical system, which facilitates cross-referencing. *Sections* within each *chapter* have been identified by their separation from the chapter number by a single full stop (for example, 3.4 and 3.5). *Sub-sections* within each of these sections have been identified by their separation from the section number by a second full stop (for example, 3.4.1 and 3.4.2). Additional numbers, placed after the sub-section number and not preceded by full stops, identify parts to these sub-sections (for example, 5.3.21).

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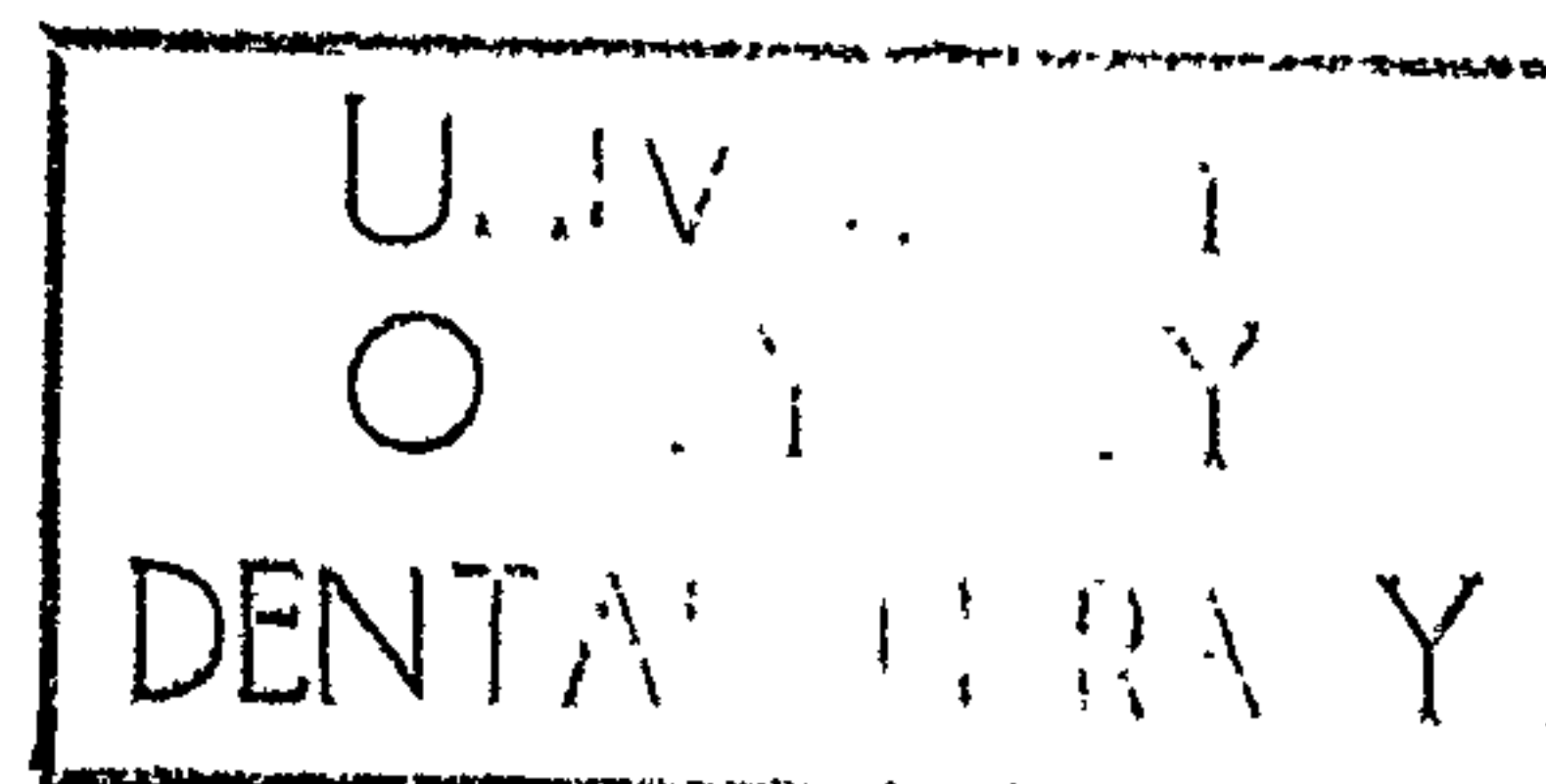
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THE REVIEW OF THE LITERATURE

CHAPTER I



THE DEVELOPMENT OF GLASS IONOMER CEMENTS

- 1.1 The development of experimental glass ionomer cements
- 1.2 The marketing of commercial glass ionomer cements

1.1 THE DEVELOPMENT OF EXPERIMENTAL GLASS IONOMER CEMENTS

A glass ionomer cement was first described in 1971 by Wilson and Kent, of the laboratory of the Government Chemist, England (Wilson and Kent, 1971). They indicated that their aims in developing this cement were to improve upon the performance of the dental silicate cement by combining the favourable features of the dental silicate and zinc polycarboxylate cements and by reducing their disadvantages.

Dental silicate cements consist of an aluminium phosphate gel, reinforced by aluminosilicate glass fillers. Setting occurs when the negatively charged aluminosilicate glass network is decomposed by hydrogen ions, and the leached cations migrate into the aqueous phase where they form an insoluble cementing gel with the phosphate ions present.

The setting mechanism of the dental silicate cement demonstrated to Wilson and Kent the important role played by the acid anions. This mechanism also indicated fields of research in which new cement systems could be formulated and developed.

Wilson and Kent (1972) proposed that alternative liquids to phosphoric acid (used in dental silicate cements) should : a) contain water, both as a reaction solvent and to hydrate reaction products, b) possess an acid function to decompose the aluminosilicate powders and to liberate the cement forming cations, and c) include anions

which would act as a "co-ordination ligand" with the ability to form stable complexes with liberated metal ions.

Polyacrylic acids satisfied the above criteria. They had been combined with zinc oxide to form polycarboxylate cements with considerable success (Smith, 1968). Attempts were made to combine dental silicate powders with 40 to 50 per cent aqueous solutions of polyacrylic acid. The resultant cement was slow setting, mechanically weak and moisture sensitive (Wilson and Kent, 1972).

The reaction between the glass powder and liquid is an acid-base one. An increase in the basicity of the glass or the acidity of the liquid increases the rate of the setting reaction. Polyacrylic acid, being a weaker acid than phosphoric acid, requires a more basic glass to produce equivalent setting. This was achieved by increasing the basic oxide : acidic oxide ratio (that is, alumina : silica ratio) in the powder (Wilson and Kent, 1972).

Modifications were also made to the liquid components by varying the molecular weight and concentration of the polyacrylic acid (Crisp et al, 1976,c; Crisp et al, 1977; Wilson et al, 1977). Other modifications have included the addition of tartaric acid, methylation of the carboxyl (-COOH) groups by methyl alcohol and the use of a special copolymer of acrylic and itaconic acids (Wilson et al, 1976; McLean and Wilson, 1977,a; Crisp et al, 1979).

The result of these progressive modifications to the powder and liquid components was the development of experimental ASPA^a I, II, III and IV materials, which culminated in the production of the commercially available glass ionomer cements.

^a ASPA -- AluminoSilicate Polyacrylate Acid.

The new cement has been found to have the good properties of dental silicate cements, for example, high compressive strength, translucency and an anticariogenic effect, without the disadvantage of poor resistance to acid attack (McLean and Wilson, 1977,a). Like the zinc polycarboxylate cement, the glass ionomer cement (in contrast with a silicate cement) has the advantages of being adhesive to calcified dental tissue and relatively "bland" in its effect on the pulp (Wilson, 1977).

1.2 THE MARKETING OF COMMERCIAL GLASS IONOMER CEMENTS

The first commercially available glass ionomer cement was ASPA^b. It was marketed as a restorative material in the form of a powder (essentially aluminosilicate glass) and a liquid (essentially modified polyacrylic acid). The product was released in Europe in 1975, Australia in 1976 and America in 1977 (Mount, 1981).

ASPA was superseded in 1981/82 by ChemFil^b for restorative use. In ChemFil, the dehydrated form of polyacrylic acid was incorporated into the powder, and the liquid consisted of distilled water (Mount, 1981).

ChemBond^b was released several years before ChemFil for use as a luting agent and is marketed as a powder containing the aluminosilicate glass and a liquid containing the modified polyacrylic acid.

Fuji Ionomer Type II^c glass ionomer cement was first released in 1977 for restorative purposes. The powder is essentially aluminosilicate glass, and the liquid contains polyacrylic acid with the required traces of other acids. Trials are being conducted

^b A.D. International Ltd., London, England.

^c G-C Dental Industrial Corporation, Tokyo, Japan.

to develop a method of encapsulation of the material. Fuji Ionomer Type I^e glass ionomer cement is a luting cement and is available as a powder and liquid.

The restorative material, Ketac^d, was released into the Australian market in 1981 and is sold in an encapsulated form (Mount, 1982). The luting material, Ketac-cem^d, is packaged as a powder containing "calcium-aluminium-fluosilicate" and a liquid of polycarbonic acid.

Hy-Bond^e glass ionomer cement was introduced into the Australian market during 1982 and marketed as a powder (composed of alumina, silica, calcium and fluorine) and liquid (carboxylate copolymer). Hy-Bond Glasionomer-F (Type I) is the restorative material and Hy-Bond Glasionomer-C (Type II) is the luting cement. These 2 cements contain HY agent. The HY agent is basically a tannin-fluoride preparation composed of zinc fluoride, strontium fluoride, tannic acid and pH adjuster. Experiments by Tanizaki and Inoue (1979) showed that the tannin-fluoride preparation acts on both the organic and inorganic matter in dentine, thus reducing the occurrence and progress of secondary caries.

^d Espe Dental Products, West Germany, New York.

^e Shofu Dental Manufacturing Company, Kyoto, Japan.

CHAPTER 2

THE CONSTITUENTS AND SETTING REACTION OF GLASS IONOMER CEMENTS

- 2.1 The glass ionomer cement powder
 - 2.1.1 Physical properties of the powder
 - 2.1.2 Chemical composition of the powder
 - 2.1.3 The formation of aluminosilicate glass powder
 - 2.1.4 Effect of fusion temperature
 - 2.1.5 Microstructure of the powder
 - 2.1.6 Summary
- 2.2 The glass ionomer cement liquid
 - 2.2.1 Introduction
 - 2.2.2 Physical properties of the liquid
 - 2.2.3 The development of the liquid component for glass ionomer cements
 - 2.2.4 Polyacrylic acid
 - 2.2.5 Copolymer of itaconic and acrylic acids
 - 2.2.6 Molecular weight of the polyacid
 - 2.2.7 Effect of polyacid concentration
 - 2.2.8 The tartaric acid component
 - 2.2.9 Formation of the glass ionomer cement liquid
 - 2.2.10 Summary
- 2.3 The setting reaction of glass ionomer cements
 - 2.3.1 The setting reaction
 - 2.3.2 The role of tartaric acid
 - 2.3.3 The structure of the set cement

2.1 THE GLASS IONOMER CEMENT POWDER

A large proportion of the basic research into the powder and liquid component of the glass ionomer cement has been carried out by Wilson, Kent, Crisp and co-workers at the Laboratory of the Government Chemist, England.

2.1.1 *Physical properties of the powder*

The powder is an opal glass composed of fluorine-containing aluminosilicate. Its density is 2.77 Mg/m^3 and its refractive index is 1.486 at 20°C (Crisp and Wilson, 1973).

The particles of powder used for restorative cements have a maximum grain size of $45 \mu\text{m}$. For clinical use in luting cements, finer powders with a maximum grain size of between 13 and $19 \mu\text{m}$ were found to be preferable. (Wilson et al, 1977).

Kent et al (1979) investigated the particle size distribution of a typical glass powder (G200) used for restorative cements. They reported that the median particle size was 10 μm in diameter and that approximately 60 per cent by weight of the particles were larger than the median particle size.

2.1.2 *Chemical composition of the powder*

2.1.21 Introduction

The chemical composition of the glass powder varies with the composition of the fusion mixture and the temperature of fusion. The constituents of the fusion mixture of a typical glass powder (G200) used in a commercial glass ionomer cement (ASPA) were found (Wilson, 1977) to be silica (SiO_2) — 29%; alumina (Al_2O_3) — 16.6%; calcium fluoride (CaF_2) — 34.2%; cryolite (Na_3AlF_6) — 5%; and aluminium phosphate (AlPO_4) — 9.9%.

Barry et al (1979) reported that the proportions of cations expressed as atom fractions were : silicon — 0.314; aluminium — 0.302; calcium — 0.286; sodium — 0.046; phosphorus — 0.053. The proportion of anions were : oxygen — 0.565 and fluorine — 0.434. The overall anion : cation ratio was 2.04:1 (Barry et al, 1979).

The physical properties of the glass ionomer cement are dependent upon the chemical composition of the powder. Most of the research in this field was carried out by Kent et al (1979). A brief synopsis of their findings is presented.

2.1.22 Effect of alumina : silica ratio

A decrease in the alumina : silica ratio was found to prolong the setting time and produce cements with inferior mechanical properties and high solubility. The explanation for this lies in the structure of the glass.

Oxide glasses have a network structure similar to polymers. Hence silicate glasses should be regarded as three-dimensional, random networks of linked silica (SiO_4) tetrahedra. The small silicon cation (ionic radius 0.041 nm) is a network-former. It resides in the interstices formed by four touching oxygen anions (ionic radius 0.41 nm). Aluminium cations (ionic radius 0.05 nm) may act either as network-formers or network-dwellers. These ions may replace silicon ions isomorphically in the network. The network thereby acquires a negative charge due to the valency difference. This is balanced by the positive charge on a network-dwelling cation, which may be either sodium or calcium ions. If such ions (sodium or calcium) are unavailable, then aluminium ions may occupy network-dwelling sites.

When the alumina : silica ratio approaches unity, the aluminosilicate structure acquires sufficient negative charge to become susceptible to attack by acids at the aluminium ion site. The network is disrupted into aluminium ions and orthosilicic acid (which polymerizes to silica gel) by hydrogen ions, which will also displace network-dwelling cations. This is thought to explain the increase in setting reaction with an increase in the alumina : silica ratio.

In some series of glasses tested by Kent et al (1979), the setting rate increased with an increase in alumina content, to a critical level, beyond which further increase in the alumina content retarded the setting reaction. The retardation of the setting reaction may be due to additional aluminium ions going into the network-dwelling sites. Thus, the charge in the network is not increased, while aluminium ions in network-dwelling sites may increase resistance to acid attack.

2.1.23 Effect of aluminium phosphate

In one series of glasses examined by Kent et al (1979), the exact amount of aluminium phosphate had little effect on working and setting characteristics. However, cements which contained no phosphate were difficult to mix, had negligible working time and set rapidly.

In another series of glasses, an increase in aluminium phosphate content increased the mobility "consistency spread", working time and setting time. The difference, in the effect of aluminium phosphate, between the two series of glasses was not explained. The aluminium phosphate content appeared to have little effect on strength.

2.1.24 Effect of fluoride

In one series of glasses investigated, an increase in the fluoride content appeared to accelerate the setting reaction. In another series, an increased fluoride content resulted in increased mobility but a retarded setting reaction. No explanation was offered for these different results.

2.1.25 Effect of calcium : sodium ratio

The working time and, to a lesser extent, the setting time were reduced as sodium replaced calcium. Increased sodium content produced a more reactive glass. The presence of sodium ions had an adverse effect on the hydrolytic stability of the prepared cements, resulting in a poorer surface resistance to aqueous attack. Despite this, the solubility figures provided by Kent et al (1979) suggested otherwise. Glasses with a high calcium ion content, for example G200, were easy to mix.

It appeared from their research that the best glasses for cement formulation were low in sodium.

2.1.26 Effect of cation substitution

Certain cation substitutions were carried out on an equimolecular basis and their effects on setting characteristics and physical properties were studied.

The replacement of calcium fluoride by magnesium fluoride created no major changes, except that the cement was more difficult to mix in some cases. The replacement of sodium fluoride by lithium fluoride resulted in a slow setting cement with poor resistance to aqueous attack. The partial replacement of alumina by titanium oxide slowed down the setting rate. The replacement of calcium fluoride by lanthanum fluoride produced a glass which yielded a rubbery cement mix but improved compressive strength. No conclusion was made by the researchers as to the desirability of replacing calcium, sodium and aluminium ions with other cations, although the results of their experiment discouraged replacement.

2.1.27 Effect of fluoride flux

Kent et al (1979) described the fluoride flux as performing twin functions. First, it lowers the temperature of fusion. Secondly, it provides a source of leachable fluoride which has a cariostatic effect.

2.1.3 *The formation of aluminosilicate glass powder*

Wilson and Kent (1971) described the formation of the aluminosilicate glass. It was prepared by melting the constituents (listed in 2.1.21) in pre-determined proportions in sillimanite crucibles at temperatures between 1050⁰C and 1350⁰C for 45-120 minutes. The melt was then quenched and ground to a fine powder. The degree of fineness of the powder was controlled by the time of milling (Wilson et al, 1977).

2.1.4 *Effect of fusion temperature*

The physical properties, final composition and structure of the glass depend on the temperature of fusion (Barry et al, 1979). Well-homogenized G200 glass, prepared by melting at 1,200°C and above, yielded cements with poor manipulative properties. The paste rapidly acquired an elastomeric cob-webbing quality (Barry et al, 1979).

The differences between the original (pre-melt) composition of the experimental glass, G200, and the final (post-melt) composition of the glasses prepared at 1150°C and 1300°C were as follows:- the higher the temperature of the melt, the greater the final aluminium content, and the lower the final fluoride content (Barry et al, 1979).

Barry et al (1979), suggested that three mechanisms were responsible for the compositional changes occurring in these glass melts during fusion: i) the loss of fluorine and silicon at high temperatures by volatilization of silicon fluoride, ii) the loss of fluorine over a wide temperature range by pyrohydrolysis of the fluorides by water present in the batch or atmosphere, and iii) an increase in the alumina and silica content of the melt (in approximately equal molar proportions) particularly at high temperatures, due to chemical reaction with the sillimanite crucible.

Barry et al (1979) concluded that glasses prepared at temperatures of 1150°C yielded more workable pastes due to their higher fluoride content.

2.1.5 *Microstructure of the powder*

Most of the research on the microstructure of the powder has been carried out by Barry et al (1979). A brief summary of their findings follows.

Examination of polished surfaces by electron microscopy of replicas revealed that the glass was comprised of a matrix interspersed

with predominantly spherical droplets (Fig. 2.1). The matrix consisted of calcium aluminosilicate.

The droplets were either glassy, or partially or wholly crystalline. Transmission electron micrographs revealed that the droplets contained a core of crystalline fluorite sheathed by an amorphous (glassy) phase. X-ray diffraction results indicated that the fluorite was in the form of calcium fluorite. Most droplets contained only one single crystal, indicating that nucleation rather than crystal growth rate was the major factor determining the proportion of droplets containing observable crystals. The completely glassy droplets tended to be smaller than the fully or partially crystalline droplets. The amorphous phase contained calcium, aluminium and silicon, but was much richer in calcium than the matrix.

Barry et al (1979) reported that the microstructure of the glass was dependent upon the temperature of fusion. Glasses formed at 1150°C had large irregular inclusions of fluorite when compared with glasses formed at 1300°C. This is consistent with the finding that at lower temperatures (around 1150°C), the liquid melt has a strong tendency to separate into two liquid phases, with one of the phases consisting mainly of calcium fluorite. In glasses melted at 1150°C, the droplet size was $1.67 \pm 0.83 \mu\text{m}$ and the volume fraction was approximately 20 per cent. The droplet size of glasses melted at 1300°C was smaller ($1.08 \pm 0.32 \mu\text{m}$) and the volume fraction was approximately 19 per cent. The droplets from the 1150°C melt showed a greater degree of crystallinity than those from the 1300°C melt.

X-ray diffraction results indicated that the proportion of calcium remaining in the glassy state was 14 per cent in the 1150°C melt as compared with 22 per cent in the 1300°C melt. Most of the droplet formation was believed to occur between the temperature range

of 1100°C and 1000°C. Whilst the 1150°C melt cools relatively slowly through this temperature range, the 1300°C melt has reached the quenching plate before its temperature falls within this range. This, together with the greater loss of fluoride from the 1300°C melt accounts for the smaller droplet size and lower crystallinity of the 1300°C melt.

The nature of the attack of the polyacrylic acid on the glass was established by replication of polished surfaces subjected to controlled etching by liquids (Barry et al, 1979). Micrographs showed that the acids selectively attacked the non-crystalline part of the droplets (Fig. 2.1).

Because the proportion of the non-crystalline phase in the droplets is dependent on the melting temperature, and because acids selectively attack the non-crystalline part of the droplets, there is a noticeable difference in the rate of setting of the cements prepared from glasses melted at different temperatures.

2.1.6 *Summary*

Most of the research has investigated the experimental G200 powder which formed the basis of commercial ASPA powders. Watts et al (1981) reported that the Fuji Type I and Fuji Type II powder components are identical; but Fuji and ASPA powders differ in the calcium : sodium ratio of their glass. Fuji glass ionomer powder is basically a high sodium silicate glass, whereas ASPA is a high calcium silicate glass. No detailed information is available in the literature on the exact chemical composition of the powder component in other glass ionomer cements.

2.2 THE GLASS IONOMER CEMENT LIQUID

2.2.1 *Introduction*

Crisp et al (1980,a) summarized the properties of an ideal liquid for a glass ionomer cement as one which promotes "low viscosity,

long shelf-life in the polyelectrolyte liquid, good mixing and handling properties, adequate working time, good strength and hydrolytic stability in the cements."

2.2.2 *Physical properties of the liquid*

The first liquid for ASPA was a liquid which was a 50 per cent w/w (weight/weight) aqueous solution of poly (acrylic acid), with a mean molecular weight of 23,000, a density of 1.22 Mg/m^3 and a refractive index of 1.4088 at 20°C (Crisp and Wilson, 1973).

2.2.3 *The development of the liquid component for glass ionomer cements*

The first experimental glass ionomer cement was designated ASPA I. The powder component remained essentially unchanged, whilst various modifications were made to the liquid, resulting in the formation of ASPA II, III and IV. The liquid used is a polyacid and for the purpose of this thesis "polyacid" refers to either polyacrylic acid or the copolymer of acrylic acid and itaconic acid. ASPA IV was the basis for the first commercially produced glass ionomer cements.

2.2.31 ASPA I liquid

This liquid consisted of a 40 - 55 per cent aqueous solution of acrylic acid homopolymer (Crisp et al, 1976,a). ASPA I was a slow hardening cement (Crisp et al, 1976,a) and was considered to be unsuitable for general clinical use (McLean and Wilson, 1977,a) because of its relatively short working time (Wilson et al, 1976).

2.2.32 ASPA II liquid

When 5 per cent tartaric acid was added to the ASPA I liquid the setting characteristics were sharpened. This new variant was designated ASPA II (Crisp et al, 1976,a). Its "post-set" hardening rate was considerably enhanced, a finding which McLean and Wilson (1977,a) attributed to two causes : i) enhancement of the extraction

of cations from the glass, and ii) formation of metal-tartrate complexes which prevented the premature binding of cations to polyanion chains.

McLean and Wilson (1977,a) found that the ASPA II cement had good adhesion to both dentine and enamel and that it maintained its surface integrity against attack by weak acids.

However, because of the thickening and gelation of polyacrylic acid (McLean and Wilson, 1977,a) ASPA II liquid had a poor shelf-life of 10 to 30 weeks (Crisp et al, 1976,a).

2.2.33 ASPA III liquid

This liquid consisted of acrylic acid homopolymer, tartaric acid and methanol. Methanol was added to methylate some of the pendant carboxylic acid groups. It was abandoned because of its inferior clinical performance (Crisp et al, 1976,a). Its main disadvantage was the increased uptake of stain on the surface (McLean and Wilson, 1977,a).

2.2.34 ASPA IV liquid

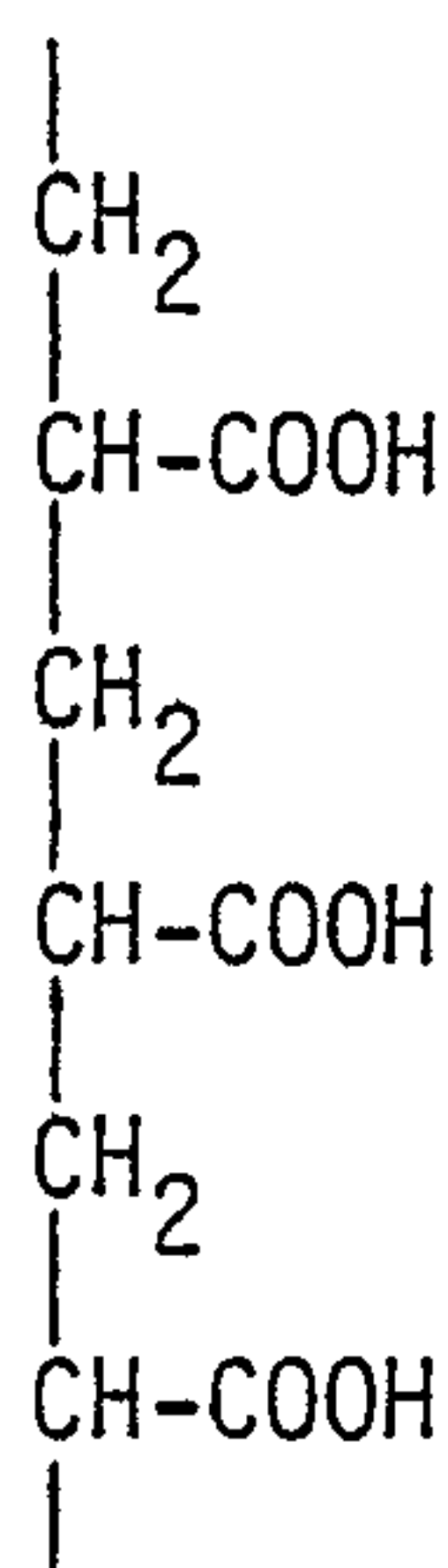
This liquid was a copolymer of acrylic acid and itaconic acid in a 3:1 mole ratio. Tartaric acid was also included (Crisp et al, 1976,a). The aqueous solution proved to be stable for at least 2 years under unfavourable conditions of storage (McLean and Wilson, 1977,a). Its viscosity was unusually low for a polycarboxylic acid solution, which made it particularly useful when mixing at low powder : liquid ratios (McLean and Wilson, 1977,a).

2.2.4 *Polyacrylic acid*

The liquid used in glass ionomer cements is a concentrated aqueous solution of polycarboxylic acids (Wilson, 1977). A carboxylic acid is an organic acid containing one or more carboxyl ($-COOH$) groups and describes a linear polymer containing pendant carboxyl groups.

Polyacrylic acid is a typical polycarboxylic acid (Wilson, 1977).

Its structure is illustrated below :

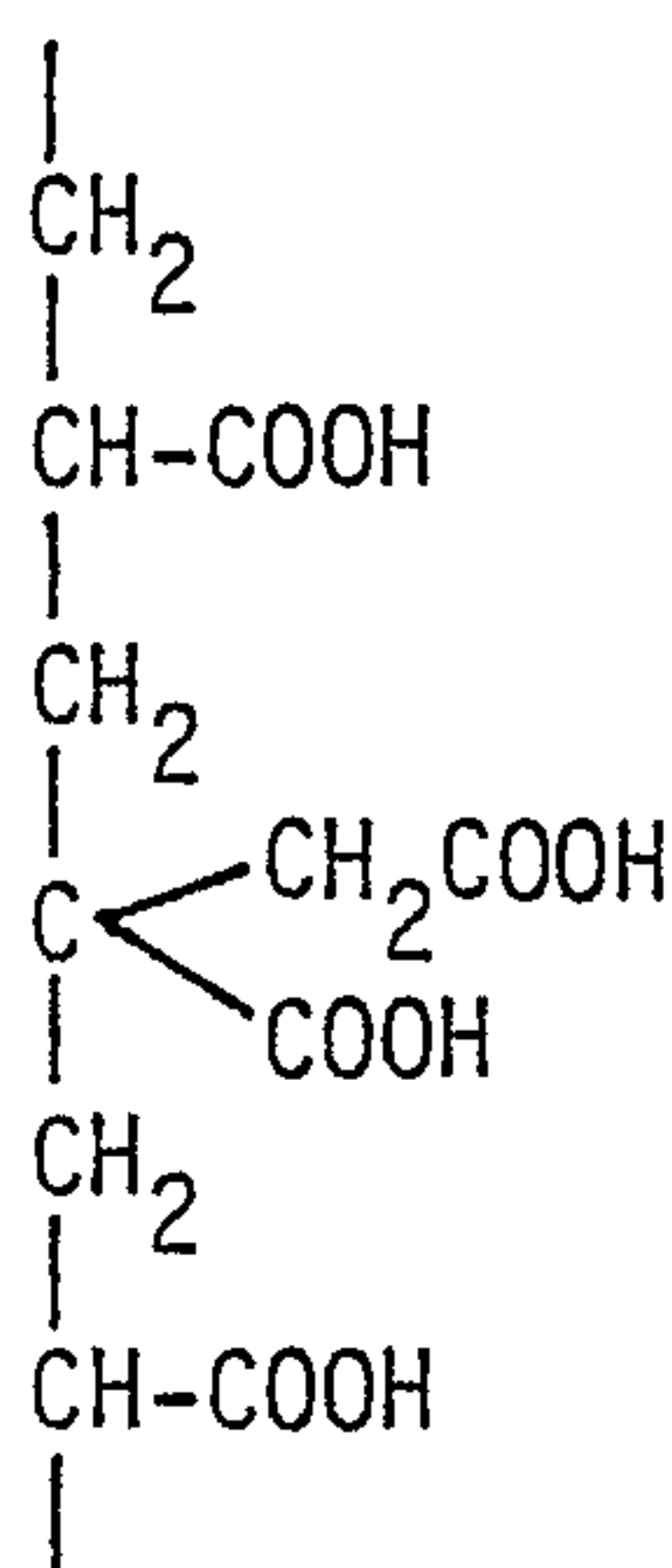


2.2.5 Copolymer of itaconic and acrylic acids

Crisp et al (1980,a) found that the copolymers of greatest importance were those of acrylic and itaconic acids. These copolymers could be prepared without residual monomer provided that a sufficient quantity of initiator was present in the reaction mixture and the itaconic : acrylic acid molar ratio did not exceed 1:2. The low viscosities of these copolymers were associated with their low molecular weight and differences in the modes of hydrogen bonding.

The stability of the copolymer solution is thought to arise from the formation of seven-membered intramolecular hydrogen-bonding rings involving both types of pendant acid groups, thereby reducing the propensity for intermolecular hydrogen bonds.

Wilson (1977) reported that in current clinical formulations the copolymer of acrylic acid and itaconic acid, on account of its low viscosity and stability when in aqueous solution, was preferred to polyacrylic acid. The formula of the copolymer is :



Wilson and Kent (1971) reported that these copolymers had a molecular weight range of 5,000 - 30,000. The copolymer of acrylic acid and itaconic acids has a lower viscosity and is "indefinitely stable" (Crisp et al, 1975).

2.2.6 *Molecular weight of the polyacid*

The properties of the glass ionomer cement are dependent on the molecular weight of the polyacid contained in the parent liquid. Increase in the molecular weight brings about a decrease in the working and setting times and an increase in the tensile and compressive strengths, provided that the polyacid concentration remains unchanged. The increase in strength is due to the increase in the matrix strength because, as the polymer chain length increases, so will the bonding between filler particles and the matrix (Wilson et al, 1977).

At equivalent acid concentration and powder : liquid ratios, polyacids of higher molecular weight yield cements of enhanced strength. Unfortunately, the higher viscosity of their aqueous solutions imposes a limitation on their use and the working time of the cement pastes is reduced. Liquids of molecular weight greater than 23,000 can only be used at a low concentration (25 per cent m/m). At this concentration, however, they produce

weaker cements than low molecular weight acids at a high concentration of 50 per cent m/m (Wilson et al, 1977).

Typical practical formulations have employed a 50 per cent m/m solution of polyacrylic acid with a mean molecular weight of 23,000 (Wilson and Kent, 1971; 1972), and a 47.5 per cent m/m solution of a copolymer of acrylic and itaconic acids with a mean molecular weight of 10,000 (Crisp et al, 1975).

2.2.7 *Effect of polyacid concentration*

An increase in the polyacid concentration produced cements with increased strengths and reduced solubility (Crisp et al, 1977; Wilson et al, 1977).

The setting time of the cement varied with the polyacid concentration in a complex manner (Crisp et al, 1977). With increased polyacid concentration the viscosity of the solution and the tendency to thicken and gel increased and adversely affected the ease of mixing and the quality of the cement (Crisp et al, 1980,a). An increased polyacid concentration of greater than 38 per cent necessitated a corresponding reduction in the powder : liquid ratio to produce cements of the same consistency (Crisp et al, 1977).

A concentration of polyacid must be selected that combines good mixing properties in the paste with adequate strength in the set cement. One satisfactory formulation employed a 50 per cent solution of polyacrylic acid with a mean molecular weight of 23,000 (Wilson et al, 1977).

2.2.8 *The tartaric acid component*

When the proportion of tartaric acid : total acid lies between 5:95 and 10:90 an optimum combination of a short working time and maximum strength and resistance to aqueous attack is obtained (Crisp et al, 1979).

2.2.9 *Formation of the glass ionomer cement liquid*

Research has investigated experimental liquids and this work is discussed in this section. Details of the formation of commercial glass ionomer cement liquids are not currently available. It may be anticipated that this occurs in a similar fashion to that in experimental liquids.

The polycarboxylic acid solutions were prepared generally by free radical polymerization in aqueous solutions using ammonium persulphate as the initiator and propan-2-ol as a chain transfer agent (Wilson et al, 1976; Crisp et al, 1980,a). The concentration of acrylic acid was kept below 25 per cent, otherwise the reaction could have proceeded with explosive violence. The final concentration of the polyacid was attained by vacuum distillation (20 mm of mercury pressure at 40 - 45°C) until the desired concentration of 50 per cent m/m was attained (Crisp et al, 1980,a).

The copolymers were prepared without residual monomer by ensuring that a sufficient quantity of initiator was present in the reaction mixture and that the itaconic acid : acrylic acid molar ratio did not exceed 1:2 (Crisp et al, 1980,a).

2.2.10 *Summary*

The liquid component of some commercial glass ionomer cements normally contain polyacrylic or modified polyacrylic acid with tartaric acid as the chelating agent. The liquid components of Fuji Type I and Fuji Type II liquids are similar and are primarily polyacrylic acid, whereas the liquid component of ASPA is a copolymer of acrylic and itaconic acids (Watts, 1979; Watts et al, 1981). Tartaric acid is present as a chelating additive in both ASPA and Fuji (Types I and II) glass ionomer cement liquids. The itaconic acid units constitute 21 per cent of the repeating units in the ASPA

liquid, and appeared to be randomly distributed along the chain sequence of the polymer (Watts, 1979). The exact proportion and type of component acids in other commercial glass ionomer cement liquids is not stated in the available literature. However Smith (1982) reported that some formulations may use more tartaric acid and/or copolymers of acrylic acid with maleic acid or polyitaconic acids. These stronger acids permitted the use of more acid resistant silicate glasses which possessed a greater degree of translucency.

2.3 THE SETTING REACTION OF GLASS IONOMER CEMENTS

2.3.1 *The setting reaction*

The setting process of the cement takes place when the glass powder is mixed with the polyacrylic acid. It has two overlapping stages (Barry et al, 1979). This double setting reaction confers interesting rheological properties on the hardening paste. Initially the cement sets to a condition which enables it to be "carved like an amalgam" -- the calcium ion-exchange stage. Later it sets "rock hard" -- the aluminium ion-exchange stage (McLean and Wilson, 1977,a). Crisp and Wilson (1974,b) have suggested that the cementation process can be divided into three overlapping phases : i) the initial attack on the glass in which ion-leaching occurs, ii) the precipitation process, and iii) long-term reactions and diffusion processes that continue for many months.

2.3.11 The calcium ion-exchange stage

Calcium-rich droplets are present in the glass particles of the powder. The outer non-crystalline (amorphous) zone of these droplets is rich in calcium and is preferentially attacked by acids (Barry et al, 1979). This results in the rapid leaching of calcium ions from the non-crystalline part of the droplets; these ions

progressively replace hydrogen in the carboxyl groups of the poly (acrylic acid) (Crisp and Wilson, 1974,b). The preferential formation of calcium polyacrylate in the early stages of the reaction is associated with gelation and the initial set of the cement (Crisp et al, 1974; Barry et al, 1979). The calcium ions react within the first few minutes and are fully combined within three hours (Crisp and Wilson, 1974,b).

The aluminium polyacrylate begins to form at least 30 minutes after the start of mixing, and prior to this, the ionomer system is highly susceptible to water absorption. If water is absorbed, the matrix becomes chalky and erodes rapidly (Council on Dental Materials and Devices, 1979).

2.3.12 The aluminium ion-exchange stage

This stage corresponds to the slow release of aluminium (and some calcium) from the main glass phase (Barry et al, 1979). The formation of aluminium polyacrylate was not observed until at least 30 minutes to one hour had elapsed (Crisp and Wilson, 1973; Council on Dental Materials and Devices, 1979). This is because aluminium must be derived from the main continuous phase (matrix) of the glass, which is less reactive than the calcium-rich glassy zone surrounding the droplets. The slow hardening process is the result of the slower attack on the main calcium aluminosilicate phase of the glass and the release of aluminium ions which are mainly present as fluoride, phosphate or complexes (Crisp and Wilson, 1974,b; Barry et al, 1979). Aluminium ions bind to the polyacrylic acid at the carboxylate groups, probably forming intermolecular ionic bridges which strengthen the gel structure (Crisp and Wilson, 1974,b). As aluminium polyacrylate begins to form, any further fluoride or phosphate eluted from the glass will be present as soluble salts (Crisp and Wilson, 1974,b).

Aluminium ions continue to react for at least 48 hours (Crisp and Wilson, 1974,b). In the fully hardened cement matrix, aluminium polyacrylate predominates over calcium polyacrylate (Barry et al, 1979). In contrast, Crisp et al (1974) found that the calcium and aluminium salts were present in approximately equal amounts. Aluminium formed stronger salts than calcium with polyacrylic acid, and some cationic exchange might occur. Aluminium is responsible for the final hardening of the cement, producing a "rock-hard" surface that is resistant to solution (Crisp et al, 1974; McLean and Wilson, 1977,a).

Many factors are responsible for the important difference between the role of calcium and that of aluminium in the setting process (Crisp and Wilson, 1973; 1974,b). The concentration radius of aluminium is 5.0 nm and that of calcium is 9.9 nm. The smaller, more highly charged aluminium ion will be more highly solvated and will have lower mobility than the calcium ion. The calcium ion is probably leached preferentially from the glass as a result of morphologic differences in ion sites. The calcium ion is satisfied electrically by reacting with two carboxylate groups, whereas aluminium requires three groups. Thus, entropy operates in favour of the formation of calcium polyacrylate (Crisp and Wilson, 1973; 1974,b).

2.3.13 The overall setting reaction

Crisp and Wilson (1974,a) stated that the initial reaction between the powder and the liquid is an acid-base one. The powder acts as a proton acceptor and the liquid as a proton donor. The essential change is that hydrogen ions in the liquid are replaced by metallic ions. The reaction is an ionic one; no toxic monomers, initiators or activators are involved in the setting reaction (Wilson, 1977).

The chemical changes in the cementation process are undoubtedly complex because the system contains many chemical species. The reactions are moderately fast, the rapid rheological changes affect ionic mobility and other transport processes. The configuration and degree of ionization of the polymer and the morphology of the glass must also be considered.(Crisp and Wilson, 1974,b).

In the freshly mixed paste, it is presumed that hydrated protons from the liquid penetrate the surface regions of the powder particles, displacing the cations (first calcium, then aluminium), and degrading the aluminosilicate network to a hydrated siliceous gel. Cations, either simple or as fluoride complexes, migrate into the aqueous phase of the cement paste where metallic salt bridges are formed between the long chains of charged polycarboxylate ions, thus cross-linking them. This causes the aqueous phase to gel, and the cement to set to an amorphous mass. Infrared spectroscopy has shown the progressive conversion of carboxylic acid groups along the polymer chain to carboxylate ions and the formation of a siliceous hydrogel (Wilson and Kent, 1972). Complexing agents have a profound effect on the cementing reaction, protecting the metal ions from becoming prematurely bound to polyacrylate chains thus preventing premature gelatinization (Wilson et al, 1976). Their role is discussed in 2.3.2.

As the reaction proceeds, the configuration of the polyacrylic acid (initially tightly packed spheres of random chains) will change. As negatively charged carboxylate ions are formed, the initial repulsive forces cause the chains to unwind into a linear configuration, an average 0.1 μm in length. This configuration aids the solution of aluminium and calcium ions and reduces ion-dipole interactions at the powder surface to insignificant proportions (Crisp and Wilson, 1974,a).

Fig. 2.2 illustrates the setting reaction of glass ionomer cements. Metal ions liberated from the glass may be precipitated as insoluble salts such as fluorides, phosphates or fluorophosphates. Alternatively, they can form different salts with polyacrylic acid, such as pendant half-salts or intra- and inter-ionic di-salts. The inter-ionic di-salts act as bridges between the polymer chains and contribute to binding the matrix (Crisp and Wilson, 1974,b), as illustrated in Fig. 2.3.

Hydrogen ions are six to twelve times more mobile than other cations, resulting in a delay between proton attack and the time when cations reach the displaced polymer chain. These factors, and the necessity for reaction with at least two carboxylate groups, account for the concentration maxima at 5 - 10 minutes of soluble calcium and aluminium in the cement. This is significant because the acid attack may be completed during the vigorous mixing of the cement. Crisp and Wilson (1974,b) considered that it was difficult to reconcile the fast setting of the cement with the slow diffusion of the ions without a driving force. They noted however, that if there is a considerable attack while mixing, the resultant temporary "electric field" accelerates the movement of calcium.

The electrical conductance studies on the setting cement showed continual changes in ionic concentration and mobility. The absence of discontinuities indicate that no sudden crystallization processes take place (Crisp and Wilson, 1974,b). Infra-red spectroscopic data have shown that the cementing reaction occurs over several hours and could continue indefinitely while free -COOH groups persist (Crisp et al, 1974). Further evidence of the setting reaction (cementation process) comes from the observed increase in recorded pH of the paste from pH 2 to pH 5.5 during the setting and hardening process (Wilson and Kent, 1971).

Crisp and Wilson (1974,a; 1974,b) reported that approximately 30 per cent of the glass is decomposed by proton attack and combine with the polymer in forming the matrix. The interpretation of the transmission and attenuated total reflectance spectra of the fully hardened cement indicated that a minor proportion of -COOH remains unconverted to -COO^- groups for steric and polar reasons which render, some -COOH group inaccessible (Crisp et al, 1974). One reason for this is that as the reaction proceeds, the cross-linking process increases the viscosity of the system, reducing ionic mobility and hence retarding the reaction. The other reason is that when the polyacrylate chain is largely ionized, the remaining hydrogen becomes very firmly bound by electrostatic forces. In effect they have little acidic function and are replaced by cations with difficulty (Crisp et al, 1974). There is no difference in the complexing behaviour of itaconic and acrylic acid units in the copolymer (Prosser et al, 1982).

2.3.14 The role of fluoride, phosphate and sodium ions

Because fluoride is an effective complexing agent for aluminium ions, the 1150°C glass, with its higher final fluoride content and consequent ability to release fluoride more quickly into acid solutions, yields more workable pastes (Barry et al, 1979). Only relatively small amounts of fluoride are extracted from the glass. The reason may be because fluoride is transported as metal cationic complexes such as AlF_2^+ , AlF^{2+} and CaF^+ , which thereby compete with polyacrylic acid for these metals (Crisp and Wilson, 1974,a; Wilson et al, 1976). Alternatively, since the pH of the cement is high, an early precipitation of calcium fluoride may occur (Crisp and Wilson, 1974,a).

Phosphate is only a minor constituent of G200 glass -- a glass with a composition typical of commercial glass ionomer cements.

Phosphate ions, together with fluoride ions, compete with the polyanion to form insoluble salts and complexes (Crisp and Wilson, 1974,b). Little phosphate goes into solution and it plays a minor part in the chemistry of the setting reaction (Crisp and Wilson, 1974,a).

Sodium appears to be present in two forms in the G200 glass (Crisp and Wilson, 1974,a). The water soluble form is rapidly extracted from the glass; altogether, approximately 30 per cent of the sodium in the glass is extracted by the polyacid (Crisp and Wilson, 1974,a). However, Crisp and Wilson (1974,b) concluded that "the sodium ion does not seem to take part in the reaction scheme."

2.3.2 *The role of tartaric acid*

The ^{13}C Fourier Transform Nuclear Magnetic Resonance (FTNMR) spectroscopy study, by Prosser et al (1982), confirmed the chemical studies by Wilson et al (1976) on the role of tartaric acid. Tartaric acid when present reacts preferentially with the glass powder, facilitating the extraction of metal ions from the glass, and combining with them in the period when the polymer is ionizing and unwinding (Wilson et al, 1976). There are a pair of ligands for chelation at each end of the molecule, bridging pairs of metal ions as illustrated in Fig. 2.4 (Wilson et al, 1976). This chelation has the effect of withholding metal ions from the polyanion chains in the early stages, preventing premature gelatinization and thus prolonging working time (Prosser et al, 1982).

Tartaric acid is fully complexed at pH 3 - pH 4 (Prosser et al, 1982). Ultimately, the complexed metal ion reacts with the polymer in either its ionized or unionized form (Wilson et al, 1976). It has been suggested that the metal tartrate complex may not dissociate but may instead become bound to the polymer chain (Wilson et al, 1976; Prosser et al, 1982).

2.3.3 *The structure of the set cement*

The fully set cement is a composite of glass particles embedded in a hard matrix (Crisp and Wilson, 1974,b).

The attacked glass particles which act as a filler are ion-depleted. The larger particles have an unattacked glass core surrounded by an aluminium ion-depleted outer zone of silica gel with isolated crystallites of calcium fluorite. The smaller particles are essentially the same, except that no inner, unattacked core remains. (Barry et al, 1979).

The polymer matrix contains only aluminium and calcium as major constituents with very little silicon. Aluminium is relatively more concentrated in the polysalt than calcium and aluminium polyacrylate predominates over calcium polyacrylate in the matrix (Barry et al, 1979). The strength and insolubility of the matrix are a result of the chains of covalent bonds in the polymer backbone and the ionic bridges cross-linking the chain (Crisp and Wilson, 1974,b).

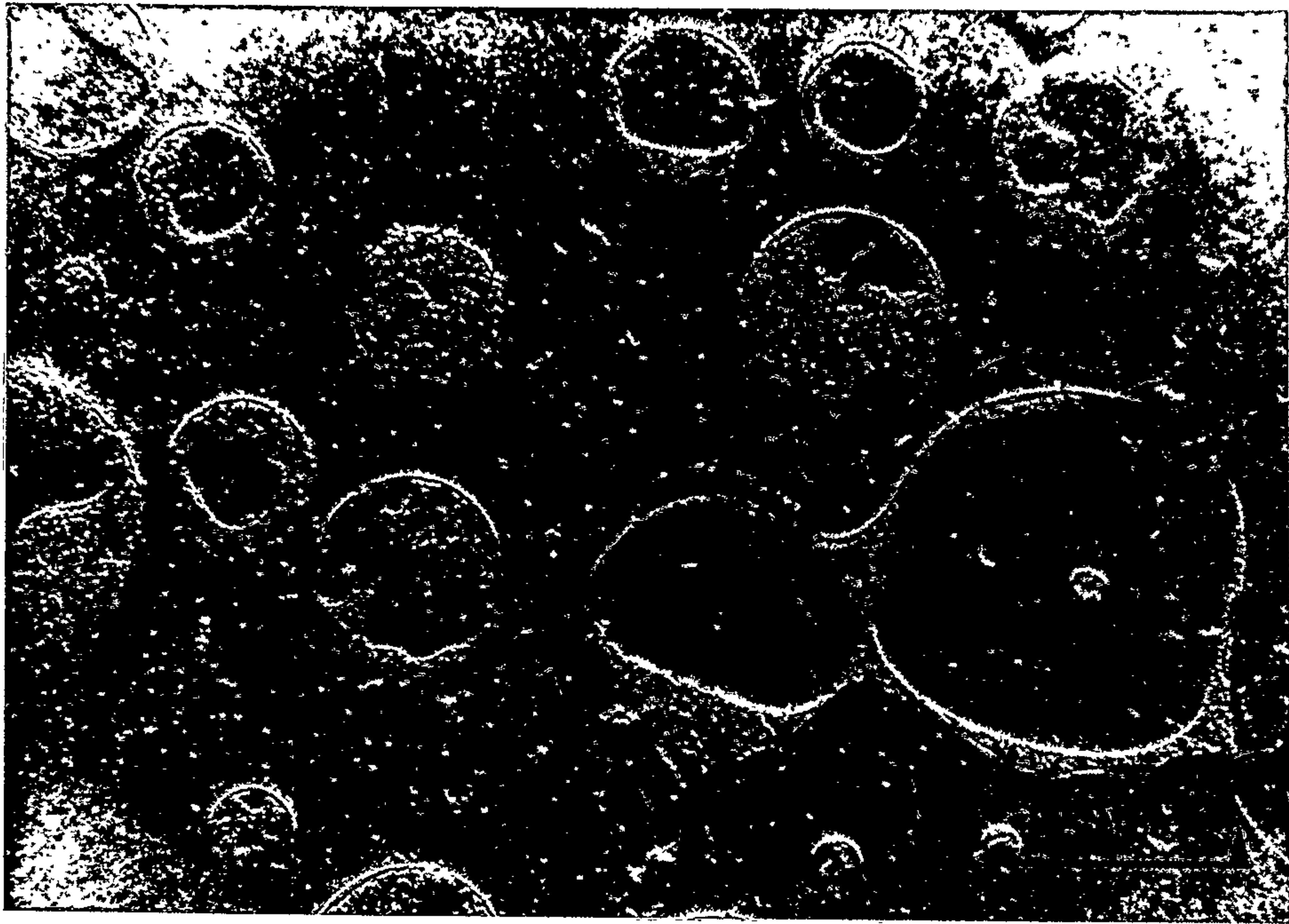
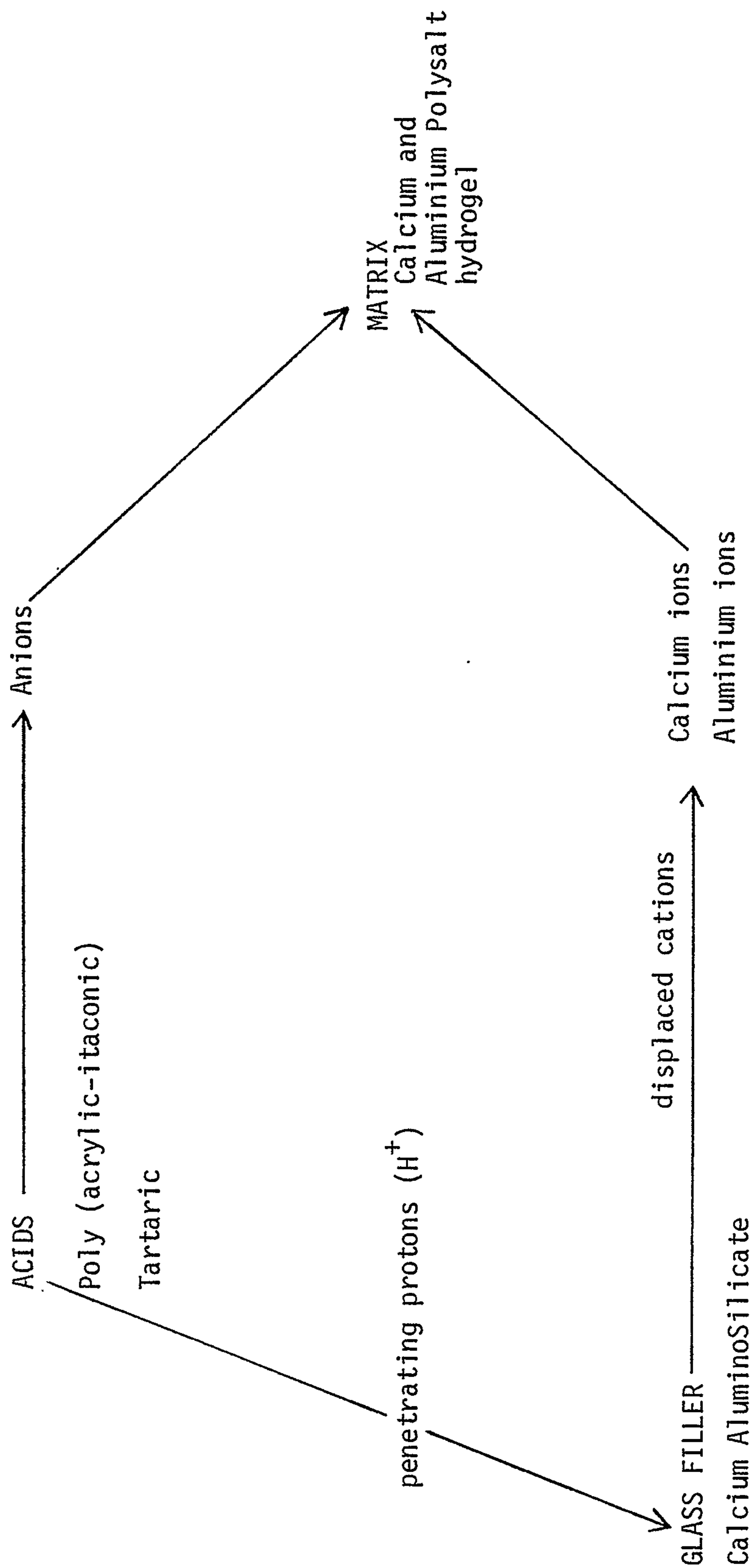


Fig. 2.1 Area of a glass sample from a 1150°C melt, polished then etched with 0.1 per cent HF for five seconds and then replicated for electron microscopy. The droplets can be clearly distinguished; the non-crystalline part of the droplets have been attacked by the etchant (from Barry et al, 1979).

Figure 2.2



The setting reaction of glass ionomer cements (McLean and Wilson, 1977,a)

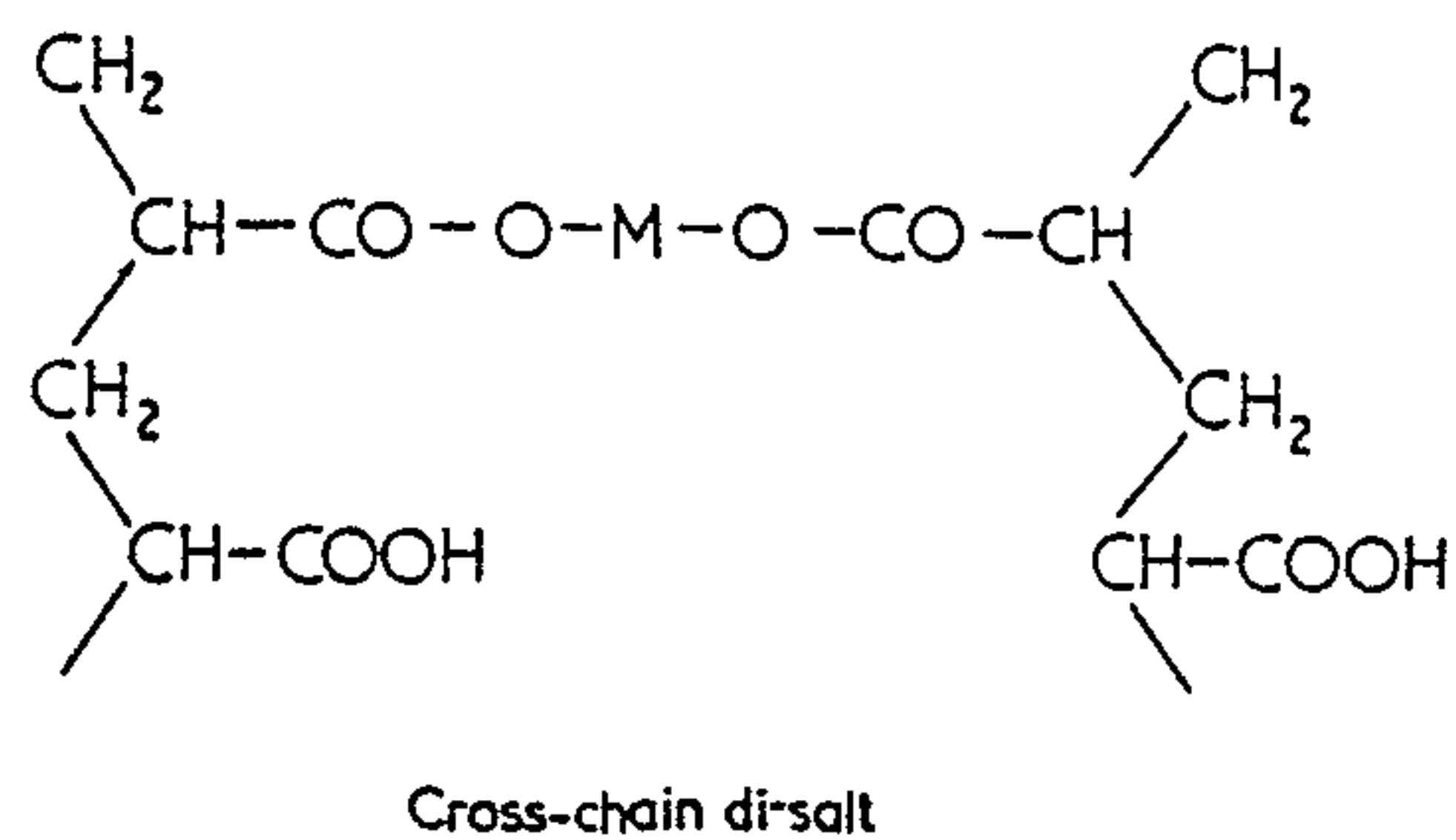
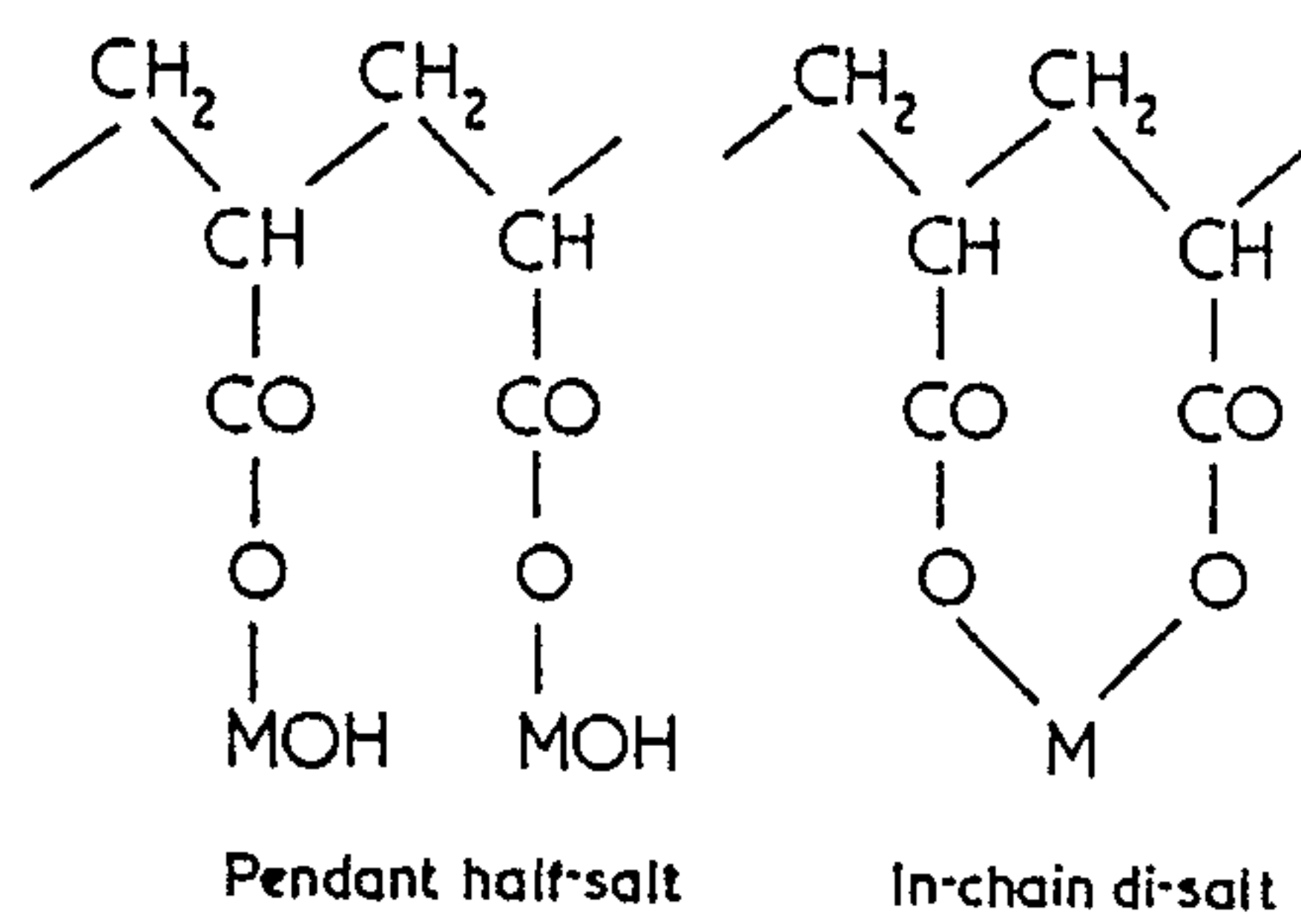


Fig. 2.3 Various types of salts formed from polyacrylic acid and divalent metal cations (Crisp and Wilson, 1974,b).

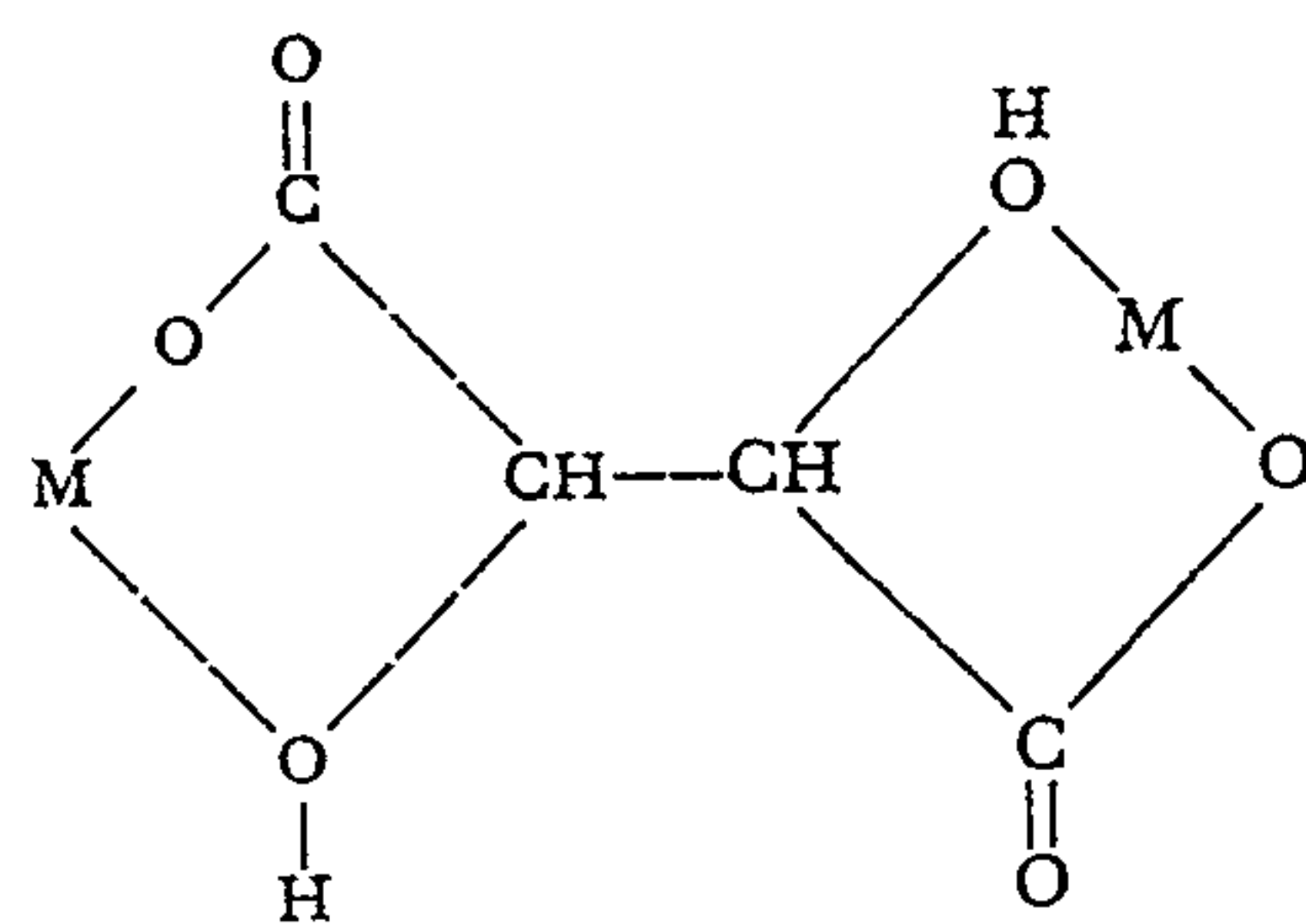


Fig. 2.4 The metal-tartrate complex (Wilson et al, 1976).

CHAPTER 3

PROPERTIES ASSOCIATED WITH THE CLINICAL PERFORMANCE OF GLASS IONOMER CEMENTS

- 3.1 The working time of glass ionomer cements
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- 3.10 Colour of the glass ionomer cements
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 - 3.12.3 Consistency
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3.1 THE WORKING TIME OF GLASS IONOMER CEMENTS

The working time of the various commercially available glass ionomer cements are stated to range from 1 minute to 2.5 minutes at 23⁰C (commercial brochures; McCabe et al, 1979; Stokes, 1980). Fuji Type II has the shortest (1 minute) and Ketac-cem the longest (2.5 minutes) working time. Chilling the glass slab has been found to prolong the working time by 0.5 to 1.0 minute (Mount and Makinson, 1978; McCabe, 1979; Stokes, 1980).

Working time has been found to decrease with increased powder : liquid ratio (Crisp et al, 1976,b; 1976,c; 1977), increased polyacid molecular weight (Crisp et al, 1976,c; Wilson et al, 1977), and with a concentration of polyacid greater than 38 per cent (Wilson et al, 1977). Working time is also affected by the composition and temperature of fusion of the glass (Kent et al, 1979).

3.2 THE SETTING TIME OF GLASS IONOMER CEMENTS

The setting times claimed by the manufacturers for the various commercial glass ionomer cements range from 2.25 to 5 minutes for the restorative cements and from 4 to 7 minutes for the luting cements. Reisbick (1981) reported that the setting times for ChemBond and Fuji Type I were 9.3 and 5.8 minutes, respectively; these were comparable with the manufacturers' claims of 7 and 5 minutes, respectively.

Setting time has been found to decrease with increased powder : liquid ratio (Crisp et al, 1976,b; 1976,c) and increased

polyacid molecular weight (Wilson et al, 1977). The addition of tartaric acid to the liquid decreased the setting time without affecting the working time (Wilson et al, 1976; McLean and Wilson, 1977,a).

Chilling the glass slab prior to mixing did not alter the setting time (Mount and Makinson, 1978). Pre-heating the ASPA powder to 100°C just prior to mixing increased the setting time (Brune, 1982). The setting time has also been found to vary with the composition and fusion temperature of the glass powder (2.1.2 and 2.1.4).

3.3 THE STRENGTH OF GLASS IONOMER CEMENTS

3.3.1 *Compressive strength*

When subjected to loading, the glass ionomer cement is intermediate in behaviour between zinc polycarboxylate and the phosphate-bonded materials like zinc phosphate and silicophosphate cements. The glass ionomer cement generally exhibits brittle fracture, although some plastic deformation occurs under compressive load (Wilson and Lewis, 1980).

3.3.11 Rate of development of compressive strength

The compressive strength of experimental glass ionomer cements was found to increase with time after mixing (Crisp and Wilson, 1973; Kent et al, 1973; Crisp et al, 1976,a; McLean and Wilson, 1977,a). ASPA IV developed approximately one-half its 24 hour wet strength in 1 hour. The strength of 1 year old specimens (235 MPa) was considerably greater than that of 24 hour specimens (170 MPa) (Crisp et al, 1976,a). Causton (1981) reported a significant increase in strength with time up to 1 year when the specimens were protected from exposure to water for 15 minutes after mixing. The manufacturer of ChemFil has claimed that the 1 hour, 24 hour and 1 month strengths are 110, 170 and 220 MPa, respectively.

3.3.12 Compressive strength of glass ionomer cements

The 24 hour compressive strength of the experimental glass ionomer cement ASPA IV ranged from 164 - 190 MPa (Crisp et al, 1975; 1976,a; McLean and Wilson, 1977,a; Wilson, 1977), and that of the corresponding luting consistency ASPA IVA was approximately 130 MPa (Wilson, 1977).

The 24 hour compressive strengths of ASPA and Fuji Type II were reported to be approximately 170 MPa and 140 MPa, respectively (Wilson and Prosser, 1982; Vougiouklakis and Smith, 1982). The 24 hour compressive strengths of ChemBond and Fuji Type I were reported to be approximately 120 MPa and 170 MPa, respectively (Wilson and Prosser, 1982).

The manufacturers of the commercial glass ionomer cements have stated that the compressive strengths of two restorative cements (ChemFil and Hy-Bond F) were 170 and 226 MPa, respectively, and that the strengths of the luting consistency materials (Hy-Bond C and Ketac-cem) were 196 and 118 MPa, respectively. All values were stated for the 24 hour compressive strength except for Ketac-cem for which the time of testing was not stated. The claims of the manufacturers have not been verified by independent research; no reports have been published on the compressive strength of ChemFil, Hy-Bond F and C, Ketac and Ketac-cem. It is evident that there is considerable variation in the strength of these cements. The results of the present investigation into the compressive strengths of ChemFil, ChemBond, Ketac, Ketac-cem, Fuji Type II and Fuji Type I are discussed in 6.2 and 6.3.

3.3.13 Comparison with other materials

The strengths of glass ionomer cements are compared to other luting cements and other restorative cements in Tables 3.1 and 3.2, respectively. The luting consistencies of glass ionomer cements

are stronger in compression than the zinc phosphate cements, the zinc oxide-eugenol cements containing o-ethoxy benzoic acid, and the polycarboxylate cements (Table 3.1). Glass ionomer cements of restorative consistency are not as strong as the composite resins but are comparable to silicate cements (Table 3.2).

It is evident from Tables 3.1 and 3.2 that there are substantial differences (in both luting and restorative consistencies) between data for the glass ionomer cements as presented by Phillips (1982), the experimental glass ionomer cements, and the commercial glass ionomer cements (data from manufacturers). No explanation has been given, to date, to account for these differences.

3.3.14 Manufacturer-controlled factors affecting the compressive strength

Manufacturer-controlled variables that may influence the compressive strength are the molecular weight of the polyacid, the polyacid concentration, the proportion of tartaric acid and the silica content of the powder.

The compressive strength has been found to increase with increased molecular weight of the polyacid (2.2.6). However, polyacids with molecular weights greater than 23,000 can only be used at a concentration of 25 per cent due to their high viscosity, producing weaker cements than low molecular weight acids at a high concentration of 50 per cent (Wilson et al, 1977).

The compressive strength has been shown to increase linearly with polyacid concentration (Crisp et al, 1977). Maximum compressive strength was attained when the tartaric acid : total acid ratio was between 2.5 : 97.5 and 10 : 90 (Crisp et al, 1979). When the proportion of tartaric acid was greater than 10 per cent, cement strength decreased due to the high concentration of metal tartaric acid chelate (Crisp et al, 1979).

Kent et al (1979) found that a greater silica content of the glass powder, corresponded with a lower compressive strength.

3.3.15 Manipulative variables affecting the compressive strength

The higher the powder : liquid ratio used by the operator, the higher the compressive strength of the set cement (Crisp et al, 1976,b; 1976,c). The manufacturers of Hy-Bond F and C have reported in their brochures that the compressive strength of both materials decreased with a reduction in powder : liquid ratio.

The compressive strength increases if exposure of the newly set cement to water is delayed (Causton, 1981). Protecting the cement for 1 hour will have the same beneficial effects as protecting it for 48 hours (Causton, 1981). Clinically this is achieved by coating the cements with a layer of varnish.

3.3.2 *Tensile strength*

The tensile strengths stated in the literature for glass ionomer cements are derived from diametral tensile strength tests.

3.3.21 Tensile strength values of glass ionomer cements

The 24 hour tensile strengths of the experimental ASPA IV cement ranged from 11.7 - 13.0 MPa (Crisp et al, 1975; McLean and Wilson, 1977,a; Wilson, 1977; Council on Dental Materials and Devices, 1979). The tensile strength of the experimental luting agent, ASPA IVA, ranged from 8.0 - 9.3 MPa (McLean and Wilson, 1977,a; Wilson, 1977; Council on Dental Materials and Devices, 1979).

Wilson and Prosser (1982) reported that the 24 hour tensile strengths of the commercial glass ionomer cements Fuji Type II, Fuji Type I, ASPA and ChemBond were 13.5, 7.5, 14 and 6.4 MPa, respectively. Vougiouklakis and Smith (1982) found that the tensile strengths of Fuji Type II and ASPA were 8.2 and 8.3 MPa, respectively; these values were approximately one-half the values quoted by Wilson and Prosser (1982). Manufacturers have stated that the 24 hour

tensile strengths of their commercial brands were 17 MPa (ChemFil) and 6.7 MPa (Hy-Bond F).

The results of research, other than by the manufacturers, on commercial products like ChemFil, Ketac, Ketac-cem, Hy-Bond F and C are not available in current literature. One of the aims of this study was to investigate the tensile strengths of a few of the commercially available glass ionomer cements. The results of this investigation are discussed in 7.2 and 7.3.

3.3.22 Comparison with other materials

The luting consistencies of glass ionomer cements are stronger in tension than zinc phosphate and zinc oxide-eugenol (EBA) cements and comparable with polycarboxylate cements (Table 3.1). The restorative glass ionomer cements are stronger in tension than silicate cements but much weaker than composite resins (Table 3.2).

3.3.23 Factors affecting the tensile strength

No studies have been reported in the literature on the effect of either powder : liquid ratio or the exposure of the cement to water on the tensile strength.

The tensile strengths of experimental glass ionomer cements were found to increase with the molecular weight (Wilson et al, 1977) and the concentration (Crisp et al, 1977) of the polyacid in the liquid.

3.4 THE ADHESIVE BOND STRENGTH OF GLASS IONOMER CEMENTS

3.4.1 *Introduction*

The glass ionomer cement is the first dental restorative material that can adhere to both enamel and dentine by physico-chemical bonding ("specific adhesion") thus reducing the need for mechanical bonding (Hotz et al, 1977; Prodger and Symonds, 1977; Öilo, 1981). The nature of the bond, the adhesive bond strengths and factors affecting the bond are discussed.

3.4.2 *Nature of the adhesive bond*

It has been postulated that the glass ionomer cements attach to tooth structure by molecular bonding. When the cements are first mixed, they are still in a fluid condition with many free pendant -COOH groups available in the polyacid for the formation of hydrogen bonds to the hydroxyapatite in enamel or to pendant amine and carboxyl groups of collagen in dentine. This promotes the wetting of the substrate (Williams and Cunningham, 1979).

As the reaction proceeds, hydrogen bonding to enamel is replaced by metal-ion bridges of the -O-M-OOO- type. The cations may be derived either from the cement or the substrate, providing a rigid and permanent attachment (McLean, 1977; McLean and Wilson, 1977,a; Williams and Cunningham, 1979; Wilson and Prosser, 1982) (Fig. 3.1).

Dentine contains both hydroxyapatite and collagen and adhesion to both components by glass ionomer cements is possible. Bonding of the cement to apatite would be similar to that for enamel, that is, by metal-ion bridges. Bonding to collagen can be by way of hydrogen bridges (Williams and Cunningham, 1979; Wilson and Prosser, 1982) (Fig. 3.1).

In general, adhesion between the cement and substrates results from dipole and ionic interactions because glass ionomer cements and substrates have a polar nature (McLean and Wilson, 1977,a). Stevens (1975) suggested that the mechanisms of adhesion of the polyacrylate based cements were: i) primary bonding due to chelation or coordination, and ii) secondary bonding due to improved wetting.

Many researchers have examined the surfaces of tooth specimens after being subjected to adhesive bond strength tests. Maldonado et al

(1978) found that 90 per cent of the failures were classified as cohesive failure which took place within the cement and the remaining 10 per cent of failures were of the cohesive-adhesive type where some of the cement remained attached to the tooth structure.

Consistent with this evidence, other researchers have reported that the failure of the bond to enamel was predominantly of the cohesive type (Hotz et al, 1977; Öilo, 1981; Vougiouklakis et al, 1982). The failure of the cement-dentine bond has been found to be of the adhesive-cohesive type (Jenkins, 1976; Hotz et al, 1977; Vougiouklakis et al, 1982).

3.4.3 *Clinical evidence of adhesion of glass ionomer cements to tooth structure*

The retention rate of glass ionomer cements used in the restoration of Class V abrasion lesions and Class II lesions in deciduous teeth is discussed in 4.3.1 and 4.3.3, respectively.

3.4.4 *Adhesive bond strength values of glass ionomer cements*

The tensile bond strength and shear bond strength of these cements to enamel, dentine and other materials are discussed. A comparison of the bond strength of glass ionomer cements and other restorative and luting cements is also made.

3.4.41 *Adhesive bond strength to enamel*

The adhesive bond strengths of some glass ionomer cements to enamel and dentine are summarized in Table 3.3.

The tensile bond strength of ASPA to enamel ranged from 1.0 MPa to 5.5 MPa (Williams et al, 1974; Prodger and Symonds, 1977; Levine et al, 1977; Maldonado et al, 1978; McCabe et al, 1979; Vougiouklakis et al, 1982). The value for ChemFil (which replaced ASPA) was reported to be 4 MPa by the manufacturer. The tensile bond strength of Fuji Type II was found to be 4.6 MPa (Lacefield

et al, 1982). Values for other glass ionomer cements are not currently available in the literature.

For the luting consistency cements, only the values for ChemBond have been reported. The 24 hour tensile bond strength of ChemBond was found to range from 1.3 to 3.9 MPa (McCabe et al, 1979; Öilo, 1981). The bond strengths of both ASPA and ChemBond to enamel increased with time (Williams et al, 1974; McCabe et al, 1979).

3.4.42 Adhesive bond strength to dentine

The tensile bond strength of ASPA to dentine has been found to range from 1 to 6 MPa (Levine et al, 1977; Prodger and Symonds, 1977; Maldonado et al, 1978; McCabe et al, 1979; Vougiouklakis and Smith, 1982; Vougiouklakis et al, 1982). The tensile bond strength of Fuji Type II ranged from 3.3 to 4.3 MPa (Kawahara et al, 1977; Lacefield et al, 1982; Vougiouklakis and Smith, 1982; Vougiouklakis et al, 1982). The manufacturer has claimed that the bond strength for Hy-Bond F is 2.3 MPa.

For the luting consistency cements, ChemBond was reported to have a bond strength of 1.3 to 3.4 MPa (McCabe et al, 1979; Öilo, 1981) and Hy-Bond C was reported to have a bond strength of 2.4 MPa by its manufacturer.

Öilo (1981) reported a decrease in the tensile bond strength of ASPA with time while McCabe et al (1979) found an increase with time. For ChemBond, Öilo (1981) reported an increase in bond strength with time while McCabe et al (1979) found no change in strength. It is interesting to note that Lipton and Smith (1977) were the only researchers who found no bonding of a glass ionomer cement (ASPA) with dentine.

The shear bond strength of ASPA to dentine was found to be 6.8 ± 2.0 MPa by Hood et al (1981). No information was available

in the literature on the shear bond strength of other glass ionomer cements to enamel or dentine.

3.4.43 Comparison of the adhesive bond strength of glass ionomer cements and other materials to tooth structure

The tensile bond strength of glass ionomer cements to enamel was found to be similar to that of polycarboxylate cements but was only approximately one-half that achieved by the use of the acid-etch composite resin system (Williams et al, 1974; Maldonado et al, 1978; Jenkins, 1976). The shear bond strength of a glass ionomer cement to enamel was found to be considerably lower than that achieved by acid-etched composite resins (Carlyle et al, 1978).

The tensile bond strength of glass ionomer cements to dentine has been found to be higher than that of a "composite resin adhesive restorative system" (Vougiouklakis and Smith, 1982). Jenkins (1976) and Lipton and Smith (1977), reported that no bonding (mechanical or chemical) of composite resin to dentine was achieved. The bond strengths to dentine of glass ionomer cements and polycarboxylate cements are very similar (Levine et al, 1977; Maldonado et al, 1978).

3.4.44 Adhesive bond strength of glass ionomer cements to other materials

Glass ionomer cements do not bond to porcelain (Hotz et al, 1977; McCabe et al, 1979; Rogers and Griffith, 1980). The adhesive bond to pure platinum ranges from 0 to 0.07 MPa (Hotz et al, 1977; McLean, 1977). The adhesive bond strength of glass ionomer cement to gold and porcelain was reported to be between 0 to 2.2 MPa (Hotz et al, 1977; McLean, 1977; McCabe et al, 1979) and the bond strength to stainless steel was 6.8 MPa (Williams and Cunningham, 1979). Techniques of improving the bond strength of glass ionomer cements to gold and platinum are discussed in 3.4.56.

3.4.5 *Factors affecting bond strength to tooth structure*

Glass ionomer cements adhere to substrates by physico-chemical bonding (3.4.1, 3.4.2). Hence the bond strength of the glass ionomer cements to tooth structure and other materials is to a large extent dependent upon the physical characteristics of the cement, for example, its compressive and tensile strength. Bond strength may also be altered by various surface treatments to the tooth structure or other materials.

3.4.51 Physical properties of the cement

Because a joint may fracture either adhesively, cohesively, or partially adhesively and partially cohesively, the tensile and compressive strength of the cement may affect its bond strength (Stevens, 1975).

Negm et al (1981) found a significant reduction in the adhesive bond strength of polycarboxylate cements to tooth structure, with increased film thickness. The reason suggested was that thick cement films were porous and contained air bubbles. It is likely that the effect will be the same for glass ionomer cements because of their similarity to polycarboxylate cements.

3.4.52 Use of citric acid conditioner

The use of citric acid pre-treatment was recommended when glass ionomer cements were first introduced and presently it is still available for use with ChemFil. The application of 50 per cent citric acid to tooth structure for a period of 30 seconds to one minute was believed to increase the adhesion of the cement to the tooth. The results of various studies on this technique have been conflicting.

Studies by Prodger and Symonds (1977) and Vougiouklakis et al (1982) found no significant increase in tensile bond strength to enamel with citric acid pre-treatment. Hotz et al (1977) however found that, for ASPA IV, the most effective form of surface treatment

of the enamel was the use of the citric acid conditioner. Yedid and Chan (1980) found that the shear bond strength of ASPA to enamel was greater after the use of citric acid pre-treatment.

The results of studies investigating the effect of citric acid pre-treatment on the adhesion to dentine have also been conflicting.

Some researchers have reported an increase in tensile bond strength of ASPA and ASPA IV with citric acid pre-treatment (Hotz et al, 1977; Yedid and Chan, 1980; Vougiouklakis et al, 1982). Vougiouklakis et al (1982) found that citric acid pre-treatment resulted in a slight decrease of the bond strength of Fuji Type II which was not statistically significant. This was confirmed by Lacefield et al (1982). The reason for the difference in behaviour between ASPA and Fuji Type II was attributed to the difference in viscosity and tartaric acid content of the two cements.

It has been suggested that pre-treatment of the dentine surface with citric acid removed the smeared layer of cutting debris and opened the dentinal tubules. SEM examination of these surfaces after adhesive bond fracture showed tubules occluded by the penetration of some glass ionomer cements; this was suggested as the probable cause of the increased bond strength found for ASPA cement (Vougiouklakis et al, 1982).

Prodger and Symonds (1977), Shalabi et al (1981) and Lacefield et al (1982) reported that there was no significant difference in tensile bond strength to dentine between treatment and non-treatment with citric acid. Prodger and Symonds (1977) also reported a decrease in bond strength after exposure of the dentine to saliva; the strength increased to the level of freshly cut dentine after conditioning with citric acid. In contrast, Hood et al (1981) reported a 40 per cent decrease in the shear bond strength of ASPA after treatment of dentine with citric acid.

The nature of the adhesive bond failure of ASPA to dentine differs from that of Fuji Type II (Vougiouklakis et al, 1982). For ASPA, the type of failure was entirely adhesive and occurred at the interface between the untreated dentine surface and the material. Adhesive failure decreased to approximately 80 per cent with citric acid pre-treatment. The remaining 20 per cent of failures were of the adhesive-cohesive or cohesive type. In contrast, for Fuji Type II, 60 per cent of the failures with untreated or citric acid pre-treated dentine were adhesive and the remainder were adhesive-cohesive or cohesive through the material.

Lacefield et al (1982) reported that the tensile bond strength of Fuji Type II to cementum was not affected by citric acid pre-treatment.

In conclusion, the desirability of using citric acid pre-treatment is controversial because of the conflicting evidence obtained (as discussed earlier). Mount (1981) reported that "clinical experience suggests it is not necessary". At present, of all the commercial glass ionomer cements, only ChemFil has been advocated for use with citric acid pre-treatment by its manufacturer.

3.4.53 Use of a mineralizing solution

A mineralizing solution increases the mineral content of the tooth surface to which it is applied. In this treatise, the terms "mineralizing" and "remineralizing" have been used synonymously (as they have been in the literature).

The mineralizing solution used in most of the studies basically consists of two parts. The first part is a 0.5 mol/l solution of potassium dihydrogen phosphate (pH 4.5) saturated with Brushite, and the second part is a 0.5 mol/l solution of disodium hydrogen phosphate (pH 9.0 and containing 2000 ppm of fluoride). The mineralizing

solution has been applied to the dentine for a period ranging from 30 seconds to 3 minutes. Examination of dentine surfaces treated with mineralizing solution has given evidence of crystal growth on the dentine surface; the crystals were incorporated into the cement (Vougiouklakis et al, 1982). No studies have been reported on the effect of this solution on the adhesive bond strength to enamel.

Garton et al (1976) and Levine et al (1977) reported a 90 and 115 per cent (respectively) increase in the bond strength of the glass ionomer cement to dentine treated with the mineralizing solution for 30 seconds and 3 minutes, respectively. Lipton and Smith (1977) and Vougiouklakis et al (1982) found that the use of the mineralizing solution did not have a statistically significant effect on the bond strengths of ASPA and Fuji Type II cements. Vougiouklakis et al (1982) reported that the use of 50 per cent citric acid for 30 seconds, followed by the application of the mineralizing solution for 3 minutes, resulted in a significant increase in the bond strength from 3.3 MPa to 5.3 MPa with the ASPA cements. In the case of Fuji Type II, however, the use of the remineralizing solution alone or in combination with the citric acid treatment did not result in a significant change in bond strength.

Hotz et al (1977) reported that the mineralizing solution was less effective than citric acid in improving the bond strength of ASPA IV.

The results of these studies have suggested that further research needs to be undertaken before advocating the routine clinical use of mineralizing solutions.

3.4.54 Effect of other solutions

Yedid and Chan (1980) reported that the bond strength of ASPA to enamel and dentine was significantly greater when the tooth surfaces had been etched with 37 per cent phosphoric acid than when ASPA was

applied to unetched surfaces. Other researchers have reported that the tensile bond strength of the cement to enamel, dentine and cementum was not affected by surface treatment with phosphoric acid (Shalabi et al, 1981; Lacefield et al, 1982).

Hotz et al (1977) reported that pre-treatment of the dentine with 20 volume hydrogen peroxide resulted in bond strengths that were significantly lower than samples which were treated with citric acid.

The use of 15 - 17 per cent EDTA solution as a surface treatment has also been studied. Shalabi et al (1981) reported a significant increase in the bond strength of the cement to dentine. In contrast, Vougiouklakis et al (1982) reported that the effect of EDTA on dentine surfaces was similar to that for citric acid and that there was no significant difference in the bond strength after pre-treatment with EDTA solution.

Shalabi et al (1981) reported that the bond strength between dentine and a glass ionomer cement could be increased by pre-treatment of the cut surface with an acidic cleansing agent, followed by the application of a low concentration of ferric chloride solution.

3.4.55 Other factors affecting the bond strength to tooth structure

Thermal cycling of the specimens did not significantly affect the bond strength of the cement to enamel but significantly reduced the bond strength to dentine (Maldonado et al, 1978).

The surface texture of the preparation has been found to influence the bond strength of cement to tooth structure (Negm et al, 1981). Surface roughness of the tooth preparation was found to decrease the tensile bond strength but improve the shear bond strength.

Prodger and Symonds (1977) found evidence that the application of varnish to the "cement margin" significantly improved the adhesion to enamel (conditioned or unconditioned with citric acid) and conditioned dentine.

3.4.56 Techniques for improving the bond strength of glass ionomer cements to other dental materials

The bond strength of these cements to gold and platinum may be increased by the electrodeposition of up to 2 μm of tin on the metal surface to provide a suitable oxide film for wetting by the cement (Hotz et al, 1977; McLean, 1977). The bond strengths of the cement to gold and platinum have been increased to 4.3 MPa and from 2.5 to 3.8 MPa respectively, by this technique. These findings may be associated with increased retention of cast restorations and platinum-bonded alumina crowns to tooth structure when glass ionomer cements are used as the luting agent.

Rogers and Griffith (1980) found that glass ionomer cement did not bond to smooth porcelain. The addition of from 20 to 50 per cent of glass ionomer particles in the porcelain powder and/or roughening of the porcelain surface increased the retentive properties. The effect of the addition of the glass ionomer particles on other properties of the porcelain needs to be investigated.

3.4.6 *Conclusion*

The glass ionomer cement bonds to active polar surfaces such as enamel, dentine and the oxide surfaces of base metals, but not to the chemically unreactive surfaces of dental porcelain and the noble metals. Adhesion is attributed to the interaction of the polar groups of the polymeric carboxylic acids with the polar surfaces of the substrates. More research and clinical data are required before the various techniques for improving bond strength can be adopted as routine procedures.

3.5 MARGINAL LEAKAGE

Ideally, a restorative or luting cement should not allow marginal leakage of oral fluids between the cement and walls of the preparation because of the potential for pulpal irritation, sensitivity

and recurrence of caries. As discussed in 3.4, glass ionomer cements exhibit specific adhesion to tooth structure. It is generally considered that little or no microleakage occurs because of this.

3.5.1 *Microleakage of glass ionomer cement restorations*

Maldonado et al (1978) reported that a good seal was obtained with glass ionomer cements even when the margin was in dentine or cementum. Kidd (1978) confirmed the good sealing ability of these cements. In contrast, experiments with glass ionomer cement restorations on thermally-cycled teeth *in vitro* have indicated that marginal leakage occurred (Hargrave et al, 1979; Kidd and McLean, 1979; Lacefield et al, 1982). Under these conditions, Lacefield et al (1982) reported that severe microleakage occurred with glass ionomer cements regardless of cavity pre-treatment with citric acid or phosphoric acid. Kidd and McLean (1979) reported that although tin-plating the fitting surface of an inlay increased the adhesion to glass ionomer cements, it did not reduce marginal leakage.

3.5.2 *Comparison with other materials*

Class V inlays cemented with glass ionomer cements exhibited less microleakage than inlays cemented with zinc phosphate cements (Kidd and McLean, 1979). Hargrave et al (1979) found evidence that there was no significant difference between the leakage of ASPA and two composite resins (Cervident and Concise) *in vitro* at both enamel and non-enamel margins. Kawahara et al (1977) however, reported that the marginal leakage around glass ionomer cement restorations was less than that associated with conventional filling and sealing materials, although they did not specify what these were.

Pitt Ford (1979) found that the addition of bismuth compound to the glass ionomer cement powder, and the reduction of the powder : liquid ratio to 2:1 produced a root filling paste which gave leakage values similar to Rickett's cement. He suggested that this modified

cement could be used as a root filling cement with a single cone method without the need for a lateral condensation technique.

3.5.3 *Clinical evidence of microleakage*

Clinically, marginal staining could be an indication of marginal leakage. Charbeneau and Bozell (1979) reported a 6.2 per cent incidence of marginal staining around glass ionomer cement restorations at 6 months. Smales (1981,b) reported a 3 per cent incidence at 3 years. McLean and Wilson (1974; 1977,c) reported the occurrence of marginal discolouration around ASPA restorations. In contrast, Flynn (1982) found no discolouration around these restorations.

3.5.4 *Conclusion*

Although the results of the *in vitro* experiments on marginal leakage are conflicting, currently available clinical evidence seems to indicate that marginal leakage does occur with glass ionomer cements, although to a limited extent.

3.6 SOLUBILITY AND DISINTEGRATION

Crisp et al (1980,b) defined "solubility" (or dissolution) as the amount of material going into solution and "disintegration" as the amount of insoluble decomposition products formed.

3.6.1 *Solubility and disintegration in distilled water*

The solubility and disintegration values of glass ionomer cements (at 24 hours) in distilled water have been found to range from 0.3 to 0.8 per cent for the restorative consistency and to be approximately 0.9 per cent for the luting consistency (Crisp and Wilson, 1973; Kent et al, 1973; Crisp et al, 1975; Wilson, 1977; Wilson et al, 1977; Council on Dental Materials and Devices, 1979).

These authors have reported that glass ionomer cements were more soluble than the zinc phosphate, zinc oxide-eugenol (simple or reinforced) and zinc polycarboxylate cements. However, the

solubility and disintegration of glass ionomer cements have been found to be less than that of silicate cements (Kent et al, 1973; Wilson, 1977; Council on Dental Materials and Devices, 1979; Phillips, 1982, Ch. 30). The manufacturers of Hy-Bond F and C, and ChemFil have claimed that the solubility of these cements after 24 hours is 0.3 per cent.

3.6.2 *Acid erosion*

Erosion is the sum of dissolution and disintegration. The acid erosion of ASPA IV (restorative consistency) was 1.05 per cent after one day and 1.2 per cent after 7 days (Wilson, 1977; Crisp et al, 1980,b). In contrast, the acid erosion for a silicate cement was 1.1 per cent at one day and 2.7 per cent at 7 days (Crisp et al, 1980,b). McCabe et al (1979) also reported that ASPA had lower acid solubility than a silicate cement. The acid erosion was greater in polycarboxylate cements than in glass ionomer cements (Crisp et al, 1980,b).

Under acid conditions, the glass ionomer cement erodes significantly less than either silicate or zinc polycarboxylate cements and the contributions to the total erosion from dissolution and disintegration are of the same order. In contrast, most of the acid erosion products of zinc polycarboxylate cements are soluble and most of the acid erosion products of silicate cements are insoluble (Crisp et al, 1980,b).

Silicate cements show a much greater disintegration than the glass ionomer cements because in the latter, the aluminium acts as an ionic cross-linking unit for the polymer chains linked by acid-resistant covalent bonds. Hence, the loss of a proportion of aluminium ions is not "catastrophic", whereas in the silicate cement,

aluminium serves as the sole connecting ionic link for isolated phosphate tetrahedra (Crisp et al, 1980,b).

3.6.3 *Composition of the eluates*

Calcium, although a major constituent of the original powder, has not been extracted under either acid or neutral conditions (Crisp et al, 1976,d; 1980,b). The same authors reported that aluminium was lost under both neutral and acidic conditions, but the loss was greater in neutral than in acid conditions. Silica and fluoride were lost under both neutral and acidic conditions but fluoride was extracted to a larger extent under acid conditions (Crisp et al, 1976,d; 1980,b). Sodium, although only a minor constituent of the glass ionomer cement is a principal constituent of eluates (Crisp et al, 1975; 1980,b).

The higher early dissolution of cements based on aluminosilicate powders in water can be attributed to two causes. First, they contain sodium which forms water-soluble salts with the matrix-forming anions. Secondly, aluminium ions react rather slowly with the matrix-forming anions and, before they are bound, are vulnerable to early leaching in water (Crisp et al, 1980,b).

Elution, under all conditions, occurs most rapidly in the initial 23 hours and is much slower thereafter (Crisp et al, 1980,b).

3.6.4 *Effect of powder and liquid composition on solubility and disintegration*

Kent et al (1979) reported that glasses with high silica content produced cements with poor resistance to aqueous attack. They also found that a high sodium content led to poorer surface resistance to aqueous attack (although solubility figures at 24 hours suggested otherwise). Replacement of sodium by lithium yielded cements with very poor resistance to aqueous attack (Kent et al, 1979).

Crisp et al (1979) reported that minimum values for water-leachable materials were obtained when the tartaric acid : total acid ratio was between 0:100 and 10:90.

Solubility and disintegration are greatest for cements prepared from liquids with polymer concentrations of between 28 and 38 per cent, and decrease linearly with increase in polymer concentration (Crisp et al, 1977). An increase in powder : liquid ratio and the molecular weight of the polyacid decreased the solubility of the cement (Crisp et al, 1976,b; 1976,c).

3.6.5 *Other factors affecting solubility and disintegration*

Degradation of the cement is affected by the molarity and pH of the medium (McCabe, 1982; Mesu, 1982). McCabe (1982) reported a four-fold increase in solubility under agitated conditions compared with static conditions in a near neutral medium. The solubility decreases as the "cure" time of the cement is extended (Crisp et al, 1976,d). Mesu (1982) however reported no difference in degradation speed with extended curing time.

3.6.6 *Clinical studies*

The solubility and disintegration tests performed in the laboratory have little value in predicting clinical behaviour (Bowen et al, 1968; Mitchem, 1972). Clinical studies are therefore the most reliable means of predicting clinical behaviour of the cements. A few studies are available on the surface contour of glass ionomer cements over a period of time. However, loss in surface contour is dependent upon the rate of solubility and erosion as well as the abrasion resistance of the material; and at present there are no clinical studies on solubility and erosion alone reported in the literature. McLean and Wilson (1977,c) reported that over a period of six months to three years the increase in the number of

restorations showing loss of surface contour was from 0.7 to 10.0 per cent. Smales (1981,b) reported a 45 per cent incidence of surface disintegration within one year after placement of the restoration. Flynn (1982) reported that ASPA restorations exhibited greater surface deterioration than composite resin restorations when evaluated six years after placement.

3.6.7 *Conclusion*

The clinical studies and laboratory research have been carried out on ASPA IV and the commercial ASPA cements. Very few studies have been reported in the literature on the solubility of the newer commercial glass ionomer cements. The general consensus however is that, due to their greater resistance to acid attack, the glass ionomer cements are less soluble clinically than the other dental cements.

3.7 FILM THICKNESS

3.7.1 *Introduction*

The luting glass ionomer cements have been advocated for the cementation of cast metal and porcelain restorations. It is necessary for the film thickness to be sufficiently thin to enable complete seating of the restoration (without interference to its fit). The American Dental Association Specification classifies cements as Type I or Type II, on the basis of their properties and their intended use. Type I is a "fine grain cement" with a film thickness of less than 25 μm , intended for cementation of precision fitting castings. Type II is a "medium grain" cement with a film thickness of less than 40 μm , used for thermal insulating bases and cementation of orthodontic bands (Phillips, 1982, Ch.29).

The thickness of the film between the casting and the tooth is determined by the cementation pressure, viscosity and temperature of

the cement, the taper of the walls of the cavity preparation, the particle size and the effective grain size (Phillips, 1982, Ch.29). The actual film thickness is usually less than the maximum particle size due to its solution in the liquid, the mixing procedure which breaks up the particles even further and the pressure exerted on the casting at the time of cementation. It is the size of the particles that have withstood these procedures, "the effective grain size", that determines the film thickness of the cement. The finer the original particles, the smaller is the effective grain size and the lower is the film thickness (Jørgensen and Petersen, 1963).

3.7.2 *Reported film thickness values*

Wilson et al (1977) reported the film thickness of ASPA IV A to be 24 μm , at a powder : liquid ratio of 1.67:1. The film thickness of ChemBond was found to be 20 μm by Mesu (1982). The manufacturer of Hy-Bond C has claimed that the film thickness of the cement is 25 μm at the recommended consistency of 1.5:1. Reisbick (1981) found that the film thickness of Fuji Type I was considerably greater than that for ChemBond and suggested that Fuji Type I might present difficulties in complete seating of a crown. Although no values of film thickness were reported, Reisbick (1981), from his laboratory tests, decided that Fuji Type I was not suitable for clinical use and omitted it from subsequent clinical tests.

The studies reported here have either made use of the powder : liquid ratio recommended by the manufacturer or have failed to state the powder : liquid ratio used. The film thickness is related to the powder : liquid ratio. Wilson et al (1977) found that the film thickness of ASPA IV A increased with the powder : liquid ratio. The manufacturers of Hy-Bond C stated in their brochure that the film thickness decreased

slightly from 25 μm to 22 μm when the powder : liquid ratio was reduced from 1.5:1 to 1.05:1 (a reduction of 30 per cent). In contrast, the film thickness of Hy-Bond C increased dramatically from 25 μm (powder:liquid ratio 1.5:1) to 39 μm (powder:liquid ratio 1.65:1) with a 10 per cent increase in the powder : liquid ratio. The effect of the powder : liquid ratio on the film thickness of other commercial glass ionomer cements was examined in this investigation (8.2).

3.7.3 *Comparison with other luting cements*

Table 3.4 shows the film thickness of the commonly used luting agents. On currently available data it is evident that glass ionomer cements have a greater film thickness than zinc phosphate cements. However, Wilson et al (1977) referred to the film thickness of ASPA IVA as being "equivalent" to that of a fine-grained zinc phosphate cement. The film thickness of glass ionomer cements is similar to that of zinc oxide-eugenol-EBA and zinc polycarboxylate cements (Table 3.4). Reisbick (1981) confirmed this in a study in which he assessed the cement thickness between the tooth and the cast restoration.

From a clinical evaluation of crowns and bridges cemented with ChemBond, Reisbick (1981) suggested that this cement was satisfactory and was associated with no post-operative pain or hypersensitivity (although a few patients did complain of momentary sensitivity following cementation on unanaesthetized teeth without prior application of varnish). None of the restorations cemented with ChemBond became loose or were dislodged 6 months after placement.

3.7.4 *Conclusion*

A film thickness not exceeding 25 μm has been stated as a requirement of cements used for luting. Although they have been widely advocated for clinical use (4.2; 4.3.2) there is little

evidence available on the film thickness of the commercial brands of glass ionomer luting cements in the literature. One of the aims of the present investigation was to measure the film thickness of these cements.

3.8 PULPAL EFFECTS OF GLASS IONOMER CEMENTS

The ability of the glass ionomer cement to adhere to tooth structure accounts for many of its suggested clinical applications. To ensure optimal adhesion to dentine, the cement is often used without the placement of any preliminary pulp protection. The effect of the material on the pulp is reviewed to confirm the efficacy of this practice. The pulpal effects have been studied *in vivo* in human and animal teeth or *in vitro* in cell cultures.

3.8.1 *Comparison with other cements*

The effect of glass ionomer cements on the pulp has often been studied using a zinc oxide-eugenol cement as a control. Tobias et al (1978) and Cooper (1980) reported that ASPA IV produced a more severe pulpal reaction *in vivo* than zinc oxide-eugenol cement. Kawahara et al (1979) and Douvitsas et al (1982) however, reported a negligible to mild reaction *in vivo* for Fuji Type II and ASPA cements. Kawahara et al (1977) reported a weaker reaction *in vitro* to glass ionomer cements than to zinc oxide-eugenol cements.

The glass ionomer cements were found by Kawahara et al (1977; 1979) to evoke a weaker reaction *in vitro* than zinc polycarboxylate cements. No other comparative studies have been reported.

Dental silicate cements produce a more unfavourable pulp reaction than glass ionomer cements (Klotzer, 1975; Dahl and Tronstad, 1976; Pameijer et al, 1981; Douvitsas et al, 1982). Wilson (1977) and Pameijer et al (1981) stated that the reasons for the milder reaction of the pulp to glass ionomer cements are : i) polyacrylic acid

is weaker than phosphoric acid, ii) polyacrylic acid, being a monomer with a higher molecular weight, has limited diffusion through the dentinal tubules to the pulp, iii) the strong electrostatic attraction between H^+ ions and the negatively charged polymer chain which results in less dissociation than in phosphoric acid, and iv) the lower heat of reaction.

3.8.2 *The cytotoxic effect of set and unset cements*

Unset glass ionomer cement has been found to have a mild cytotoxic effect *in vitro* when compared with polycarboxylate and zinc oxide-eugenol cements which had a strong cytotoxic effect. The set glass ionomer cement had no significant cytotoxic effect *in vitro* (Dahl and Tronstad, 1976; Kawahara et al, 1979). This contrasted with the set zinc polycarboxylate and zinc oxide-eugenol cements which showed a decrease in cell growth and evidence of cell degeneration (Kawahara et al, 1979).

3.8.3 *Pulpal effects of luting consistencies of glass ionomer cements*

The luting consistencies of glass ionomer cements have been found to evoke a greater pulpal response than the restorative consistencies (Tobias et al, 1978; Cooper, 1980). However, Tobias et al (1978) reported that, 7 days after insertion, there was no difference in the pulpal reactions to the restorative and luting consistencies.

3.8.4 *Pulpal effects of glass ionomer cements with citric acid pre-treatment*

Treatment of cavities with 50 per cent citric acid prior to restoring with glass ionomer cements has been found to result in significantly more irritation than the placement of glass ionomer cements into untreated cavities (Tobias et al, 1978). This has been attributed to : i) additional irritation from the citric acid

itself, and ii) greater penetration of toxic constituents of the restorative material, due to the removal of the plug of debris from the dentinal tubules.

3.8.5 *Pulpal histopathology*

The histopathological features commonly associated with the pulp subjacent to a glass ionomer cement restoration are pulpal hyperaemia, round cell infiltration, degeneration of odontoblasts, irregularities in the predentine and reparative dentine formation (Tobias et al, 1978; Kawahara et al, 1979; Yakushiji et al, 1979; Cooper, 1980; Pameijer et al, 1981; Kouvelas et al, 1982).

When glass ionomer cements have been placed in contact with the pulpal tissues, pulp necrosis occurred in all cases and 75 per cent of the cases had apical inflammation (Paterson and Watts, 1981).

3.8.6 *The use of a calcium hydroxide base*

Kawahara et al (1979), Yakushiji et al (1979), and Cooper (1980) reported the mild effect the glass ionomer cements have on the pulp. This evidence appeared to suggest that a base of calcium hydroxide beneath the glass ionomer cement is not necessary. However, Paterson and Watts (1981) and Lampert (1982) observed a marked reaction *in vivo* and *in vitro*, respectively, and proposed that a calcium hydroxide base should be used. Mount (1981) recommended that a calcium hydroxide base be placed where the thickness of the remaining dentine was less than 1 mm.

3.8.7 *Conclusion*

Currently, the balance of evidence indicates that glass ionomer cements provoke a mild response in the pulp and that the placement of calcium hydroxide as a base is required only in deep cavities where there are possible microexposures of the pulp.

3.9 CARIOSTATIC PROPERTIES OF GLASS IONOMER CEMENTS

The cariostatic property of glass ionomer cements has been associated with the release of fluoride ions from the cement.

3.9.1 *Fluoride release*

The fluoride content in the powder of a commercial glass ionomer cement (ASPA) has been reported to be 22.7 per cent by Hotz et al (1977) and 13.2 per cent by Forsten (1977); no explanation has been given to account for this difference. The total amount of fluoride released from ASPA relative to the fluoride content in test specimens was found by Tveit and Gjerdet (1981) to be 0.12 per cent after seven weeks. This represented more fluoride than the quantity released by a fluoride-containing amalgam, but less fluoride than the quantity released by a silicate cement (Tveit and Gjerdet, 1981). In contrast, Maldonado et al (1978) reported a significantly greater release of fluoride from a glass ionomer cement (ASPA) than from a silicate cement. Swartz et al (1977) found that a glass ionomer cement released similar amounts of fluoride to a silicate cement. Derkson et al (1982) reported that glass ionomer cements released greater amounts of fluoride than the silicophosphate type of cements.

It has been found that the greatest release of fluoride from glass ionomer cements occurred during the initial period of immersion and that the release diminished later to a fairly constant value (Forsten, 1977; Maldonado et al, 1978; Swartz et al, 1980; Derkson et al, 1982), and was found to cease within six months of exposure to water (Causton, 1981). The total quantity of fluoride ions released decreased with the length of time the cement was protected from water. It has been suggested that this indicated that the gel matrix was the source of fluoride ions (Causton, 1981).

3.9.2 *Effect of glass ionomer cement on tooth structure*

Tooth structure adjacent to a glass ionomer cement restoration has demonstrated rapid fluoride uptake (Wesenberg and Hals, 1980,a; 1980,b; Swartz et al, 1980; Smith et al, 1982; Retief et al, 1982). The rate and amount of fluoride uptake has varied with different brands of glass ionomer cements (Smith et al, 1982). Sites closer to the restoration showed a greater uptake of fluoride than sites further away; for example, sites 1 mm and 3 mm away showed an increase in fluoride content of 4,500 and 400 per cent, respectively (Swartz et al, 1980). Retief et al (1982), however, found contrary evidence; it appeared that fluoride acquisition was not influenced by the distance from the restoration.

Wesenberg and Hals (1980,a; 1980,b) reported that, in the region of the tooth surrounding the restoration, the concentration of fluoride and of aluminium increased by 0.3 and 1.15 per cent (respectively), the concentration of calcium and phosphate increased by 5 to 10 per cent, and there was a concomittant decrease in zinc.

Some studies have reported evidence of mild demineralization along the cavity wall (Kidd, 1978; Kidd and McLean, 1979; Wesenberg and Hals, 1980,a). It has been suggested that this initial demineralization was caused by the liquid (polyacid) in the cement and was followed by remineralization which was enhanced by the release of fluoride ions from the cement (Wesenberg and Hals, 1980,a).

After contact with a glass ionomer cement, the solubility of enamel has been found to decrease by about 50 per cent (Swartz et al, 1977; Maldonado et al, 1978). Enamel adjacent to silicate cements exhibited a smaller decrease in solubility (Swartz et al, 1977; Maldonado et al, 1978).

3.9.3 *Clinical studies*

To date, all clinical studies have been of relatively short duration. Longer term studies are generally required to assess cariostatic properties of materials.

McLean and Wilson (1974) reported that the incidence of occlusal caries, where ASPA II was used as a sealant, was "small" except where the sealant was lost. McLean and Wilson (1977,c) and Smales (1981,b) reported that there was no incidence of recurrent caries around glass ionomer cement (ASPA IV) restorations after three years. Low (1981) reported that there was no incidence of recurrent caries around the margins of cervical abrasion lesions restored with a glass ionomer cement (ASPA) after 6 - 15 months.

Williams and Winter (1976) and Williams et al (1978) reported that there was no statistical difference between ASPA and Nuva Seal in their ability to prevent pit and fissure caries when used as a fissure sealant for up to 2 years. However a longer-term clinical study of 4 years (Williams and Winter, 1981) indicated that ASPA was more effective than Nuva Seal. Williams et al (1978) and Williams and Winter (1981) reported that Concise, when used as a fissure sealant, had a statistically significant lower caries incidence than ASPA in a 2 and 4 year follow-up study.

3.9.4 *Conclusion*

The relatively short term studies conducted so far have shown that glass ionomer cements appear to have a mild anticariogenic effect on the neighbouring tooth structure that is probably related to the fluoride release from the cement. Clinical studies with the experimental glass ionomer cements and the commercial ASPA have found that over a 4 year period, ASPA was more effective than Nuva Seal but less effective than Concise in reducing the incidence of caries in

pits and fissures, when used as a fissure sealant. However, no clinical reports are available in the literature on the anticariogenic effect of the newer glass ionomer cements.

3.10 COLOUR OF THE GLASS IONOMER CEMENTS

The opacity of 24 hour specimens of ASPA IV and De Trey's ASPA has been measured using a reflectometer. Their $C_{0.70}$ values ranged from 0.68 to 0.69 (Kent et al, 1973; Crisp and Wilson, 1973; Wilson, 1977; Council on Dental Materials and Devices, 1979). The luting consistency, ASPA IVA was slightly more opaque with a $C_{0.70}$ value of 0.7 (Wilson, 1977). No quantified data on the colour of the other commercial glass ionomer cements are available in the literature.

The glass ionomer cement resembles the silicate cement in possessing a degree of translucency, but has a slightly higher $C_{0.70}$ opacity (Kent et al, 1973). The translucency, which is related to the physical nature of the cement powder (Kent et al, 1973), is generally considered to be insufficient for a fully aesthetic restoration of large labial cavities (Wilson, 1977). Wilson (1977) considered the glass ionomer cements to be less translucent than most of the modern composite filling materials.

A decrease in the potential translucency results if the cement is contaminated with water in the first 60 minutes after placement (Mount, 1981; 1982). In addition, dehydration during the first 60 minutes resulted in cracks and craze patterns on the restoration (Mount, 1981; 1982). McCabe et al (1979) tested for ultra-violet colour stability and found no colour change after ultra-violet radiation for 24 hours.

A number of clinical studies have reported that ASPA was not sufficiently translucent for the restoration of anterior teeth

(McLean and Wilson, 1977,c; Smales, 1981,b; Flynn, 1982). There are no reports in the current literature on the clinical assessment of the colour of the newer glass ionomer cements.

3.11 THE CLINICAL SURFACE OF GLASS IONOMER CEMENTS

The surface finish and abrasion resistance of the cement are important clinical considerations as these properties influence plaque retention, the uptake of stains and the durability of the cement. The surface finish and abrasion resistance of glass ionomer cements are discussed in 3.11.1 and 3.11.2.

3.11.1 *Surface finish*

It has been suggested that surface finishing should not be carried out prior to 24 hours after insertion (Mount and Makinson, 1978; Mount, 1981; 1982). The Council on Dental Materials and Devices (1979) recommended the finishing of these cements with sharp knives, scalers or excavators in preference to the use of rotary instruments. In contrast, Smales and Joyce (1978) reported that finishing with a scalpel produced a rough, pitted surface. Smales and Joyce (1978) also found that ASPA polymerized in contact with a matrix showed a granular, irregular surface with more air entrapment than Concise. The smoothest surface for ASPA was obtained with a "hand-held dry silicon carbide disc". Surfaces finished with the silicon carbide disc had a smooth, undulating surface with some scoring of the surface by the abrasive. This surface also had a smeared appearance which may have accounted for the smoothness and lack of exposed air bubbles.

It is currently recommended that finishing procedures (at 24 hours) should initially be carried out under a fine water spray with fine diamonds or steel finishing burs (Mount, 1981; 1982). The final finish is achieved with the use of silicon mounted points, white alpine

finishing points and graded silicon carbide discs (Charbeneau and Bozell, 1979; Mount, 1981; 1982). Where a water spray is not used, a water soluble lubricant should be used to prevent dehydration (Charbeneau and Bozell, 1979). Mount (1981) also advocated the use of a polishing paste for final finishing of the restoration.

Smales (1981,a) found that the surface roughness of ASPA and Concise (a conventional, relatively coarse composite resin) were not significantly different from each other. However, both ASPA and Concise had significantly greater surface roughness than amalgams. He also reported that ASPA retained significantly more plaque than any of the other materials tested.

Mount and Makinson (1978) reported that the surface finish of glass ionomer cements was well maintained after 12 months in the mouth. In contrast, Charbeneau and Bozell (1979) found, in approximately one-third of their restorations, that the surface roughness increased over a period of six months.

3.11.2 *Abrasion resistance*

Resistance to toothbrush and/or dentrifice abrasion is an important property of glass ionomer cements as one of their major applications is in the restoration of abrasion or erosion type cavities in the cervical region of teeth.

McCabe et al (1979) found that De Trey's ASPA had a similar abrasion resistance to a silicate cement (Silicap) when measured *in vitro* using a toothbrush/dentrifice test system. The surface layer of ASPA had a similar abrasion resistance to the subsurface region (McCabe et al, 1979). ASPA was found by Smales and Joyce (1978) to abrade three times more rapidly than Concise (a filled composite resin). Mount (1981, 1982) observed that the abrasion resistance decreased as the powder : liquid ratio decreased.

The results of several clinical studies indicated that ASPA had poor abrasion resistance (McLean and Wilson, 1977,c; Smales, 1981,b; Flynn, 1982). Mount and Makinson (1978) however, stated that the abrasion resistance was satisfactory. McLean and Wilson (1974) reported that only 7 per cent of fissure fillings using ASPA showed any defect in surface contour after 2 years. The surface finish of Class I, Class II and Class V ASPA restorations in primary teeth was reported by Vlietstra et al (1978) to be satisfactory after 13 months.

3.12 OTHER PROPERTIES OF GLASS IONOMER CEMENTS

3.12.1 *Transverse strength*

The 24 hour transverse strengths of ASPA and ChemBond were found by McCabe et al (1979) to be 11.2 MPa and 9.2 MPa, respectively. The transverse strength increased with time and the values at 7 days were 15 MPa and 11.4 MPa, respectively (McCabe et al, 1979).

Glass ionomer cements have lower transverse strengths than silicate cements (16 MPa) (McCabe et al, 1979) and composite resins (85 MPa) (Jones et al, 1977).

3.12.2 *Creep*

The resistance to creep of various luting cements was tested by Wilson and Lewis (1980). The 24 hour creep value for one glass ionomer cement (Fuji Type I) was 0.32 per cent, which was greater than zinc phosphate cements but less than zinc oxide-eugenol (reinforced) cements (Wilson and Lewis, 1980). The glass ionomer cements have a higher resistance to creep than carboxylate cements (Council on Dental Materials and Devices, 1979).

3.12.3 *Consistency*

Crisp et al (1976,b) reported that the disc diameter was 33.5 mm for ASPA IV at a powder : liquid ratio of 3.0:1. The disc

diameter for ASPA IVA was 29 mm at a powder : liquid ratio of 1.67:1 (Council on Dental Materials and Devices, 1979). Although ChemBond had a disc diameter of 19 mm, which was considered to be "acceptable", Fuji Type I exhibited poor spreading characteristics (Reisbick, 1981).

The fluidity of the cement was found to decrease with increased powder : liquid ratio (Crisp et al, 1976,b) and with increased molecular weight of the polyacid (Crisp et al, 1976).

3.13

CONCLUSION

Glass ionomer cements adhere to tooth structure, are considered to be "non-irritant" or "mildly irritant" to pulpal tissues, possess a degree of translucency and some anticariogenic properties. The cements possess strengths which are comparable to dental silicate cements, exhibit quite limited marginal leakage and are less soluble than the other dental cements. Because of these properties the glass ionomer cements have been advocated for a wide range of applications in dentistry. These are discussed in Chapter 4.

TABLE 3.1

24 hour compressive and tensile strengths of some luting cements

Cement	Compressive strength (MPa)	Tensile strength (MPa)
Zinc phosphate *	103	5.5
Zinc oxide-eugenol (EBA) *	55	4.1
Zinc polycarboxylate *	55	6.2
Glass ionomer *	86	6.2
Experimental glass ionomer **	128	8.0 - 9.3
Commercial glass ionomer **	118 - 196	6.2

* From Phillips (1982, p.457)

** As discussed in 3.3.12 and 3.3.21

TABLE 3.2

24 hour compressive and tensile strengths of some
restorative materials

Material	Compressive strength (MPa)	Tensile strength (MPa)
Silicate cement *	180	13.0
Conventional composite resin **	235	45
Microfilled composite resin **	276	32
Glass ionomer cement **	140	2.7
Experimental glass ionomer cement***	164 - 190	11.7 - 13.0
Commercial glass ionomer cement ***	170 - 226	6.7 - 17

* Kent et al, 1973

** Phillips (1982, pp.219; 481)

*** as discussed in 3.3.12 and 3.3.21

TABLE 3.3

Tensile bond strengths* of glass ionomer cements to enamel and dentine

Cement	Cement type	Bond strength (MPa)	
		Enamel	Dentine
ASPA	Restorative	1.0 - 5.5	1.1 - 4.3
ChemFil	Restorative	4.0	—
Fuji Type II	Restorative	4.6	3.3 - 4.3
Ketac	Restorative	—	—
Hy-Bond F	Restorative	—	2.3
ChemBond	Luting	1.3 - 3.9	1.3 - 3.4
Fuji Type I	Luting	—	—
Ketac-cem	Luting	—	—
Hy-Bond C	Luting	—	2.4

* as discussed in 3.4.41 and 3.4.42

TABLE 3.4

Film thickness of some luting cements

Cement	Film thickness (um)
Zinc phosphate *	18
Zinc oxide-eugenol-EBA *	25
Zinc polycarboxylate *	21
Glass ionomer *	24
Commercial glass ionomer **	20 - 25

* From Phillips (1982, p.457)

** As discussed in 3.7.2

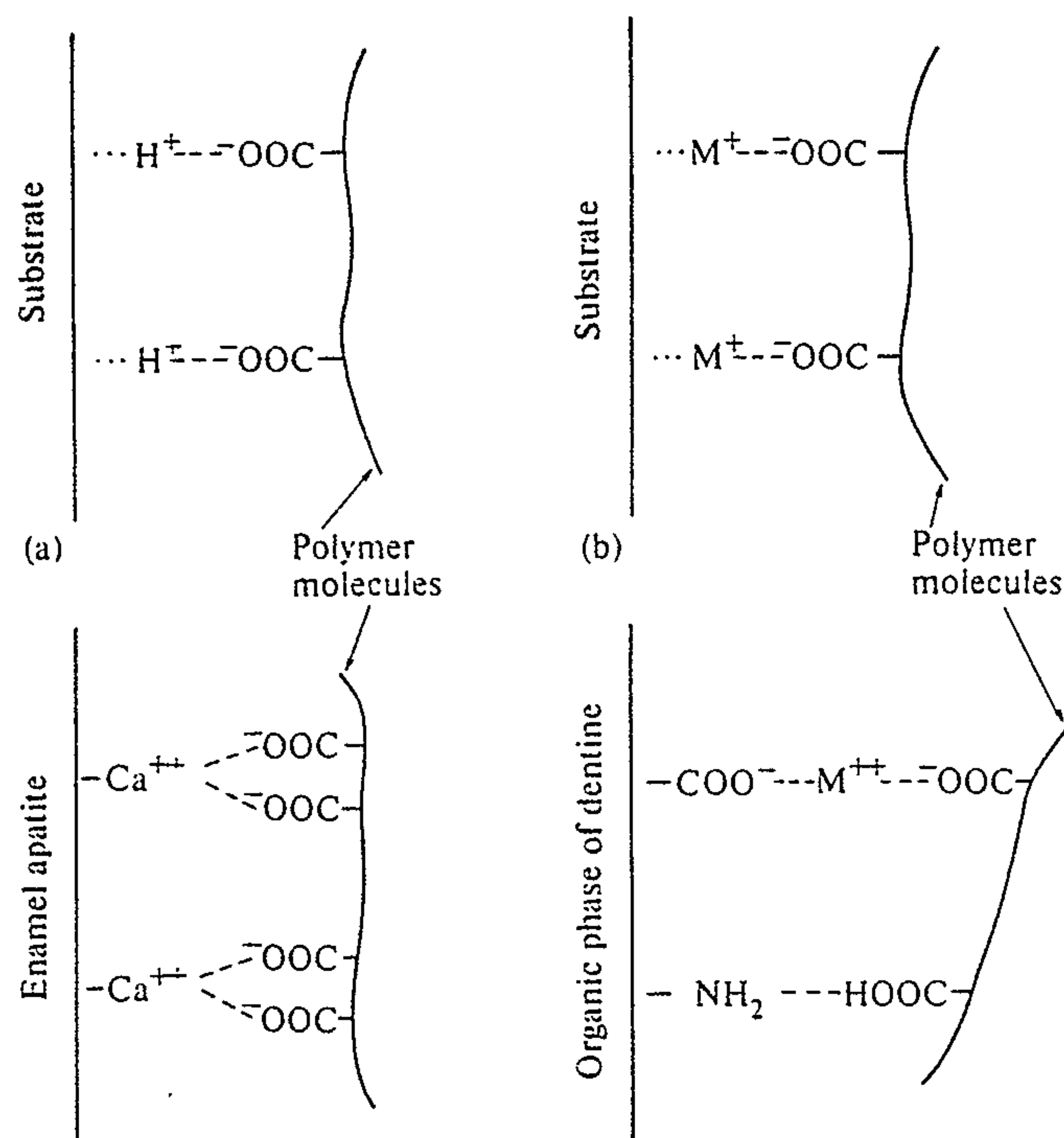


Fig. 3.1 Specific adhesion of polyacrylic acid based materials to tooth substances

- (a) Hydrogen bonds linking polymer to substrate;
- (b) replacement of hydrogen bonds by ionic bonds;
- (c) ionic bridge to enamel apatite;
- (d) bonding to amino acid and carboxyl groups in organic phase of dentine.

(Williams and Cunningham, 1979, p.82)

CHAPTER 4

THE USE AND CLINICAL STUDY OF GLASS IONOMER CEMENTS

- 4.1 Introduction
- 4.2 Clinical applications of glass ionomer cements
- 4.3 A review of clinical studies on glass ionomer cements
 - 4.3.1 The use of glass ionomer cements in the restoration of cervical erosion and abrasion lesions
 - 4.3.2 The use of glass ionomer cements in the sealing and filling of occlusal pits and fissures
 - 4.3.3 The use of glass ionomer cements in the restoration of deciduous (primary) teeth
 - 4.3.4 Other uses of glass ionomer cements
- 4.4 Conclusion

4.1 INTRODUCTION

When the glass ionomer cements were first introduced, the principal applications for the cement were the restoration of abrasion lesions and the sealing of pits and fissures. The number of potential applications for the cement have increased since then and superior formulations have been developed.

4.2 CLINICAL APPLICATIONS OF GLASS IONOMER CEMENTS

Suggested indications for the use of glass ionomer cements have included : the restoration of cervical erosion and abrasion lesions, the sealing and filling of occlusal pits and fissures, the restoration of deciduous (primary) teeth (cavity type not specified by the authors), the restoration of Class III and Class V cavities (principally on root surface cementum or dentine), the repair of defective margins in crown or bridge restorations, and the use as a base and as a luting agent (McLean and Wilson, 1977,b; McCabe et al, 1979; Council on Dental Materials and Devices; Mount, 1982; Wilson and Prosser, 1982). In addition Mount (1981; 1982) suggested that the cement could be used for restoring access cavities

and for short-term protection of newly exposed dentine in traumatized anterior teeth, but this suggestion has, to date, not received any support in the literature.

The use of glass ionomer cements is contraindicated in Class II and Class IV cavities, and in the replacement of large cusp areas in posterior teeth or large labial areas in anterior teeth (Wilson, 1977; Council on Dental Materials and Devices, 1979). The reasons for this include the low strength characteristics and the inadequate translucency of the cements compared with alternative materials.

The manufacturers of several brands of the glass ionomer cements have been more optimistic than most authors and have suggested other uses, in addition to those mentioned previously. The manufacturers of Hy-Bond F and C and Fuji Type I (rather than Fuji Type II) have stated that these cements can be used for core build-up. The manufacturers of Hy-Bond F and C and Ketac-cem have suggested that these cements can be used for multi-band setting in orthodontics. The manufacturer has suggested that Ketac is suitable for the restoration of Class II cavities with extensive caries; it is not clear whether this reference was to primary teeth, permanent teeth or both.

The Department of Pedodontics^a (Craig, 1981) recommended the use of glass ionomer cements for the restoration of proximal cavities in deciduous (primary) molar teeth. No reference was made to the use of these cements for the restoration of anterior primary teeth or as fissure sealants.

4.3 A REVIEW OF CLINICAL STUDIES ON GLASS IONOMER CEMENTS

A number of clinical studies have been conducted to examine the use of glass ionomer cements. The findings of these studies are briefly discussed in the following sections (4.3.1 — 4.3.4).

^a Faculty of Dentistry, University of Sydney.

4.3.1 *The use of glass ionomer cements in the restoration of cervical erosion and abrasion lesions*

Glass ionomer cements have been recommended for the restoration of cervical erosion and abrasion lesions for which minimal, if any, cavity preparation is normally undertaken. McLean and Wilson (1977,c) reported that the majority of failed glass ionomer restorations in these lesions were lost within the first six months of placement; therefore the retention was good. Clinical follow-up studies of these restorations for a period of from six months to three years after placement indicated that the retention rate was 80 to 95 per cent (McLean and Wilson, 1977,c; Charbeneau and Bozell, 1979; Flynn, 1979; Lawrence, 1979; Low, 1981). In contrast, two other clinical studies found that the retention rate of ASPA restorations was poor and ranged from 30 to 50 per cent after three years and six years, respectively (Smales, 1981,b; Flynn, 1982).

The reported reduction in, or elimination of, hypersensitivity by the placement of a glass ionomer cement restoration in a cervical abrasion or erosion lesion has ranged from 90 to 100 per cent (Charbeneau and Bozell, 1979; Low, 1981). Most authors have indicated that ASPA was insufficiently translucent, had poor abrasion resistance and exhibited constant wear and surface deterioration (McLean and Wilson, 1977,c; Smales, 1981,b; Flynn, 1982). McLean and Wilson (1977,c) reported a loss of surface contour and marginal discolouration. Flynn (1982), however, found no marginal discolouration around these restorations, and Mount and Makinson (1978) reported that the abrasion resistance was satisfactory. Most researchers have reported little evidence of caries and none reported any pulpal death directly attributable to the cement (McLean and Wilson, 1977,c; Low, 1981).

There are no reports in the literature on the clinical performance of other commercial glass ionomer cements in cervical erosion and abrasion lesions.

4.3.2 *The use of glass ionomer cements in the sealing and filling of occlusal pits and fissures*

Glass ionomer cements have been recommended for fissure sealing and fissure filling. The cement may be used as a fissure sealant in fissures "which are wider than 100 μ m" (McLean and Wilson, 1977,b; Council on Dental Materials and Devices, 1979). This size of fissure allows a sharp probe to enter the crevice and is easily detectable. In fissure filling, the material is used to fill sticky pits and fissures with minimum cavity preparation. The two-year retention rates of experimental and commercial ASPA as fissure sealants have been stated to range from 15 to 80 per cent (McLean and Wilson, 1974; Williams and Winter, 1976; Williams et al, 1978; Smales, 1981,b). The four-year retention rate was 35 per cent (Williams and Winter, 1981).

McLean and Wilson (1974) reported that, for fissure fillings, only 7 per cent showed any defect in surface contour after two years; marginal adaptation was good and marginal discolouration was not severe. They also reported slight staining in 50 per cent of cases; erosion of the cement was mild after two years. The occurrence of occlusal caries was negligible in fissure sealants and was associated with the partial or complete loss of the cement sealant (McLean and Wilson, 1974). Smales (1981,b), however, reported frequent adhesive fractures of the sealants, rough eroded surfaces, chipped margins and unsatisfactory shade matching.

Studies have found no statistically significant differences in the retention rate and the incidence of caries in pits and fissures

sealed by ASPA and by Nuva Seal (an unfilled resin) (Williams and Winter, 1976). Concise composite resin (a filled resin) used with Enamel Bond (an unfilled resin) was found to have significantly better retention and greater reduction in the incidence of caries than ASPA, when used as a fissure sealant (Williams et al, 1978; Williams and Winter, 1981). No studies have been reported on the use of other commercial glass ionomer cements for this purpose.

4.3.3 *The use of glass ionomer cements in the restoration of deciduous (primary) teeth*

Glass ionomer cements have been recommended for use in deciduous teeth because of their adhesive property which reduced the necessity for classical cavity form in the restoration of teeth in young children. The reduced time required for cavity preparation resulted in a desirable reduction in chair-side time. Plant et al (1977) and Vlietstra et al (1978) advocated a modified Class II cavity preparation with a shallow winged-shaped dovetail, flared outwards through the enamel and cut by a "fissure bur" held at an angle of 45° -- no undercuts were required. The Department of Pedodontics^a (Craig, 1981) has advocated a similar design for cavity preparation except for an additional feature whereby retentive grooves were placed in the buccal and lingual walls of the proximal cavity.

Vlietstra et al (1978) reported no difference in the retention in primary teeth of Class I, Class II and Class V ASPA restorations in cavities with and without undercuts. They reported that the retention rate was approximately 75 per cent after 13 months and that the marginal adaptation, contour and surface finish were acceptable (Vlietstra et al, 1978).

To date, no other studies have been reported in the literature on the clinical performance of different glass ionomer cements in deciduous teeth.

4.3.4 *Other uses of glass ionomer cements*

Despite their being frequently advocated for this purpose, only one study has been reported in the literature on the clinical performance of the glass ionomer cements as luting agents. Reisbick (1981) reported that at 6 months, there were no signs and symptoms associated with the restorations cemented with a glass ionomer cement (ChemBond). No clinical studies are currently available in the literature on the remaining uses of glass ionomer cements mentioned in 4.2.

4.4

CONCLUSION

To date, relatively few papers have reported the results from investigation into the clinical performance of glass ionomer cements.

Currently, glass ionomer cements are most commonly used for the restoration of cervical abrasion and erosion lesions in the root surface regions of permanent teeth and for the restoration of deciduous (primary) teeth. They are increasingly being used as luting agents. The cement is rarely used in high stress regions and, for restorations where tooth-coloured aesthetics is required or where the margin of the cavity is principally on enamel, composite resin is usually preferred.

CHAPTER 5

METHOD USED IN THE INVESTIGATION

- 5.1 Method A -- The investigation of the compressive and tensile strengths of glass ionomer cements
 - 5.1.1 Materials used in the investigation
 - 5.1.2 An investigation of the accuracy of the dispensers provided by the manufacturers
 - 5.1.3 The investigation of compressive and tensile strengths
- 5.2 Method B -- The investigation of the film thickness of glass ionomer cements of luting consistency
 - 5.2.1 Materials and instruments used in the investigation
 - 5.2.2 Method of investigation
 - 5.2.3 Calculation and statistical analysis of the results
- 5.3 Method C -- The scanning electron microscope (SEM) examination of the glass ionomer cements
 - 5.3.1 Introduction
 - 5.3.2 Specimen preparation techniques for SEM examination of glass ionomer cements -- description and investigation
 - 5.3.3 An investigation of the surface finish obtained with various clinical finishing techniques
 - 5.3.4 An investigation of the particle size of a number of glass ionomer cements

5.1 METHOD A

THE INVESTIGATION OF THE COMPRESSIVE AND TENSILE STRENGTHS OF GLASS IONOMER CEMENTS

5.1.1 *Materials used in the investigation*

Six materials were investigated. Three materials are supplied as restorative cements, namely, Ketac, Fuji Type II and ChemFil. The other three are supplied as luting agents, namely, Ketac-cem, Fuji Type I and ChemBond (Table 5.1).

5.1.11 Ketac

Ketac cement is marketed as pre-proportioned Ketac "Applic-Capsules" containing powder and liquid. The capsules are available in yellow, brown and grey shades as indicated by the colour of the plunger and sealing pin of the capsule (Fig. 5.1). The brown shade was used in

all experiments. Prior to mixing, a notch was made with a razor blade around the circumference of the nozzle at a distance of 4 mm from the tip. (A shorter nozzle allowed the material to be placed more quickly into the mould without a loss of gloss from the surface of the cement.)

The "Applic-Capsule" powder-liquid seal (Fig. 5.2) was broken in the "Activator unit" (Fig. 5.3) and was then mechanically mixed in a Silamat^a mixer for 10 seconds and inserted into the "Applier" (Fig. 5.4). After three priming strokes of the "Applier", the sealing pin was removed, the tip of the nozzle was broken off at the notch and the fourth stroke expressed the mixed material from the capsule and applied it into the mould.

5.1.12 Ketac-cem

Ketac-cem is supplied in a 33 g container of powder and a 12 ml bottle of liquid (Fig. 5.5). A plastic powder dispenser and a dosing dropper for dispensing the liquid are also supplied. The required amounts of powder and liquid were dispensed by mass (5.1.23) and mixed with a plastic spatula on a mixing pad for one minute. The powder was divided into three parts and was added to the liquid in an incremental manner. The first one-third was mixed for 15 seconds, the second one-third for 15 seconds, and the first and second halves of the final one-third were mixed for 10 seconds each. The complete mix was spatulated for another 10 seconds giving a total mixing time of 60 seconds. This technique of mixing was indirectly derived from a consideration of all methods suggested by the manufacturers of the glass ionomer cements. It was designed to allow for standardization and ease in mixing.

5.1.13 Fuji Type II

Fuji Type II is marketed in a container of 15 g powder and a

^a Vivadent, Schaan-Liechtenstein, Ivoclar Dist. of Australia Pty.Ltd.

plastic container of 10 g liquid (Fig. 5.6). The powder is available in six shades, shades 21 to 25 (ranging from pale yellow to cervical brown) and shade 28 (a pale grey). A shade guide, cocoa-butter, varnish, mixing pad, spatula and a plastic powder dispenser are also provided. In this series of experiments powder of shade 23 was used. The required powder and liquid were dispensed (by mass) and the cement was mixed for one minute using the incremental technique described for Ketac-cem in 5.1.12.

5.1.14 Fuji Type I

Fuji Type I is supplied in a container of 30 g powder and a plastic container of 25 g liquid (Fig. 5.7). It is supplied together with a mixing pad, spatula, plastic powder dispenser and cocoa-butter. The required powder and liquid were dispensed by mass and mixed as described in 5.1.12.

5.1.15 ChemFil

ChemFil is supplied as a 10 g powder pack and an empty liquid dispenser (Fig. 5.8). The user is required to fill up the liquid dispenser with distilled water prior to use. A powder measure and shade guide are also supplied. A 10 ml container of conditioner (50 per cent citric acid) is available for use, if required. There are four shades of powder (shades 2, 4, 5, 7) which range from light yellow to yellow-grey. The required amounts of powder and liquid were dispensed by mass (5.1.23). Initial study indicated that the recommended powder : liquid ratio of 6.8:1 could not be obtained within the recommended maximum mixing time of 30 seconds. The mix was dry and crumbly and there was no surface gloss. The powder : liquid ratio was gradually decreased until a manageable mix, that was able to be prepared within 30 seconds without a loss in surface gloss, could be consistently obtained. A powder : liquid ratio of 5.2:1 was adopted for all experiments.

The method of mixing was the incremental one suggested by the manufacturer. The powder was divided into three equal parts. The first part was mixed with the liquid in 10 seconds or less; the second part was added and mixed for a further 10 seconds. The third part was added incrementally to the mix over the final 10 seconds.

5.1.16 ChemBond

ChemBond is supplied in a 15 g powder pack and a 15 ml liquid pack (Fig. 5.9). A powder measure and varnish are also supplied. The required amounts of powder and liquid were dispensed by mass. The mixing time was one minute and the technique used was similar to that for Ketac-cem.

The dispensing of the powder and liquid was examined and is discussed in 5.1.2. The powder : liquid ratios used in most of the experimental work are listed in Table 5.4.

5.1.2 *An investigation of the accuracy of the dispensers provided by the manufacturers*

It was observed that most manufacturers, in the commercial literature accompanying the material, made reference to the use of a supplied instrument (dispenser) to dispense the powder from the container to the mixing pad.

With the exception of Fuji Type II and ChemBond, no indication was given by the manufacturers as to whether the dispensed powder should be completely used in preparing the mix or whether a small quantity should normally remain as excess. The manufacturers of Fuji Type II and ChemBond indicated that the dispensed powder was only a guide to obtaining the correct consistency.

5.1.21 Method

Five of the seven materials in Table 1 were examined. These were Ketac-cem, Fuji Type II, Fuji Type I, ChemFil and ChemBond.

Each bottle of powder was inverted and shaken before dispensing. The powder dispenser provided by the respective manufacturer was pressed firmly into the powder and the excess removed with a spatula, except for Ketac-cem where, as recommended by the manufacturer, the excess was removed by placing the dispenser against the plastic segment of the bottle opening, so that the powder was "flush" with the end of the dispenser.

The powder was emptied onto a mixing pad by tapping the dispenser with a spatula. Care was taken to ensure that excess powder was removed from the external surface of the dispenser (before transferring to the pad) and that all powder within the dispenser was placed onto the mixing pad for measuring. Either one or two scoops of powder, dispensed in this way, were then weighed^b to the nearest 0.001 g.

Five dispensings were obtained from each powder measure and the average quantity was calculated (Table 5.2). Four different dispensers were tested for Ketac-cem powder and for Fuji Type I powder. Five different dispensers were tested for each of the remaining glass ionomer cement powders.

Liquid was dispensed by holding the liquid bottle vertically downwards and gently squeezing it. Care was taken to ensure that the top of the dropper was always free of air-bubbles. In the case of ChemFil, care was taken to ensure that the liquid did not run back up the metal insert. If this occurred, the insert was dried with tissue paper. Either one or two drops were dispensed as recommended by the manufacturer. The quantity of liquid was then weighed to the nearest 0.001 g.

Five measurements were obtained from each bottle and the

^b Mettler CH-8606 Greifensee - Zurich, Switzerland.

average was calculated (Table 5.2). Four bottles of each of Ketac-cem and Fuji Type I and five bottles of each of the remaining glass ionomer liquids were tested (Table 5.2).

5.1.22 Results and discussion

The results are presented in Table 5.2. The variation in the quantity dispensed by a particular dispenser, the variation between different dispensers and the variation in the measured powder:liquid ratios are discussed.

5.1.221 Variation in the quantity dispensed by a particular dispenser

Table 5.2 presents the results for the testing of the variability in the dispensing of powder and liquid. Variation in the quantity dispensed by a particular dispenser is illustrated by the fact that the standard deviation for the various types of dispensers, ranged from approximately 0.002 g to 0.012 g for Ketac-cem and Fuji Type I liquid dispensers, respectively. For the powder dispensers, the standard deviation ranged from approximately 0.004 g (Fuji Type II) to 0.010 g (Ketac-cem).

5.1.222 Variation between different dispensers

There was also variation between different dispensers supplied for the same material. For example, for the ChemFil powder dispensers, the quantity of powder dispensed ranged from a mean of 0.240 g for dispenser No. 1, to a mean of 0.213 g for dispenser No. 5. In contrast, there was little difference between ChemFil liquid dispensers.

5.1.223 Variation in the measured powder : liquid ratios

The maximum and minimum powder : liquid ratios for each material were calculated using the data in Table 5.2. The maximum possible powder : liquid ratio was calculated by dividing the maximum powder by the minimum liquid. For example, for Ketac-cem the maximum possible powder : liquid ratio was calculated by dividing the maximum

powder (0.236 g) by the minimum liquid (0.071 g). The minimum possible powder : liquid ratio was calculated by dividing the minimum powder by the maximum liquid.

The recommended and measured powder : liquid ratios are compared in Table 5.3. In general, the measured maximum and minimum powder : liquid ratios possible were approximately 2 to 17 per cent greater or less than the recommended ratios. The notable exception was Fuji Type II where the relative quantities of powder and liquid dispensed appeared to have no relationship to the recommended ratio. It is of interest that, for both Fuji Type I and Fuji Type II, both the measured maximum and minimum powder : liquid ratios were greater than the recommended ratios.

5.1.23 Conclusions

Although it is not clear exactly how the manufacturers intend the dispensers should be used, it is evident that gross inaccuracies in powder : liquid ratios could occur if the manufacturers' techniques of dispensing were followed. Because of the potential size of these inaccuracies, the clinical performance of the material could be affected; decreased powder : liquid ratios produced cements with low strengths and high solubility (3.3.15; 3.6.4); increased powder : liquid ratios may result in cements with a greater film thickness.

To ensure accuracy and reproducibility of the results in this investigation, the dispensers provided by the manufacturers were discarded and the quantities of powder and liquid used for specimen preparation were dispensed by mass (to the nearest 0.001 g).

The powder : liquid ratios used in this investigation (strength, film thickness and surface finish) were, unless otherwise stated, the recommended ones except for ChemFil where a powder : liquid ratio of

5.2:1 was used (Table 5.4). Where a range was indicated by the manufacturer (Fuji Type II and Fuji Type I), the upper limit of the range was used. The powder : liquid ratios of specimens used in scanning electron microscope study were similar to those for the strength tests.

5.1.3 *The investigation of compressive and tensile strengths*

The rate of development of compressive and tensile (by diametral compression) strengths were investigated.

5.1.31 Specimen preparation

The cements were mixed as described in 5.1.1 according to the powder : liquid ratios described in 5.1.23 and presented in Table 5.4. Times were calculated from the start of mixing. The mixed cement was immediately placed into stainless steel split moulds, 4 mm in diameter and 8 mm high, which were clamped tightly together with G-clamps.

Techniques for placing the cement into the mould with the minimum incorporation of air-bubbles were examined. The technique of condensing or packing the cements into the mould was unsuitable as the cement adhered to the plugger. It was found that the best technique was to insert the cement with a "wiping action".

The mould surface had previously been painted with a thin solution of wax in chloroform to prevent the cement from adhering to the mould. After insertion, a glass slide was placed on the top of the clamped split mould to ensure that the cement was thoroughly "condensed" into the mould. Approximately two minutes after mixing commenced, the whole apparatus was placed into an oven at $37 \pm 1^{\circ}\text{C}$. The apparatus was removed from the oven at 7 minutes (for a restorative material) or 12 minutes (for a luting material). The ends of the specimen were trimmed "flush" with the surface of the

mould with a razor blade, painted with varnish^c and the specimens were replaced into the oven. Five minutes later, the specimen was removed from the oven and from the mould, and painted with a layer of varnish which was dried in compressed air. The specimen was then placed in distilled water and stored at 37°C. [Crisp et al (1976,a) noted that specimens stored in paraffin had greater compressive strength than those stored in water.] The tensile strength specimens were stored in distilled water until the time of testing.

The ends of the compressive strength specimens required preparation before testing. These specimens were removed from the oven at 20 minutes and the two ends of each specimen were manually planed flat (and perpendicular to the long-axis of the specimen using a metal holder) with 600 grade wet or dry silicon carbide paper^d lubricated with propylene glycol. The specimen was rotated one quarter-turn once every few strokes. The ends of the specimen were revarnished and dried, the specimens were replaced in distilled water in the oven until the time of testing.

5.1.32 Times of testing

Specimens for compressive and tensile strength experiments were tested at 30 minutes, 1, 2, 8 and 24 hours and at 1 week (except for ChemFil and ChemBond which were not tested at 1 week). In addition, compressive strength specimens were also tested at 5 hours. Fuji Type I (powder : liquid ratio 1:1) was unable to be tested for compressive strength at 30 minutes because of excessive flow. Instead, it was tested at 45 minutes, 1 and 24 hours.

5.1.33 Testing the specimens

A Hounsfield Tensometer^e with a cross-head speed of 0.3 mm/min

^c Fuji Varnish, G-C Dental Industrial Corporation, Tokyo.

^d 3 M Company, Minnesota, U.S.A.

^e Tensometer Ltd., Croydon, England.

was used for the testing of compressive and tensile strengths. A small disc of damp filter paper was placed between each end of the specimen and the crushing heads to reduce the spread of the results arising from surface roughness of the ends of the specimens in the compressive strength tests (British Standards Specification for dental glass ionomer cements, Brit. Stand. 6039:1981)^f. The success of this technique (using damp filter paper) was confirmed by the observations of this researcher.

The Diametral Compression test, used principally in the testing of concrete, coal and rock was first applied to dental materials by Eden and Waterstrat (1967) using amalgam and by Phillips et al (1968) for base forming materials. It has been widely used for the testing of the tensile strength of glass ionomer cements (Crisp et al, 1975; McLean and Wilson, 1977; Wilson, 1977; Vougiouklakis and Smith, 1982). Mitchell (1961) observed that this test is simple and that the results were in good correlation with other more complex tension testing, while Addinall and Hackett (1965) considered that the values obtained tended to be fairly low.

In this test, cylindrical specimens, identical with those used in compressive strength tests, are compressed diametrically between the two flat platens by the testing machine, causing the specimen to fracture along the diametral plane joining the points of contact of the specimen with the platen (Mitchell, 1961; Rudnick et al, 1963). The placement of a "cushion material" between the specimen and the platen promotes a uniform distribution of stress by "ironing out" slight surface irregularities and reduces the magnitude of the

^f The British Standards Specification is the only one presently available. The Australian Standards Specification for glass ionomer cements is currently being formulated.

compressive and shear stress (Rudnick et al, 1963). Mitchell (1961) observed that "cardboard plates" were suitable as a "cushion material".

In this investigation, the tensile strengths of specimens identical to those used in compressive strength tests were examined using the Hounsfield Tensometer. Soft cardboard (0.225 mm thick) was chosen as the "cushion material".

5.1.34 Classification of specimens

Despite the care taken in mixing and specimen formation, inconsistencies in the form of voids were at times observed. The specimens were classified according to the number and size of the voids following Jackson's (1971) classification (using silicate cements):

- i) NVS — no apparent voids on the surface
- ii) VOS1 — 1 or 2 voids on the surface of up to 1 mm diameter
- iii) VOS2 — 1 or 2 voids on the surface greater than 1 mm but less than 2 mm diameter
- iv) VOS3 — 1 or more voids of 2 mm or more in diameter.

Jackson (1971) found that specimens from category (iv) routinely gave abnormally low compressive strengths. He also reported that, for recently mixed silicate cements (0.5 - 2 hours old), VOS2 defects tended to reduce compressive strength.

It was decided, based on his evidence, to exclude specimens with VOS2 defects from early compressive strength testing. Specimens with VOS3 defects were discarded without testing.

During the investigation, specimens with defects greater than the VOS1 category were seldom obtained.

5.1.35 Calculation and statistical analysis of the results

Sufficient specimens were tested to obtain five readings within 15 per cent of their mean. The mean of the five readings and the

standard deviation were calculated. The standard deviation "sd" is a measure of the deviations of readings from a mean value. The standard deviation was calculated using the expression (Alder and Roessler, 1964),

$$sd = \left[\sum (x - \bar{x})^2 / (n-1) \right]^{1/2}$$

where x was the value for a single specimen, $\bar{x}$ was the mean value for n specimens, and n was the number of specimens.

The Student 't' test was used to determine the significance of the difference between results. In this investigation, a value for t was calculated from the expression (Spiegel, 1961, p.190),

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sigma \sqrt{1/N_1 + 1/N_2}} \quad \text{where } \sigma = \sqrt{\frac{N_1 s_1^2 + N_2 s_2^2}{N_1 + N_2 - 2}}$$

The subscripts "1" and "2" referred to the two groups and N, $\bar{X}$ and s, to the number of values, the mean value and the value for one standard deviation respectively for the particular groups of data.

The differences between means were stated to be statistically significant when the probability (P) of the difference being due to chance was less than one per cent ($P < 0.01$), that is a confidence level of 99 per cent was achieved.

5.2

METHOD B

THE INVESTIGATION OF THE FILM THICKNESS
OF GLASS IONOMER CEMENTS OF LUTING CONSISTENCY

5.2.1 *Materials and instruments used in the investigation*

Four glass ionomer cements of luting consistency, namely, Ketac-cem, Fuji Type I, ChemBond and Hy-Bond C were used in this investigation (Table 5.1). The first three cements were described in 5.1.1.

Hy-Bond C is supplied in a container of 60 g powder and a plastic container of 40 g liquid (Fig. 5.10). A measuring spoon, spatula and mixing pad are also provided. The required amounts of powder and liquid were dispensed by mass. The mixing time was 1 minute and the technique used was similar to that for Ketac-cem (5.1.12).

Optically-flat, square glass cover slips, having a contact surface area of approximately 517.5 mm^2 and a uniform thickness of approximately 0.136 mm, were used. The plates were cleaned with ethanol and dried prior to use.

An instrument manufactured by A. J. Wilcock (Australia) was used for load application. The lower surface of the rod supporting the load of 15 kg was horizontal (and parallel to the base) and was large enough to cover the square glass plates containing the cement. This device applied the load smoothly and with no rotational motion.

A micrometer screw gauge^g was used to determine the thickness of cements and glass plates to an accuracy of 2 μm . Using a stopclock^h,

^g Moore and Wright (Sheffield) Ltd., England.

^h English clock systems, Gt. Britain.

all times were measured from the commencement of mixing.

5.2.2 *Method of investigation*

Two clean glass cover slips were stacked in contact, and the combined thickness was measured at three different sites with the micrometer screw gauge, and an average thickness was calculated (Reading A).

The powder and liquid were dispensed by mass at the powder : liquid ratios shown in Table 5.4. Each cement was mixed for one minute as described in 5.1.12 (at room temperature and humidity). A small quantity of cement was placed in the centre of one of the cover slips with a spatula, taking care not to incorporate air bubbles. The second cover slip was carefully placed over the first. They were then placed in the centre of the base plate of the loading device.

The upper plate was gently lowered, and the placement of the load of 15 kg was commenced at 1 m 50 s. The loading procedure was completed 2 minutes from the commencement of mixing, in accordance with the British Standards Specifications. (In a preliminary study using Fuji Type I, it was found that the film thickness obtained when the load was applied at approximately 2 minutes did not differ significantly from the thickness obtained when the load was applied at approximately 1 m 30 s.)

The glass cover slips, containing the cement, were removed from the device at 9 minutes. The thickness of the two glass plates and the cement film was measured at 10 minutes with a micrometer screw gauge at three different sites and averaged (Reading B). The result was disregarded and the experiment repeated if the cover slips cracked during the process of measurement.

For the testing of film thickness, each material was initially tested at the recommended powder : liquid ratio; where a range was

given, the upper limit of the range was tested initially. The powder : liquid ratio was progressively decreased in stages and, at each ratio, the film thickness was determined. The ratio was decreased to a point where the cement was still "not set" 9 minutes from the commencement of mixing in order to determine the minimum clinically possible film thickness (discussed in 8.3.2) for the particular cement. In this context, the cement was defined as "not set" when, at 9 minutes, excess failed to fracture cleanly away from the cover slips.

5.2.3 *Calculation and statistical analysis of the results*

For each specimen tested, Readings A and B were calculated to the nearest 1 μm . The difference between Reading A and Reading B was the film thickness of the cement. Four such readings were obtained for each cement at each of the powder : liquid ratios tested. The film thickness of each cement at a specific powder : liquid ratio was taken to be the average of these four readings. (The British Standards Specification for dental glass ionomer cements, Brit. Stand. 6039:1981, recorded the average of three readings as the film thickness of a particular cement.) The standard deviation at each ratio was also calculated.

The Student 't' test was used to determine the significance of the difference between results (5.1.35). A confidence level of 99 per cent ($P < 0.01$) was regarded as significant.

5.3

METHOD C

THE SCANNING ELECTRON MICROSCOPE (SEM) INVESTIGATION OF THE GLASS IONOMER CEMENTS

5.3.1 *Introduction*

There is a relative lack of information in the literature on the preparation of glass ionomer cement specimens for scanning electron microscopy. Barry et al (1979) and Vougiouklakis et al (1982) reported the presence of extensive cracks in glass ionomer cement specimens examined under the scanning electron microscope. These cracks were considered to be artifacts caused by the "drying out of the cements in the vacuum of the specimen chamber of the electron microscope" Barry et al (1979). They did not associate the presence of the cracks with the process of coating the specimens prior to electron microscopy.

Cracking of the specimens upon dehydration was anticipated from requirements relating to the clinical use of the material which stressed the importance of protecting the cements from dehydration (Mount, 1981; 1982). The presence of cracks and crazes on specimens exposed to dehydration was confirmed by this researcher.

A preliminary study using mainly Ketac was done to investigate the efficacy of five different techniques in reducing the incidence of cracks. The techniques involved subjecting the polished specimens to :

1. coating within 30 minutes of polishing
2. dehydration in silica gel for three days prior to coating
3. dehydration in serial alcohol dilutions prior to coating
4. dehydration in serial alcohol dilutions followed by further dehydration in silica gel prior to coating

5. dehydration in serial alcohol dilutions followed by critical point drying.

These techniques are described in 5.3.2. Although not markedly superior to the other techniques, Technique 2 (5.3.22) was selected for routine use (with minor modifications) to investigate : a) the surface finish obtained with various clinical finishing techniques (5.3.3), and b) the particle size of various glass ionomer cements (5.3.4).

The specimens were examined in the scanning electron microscopeⁱ with an accelerating voltage of 10 kV. The specimens were examined under various magnifications ranging from X240 to X6,000. Photographs were taken at these magnifications. The use of the scanning electron microscope (SEM) in this investigation is discussed in 5.3.32.

5.3.2 *Specimen preparation techniques for SEM examination of glass ionomer cements -- description and investigation*

A Ketac "Applic-Capsule" was mixed and inserted into the split metal mould, as described in 5.1.31. The specimen was left in the mould, in the oven at 37°C for one hour. It was then removed from the mould and the lower half partially embedded lengthwise in a perspex mount (25 mm in diameter and approximately 5 mm high) with Epimount Compound^j (Fig. 5.11). After a further 24 hours, the specimens were flattened using 200 grade and 600 grade wet or dry silicon carbide paper^k lubricated with propylene glycol. The principal phase of polishing made use of three grades of diamond paste^l (15 µm, 6 µm,

ⁱ JEOL JSM-35C -- Japan Electron Optics Laboratory Co. Ltd., Tokyo.

^j Epirez, Indelab Pty. Ltd., Granville, N.S.W.

^k 3M Co., St. Paul, Minnesota, U.S.A.

^l Metadi diamond compound for metallurgy. Buehler Ltd., Ill., U.S.A.

1 μm), carried on microcloths^m, on a slowly rotating polishing machineⁿ. A lubricant consisting of equal parts of propylene glycol and water was used (Wing, 1965).

The subsequent preparation of the specimens is described in 5.3.21 - 5.3.25.

5.3.21 Technique 1

One specimen was gold-coated 30 minutes after the flattening procedure and examined on the same day under the SEM. Numerous cracks were present within the specimen (Fig. 5.12).

5.3.22 Technique 2

One specimen was placed in silica gel for three days and then gold coated. It was examined under the SEM the next day.

The results indicated that prolonged dehydration of the specimen in silica gel prior to coating, together with a further delay before examination, did not significantly decrease or increase (compared with Technique 1) the number of cracks present in the specimen (Fig. 5.13).

5.3.23 Technique 3

The specimens were prepared as described in 5.3.2 and then subjected to a regime of serial alcohol dilutions to dehydrate the specimen gradually. It was thought that a more gradual rate of dehydration might reduce the incidence of cracks.

Three glass ionomer cements (Ketac, ChemFil and Fuji Type II) were embedded in the one mount. After the surfaces were flattened and polished, the mount was placed in serial alcohol dilutions as follows :

^m Buehler polishing microcloth. Buehler Ltd., Evanston, Ill., U.S.A.

ⁿ Buehler Ltd. Metallurgical Apparatus. Master electric division.

Reliance electric and engineering company, Dayton, Ohio, U.S.A.

Alcohol : water dilution	Time of immersion (hours)
70 : 30	4
80 : 20	17
90 : 10	6
100 : 0	18

The specimens were then gold-coated and immediately examined under the SEM.

There was no difference in the incidence of cracks between the Ketac specimens prepared using Techniques 1 and 2, and those prepared using the method described here (Technique 3) (Fig. 5.14). No difference was found in the incidence of cracks between Ketac, ChemFil and Fuji Type II specimens.

5.3.24 Technique 4

Specimens of Ketac and Ketac-cem were embedded in the same mount and placed in a sequence of alcohol dilutions as follows :

Alcohol : water dilution	Approximate time of immersion
70 : 30	3 days
80 : 20	4 hours
90 : 10	5 hours
100 : 0	3 days

The mount was then removed and placed in silica gel for four days before coating. It was examined the next day.

The aims of this experiment were to determine whether prolonged immersion in serial alcohol dilutions, followed by dehydration in silica gel, reduced the incidence of cracks, and also to discover any differences in the incidence of cracks in restorative and luting cements.

The results indicated that there was no significant difference in the incidence of cracks obtained by this method of preparation compared with methods described in 5.3.21 - 5.3.23 (Fig. 5.15). No difference in the incidence of cracks was observed in the restorative (Ketac) and luting (Ketac-cem) cements.

5.3.25 Technique 5

One specimen was placed in a series of alcohol dilutions as follows :

Alcohol : water ratio	Time of immersion
70 : 30	1 day
80 : 20	3 hours
90 : 10	3 hours
100 : 0	1 week

The specimen was then subjected to critical point drying^o and gold-coated. It was examined in the SEM several days later.

The reason for examining the effect of critical point drying was because it was thought, that the occurrence of cracking, might be attributable to the surface tension set up as the material underwent dehydration. Subjecting the material to critical point drying avoided these surface tension forces.

^o Nupro Co., Willoughby, Ohio, U.S.A.

The results however indicated that there was no significant difference, in the incidence of cracks, between the specimen prepared by this technique (Fig. 5.16) and specimens prepared using previously described techniques.

5.3.26 Conclusion

The results of this preliminary study indicated no observable difference in the incidence of cracks between specimens prepared using the five techniques described. There was also no observable difference in the incidence of cracks between restorative and luting materials.

For reasons of maximum convenience, the principles outlined in Technique 2 (5.3.22) were therefore chosen for use (with minor modifications) in subsequent investigations.

5.3.3 *An investigation of the surface finish obtained with various clinical finishing techniques*

A smooth surface finish is important to minimize the accumulation of plaque and the uptake of stains in the restorative glass ionomer cements. Because it was anticipated that results would be similar for the three restorative materials (Ketac, Fuji Type II and ChemFil), only Ketac was examined for the effect of finishing techniques on the surface. Ketac was supplied in an encapsulated form with a powder : liquid ratio that was predetermined by the manufacturer.

5.3.31 Method of specimen preparation

The method of specimen preparation was similar to that described in 5.3.2. The specimens were not embedded lengthwise but upright with the uncut surface free of the mount as illustrated in Fig. 5.17. (Prior to embedding, the specimens were shortened by half, to enable their placement in the SEM.) After 24 hours, each specimen was finished

using one of a number of different clinically available finishing techniques (instead of being flattened and polished as described in 5.3.2) :

A--Finished with a low-speed relatively coarse diamond^p, rotating in a forward direction only, in a low-speed handpiece^q (no water spray)

B--Finished with a fine sandpaper disc^r in a low-speed handpiece

C--Finished with a coarse grade sandpaper disc^s in a low-speed handpiece

D--This specimen was prepared by placing the cement into the mould, against which was placed a matrix strip^t, and was embedded with this end upward. The aim was to investigate the surface obtained against a matrix strip.

E--Finished with a white stone^u using high-speed^v and a water spray

F--Finished with a tungsten carbide^w bur using high-speed and a water spray

p 297/016 W, Horico, Germany.

q Kavo "Blue Ring" contra-angle handpiece, West Germany.

r 3M Fine, Zirconium silicate, Dental finishing and polishing discs, Minnesota, U.S.A.

s 3M Coarse, Garnet, Dental finishing and polishing discs, Minnesota, U.S.A.

t Ash Alpine "Melinex" Polyester Matrix strips, Amalgamated Dental, London, England.

u Busch and Co., Germany.

v Kavo super torque, 625 A, West Germany.

w Komet TCB H23008, West Germany.

G--Finished with pumice and glycerine, using a rubber cup^x at low speed for one minute

H--Finished by using a commercial brand of polishing paste^y on a rubber cup at low speed for one minute

The specimens were then dehydrated in silica gel for three days and coated with gold (approximately 20 nm thick) in a sputter coating unit^z. The specimens were placed in a desiccator until the time of observation. Because the preliminary study (5.3.2) indicated that the time of observation was not critical, SEM examination was carried out at the convenience of the operator (within 7 - 10 days of coating).

5.3.32 Method of investigation

The specimens embedded in the perspex mounts were examined in the SEM using the secondary electron emission mode and an accelerating voltage of 10 kV. Each specimen was given an overall examination at a low magnification. The specimen was then arbitrarily divided into four quadrants. Each quadrant was examined through a range of magnifications. Photographs were taken at magnifications of X240, X480, X1,000, X3,000 and X4,800 using the camera which was attached to the microscope. Ilford FP4 Roll Film^{aa} (a non-polaroid type film) was used for photography. Subsequent prints were obtained from the original negatives.

^x Ash Alpine, Amalgamated Dental, London, England.

^y Floran zirconium silicate, 10 per cent stannous fluoride, prophylaxis paste, Creighton Pharmaceuticals, Sydney, N.S.W.

^z Dynavac (modified into a magnetron sputter coating unit) -- Dynavac High Vacuum Pty. Ltd., Victoria, Australia.

^{aa} Ilford Ltd., Basildon, Essex, England.

5.3.4 *An investigation of the particle size of a number of glass ionomer cements*

The particle sizes of the various glass ionomer cements were compared to assess the possibility of a correlation between particle size and strength. In addition to this, the luting cements were examined to determine if there was a correlation between the particle size and film thickness.

The investigation was divided into two parts. The first part involved the examination of unreacted powder particles; the second part involved the examination of the particles size in the set cement.

The unreacted powder particles in four luting materials (Ketac-cem, Fuji Type I, ChemBond, Hy-Bond C) were investigated. The bottle of powder was given a thorough shake before use. A small quantity of powder was placed into the cover of the bottle. The cover, with the powder was inverted over a stub (8 mm diameter, 10 mm high), to which a piece of sticky aluminium tape^{bb} had been previously attached. The excess powder was vibrated off, until only a thin film remained attached to the tape. A drop of 70 per cent alcohol was placed over the powder. The alcohol dissolved the glue on the sticky tape and improved the adhesion of the powder; it also dispersed the powder particles thereby reducing the incidence of "clumping" of the powder. The specimen was gold-coated and examined in the SEM as described in 5.3.32.

The investigation of particle size in the set cement used the seven glass ionomer cements listed in Table 5.1. The powder : liquid ratio used for each material was the same as that used for the strength tests (Table 5.4). Hy-Bond C was prepared at the recommended powder : liquid ratio of 1.5:1.

^{bb} Scotch pressure sensitive tape. 3M Australia, Pty. Ltd., 2169D.

Two methods were used to investigate the particle size in the set cement. The first method was similar to that described in 5.3.2 (the specimens were dehydrated as described in Technique 2). It was found, however, that it was extremely difficult to distinguish the particles from the matrix by this technique (9.3.2).

A second method was used. It was observed in the investigation of the surface finishes, that the surfaces obtained by finishing with either pumice and glycerine or a commercial brand of polishing paste on a rubber wheel, revealed the structure of the set cement. Because of the different abrasion resistance of the matrix and the glass particles, the glass particles protruded from the surface and could be easily distinguished from the matrix. In this investigation, the specimens were prepared as described in 5.3.31 and finished with pumice and glycerine. The specimens were examined as described in 5.3.32.

Glass ionomer cements investigated

Material	Use	Manufacturer	Batch number	
			Powder	Liquid
Ketac	Restorative	Espe Dental Products W. Germany, New York.	1008 (capsules)	
Ketac-cem	Luting		PH22607	LH14256
Fuji (Ionomer) Type II	Restorative	G-C Dental Industrial Corporation, Tokyo.	211211	161211
Fuji (Ionomer) Type I	Luting		251111	161111
ChemFil	Restorative	AD International Limited, London.	AL5681712	-
ChemBond	Luting		AD3381/08	YL681/08
Hy-Bond (Glasionomer) C	Luting	Shofu Dental Manufacturing Company, Kyoto, Japan.	028241	028214

TABLE 5.1

TABLE 5.2

Variability in the dispensing of powder and liquid

Material	Powder			Liquid		
	Number of scoops	Dispenser number	Mass (g) (Mean of 5 tests)	Number of drops	Bottle number	Mass (g) (Mean of 5 tests)
Ketac*						
Ketac-cem	1	1	0.227 (0.005) **	2	1	0.071 (0.003)
		2	0.233 (0.009)		2	0.078 (0.003)
		3	0.236 (0.012)		3	0.077 (0.001)
		4	0.230 (0.013)		4	0.078 (0.001)
Fuji II	1	1	0.181 (0.004)	1	1	0.057 (0.007)
		2	0.178 (0.004)		2	0.052 (0.008)
		3	0.178 (0.003)		3	0.052 (0.005)
		4	0.176 (0.004)		4	0.051 (0.004)
		5	0.173 (0.004)		5	0.055 (0.005)
Fuji I	1	1	0.107 (0.008)	1	1	0.067 (0.007)
		2	0.105 (0.002)		2	0.074 (0.015)
		3	0.104 (0.004)		3	0.060 (0.014)
		4	0.097 (0.005)		4	0.069 (0.013)
ChemFil	2	1	0.240 (0.011)	2	1	0.033 (0.001)
		2	0.223 (0.011)		2	0.032 (0.001)
		3	0.220 (0.007)		3	0.034 (0.001)
		4	0.220 (0.008)		4	0.033 (0.001)
		5	0.213 (0.010)		5	0.034 (0.001)
ChemBond	1	1	0.088 (0.010)	1	1	0.073 (0.004)
		2	0.085 (0.008)		2	0.069 (0.008)
		3	0.090 (0.004)		3	0.077 (0.004)
		4	0.097 (0.005)		4	0.078 (0.007)
		5	0.082 (0.008)		5	0.074 (0.008)

* Ketac supplied in encapsulated form - not measured.

** Value for one standard deviation in brackets.

Recommended and measured powder:liquid (P/L) ratios

Material	Recommended P/L ratios (:1)	Measured P/L ratios (:1)	
		Maximum	Minimum
Ketac	*		
Ketac-cem	3.4	3.32	2.91
Fuji Type II	2.2 - 2.4	3.55	3.04
Fuji Type I	1.3 - 1.4	1.78	1.31
ChemFil	6.8	7.50	6.26
ChemBond	1.2	1.41	1.05

* Ketac supplied in encapsulated form - P/L ratio not provided.

TABLE 5.3

Powder : liquid (P/L) ratios used in the investigation

Material	Recommended P/L ratios (:1)	P/L ratios used for strength tests (:1)	P/L ratios used for film thickness tests* (:1)
Ketac**			—
Fuji Type II	2.2 - 2.4	2.4	—
ChemFil	6.8	5.2	—
Ketac-cem	3.4	3.4	3.4, 3.0
Fuji Type I	1.3 - 1.4	1.4	1.4, 1.2, 1.0, 0.8
ChemBond	1.2	1.2	1.2, 1.0, 0.8
Hy-Bond C	1.5	—	1.5, 1.3, 1.1, 0.9, 0.7

* Refer method (5.2.2)

** Ketac supplied in encapsulated form - P/L ratio not stated by manufacturer.

TABLE 5.4

Figure 5.1 - 5.2

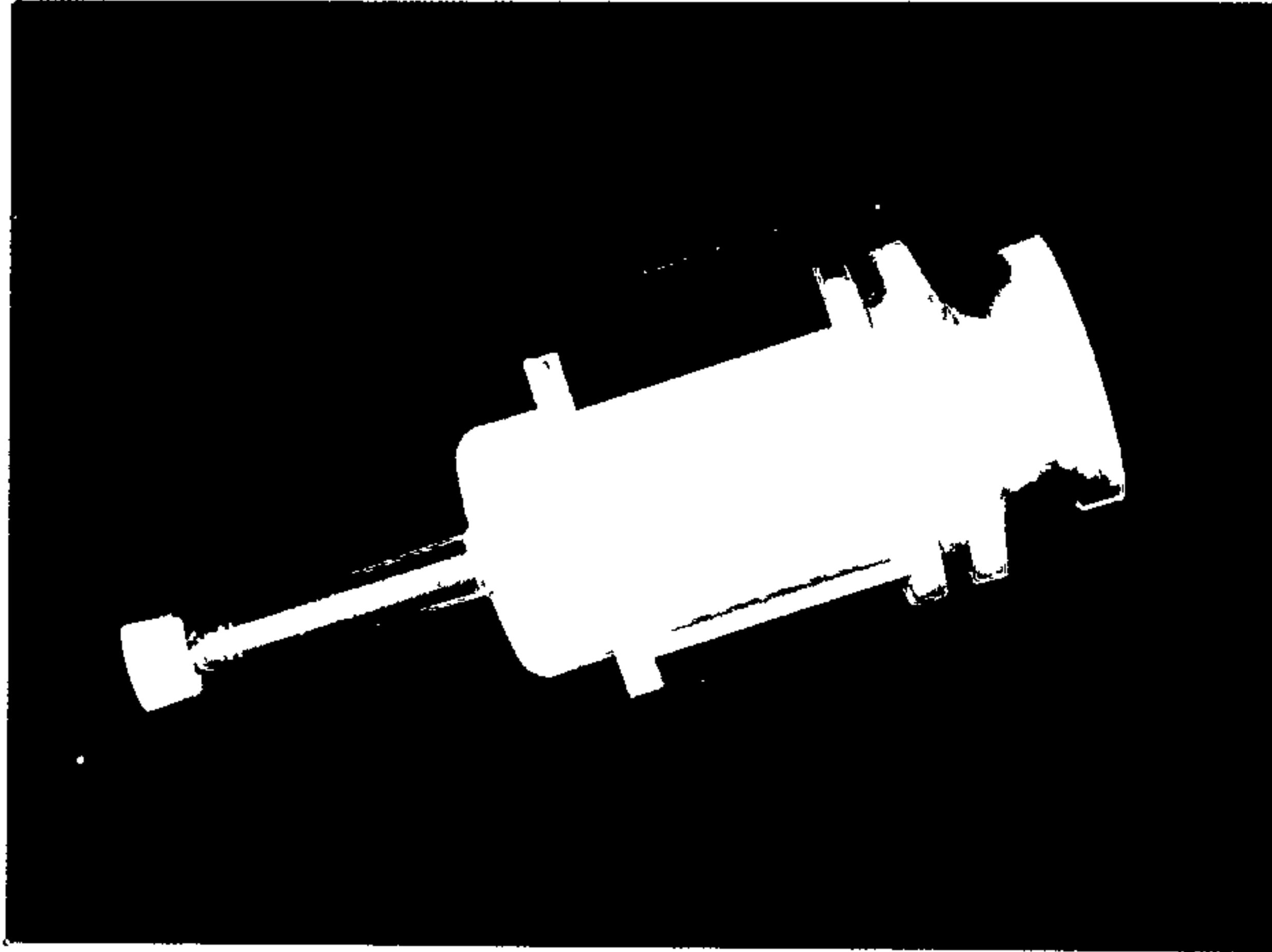


Fig. 5.1 The Ketac "Applic-Capsule".

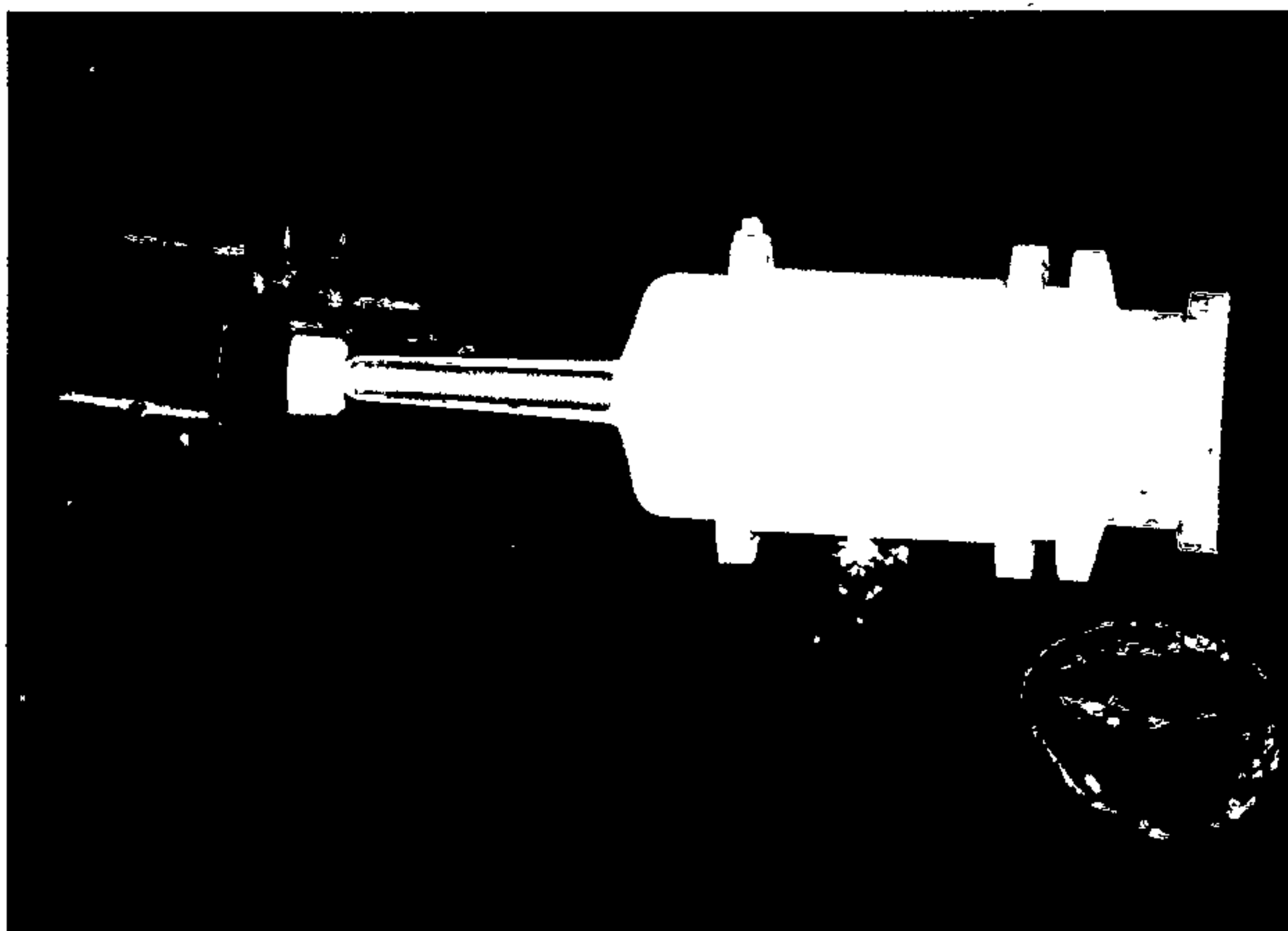


Fig. 5.2 Ketac "Applic-Capsule" dismantled.
The powder is contained in the main capsule
while the liquid is contained in the small
green pack.

Figure 5.3 - 5.4

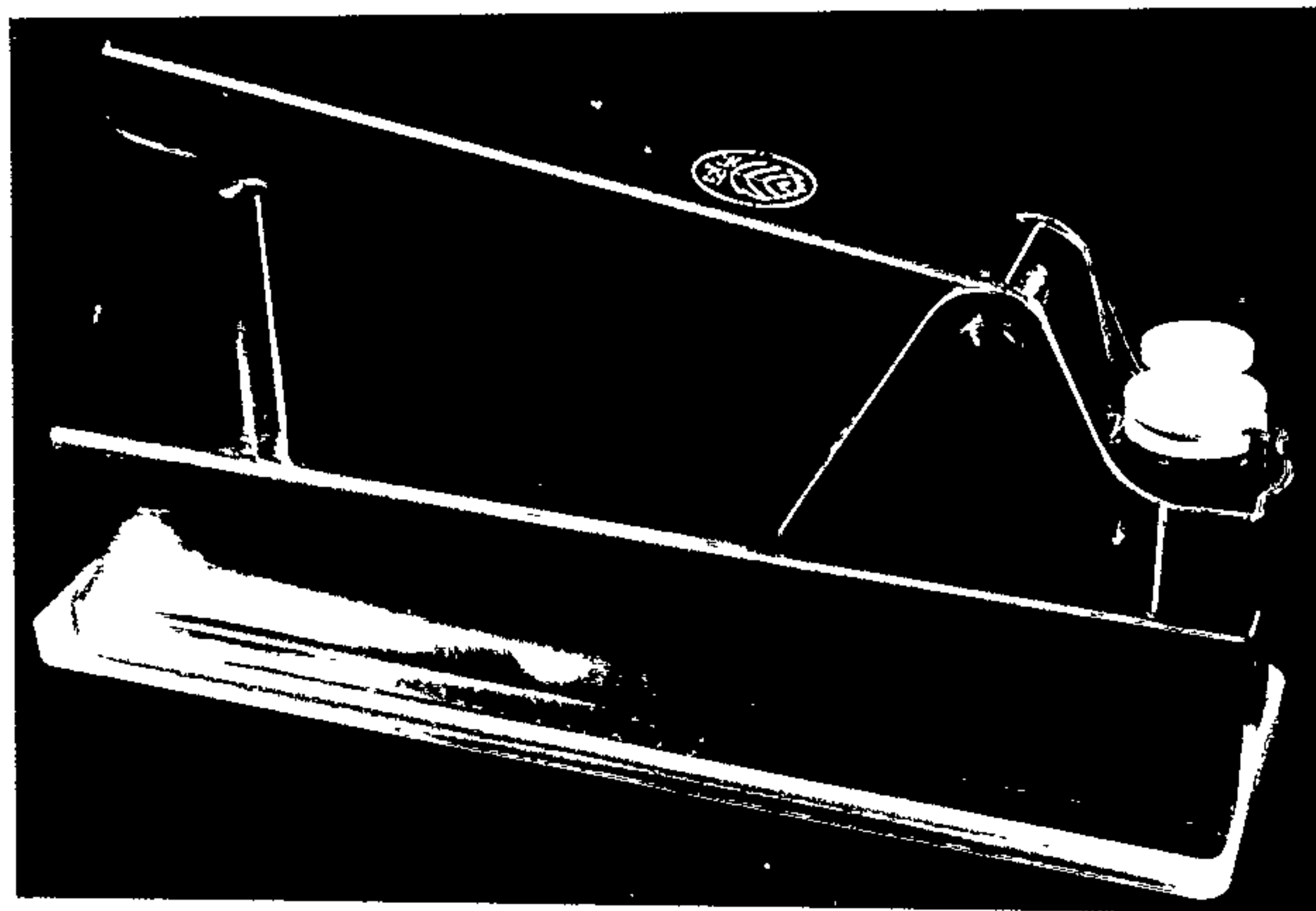


Fig. 5.3 "Activator unit" with Ketac "Applic-Capsule".

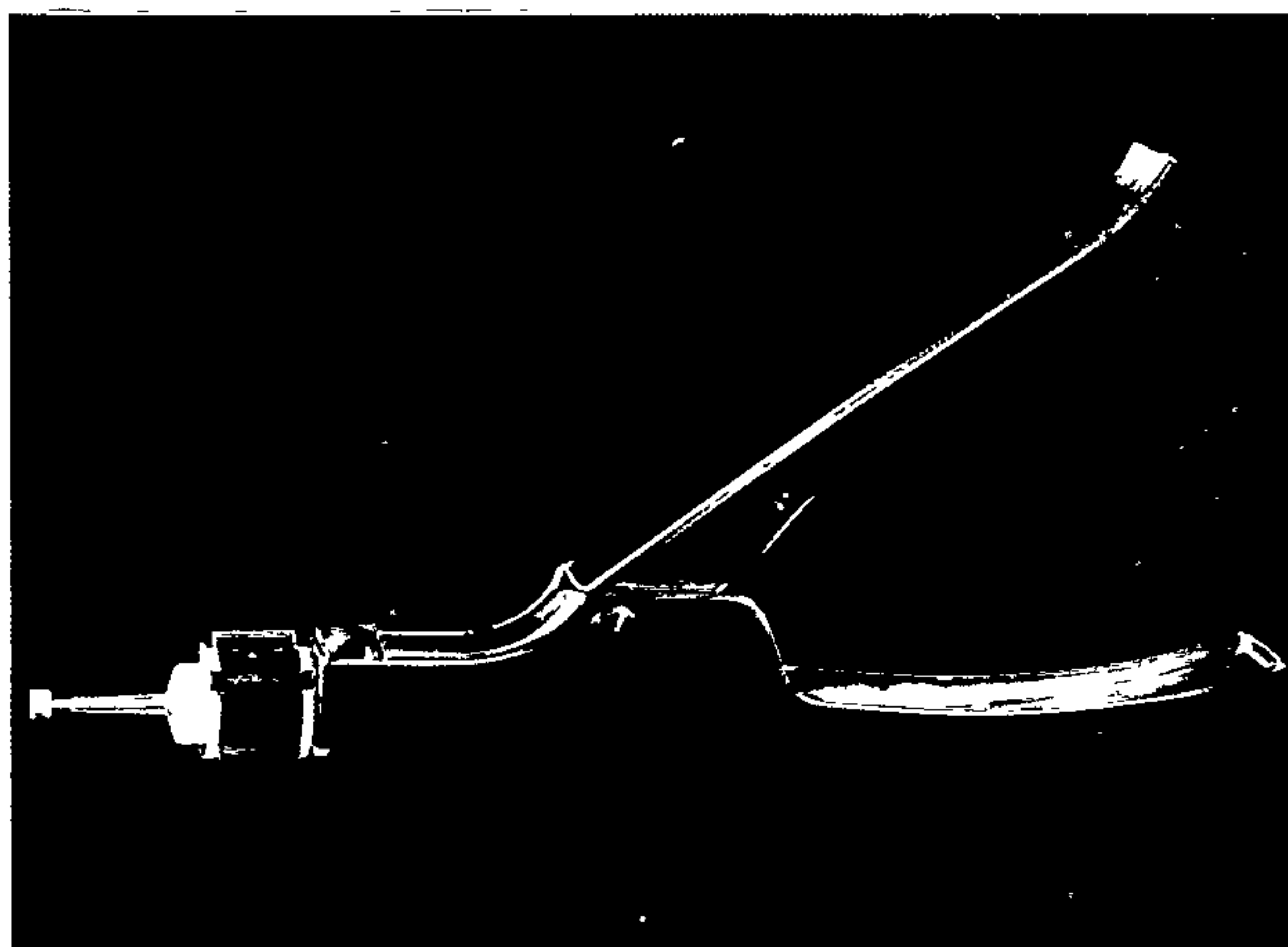


Fig. 5.4 "Applier" with Ketac "Applic-Capsule".

Figure 5.5 - 5.6

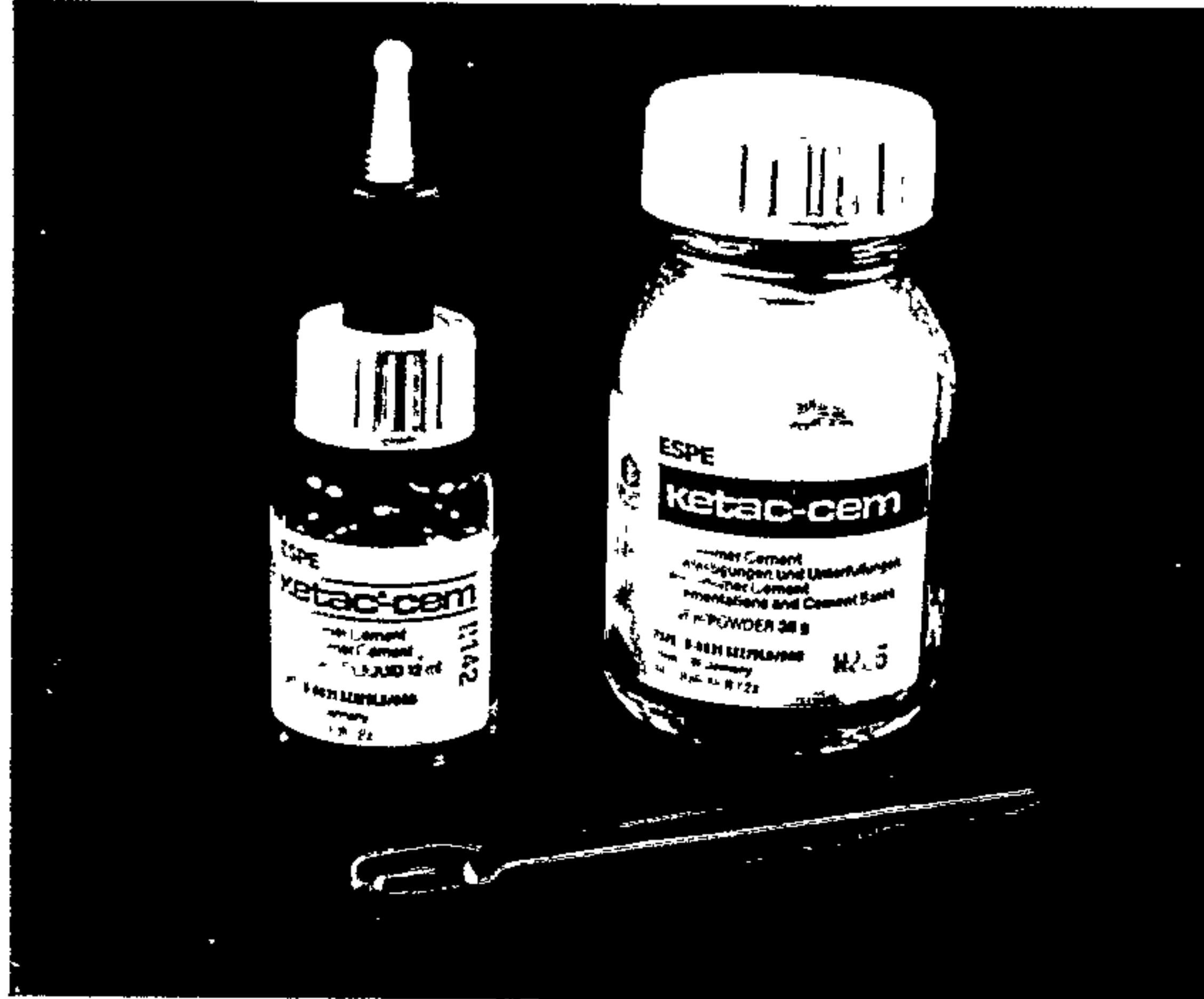


Fig. 5.5 Ketac-cem powder, liquid and powder dispenser.



Fig. 5.6 Fuji Type II powder and liquid, powder dispenser, plastic spatula, cocoa-butter and Fuji varnish.

Figure 5.7 - 5.8

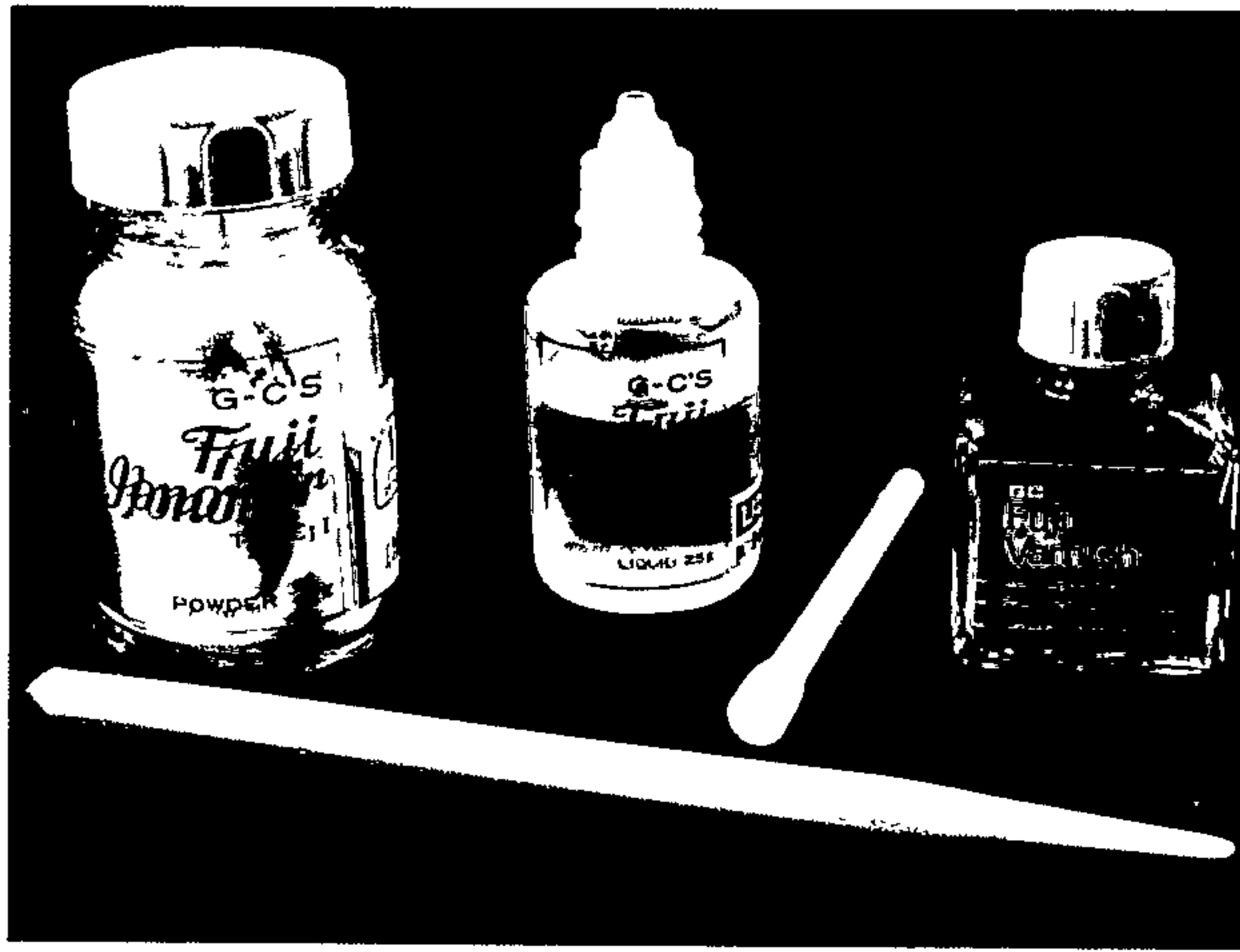


Fig. 5.7 Fuji Type I powder and liquid, powder dispenser, plastic spatula and Fuji varnish.



Fig. 5.8 ChemFil powder and liquid, and powder dispenser.

Figure 5.9 - 5.10



Fig. 5.9 ChemBond powder and liquid.



Fig. 5.10 Hy-Bond C powder, liquid, and powder dispenser.



Fig. 5.11 Perspex mount with glass ionomer cement specimen embedded.

Fig. 5.12 -- Photomicrograph of a glass ionomer cement specimen prepared for SEM examination using technique numbered "1" (5.3.21). Original magnification X1,000.

Fig. 5.13 -- Photomicrograph of a glass ionomer cement specimen prepared for SEM examination using technique numbered "2" (5.3.22). Original magnification X1,000.

Fig. 5.14 -- Photomicrograph of a glass ionomer cement specimen prepared for SEM examination using technique numbered "3" (5.3.23). Original magnification X1,000.

Fig. 5.15 -- Photomicrograph of a glass ionomer cement specimen prepared for SEM examination using technique numbered "4" (5.3.24). Original magnification X1,000.

Fig. 5.16 -- Photomicrograph of a glass ionomer cement specimen prepared for SEM examination using technique numbered "5" (5.3.25). Original magnification X1,000.

Figure 5.12 - 5.16

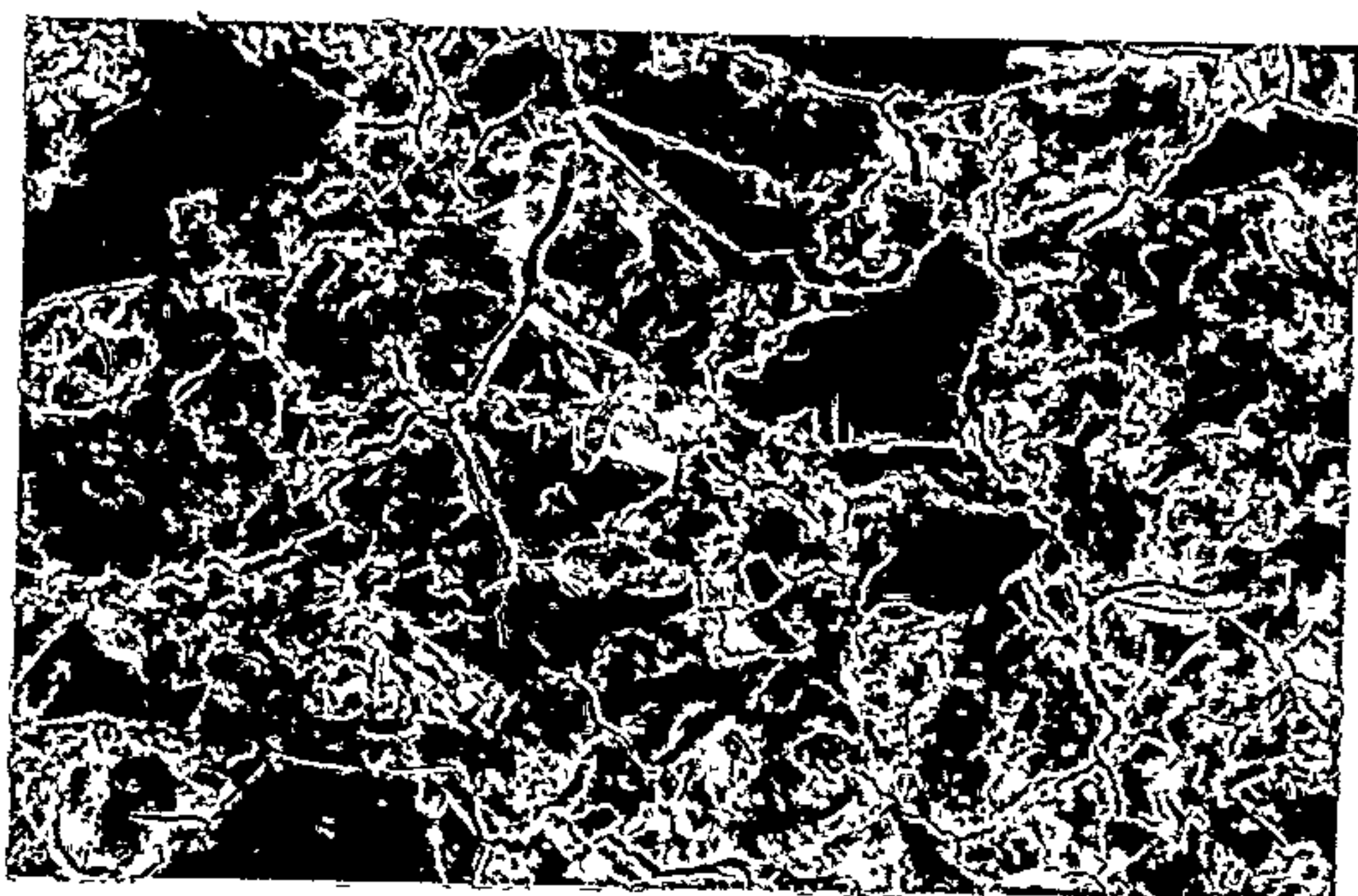


Fig. 5.12



Fig. 5.13

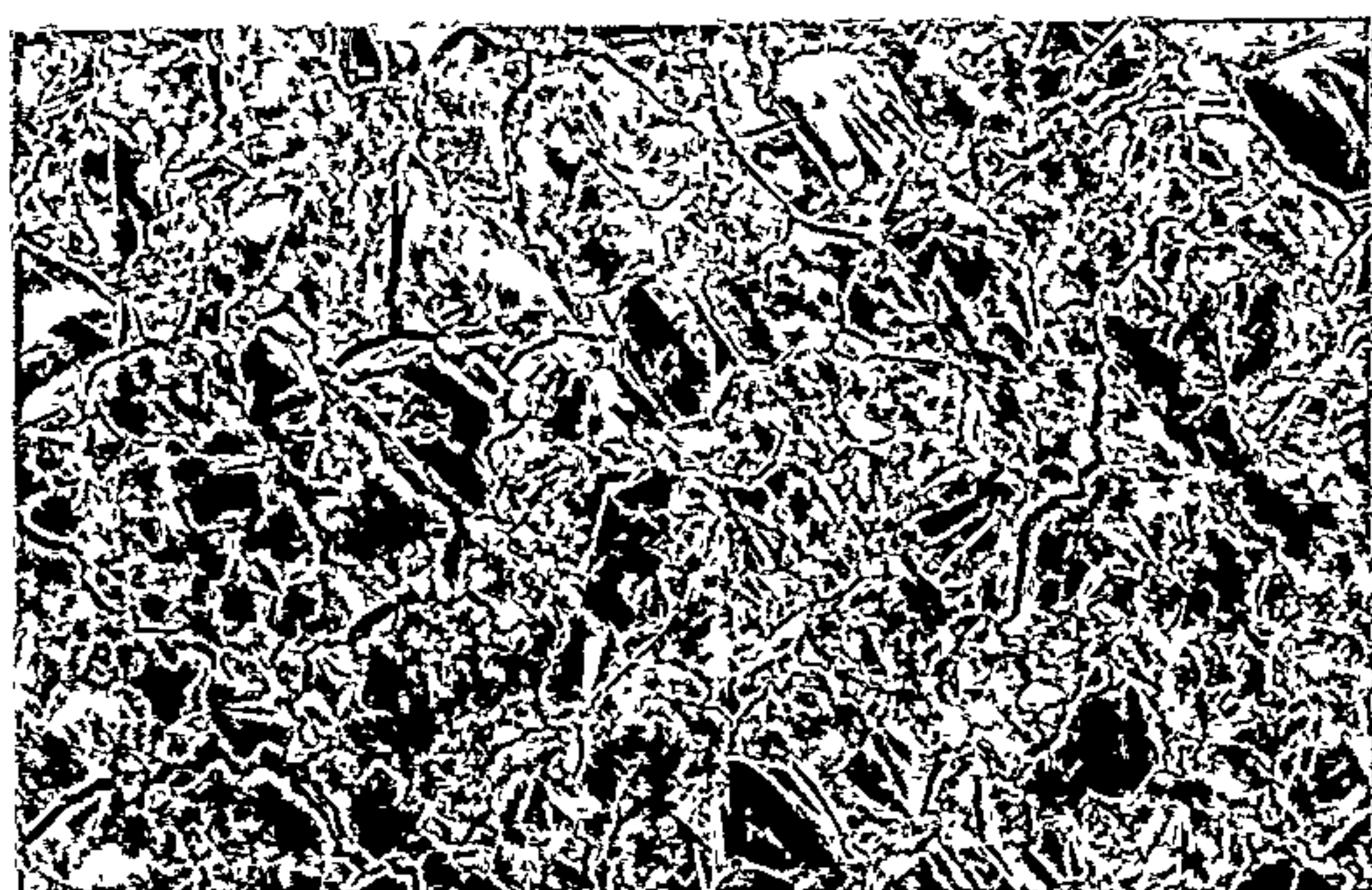


Fig. 5.14

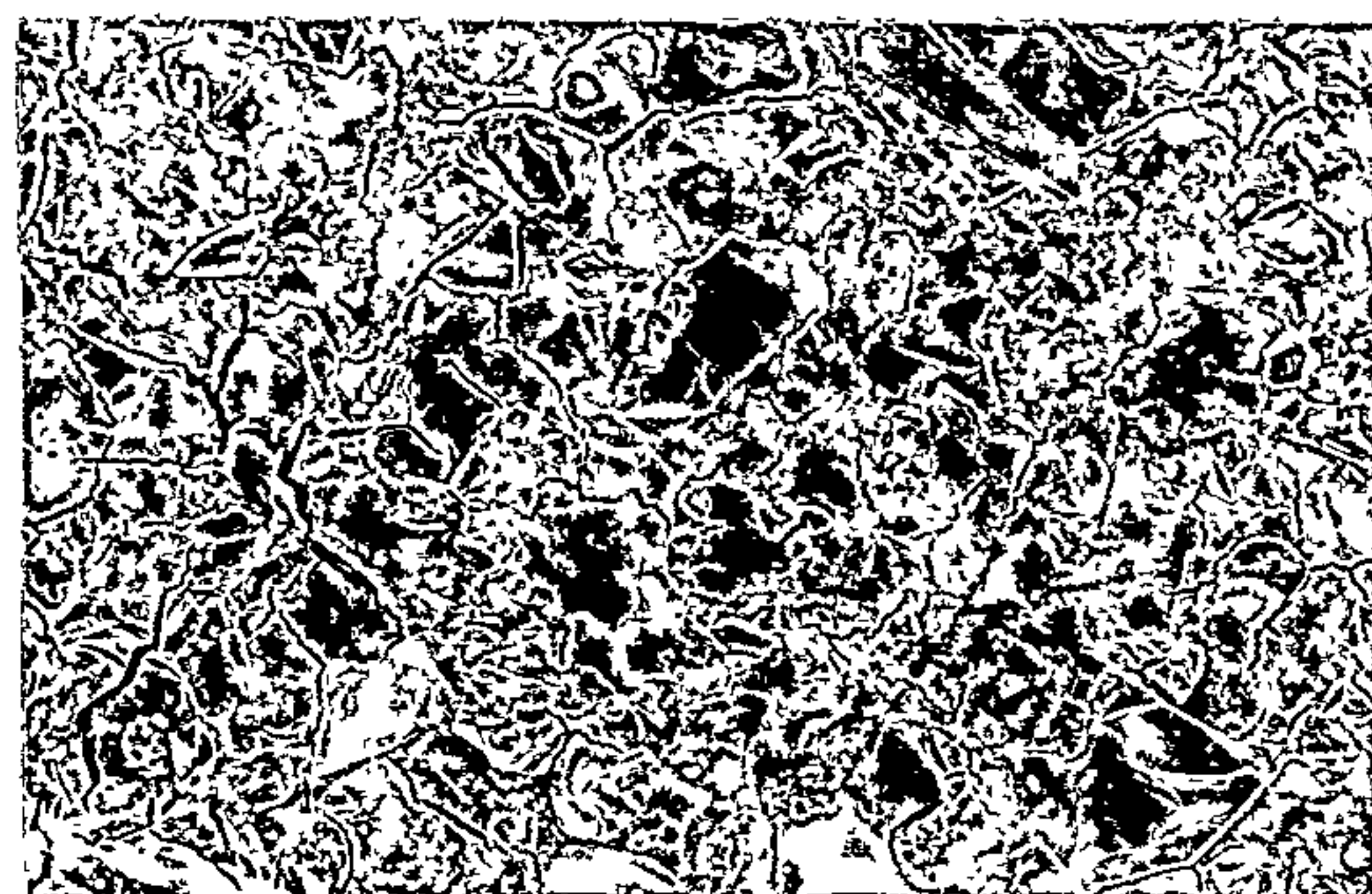


Fig. 5.15

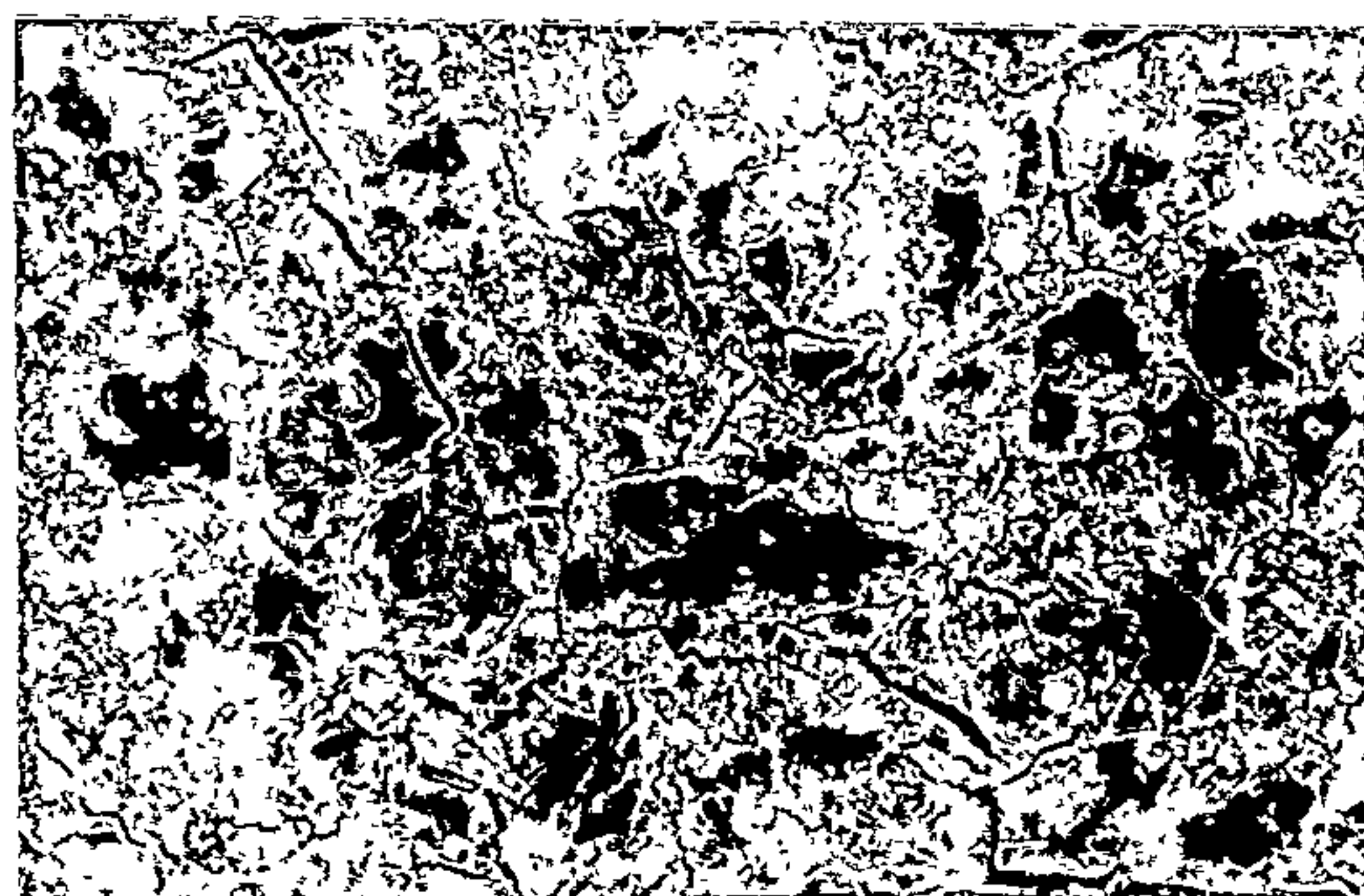


Fig. 5.16

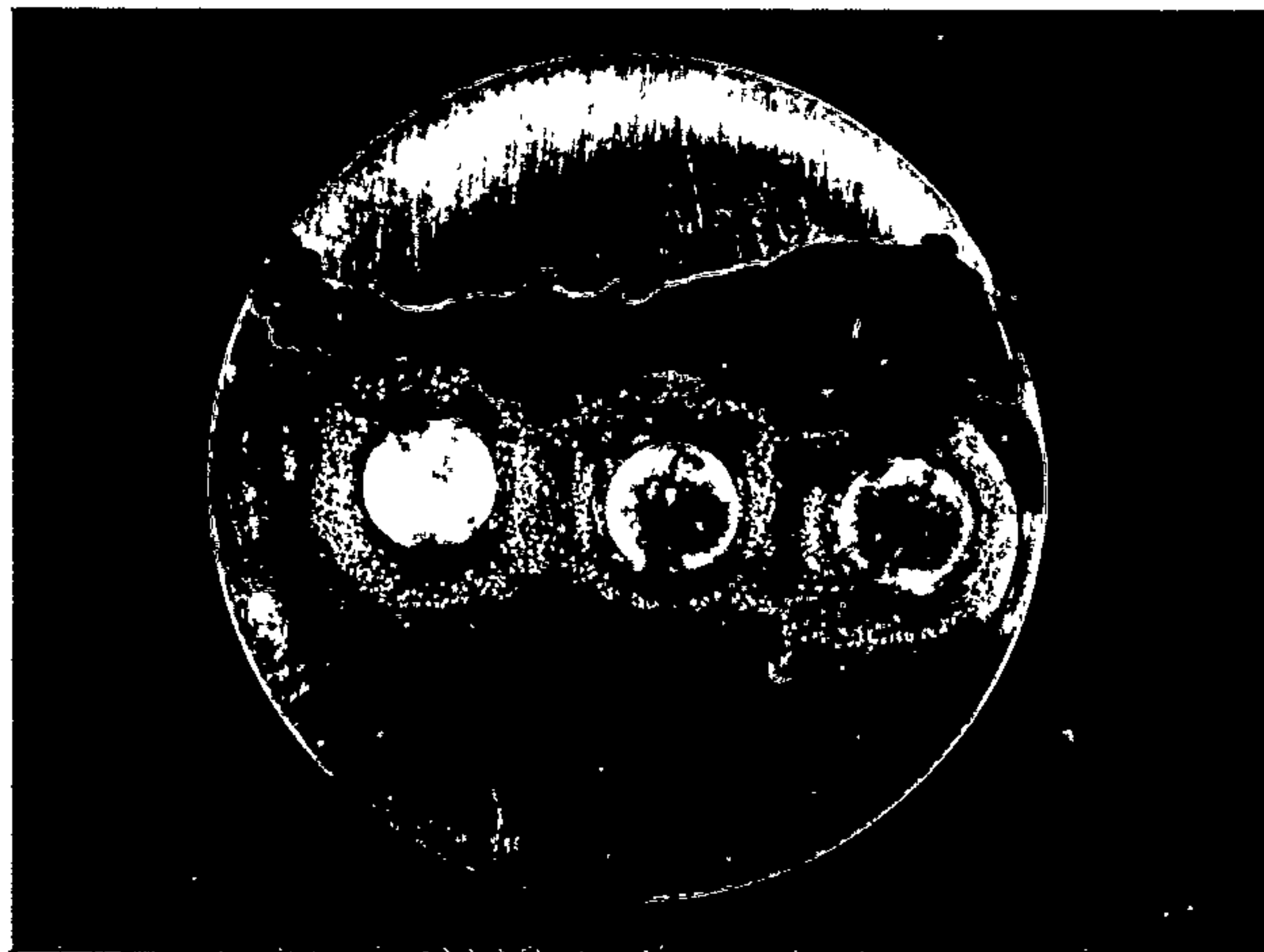


Fig. 5.17 Perspex mount containing three specimens for examination of the effectiveness of various finishing techniques.

CHAPTER 6

COMPRESSIVE STRENGTH OF GLASS IONOMER CEMENTS

- 6.1 Introduction
- 6.2 The development of compressive strength of the restorative glass ionomer cements
- 6.3 The development of compressive strength of the glass ionomer cements used for luting
- 6.4 Comparison of the compressive strengths of the restorative and luting types of glass ionomer cements
- 6.5 Discussion
 - 6.5.1 Experimental method
 - 6.5.2 The compressive strength of the glass ionomer cements
- 6.6 Summary

6.1 INTRODUCTION

The compressive strengths of the glass ionomer cements prepared to the consistencies stated in Table 5.4 are presented in Tables 6.1 and 6.2. In these tables, the connecting bar lines indicate that the difference between the two strengths is statistically significant. The compressive strength results for Fuji Type I at a powder : liquid ratio of 1:1 are discussed in 8.2. The rates of development of compressive strength are illustrated in Fig. 6.1 and 6.2.

6.2 THE DEVELOPMENT OF COMPRESSIVE STRENGTH OF THE RESTORATIVE GLASS IONOMER CEMENTS

The compressive strengths of the three restorative materials tested are presented in Table 6.1 and the rates of development of compressive strength are illustrated in Fig. 6.1.

Ketac had the greatest compressive strength of the three restorative materials and showed significant increases in strength between 0.5 and 1 hour and between 2 and 5 hours. Fuji Type II showed significant increases in compressive strength between 0.5

and 1 hour, 5 and 8 hours and between 24 hours and 1 week. ChemFil had the lowest compressive strength of the three materials tested and showed significant increases in strength between 0.5 and 1 hour, 2 and 5 hours and between 24 hours and 1 week.

All three restorative materials tested showed a significant increase in compressive strength between 0.5 and 1 hour. Only Ketac and ChemFil showed a significant increase in strength between 2 and 5 hours, while Fuji Type II showed a significant increase between 5 and 8 hours. Both Fuji Type II and ChemFil showed a significant increase in strength between 24 hours and 1 week.

The 0.5 hour compressive strength of Ketac is approximately one and one-half times greater than that of Fuji Type II and approximately three times that of ChemFil. Although the 24 hour and 1 week strengths of Ketac were also approximately one and one-half times greater than that of Fuji Type II, the compressive strength of ChemFil increased relatively rapidly within 1 week so that the compressive strength of Ketac at 1 week was only twice that of ChemFil.

6.3 THE DEVELOPMENT OF COMPRESSIVE STRENGTH OF THE GLASS IONOMER CEMENTS USED FOR LUTING

The compressive strengths of the glass ionomer cements used for luting are presented in Table 6.2 and the rates of development of strength are illustrated in Fig. 6.2.

Fuji Type I had the greatest compressive strength of the three materials. Fuji Type I showed a significant increase in strength between 0.5 and 1 hour and between 8 and 24 hours; the 24 hour strength was more than twice that of its 0.5 hour strength. Ketac-cem showed significant increases in compressive strength between 0.5 and 1 hour, 1 and 2 hours, 2 and 5 hours, and between 8 and 24 hours. The

24 hour strength of Ketac-cem was approximately twice that its 0.5 hour strength. ChemBond had the lowest compressive strength of the three materials. It showed significant increases in strength between 0.5 and 1 hour, 1 and 2 hours, 2 and 5 hours and between 24 hours and 1 week. The 24 hour strength of ChemBond was approximately three times greater than its strength at 0.5 hours.

Each of the three luting materials exhibited a significant increase in strength between 0.5 and 1 hour. Both Ketac-cem and ChemBond showed significant increases in strength between 1 and 2 hours and between 2 and 5 hours. Both Ketac-cem and Fuji Type I showed significant increases between 8 and 24 hours; only ChemBond showed a significant increase between 24 hours and 1 week.

The compressive strength of Fuji Type I was approximately one and one-half times greater than that of Ketac-cem at all times of testing and it was approximately three times greater than ChemBond at 0.5 hours. However, ChemBond increased relatively rapidly in strength with time so that at 1 week, the compressive strength of Fuji Type I was approximately only twice that of ChemBond.

6.4 COMPARISON OF THE COMPRESSIVE STRENGTHS OF THE RESTORATIVE AND LUTING TYPES OF GLASS IONOMER CEMENTS

Ketac was approximately twice as strong (in compression) as Ketac-cem at all times of testing. The compressive strengths of Fuji Type I and II were generally comparable at all times of testing. The early strengths (up to one hour) of ChemFil and ChemBond were significantly different, with ChemFil being stronger than ChemBond. After one hour, the differences between the compressive strengths of ChemFil and ChemBond were not significant.

Somewhat surprisingly, ChemFil (a restorative material) was found to be only comparable in compressive strength to Ketac-cem

(a luting material) and significantly weaker than Fuji Type I, another luting material, at all times of testing.

6.5

DISCUSSION

6.5.1 *Experimental method*

Wilson et al (1970) stated that "the compressive strength of cements is taken as a measure of the degree of cementation" (or set). Careful examination of early strength specimens loaded to just short of fracture revealed deformation in the specimens (Fig. 6.3). Bryant (1968) reported that deformation occurred in some base forming materials (Caulk zinc oxide-eugenol and Opatow EBA cements). The flow (deformation) was greatest in cements tested at 30 minutes from the time of mixing, the deformation was only very slight at one hour. Glass ionomer cements with low compressive strengths (ChemBond, ChemFil and Ketac-cem) showed greater evidence of deformation than the stronger cements. Because of the presence of deformation, the compressive strength values obtained at 30 minutes for the glass ionomer cements are probably inaccurate and should not be treated as absolute values. They are of value however, in comparing the early strengths of the various cements. They probably also reflect the setting rate of the cements.

Groffman and Wilson (1981) reported that the incremental method of packing silicate cements into moulds was inferior to the "single-shot" technique because it increased the porosity *within* the specimen. An incremental technique (combined with a wiping action during placement) was used in this investigation because it was found to reduce the incidence of voids *on the surface* of the specimen. However, the use of this technique may have contributed to the lower values obtained in this investigation as compared to some values previously quoted in the literature (3.3.11 and 3.3.12).

6.5.2 *The compressive strength of the glass ionomer cements*

Only data for the experimental and a limited number of commercial glass ionomer cements are currently available in the literature (3.3.12).

The results obtained in this investigation for the commercial glass ionomer cements indicate that, like the experimental glass ionomer cements (Crisp and Wilson, 1973; Kent et al, 1973; Crisp et al, 1976,a; McLean and Wilson, 1977,a), the compressive strength increased with time after mixing. Like the ASPA IV cements (Crisp et al, 1976,a), these commercial glass ionomer cements developed approximately one-half their 24 hour strength in one hour.

The one hour and 24 hour compressive strengths of ChemFil were found to be 36.7 and 67.4 MPa, respectively. These were approximately one-third the value for the one hour (110 MPa) and 24 hour (170 MPa) strength claimed by the manufacturer. The difference in compressive strength may be attributed, in part at least, to the different powder : liquid ratios used. As explained in 5.1.15, a powder : liquid ratio of 5.2:1 was used in this investigation, instead of the recommended ratio of 6.8:1.

The 24 hour compressive strengths of the restorative materials indicated that Fuji Type II and ChemFil were considerably weaker than the experimental ASPA IV cement (164-190 MPa). The 24 hour strength of Ketac (155.3 MPa) was comparable to that of ASPA IV cement. As discussed in 3.3.12, the 24 hour compressive strengths of Fuji Type II and ChemFil were reported by Wilson and Prosser (1982) and Vougiouklakis and Smith (1982) to be 140 and 170 MPa, respectively. The results obtained from this investigation for Fuji Type II (106.3 MPa) and ChemFil (67.4 MPa) were considerably lower. (One cause for the low ChemFil strength has already been suggested; the differences are examined further in subsequent discussion.)

The results obtained for the 24 hour compressive strength of the luting materials tested indicated that Ketac-cem (79.8 MPa) and ChemBond (63.8 MPa) were considerably weaker than the experimental ASPA IVA luting cement (130 MPa -- refer, 3.3.12). The 24 hour strength of Fuji Type I (120.4 MPa) was comparable with that of ASPA IVA. The compressive strengths of Fuji Type I, ChemBond and Ketac-cem have been previously reported to be 170, 120 and 118 MPa, respectively (3.3.12). The 24 hour compressive strengths obtained in this investigation for Fuji Type I, ChemBond and Ketac-cem were 120.4, 63.8 and 79.8 MPa, respectively, which were significantly lower than the values reported in the literature.

The differences between the results obtained in this investigation and the small number of results reported in previous literature may be attributed to one or more potential causes. 1) The manufacturer - introduced modifications and developments in the composition of the powder and liquid of various brands of glass ionomer cements. 2) The size of the specimen tested -- the larger the specimen, the higher the value obtained (Groffman and Wilson, 1981). The specimens used in this investigation were 4 mm in diameter and 8 mm high. The British Standards Specification for glass ionomer cements recommended specimens 6 mm in diameter and 12 mm high. Crisp and Wilson (1973), Kent et al (1973) and Crisp et al (1975; 1976,a) used specimens which were similar in size to the British Standards Specification. Vougiouklakis and Smith (1982) however used specimens which were 3 mm in diameter and 6 mm high. 3) The shape (length:diameter ratio) of the specimen -- the lower the length:diameter ratio, the higher the compressive strength value obtained (Wilson, 1976). Despite the different sizes of specimens reported in the literature, the length:diameter ratio remained constant at 2:1 (Crisp and Wilson, 1973; Kent et al, 1973; Crisp et al, 1975; Crisp et al, 1976,a;

Vougiouklakis and Smith, 1982). The specimens used in this investigation and those specified in the British Standards had a similar length:diameter ratio of 2:1. 4) The storage medium prior to testing (Crisp et al, 1976,a). This investigator, the British Standards Specification, Crisp and Wilson (1973), Kent et al (1973) and Crisp et al (1975) used distilled water as the storage medium. Crisp et al (1976,a) used both paraffin and water as the storage medium. 5) The use or non-use of varnish (Causton, 1981). Varnish was used in the present investigation. The use of varnish was not specified in the British Standards Specification. 6) The cross-head speed used. The present investigator used a cross-head speed of 0.3 mm/min; in contrast, the British Standards specified a cross-head speed of 1.0 mm/min. Although Mahler and Mitchem (1964) and Wing (1961) reported that the cross-head speed influenced values for the compressive strength, Wilson (1976) and Groffman and Wilson (1981) found no difference between results for different cross-head speeds. 7) Differences between operators. Groffman and Wilson (1981) found that the differences between the results of various operators performing the same experiment were highly significant and this was probably due to the packing (into the mould) technique used. The incremental method was found by them to be inferior to the "single-shot" technique, presumably because it increased the porosity of the mix.

It is not possible therefore to compare in detail the compressive strength values obtained in this investigation with the findings of some other investigators because i) there is currently limited data available on commercial glass ionomer cements in the literature, and ii) there is inadequate information provided by some authors on the exact details of their method. For example,

Vougiouklakis and Smith (1982) did not specify the storage medium; both Crisp et al (1976,a) and Vougiouklakis and Smith (1982) did not state the cross-head speed used or whether or not varnish had been applied to the specimens.

The British Standards Specification for glass ionomer cements (British Standards 6039, 1981) has stated that the minimum 24 hour compressive strength should be 125 MPa for the restorative materials and 65 MPa for the luting consistencies. The results of this investigation indicated that, of the three restorative materials tested (Ketac, Fuji Type II and ChemFil), only Ketac met the British Standards Specification for compressive strength. Of the three luting materials examined (Ketac-cem, Fuji Type I and ChemBond), only Ketac-cem and Fuji Type I met the British Standards Specification for compressive strength. However, experimental conditions were different. A different specimen size (12 mm high by 6 mm diameter) and cross-head speed (1.0 mm/min) were used in the British Standard Specification.

6.6

SUMMARY

All materials showed a general increase in compressive strength with time. The rate of increase was greatest in the first one hour, followed by a slower increase in the period of up to one week. Most materials showed at least a 100 per cent increase in strength between 0.5 and 24 hours.

Of the three restorative materials tested, Ketac had the highest and ChemFil the lowest compressive strength. Ketac was significantly stronger than Fuji Type II and was twice as strong as ChemFil. For the luting materials, Fuji Type I had the highest and ChemBond the lowest compressive strength. The compressive strength of the restorative material Ketac was almost twice that

of the luting material Ketac-cem. In contrast, the compressive strengths of Fuji Type II and ChemFil (both restorative materials) were similar to those of their luting counterparts, Fuji Type I and ChemBond, respectively.

Comparison of the results obtained with the findings of other researchers is difficult because of the number of variables that affect the compressive strength and because of the very few other similar studies reported.

Of the six materials tested, only Ketac, Ketac-cem and Fuji Type I met the requirements for compressive strength stated by the British Standards Specification for glass ionomer cements. Experimental testing conditions were, however, different.

Development of compressive strength of glass ionomer cements (restorative)

TABLE 6.1

Compressive strength (MPa) at times after beginning of mixing							
Material	0.5 h	1 h	2 h	5 h	8 h	24 h	1 wk
Ketac	78.2 (7.7)*	95.1 (8.3)	107.5 (7.3)	136 (11.3)	146.2 (7.5)	155.3 (12.7)	177.6 (16.3)
Fuji Type II	56.1 (2.9)	69.6 (5.1)	73.1 (4.9)	74.8 (6.7)	98.5 (3.8)	106.3 (3.8)	118.6 (6.7)
ChemFil	24.0 (1.8)	36.7 (2.2)	39.0 (2.4)	58.5 (3.5)	61.2 (2.7)	67.4 (4.5)	90.0 (9.5)

* Value for one standard deviation in brackets.

┐ The difference between the two values is statistically significant.

Development of compressive strength of glass ionomer cements (luting)

TABLE 6.2

Compressive strength (MPa) at times after beginning of mixing							
Material	0.5 h	1 h	2 h	5 h	8 h	24 h	1 wk
Ketac-cem	37.5 (3.9)*	46.3 (2.9)	56.3 (2.3)	66.4 (5.2)	67.6 (2.8)	79.8 (5.9)	83.3 (3.0)
Fuji Type I	54.0 (5.9)	70.6 (6.2)	77.8 (2.0)	86.7 (9.7)	99.6 (2.0)	120.4 (9.6)	124.6 (9.8)
ChemBond	18.3 (1.3)	28.1 (1.5)	38.1 (2.3)	46.0 (3.8)	54.5 (4.9)	63.8 (4.0)	77.2 (5.4)

* Value for one standard deviation in brackets.

┐ The difference between the two values are statistically significant.

Figure 6.1

Development of compressive strength of glass ionomer cements (restorative)

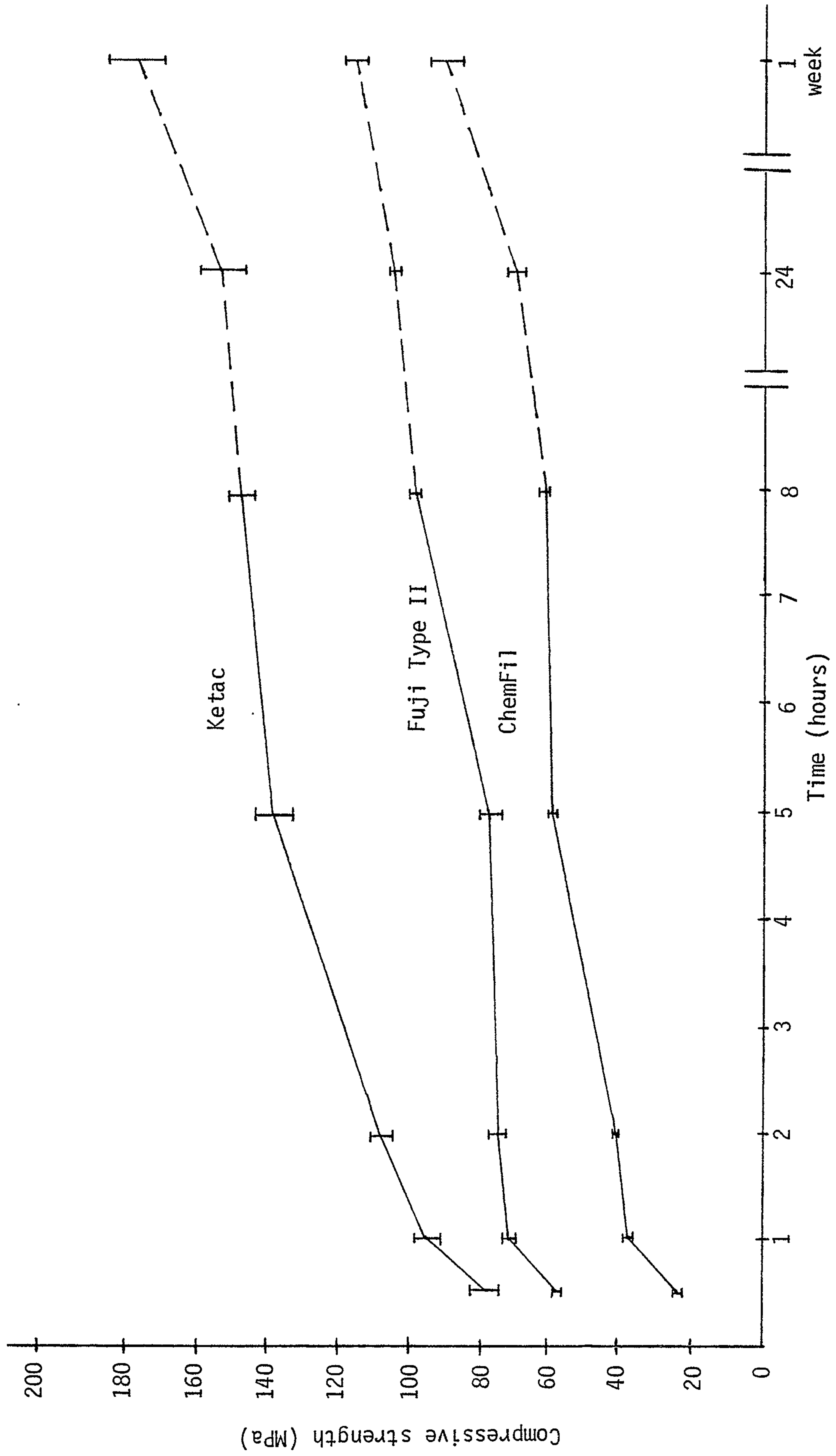
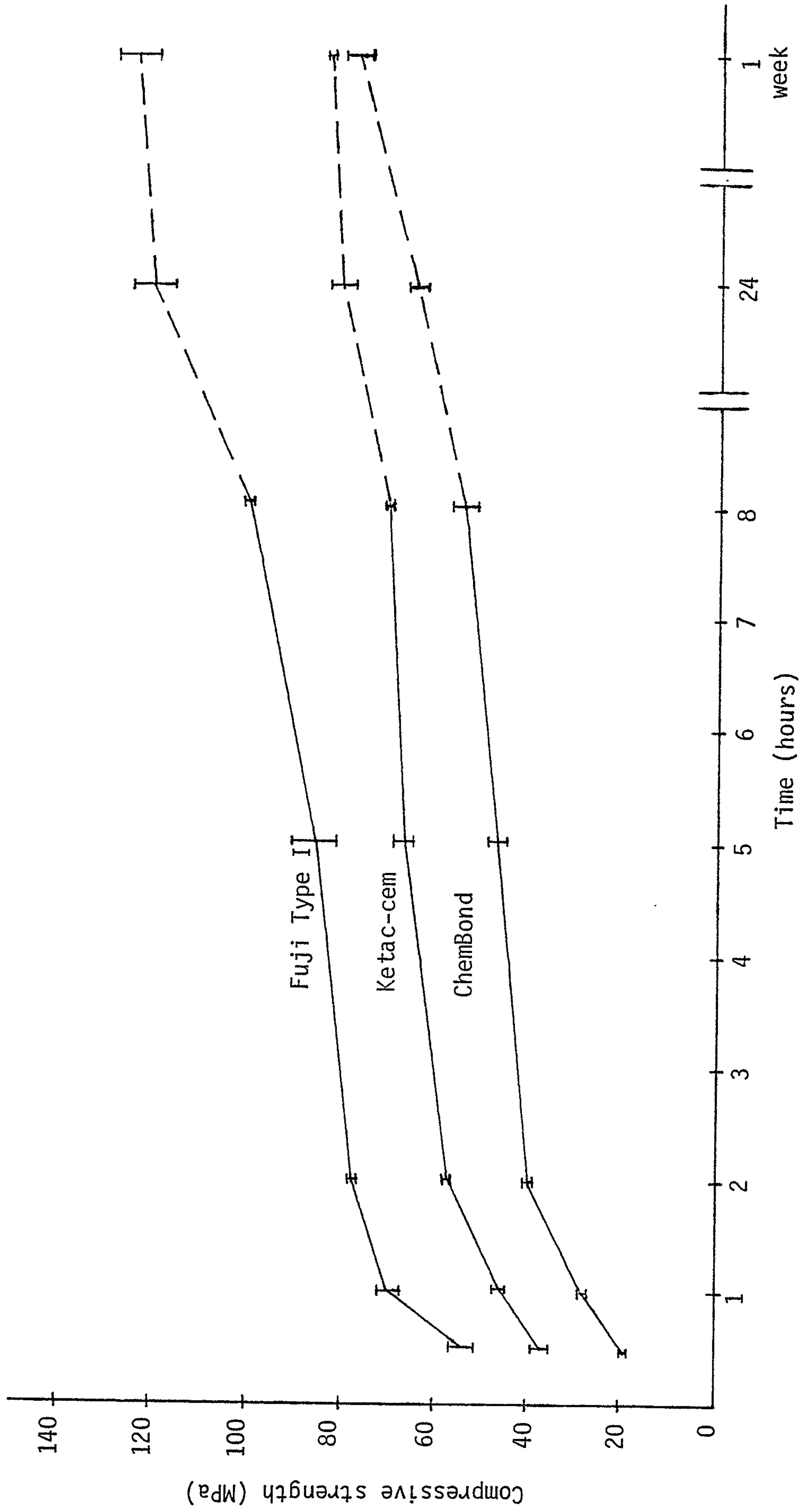


Figure 6.2

Development of compressive strength of glass ionomer cements (luting)



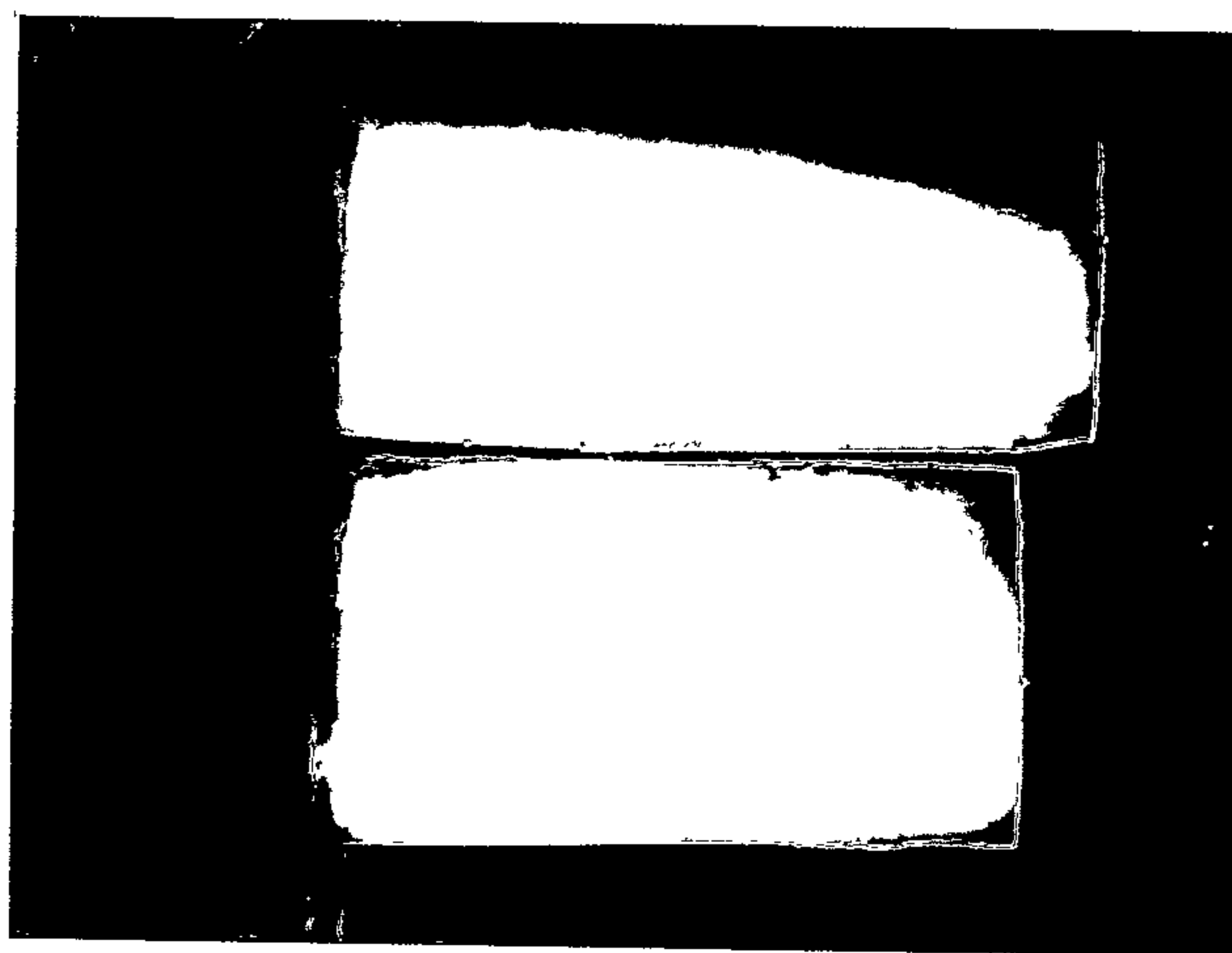


Fig. 6.3 A comparison of the length of a specimen before loading (the longer one) with the length of another specimen subjected to the compressive strength test at 30 minutes after mixing and removed from the testing machine at a loading near the failure value. Observe the deformation in the test specimen.

CHAPTER 7

TENSILE STRENGTH OF GLASS IONOMER CEMENTS

- 7.1 Introduction
- 7.2 The development of tensile strength of the restorative glass ionomer cements
- 7.3 The development of tensile strength of the glass ionomer cements used for luting
- 7.4 Comparison of the tensile strengths of the restorative and luting types of glass ionomer cements
- 7.5 Discussion
 - 7.5.1 Experimental method
 - 7.5.2 Comparison of results
- 7.6 Summary

7.1 INTRODUCTION

The tensile strengths of the glass ionomer cements are presented in Tables 7.1 and 7.2. The standard deviation is indicated in brackets and a connecting bar line indicates that the difference between two readings is statistically significant. The rates of development of tensile strength are illustrated in Fig. 7.1 and 7.2.

7.2 THE DEVELOPMENT OF TENSILE STRENGTH OF THE RESTORATIVE GLASS IONOMER CEMENTS

The development of tensile strength of the three materials tested is illustrated in Fig. 7.1.

Ketac had the greatest tensile strength of the three restorative materials and showed significant increases in strength between 0.5 and 1 hour and between 24 hours and 1 week. As illustrated in Fig. 7.1, the development of strength in Fuji Type II appeared somewhat erratic. Statistical analysis, however, indicated that the decreases in strength from 0.5 to 1 hour and from 8 to 24 hours to 1 week were not significant. Fuji Type II gradually increased in strength up to a period of 8 hours, the maximum increase

occurring between 2 and 8 hours. ChemFil exhibited a significant increase in strength between 0.5 and 2 hours and between 2 and 8 hours.

ChemFil had a low initial strength (approximately one-half that of Ketac and Fuji Type II). By 24 hours, it had attained a similar tensile strength to Fuji Type II. The tensile strength of Ketac (in contrast with Fuji Type II) generally increased over the period of testing.

Ketac was significantly stronger than Fuji Type II and ChemFil at all times of testing except at 0.5 hours (when the difference in tensile strength between Ketac and Fuji Type II was not significant). Fuji Type II was significantly stronger than ChemFil at all times up to and including 8 hours after mixing. At 24 hours, their strengths were similar.

7.3 THE DEVELOPMENT OF TENSILE STRENGTH OF THE GLASS IONOMER CEMENTS USED FOR LUTING

The rate of development of tensile strength of the glass ionomer cements used for luting is illustrated in Fig. 7.2. Each material showed a significant increase in strength between 0.5 and 1 hour, followed by a gradual increase in strength up to 24 hours.

Fuji Type I had the highest tensile strength of the three luting cements investigated. (This was associated with a relatively high film thickness -- Table 8.1). Only Fuji Type I exhibited a significant decrease in tensile strength after 24 hours. A similar apparent decrease in strength of set cements (in this case, of base forming materials) has been observed previously by Bryant (1968). At all times of testing, there were no significant differences in the tensile strengths of ChemBond and Ketac-cem. In contrast there were significant differences between the strengths of Ketac-cem and Fuji Type I at all times of testing except at 8 hours. Fuji Type I was significantly stronger than ChemBond at all times of testing.

7.4 COMPARISON OF THE TENSILE STRENGTHS OF THE RESTORATIVE AND LUTING TYPES OF GLASS IONOMER CEMENTS

Ketac was approximately two to three times as strong as Ketac-cem at all times of testing (Tables 7.1 and 7.2). In contrast the strengths of Fuji Type II and Fuji Type I were comparable. Although the early strengths of ChemFil and ChemBond were similar, ChemFil (unlike ChemBond) showed a significant increase in strength between 2 hours and 8 hours, and possessed a final strength that was approximately twice that of ChemBond.

7.5 DISCUSSION

7.5.1 *Experimental method*

The results suggested a somewhat irregular development of tensile strength in the glass ionomer cements investigated. This is in contrast with the relatively steady increase in compressive strength with time (Fig. 6.1 and 6.2).

Since it could be expected that the development of these two strength properties would be related (Mahler and Mitchem, 1964), the use of the diametral tensile strength test in this investigation was considered.

The validity of the diametral tensile strength test is based on certain pre-requisites (Wright, 1955; Turchyn and Youdelis, 1970; Mori and Earnshaw, 1983). These are : i) the material tested is homogeneous and isotropic, ii) the material obeys Hooke's law and strain is proportional to stress.

Specimen deformation invalidates the pre-requisite of point loading and may introduce a substantial error into the calculation of tensile strength.

The glass ionomer cement is heterogeneous (as discussed in 2.3.3). Although it is generally considered a brittle material, it does undergo some plastic deformation (Wilson and Lewis, 1980).

In the presence of plastic deformation, point loading does not occur and the load is actually distributed over an area of appreciable width. The value thus obtained will be higher than the true value (Mori and Earnshaw, 1983). This may have been responsible for the relatively large proportion of the final tensile strength apparently achieved in the first two hours. Proper load distribution "irones out" irregularities and is essential for successful application of the diametral tensile strength test (Rudnick et al, 1963). This was achieved in this investigation by placing a piece of cardboard (approximately 1 cm wide and 0.225 mm thick) between the specimen and the loading platens. Shear and compressive stresses are potential causes of fracture in materials subjected to some plastic deformation during diametral tensile strength testing (Rudnick et al, 1963) and could have contributed to the irregular development of tensile strength (when compared with the relatively steady development of compressive strength).

Several problems in experimental technique were encountered in the course of this investigation. Many early specimens (tested at 0.5 and 1 hour after mixing) displayed noticeable deformation (Fig. 7.3, Fig. 7.4, Fig. 7.5). There was no observable deformation of specimens tested at one week (Fig. 7.6). The results obtained for the early strengths should not be taken as absolute values (for reasons stated above), but they can be used to compare the stage of set of the materials and their relative early strengths. A second problem was encountered in ascertaining the exact time of fracture (particularly for relatively weak specimens). One of two criteria was used. The applied load was recorded either when a "crack" sound was heard, or when a "fracture" line appeared on the specimen (whichever occurred first). When doubt existed the lower value was used.

7.5.2 *Comparison of results*

As discussed in 3.3.21, only data for the experimental and a limited number of commercial glass ionomer cements are available in the literature.

The 24 hour tensile strengths of the restorative materials tested in this investigation were within the range of values for ASPA IV (11.7 to 13.0 MPa) with the exception of Ketac which was clearly superior. The 24 hour tensile strength of Fuji Type II (12 MPa) was comparable to the value reported by Wilson and Prosser (1982), but significantly higher than the value of 8.2 MPa reported by Vougiouklakis and Smith (1982). However, the 24 hour tensile strength for ChemFil (11.8 MPa) was considerably lower than the value of 17 MPa indicated by the manufacturer. This difference in the tensile strength for ChemFil may be attributed, in part at least, to the different powder : liquid ratios used. As explained in 5.1.15, a powder : liquid ratio of 5.2:1 was used in this investigation, instead of the recommended ratio of 6.8:1.

The results obtained for the 24 hour tensile strengths of the three luting cements indicated that both Ketac-cem and ChemBond were weaker than the experimental cement, ASPA IVA (8.0 to 9.3 MPa). Although Fuji Type I had significantly greater tensile strength at 24 hours, the tensile strength appeared to decrease significantly by one week. The 24 hour tensile strength of Fuji Type I (14 MPa) was approximately twice the value reported by Wilson and Prosser (1982). The value obtained for ChemBond in this investigation (6.6 MPa) is similar to the value of 6.4 MPa reported by Wilson and Prosser (1982).

Differences between the results obtained in this investigation and those reported in the literature may be attributed to one or more potential causes. 1) The different composition of the powder and liquid

of various brands of glass ionomer cements. 2) The size of the specimen tested -- the smaller the specimen, the higher the value (Wright, 1955). 3) The storage medium prior to testing-- 5.1.31 (Crisp et al, 1976,a). 4) The use or non-use of varnish (Causton, 1981). 5) The type of cushioning material used--the softer the cushioning material, the higher the tensile strength and the greater is the range of values obtained (Addinall and Hackett, 1964). 6) The cross-head speed (rate of loading) -- Mitchell (1961) reported that the higher the cross-head speed, the higher the tensile strength values obtained. In contrast, Mahler and Mitchem (1964) found no change in tensile strength as the rate of loading was varied.

Detailed comparison of the diametral tensile strength results of this investigation, with the findings of other researchers, is not possible because of the very few reports currently available in the literature and the limited information provided by these researchers on their experimental method.

The British Standards Specification for glass ionomer cements (British Standards 6039, 1981) states that the minimum 24 hour tensile strength should be 10 MPa for the restorative materials and 6 MPa for the luting consistencies. All the materials tested in this investigation (both restorative and luting) satisfied these requirements. As noted with respect to compressive strength results, however, the experimental method used differed from that defined in the British Standards Specification.

7.6

SUMMARY

It is evident that, because of some plastic deformation, the diametral tensile strength test is unsuitable for testing the early strengths of glass ionomer cements. However, the results obtained can be used in a comparative way.

With the exception of Fuji Type I and Fuji Type II, which exhibited a somewhat irregular development of tensile strength, all materials were found to have a relatively consistent increase in strength with time. Of the three restorative materials tested, Ketac was found to have the highest tensile strength. The tensile strengths of Fuji Type II and ChemFil were comparable. For the luting materials, Fuji Type I had the highest tensile strength, and the tensile strengths of Ketac-cem and ChemBond were similar. The tensile strengths of the restorative materials Ketac and ChemFil were almost twice the strength of the luting materials Ketac-cem and ChemBond. The tensile strengths of Fuji Type II (restorative) and Fuji Type I (luting) were comparable.

Comparison of the results obtained with the findings of other researchers is difficult because of different experimental methods and because of the very few other similar studies currently reported.

Although the six materials tested met the requirements for the 24 hour tensile strength stated in the British Standards Specification for glass ionomer cements, differences in experimental method preclude further comparison.

TABLE 7.1

Development of tensile strength of glass ionomer cements (restorative)

Tensile strength (MPa) at times after beginning of mixing						
Material	0.5 h	1 h	2 h	8 h	24 h	1 wk
Ketac	10.7 (1.0)*	13.8 (1.4)	16.5 (1.4)	15.6 (0.6)	17.8 (2.3)	22.3 (2.3)
Fuji Type II	10.2 (0.5)	9.5 (1.0)	9.9 (0.9)	13.4 (1.2)	12.0 (1.6)	11.4 (0.8)
ChemFil	4.9 (0.2)	6.2 (0.3)	7.8 (0.2)	10.2 (0.6)	11.8 (1.2)	**

* Value for one standard deviation in brackets.

** Not tested at one week.

┌ The difference between the two values is statistically significant.

Development of tensile strength of glass ionomer cements (luting)

TABLE 7.2

Tensile strength (MPa) at times after beginning of mixing

Material	0.5 h	1 h	2 h	8 h	24 h	1 wk
Ketac-cem	4.2 (0.4)*	6.1 (0.4)	5.6 (0.6)	6.8 (0.5)	7.6 (0.8)	6.6 (0.7)
Fuji Type I	6.3 (0.4)	9.4 (0.7)	8.8 (0.8)	8.3 (0.9)	14.0 (0.9)	9.3 (0.6)
ChemBond	4.1 (0.4)	5.3 (0.4)	5.7 (0.5)	6.1 (0.4)	6.6 (0.7)	**

* Value for one standard deviation in brackets.

** Not tested at one week.

— The difference between the two values is statistically significant.

Figure 7.1

Development of tensile strength of glass ionomer cements (restorative)

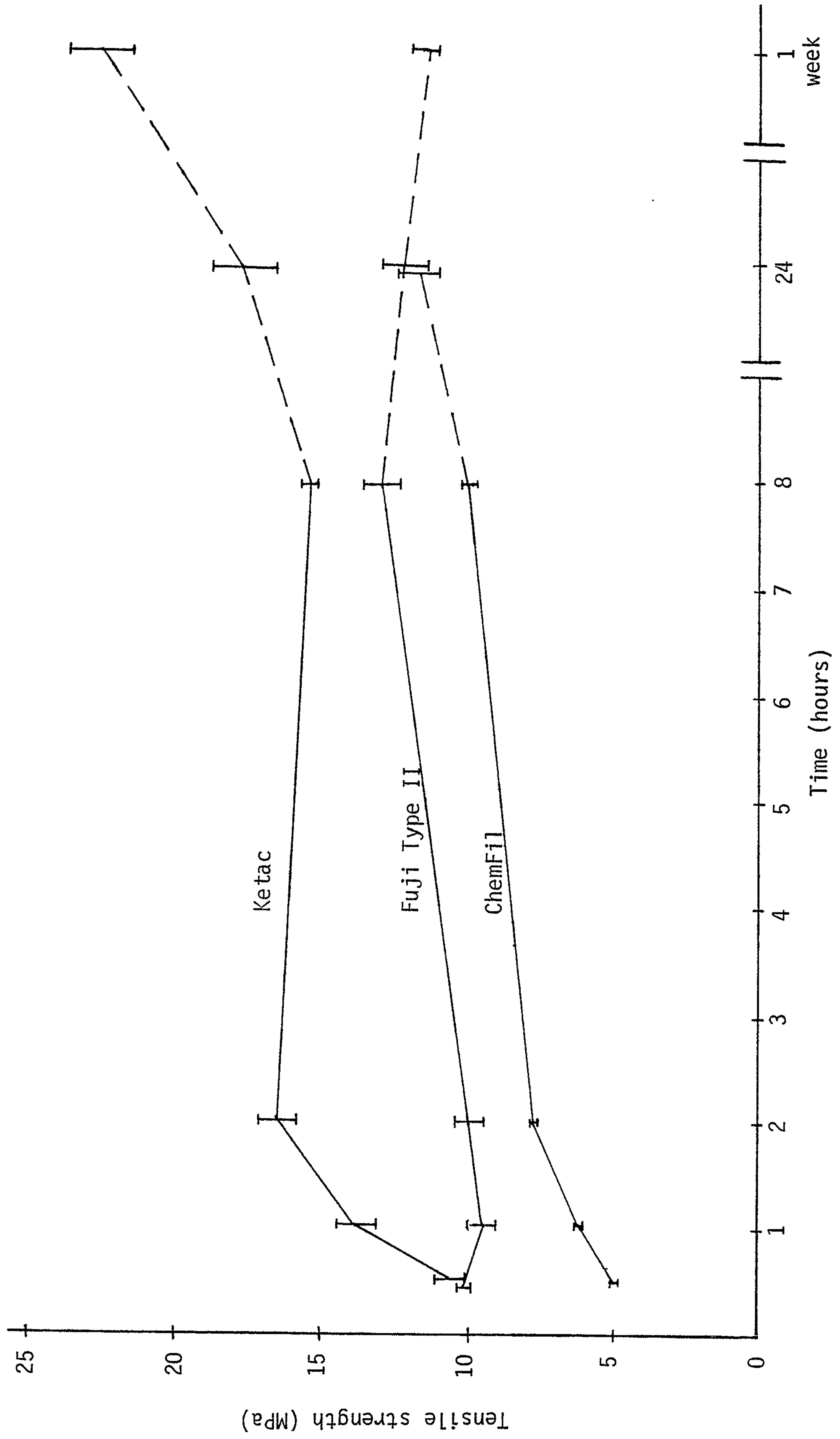


Figure 7.2

Development of tensile strength of glass ionomer cements (luting)

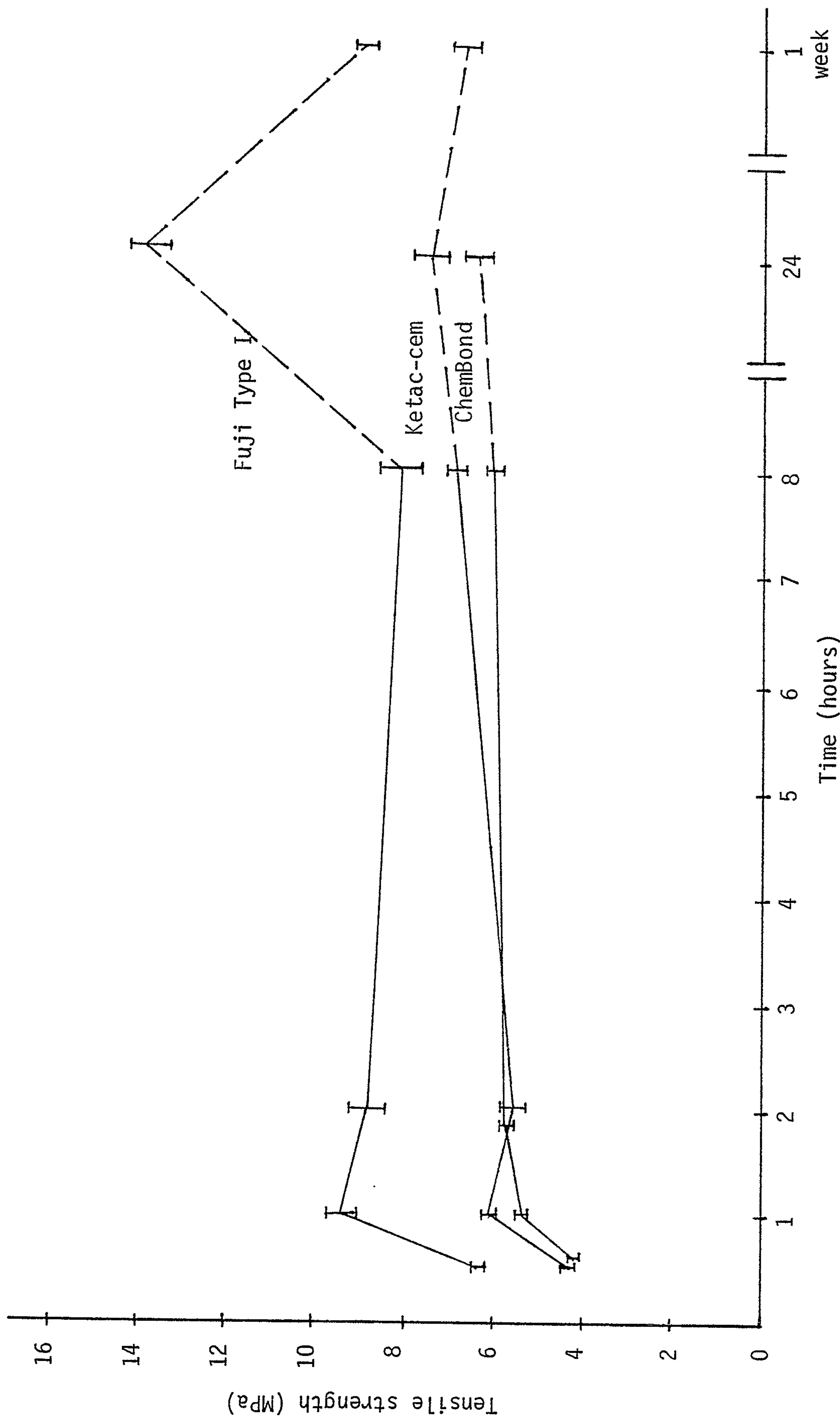


Figure 7.3 - 7.4

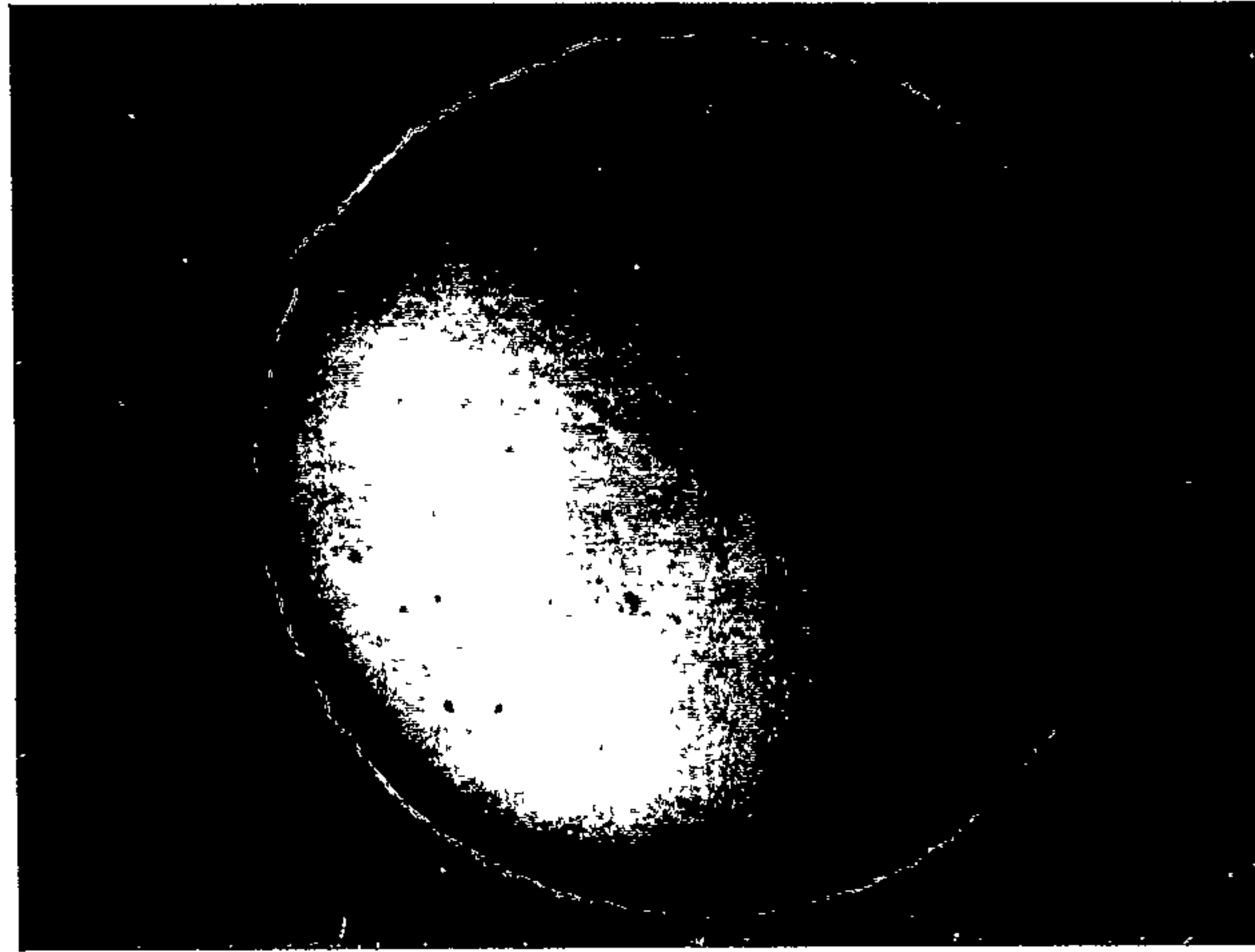


Fig. 7.3 A glass ionomer specimen not subjected to tensile stress.

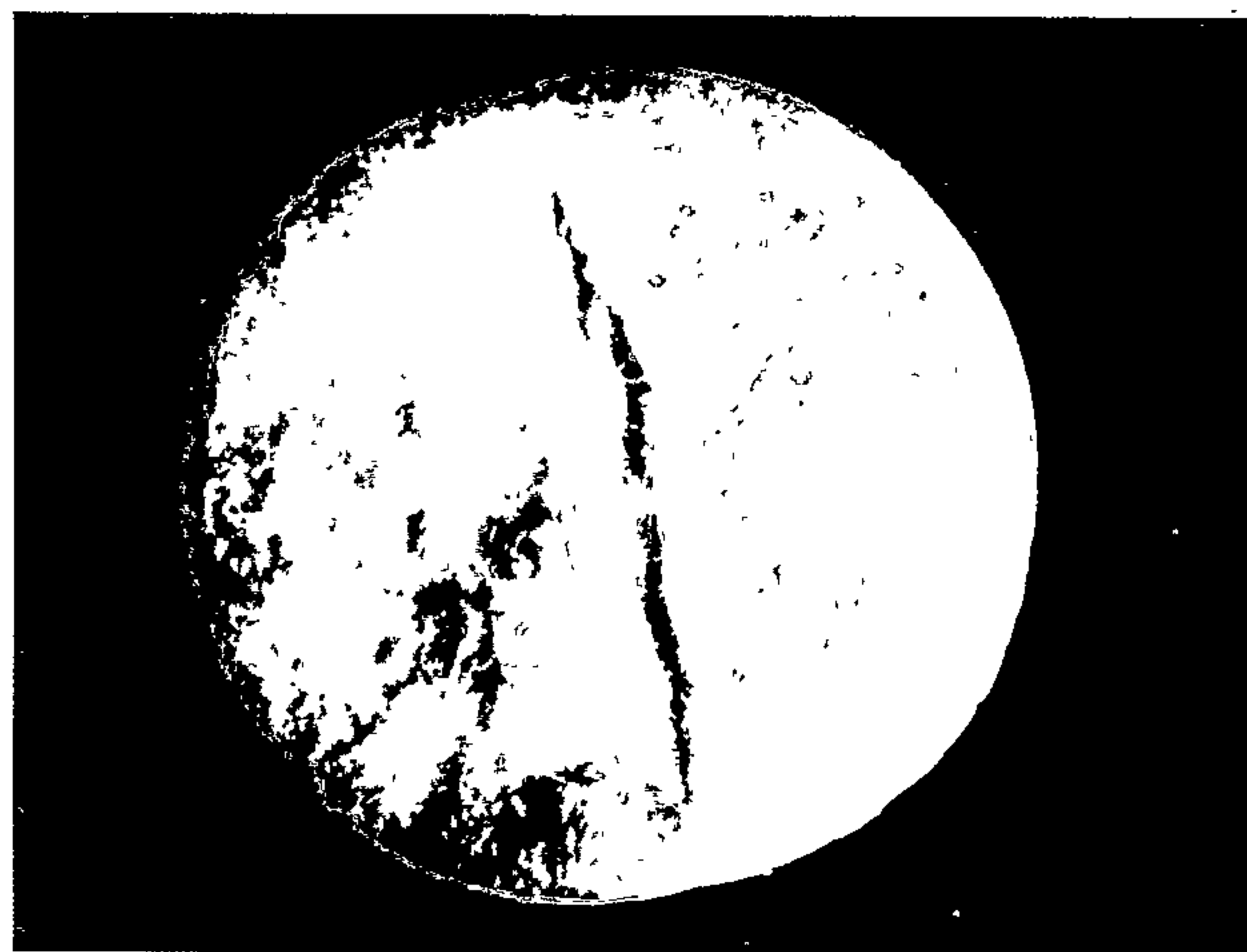


Fig. 7.4 Deformation of a glass ionomer cement specimen tested at 30 minutes from the time of mixing.

Figure 7.5 - 7.6

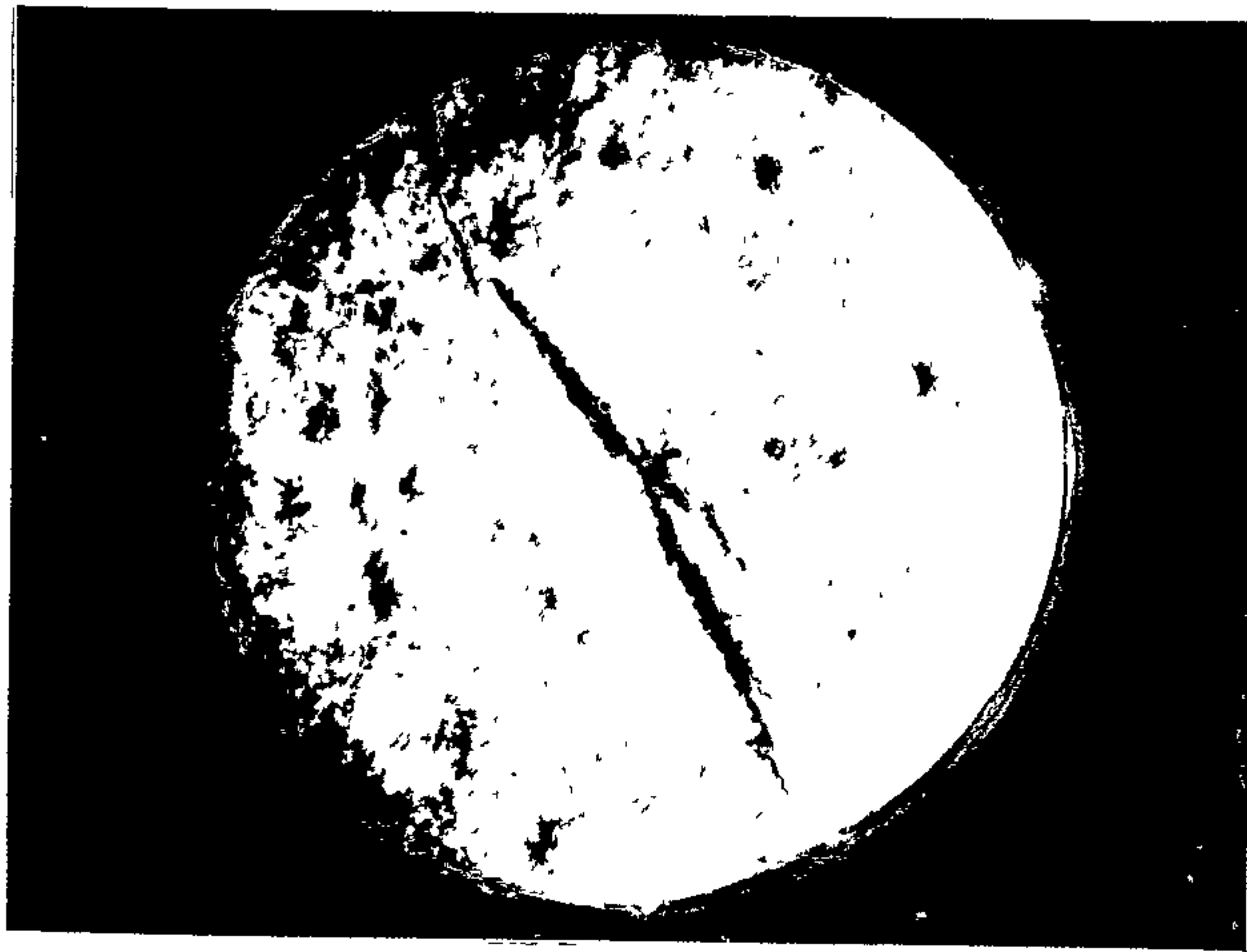


Fig. 7.5 Deformation of a glass ionomer cement specimen tested at one hour from the time of mixing.

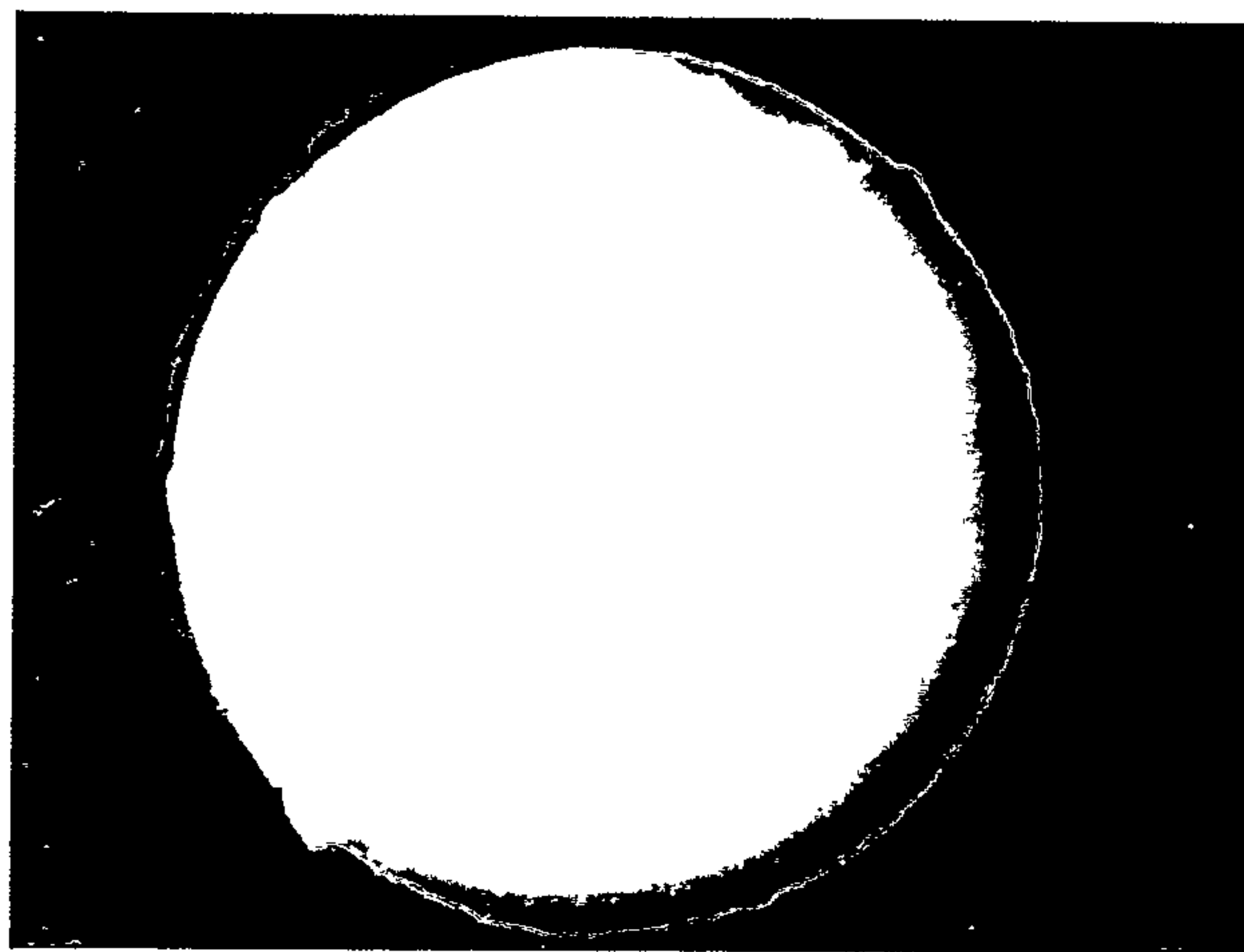


Fig. 7.6 No noticeable deformation of a glass ionomer cement specimen tested at one week from the time of mixing.

CHAPTER 8

THE FILM THICKNESS OF LUTING GLASS IONOMER CEMENTS

- 8.1 Introduction
- 8.2 The film thickness of four luting glass ionomer cements
- 8.3 Discussion
 - 8.3.1 Experimental method
 - 8.3.2 Comparison of the film thickness of four cements
- 8.4 Summary

8.1 INTRODUCTION

The film thickness of the four luting glass ionomer cements are presented in Table 8.1. The values are the means obtained from four specimens and the standard deviations for these data are indicated in brackets. The powder : liquid ratio for each material at which the cement was not set 9 minutes after the commencement of mixing is denoted **.

8.2 THE FILM THICKNESS OF FOUR LUTING GLASS IONOMER CEMENTS

Ketac had a film thickness of 27 μm at the recommended powder : liquid ratio (3.4:1). Although the film thickness decreased when the powder : liquid ratio was decreased to 3.0:1, the material remained unset at 9 minutes.

The recommended range for the powder : liquid ratio for Fuji Type I is 1.3:1 to 1.4:1. At the upper limit of the range (1.4:1), the film thickness of Fuji Type I was 47 μm . The film thickness decreased with a decrease in the powder : liquid ratio. At a powder : liquid ratio of 1:1, the film thickness was 27.5 μm . A similar film thickness was obtained at a powder : liquid ratio of 0.8:1 at which consistency the cement was not set at 9 minutes.

Because the film thickness obtained for Fuji Type I at a ratio of 1:1 was considered to be more clinically acceptable than

the thickness obtained using thicker mixes, the compressive strength of the cement was examined at the 1:1 powder : liquid ratio. The compressive strengths at 45 minutes, 1 hour and 24 hours were 45.8 (3.4)^a, 55.2 (3.2) and 88.4 (6.7) MPa, respectively. The material was not testable for compressive strength at 30 minutes (because of excessive specimen deformation). In contrast, the compressive strengths of Fuji Type I (powder : liquid ratio 1.4:1) at 30 minutes, 1 hour and 24 hours were 54.0, 70.6 and 120.4 MPa, respectively (Table 6.2).

The film thickness of ChemBond at the recommended powder : liquid ratio of 1.2:1 was 30 μm . The film thickness did not decrease substantially as the powder : liquid ratio was reduced to 0.8:1.

The film thickness of Hy-Bond C was 41.5 μm at the recommended powder : liquid ratio (1.5:1.0). The film thickness decreased by approximately 50 per cent to 21 μm at a powder : liquid ratio of 0.7:1, at which consistency the cement remained unset 9 minutes after the commencement of mixing.

A comparison of the four cements tested indicated that, at the recommended powder : liquid ratios, the film thickness was greatest for Fuji Type I (47 μm) and least for Ketac-cem (27 μm). The differences between the film thickness of Fuji Type I and Hy-Bond C, and between Ketac-cem and ChemBond were not statistically significant.

The powder : liquid ratios of Fuji Type I, ChemBond and Hy-Bond were reduced substantially (to contain approximately 40 per cent less powder for the quantity of liquid) before the cement remained "not set" 9 minutes after the commencement of mixing. In the case of Ketac-cem, this stage was achieved when the powder : liquid ratio was decreased by approximately 10 per cent.

^a Value for one standard deviation in brackets

8.3

DISCUSSION

8.3.1 *Experimental method*

Several problems were encountered during the course of the investigation. One of these was the occurrence of cracks in the thin cover slips after the weights were removed at 9 minutes. This occurred in approximately 10 per cent of tests and in such cases the results were considered invalid and the tests repeated. Another problem with the use of thin cover slips (0.136 mm thickness) was their flexibility which resulted in inaccurate readings. These problems could be overcome by using thicker glass plates (for example, the 5 mm or greater thickness recommended by the British Standards Specification for glass ionomer cements -- British Standards 6039, 1981).

The occurrence of small air bubbles between the cover slips for all materials at the lower powder : liquid ratios may also have contributed to inaccurate readings.

8.3.2 *Comparison of the film thickness of four cements*

The findings indicated that the film thickness of the luting glass ionomer cements decreased with a reduction in the powder : liquid ratio. It was of particular interest to note that, at the lowest powder : liquid ratio at which each material was set at 9 minutes, the film thickness of the materials were in the relatively narrow range of 27 to 28.8 μm . The criterion of "set at 9 minutes" was chosen for two reasons; it is clinically appropriate, and it is the time stated in the British Standards Specification (British Standards 6039, 1981) at which the film thickness specimen is removed from the loading device for the measurement of film thickness. On this basis, it is possible to conclude that the thinnest clinically appropriate film thickness of glass ionomer cements is currently approximately 28 μm .

However, in some materials this film thickness was achieved by reducing substantially the powder : liquid ratio recommended by the manufacturers. On the evidence obtained from the investigation of the effect of reduced powder : liquid ratio on the compressive strength of Fuji Type I, it could be concluded that the reduction in film thickness to this minimum clinically appropriate level is at the expense of strength. In addition, a further reduction in powder : liquid ratio below this critical level prolonged the setting time to beyond 9 minutes. The evidence tended to support the observation by Crisp et al (1976,b; 1976,c; 1976,d) that a reduction in powder : liquid ratio to achieve decreased film thickness may be clinically unacceptable because of the accompanying detrimental effects of decreased strength, prolonged setting time and increased solubility and disintegration. On the other hand, failure to reduce the powder : liquid ratio of currently available glass ionomer cements to less than the recommended ratio may result in an unacceptably thick film of cement.

As discussed in 3.7.2, only data for the experimental and a limited number of commercial glass ionomer cements are currently available in the literature. Of the luting cements tested, at the recommended powder : liquid ratio only Ketac-cem (27 μm) was found to have comparable film thickness to ASPA IVA (24 μm). The film thickness of ChemBond (30 μm) was found to be 50 per cent greater than the value (20 μm) reported by Mesu (1982). The manufacturer of Hy-Bond C has claimed that the film thickness of the cement was 25 μm ; in this investigation it was found to be 41.5 μm at the same powder : liquid ratio. The results obtained in this investigation confirmed the observation of Reisbick (1981) that the film thickness of Fuji Type I was "considerably greater" than that for ChemBond.

The British Standards Specification for glass ionomer cements (British Standards 6039, 1981) states that the maximum film thickness for the Type I luting cement is 25 μm . The British Standards requires that the mean result of three tests, to the nearest 5 μm , should be recorded as the film thickness of the material. In this investigation the mean of four tests was calculated to the nearest 1 μm and recorded as the film thickness of the cement. If the results had been recorded to the nearest 5 μm , only Ketac-cem would have met the specification for film thickness.

The results of this investigation indicated that the film thickness of Ketac-cem at the recommended consistency was comparable to that of zinc oxide-eugenol-EBA cements, but greater than that of zinc phosphate and zinc polycarboxylate cements (Table 3.4). The film thicknesses of ChemBond, Fuji Type I and Hy-Bond C (at the recommended consistency) were considerably greater than that of zinc oxide-eugenol-EBA, zinc phosphate and zinc polycarboxylate cements.

The film thickness of the thinnest clinically appropriate consistency (set at 9 minutes), obtained by reducing the powder : liquid ratio, was considerably lower (in most cases) than the film thickness at the recommended consistency (Table 8.1). At the former consistency, the film thicknesses of all the luting glass ionomer cements tested (27 to 28.8 μm) were comparable to that of zinc oxide-eugenol-EBA but greater than that of zinc phosphate and zinc polycarboxylate cements.

8.4

SUMMARY

Of the luting glass ionomer cements tested (at the recommended consistency), Fuji Type I had the greatest and Ketac-cem the lowest film thickness. The film thickness of Fuji Type I was comparable to Hy-Bond C, and that of Ketac-cem was comparable to ChemBond. With the

exception of Ketac-cem, which met the British Standards Specifications for film thickness, the other glass ionomer cements (mixed at the recommended consistency) had film thickness substantially greater than 25 μm .

All materials exhibited a decrease in film thickness as the powder : liquid ratio was reduced. The thinnest clinically appropriate film thickness (set at 9 minutes) obtained was approximately 28 μm for all luting glass ionomer cements tested.

It is evident from the findings that thinner mixes should be used with most cements to reduce the film thickness to that comparable with zinc oxide-eugenol-EBA cements. However, the reduction (substantial in some cements) in powder : liquid ratio required to achieve this probably has a detrimental effect on other properties (strength, setting time, solubility and disintegration).

TABLE 8.1

Film thickness of glass ionomer cements
at various powder : liquid (P/L) ratios

Material	P/L ratio (:1)	Film thickness (μm)	
Ketac-cem	3.4*	27.0	(4.1) ⁺
	3.0**	20.5	(1.0)
Fuji Type I	1.4*	47.0	(3.2)
	1.2	35.5	(1.3)
	1.0	27.5	(2.1)
	0.8**	27.3	(3.8)
ChemBond	1.2*	30.0	(2.2)
	1.0	28.3	(3.0)
	0.8**	25.3	(2.5)
Hy-Bond C	1.5*	41.5	(3.5)
	1.3	32.5	(1.9)
	1.1	31.5	(1.3)
	0.9	28.8	(2.4)
	0.7**	21.0	(1.2)

+ Value for one standard deviation in brackets.

* Cement prepared at the recommended powder : liquid ratio.

** Cement not set at 9 minutes from the commencement of mixing.

CHAPTER 9

THE SCANNING ELECTRON MICROSCOPE (SEM)

EXAMINATION OF GLASS IONOMER CEMENTS

- 9.1 The investigation of the surface obtained with various clinical finishing techniques. Results
- 9.2 The investigation of the surface obtained with various clinical finishing techniques. Discussion
- 9.3 SEM investigation of the particle size of a number of glass ionomer cements. Results
 - 9.3.1 The glass particle sizes in unreacted cement powders
 - 9.3.2 The glass particle sizes in set cements
- 9.4 SEM investigation of the particle size of a number of glass ionomer cements. Discussion
- 9.5 Summary

9.1 THE INVESTIGATION OF THE SURFACE OBTAINED WITH VARIOUS
CLINICAL FINISHING TECHNIQUES. RESULTS

The surface obtained when Ketac was finished with a low-speed diamond, rotating in a forward direction only is illustrated in Fig. 9.1 and 9.2. Deep grooves (10-20 μm wide) were observed on the surface of the cement, running across both the matrix and particle components. At higher magnification (X1,000--Fig. 9.2) the surface appeared rough and particles were observed to be protruding from the surface.

Fig. 9.3 and 9.4 illustrate a surface which had been finished with a coarse grade sandpaper disc. At a magnification of X1,000, scratch marks present on the surface (Fig. 9.4) were coarser than those present on a surface finished with a fine sandpaper disc (Fig. 9.6). Scratches were present both on the particles and matrix portions of the cement.

The surface obtained when the cement was finished with a fine sandpaper disc in a low-speed handpiece is illustrated in Fig. 9.5

and 9.6. The surface appeared to be smooth; fine scratches could only be observed at high magnifications (Fig. 9.6). Certain parts of the surface appeared to be irregular and these areas appeared to have been untouched by the sandpaper disc.

Fig. 9.7 and 9.8 illustrate the surface obtained when the Ketac cement set against a matrix strip. Numerous voids (which varied in size) were present on the surface where air-bubbles had been trapped between the cement and the matrix during the setting reaction. Numerous cracks were also present on the untouched surface.

Fig. 9.9 and 9.10 illustrate the surface obtained when the Ketac cement was finished with a white stone at high-speed. Scratches were present on the surface. The white stone produced a relatively rough surface finish.

The surface obtained when Ketac was finished with a tungsten carbide bur at high-speed is illustrated in Fig. 9.11 and 9.12. The resulting surface was rough with scratches present.

Fig. 9.13 and Fig. 9.14 illustrate the surface produced when Ketac was finished with pumice and glycerine in a rubber cup. The softer matrix was preferentially reduced so that the aluminosilicate glass particles were left protruding. No deep scratch marks were present. A similar finding was observed when the cement was finished with Floran polishing paste in a rubber cup (Fig. 9.15 and 9.16).

Comparison of the surface produced by the various finishing techniques indicated that the smoothest finish was obtained with a fine sandpaper disc and the roughest finish was obtained using a low-speed diamond. The white stone produced a slightly rougher finish than a tungsten carbide bur. The surface finish produced with pumice and glycerine was similar to that produced with Floran finishing paste; although the surface was scratch-free, it was rough

because of the protruding glass particles. The surface produced against a matrix strip exhibited numerous voids and cracks.

9.2 THE INVESTIGATION OF THE SURFACE OBTAINED WITH VARIOUS CLINICAL FINISHING TECHNIQUES. DISCUSSION

The results obtained in this investigation indicated that the best surface finish was that obtained using a low-speed fine sandpaper disc.

The surface obtained against a matrix strip had numerous voids and cracks. The voids were present although care was taken in specimen preparation. The cracks may be due to the dehydration of the cement (Mount, 1981; 1982) after removal from the mould. A layer of varnish was not applied to the specimen after matrix removal in order that the surface could be observed in the SEM without being obscured by varnish. Clinically, a layer of varnish is applied to the restoration immediately after removal of the matrix and this would prevent the occurrence of cracks. It could be anticipated, that the voids would still be present.

Little evidence is available in the literature on the effects of similar clinical finishing techniques on the surface of the glass ionomer cements. Only Smales and Joyce (1978) have reported the effects of finishing techniques in a study in which they used a sharp scalpel blade, a hand-held dry rubber Burlew wheel and a Mylar matrix strip. This investigation confirmed their findings of air entrapment when the cement was polymerized against a matrix strip.

Various techniques have been advocated for the finishing of glass ionomer cement restorations (3.11.1). Charbeneau and Bozell (1979), and Mount (1981; 1982) recommended the use of fine diamonds for gross finishing followed by a final finish with white alpine finishing points, silicon mounted points and graded silicon carbide

discs. Although the effects of silicon carbide points and discs were not investigated, the results of this investigation indicate that the white alpine finishing stones do not produce a smooth surface and that, where access permits, their use should be followed by the use of fine sandpaper (zirconium silicate) discs. Although Mount (1981) suggested the use of a polishing paste for final finishing, the results of this investigation indicated that a polishing paste produces a less than satisfactory surface finish.

Based on the evidence of this investigation, it is recommended that the final finishing of glass ionomer cements should be carried out using :

- i) either a high-speed white stone or tungsten carbide bur (at high-speed) or, where access permits, a coarse sandpaper disc (low-speed), to reduce gross excess, and to obtain correct contour and marginal finish.
- ii) a fine sandpaper disc (low-speed) to produce the surface with the fewest deep scratches. It could be anticipated that this surface would provide the least plaque retention. In areas inaccessible to the disc, it is probable (although not examined in this investigation) that, an equally satisfactory surface would be achieved by using an abrasive strip with a fine (zirconium silicate) abrasive.

A smooth, scratch-free surface was not obtained on the glass ionomer cements with any of the finishing techniques investigated.

9.3 SEM INVESTIGATION OF THE PARTICLE SIZE OF A NUMBER OF GLASS IONOMER CEMENTS. RESULTS

The findings of the investigation of the particle sizes in glass ionomer cement powders are illustrated in Fig. 9.17 to 9.26.

Photomicrographs providing evidence of the particle sizes in the set glass ionomer cements are presented in Fig. 9.27 to 9.35. These photomicrographs were selected because they were considered to be representative of the photomicrographs obtained for each material in the SEM investigation.

9.3.1 *The glass particle sizes in unreacted cement powders*

Fig. 9.17 illustrates the appearance of the powder particles when mounted on the aluminium tape without the use of alcohol. The finer powder particles tended to be clumped together. Fig. 9.18 illustrates the appearance of the aluminium tape to which a drop of alcohol had been added to dissolve the glue. The tape appeared wrinkled and the photomicrograph confirmed that there was no visible evidence of the glue at a magnification of X1,000. Fig. 9.19 illustrates the appearance of the powder particles when a drop of alcohol was placed onto the particles after they had been mounted on the tape. The particles were more uniformly distributed and the finer particles were no longer clumped together (contrast with Fig. 9.17). Because of this, it was decided to use alcohol in the mounting of all powder samples for SEM investigation (5.3.4).

The appearance of the powder particles in four glass ionomer cements used for luting is shown in Fig. 9.19 to 9.26. Each material is illustrated by two photomicrographs, one at X240 and the second at X1,000. The distribution of particle sizes can be observed at a magnification of X240; greater detail of the size and shape of individual particles is evident at the higher magnification (X1,000).

In all the materials examined the powder particles varied in shape and size. There was a wide range in the sizes of the particles present in each material. The larger particles, of up to 20 μm minimum cross-section, were interspersed with an abundance of very

fine particles of 1 μm minimum cross-section or less. Ketac-cem, Fuji Type I and Hy-Bond C appeared to have a similar range of particle size. A subjective impression was that some of the larger powder particles in ChemBond were slightly larger than those in the other three materials; the finer particles were in the same size range.

9.3.2 *The glass particle sizes in set cements*

The SEM examination of the set cement, prepared (flat-polished) as described in 5.3.2, revealed the difficulty of distinguishing the particles from the matrix in both restorative and luting glass ionomer cements (Fig. 9.27 and 9.28). Similar results were obtained for the seven glass ionomer cements investigated.

The particles could be distinguished from the matrix in the set cement when the specimens were prepared as described in 5.3.31 and finished with pumice and glycerine (Fig. 9.29 to 9.35).

Examination of the photomicrographs of the three restorative cements (Fig. 9.29 to 9.31) revealed the presence of particles of varying shapes and sizes. In the regions examined, there did not appear to be a substantial difference in the range of particle sizes between Ketac and Fuji Type II. However, the larger particles in ChemFil generally appeared to be slightly larger than those in Ketac and Fuji Type II.

The glass particles in set luting glass ionomer cements were also of varying shapes and sizes. The particle sizes in all four luting cements (Fig. 9.32 to 9.35) appeared to be similar.

When the glass particles in the restorative cements were compared with those in the luting cements, it was apparent that the largest particles in the restorative cements were commonly two to three times larger than those in the luting cements.

9.4 SEM INVESTIGATION OF THE PARTICLE SIZE OF A NUMBER OF GLASS IONOMER CEMENTS. DISCUSSION

The principal problem encountered in this part of the investigation was the potential for sampling error. Although precautions were taken to ensure a representative sample, sampling errors may arise during the placement of the powder onto the aluminium tape and the subsequent removal of excess powder by vibration. Sampling errors may also occur in the taking of photographs during the SEM examination. To minimize this tendency, at least four photographs were taken at each magnification.

Although the glass particle sizes in the restorative cements, Ketac and Fuji Type II, appeared to be similar, the 24 hour compressive strengths of these cements differed substantially (155.3 and 106.3 MPa, respectively--6.2). ChemFil, with a 24 hour compressive strength of 67.4 MPa, was found to be significantly weaker than Ketac and Fuji Type II; the larger particles in ChemFil generally appeared to be slightly larger than those in Ketac and Fuji Type II. The available evidence, therefore, failed to indicate a relationship between the larger glass particle sizes and the compressive strength of the cement.

Similarly, no relationship could be established between the particle size and the 24 hour tensile strength (7.2) of the restorative glass ionomer cements.

The 24 hour compressive strength of Fuji Type I was found to be approximately 50 and 100 per cent greater than Ketac-cem and ChemBond, respectively (6.3). The 24 hour tensile strength of Fuji Type I was approximately twice that of Ketac-cem and ChemBond (7.3). The glass particle sizes however, were similar in the three luting cements. Again no relationship between the particle size of the larger glass

particles and the strength of the luting glass ionomer cements was evident. It is possible that differences in the quantity and size of the abundant very small particles in the unreacted powder of each material may have been responsible for the differences in strength. The presence of any such differences between the small particles were not detectable within the limits of this investigation.

The restorative cements were generally found to be twice as strong as their luting counterparts (with the exception of Fuji Type II and Fuji Type I) (6.4; 7.4). The particle sizes in the restorative cements were found to be two to three times larger than those in the luting cements. It is interesting to note that although the glass particles in Fuji Type I were smaller than those in Fuji Type II (and similar to those in other glass ionomer luting cements), Fuji Type I was as strong as Fuji Type II and was approximately twice as strong as the other luting cements (ChemBond and Ketac-cem). It is possible that the general differences in the particle sizes between restorative and luting cements (with the exception of Fuji Type II and I) may be associated with differences in strength.

At the recommended consistency, the film thicknesses of the four luting glass ionomer cements, Ketac-cem, Fuji Type I, ChemBond and Hy-Bond C, were found to be 27, 47, 30 and 41.5 μm , respectively (8.2). An examination of the glass particles, however, showed that these four luting cements had similar particle sizes of the larger particles. The findings suggested that there was no relationship between particle size and film thickness, at the recommended powder : liquid ratio.

In contrast, the similarity in the particle sizes in the four luting cements is consistent with the finding that the four luting cements had similar "smallest clinically appropriate film thicknesses".

The differences in film thickness at the recommended consistencies appear to be attributable, in large part, to the powder : liquid ratios used.

The sizes of the larger particles in the restorative cements were found to be greater than those in the luting cements. This finding was consistent with the requirement that luting cements should possess low film thickness and consequently a small particle size (Wilson et al, 1977).

The range of particle sizes in the luting glass ionomer cement powders was surprising. The powders generally contained a small number of relatively large particles (up to 20 μm in minimum cross-section) interspersed within an abundance of very fine particles (less than 1 μm in minimum cross-section) many of which, it can be assumed, have completely reacted in the set cement.

No comparison of these findings with those of other investigators is possible, because of the current lack of published data on this aspect of glass ionomer cements.

9.5

SUMMARY

The luting glass ionomer cement powders contain a relatively small number of large particles up to 20 μm in minimum cross-section. In addition, the luting glass ionomer cement powders contained an abundance of very fine (less than 1 μm minimum cross-section) particles. The restorative glass ionomer cement powders (unreacted) were not investigated; examination of the particles in the set restorative cements indicated the presence of particles with a minimum cross-section of up to 40-50 μm .

Of the restorative cements, Ketac and Fuji Type II have similar particle size; ChemFil may have slightly larger particles. The particle sizes of the larger particles in the four luting cements were

similar. There did not appear to be any correlation between the glass particle size and the strength of the glass ionomer cements. Very similar smallest "clinically appropriate film thicknesses" were consistent with the similarity in the particle sizes of the larger glass particles in the luting cements.

- Fig. 9.1 -- Photomicrograph of a Ketac specimen finished with a low-speed diamond. Original magnification X480.
- Fig. 9.2 -- Photomicrograph of a Ketac specimen finished with a low-speed diamond. Original magnification X1,000.
- Fig. 9.3 -- Photomicrograph of a Ketac specimen finished with a coarse grade sandpaper disc in a low-speed handpiece. Original magnification X1,000.
- Fig. 9.4 -- Photomicrograph of a Ketac specimen finished with a coarse grade sandpaper disc in a low-speed handpiece. Original magnification X3,000.
- Fig. 9.5 -- Photomicrograph of a Ketac specimen finished with a fine sandpaper disc in a low-speed handpiece. Original magnification X240.
- Fig. 9.6 -- Photomicrograph of a Ketac specimen finished with a fine sandpaper disc in a low-speed handpiece. Original magnification X1,000.

Figure 9.1 - 9.6

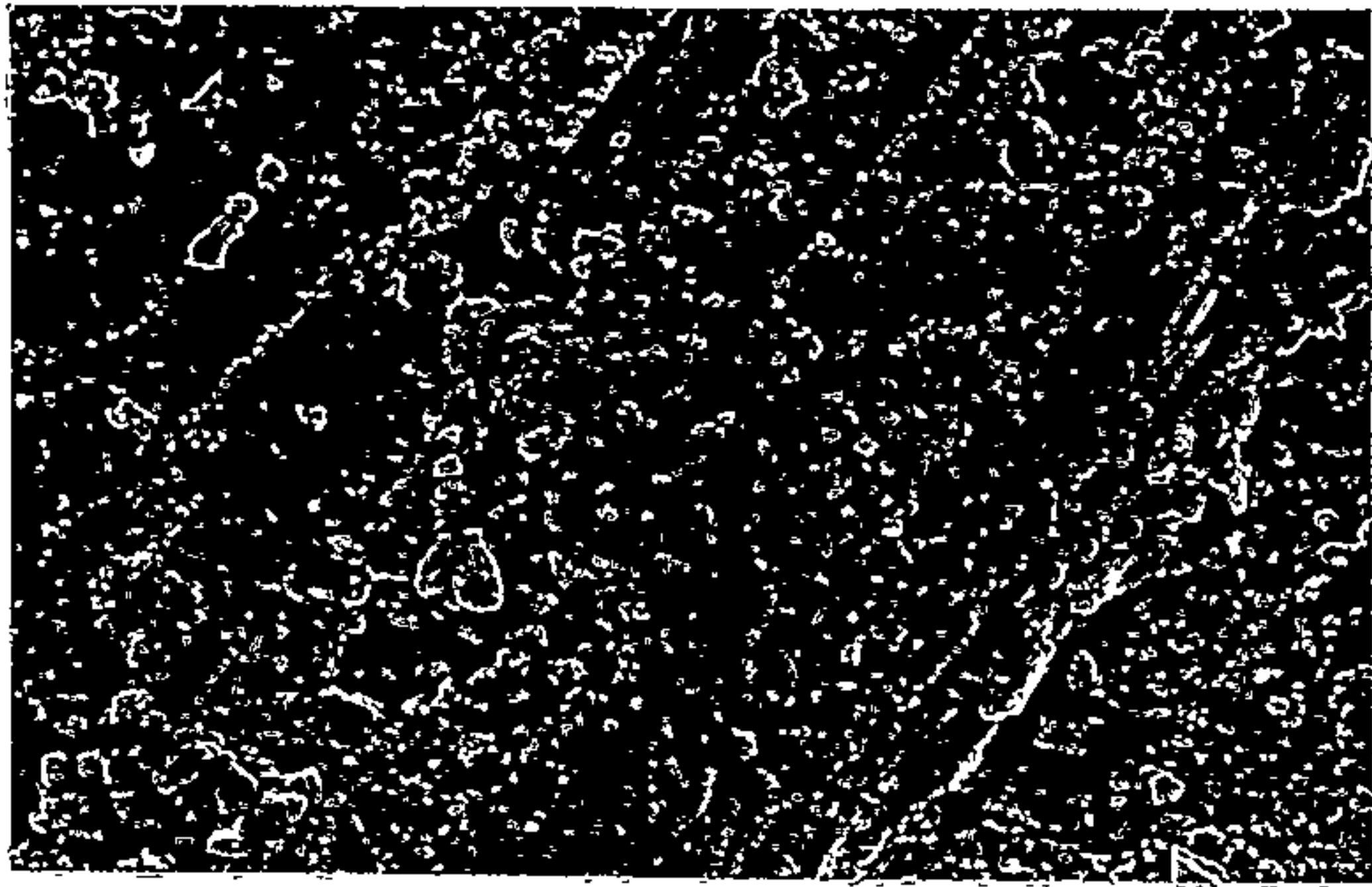


Fig. 9.1

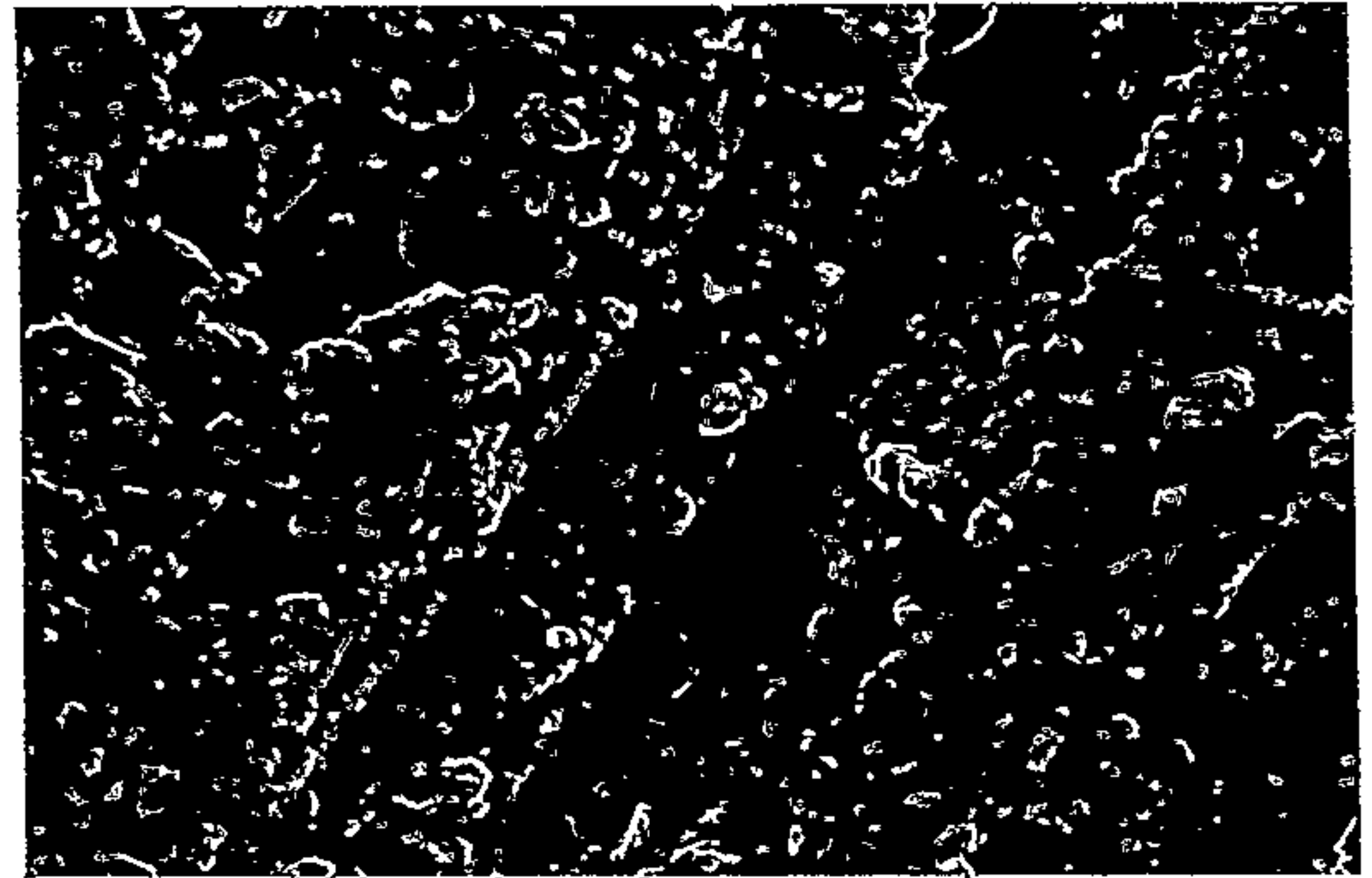


Fig. 9.2

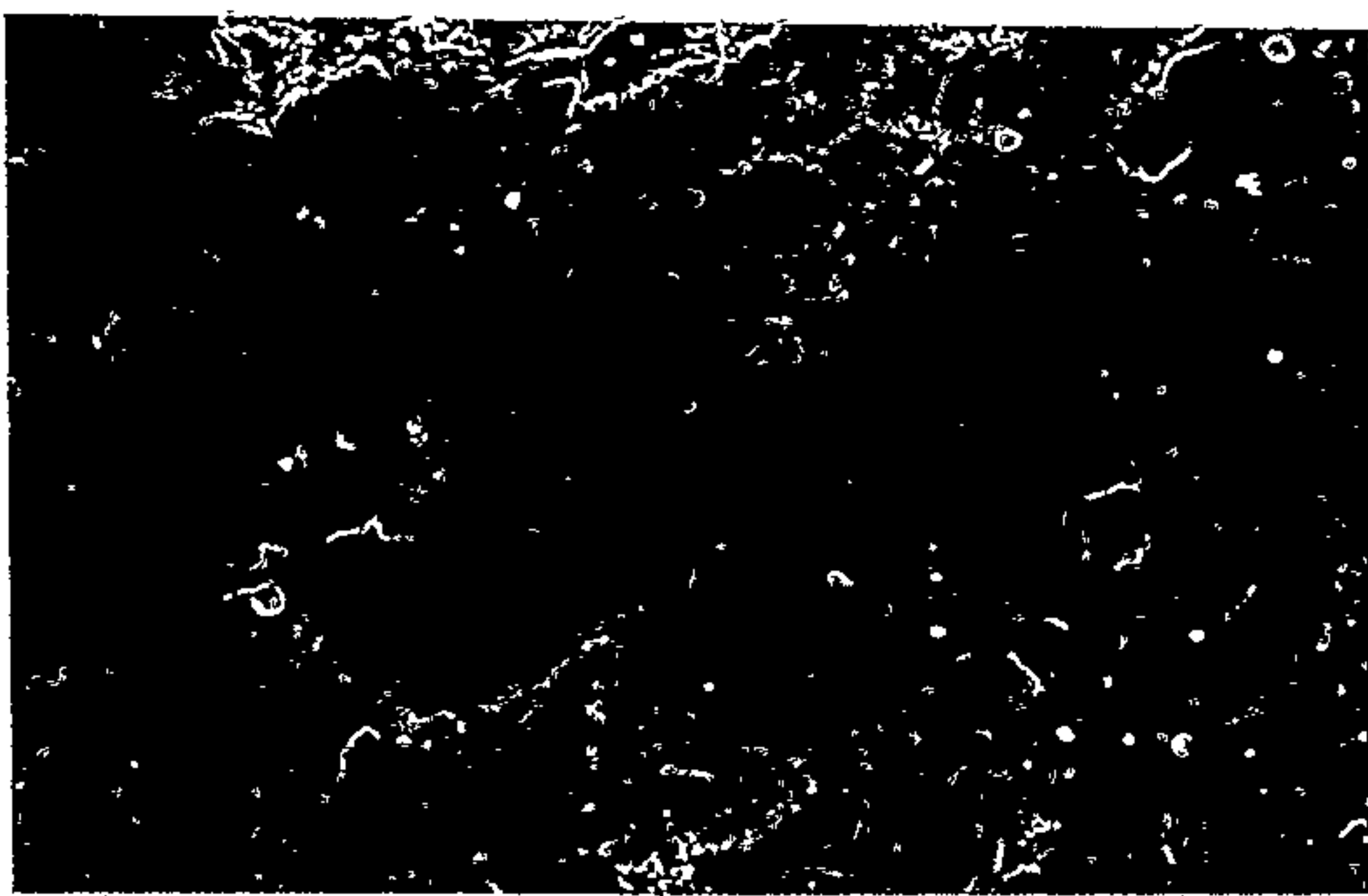


Fig. 9.3

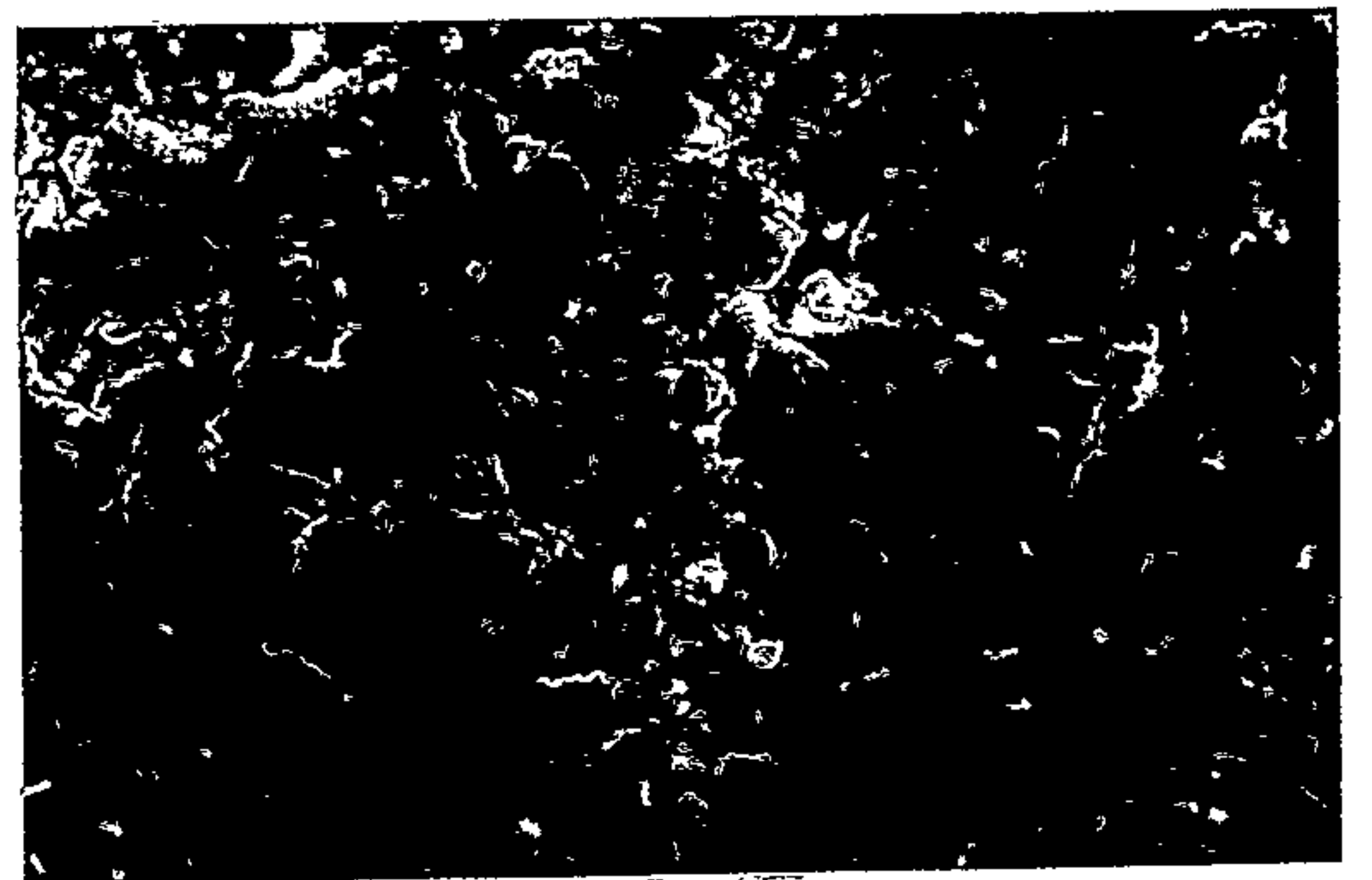


Fig. 9.4

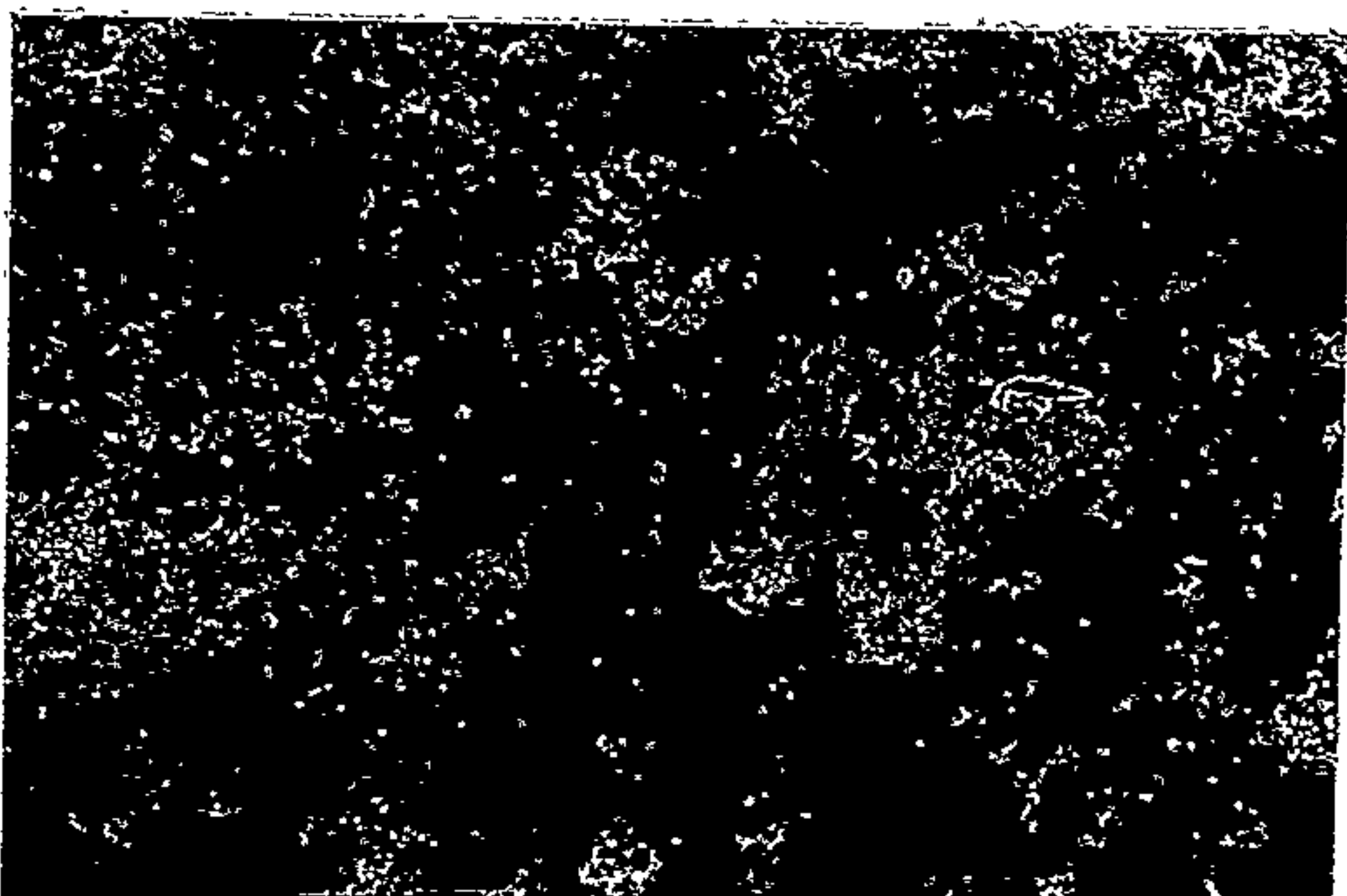


Fig. 9.5

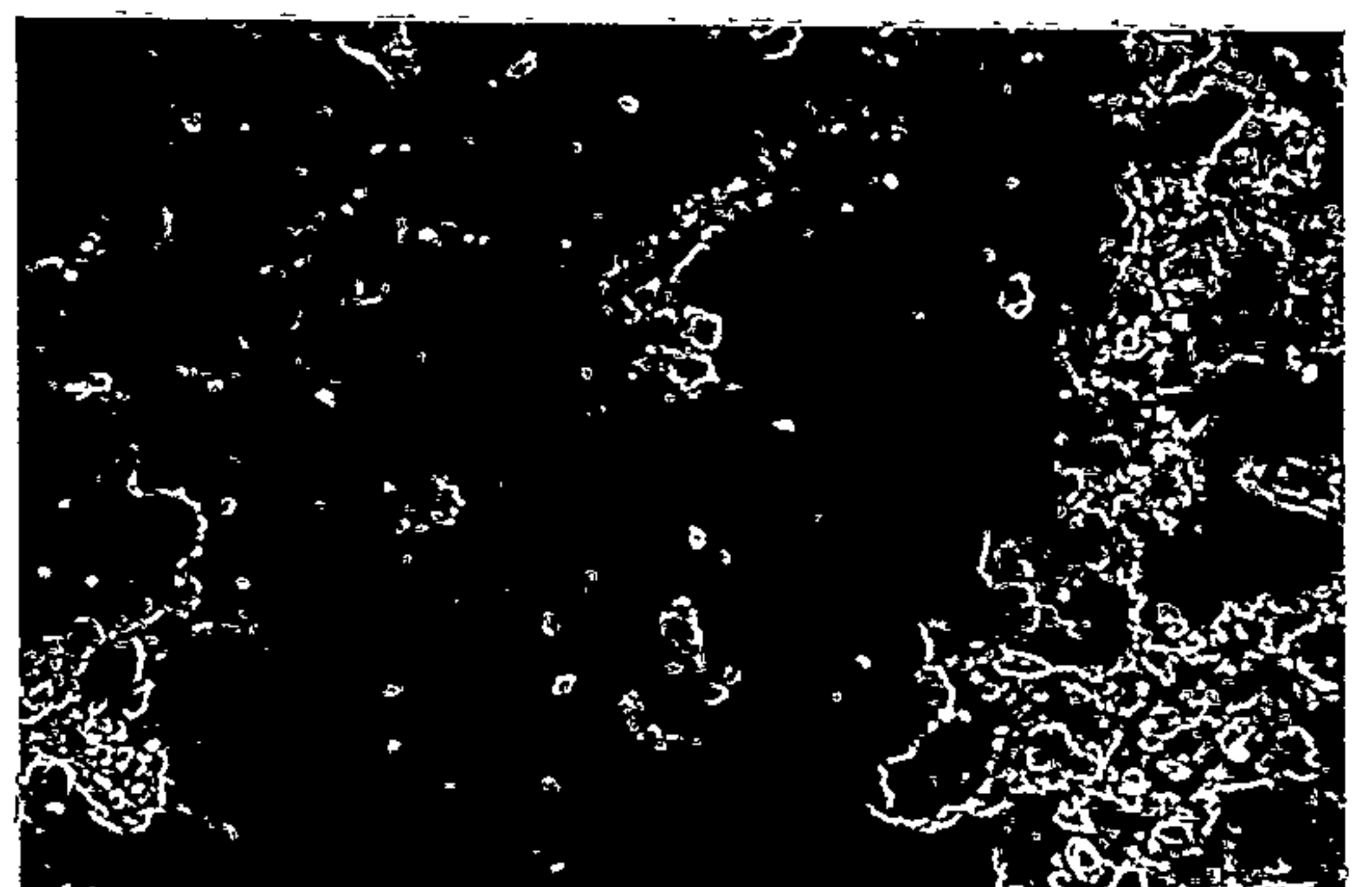


Fig. 9.6

Fig. 9.7 -- Photomicrograph of a Ketac specimen polymerized against a matrix strip. Original magnification X240.

Fig. 9.8 -- Photomicrograph of a Ketac specimen polymerized against a matrix strip. Original magnification X480.

Fig. 9.9 -- Photomicrograph of a Ketac specimen finished with a white stone using high-speed and a water spray. Original magnification X480.

Fig. 9.10 -- Photomicrograph of a Ketac specimen finished with a white stone using high-speed and a water spray. Original magnification X1,000.

Fig. 9.11 -- Photomicrograph of a Ketac specimen finished with a tungsten carbide bur using high-speed with water spray. Original magnification X240.

Fig. 9.12 -- Photomicrograph of a Ketac specimen finished with a tungsten carbide bur using high-speed with water spray. Original magnification X1,000.

Figure 9.7 - 9.12

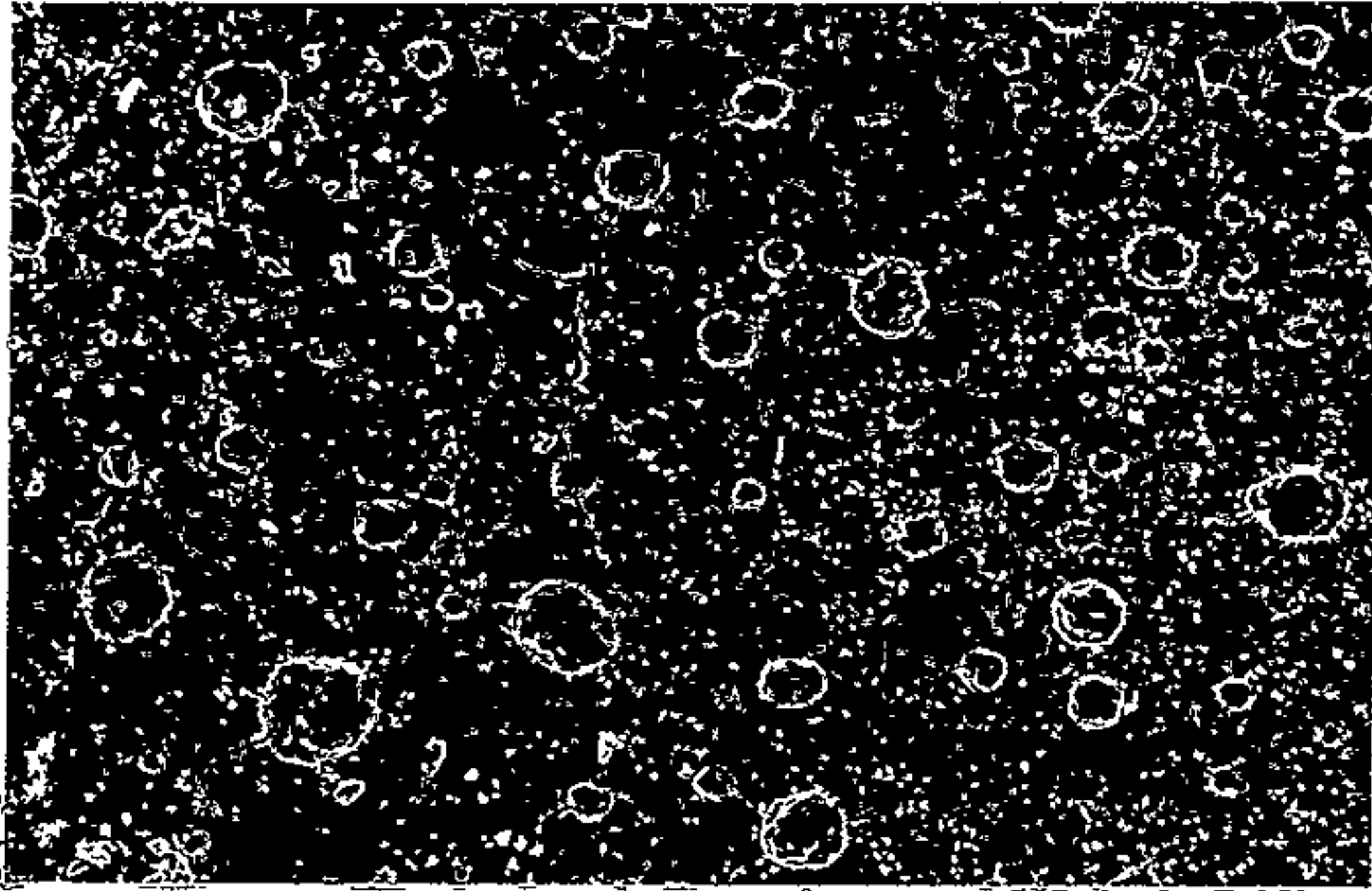


Fig. 9.7

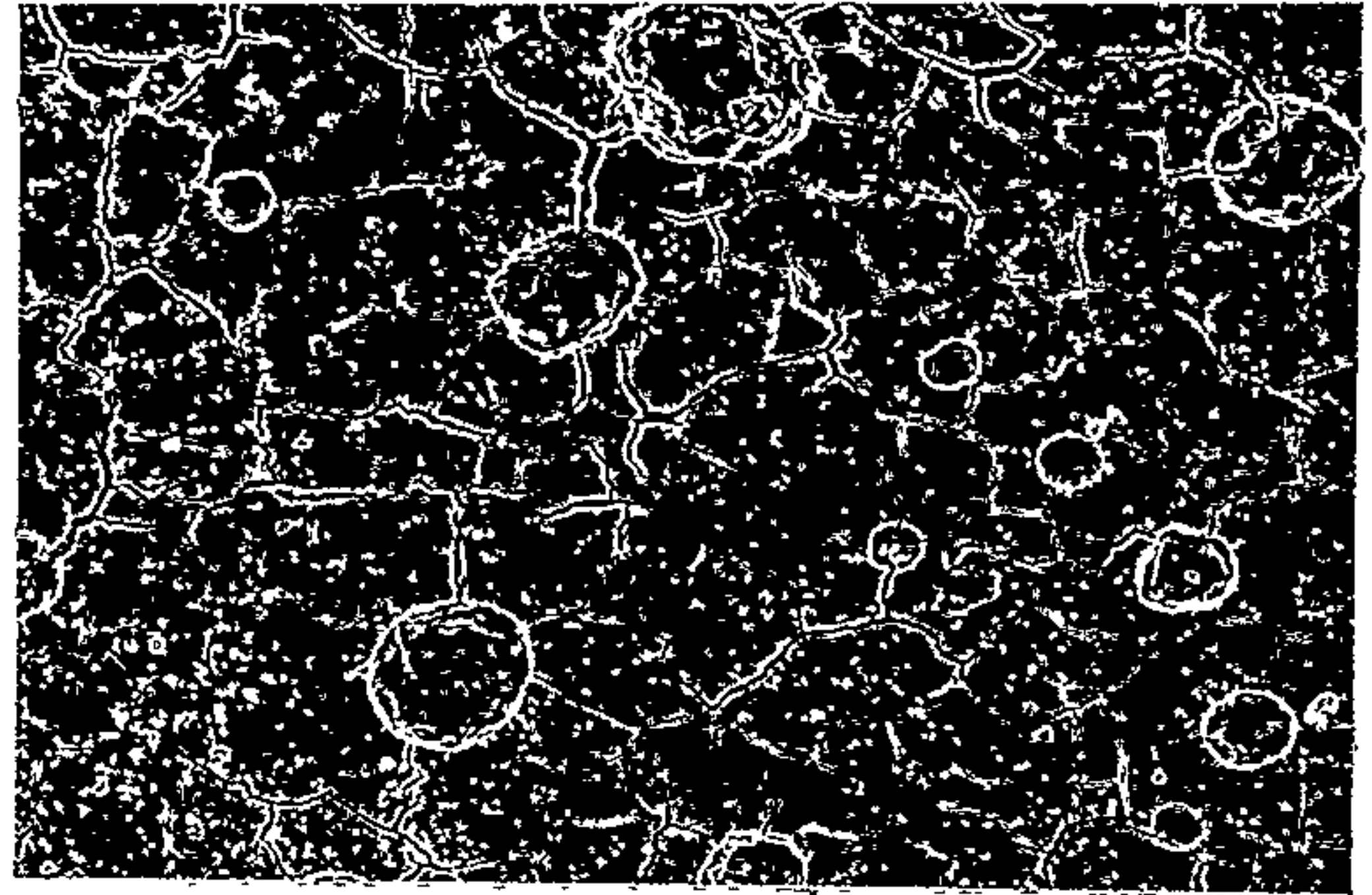


Fig. 9.8

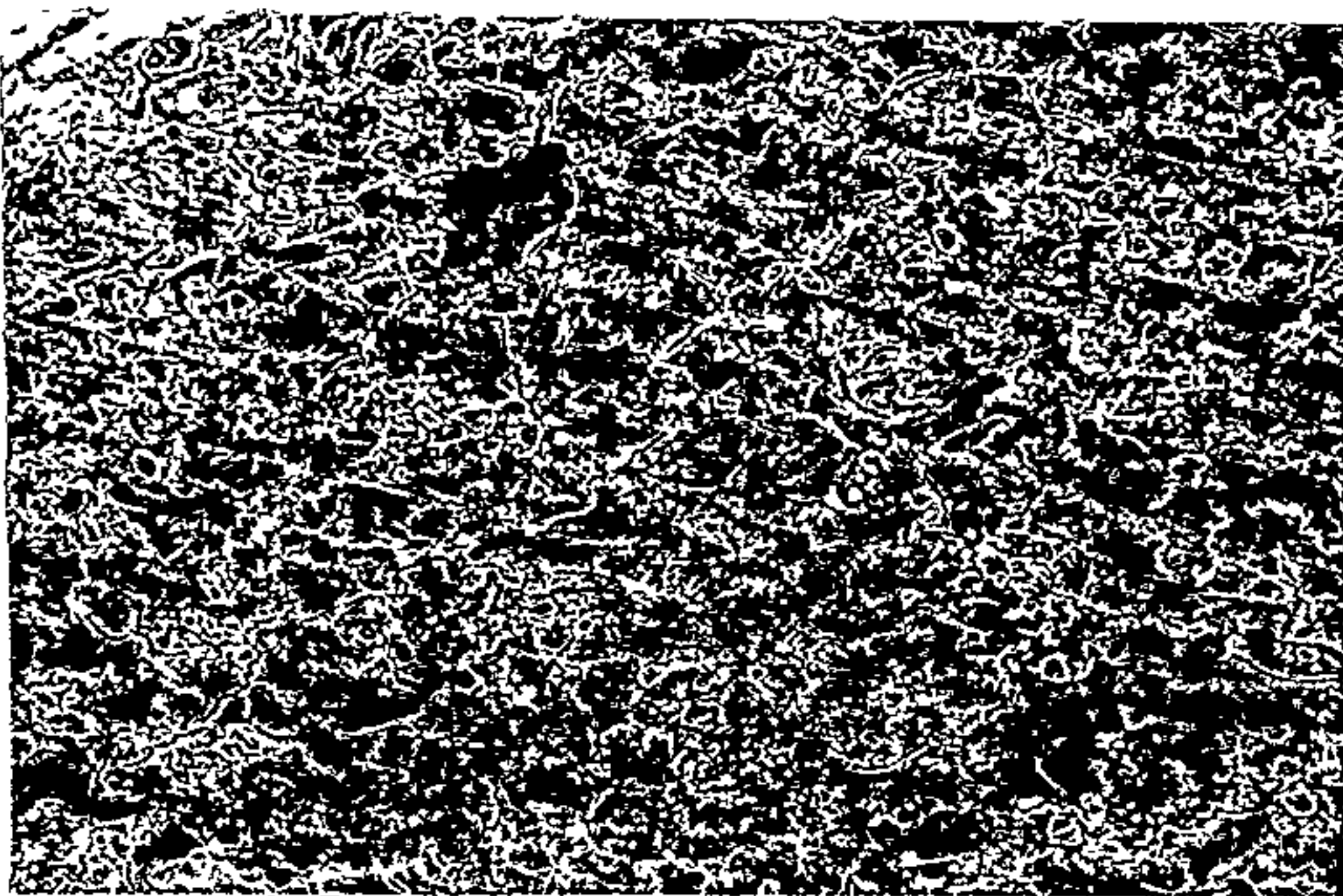


Fig. 9.9

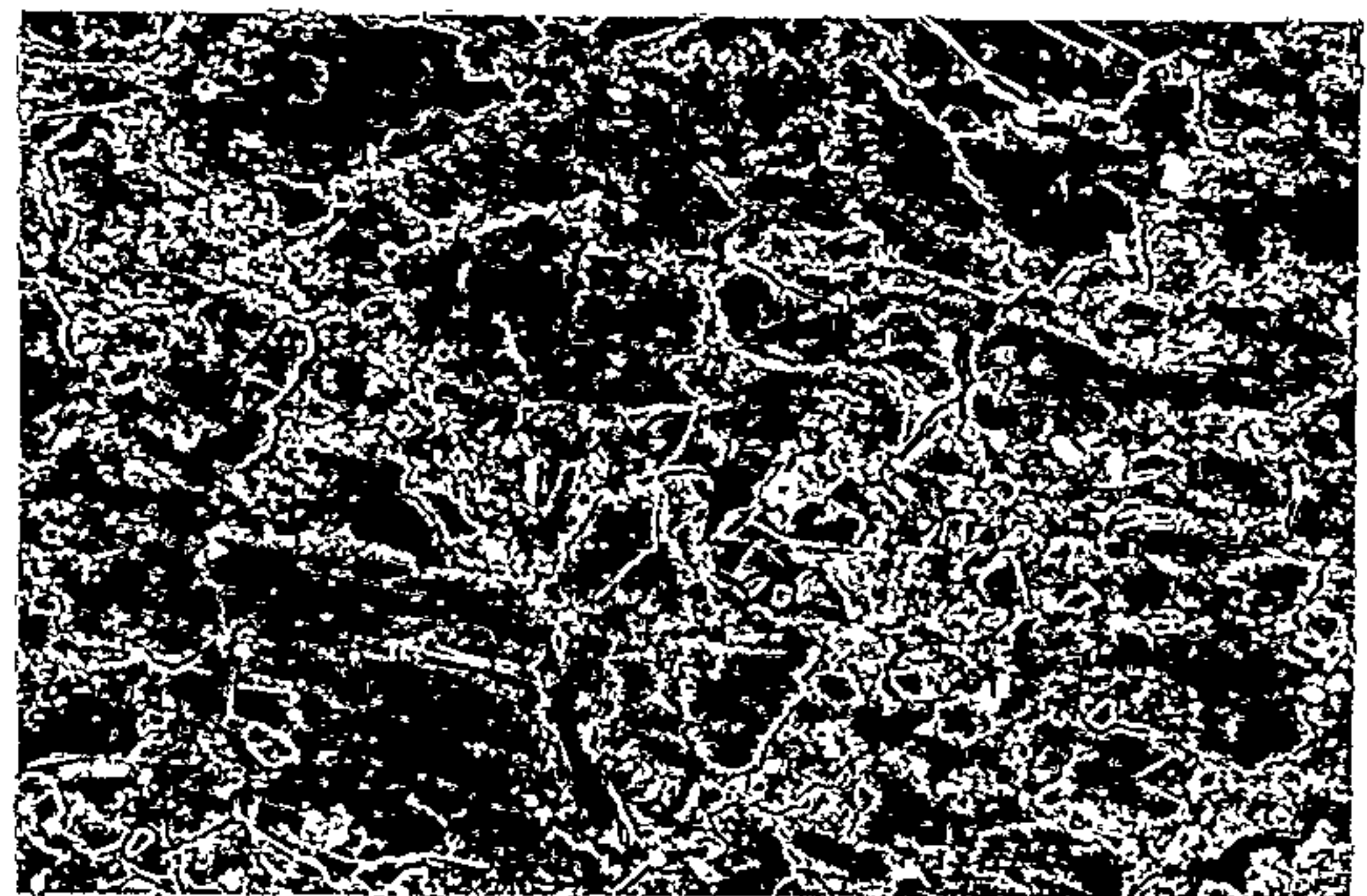


Fig. 9.10

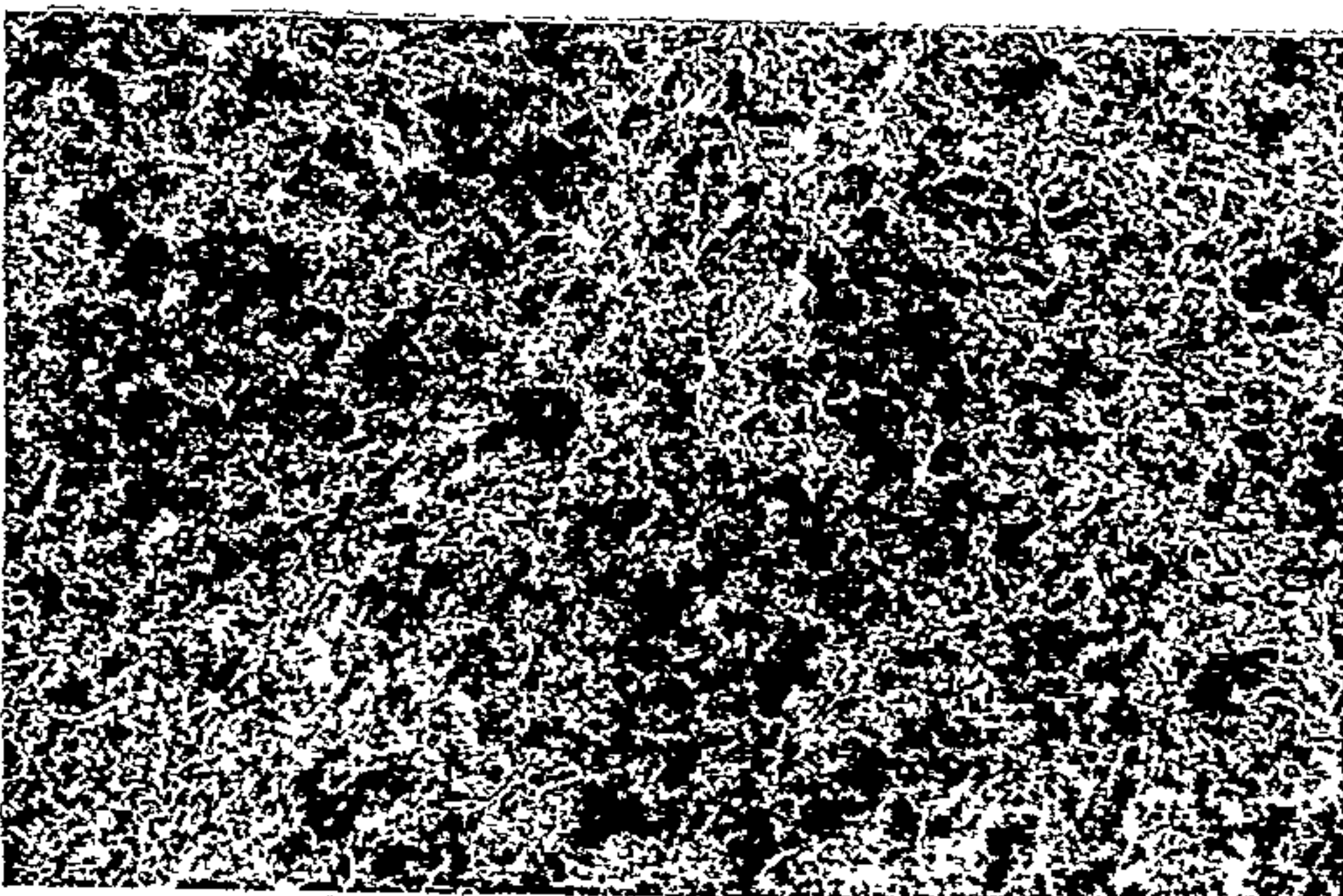


Fig. 9.11

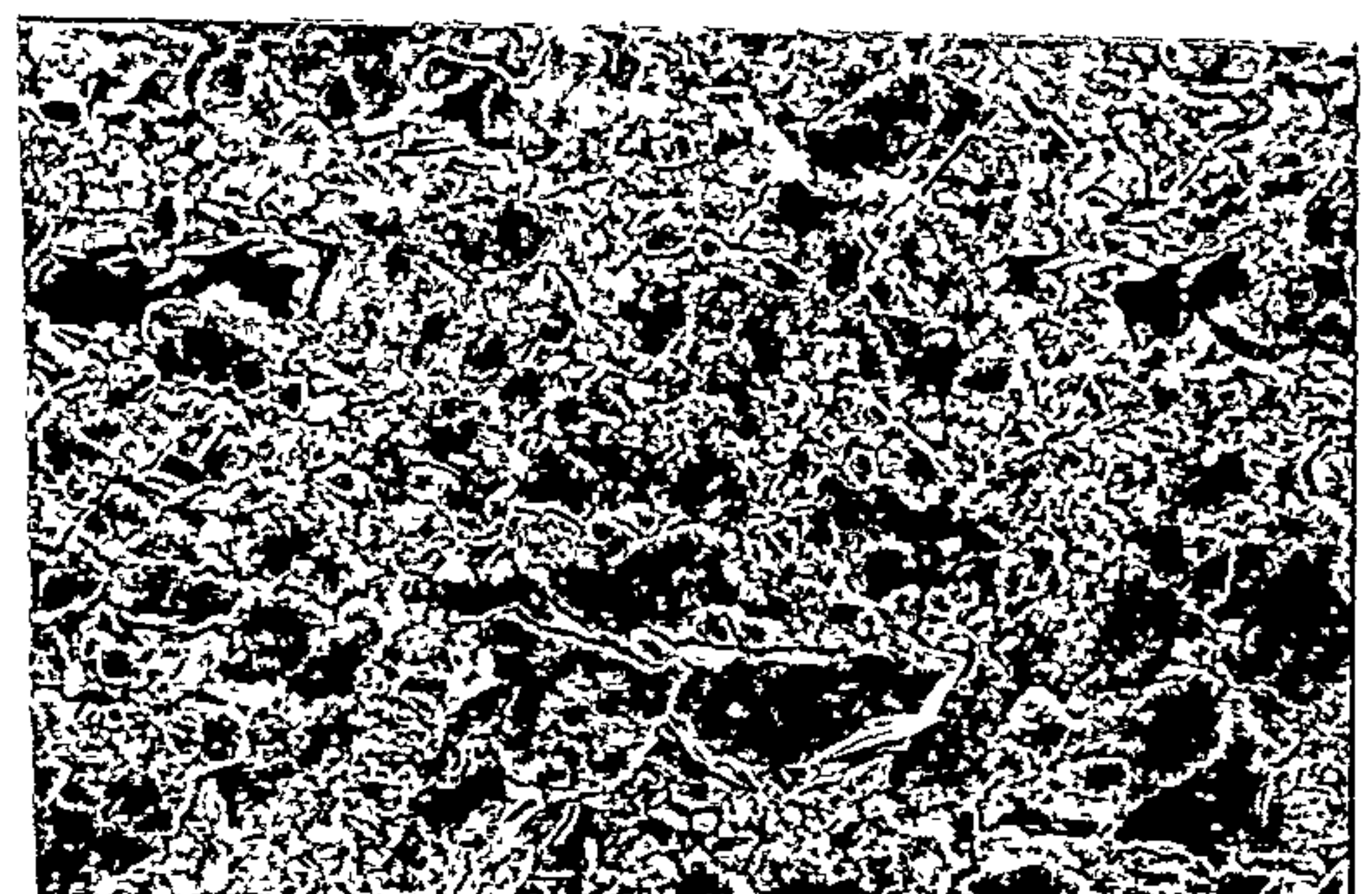


Fig. 9.12

Fig. 9.13 -- Photomicrograph of a Ketac specimen finished with pumice and glycerine, using a rubber cup at low speed for one minute. Original magnification X240.

Fig. 9.14 -- Photomicrograph of a Ketac specimen finished with pumice and glycerine, using a rubber cup at low speed for one minute. Original magnification X1,000.

Fig. 9.15 -- Photomicrograph of a Ketac specimen finished with Floran polishing paste on a rubber cup, at low speed for one minute. Original magnification X240.

Fig. 9.16 -- Photomicrograph of a Ketac specimen finished with Floran polishing paste on a rubber cup, at low speed for one minute. Original magnification X1,000.

Fig. 9.17 -- Photomicrograph of Ketac-cem powder particles mounted on aluminium tape without the use of alcohol. Original magnification X1,000.

Fig. 9.18 -- Photomicrograph of the aluminium tape to which a drop of alcohol had been previously applied. Original magnification X1,000.

Figure 9.13 - 9.18

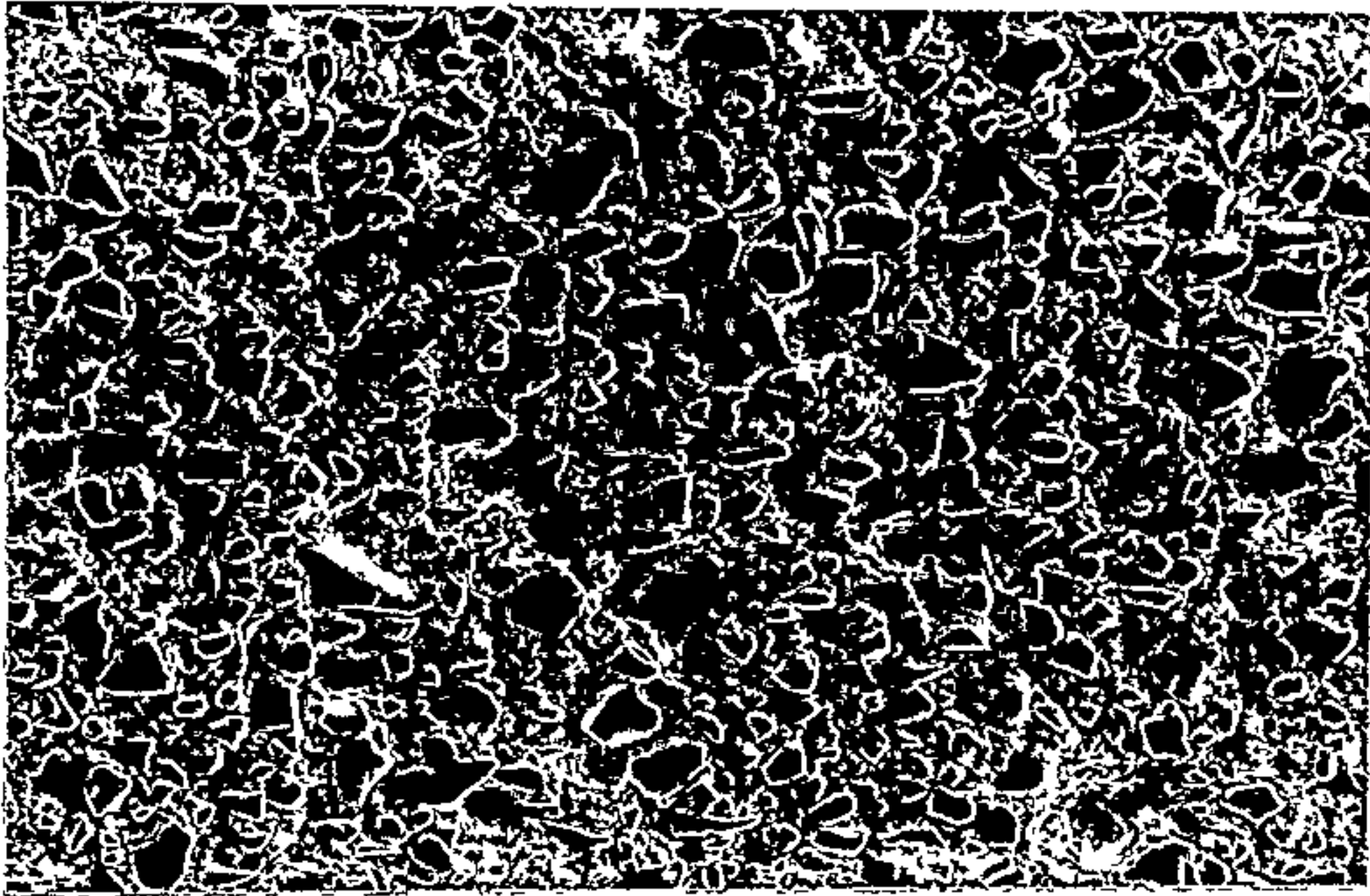


Fig. 9.13

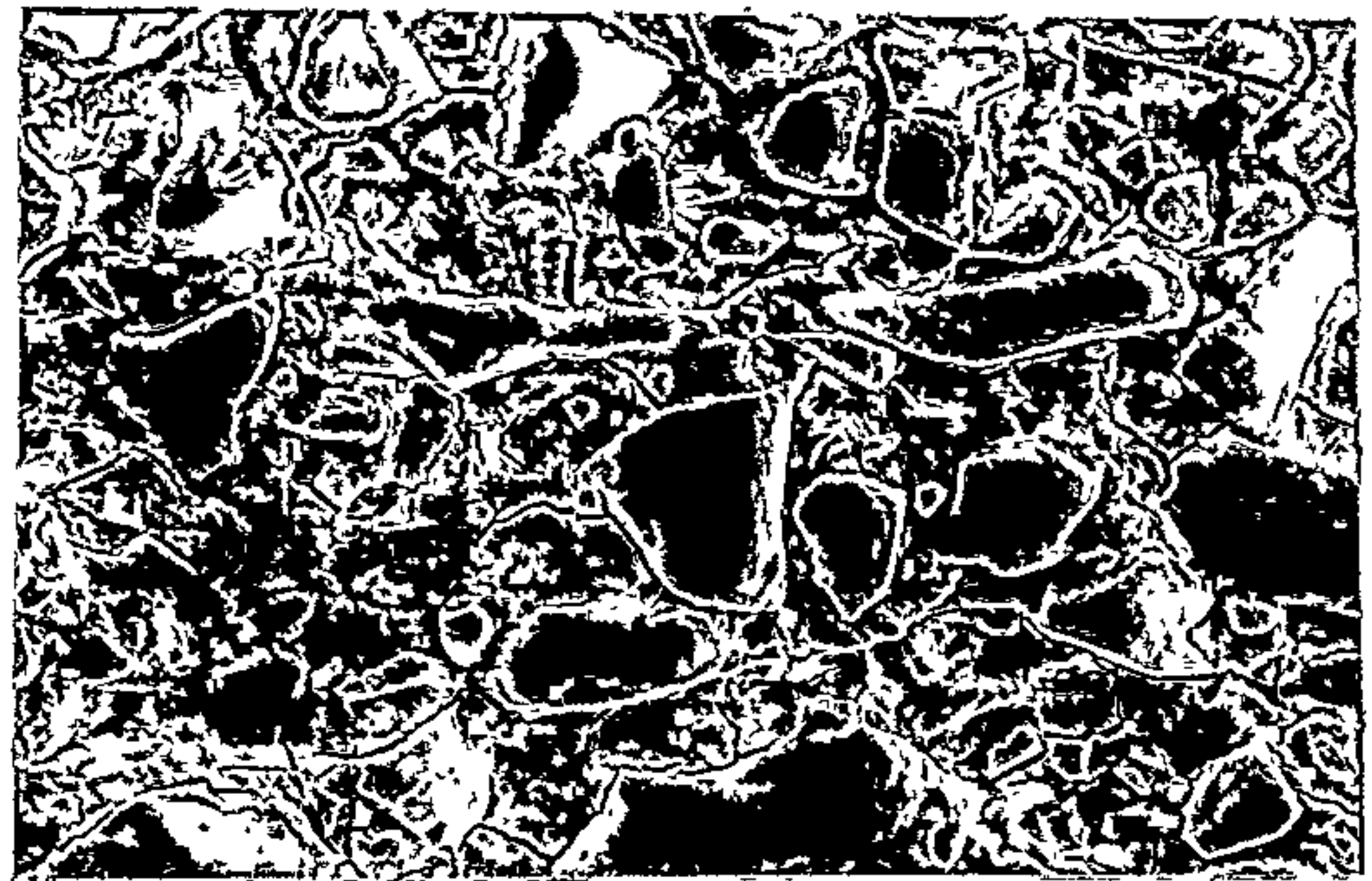


Fig. 9.14

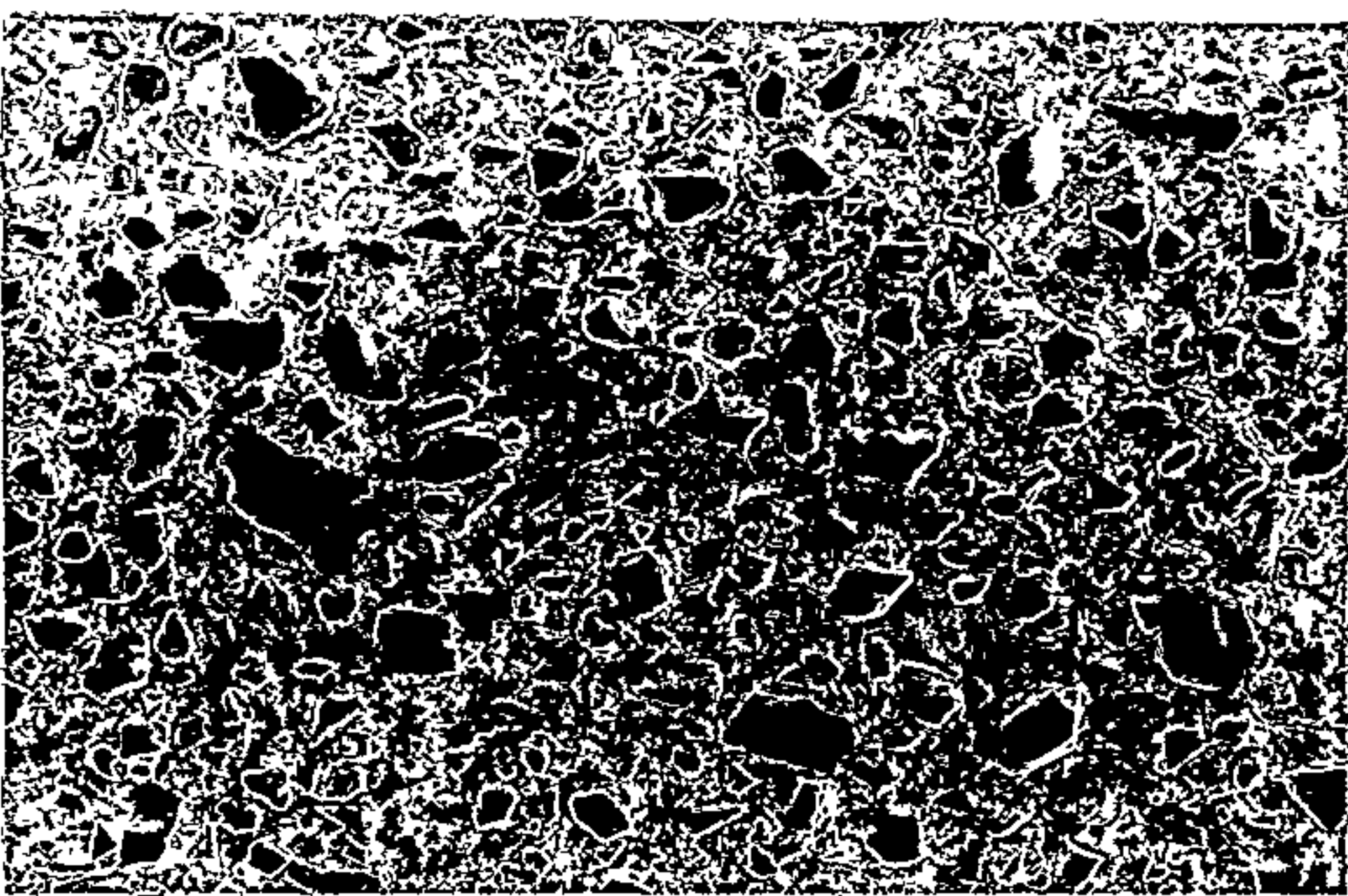


Fig. 9.15

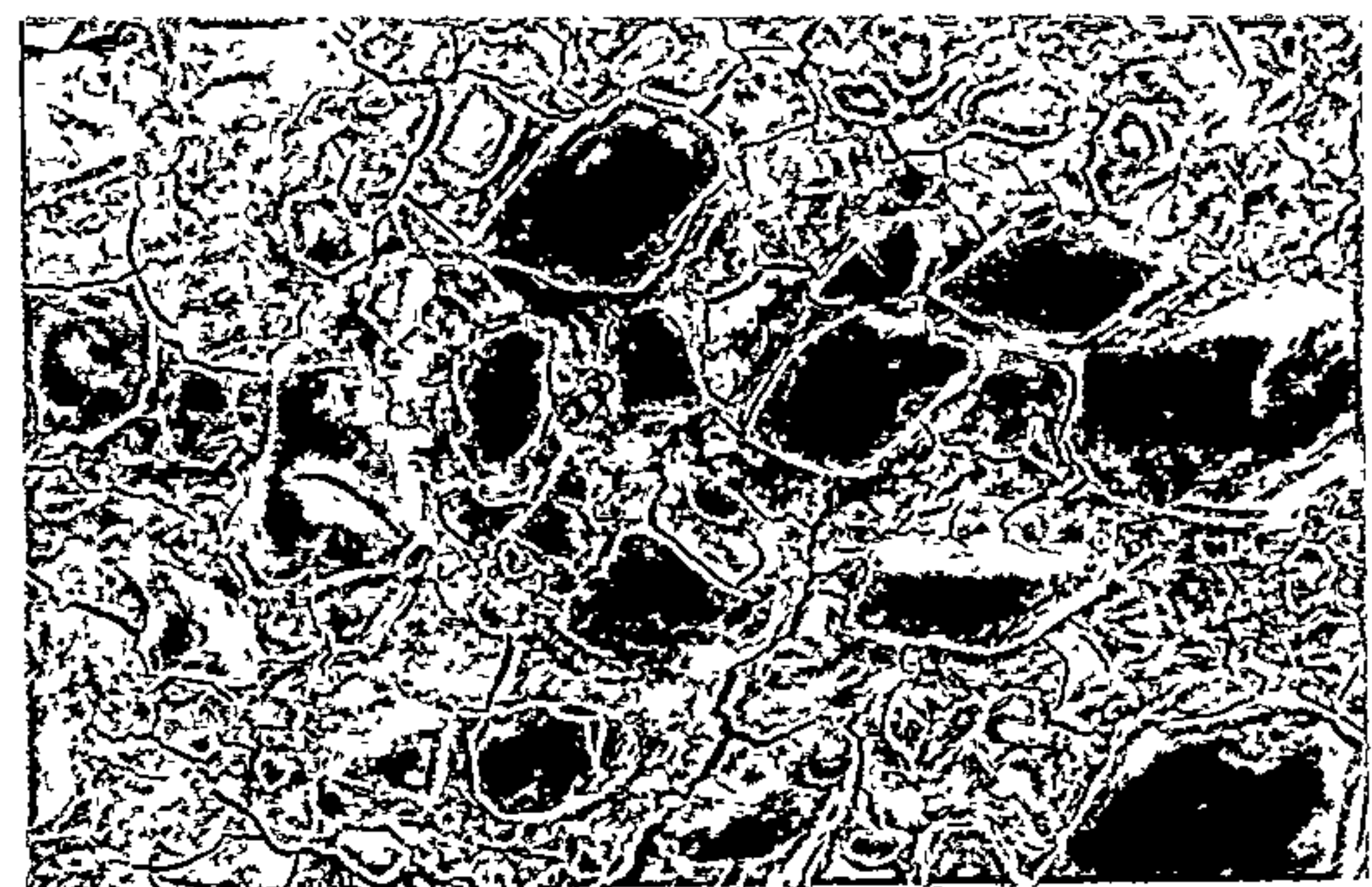


Fig. 9.16

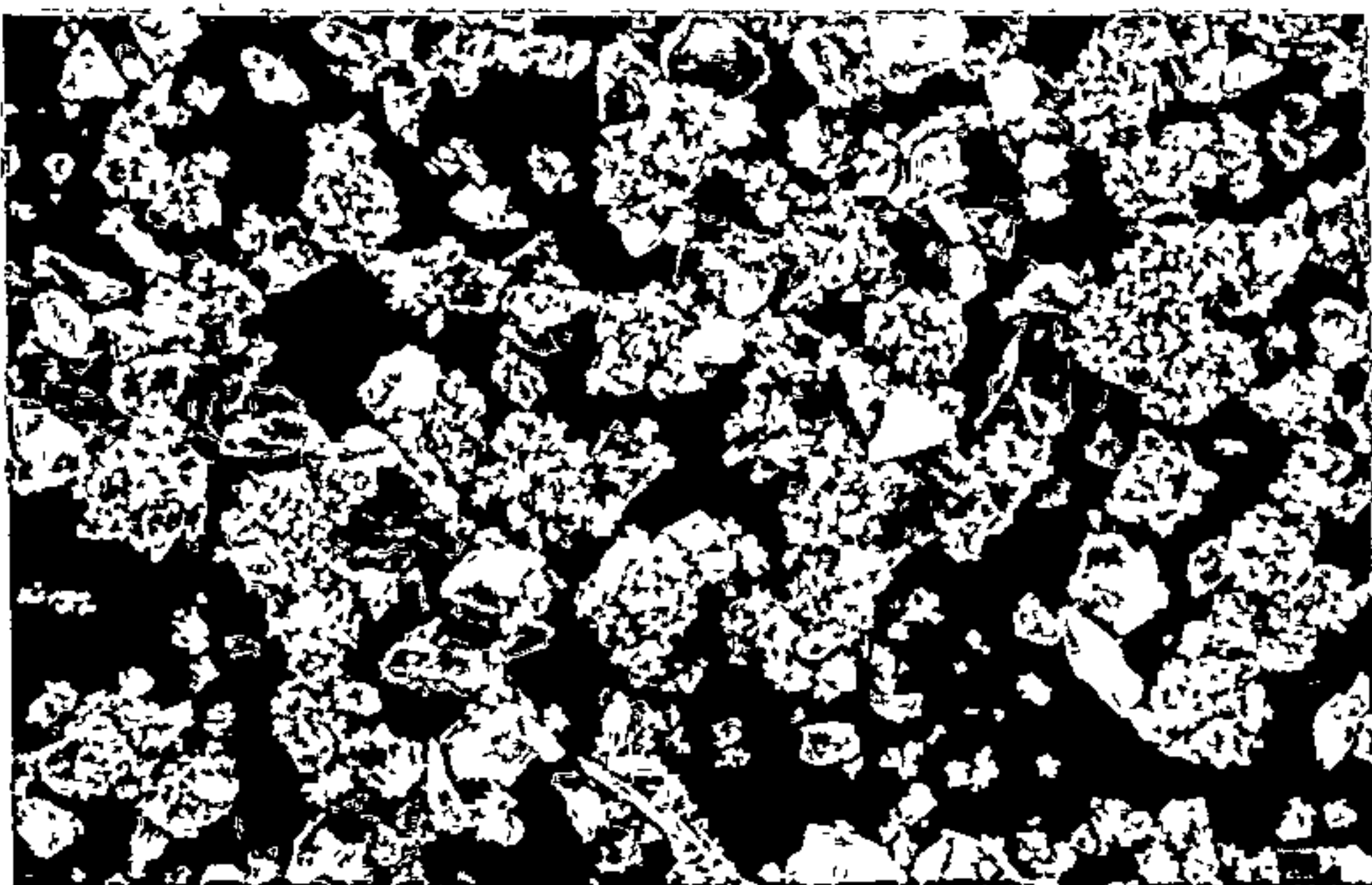


Fig. 9.17

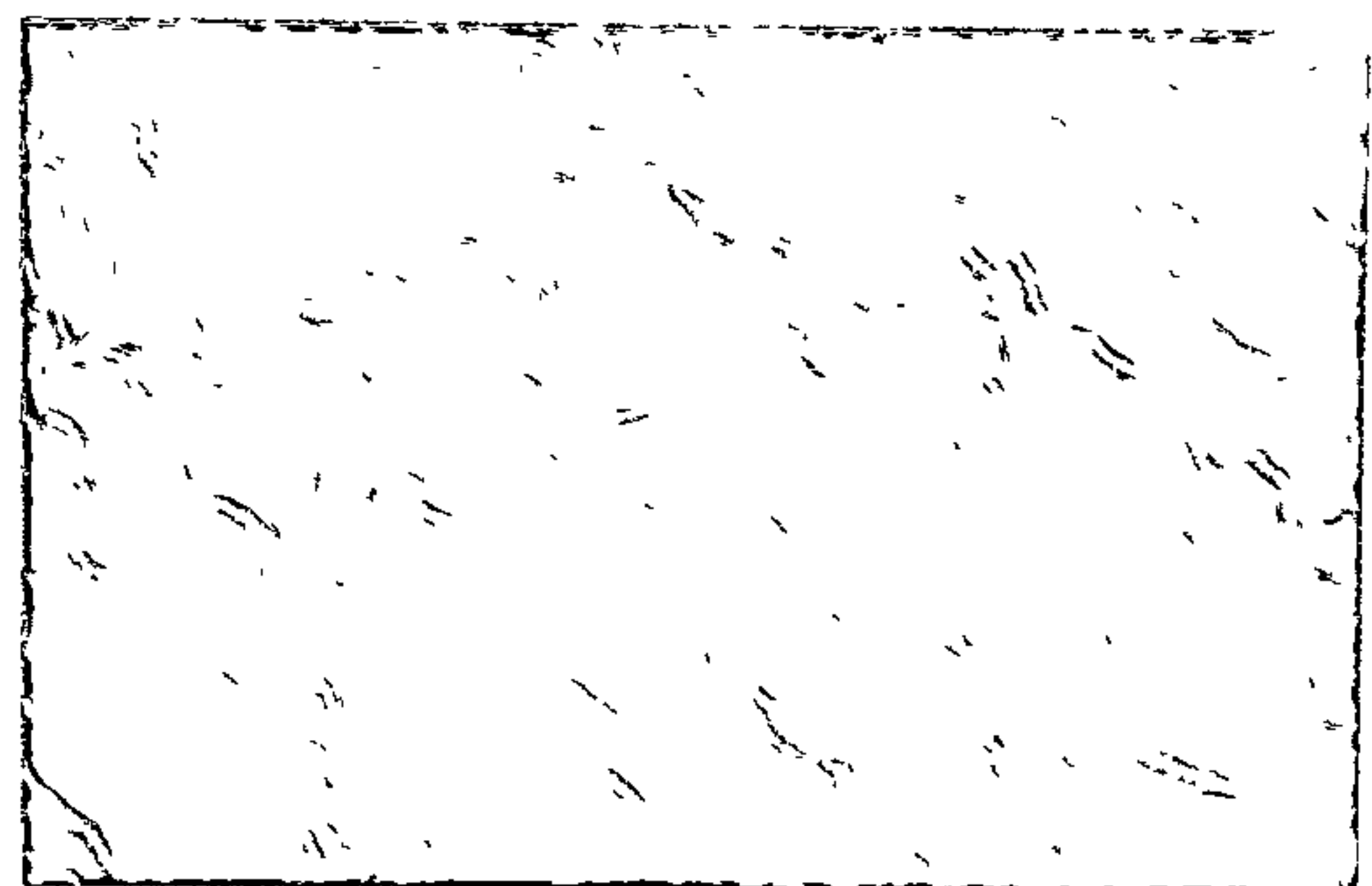


Fig. 9.18

Fig. 9.19 -- Photomicrograph of Ketac-cem powder particles
(mounted on aluminium tape) onto which a drop
of alcohol had been previously placed (as in
Fig. 9.20 - 9.26). Original magnification X1,000.

Fig. 9.20 -- Photomicrograph of Ketac-cem powder particles.
Original magnification X240.

Fig. 9.21 -- Photomicrograph of Fuji Type I powder particles.
Original magnification X1,000.

Fig. 9.22 -- Photomicrograph of Fuji Type I powder particles.
Original magnification X240.

Fig. 9.23 -- Photomicrograph of ChemBond powder particles.
Original magnification X1,000.

Fig. 9.24 -- Photomicrograph of ChemBond powder particles.
Original magnification X240.

Figure 9.19 - 9.24

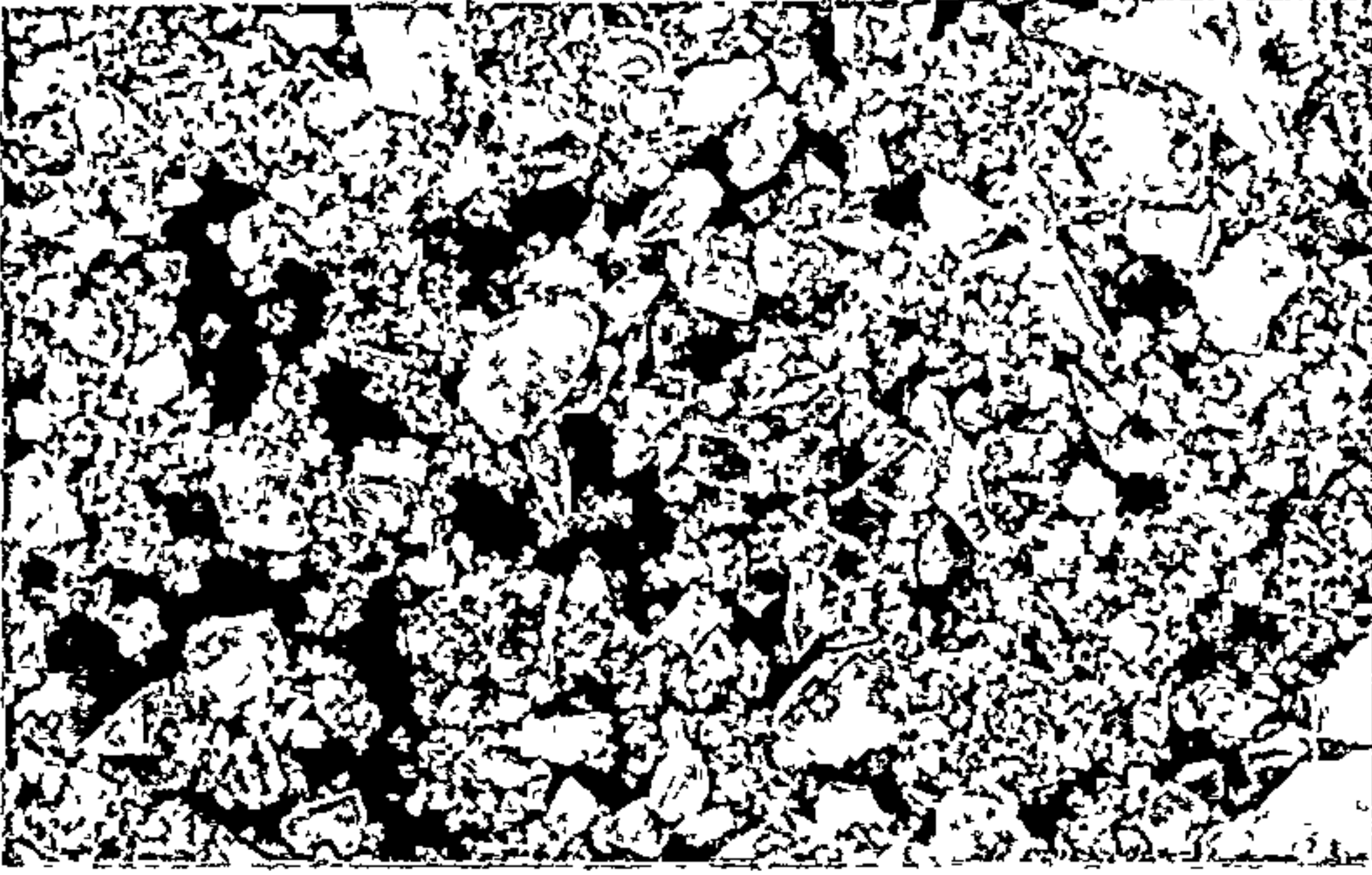


Fig. 9.19

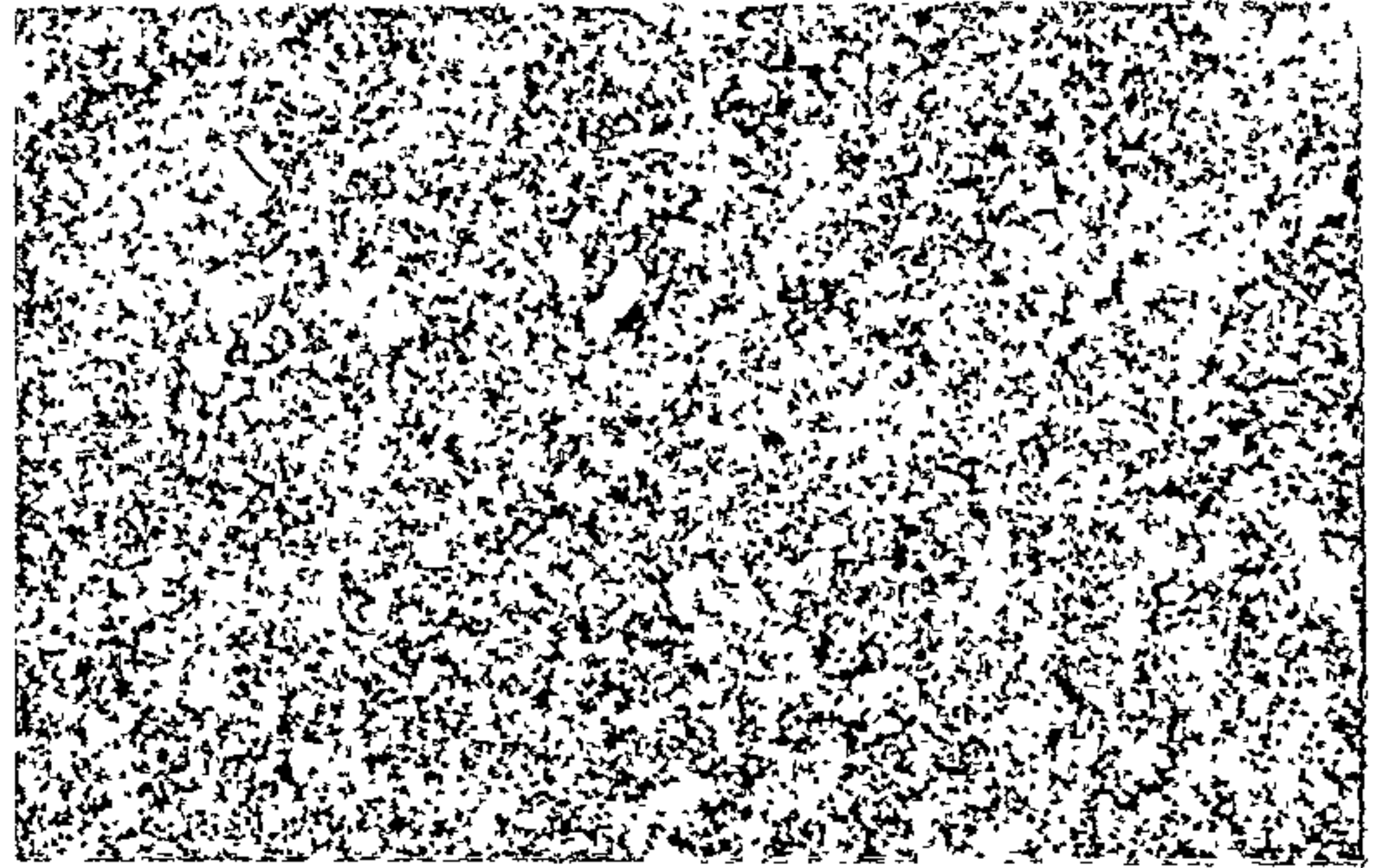


Fig. 9.20

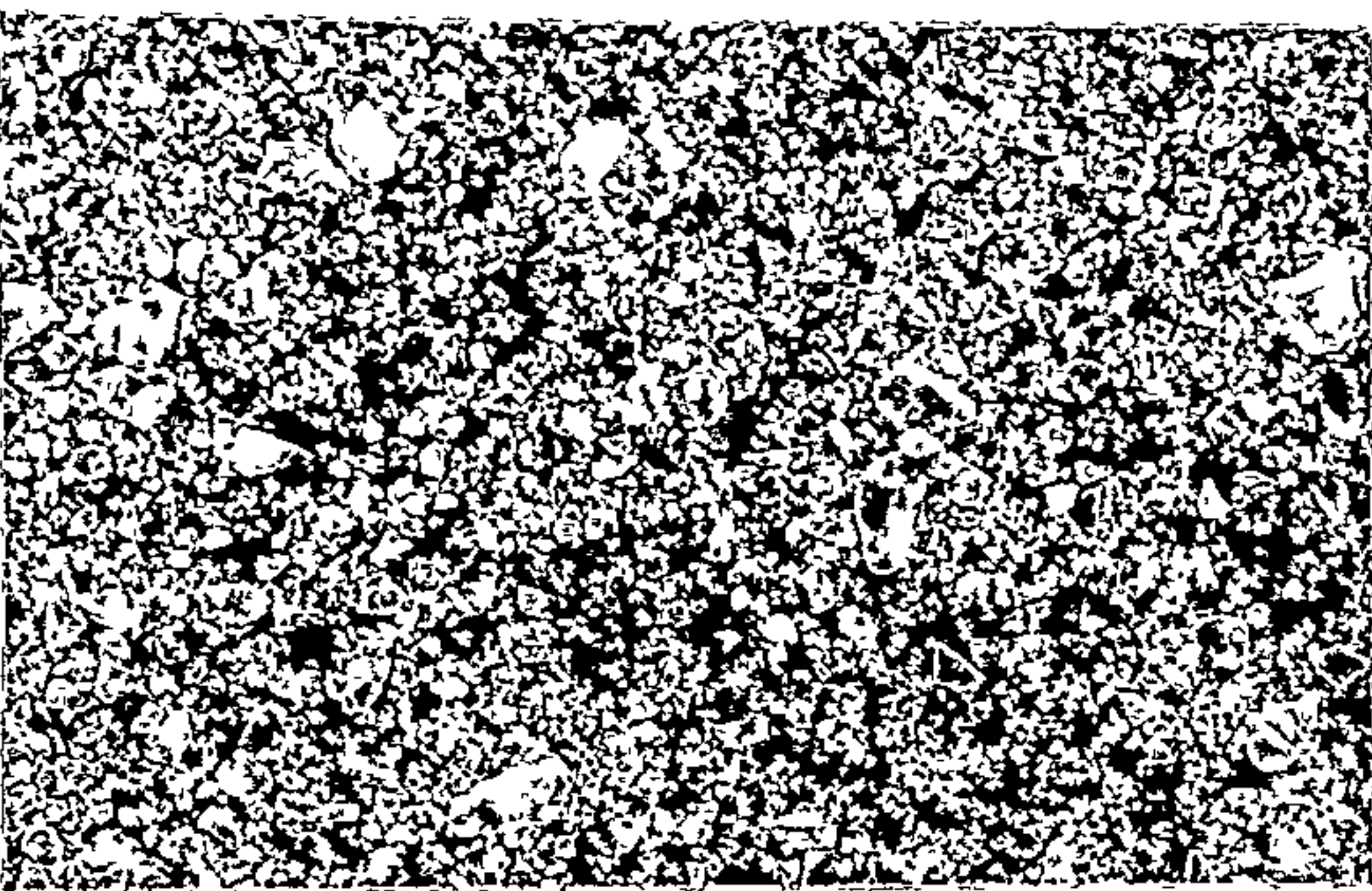


Fig. 9.21

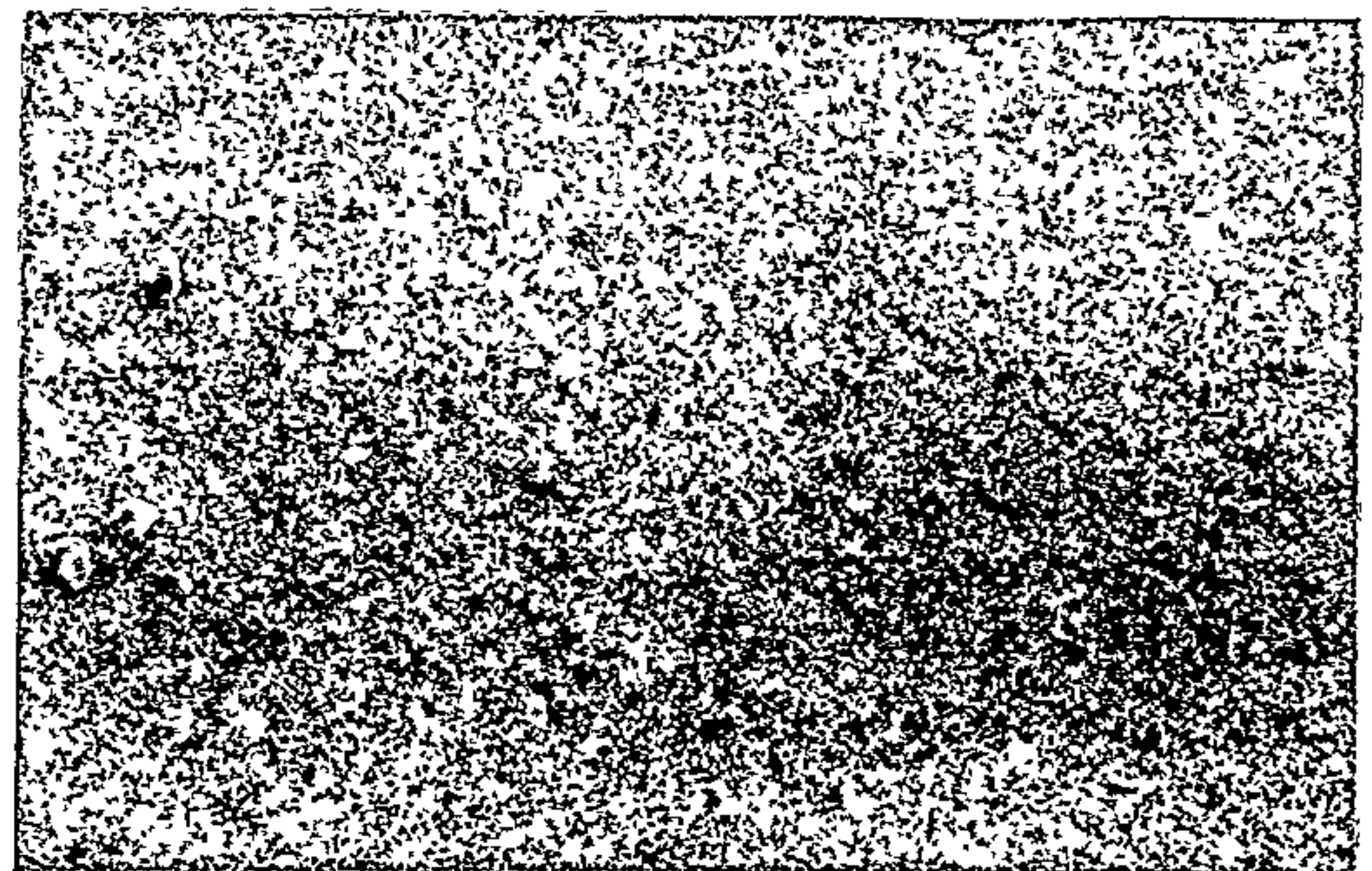


Fig. 9.22

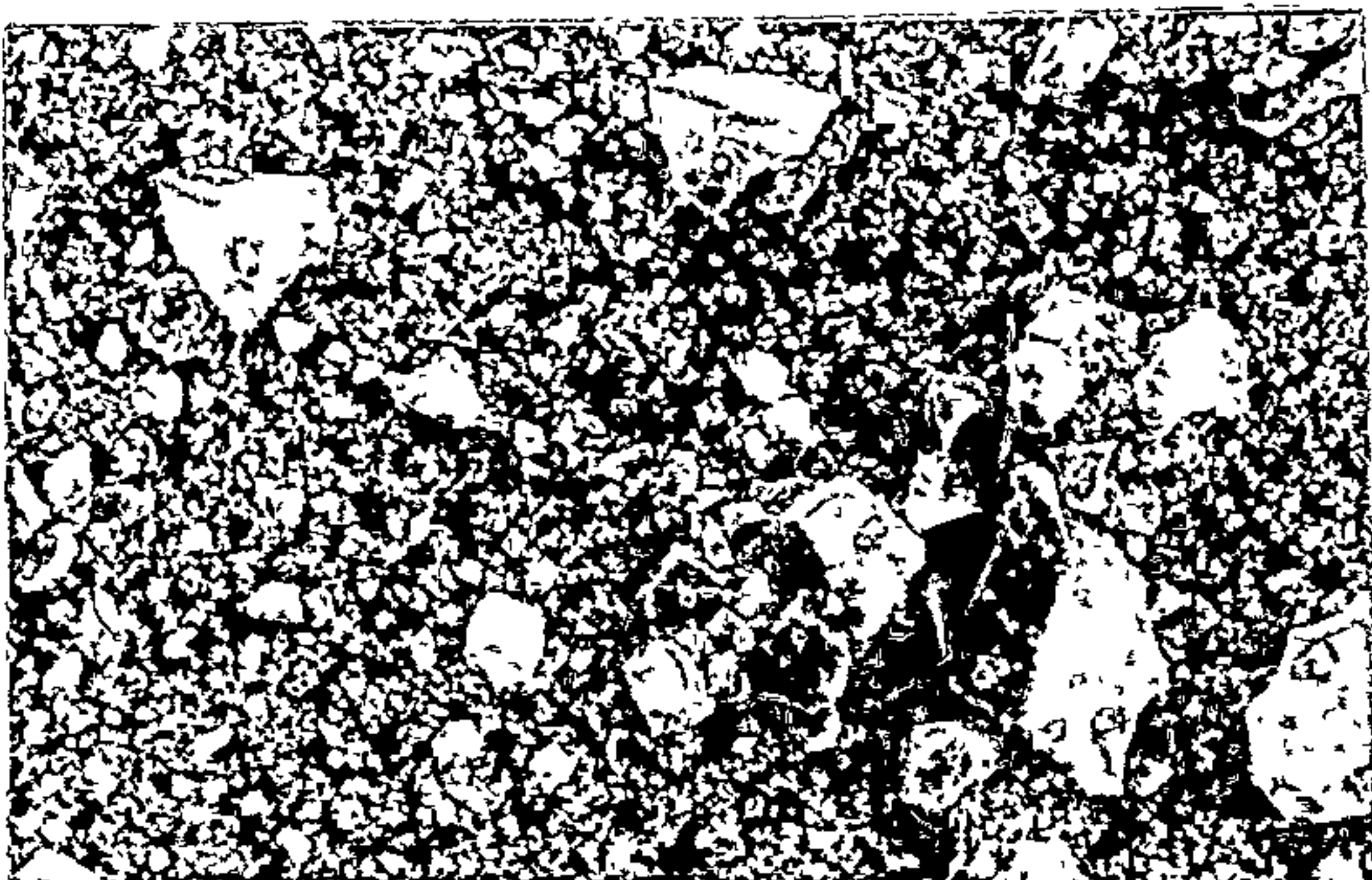


Fig. 9.23

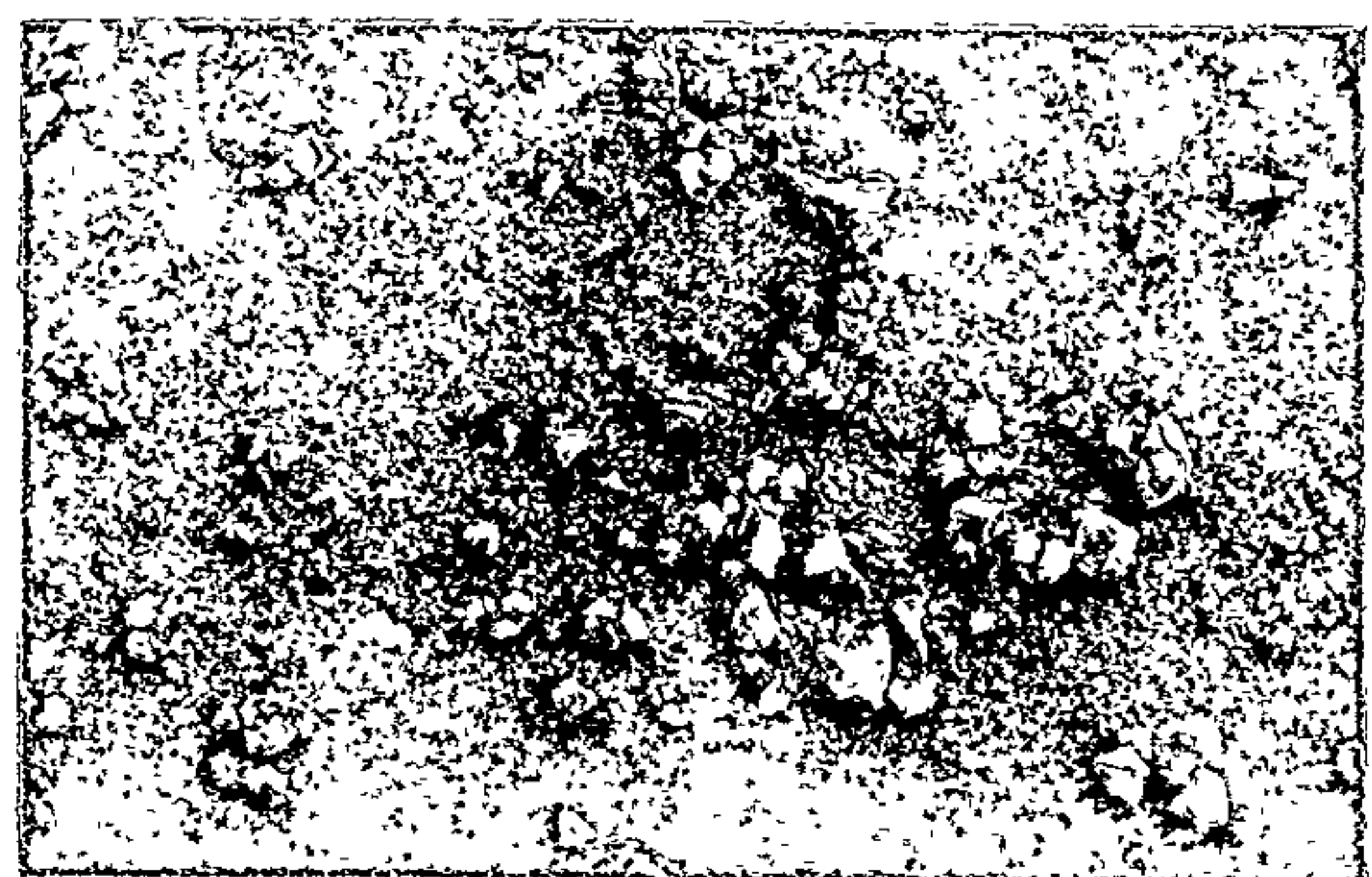


Fig. 9.24

Fig. 9.25 -- Photomicrograph of Hy-Bond C powder particles.

Original magnification X1,000.

Fig. 9.26 -- Photomicrograph of Hy-Bond C powder particles.

Original magnification X240.

Fig. 9.27 -- Photomicrograph of Fuji Type II glass ionomer cement.

Identification of glass particles is difficult.

Original magnification X480.

Fig. 9.28 -- Photomicrograph of ChemBond glass ionomer cement.

Identification of glass particles is difficult.

Original magnification X480.

Fig. 9.29 -- Photomicrograph of Ketac glass ionomer cement.

Original magnification X480.

Fig. 9.30 -- Photomicrograph of Fuji Type II glass ionomer cement.

Original magnification X480.

Figure 9.25 - 9.30



Fig. 9.25

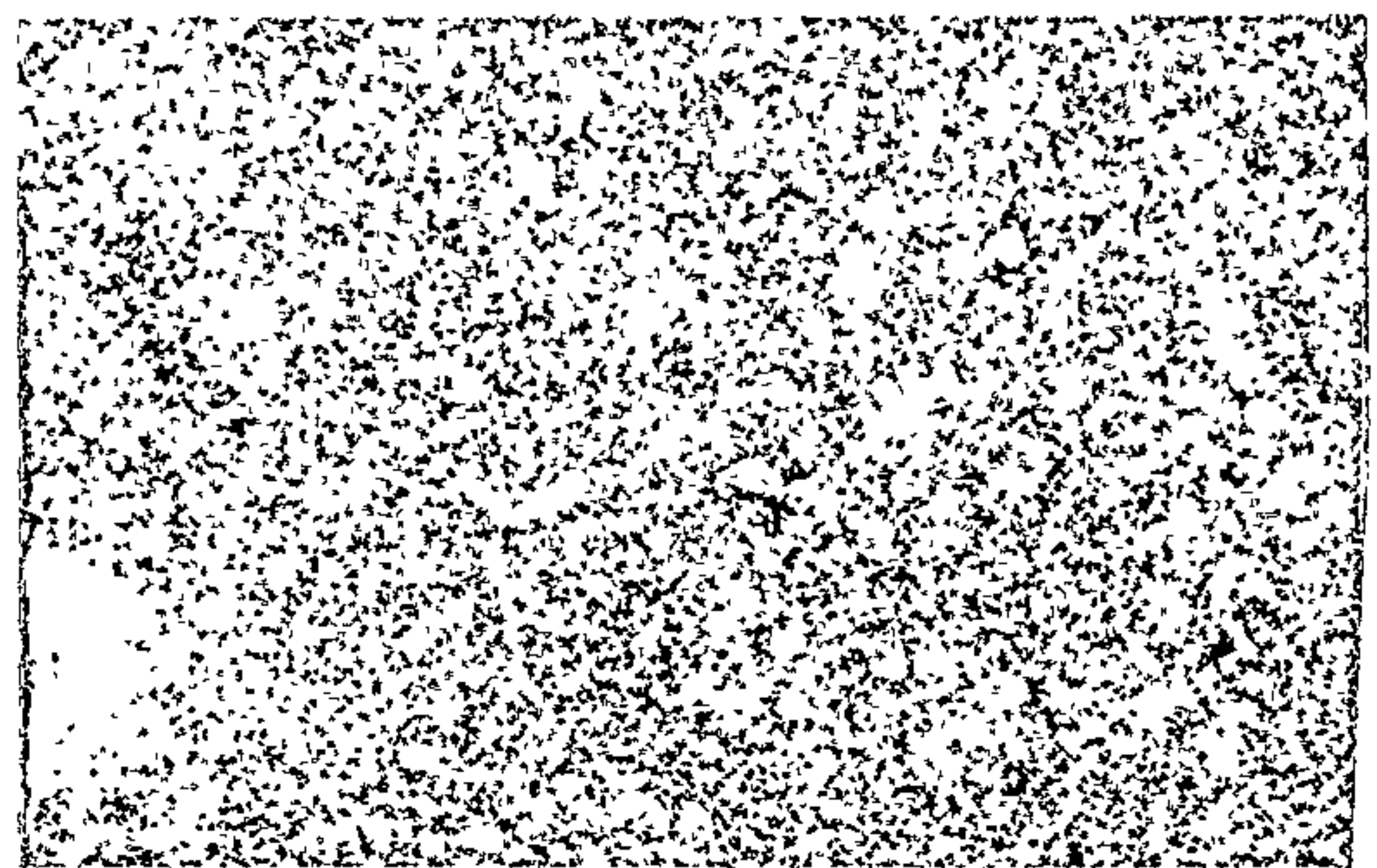


Fig. 9.26

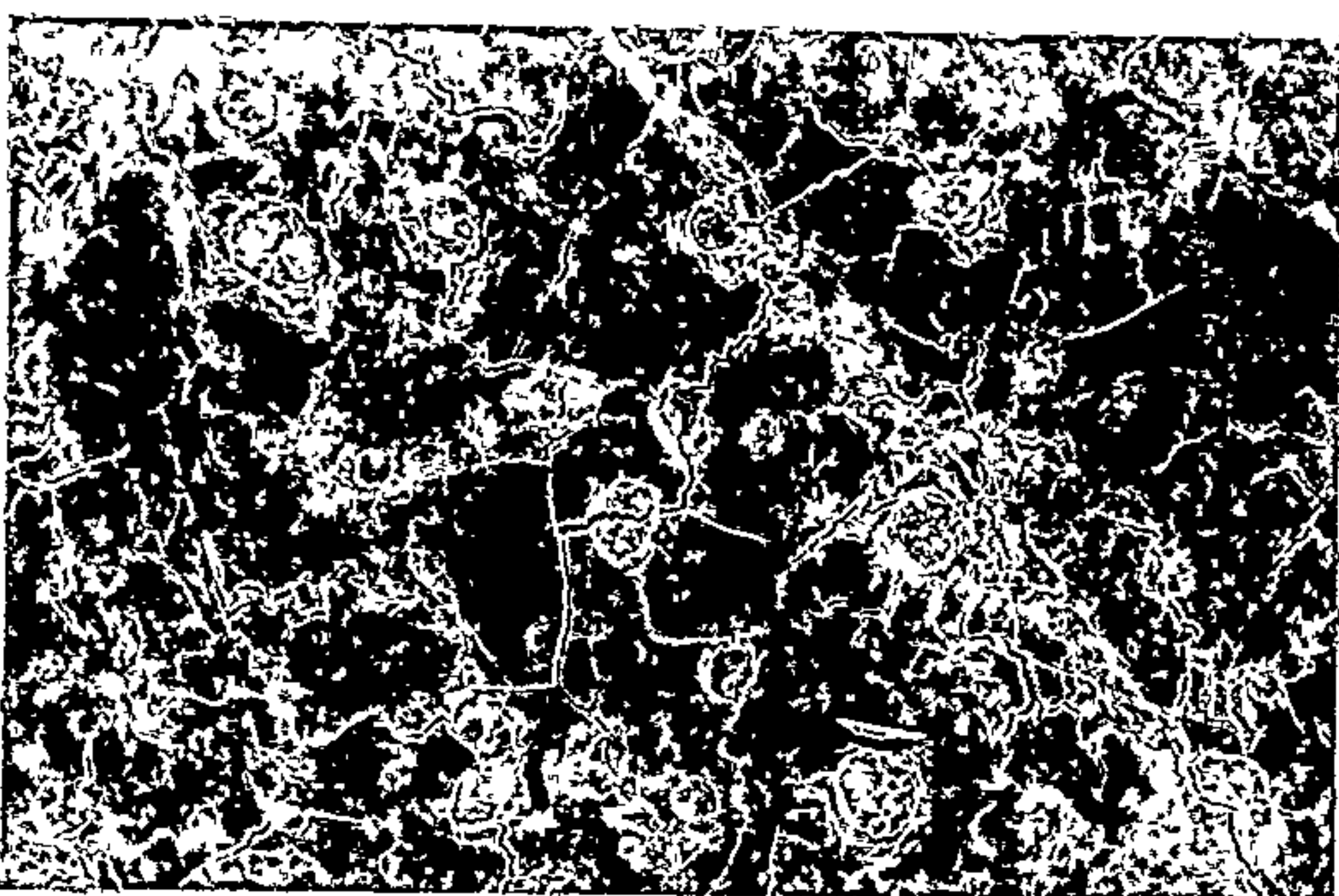


Fig. 9.27

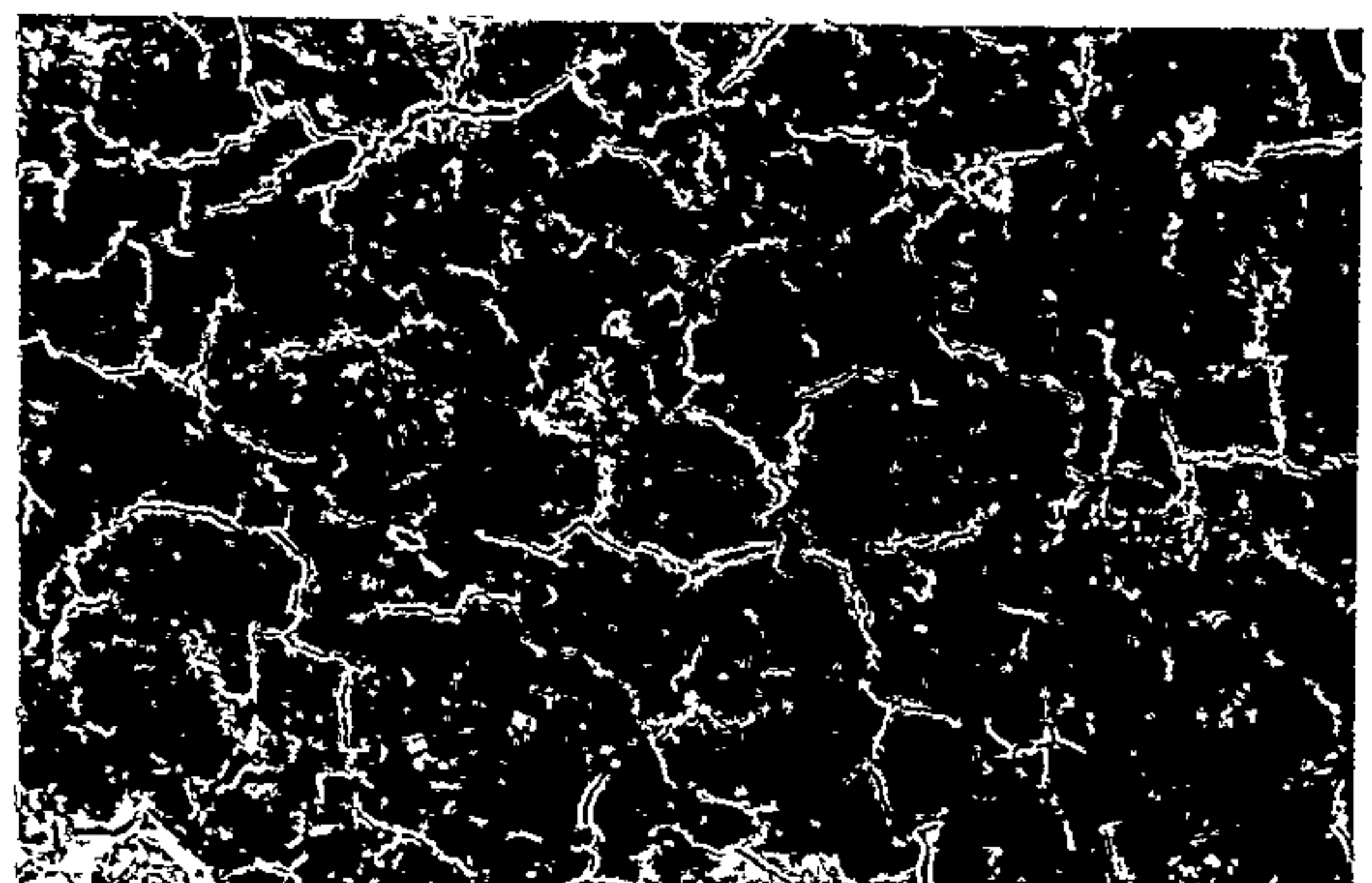


Fig. 9.28

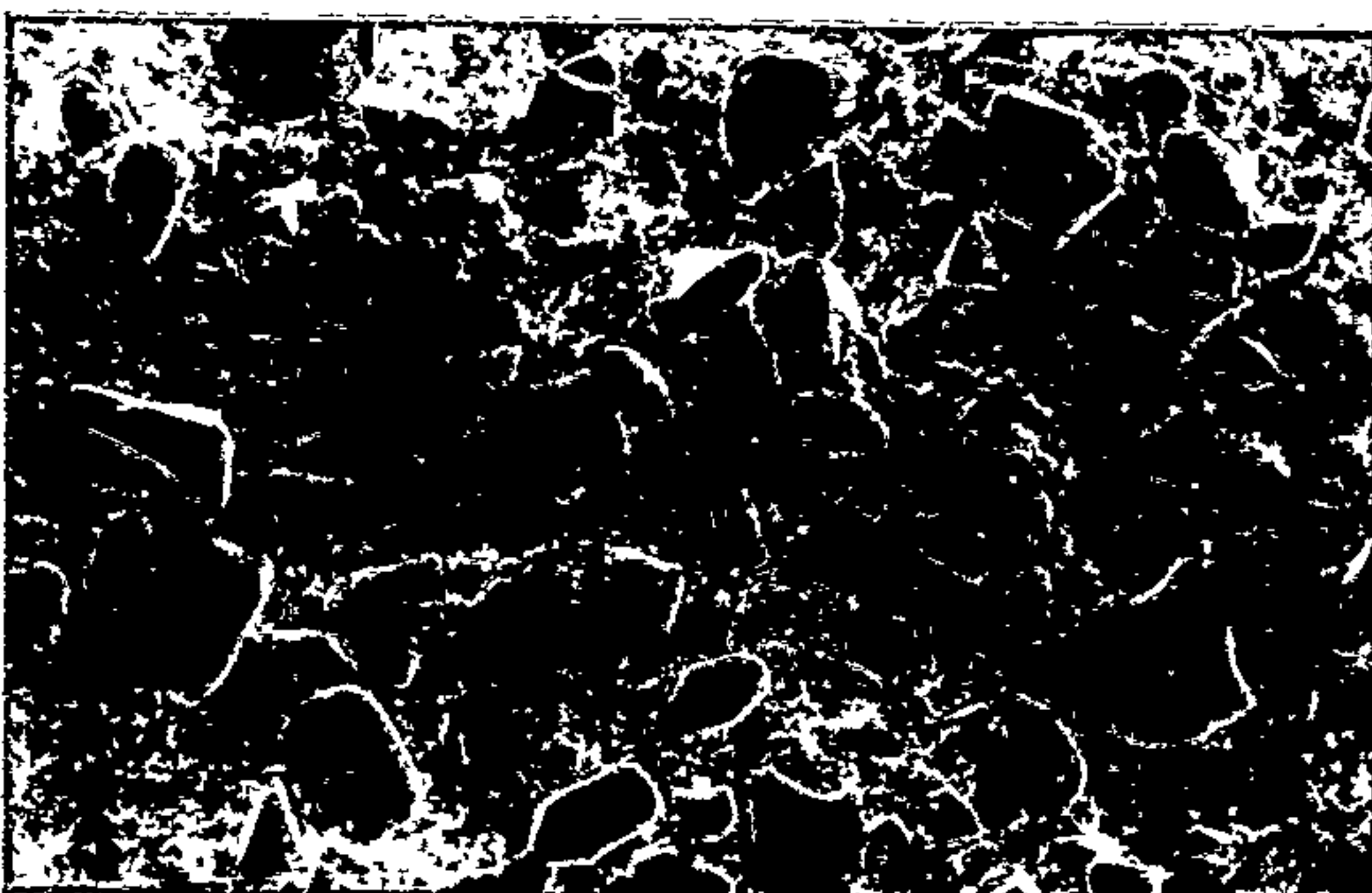


Fig. 9.29



Fig. 9.30

Fig. 9.31 -- Photomicrograph of ChemFil glass ionomer cement.

Original magnification X480.

Fig. 9.32 -- Photomicrograph of Ketac-cem glass ionomer cement.

Original magnification X480.

Fig. 9.33 -- Photomicrograph of Fuji Type I glass ionomer cement.

Original magnification X480.

Fig. 9.34 -- Photomicrograph of ChemBond glass ionomer cement.

Original magnification X480.

Fig. 9.35 -- Photomicrograph of Hy-Bond C glass ionomer cement.

Original magnification X480.

Figure 9.31 - 9.35

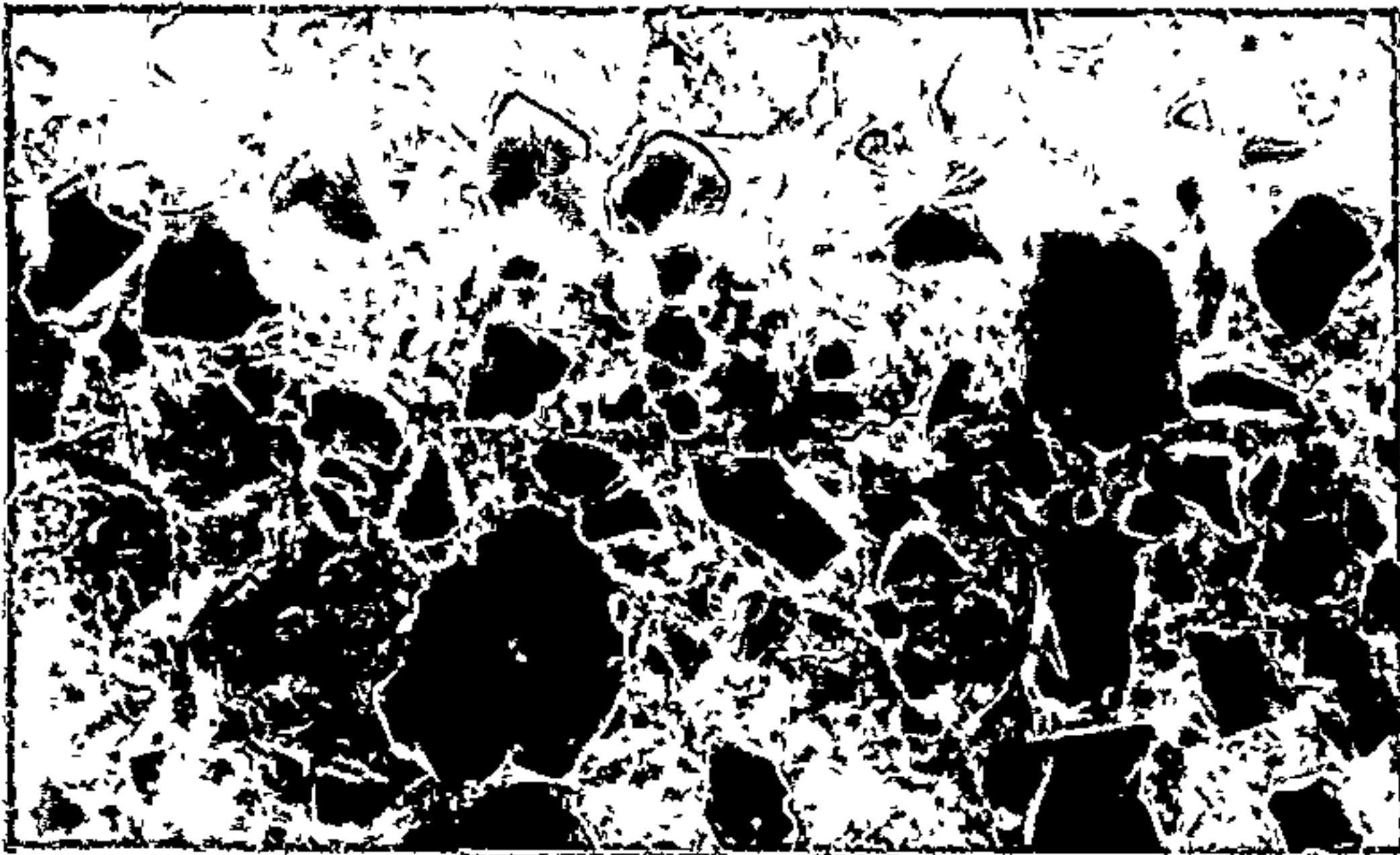


Fig. 9.31

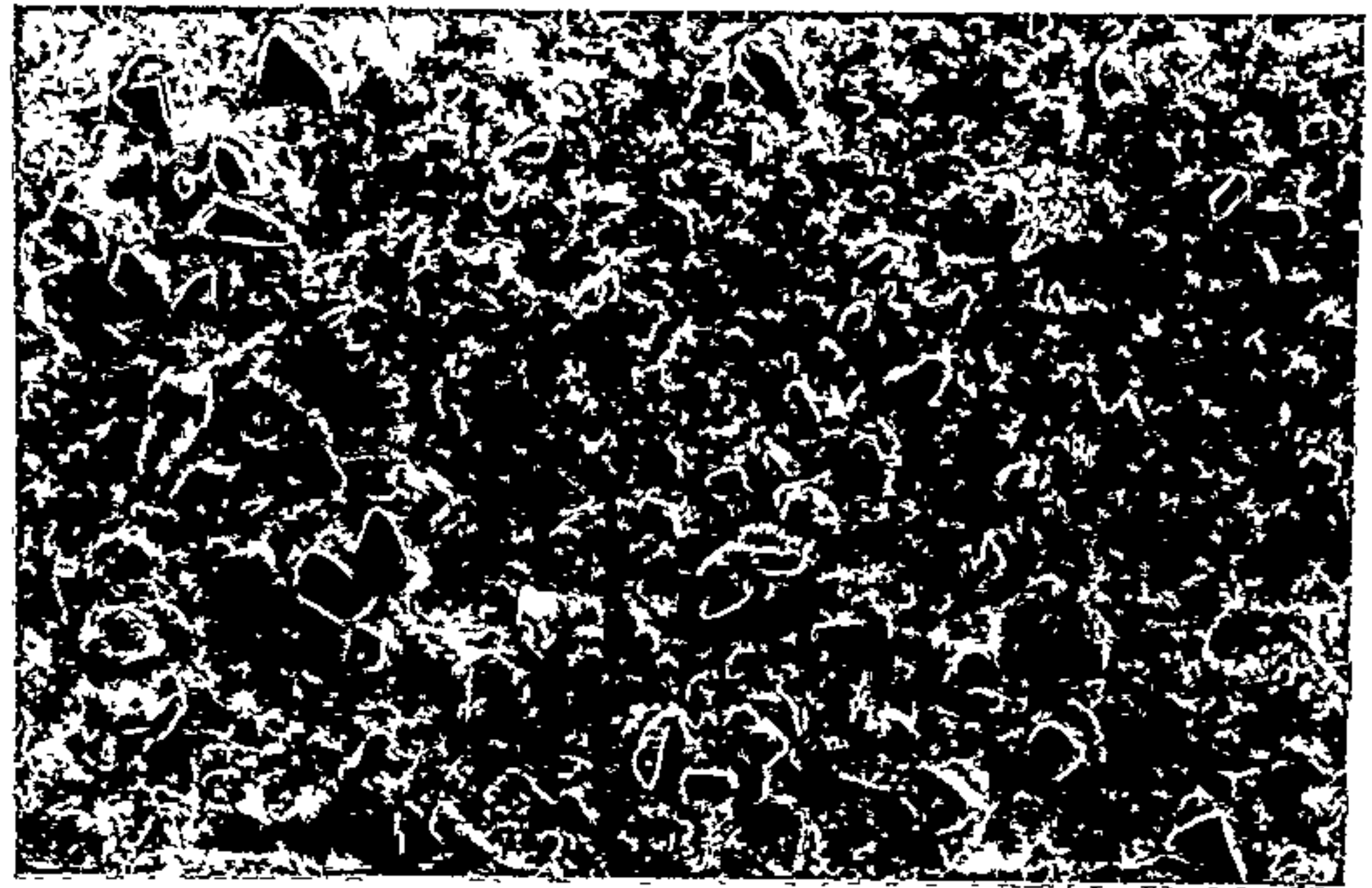


Fig. 9.32

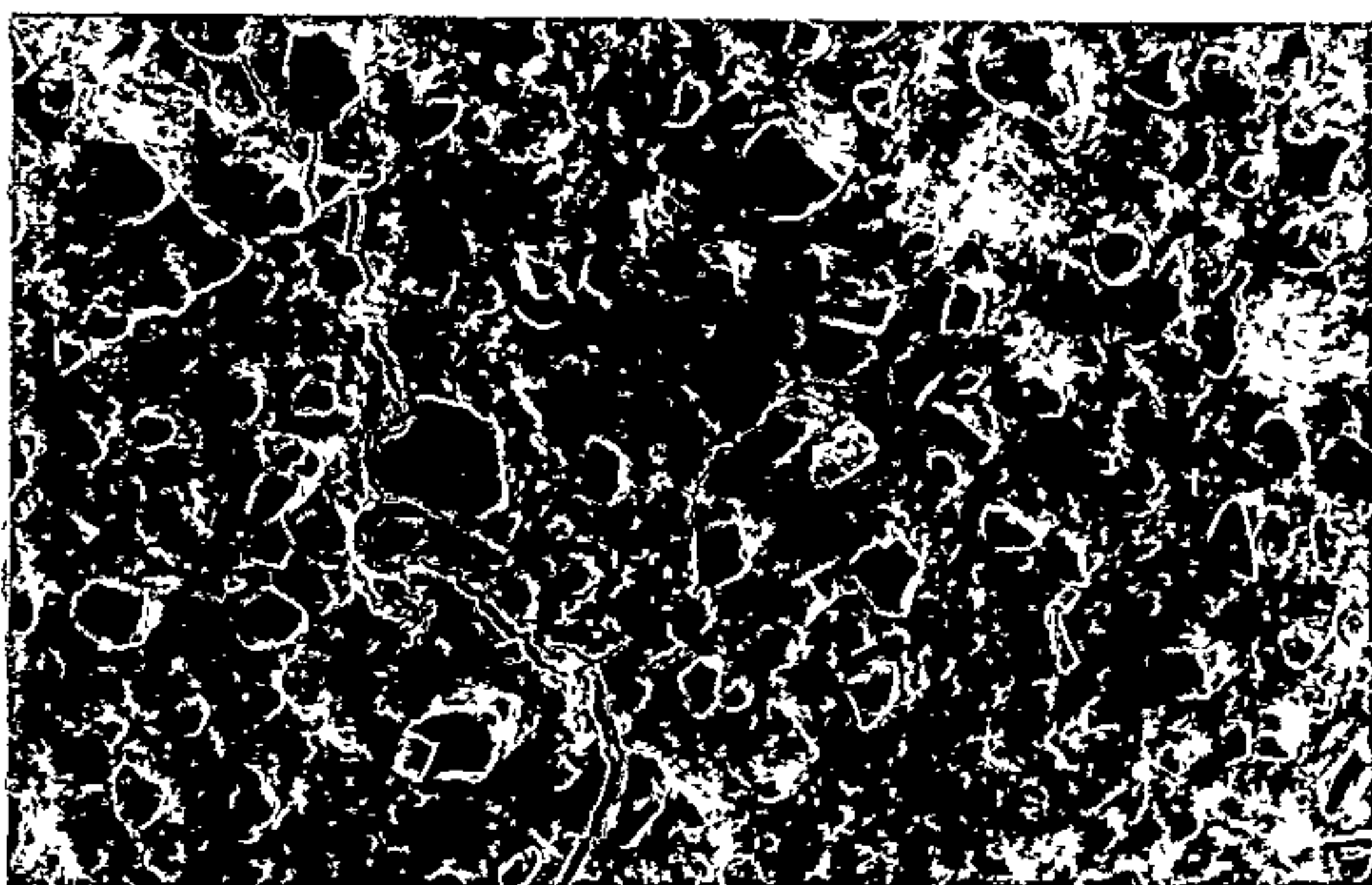


Fig. 9.33

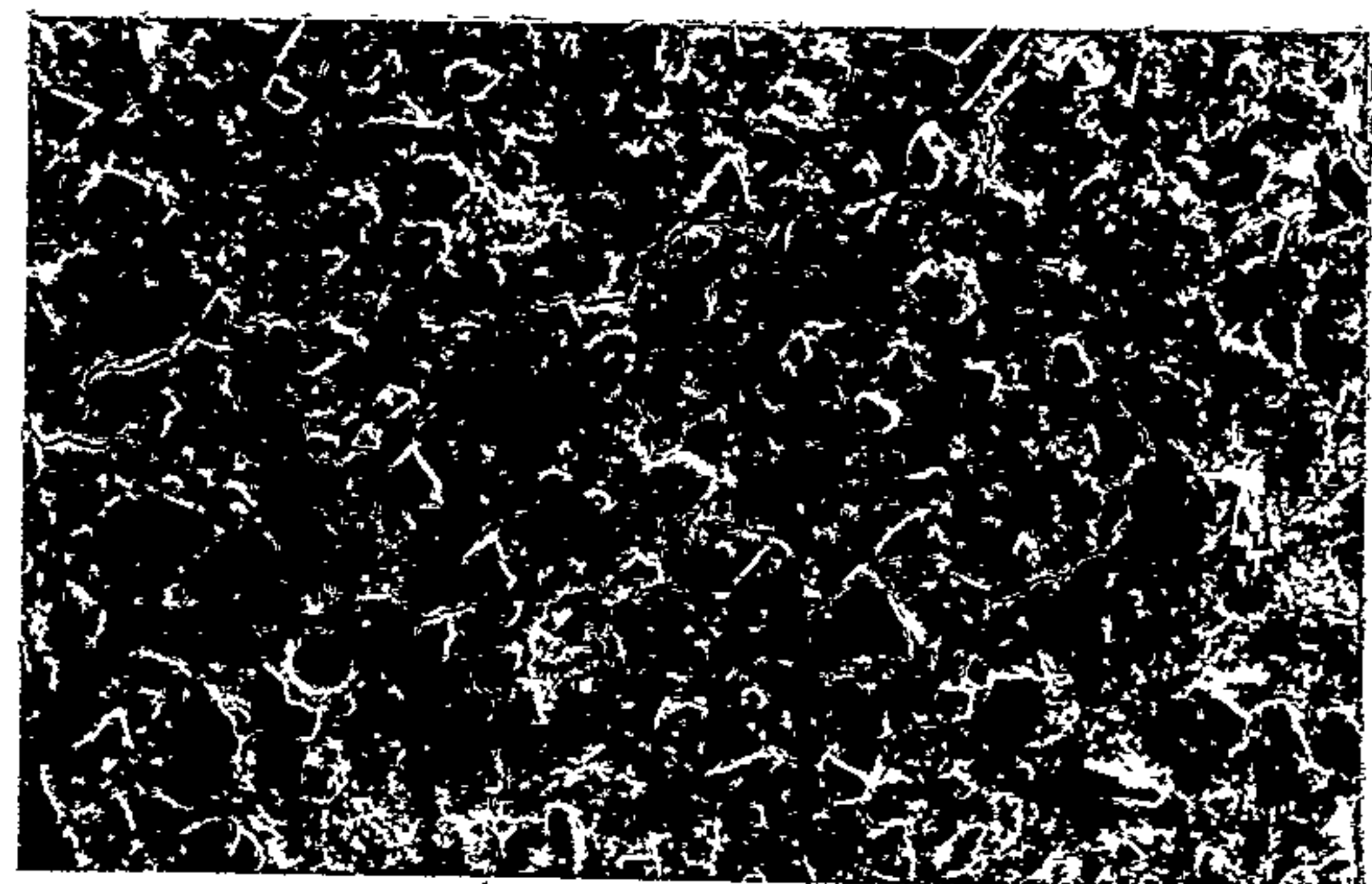


Fig. 9.34

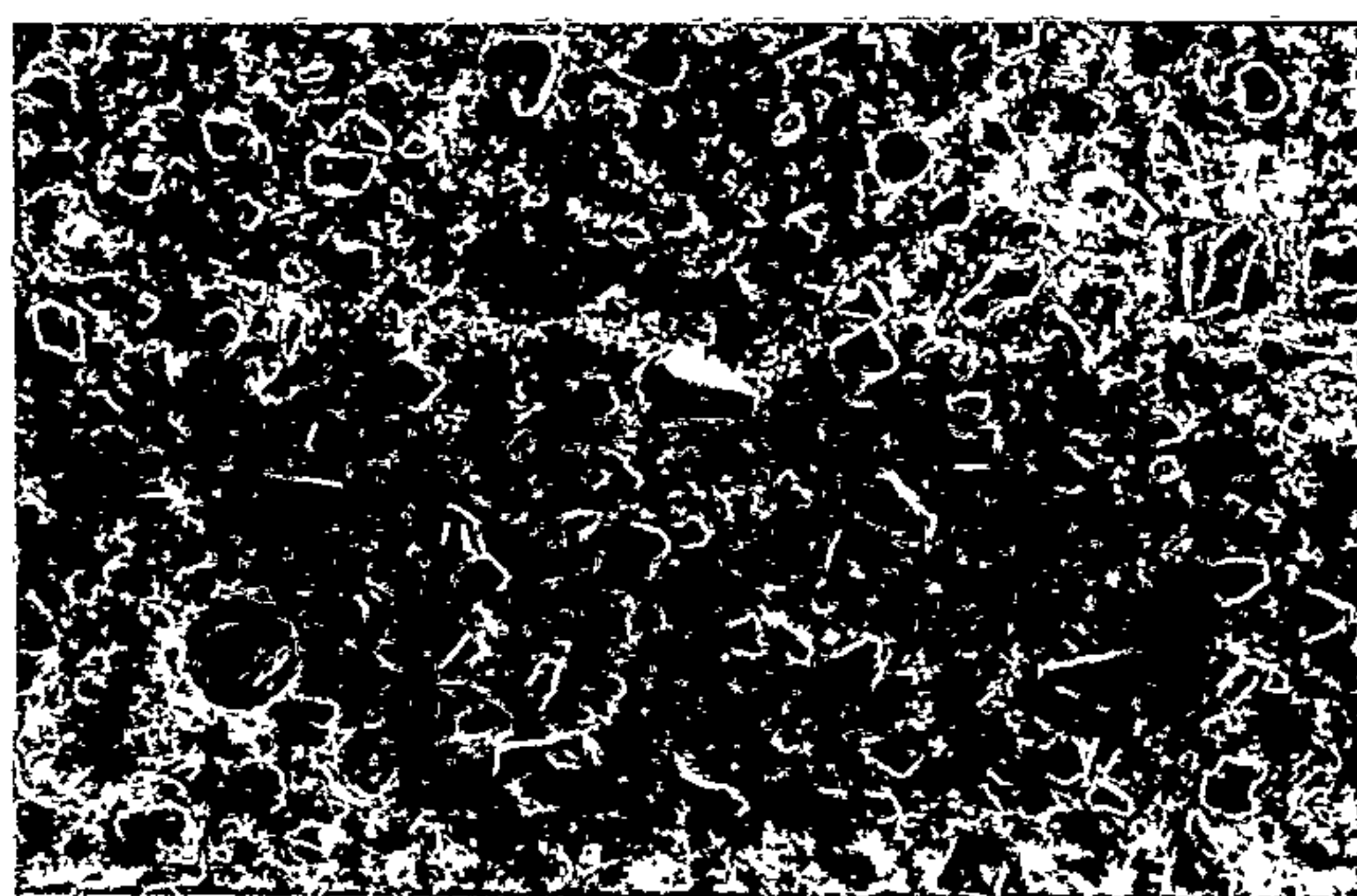


Fig. 9.35

CHAPTER 10

CONCLUSION

The seven commercially available glass ionomer cements examined in this investigation included three restorative cements (Ketac, Fuji Type II and ChemFil) and four luting cements (Ketac-cem, Fuji Type I, ChemBond and Hy-Bond C). Currently, there are relatively few reports in the literature on these commercial glass ionomer cements.

Three aspects of the method were examined. One of these was the accuracy of dispensing using the powder and liquid measures provided by the manufacturers. A second was an investigation of specimen preparation techniques in order to eliminate or minimize cracks in the cements prepared for scanning electron microscopy. The other aspect of the method examined was a technique for comparing the particle sizes of the glass particles in the cements.

The principal part of the investigation examined the strength (compressive and tensile), film thickness, particle size and finished surface of glass ionomer cements. The more important conclusions resulting from this investigation are summarized in the following paragraphs.

1. The accuracy of dispensing using the powder and liquid measures provided by the manufacturers

The results showed that there were differences in the quantity of material (powder or liquid) dispensed by a particular dispenser on different occasions and also by different dispensers. For most materials, the measured minimum and maximum powder : liquid ratios possible were approximately 2 to 17 per cent greater or less than the recommended ratios. For Fuji Type I and Fuji Type II, both the

measured maximum and minimum powder : liquid ratios were substantially greater than the recommended ratios. In the case of Fuji Type II especially, the relative quantities of powder and liquid dispensed appeared to have no relationship to the recommended ratio. Inaccuracies in the dispensers provided are particularly undesirable because glass ionomer cements are relatively new materials in the market and many dentists are unfamiliar with the consistency that produces optimal properties for the luting and restorative materials. Some dentists and their assistants will therefore tend to rely upon the dispensers supplied by the manufacturers to provide an accurate guide to the correct consistency.

Based on the evidence from this study, the variations in powder : liquid ratio associated with the use of the same or different dispensers indicate the advantage of using these dispensers only as an approximate guide (rather than as an exact measure) to obtain the required consistency.

2. The method of specimen preparation for scanning electron microscopy (SEM)

Techniques investigated to reduce the incidence of cracks in the specimens included subjecting the polished specimens to : i) gold-coating within 30 minutes of polishing, ii) dehydration in silica gel, iii) dehydration in serial alcohol dilutions, iv) dehydration in serial alcohol dilutions followed by storage (and further dehydration) in silica gel, and v) critical point drying, prior to coating. There was no noticeable difference in the incidence of cracks with any of the techniques. All specimens exhibited extensive cracking. Because of this, it was decided, largely for reasons of convenience, that dehydration of the polished specimen in silica gel for 3 days prior to coating would be used for all specimen preparation for electron microscopy.

3. Examination of the particle size in glass ionomer cements

Three techniques were examined to determine a method of specimen preparation for examining the glass particle size in glass ionomer cements : i) flat-polishing the set cement with various grades of diamond polishing paste on a lubricated slowly rotating cloth, ii) polishing the set cement with pumice and glycerine which achieved preferential polishing of the softer matrix, and iii) examination of the unreacted powder. Techniques (ii) and (iii) were of use in the examination of particle size. It was not possible to identify with any certainty the glass powder particles in the flat-polished cement specimens.

An unexpected finding of the investigation was the observation that all luting glass ionomer cement powders contained, before reaction, many relatively large glass particles surrounded by an abundance of very fine particles. The presence of these very fine particles in the restorative glass ionomer cements was not investigated.

4. Strength of glass ionomer cements

Both restorative and luting cements showed a general increase in strength with time. (In this section, unless otherwise stated, "strength" refers to both compressive and tensile strengths). Most cements developed one-half their 24 hour strength in the first hour. It is possible, however, that observable deformation of the early strength specimens may have influenced these strengths.

Of the restorative materials, Ketac had the highest and ChemFil the lowest strength; of the luting materials Fuji Type I had the highest and ChemBond the lowest strength. The restorative materials were approximately twice as strong as the luting materials except in the case of Fuji Type I and Fuji Type II for which the strengths were similar. Under the conditions of testing, of the restorative materials,

only Ketac met the British Standards Specifications for compressive and tensile strengths. Of the luting materials, Ketac-cem and Fuji Type I achieved adequate strength; however only Ketac-cem met the British Standards Specification for film thickness (at the recommended consistency, Fuji Type I possessed an unacceptably high film thickness).

It has been noted that other researchers have used different conditions of testing, and the conditions in the present investigation differed from those in the British Standards Specifications. These factors made direct comparisons of the results of this investigation, with those of other researchers and with the Standards, difficult.

The SEM investigation of particle size indicated that the three restorative glass ionomer cements had similar particle size. The particle sizes in three of the luting glass ionomer cements (Ketac-cem, Fuji Type I and ChemBond) were similar. The larger particles in the luting cement powders were generally smaller than the larger particles in the restorative glass ionomer cements. On the basis of the evidence available, it appeared that differences within the strengths of restorative cements or the luting glass ionomer cements were unrelated to the size of the larger particles. General particle size differences may, however, be partly responsible for the generally lower strength of the luting glass ionomer cements compared to the restorative glass ionomer cements.

5. Film thickness of the glass ionomer cements

The film thickness of the luting glass ionomer cements at the recommended consistency was greater than 25 μm . At this consistency, Fuji Type I had the greatest (47 μm) and Ketac-cem the smallest (27 μm) film thickness and only Ketac-cem met the requirements of the British Standards Specification for film thickness.

Reducing the powder : liquid ratio resulted in a smaller film thickness. It was found that the smallest "clinically appropriate

film thickness" (cement set at 9 minutes) was approximately 28 μm for all the cements investigated. Examination revealed that although a reduction in the powder : liquid ratio decreased the film thickness, it also decreased the strength of the cement.

Further investigation is required to determine the actual powder : liquid ratio used by different clinicians to cement restorations with a glass ionomer luting cement. One of the potential problems in such an investigation may be the clinicians' lack of experience in handling the material. As mentioned previously (1), the dispensers supplied by the manufacturers generally provide an unreliable guide to the inexperienced.

The variation in the film thickness of the glass ionomer cements mixed at the recommended consistency seemed to be inconsistent with the similar particle sizes observed for the four luting glass ionomer cements by SEM examination. At the smallest "clinically appropriate film thickness", the film thickness of the four cements were similar. This finding was consistent with SEM observations and emphasized the potential influence of powder : liquid ratio on the film thickness of a cement.

6. The surface obtained by clinical finishing techniques

The SEM investigation indicated that the smoothest surface was obtained with a fine sandpaper disc and the roughest with a coarse diamond used at low-speed. A white stone (high-speed), a tungsten carbide bur (high-speed), and a coarse sandpaper disc (low-speed) produced surface finishes that were intermediate in degree of roughness. The surface of the cement adjacent to a matrix strip had numerous voids and cracks. Finishing with pumice and glycerine or a commercial polishing paste (Floran) produced an unacceptable surface as the softer matrix was preferentially abraded,

leaving the harder glass particles protruding from the surface. To avoid plaque accumulation on the rough surface, glass ionomer cement restorations should not be polished with such pastes.

Based on the evidence of this investigation, it is suggested that either a high-speed white stone or tungsten carbide bur, or a coarse sandpaper disc (at low-speed), or a combination of these instruments may be used to obtain the correct contour in the final finishing of glass ionomer cements. Finally, the surface should be smoothed with fine sandpaper discs or finishing strips impregnated with zirconium silicate to produce a surface with the fewest deep scratches.

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