

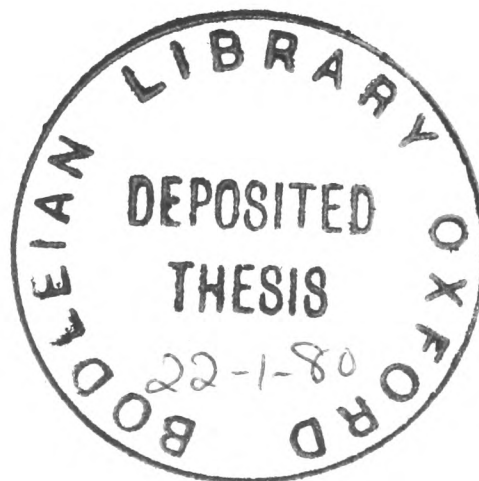
ADHESION OF CHLORINATED-RUBBER BASED LACQUERS TO MILD STEEL

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Thesis submitted for the degree of Doctor of Philosophy in the
University of Oxford

September 1979



"You know, this applied science is just as interesting
as pure science, and what's more it's a damned sight
more difficult."

Sir William Bate Hardy 1864-1934 to Sir Henry Tizard

Sir Henry Tizard, Haldane Memorial Lecture, Birkbeck College,
University of London, 1955

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Abstract

This thesis reports work carried out to investigate the adhesive properties of chlorinated-rubber based lacquers on mild steel. Tensile tests were used to measure the failure stresses of such coatings, and it was established that a mixture of cohesive and weak boundary layer failure occurred. Consideration was given to the influence of lacquer storage, film thickness, drying time and binder molecular weight on the failure stress of the coating.

In Chapters 1 and 2 the theories of adhesion are discussed, the system under investigation is described and methods of testing the adhesive and cohesive strengths of coating/substrate systems are considered. The development of a suitable test method, preparation and testing of specimens are described in Chapter 3, and the experimental values of stress to cause failure of the coating are discussed. Chapter 4 describes the detailed surface analytical work which was carried out to establish the mode of failure of the coating, and investigate the inhomogeneities occurring within the cured film. It was found that the plasticiser migrated towards the lacquer/air interface as the film cured, leaving a "binder-rich" region at the lacquer/substrate interface. It was also found that chemical interaction occurred between the lacquer and the substrate, under certain circumstances, and in Chapter 5 these interactions are considered.

Theoretical work was carried out to investigate the application of various expressions for calculating the Van der Waals forces acting between two molecules, to the system under investigation. This is described in Chapter 6. The numerical values of the Van der Waals forces obtained using these expressions are compared, and their relevance to the experimentally measured failure stresses considered.

The conclusions which may be drawn from the results of the work described in Chapters 3-6 are considered in Chapter 7, and suggestions made of areas for further work.

Preface

The work described in this thesis was carried out by the author in the Department of Metallurgy and Science of Materials, University of Oxford, between October 1976 and September 1979 under the supervision of Dr. D. A. Smith. No part of this thesis has been submitted for a degree at this, or any other university. The work of others has been freely drawn upon and duly acknowledged in the text. A list of references in alphabetical order is included at the end of the chapter to which they pertain, and the trade names used in the thesis are listed in the appendix, at the end of Chapter 7.

The work discussed in Chapter 3 forms the basis of a paper accepted for publication by the Journal of Materials Science, entitled "Investigation of Failure in Paint Films".

I would like to thank Professor Sir Peter Hirsch, F.R.S., and I.C.I. Ltd. Mond Division for provision of laboratory facilities; also the Science Research Council and I.C.I. Ltd. for financial support, through the CASE Award scheme.

It is a pleasure to express my gratitude to Dr. D. A. Smith for supervising this work, also for his conscientious reading of the final draft of this thesis, and many helpful and stimulating discussions; to Dr. W. W. Harper (now of International Paints Ltd.) for his guidance, assistance and hospitality during many visits to I.C.I. in Runcorn; and to Dr. J. Padget and Mr. D. F. Bowerman of I.C.I. Ltd. for their help and advice on many occasions.

I would also like to thank the following people for the part they have played in the work discussed in this thesis:-

Dr. A. Dilks of the Chemistry Department, University of Durham, for

carrying out the ESCA investigation described in Chapters 4 and 5, and for assistance in interpreting the results,

Mr. P. Carr for carrying out the Auger analysis, also described in

Chapters 4 and 5, and for his guidance in interpreting the results,

Mr. G. Spiller for assistance in carrying out the TEM work described
in Chapter 5,

Mr. J. Short for his inspiration and assistance, and the cheerful
atmosphere of his workshop,

Mr. D. Pinfold for willingly transforming designs submitted to him into
working items of equipment,

Mr. A. McKnight and Mr. S. Bowers for the photographic work carried out
over the past three years, and in particular for this thesis,

Mrs. J. Pavlovic for the many letters, manuscripts etc. which she has
typed so professionally,

Miss L. Brooks for her care and efficiency in typing this thesis.

I would like to thank all those in laboratories 211 and 212 at
I.C.I. Runcorn, for their help and hospitality; and all members of
the "Interfaces" group in Oxford, both past and present, for their
friendship and assistance in many ways, particularly Dr. K. Reading;
my fiancé, Ian, for his love, encouragement and understanding; and
finally my parents, without whose support, in every way, this work
could not have been carried out, and to whom this thesis is dedicated.

The author's signature has been redacted
from the online version of this thesis

D. H. Smelt

Linacre College

September, 1979

Symbols

k = Boltzmann's constant = $1.38 \times 10^{-23} \text{ Jk}^{-1}$

h = Planck's constant = $6.626 \times 10^{-34} \text{ Js}$

L = Loschmidt's number = $2.687 \times 10^{25} \text{ m}^{-3}$

e = electronic charge = $1.602 \times 10^{-19} \text{ C}$

m = electronic mass = $9.109 \times 10^{-31} \text{ kg}$

ρ = electron density in metal

ϵ_0 = permittivity of vacuum = $8.85 \times 10^{-12} \text{ Fm}^{-1}$

T = absolute temperature

c = velocity of light = $2.998 \times 10^8 \text{ ms}^{-1}$

R = separation of atoms or molecules

I = ionisation potential of atom or molecules

ν_0 = proper frequency of oscillations

μ = dipole moment of atom or bond

α = polarisability of atom or molecule

α_0 = distortion polarisability of atom or molecule

ϵ = dielectric constant of medium

χ = magnetic susceptibility of atom or molecule

N = number of electrons in outer shell

W_A = atomic weight

n_0 = number of atoms per unit volume

v_0 = volume occupied by one atom

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CHAPTER ONE

INTRODUCTION

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INTRODUCTION

1.1 ADHESION

Adhesion between two solid materials is defined as the mechanism by which mechanical force may be transferred from one material to the other, in tension or in shear, without interfacial slip or inelastic displacement of either material with respect to the other. The strength of the interaction between the two materials is characterised by the amount of energy, per unit area of the interface, which must be supplied in order to bring about their separation.

The references marked with an asterisk provide a comprehensive view of the properties of adhesives, and mechanisms involved in adhesion. A great deal of work has been carried out by many research workers, to try to establish the most important aspects of this phenomenon, and to identify the properties which define a good adhesive.

There are many theories concerning the actual mechanisms of adhesion, most of which have been discussed several times in a series of books entitled "Aspects of Adhesion" [1]. Those which have achieved some degree of general acceptance will be discussed below.

(i) The chemical, or molecular theory

The forces acting at the interface are due to long or short range molecular interactions.

(a) Chemical bonding. This requires the presence of chemically active groups within the adhesive, which may react with the substrate to which it is applied forming a new compound. This involves primary forces, which are long range and theoretically very large; e.g. covalent, electrostatic or metallic bonding.

(b) Physical, secondary or Van der Waals bonding. This is sometimes

referred to as the adsorption theory, and is favoured by both Eley [14] and Schonhorn [27]. The forces which are involved here are produced by the interactions between permanent and instantaneous dipoles in the adhesive surface at the interface, with permanent and induced dipoles in the substrate at the interface. These are of shorter range than the primary forces, and are considered in detail by Heitler in reference 1 vol.4, and Dunning [12].

(ii) Mechanical theory

This is the oldest theory of adhesion; the central concept is of the fluid adhesive which wets the substrate flowing into grooves and re-entrant cavities in the substrate surface, this action being accelerated by capillarity. As the adhesive cures, or dries, it is locked into the cavities, and the film is held onto the substrate by a series of "hooks" or "plugs".

Alternatively, it may be argued that the adhesive in the grooves and cavities is attracted to the walls, and adheres to them, according to (ia) or (ib). The effective surface area of the substrate at the interface is much larger than the apparent area of contact between the two media, due to the surface roughness, and the force per unit of apparent surface area required to remove the film is correspondingly larger. It is observed by Patton [24] that most of the adhesion that is attributed to mechanical interlocking is undoubtedly due to the improved spreading (and penetration) that is provided by a rough surface.

It may be that both these mechanisms occur at the same time, giving the same overall effect.

(iii) Electrostatic theory

This theory was initially due to Deryaguin [11], but some doubt is cast upon it by other workers, for example Huntsberger in reference 22, and Voyutskii [31]. The well known phenomenon of an electrical double-layer formed at the junction of two materials is applied in

considering the system as similar to a charged capacitor, with the substrate and adhesive layer forming the two plates. Work must be done to separate the double-layer, which is postulated to raise the level of adhesion of the two materials. Roberts [26] has investigated the contribution of surface charge to the adhesion and friction of rubber.

(iv) Diffusion theory

This theory has been propounded by Vasenin [30] and Voyutskii [31], and is based on the idea that adhesion arises through the interdiffusion of the adhesive and substrate. The two media are thus mechanically "locked" together by the combination of their interfacial regions. The theory has been applied mainly to joints involving two polymeric materials, and cannot be extended, for example, to cover polymeric coatings on metals.

The interpenetration of the polymer chains occurs as a result of thermal motion, and those which have diffused are held together by intermolecular forces, and the strength of the joint depends on the number of chains crossing the phase boundary, the depth of the interpenetration, and the strengths of the individual chains.

This theory is discussed by Allen in reference 1, vol.5; Mittal [20] gives a clear consideration of all the above theories which are also considered by Huntsberger [19].

It may be that all these mechanisms have some part to play in the process of adhesion, their relative significance depending upon the nature of the adhesive and the substrate. In the case of the electrostatic contribution it has been found by Roberts [26] that even in a system where the contribution to the adhesion was expected to be large it was, in fact, less than 10%, and often as little as 0.1-1%. Although the diffusion theory can be applied to joints involving two polymeric materials, whose strength depends upon the nature of the polymers, it is unlikely that it can contribute to an understanding of the adhesion of polymers, for example, to metals.

The theory of mechanical adhesion is relevant to rough surfaces. If the mechanism of adhesion is that of "hooks" the joint strength will approach the cohesive strength of the adhesive; however, if the effective increase in the surface area of the substrate is the dominant effect, then the joint strength will be proportional to the strength of the chemical or physical bonds formed at the interface. The contribution to the total adhesive interaction at the interface due to the formation of chemical bonds depends upon the number of active groups present at the interface, and the strength of each individual interaction. However, Van der Waals interactions occur to some extent in all materials, and are considered by many [6, 7, 22] to be sufficient for the formation of strong bonds between a polymeric film and metal substrate, regardless of any other contributions.

1.2 PAINTS AND LACQUERS

In the section above adhesion has been discussed in terms of interactions between two materials, the natures of which have not been specified. In a paper by Brown and Garnish [6] the system is described as follows:

"A junction is usually formed in practice by applying a liquid on a solid and then hardening the liquid. When there is only one solid the liquid is termed a surface coating, when the liquid bridges a gap between two solids it is termed an adhesive. The coating, therefore, is an adhesive that sticks on one side only".

The work described in the following chapters is concerned with surface coatings - paints and lacquers. Paints are applied to various substrates not simply for decorative purposes, but also to provide a protective coating. This protection is not provided only by the isolation of the substrate from the corrosive constituents of its environment, but a well formulated paint may form bonds at certain sites on the substrate surface which are susceptible to attack by corrosive chemicals, or it may even react with those chemicals, and so prevent them from attacking the substrate [29]. Svoboda and Mleziva have written a very interesting paper [28] concerning the protective properties of organic coatings, and the penetration of inorganic compounds into such coatings.

Eley [13] has defined the three requirements for a paint film as "wetting, setting and deformation", and Bullett and Rudram [9] enlarge upon this in a very useful paper concerning the properties of the coating and substrate - for example, the resistance to mechanical damage and weathering, moisture permeability and corrosion.

Wetting is the process by which molecules of air, water, grease etc. originally in contact with the surface of the substrate, are replaced by molecules of the coating, or paint. The rate at which this displacement occurs depends on several variables, for example

the rheology of the paint and the configuration of the substrate. The material displaced may be incorporated into the paint, or emulsified, or just pushed aside as the paint film advances.

The coating sets, or cures, either by cross-linking or by solvent evaporation. In the former mechanism the polymer chains combine and join together to form a complex web, becoming solid in the process. In the latter process the chain length is unchanged, but as solvent evaporates the chains come into closer proximity to each other, and the secondary, interchain bonds increase, and the film forms a solid structure. It is necessary that the volume of the film should not change too much during the setting process, as stresses are induced in the film on shrinkage, which could destroy the bonds between the film and substrate, or cause rupture within the film itself.

Deformation of the film goes some way to relieving the shrinkage stresses in the film, and it is also necessary to have a deformable coating if the substrate is not rigid, or is likely to undergo thermal expansion and contraction. Otherwise the film could crack and flake away from the substrate.

A paint is composed of many compounds. Firstly the binder, which is the major component and is primarily responsible for the adhesive forces which bind the film to the substrate, and cohesive forces within the film itself. This is dissolved in a suitable solvent, and plasticiser is combined into the solution. This is added to the binder to improve the flexibility of the dried film, and must be completely compatible with it, in order to form an homogeneous composition under all circumstances. The tensile properties of the film depend very strongly upon the nature and level of plasticisation. Bhatnagar and Bhatnagar have considered the subject of plasticisation in some detail [4].

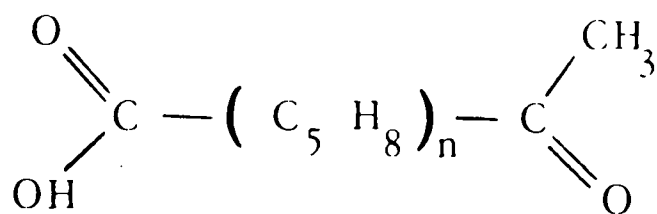
This mixture of binder and plasticiser is termed a lacquer, and contains the basic constituents of a paint. It will probably also

contain some stabiliser, which is added to maintain the physical and chemical properties of the lacquer, or paint, at their initial values throughout processing and use.

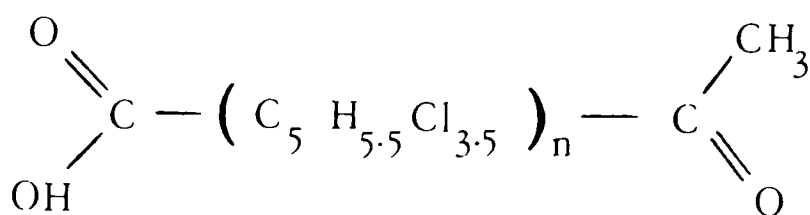
A lacquer containing pigment in suspension is normally termed a paint. This pigment is usually added to provide colouration and opacity to the film, but may have properties inhibiting the corrosion of the substrate, either by external agents, or by the coating itself. Pigments can influence the cohesive properties of a paint film, as may extenders, which are added to reduce the amount of binder required per unit volume of the film, and contribute to some degree towards its adhesive properties. Fillers and extenders both improve the application properties of a paint, and often increase the viscosity.

Thixotropes are added to prevent pigment settlement during storage, and also to improve the application properties. The viscosity of the fluid paint decreases as it is stirred or brushed, but increases again after the disturbance, thus preventing "sag" of a thick coating on a vertical substrate.

The effects of solvents, pigments and extenders on the adhesive properties of polymer films are considered briefly by Ason [2], Müller [21] and Petit [25], and the factors affecting the adhesion of paint films to metal substrates are discussed by Bascom and Patrick [3], Bullett [7], and Bullett and Prosser [8].



On chlorination a combination of addition and substitution reactions occur, and the final structure is



where the chlorine content is approximately 65% by weight. This product, which in this case is marketed by ICI, is called "Alloprene", and for the particular grade of binder used in the work to be discussed $n \approx 300$, with a chain length of $\sim 0.2\mu\text{m}$. It decomposes at temperatures above 80°C , liberating hydrogen chloride gas.

The solvent used was an Analar toluene, which is the cheapest useful solvent used in inks, paints and adhesives.

The plasticiser was a chlorinated paraffin, derived from a petroleum wax of carbon chain length 22-24 and chlorine content of $\sim 42\%$ by weight. This is also produced by ICI, under the trade name "Cereclor 42". It is the most frequently used plasticiser for "Alloprene", and the "Cereclor" group is the most important type of plasticiser for anticorrosive, chemically resistant surface coatings.

A small proportion of stabiliser is added to all "Alloprene" during production to stabilise the polymer in all but the most severe conditions; this is in the form of an epoxidised oil, which acts as an acid acceptor and prevents autocatalytic dehydrochlorination of the polymer

The glass transition temperature, T_g , of pure "Alloprene" is in the region of 138°C ; this value is reduced by the addition of plasticiser, and for most paint systems it is around room temperature. These are described as "soft" systems.

The substrate used was mild steel, as "Alloprene" based coatings are frequently used as a protection for steelwork. Single coatings up to $\sim 150\mu\text{m}$ are often encountered, and the atmospheric environments are often highly corrosive.

A single lacquer coating was studied in order to avoid problems of intercoat failure, or inhomogeneities.

1.4 OBJECTIVES

The main objective of the work reported here was to investigate the nature of the adhesive interaction occurring between the chlorinated-rubber based lacquer, and mild steel substrate.

A method for testing this property of the film had to be selected. This method was to be relatively simple to employ, and give easily reproducible results. It was also necessary that many specimens could be prepared and tested at one time, in order to minimise the number of variables affecting the results.

It was proposed to investigate the stresses required to cause failure of a film, and to identify the mechanisms by which failure occurred. It was realised that there are many factors which affect the magnitude of this stress, and only some of these were to be investigated in the course of the work.

Parallel theoretical work was to be carried out to estimate the magnitude of the contribution of the Van der Waals interactions to the adhesive and cohesive strengths of the film, as these are considered to be the most important interactions involved in the adhesion of polymer coatings to metal substrates, and cause interchain attraction within the film itself. These were to be compared with the results obtained from the experimental work.

Finally, the results of all these investigations had to be considered to identify their relevance to pigmented coatings, or paints.

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CHAPTER TWO

TESTING ADHESION

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TESTING ADHESION

2.1 INTRODUCTION

Many destructive test methods have been developed for investigating the strength of adhesives and coatings; these are usually designed to evaluate the magnitude of the adhesive forces acting between the coating and the substrate, but in practice the cohesive strength of the film is often measured, or the strength of a weak boundary layer occurring at the coating/substrate interface. Careful analysis is required to identify the mode of failure of a coating, which is often quoted as being adhesive in nature, although more detailed study of the substrate surface would reveal a very thin layer of the coating remaining there.

According to Macmillan [25] the ideal, maximum or theoretical strength of a specimen is a function of geometry, mode of deformation, temperature, strain rate and the type of loading imposed by the loading device. For this reason it is impossible to compare the results obtained using one test method with those obtained using similar specimens, but a different test.

Huntsberger [17] considered that the progress in the study of adhesion has been retarded by the extreme complexity of the tests employed to appraise the adhesion. All the destructive tests involve several factors which cannot be quantitatively defined, and in his opinion no satisfactory non-destructive test had then been devised. He regarded the only absolute measure of adhesion as being the energy of interaction between the coating and the substrate at equilibrium, and he could quote no way of measuring the interfacial energy between two solid surfaces.

In this chapter the various methods of destructive testing will

be described, and the reasons for selecting a particular method for use in the present work will be discussed. Two books which give a useful introduction to this subject are those by Anderson *et al.* [1] and Weiss [34].

2.2 TEST METHODS

Many test methods have been devised in which a stress is applied to the coating, to remove it from the substrate. These are:

- a) Ultracentrifuge
- b) Ultrasonic vibration
- c) Centrifugal hammer and impact testing
- d) ICI gun
- e) Torque-wrench test
- f) Blister test
- g) Direct pull-off method
- h) Bend test
- i) Scratch test
- j) Ploughing
- k) Peeling
- l) Shear and lap tests

There are also non-destructive test methods, as discussed by Sharpe and Thompson in reference 16, vol.5, for example:

- m) Measurement of capacitance
- n) Ultrasonic resonance (Lloyd, reference 16, vol.8)
- p) Thermal testing

Many of these test methods are discussed by Bullett [9], Bullett and Prosser [10], Sathyanarayana *et al.* [32], and Zorll [39].

Only destructive tests were considered for the present work, as the mode of failure was also to be studied. Each of these tests will now be described in more detail, and their relative merits for studying "Alloprene" based lacquers on mild steel will be considered.

(a) Ultracentrifuge

This is described in detail by Malloy *et al.* [26]. A spot of paint is placed on the central metal rotor of an ultracentrifuge, and accelerated until the spot is removed by the centrifugal forces acting upon it. If r_o is the radius of the rotor, and r_s the radius to the

outer surface of the paint the force at the paint/metal interface is

$$F = \frac{A\sigma\omega^2}{2} (r_s^2 - r_o^2), \text{ where } A \text{ and } \sigma \text{ are the cross-section area and}$$

density of the paint spot, respectively; and ω is the angular velocity of the rotor. The force on the paint spot is thus greatest at the interface, and if the cohesive and adhesive strengths were the same it would fail in the adhesive mode. However, the cohesive strength is often less than the adhesive, and premature failure may occur within the film itself. Also, a spot of constant thickness is required for this test, as failure otherwise occurs first at the thickest points on the film.

(b) Ultrasonic vibration

A spot of paint is applied to the end-surface of a metal cylinder, which is placed in a solenoid with an alternating current passing through it. The frequency of the resultant vibrations is altered until the paint is detached, and the force required to cause this may be calculated from the electrical and mechanical properties of the system.

(c) Centrifugal hammer and impact tests

In these tests a spot of paint is applied to one side of a metal plate, and allowed to cure. The centrifugal hammer is rotated to a given angular velocity, and then allowed to hit the reverse side of the plate. If the correct velocity, and hence momentum is chosen, the paint spot will fly off the plate. The calculation of the force required to remove the spot involves the conservation of momentum within the system. Similarly in the impact test, a missile is raised to a chosen height above the back of the plate and allowed to fall. When the correct height is chosen the impact velocity of the missile is such that the paint spot is detached from the plate. This method was used by Zorll [40], who found both normal and shear stresses at the coating/substrate interface affect the mode of failure.

(d) ICI gun

This is similar to method c, but in this case a disc of metal with a paint spot on one side is fired from a gun, with the paint side leading, at a given velocity. The disc strikes a solid support with a small hole in it, through which the paint spot may pass. When the muzzle velocity is correct the momentum of the paint spot is such that it is removed from the metal disc, and continues through the hole in the support, when the disc is stopped.

None of the above tests was used in this work, as it is not possible to study the response of the coating to stresses lower than the failure stress. Also, in the case of c and d the applied stress at the interface is, in fact, a mixture of shear and tension, and somewhat difficult to define.

(e) Torque-wrench test

The mechanisms of this test are sometimes quoted as those most closely matching the stresses experienced by coatings in normal use. A small, circular plate is attached to the surface of the coating, using an adhesive which has a very small volume change on curing. This plate has a knob attached to it which enables it to be pulled away from the substrate using a special device which both twists and pulls the plate in a direction perpendicular to the coating/substrate interface.

This is similar to a test usually referred to as the "napkin-ring" test.

The stresses applied at the interface during these tests are very complex, and very little theoretical work has been carried out on them. Also, it is difficult to monitor the response of the coating to the various levels of stress applied to it. However, these tests are very useful if simply the mode of failure is to be studied.

(f) Blister test

This test is generally accredited to Dannenberg [11], and is designed to measure the adhesion of the coating to the substrate in

preference to the cohesion within the coating itself. It can also be applied to a wide range of specimens.

The basic principles of the technique are that a fluid is injected between the substrate and coating to form a blister; the pressure and volume of the fluid are measured, and also the rate of increase of the volume of the blister. Thus, the work required to detach the film from the substrate may be calculated.

The experimental procedure is well documented by Dannenberg, and many authors have considered the fracture mechanisms involved, among them Bennett *et al.* [5], Burton *et al.* [12], Williams [35 & 36], and Williams and Anderson [37].

This test appears to be very useful, as it can be applied to most adhesives and coatings; a great deal of work has been carried out on the analysis of the stresses involved and the mechanisms of crack propagation. It was not used in this work simply because it is not as suitable for application in an industrial situation as other methods, although it is considered to be a very promising test.

The direct pull-off test, g, will be discussed at the end of this section, after considering all the others, as this was selected for use on the system under investigation.

(h) Bend test

This test is often used in industrial laboratories to give a quick measure of the quality of a particular coating. A strip of metal, coated with the film under test, is bent around a mandrel of a specific diameter and the film examined to detect any cracks or areas of flaking. It is not possible to determine the exact site of failure, or the stresses which cause it. Thus, it is a highly empirical test, and not suitable for application to the investigations to be carried out in the present work.

(i) Scratch or cross-hatch test

This is also an empirical test which is frequently used in industrial

laboratories. A cured coating is scribed using a specially designed cutting tool, with ten equally spaced wheels, and a net of one-hundred squares of equal area is produced. A piece of "Sellotape" is then placed over the scribed area and pressed firmly onto the surface; this is stripped quickly from the substrate, and the number of squares remaining on the substrate gives a measure of the properties of the film. Stone [33] has developed a test called the "PASS" test, in which he studies the relative paint loosening along a scribed line through the film, after exposure to a corrosive environment.

However, neither of these tests was suitable for use in this case.

(j) Ploughing

This method is discussed in detail by Asbeck [3, 4] and involves the controlled removal of the coating, using a sharp knife blade. The knife is of a fixed, accurately known geometry, and the force required to cause removal of the film is plotted versus distance along a specimen, or coating thickness. Three types of film failure may occur: cutting, which is pure cohesive failure; peeling, which is pure adhesive failure; or chipping, which is consecutive interfacial rupture (adhesive) followed by cohesive failure of the film.

An abrupt change occurs in the removal force as the failure mechanism changes from one to the other. From a knowledge of the many parameters involved in this system the adhesive forces between the film and substrate, and the cohesive forces within the film itself may be calculated.

Asbeck refers to the device as a "Hesiometer", while Malloy *et al.* [27] describe a similar device called the "Interchemical Adherometer".

The results are reputed to be rapidly obtained and reproducible, but are dependent on many variables of the system. Although it is clearly a useful tool it is considered to require more complex theoretical back-up than other test methods considered.

(k) Peeling

This is a very popular technique for studying the strength of the

adhesive bonds between a coating and the substrate, and has been reviewed in a very useful paper by Hardy [16]. There are many different forms of this test, all involving the peeling of a coating from its substrate, the main variation being the angle at which it is peeled which ranges from 0° [24] to 180° .

The analysis of the results of this test method are complicated as they depend on many variables, such as the width of the specimen, the thickness of the coating, the modulus of the coating material, angle and rate of peeling, and temperature. The coating may be stripped from the substrate at a constant rate, or a given load applied and the time noted for the bond to strip a measured distance.

May *et al.* [29] give a useful discussion of the peel test, and the energetics are considered by Kendall [22]. However, the most thorough consideration of the theory of peel testing is given by Kaelble [19, 20].

These tests cannot be carried out on rigid coatings as the film will simply crack, and it is considered that tests of this type are involved more in measuring the rheological properties of the coating than the strength of the adhesive bonds with the substrate.

(1) Shear and lap tests

In a shear test the direction of stress is parallel to the plane of the joint, and the whole coating is stressed at one time. However, in the simple lap shear test, where a film of the adhesive under test is positioned between two, overlapping lengths of the substrate material, each of which is pulled in the opposite direction. distortion may occur as the forces at each interface are not in line, introducing an element of cleavage at the interface. Many other types of lap joint have been designed [6] to eliminate this distortion, but the applied stress has components of both tension and shear.

These joints are extremely useful from a practical point of view, as they are very strong; however, as tests for investigating the adhesive

interaction between the coating and the substrate they are of little use, as the applied stresses are complex to analyse [18, 23].

(g) Direct pull-off method

In this test the coating is sandwiched between two specimens of the substrate material, usually circular or square in cross-section, and stress is applied in a direction perpendicular to the coating/substrate interface. These are called butt joints, and the whole of the sample is stressed equally. Malyshev and Salganik [28] favour this method to determine the work of adhesion using the average breaking stress of the specimen, as failure occurs very rapidly across the tested area and does not allow time for extension of cracks arising from weakened regions of the joint. The strain of the specimen may easily be defined, and the duration of the test. This is unlike the peel test where each element of the interface is stressed for a very short time, and the strain of the specimen is complicated by the fact that part of the coating is detached while the remainder is supported by the substrate, the proportions of each changing continuously.

The stresses involved in the testing of butt joints have been considered by several authors, for example Anderson *et al.* [1], Bikerman [7] and Gent and Lindley [13], and are less complex than in many of the tests outlined above.

The direct pull-off method was chosen for investigating the adhesive and cohesive strength of the lacquer/mild steel system for the following reasons:

- (i) The experimental procedure is straightforward and suitable for use in an industrial laboratory;
- (ii) the results are relatively easy to interpret, and the applied stresses less complex than in many other tests;
- (iii) The response of the coating to various levels of stress may be investigated, and the relative magnitudes of the adhesive and cohesive interactions considered;

- (iv) results recorded in the literature suggest a good level of reproducibility is possible; for example, those recorded by May *et al.* [29].
- (v) The test can be applied to many types of coating on a variety of substrates.

2.3 THERMODYNAMIC APPROACH

The thermodynamic work of adhesion is defined as the difference in surface free energies between the separated surfaces of the adhesive (or coating) and substrate, and the intact interface. There is conflict in the literature concerning the correlation between this value and the measured strengths of adhesive joints - some authors report such a correlation, while others have found none. This conflict is probably caused by the fact that most of the test methods used to measure the strengths of adhesive joints are not well suited to theoretical analysis.

Andrews and Kinloch [2] have discussed this problem from both the theoretical and experimental points of view. They measured the adhesive failure energy per unit area of a fracture plane, θ , and calculated the thermodynamic work of adhesion, W_A , for a series of joints. They found that for any particular joint the adhesive failure energy decreased with decreasing rate of crack propagation, and with increasing temperature, suggesting that θ included energy dissipated viscoelastically in the coating around the propagating crack. In some joints at low values of the crack propagation rate, when the viscoelastic contribution was minimal, the adhesive failure energy was found to approach the value of the thermodynamic work of adhesion.

Thus, they concluded that θ has two main components; the intrinsic adhesive failure energy, θ_o , which is the energy required to propagate a crack through unit area of an interface in the absence of viscoelastic energy losses, and should be rate-temperature independent; and ψ , the energy dissipated viscoelastically within the coating, which is the dominant term but is itself proportional to θ_o .

If the values of θ_o and W_A are in agreement this indicates that the main mechanism of adhesion is the formation of interfacial secondary bonds. However, if θ_o is greater than W_A it implies that a stronger type of bonding force is active at the interface, for example covalent bonding.

This type of study provides a useful method for investigating the mechanisms of adhesion between the coating and the substrate, but requires a great deal of careful experimental and theoretical work. Many other workers have considered the subject, among them Gent [14] and Gent and Kinloch [15], while others have discussed the computation of thermodynamic work of adhesion, for example Kaelble [21], Owens and Wendt [30], Patton [31] and Zettlemoyer [38].

This could be a particularly fruitful method for investigating the type of bonding occurring between a coating and substrate under various conditions, provided the difficulties involved in the experimental procedure could be overcome. However, it does not yield sufficient information concerning the properties of the film itself, which are required in this work, so the more basic experimental approach was employed.

References - Chapter Two

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CHAPTER THREE

EXPERIMENTAL

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3.1 PRELIMINARY TESTS

Preliminary tests were carried out using the standard laboratory tensile test method. This will be described and discussed in detail, and its shortcomings evaluated. The methods of lacquer and specimen preparation will also be described, as they became standard procedure for all the tests which were performed.

"Alloprene R20" from batch 300 was used in all tests, and the infrared adsorption spectrum of the polymer was obtained to check that no other chlorinated polymers were present, apart from chlorinated cis-polyisoprene. The spectrum is shown in Figure 3.1, which also illustrates the variation observed when a small proportion of chlorinated polybutadiene is present. For each sample of lacquer 0.25kg of "Alloprene" was dissolved in 0.25kg of Analar toluene, in a glass jar with a sealed lid. This jar was placed on rollers overnight to ensure complete dissolution of the polymer.

All "Alloprene" contains a small amount of carbon tetrachloride (CTC), and the theoretical proportion for this batch was 6.75% by weight. However, a gas chromatogram was obtained (Figure 3.2) for this specimen. By taking the ratio of the CTC peak height to the peak height of the chloroform internal standard, and comparing this with the calibration curve of the column it was found that the CTC content had fallen to $6.45 \pm 0.05\%$, during the storage of the polymer. In solution this value falls to approximately 1% by weight.

"Cereclor 42" from batch H418 was used as the plasticiser, and was added in the ratio 70:30 w/w of binder to plasticiser, as suggested by Caldwell and Ferguson [14]. The resulting lacquer was

Figure 3.1

Infra-red spectra obtained from chlorinated-polyisoprene, chlorinated-polybutadiene and mixed chlorinated-polyisoprene and chlorinated-polybutadiene, to check the purity of the sample used for tests.

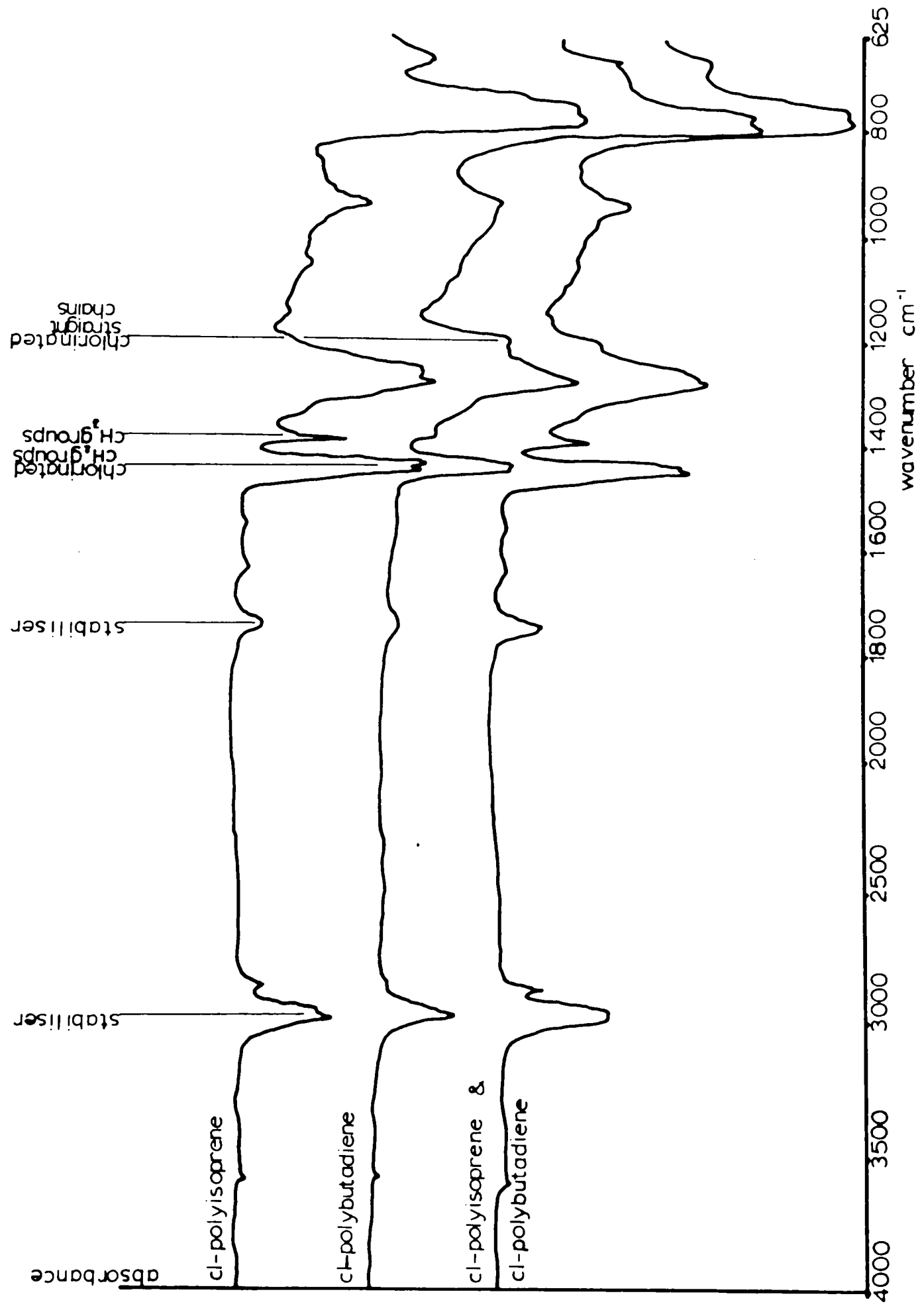
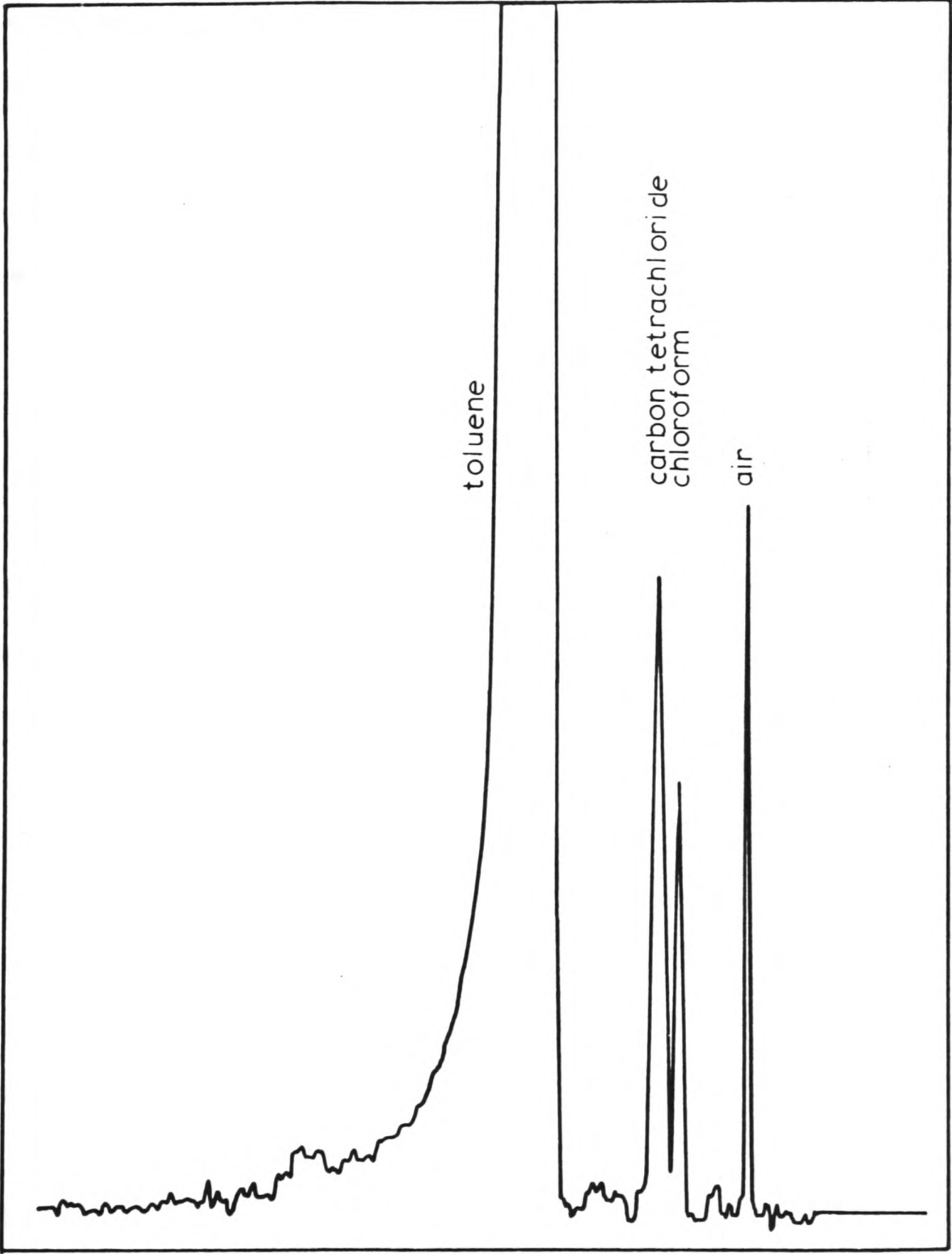


Figure 3.2

Gas chromatogram obtained to check carbon tetrachloride content in "Alloprene" sample. 1g of "Alloprene R20" dissolved in toluene with 1ml of 3% w/w chloroform in toluene as internal standard. Column temperature 80°C.



rolled for at least four hours to ensure complete mixing of the components, and then allowed to stand overnight to ensure that any trapped air bubbles could escape from the lacquer.

The dry film thickness of an industrial paint coating is in the region of 100µm, so it was considered necessary to study films of a comparable thickness. The necessary wet film thickness is calculated in the following way:

Considering 0.25kg of "Alloprene", density 1.6kg/l; 0.25kg of toluene, density 0.867kg/l; and 0.107kg of "Cereclor", density 1.16kg/l. The total volume of this lacquer is

$$\left[\frac{0.25}{1.6} + \frac{0.25}{0.867} + \frac{0.107}{1.16} \right] L = 0.537 L$$

The percentage of this volume due to solvent alone is $25/(0.867 \times 0.537)\% = 53.70\%$. Thus, if all the solvent is lost on curing, the film thickness decreases by 53.7%; so far a dry film thickness of 100µm, a wet film thickness of 216µm is required. A draw-down bar was to be used for applying the film. This has an accurately measured clearance between the bar and the substrate, but is recognised to carry about 40-50% of this depth of lacquer along with it. Thus, if a bar with 375µm clearance was used, it should leave a wet film 188-225µm thick resulting in a dry film thickness of 87-104µm, which is within the required range.

The substrates used were mild steel plates supplied by "Pyrene", measuring 152 x 102 x 1.27 mm. These were coated in oil for storage, and first had to be degreased in a bath of boiling trichlorethylene for two minutes, and about a minute in the vapour. In order to make any useful observations concerning film performance, a balance had to be struck between studying the often highly contaminated surfaces encountered in the industrial application of paints, and surfaces which had been rigorously chemically cleaned in the laboratory. Thus, each plate was abraded to "British Standard" [8] specifications using

280 grade emery paper, until there was no preferred direction of the surface abrasions. They were then washed in "solveso" and dried by compressed air. The plates were coated as soon as possible after cleaning, to prevent undue contamination of the surface.

The roughness of the surface thus produced was measured using the centre line average technique (CLA), also called the Ra method, where

$$Ra = \frac{1}{L} \int_0^L |y| dx \quad \text{approximately}$$

L = total length of specimen

y = peak height above and below centre line

x = position along specimen

The actual height of any single peak can only be estimated from the chart obtained.

The CLA obtained varied between 0.3 μ m and 0.4 μ m, and the average maximum peak height was between 0.75 μ m and 1.25 μ m.

The effects of surface roughness and surface cleaning are discussed by Harris [22], Bullett and Prosser [9], and Jennings [24]. On a rough surface the larger surface peaks give a stress concentration leading to failure at low stress, but the so-called "creep" of the failure due to peeling occurs more readily on a smooth surface. Thus, a smooth surface will give a greater adhesive strength, but once failure occurs more of the film will be detached. It is suggested that when a steel surface is cleaned thoroughly, the cohesive strength of the applied film is usually less than the adhesive force binding it to the substrate, and few films, if any, can be detached with clean interfacial failure.

Each plate was coated with a single film of lacquer which was allowed to dry in air at 25°C for twenty-four hours, and in an oven at 40°C for a further seventy-two hours. The film thickness on each

plate was measured using a magnetic flux meter, after complete drying had occurred, and for twenty-two plates coated the average film thickness was $74.6 \pm 3.2 \mu\text{m}$, rather lower than the predicted value. Each plate was cut in half, and one 20mm diameter aluminium "dolly" was attached to each film surface using "Araldite" resin MY753 and hardener HY951 (Figure 3.3). The plates were then put aside for a further twenty-four hours at 25°C to allow the adhesive to cure.

Six specimens were tested in tension using an "Instron" tensile testing machine, in order to find some measure of the force required to detach the film from the substrate. A cross-head speed of 5mm min^{-1} was used, and the mean stress required to cause failure of the specimen was $0.588 \pm 0.073 \text{ MN m}^{-2}$.

The remaining specimens were tested using a bench-top "Elcometer" tensile testing device, which was employed simply to detach the film in order to study the types of failure occurring, and the possible weaknesses in the film.

Figure 3.3

Aluminium "dolly" mounted on coated substrate.



3.2 OBSERVATIONS AND DEDUCTIONS

An important part of any test of this kind is the identification of the site of initiation and subsequent path of failure, whether it is adhesive failure between film and substrate, or cohesive failure within the film itself. The solutions to these problems are not always simple to obtain.

The first points to be noted from these preliminary tests were:

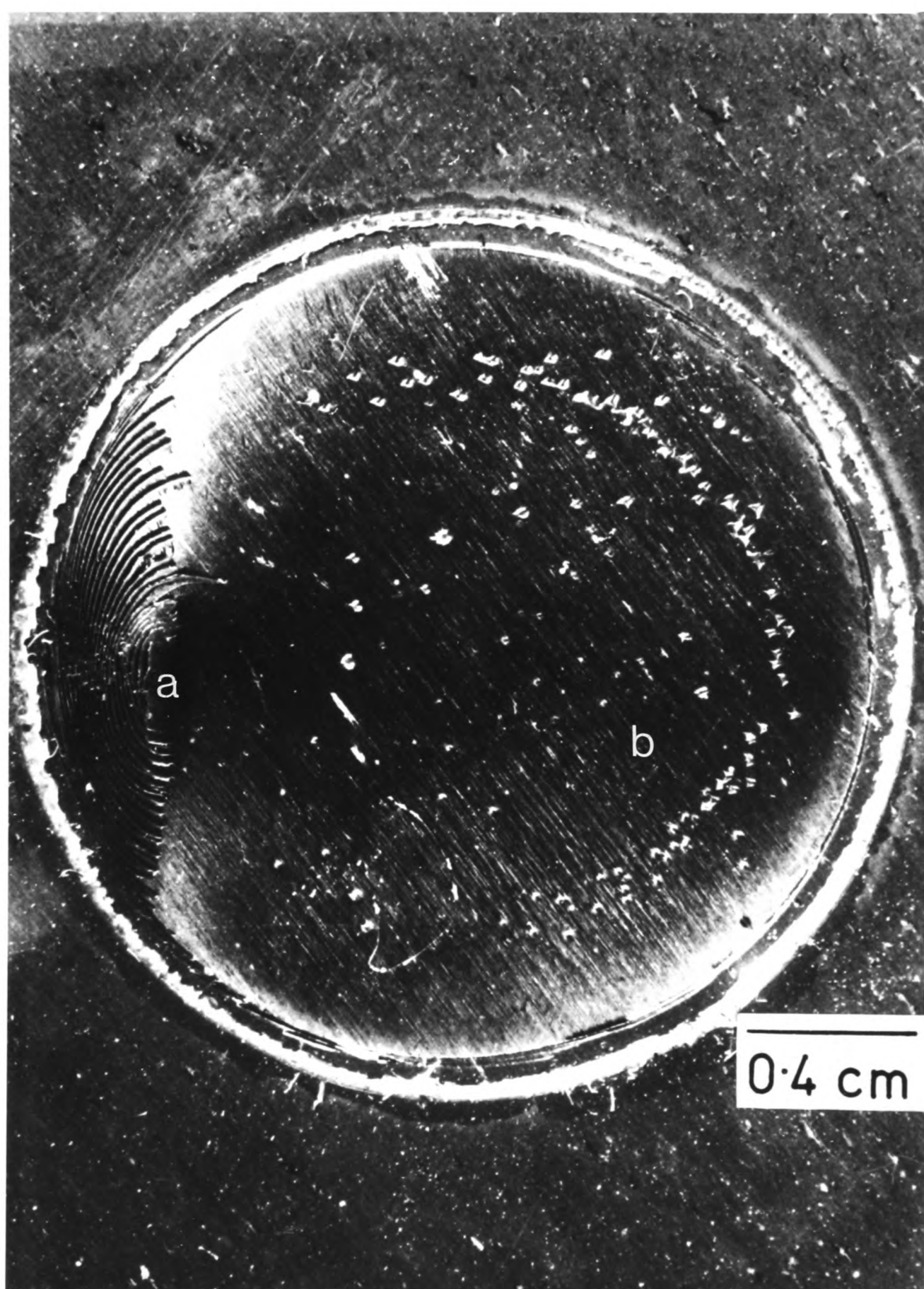
- (i) that the stress at failure was much lower than those predicted for an unsupported film of this formulation. Values ranging from 1.96 MN m^{-2} [23] to 11.04 MN m^{-2} [31] have been recorded at a cross-head speed of 5 cm min^{-1} ;
- (ii) that the surface markings on all the tested areas were very similar (Figure 3.4);
- (iii) that most of the specimens appeared to have failed mainly in the adhesive mode.

The interpretation of the surface markings observed in these areas leads to an explanation of point (i) above, as follows: each specimen exhibited an area of rib markings, as shown in Figure 3.4, and each one was in a similar position on the tested area. These were caused by "stick-slip" propagation of the crack within the body of the film [3].

A propagating crack tends to accelerate as more energy becomes available through its propagation. It would be expected that this acceleration would continue until some specific terminal velocity had been reached, and the fracture would then continue at this maximum speed. However, the acceleration of the fracture front often appears to give rise to instability, and the most common example of this is crack forking, in which the fracture divides into two separate branches and is either halted, or slowed down, before one of the branches continues to propagate. This process may occur many times, giving rise to a quasi-periodic effect.

Figure 3.4

Typical example of a tested area. (a) Rib markings, (b) area of apparent adhesive failure showing "lumps" of lacquer remaining on the surface.



0.4 cm

Crack forking can only occur if the stress distribution at the fracture tip changes in such a way as to encourage propagation along two loci instead of the usual single axial direction (Figure 3.5).

Under normal circumstances the stress distribution moves along with a propagating crack, so that the locus of maximum stress (b) coincides with the crack axis, (Figure 3.5), and this is the direction along which fracture will always occur. It is for this reason that a crack in a uniform field of force propagates in a straight line. However, if the stress distribution at the propagating crack changes then the crack will follow one or both of the loci of maximum stress (a). This causes forking at the crack tip. As the crack grows in this way it will encounter successively lower stresses, and will come to a halt unless the overall stress in the specimen is increased to compensate for this. When a high overall stress is achieved the conditions maintaining the steady state are overcome, and as the stress in the test piece is far in excess of that necessary for propagation, a catastrophic phase of failure will follow. The process recurs many times, and the "stick-slip" fracture is thus accounted for. Figures 3.6 and 3.7 show typical areas of "stick-slip" fracture observed in the specimens, and as described by Andrews [3].

The remaining area of each specimen was apparently a region of adhesive failure - the film appearing to have been completely removed from the substrate, leaving only occasional "lumps" of lacquer on the steel surface. This "adhesive" failure will be discussed in greater detail in following chapters. However, on closer examination, using an optical microscope, these lumps were found to have a particular structure, and showed clear surface markings (Figure 3.8).

This structure will be described as "nose-and-tail", and it was found that all the "noses" of the lumps pointed towards one particular area of the tested surface - this point was also the

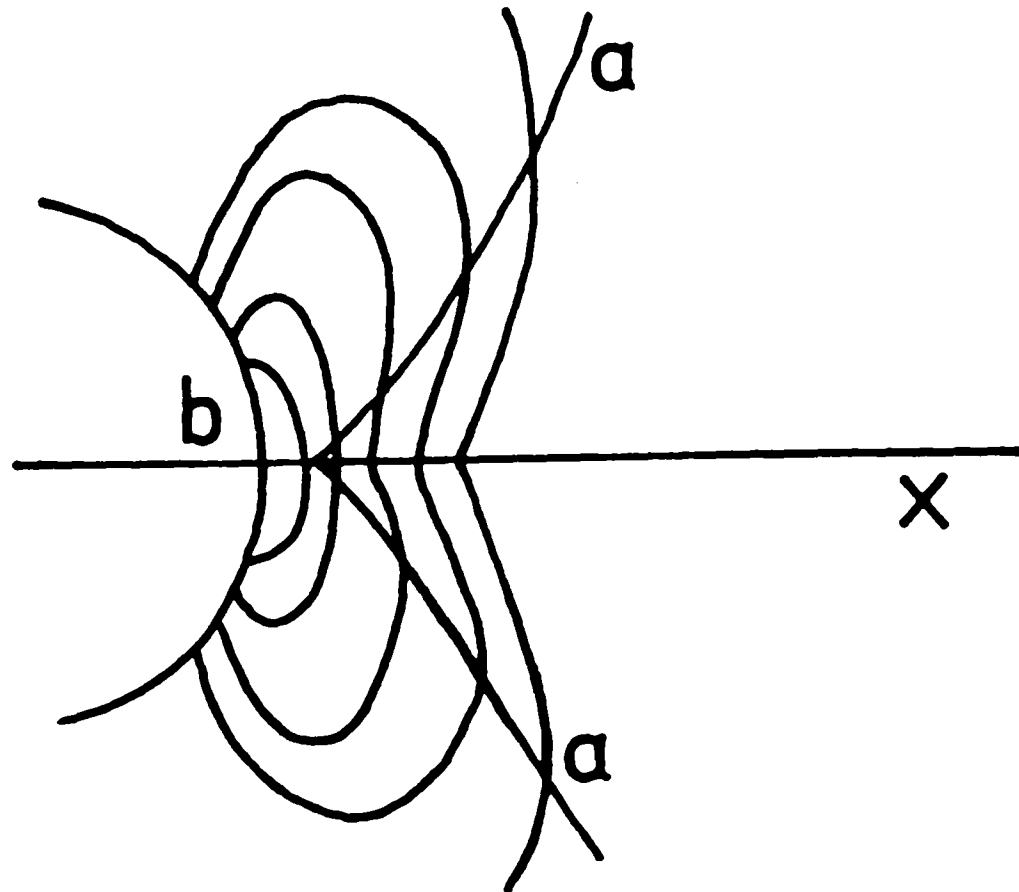


Figure 3.5

Stress distribution at crack tip. (a) Loci of maximum stress.
(b) Normal crack axis. (x) Normal path of fracture.

Figure 3.6

Area of "stick-slip" fracture showing intersection of two fracture fronts.

Figure 3.7

Area of "stick-slip" fracture showing the typical curvature of the markings, and their periodicity.

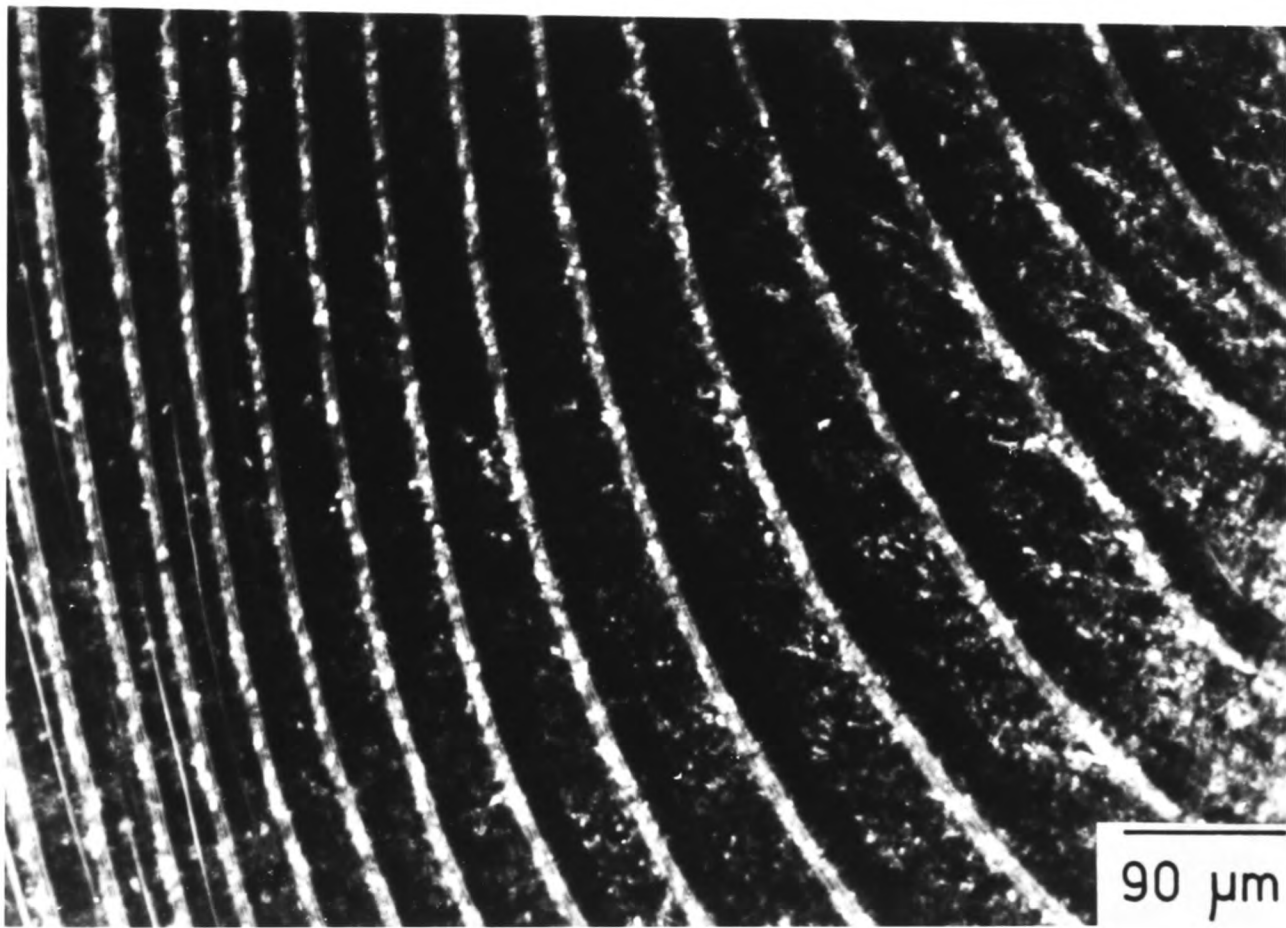
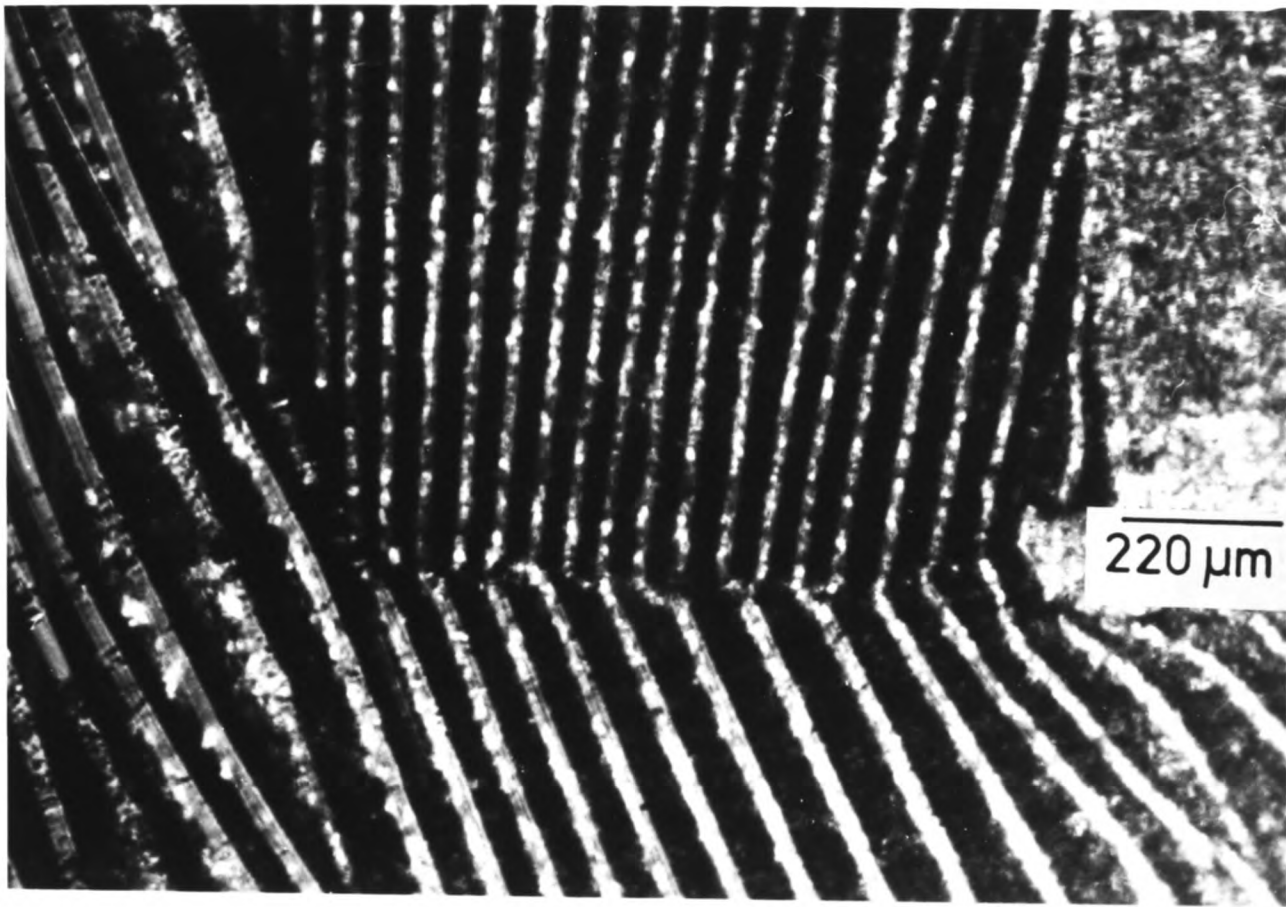
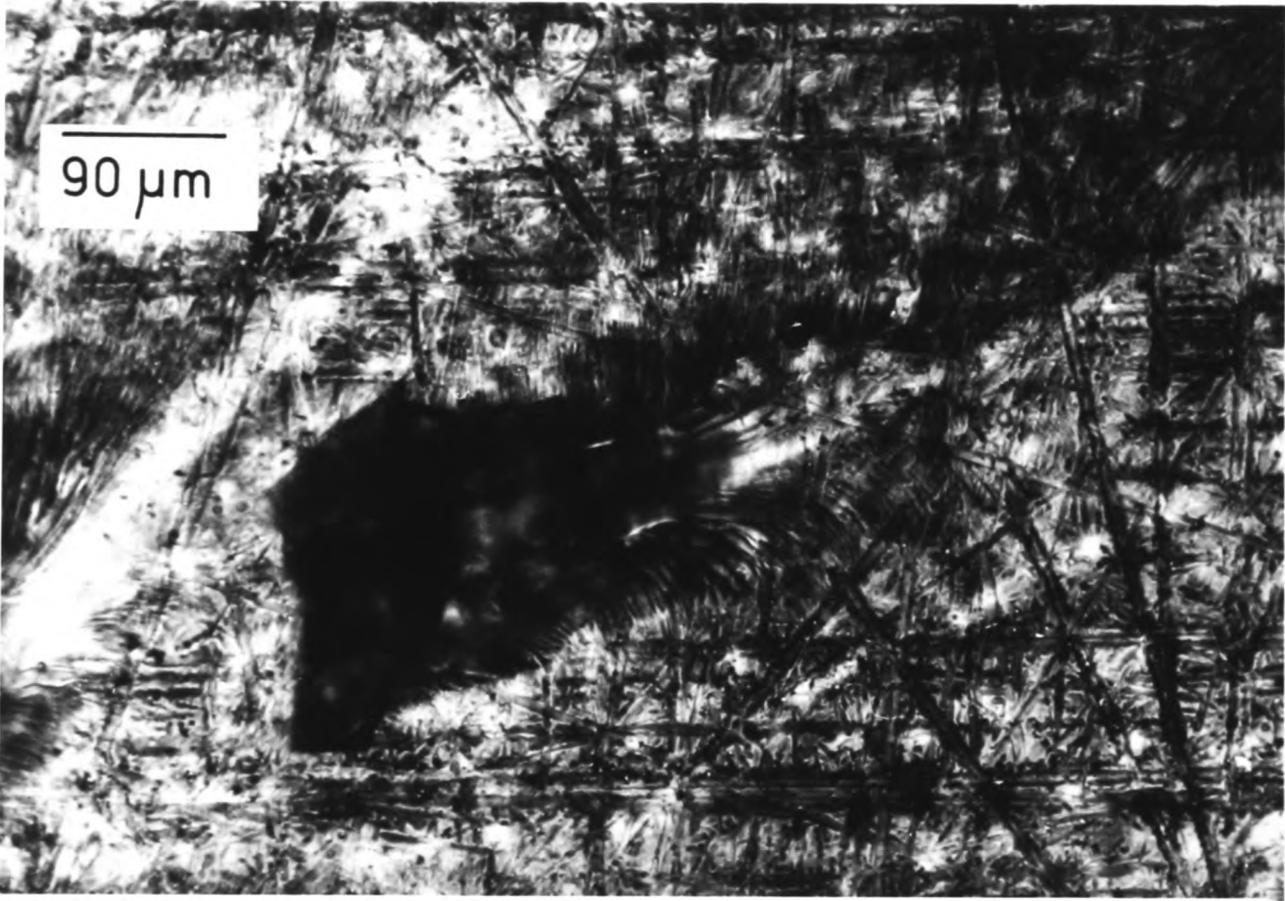
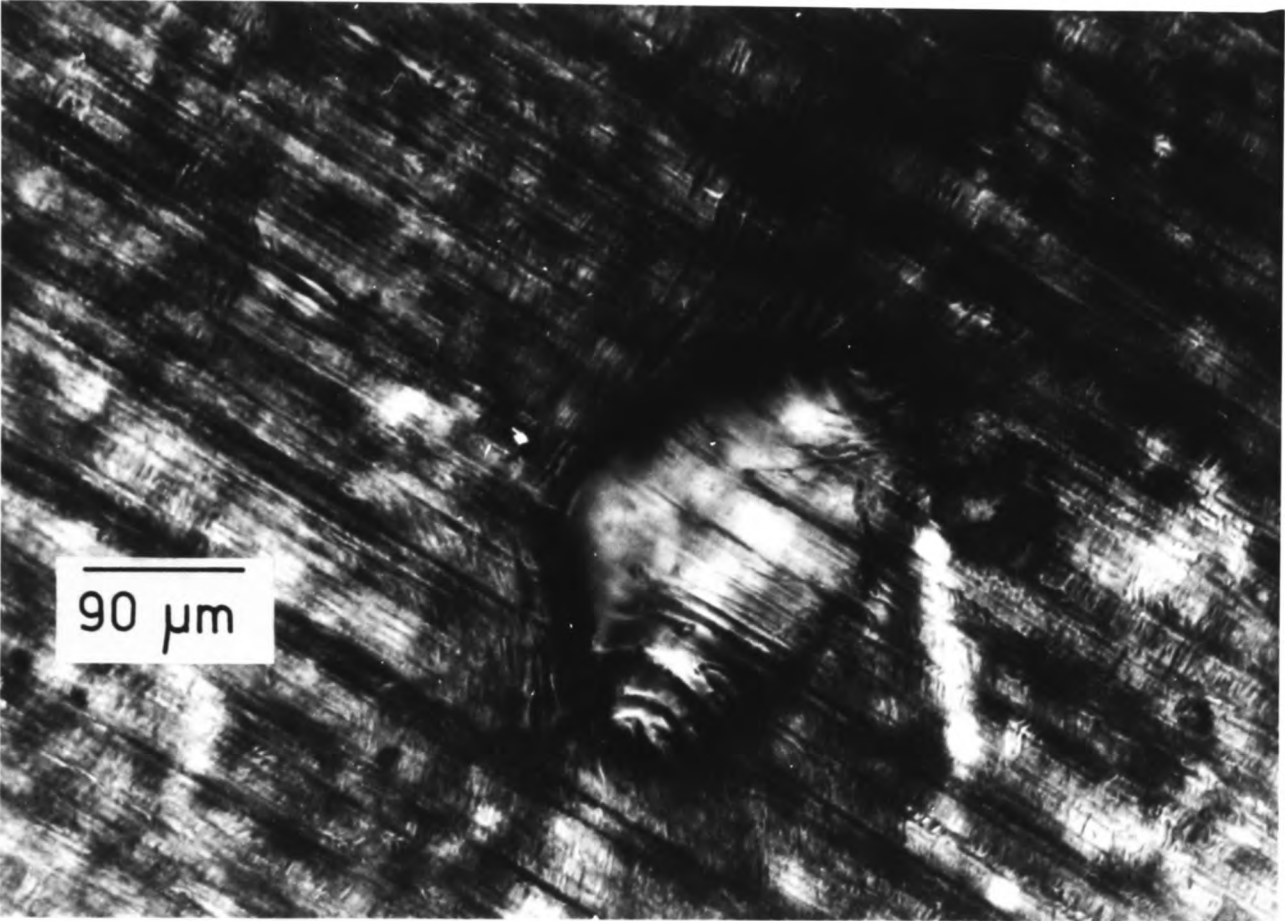


Figure 3.8

Typical examples of areas of lacquer remaining on the substrate surface, showing "nose-and-tail" structure.



focus of the "stick-slip" markings. This is illustrated in Figure 3.9. It was inferred that this was the point at which the initial failure occurred, and it is suggested that the surface features were formed in the following way (Figure 3.10). Assume that crack x is propagating at constant velocity at the interface between the lacquer and the substrate. Area y is an area of enhanced adhesion, for example where the lacquer is strongly keyed into the surface. When the crack reaches y those parts of it to the right and left of this area continue to propagate, but the portion at y is held up, as the stress is insufficient to cause fracture here. As the crack moves further across the specimen the stress at y builds up, until it is sufficiently high either to cause interfacial failure here or for the crack to climb through the film to a region of lower strength, and move past the hold-up. It is the latter case which causes the "nose-and-tail" structure of the lumps, because once the hindrance to crack propagation is by-passed the crack front moves rapidly forward and down through the film to rejoin the main fracture front propagating at the weakest level in the film/substrate system.

Thus, the detailed markings on each surface may be examined using an optical microscope, and the point of initial failure deduced. Some effort was made using the optical microscope, to identify the cause of the areas of increased adhesive strength - to detect some change in the structure of the interface - but no apparent causes could be found.

In all cases the crack had initiated at a point 2-3mm from the edge of the tested area, and the fracture front had expanded radially from this point. The mode of fracture must be related to the loading of the specimen, but the loading of the discs was intended to be symmetrical while the fracture pattern was non-symmetrical.

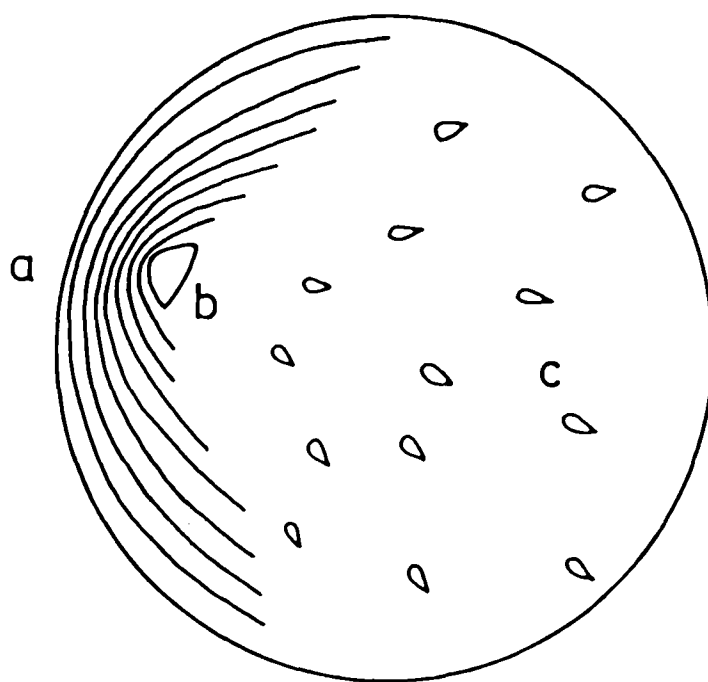
Dannenberg [17] found that a bubble with a low angle of advance tends to propagate by peel, while one with a high angle tends to

Figure 3.9

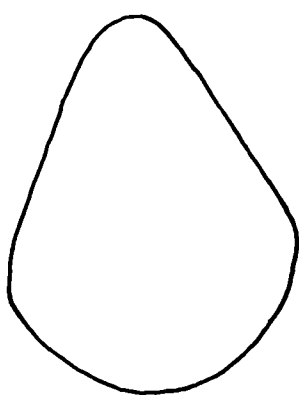
Schematic diagram of a typical tested area. (a) Rib markings. (b) Focus of all fracture markings. (c) Exaggerated view of the pattern of the remaining lumps of lacquer.

Figure 3.10

(i) Typical shape of a remaining lump of lacquer, plan view and elevation. (ii) Schematic representation of the process by which the lumps are formed, progressing a to d. (See text.)



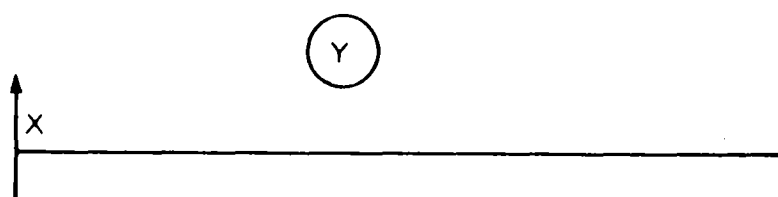
i



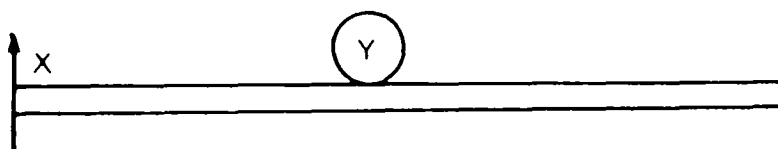
ii



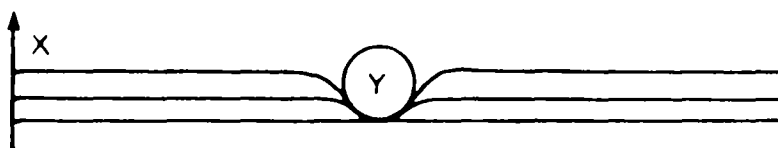
a.



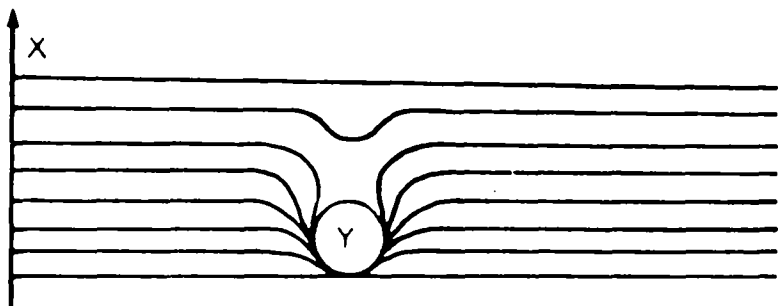
b.



c.



d.



move by the "stick-slip" mechanism. Figure 3.11 shows an exaggerated view of uneven loading on a specimen, due to bending and inaccurate alignment. To the right-hand side the crack has a smaller angle of advance, and on the left-hand side a larger angle. Thus, the crack tends to propagate by a "peel-like" mechanism to the right, and "stick-slip" to the left. The sharper crack would tend to propagate more readily than the less sharp [32], which indicates that peel probably occurs before "stick-slip" failure. As this description coincides exactly with the markings observed on all the tested specimens it must be inferred that they are produced as a result of bending occurring within the system.

It was clear from these preliminary tests that a significant amount of bending occurred within the system, so the method of testing required some review and improvement to eliminate this completely. This bending probably caused a large increase in the local stress at the point of initial failure, and hence premature failure of the specimen, which explains (i) above. Also, the fact that the "dolly" was attached to the surface of a large area of lacquer made it impossible to define the exact area of lacquer which was influenced by the applied force, and the restraining effect of the film surrounding the area beneath the "dolly" could not be described.

A more rigorous cleaning program for the components in the system would not draw too far from the types of surface encountered in industrial situations, but would reduce the number of random variables introduced into the properties of the interface.

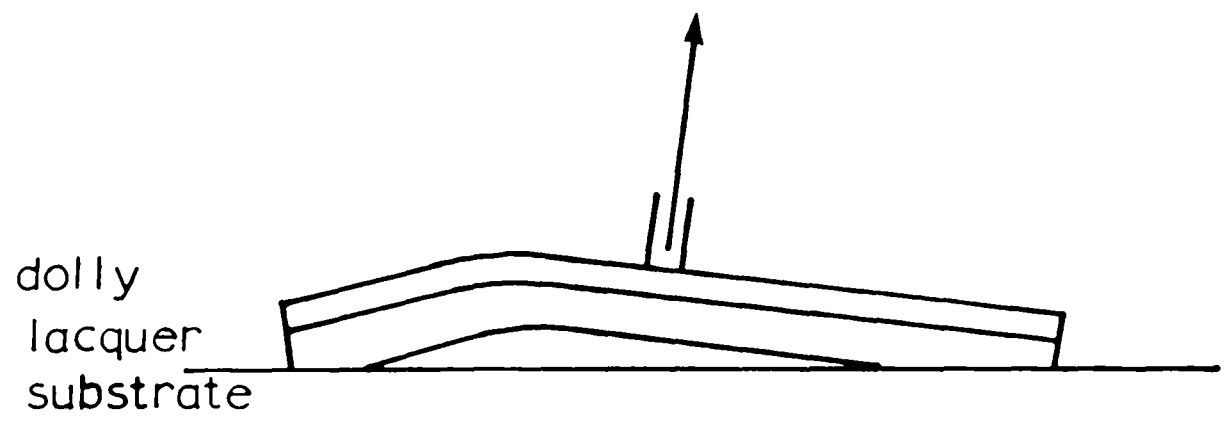


Figure 3.11

Exaggerated view of the effects of uneven loading on a specimen.

3.3 MAIN METHOD OF TESTING

A test method was required where the total area of the specimen was confined beneath the "dolly" so that the boundaries of the specimen could be clearly defined, and the substrate well supported to prevent bending.

Several variations are described in the literature. Gent [19] used a disc of a viscoelastic polymer pressed between two mylar sheets to form a "sandwich", and cemented the whole between steel cylinders to form a tensile specimen. He measured the mean tensile stress at break. Gent and Lindley [20] prepared butt joints of vulcanised rubber between plane metal cylinders 2cm in diameter; and Jennings [24] reports an experiment using specimens bonded between stainless steel plugs 2.54cm in diameter, and 2.54cm long. He gives a detailed description of specimen preparation, testing and evaluation, and refers to a method of aligning the specimens reported by DeLollis [18].

Bullett and Prosser [9] used discs which were stamped from a metal sheet before coating, and were 3.175cm in diameter. These were used to form butt joints between steel cylinders 2.54cm in diameter, with the faces in contact with the coating relieved to leave a diameter of 1.905cm in contact with the paint, to concentrate the force on this side of the disc.

A method of testing was devised, which was based on these outlines, and which could be used to study a significant number of specimens at one time.

"Pyrene" mild steel plates were used, measuring 305 x 102 x 1.27 mm, which were first degreased in a bath of boiling trichlorethylene, and twenty 19.05mm ($\frac{3}{4}$ inch) diameter discs were punched from each one using a fly-press. It was decided to punch the discs before coating the plates to avoid any damage occurring to the film. A specially designed die was used in the fly-pass to prevent "dishing" of the discs (Figure 3.12). The disc was pressed out by the punch, and

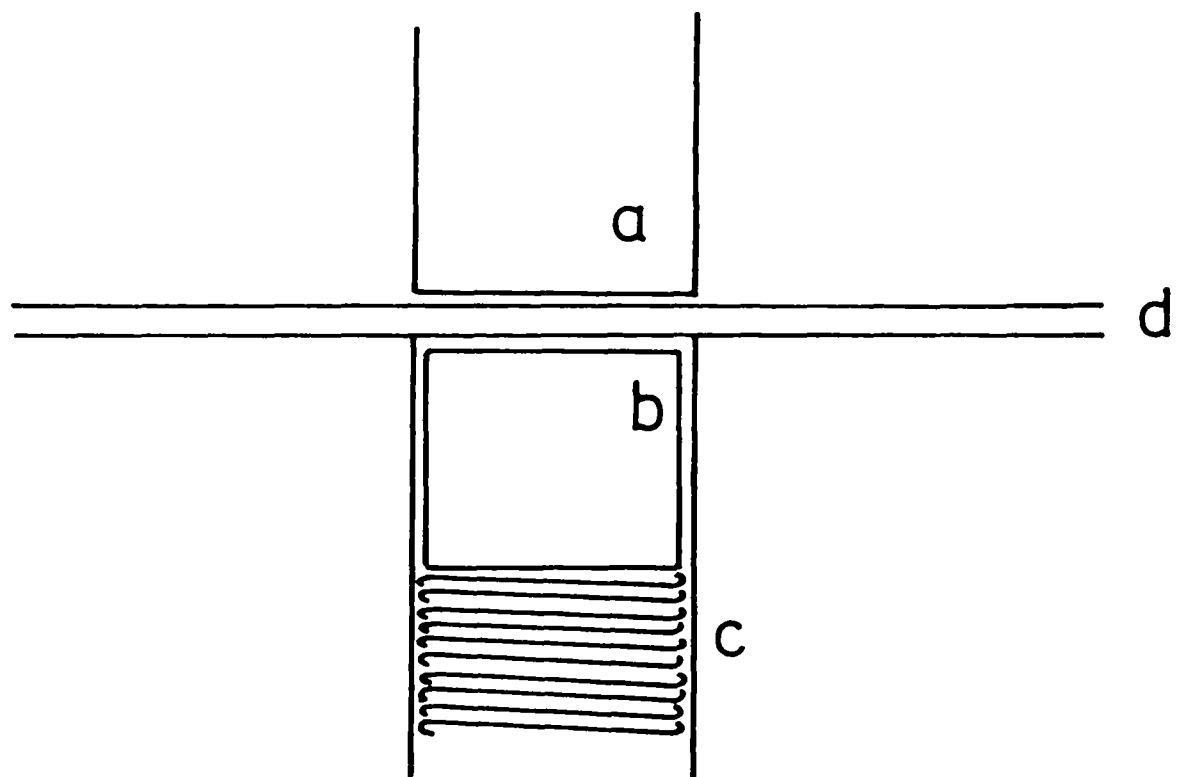


Figure 3.12

Diagram of the technique used for punching discs from mild steel plates. (a) Punch. (b) Solid cylinder mounted in die. (c) Strong spring. (d) Steel plate.

flattened against the cylinder mounted in the die; it was then ejected by the strong spring positioned below the cylinder. The system is quick and easy to use, and appears to work well.

The burrs were removed from the reverse side of each disc using emery paper, and each set of twenty was stuck reverse-side down to a glass plate using double-sided tape, to improve the ease of handling them. The discs were then abraded to "British Standard" specifications using 280 grade emery paper, so that there was no preferred direction of the surface abrasions; the plates initially showed abrasions parallel to their length.

The discs were at once ultrasonically degreased for five minutes in boiling trichlorethylene, shaken vigorously in distilled water to remove any remaining surface particles and finally in acetone to dry the surface. At all times they were handled with clean tweezers.

The dimensions of the specimens were chosen to give a large value for the ratio of the diameter of the disc, to the film thickness. This followed the suggestions put forward by Anderson, Bennett and Devries [2] in their discussion of the variation of the normal (axial) and shear stresses across the diameter of such a specimen, Figures 3.13 and 3.14. They considered a diameter to thickness ratio (D/h) in the region of 100 for a Poisson's ratio (γ) of 0.5, and found that the ratio of bond plane axial stress to average axial stress was between 1.0 and 1.1 to within a distance of $0.15D$ from the edge of the disc. Beyond this point the ratio fell below 1.0, and at the edge was about 0.2. The uniformity of the axial stress across the diameter was found to increase as Poisson's ratio decreased from 0.5.

The shear stress at the bond plane for a butt joint with γ less than 0.5 was found to be zero to within a distance of about $0.07D$ from the edge of the disc, where it was small for specimens with D/h greater than 100.

Alwar and Nagaraja [1] also discuss this phenomenon.

Figure 3.13

(a) Axial stress distribution at bond plane for butt joint specimens with Poisson's ratio of 0.50 [2].

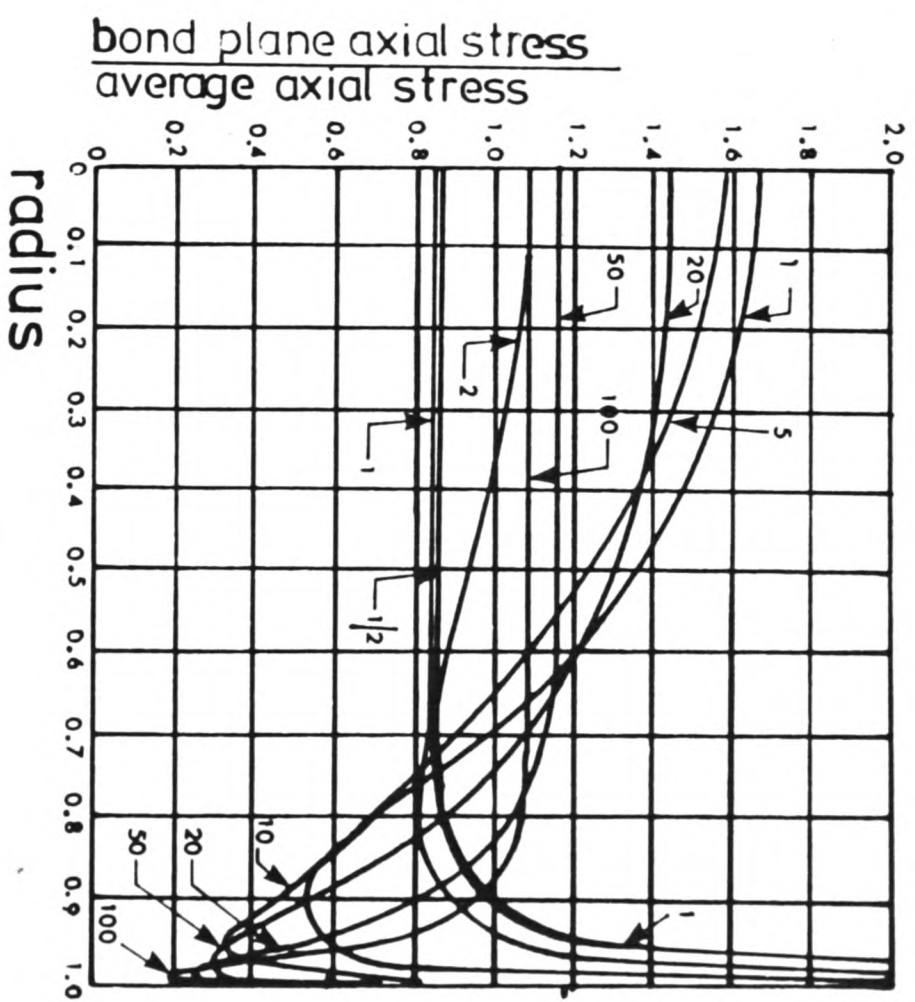
(b) Axial stress distribution at the bond plane for butt joint specimens with Poisson's ratio of 0.49 [2].

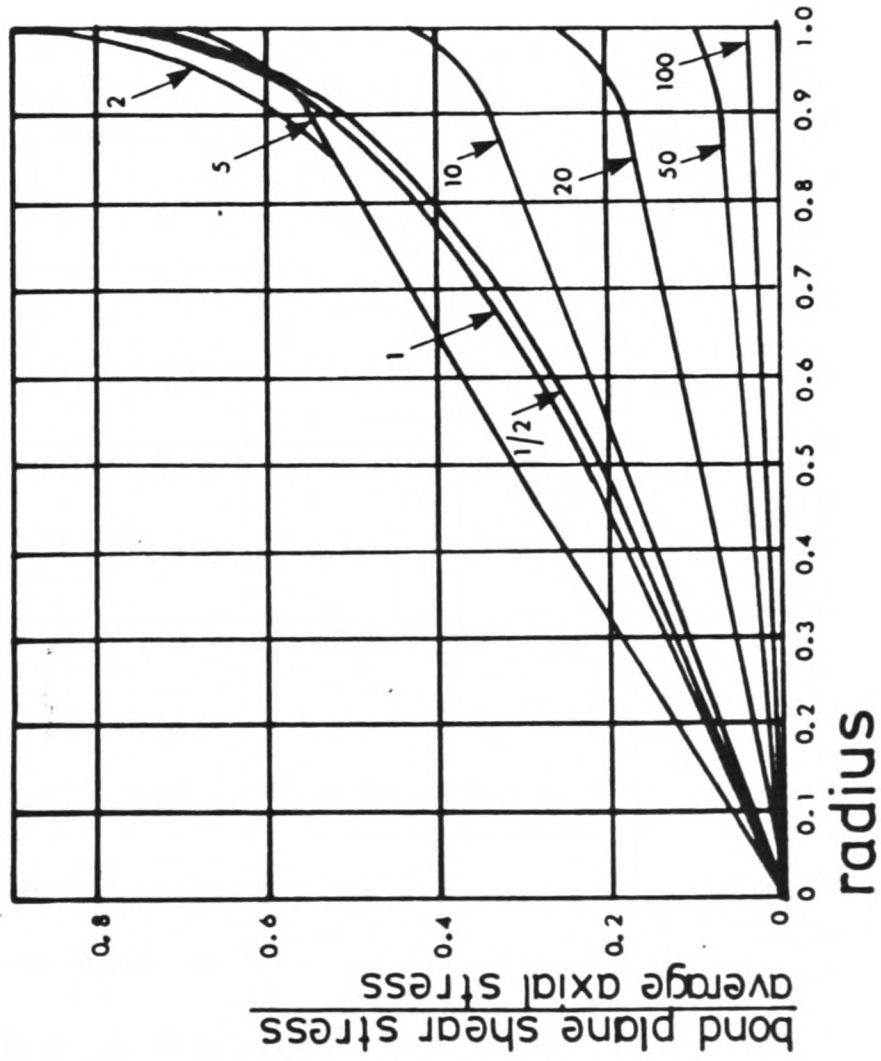
Figure 3.14

(a) Shear stress distribution at the bond plane for butt joint specimens with Poisson's ratio of 0.50 [2].

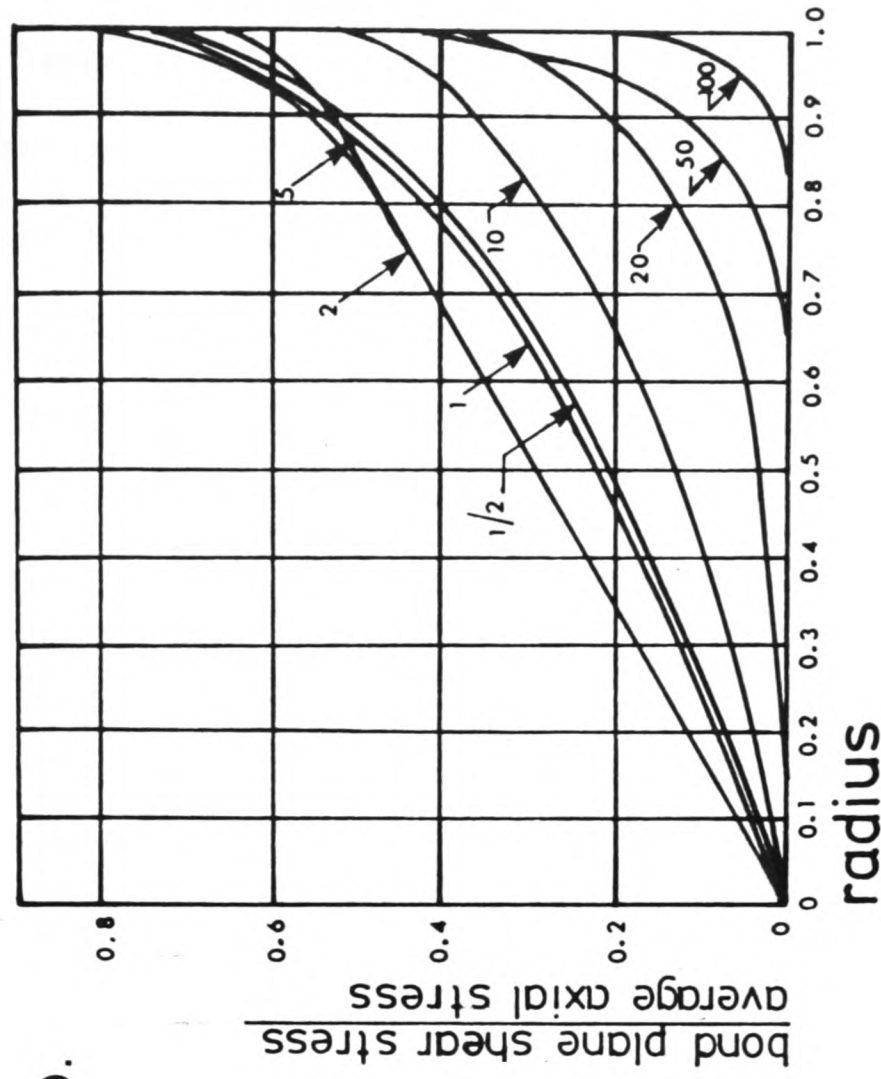
(b) Shear stress distribution at the bond plane for butt joint specimens with Poisson's ratio of 0.49 [2].

८





a.



b.

The dimensions of the specimens were thus designed to give a diameter to thickness ratio of about 200, so that the axial stress would be uniform across a large proportion of the diameter, and equal to the average axial stress; and the shear stress should only be non-zero at the very edge of the specimens, and here only very small.

A film thickness of approximately 100 μ m was required, and the 350 μ m "draw-down" bar was used once again. Two methods were tried for casting the films, and were carried out as follows:

1. Immediately after cleaning, the twenty discs from each set were mounted in a double row, using double-sided tape, down the centre of a cleaned steel plate, as shown in Figure 3.15. The shoulders were removed from the spreader bar to enable it to run easily along the side-plates. A film of the required thickness was cast on the discs, while the surrounding film was approximately ten times thicker, due to the depth of the plates. This film could easily be cut to remove the discs at the appropriate time.
2. The second method consisted of placing the cleaned discs in holes carefully cut in a clean steel plate 1.27mm thick. These holes were 20mm in diameter to allow a clearance for the discs, (Figure 3.16), and the shoulders were kept on the spreader bar to assist the application of the film (Figure 3.17). A film of the required thickness was cast, and the discs could be cut from the surrounding film using a specially prepared cylindrical blade.

In both cases the discs remained on the base plate while the films were dried in moving air for approximately 75 hours at 25°C. Prosser [29] found that chlorinated rubber based films retain less solvent when allowed to dry in a draught than in stagnant air. The discs were carefully cut from the surrounding film, and placed in an oven at 40°C for approximately 65 hours. This heat treatment was

Figure 3.15

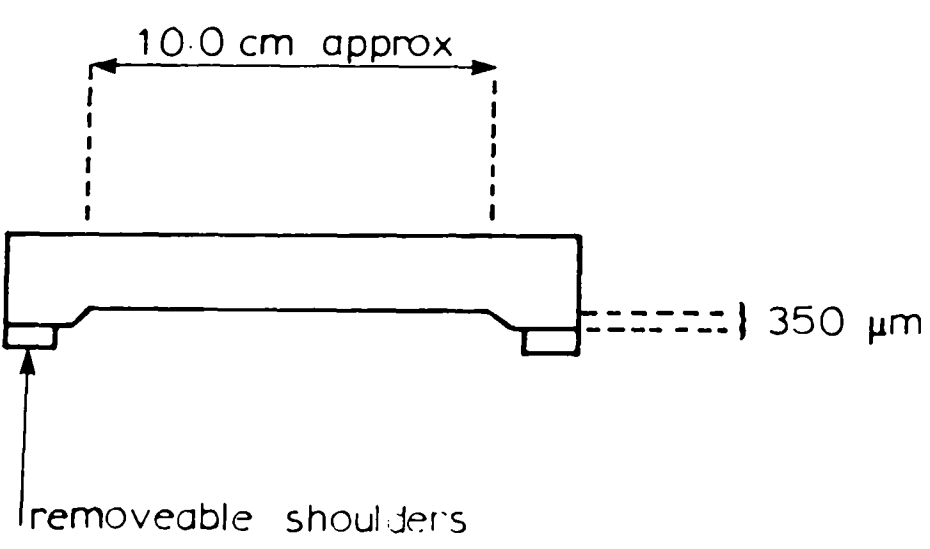
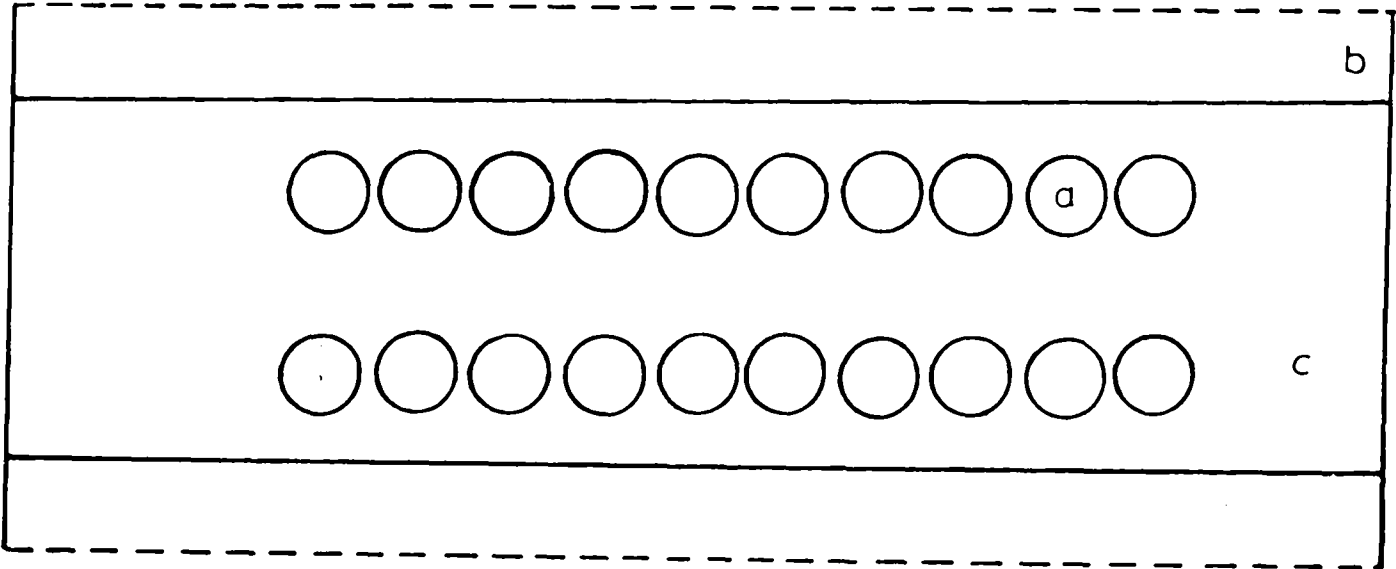
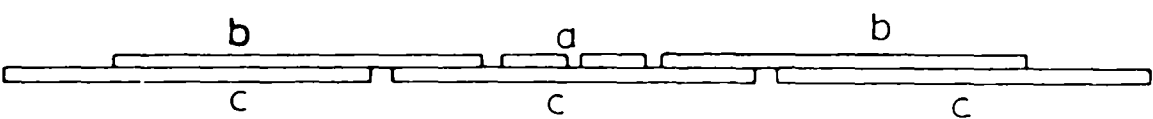
Mounting of discs ready for coating. (a) Double row of discs.
(b) Side-plates along which spreader bar runs. (c) Base plates.

Figure 3.16

Plan view of the mounting of discs for coating. (a) Discs.
(b) Side-plates in position when method (1) is used, but not required using method (2). (c) Base plate.

Figure 3.17

Diagram of spreader bar used for applying coatings.



intended to relax any stresses introduced into the films during curing and cutting. Sathyanarayana et al. [30] discuss this point in their excellent review paper, and Bullett [10] considers the stresses set up within a film on curing. Bullett and Prosser [11] consider the shrinkage stresses set up within a polymer, and the effects of internal stresses on the strength of a film.

The thickness of the dried films was measured using a magnetic flux meter, and also a micrometer screw gauge. The latter was found to be more reliable.

The first method of coating the discs was found to give the smaller variability of film thickness through the set of discs, and also across the diameter of each disc, and this was adopted as the standard method. The standard error in film thickness for each set was between 1.6% and 5.5%. However, it was also found that the predicted film thickness was rarely achieved, and films were often much thicker than expected, particularly the less viscous films where a smaller proportion of the lacquer thickness was carried away by the spreader bar.

Instead of the original aluminium "dollies", mild steel cylinders were used this time, as they are more rigid than the aluminium, and because of their design they can be more accurately aligned to prevent off-axis stress on the specimen. The dimensions of these "dollies" are given in Figure 3.18, which also shows how each disc was bonded between two "dollies" using a cold setting, epoxy adhesive, "Araldite". Before the discs were bonded in this way all the surfaces were thoroughly cleaned using methanol, which is not a solvent for the lacquer. The surface of the "dolly" next to the film surface was abraded thoroughly, using emery paper, and after initial tests it was found to be necessary for the surface of the "dolly" at the back of the disc to have a series of V-shaped, concentric, circular grooves, 0.127mm deep machined into the surface, to afford a more

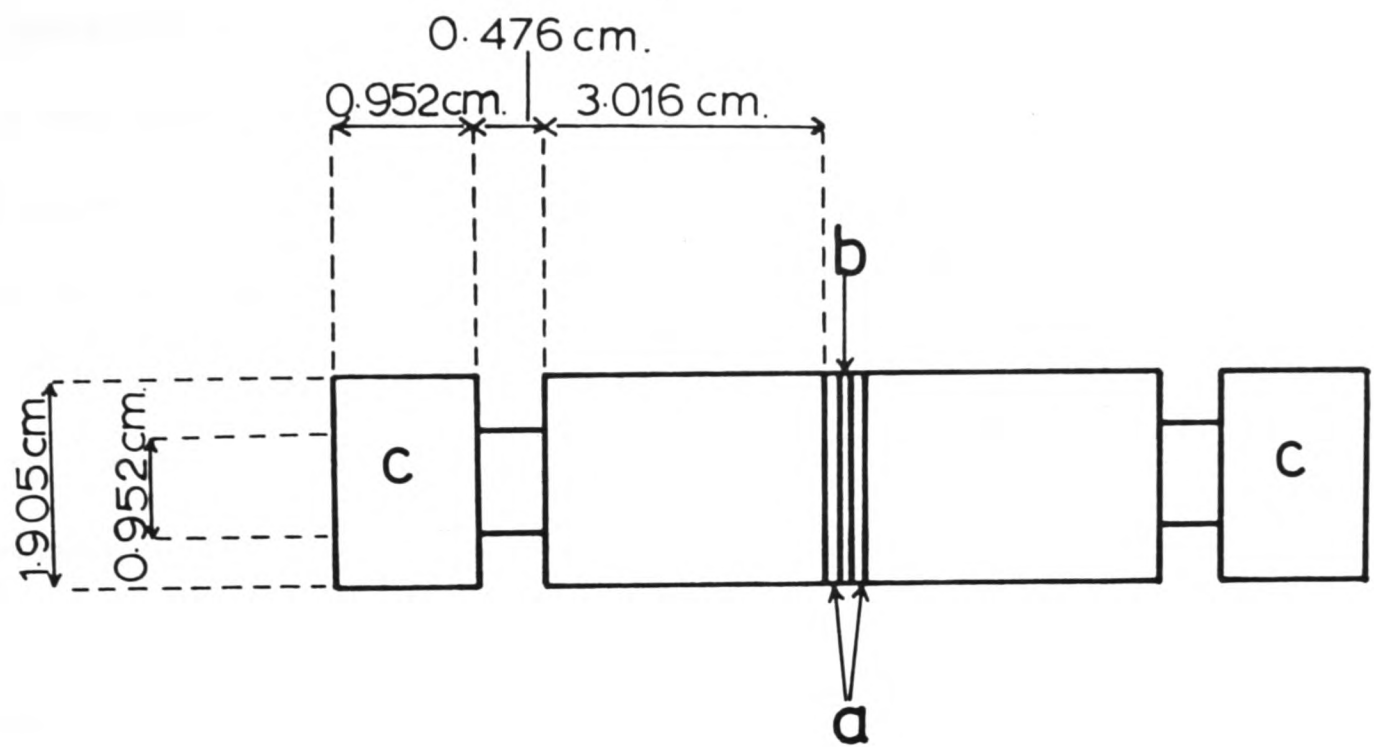


Figure 3.18

Preparation of specimen for test. (a) "Araldite". (b) Steel disc with lacquer on one face. (c) Mild steel cylinders or "dollies".

suitable surface for the "Araldite" to key into. Both "dollies" were placed in methanol in an ultrasonic bath for five minutes, before being swabbed with clean methanol and allowed to dry.

Fifteen discs were chosen from each set, discarding any which showed imperfections in the film, which could cause premature failure. Each disc was bonded between two "dollies", as shown in Figure 3.18, and laid on specially designed alignment jigs to ensure the correct alignment of the specimens, and to standardise the thickness of the "Araldite" in each specimen (Figure 3.19 and 3.20) [13]. The end-stops were screwed up to exert a force of approximately 5kg along the axis of each specimen. French chalk was spread lightly over the rods to decrease the friction, and to prevent any excess adhesive which may be squeezed from the joints from sticking to the jig. The specimens were held in this way until the adhesive had completely cured. Bullett and Prosser [12] mention the importance of the correct alignment of specimens to ensure even stress on testing.

Great care must be taken with the dimensions of the "dollies" as their diameter must not be larger than that of the disc. If this happens a situation similar to that illustrated in Figure 3.21a develops on alignment, and there will be a point of increased stress near the right-hand edge of the specimen when under test. However, the "dollies" may be slightly smaller than the discs, as Figure 3.21b shows, as there is no point of increased stress here, but it is preferable for the dimensions to be the same.

Two sets of clamps were specially designed for an "Instron" to hold the specimens firmly, and prevent any movement of the test-pieces away from the stress axis. These are shown in Figure 3.22. The specimens were tested at constant strain rate, and the stress required to cause failure in each specimen was recorded.

This method of testing was found to be quite simple to carry out, and considers a suitable number of specimens from each sample.

It can easily be implemented in an industrial laboratory, and is now being used by ICI Mond Division to test some of their own paint formulations.

Figure 3.19

Diagram of alignment jig for preparation of nine specimens.
A - elevation, B - plan view. (a) Ground silver steel rods. (b) Screw.
(c) Compression spring. (d) Fixed supports. (e) Support bar.

Figure 3.20

A. Diagram of alignment jig for preparation of six specimens.
(a) Ground silver steel rods. (b) Screw. (c) Compression spring.
(d) Fixed supports. (e) Support bar.

B. Photograph (above) jig in use, and (below) not in use.

Figure 3.21

- (a) Situation occurring when "dollies" are too large.
- (b) Situation occurring when "dollies" are too small.

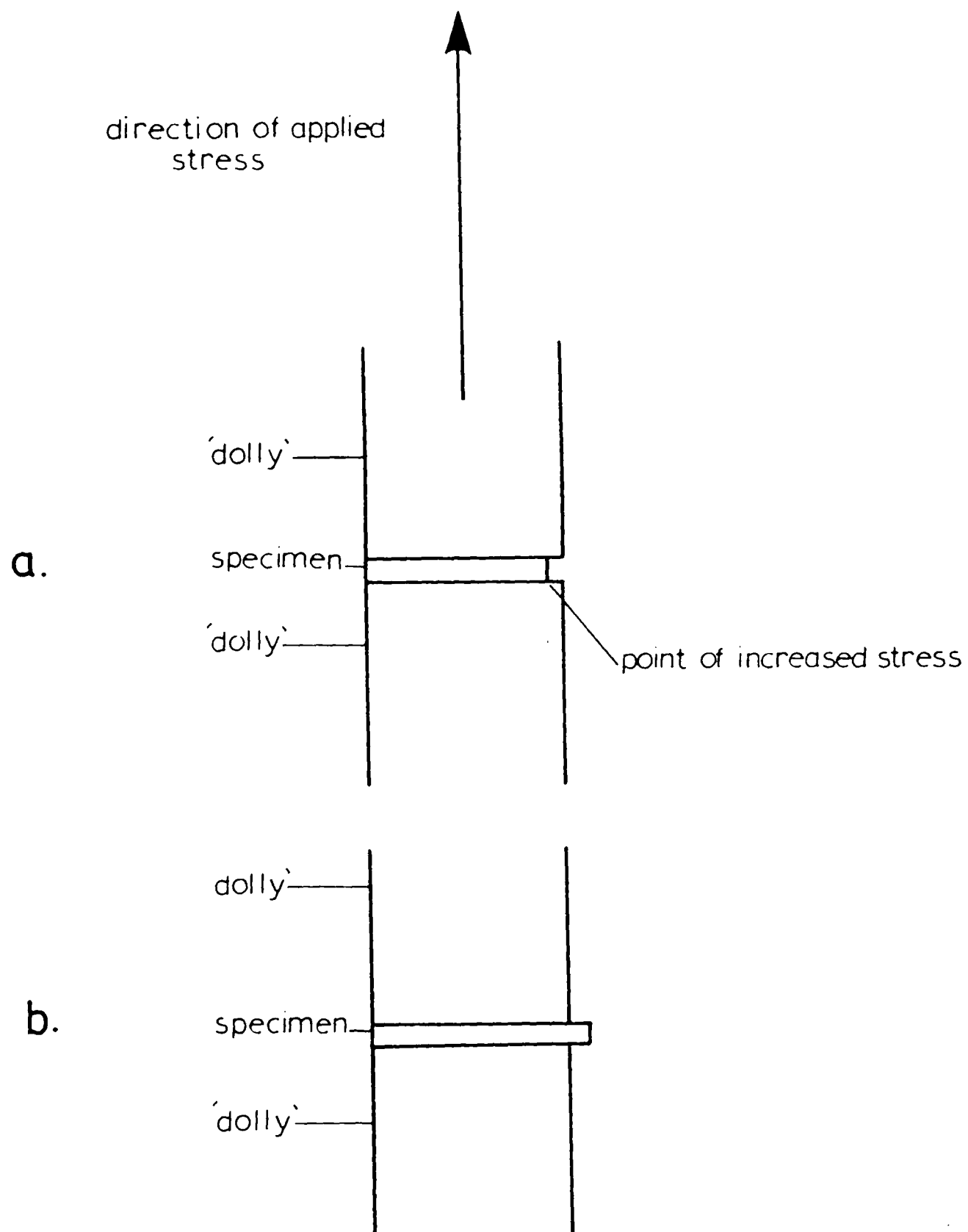
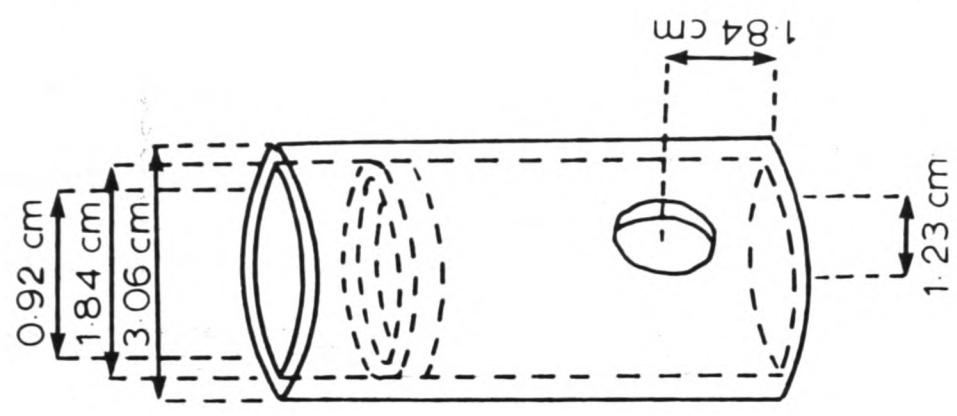
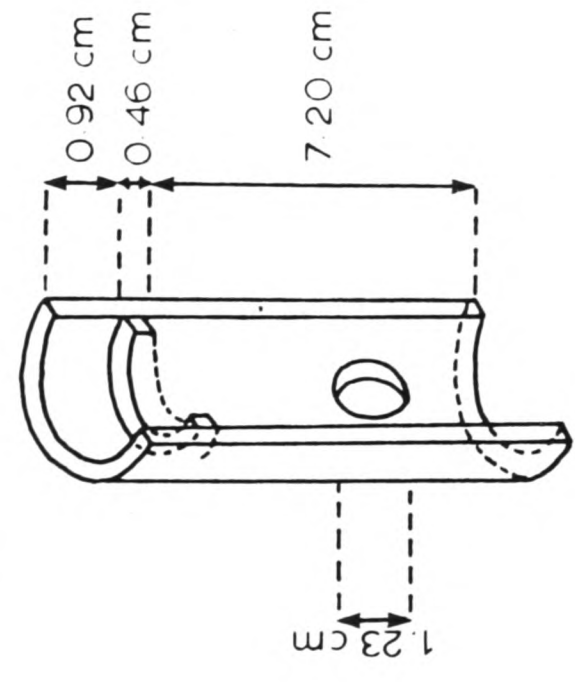


Figure 3.22

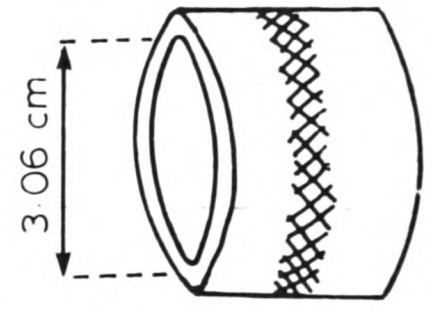
- Clamps designed to hold specimen firmly in tensile testing machine.
- (a) Half of clamp showing inner collar which fits into groove on "dolly".
 - (b) Clamps in the form of a hollow cylinder surrounding the "dolly".
 - (c) Collar holding the assembly firmly together.



b.



a.



c.

3.4 RESULTS

Over a period of eighteen months, twelve different sets of specimens were prepared and tested. The main problem encountered was that of choosing the correct variety of "Araldite" to withstand the stresses involved. Two systems were tried, Resin AV100 with hardener HV100, and Resin MY753 with hardener HY951. The former was found to make good adhesive bonds with the metal, but its cohesive strength occasionally proved inadequate; and the latter showed the opposite trend. Thus, several specimens had to be discarded as failure occurred in the "Araldite" layer before the lacquer itself failed. However, despite these problems "Araldite" is recognised as a good adhesive to use in tensile test specimens as it shows very little volume change on curing, and has a high modulus of elasticity. The AV100/HV100 system has a modulus of 2.7 GN m^{-2} [15] and the MY753/HY951 system has a modulus of 2.3 GN m^{-2} ; it is also reported to exhibit a tensile strength of $55\text{--}60 \text{ MN m}^{-2}$ and an elongation at break of only 2.5–3.5% [16].

Table 3.1 gives the results of the tests. Each set is numbered according to the year in which it was tested, and seven months elapsed between each batch of tests. The lacquer prepared for the first three sets was stored in sealed glass jars, in a dark cupboard and used to prepare the next three sets of specimens; it was then stored for a further seven months, in the same way, and used to prepare set 79.6. This was in order to study the effects of storage time on the film properties.

It was suspected that the lacquer degraded on storage, releasing hydrogen chloride, which interacted with the substrate when a film was cast. To investigate this hypothesis a new sample of lacquer was prepared, using R20 grade "Alloprene", and hydrogen chloride gas was passed through it, to produce a low concentration of gas in the lacquer. Films were then cast and tested in the normal way - these are numbered 79.5.

SET NUMBER	LACQUER SPECIFICATIONS	FILM THICKNESS μm	DRYING TIME HOURS (APPROX.)	CROSS-HEAD SPEED mm min^{-1}	APPLIED STRESS AT FAILURE kgf cm^{-2} MN m^{-2}		MAXIMUM STRESS TO FAILURE MN m^{-2}
77.1	R20	125 ± 2	140	5	53.00 ± 6.73	5.20 ± 0.66	9.46
77.2	R20	200 ± 11	140	5	43.62 ± 2.63	4.28 ± 0.26	6.03
77.3	R20	215 ± 10	2 months	5	97.26 ± 8.71	9.54 ± 0.85	14.61
78.1	STORED R20 '77	132 ± 5	140	0.5	147.00 ± 9.63	14.42 ± 0.94	19.66
78.2*	STORED R20 '77	87 ± 4	140	0.5	$155.31 \pm 16.11^*$	$15.24 \pm 1.58^*$	18.05*
78.3	STORED R20 '77	71 ± 3	140	0.5	151.48 ± 17.36	14.86 ± 1.46	19.98
79.1	R5	231 ± 4	140	0.5	38.23 ± 7.15	3.75 ± 0.70	9.57
79.2	R20	163 ± 4	140	0.5	83.24 ± 6.79	8.17 ± 0.67	10.94
79.3	R40	162 ± 4	140	0.5	87.89 ± 6.43	8.62 ± 0.63	11.99
79.4*	R90	127 ± 2	140	0.5	$84.32 \pm 7.15^*$	$8.27 \pm 0.70^*$	9.53*
79.5*	HYDROCHLORINATED R20	172 ± 7	140	0.5	$72.17 \pm 12.15^*$	$7.08 \pm 1.19^*$	10.76*
79.6*	STORED R20 '77	145 ± 4	140	0.5	$135.05 \pm 21.08^*$	$13.25 \pm 2.07^*$	18.16*

* The data relating to these sets can only be used to deduce trends in the results, as more than half of the specimens in each set had to be discarded due to failure in the "Araldite".

TABLE 3.1

It was considered necessary to investigate the effect of varying the molecular weight of the "Alloprene" on the force required to cause failure of the film. Thus, sets 79.1 to 79.4 were prepared using four different grades; R5, R20, R40 and R90 respectively. Each lacquer was prepared and applied in the normal way.

It was assumed that the results conformed to a Gaussian distribution, although Kurzmann and Klemme [26] suggest that such results conform to a negatively skewed Kase distribution, and that the bond strength should be characterised by the mode instead of the mean. However, this is only possible if a very large sample is taken.

The first point which must be noted is the magnitude of the values for the applied stress at failure, compared with those measured in the preliminary tests, which gave a mean value of $0.588 \pm 0.073 \text{ MNm}^{-2}$. The stresses measured here are a factor of between six and twenty-six larger than the preliminary results. The implications of this will be considered later.

The results will be reviewed under five headings:

- 1) Film thickness
 - 2) Drying time
 - 3) Storage of lacquer
 - 4) Hydrochlorination
 - 5) Molecular weight
- 1) Film thickness

Comparing the results of set 77.1 with set 77.2, and 78.1 with 78.3, it is observed that the thinner films require a slightly greater stress to cause failure than the thicker films. This is a well recognised effect, discussed in detail by Gent [19] and Anderson, Bennett and Devries [2] where various suggestions for its cause are discussed, although the phenomenon is not well understood. The most frequently proposed cause [6] is the higher probability of a flaw of a given critical size occurring in a thick film than in a thin one. This

crack size is specified by the Griffith-Irwin crack criterion [3].

However, this is only one possible explanation, and an important factor may be the variation in the D/h ratio, as discussed earlier, and the associated change in stress contours.

2) Drying time

Comparing the results for sets 77.2 and 77.3 the effects of increasing the length of time between casting the film and testing it may be observed. It is clear that the stress to cause failure in set 77.3 is over twice that required by set 77.2

The specimens of set 77.3 were stored at room temperature in a closed wooden box for two months before testing. After this time a rust-like discolouration was observed on each disc, particularly towards the edges, which appeared to be at the lacquer/metal interface. This change will be discussed in greater detail later. However, the increase in strength may be caused by some change within the film itself, for example a reduction in the residual solvent content, or by a change in the composition of the lacquer/substrate interface.

3) Storage of Lacquer

A marked change in the properties of the lacquer can be observed by comparing the results for sets 77.1, 78.1 and 79.6. It should first be noted that a subsidiary test was carried out to investigate any effects of changing the cross-head speed from 5mm min^{-1} to 0.5mm min^{-1} . No variation in fracture stress, as described by Gent [19] and Gent and Kinloch [21] was observed, and it was thus considered to be a valid comparison.

Set 77.1 was coated using freshly prepared lacquer, while sets 78.1 and 79.6 were coated with the same lacquer seven and fourteen months later, respectively. The stress required to produce failure in set 78.1 is a factor of 2.8 larger than that required by set 77.1, and set 79.6 appears to follow the same trend, within the range of experimental error. There is clearly a much greater effect than

could be caused by the small variation in film thickness.

This change may be explained in two ways. Firstly it is suggested that during the storage time the atmospheric gases, which become dissolved in the lacquer during the vigorous rolling involved in preparation, diffuse out of the lacquer. Also that any small bubbles of gas trapped in the lacquer will slowly be released. Although the lacquer is allowed to stand overnight after mixing, to allow all visible bubbles to be released, it is possible that microscopic pockets of air may remain trapped. However, it must be noted that no evidence of such bubbles has been found from either optical or scanning electron microscopical studies of the tested films.

The second suggestion is that the lacquer degrades during storage, as mentioned above, and that the products thus released may interact with the substrate to produce a strong bond between the lacquer and the substrate. This may be a chemical bond or it may be a physical bond involving a different type of molecule from those known to be present in the original lacquer. The degradation may involve the partial dehydrochlorination of the polymer molecules, thus releasing free hydrogen chloride into the lacquer. This theory has been tested by passing hydrogen chloride gas through a newly prepared lacquer, and coating the discs of set 79.5 with the resulting lacquer.

4) Hydrochlorination

A comparison can be made between the results for sets 79.2 and 79.5, particularly the values of maximum stress to failure. Within the range of experimental error, the trend suggests that the presence of free hydrogen chloride within the film does not effect the failure stress of the film, although the specimens showed severe discolouration at the film/substrate interface after only a few days. The nature of this discolouration will be discussed later.

5) Molecular weight

Sets 79.1, 79.2, 79.3 and 79.4 were prepared using "Alloprene"

of four different molecular weights, which are detailed in Table 3.2. Müller [28] has mentioned the fact that the higher the mean molecular weight of the polymer the more strongly it will be bound to the substrate. It is also expected that the cohesive strength would increase due to the greater degree of chain entanglement. Thus, the failure stress would be expected to increase with increasing molecular weight.

Sets 79.2 and 79.3 are ideal for comparison, as the film thickness is almost the same. The failure stresses for these two sets can hardly be distinguished within the range of experimental error, and although set 79.4 can only suggest a trend in the results, and has a slightly lower film thickness, there is no clear variation of failure stress over this range of molecular weight. However, set 79.1 shows a much lower value of failure stress, and although the film thickness is a factor of almost 0.5 larger than 79.2 and 79.3, this is not sufficient to account for the difference. It appears that the failure stress may be sensitive to molecular weight variation below a certain critical value, or that there is some other factor which should be taken into account here.

It should be noted, however, that the proportion of the area of the specimen which appeared to have failed in an adhesive mode increased with increasing molecular weight, such that the specimens of set 79.4 exhibit no cohesive failure at all, but those of set 79.1 show mostly cohesive failure, and a very little apparent adhesive failure. This seems to contradict Müller's observation [28].

The shape of the force versus extension plot obtained from the "Instron" is shown in Figure 3.23. There is no yield point, and as the extension of the specimen increases at a constant rate the applied force begins to increase rapidly in the manner of rubber-like elasticity [5]. A simple description of the processes involved is as follows:

Region 'a': In this region the polymer chains are disentangled,

<u>"Alloprene" Grade</u>	<u>Number Average Molecular Weight</u>	<u>Viscosity Average Molecular Weight</u>
R5	15,000	28,000
R10	(29,000)	(54,000)
R20	57,000	88,000
R40	(80,000)	(118,000)
R90	(115,000)	(174,000)
R125	125,000	200,000

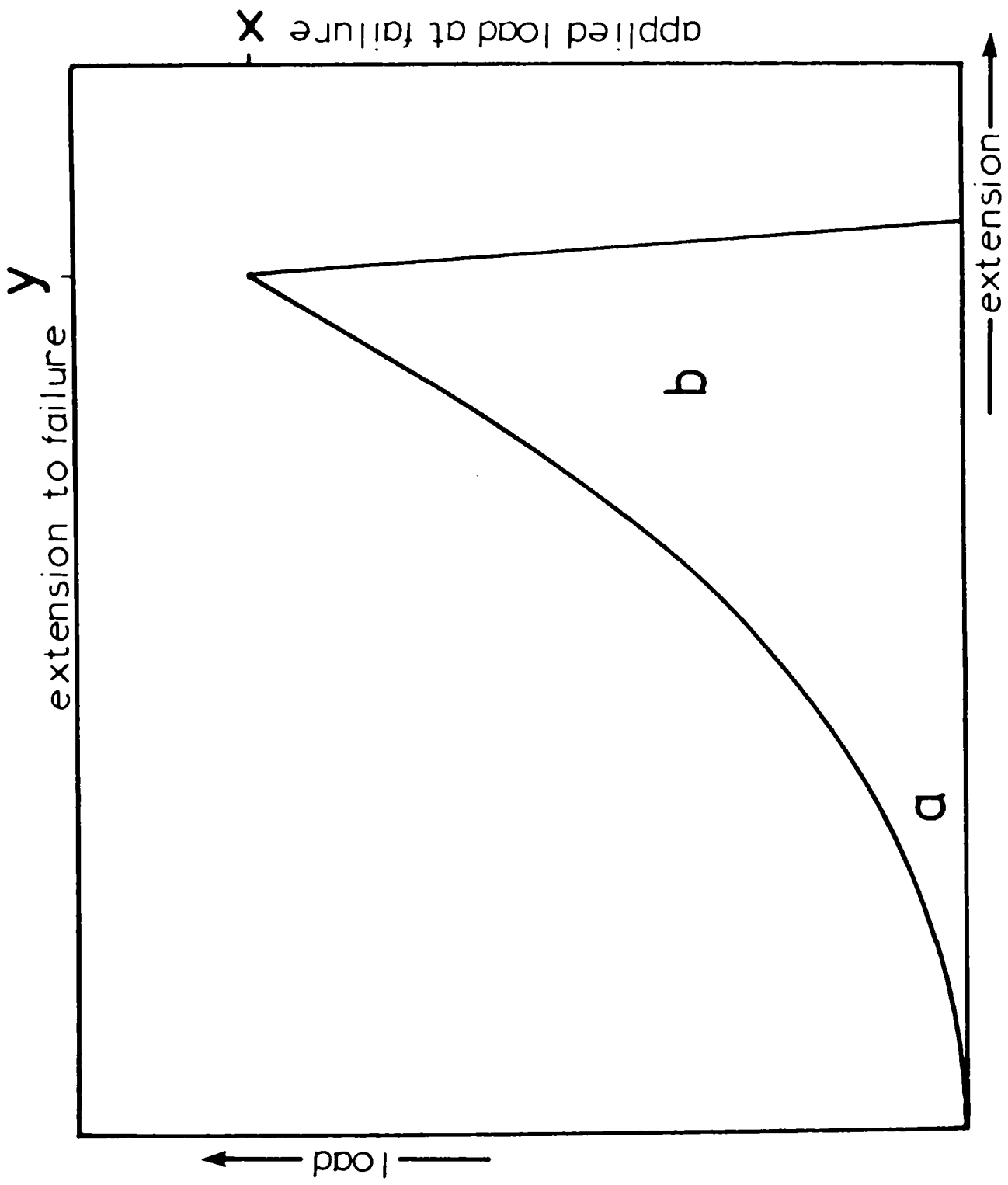
Data in brackets were obtained by interpolation

TABLE 3.2

Molecular Weight of Grades of "Alloprene" [23]

Figure 3.23

Load versus extension chart obtained from the Instron testing machine, showing rubber-like behaviour of the specimen.



and gradually straightened out in the direction of the applied force (Figure 3.24).

Region 'b': Here the chains lying parallel to the plane of the film begin to separate against the Van der Waals forces, which hold them together. The chains lying parallel to the direction of applied force are slowly extended, as their covalent bonds are slightly stretched (Figure 3.25).

The processes involved in region 'b' require much greater forces to produce a constant strain rate, and the abscissa rises steeply.

Figure 3.26 shows the force/extension chart obtained when a specimen was stressed to a point below failure, and then the stress was relaxed to detect any permanent changes in the dimensions of the film, and hence any plastic flow. This is superimposed on a similar chart obtained for a solid steel specimen, with the two "dollies" remaining as a continuous rod.

It is clear that the two specimens respond in a similar way, and that the residual extension appearing on the chart is due to the response of the testing machine, and is not a residual plastic deformation within the film.

Thus, it may be deduced that when the film is in the form of a coating on a mild steel substrate it exhibits rubber-like elasticity when subjected to a stress in a direction perpendicular to the plane of the substrate.

Failure initiates at the weakest point in the film, possibly a flaw, or a weak boundary layer at the film/substrate interface, at the critical stress for the propagation of that failure. This stress is recorded at the point 'x' on the plot, as the applied force at failure; and the extension of the specimen is measured to point 'y'.

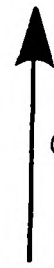
Difficulties were encountered when trying to estimate the extension of each specimen during the test. Ostensibly it was a simple task, as the "Instron" chart and cross-head were both driven

Figure 3.24

Schematic representation. (a) Unstressed polymer chains.
(b) Stressed chains disentangled and straightened in direction of applied stress.

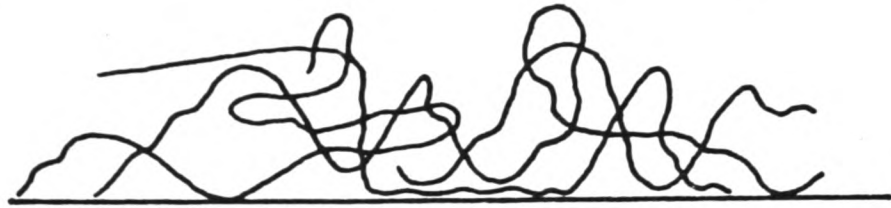
Figure 3.25

Chains perpendicular to direction of applied stress are separated.
Those parallel to direction of stress are extended.



direction of applied stress

a.



b.

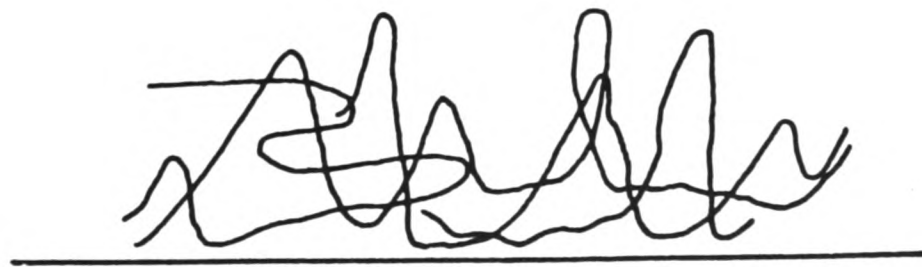
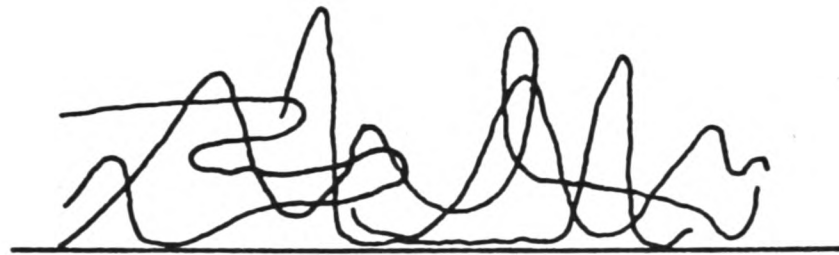
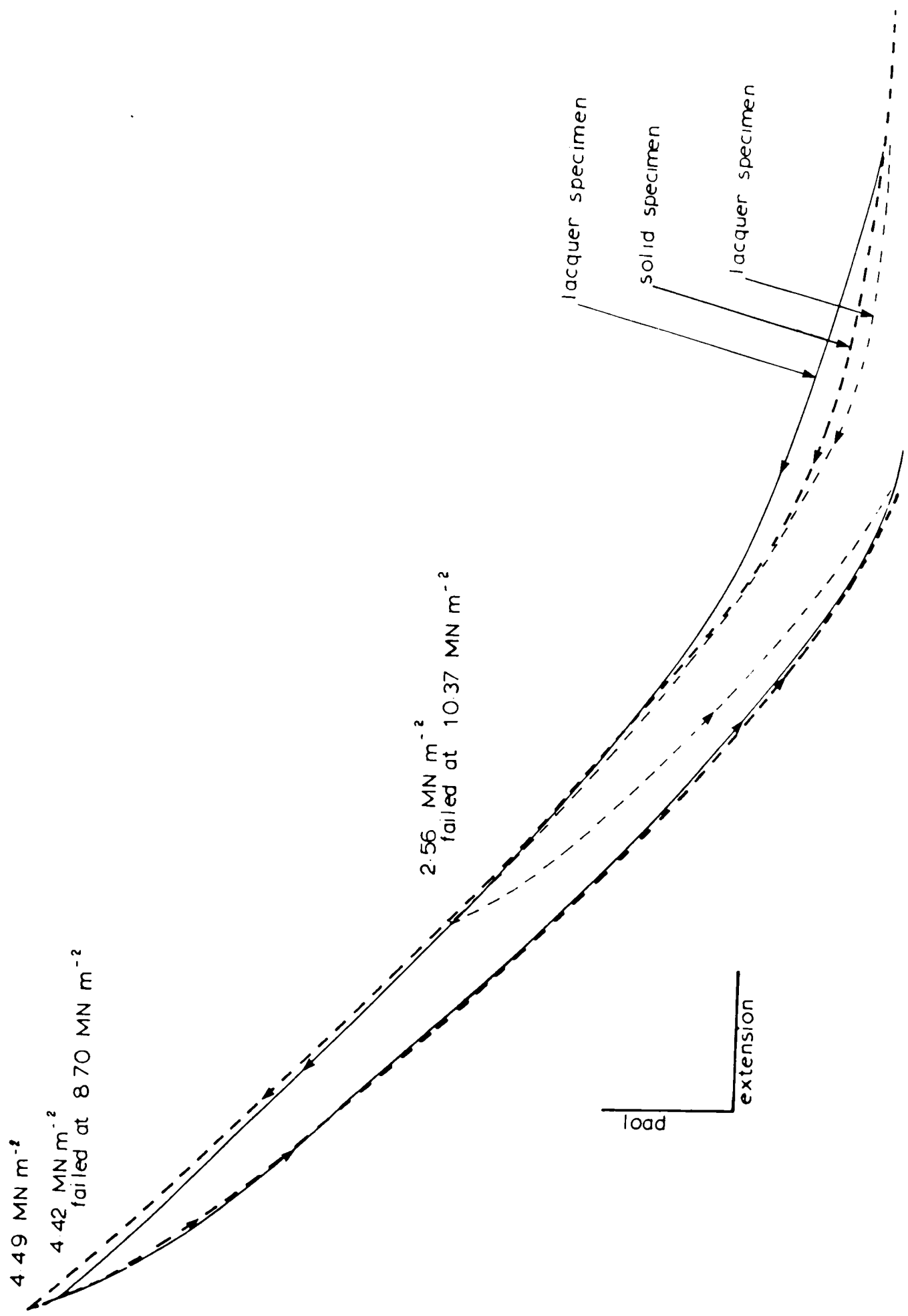


Figure 3.26

Load versus extension chart as obtained from the Instron testing machine.

Specimens are stressed to points below failure, and then stress is relaxed. Extension increases from right to left.



at constant speeds, and the distance on the chart between the first point of applied stress, and the point of failure could be used to calculate values for the duration of the test, and specimen extension. However, the extensions calculated in this way were up to 400% of the original film thickness, which was clearly wrong. It is not unusual to measure extensions up to 100% of thickness for these films, and it was deduced that the remaining 300% was due to strains within the instrument itself. Therefore, several specimens were photographed during the test to observe their deformation under stress, and to measure the extension of the film. The extension observed was $123 \pm 20 \mu\text{m}$, while that calculated was $485 \pm 23 \mu\text{m}$, a factor of four larger. Thus, the values given in Table 3.3 are an estimate of the extension, and are simply the values calculated from the "Instron" plot divided by four. The most accurate method of measuring extensions would be to use strain gauges, but as this aspect was not part of the major line of study it was decided not to pursue this further.

Tests were carried out on unsupported films to obtain some information about the film itself. The films were cast on sheets of plate glass coated with a parting agent, polyvinyl alcohol (PVA), which is soluble in water. The $375\mu\text{m}$ spreader bar was used and the film thickness was approximately $100\mu\text{m}$. The dried films were removed from the plates by soaking them in water, and were dried at room temperature for about four hours. Dumb-bell shaped specimens were cut from the film, with a gauge length of 5cm and width 0.5cm. These were tested using the same technique as for the supported films, with 100% extension per minute. The results for a typical film are shown below:

$$\text{Cross-sectional area} = 5 \times 10^{-7} \text{ m}^2$$

$$\text{Extension at yield} = 5\%$$

$$\text{Extension at break} = 156\%$$

$$\text{Yield stress} = 8.10 \text{ MN m}^{-2}$$

$$\text{Fracture stress} = 11.04 \text{ MN m}^{-2}$$

SET NUMBER	ESTIMATED EXTENSION μm	DURATION OF TEST S
77.1	94 ± 10	4.41 ± 0.41
77.2	76 ± 4	3.65 ± 0.18
77.3	119 ± 7	5.71 ± 0.32
78.1	121 ± 6	57.0 ± 4.2
78.2	125 ± 6	60.0 ± 3.0
78.3	116 ± 8	55.8 ± 4.2
79.1	80 ± 11	38.4 ± 5.4
79.2	103 ± 8	49.2 ± 3.6
79.3	106 ± 6	51.0 ± 3.0
79.4	103 ± 15	49.2 ± 7.2
79.5	100 ± 6	48.0 ± 3.0
79.6	131 ± 10	63.0 ± 4.8

TABLE 3.3

Extension of Specimen and Duration of Test

The stresses were compensated for change in cross-sectional area on extension.

Caldwell and Ferguson [14] report a tensile strength of 2.45 MN m^{-2} and extension at break of 190% using a two-coat system.

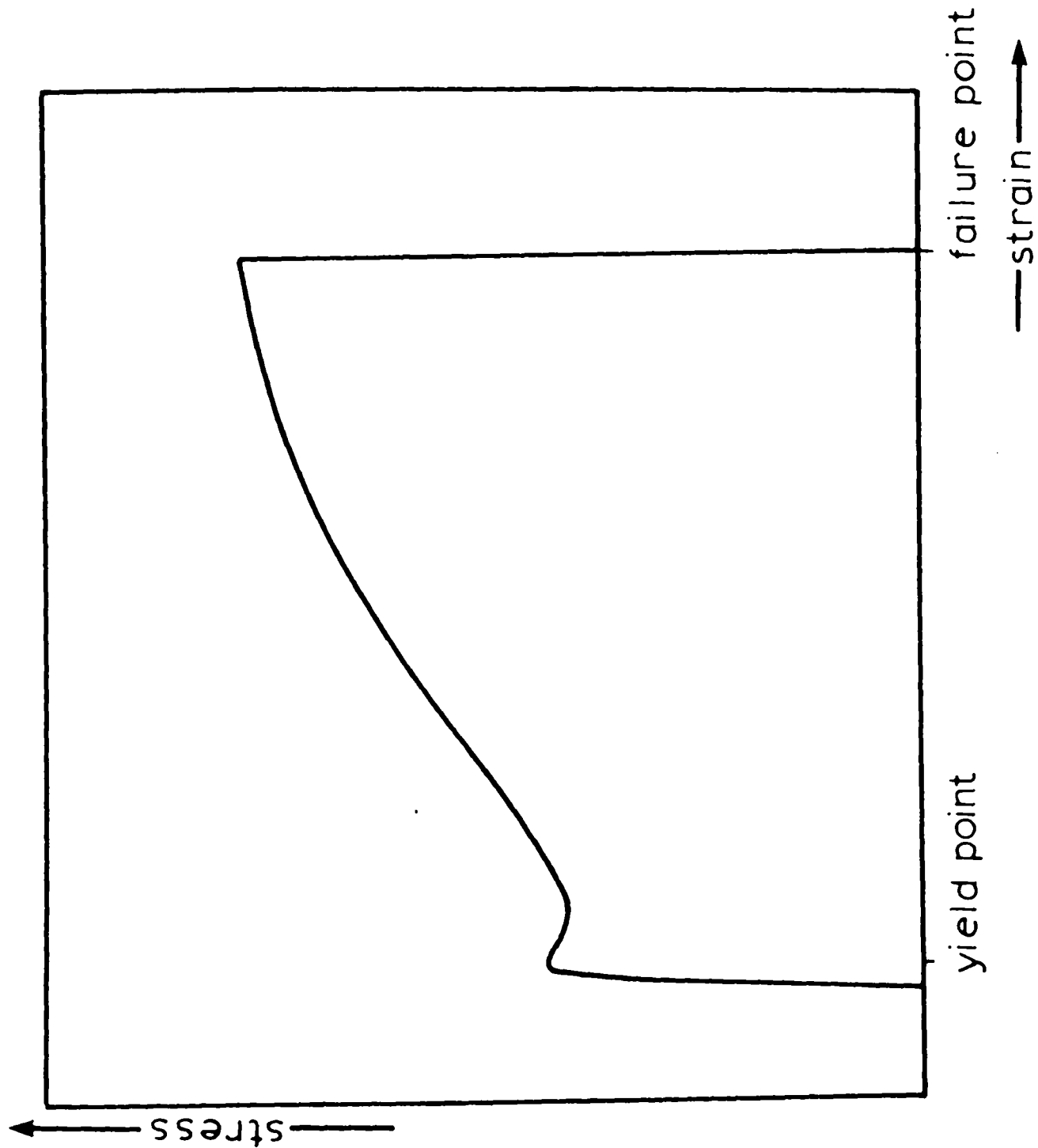
The extension versus load plot obtained from the "Instron" confirms that the ratio of plasticiser to binder in the lacquer used gives optimum plasticisation of the film (Figure 3.27). Other deductions which may be made from these results are that large extensions do occur in unsupported films, and they will withstand high stresses. However, these results cannot be directly related to the results obtained for supported films, as the presence of the substrate and test "dollies" have a large constraining effect on the film.

Optical examination of the main, supported specimens revealed that all specimens showed mixed modes of failure, with varying proportions of the area appearing to have failed adhesively, cohesively, or occasionally at the "Araldite"/film interface as Kraus and Manson found in their study of polystyrene and polyethylene on steel [11]. Some effort was made to correlate the main mode of failure with the failure stress of the specimen. However, only the specimens of sets 78.1, 78.2 and 78.3 showed any correlation, and it was found that the highest failure stresses were exhibited where the largest proportion of the area appeared to have failed adhesively, and vice versa.

A few of the specimens had contained very small bubbles on the surface of the lacquer, before bonding to the "dollies". These specimens were also examined after testing, and their individual failure stresses noted. No weakening of the system was observed, which is in agreement with Bikerman's suggestion [7], that bubbles are particularly dangerous when situated near the three-phase line, but relatively innocuous when within the body of the film, and away from the film/substrate interface.

Figure 3.27

Example of stress versus strain chart obtained from the Instron testing machine, for tensile testing of unsupported films.



3.5 DISCUSSION

The results must now be viewed as a whole, and in the light of the results and observations made from the preliminary tests described in sections 3.1 and 3.2.

Primarily the specimens were redesigned to eliminate the bending which occurred in the steel plates used earlier. This feature was evidenced by the characteristic markings appearing on the fractured surfaces, so the surfaces of the new type of specimens had to be examined for any such features.

No consistent trend was observed in the types of markings occurring on the fractured surfaces, and there was no indication that there was any deviation from stress in a direction perpendicular to the plane of the specimen. However, in regions where cohesive breakdown had occurred, markings similar to those in Figures 3.28 and 3.29 were observed. These have not previously been reported in the literature, but it is suggested that they are produced by a similar mechanism to "Wallner" lines, and a useful account of this is given by Andrews [4]. This will be considered under three headings:

- (i) Propagation of fracture
 - (ii) Origin of stress waves
 - (iii) Interaction of fracture front and stress waves
- (i) It is suggested that the crack propagates more rapidly than the rate at which the "Instron" jaws are separating; therefore it will move in short jumps. The crack will move until there is insufficient energy available for its continued propagation, and it will then remain stationary until the stress has built up sufficiently to propagate the failure further.
 - (ii) A stress wave is generated at the point of fracture by a sudden release of energy as the crack begins to propagate. As the stress on a stationary crack builds up it has to reach some excess over the stress necessary for continuous propagation -

Figure 3.28

Example of markings observed in areas of cohesive failure.

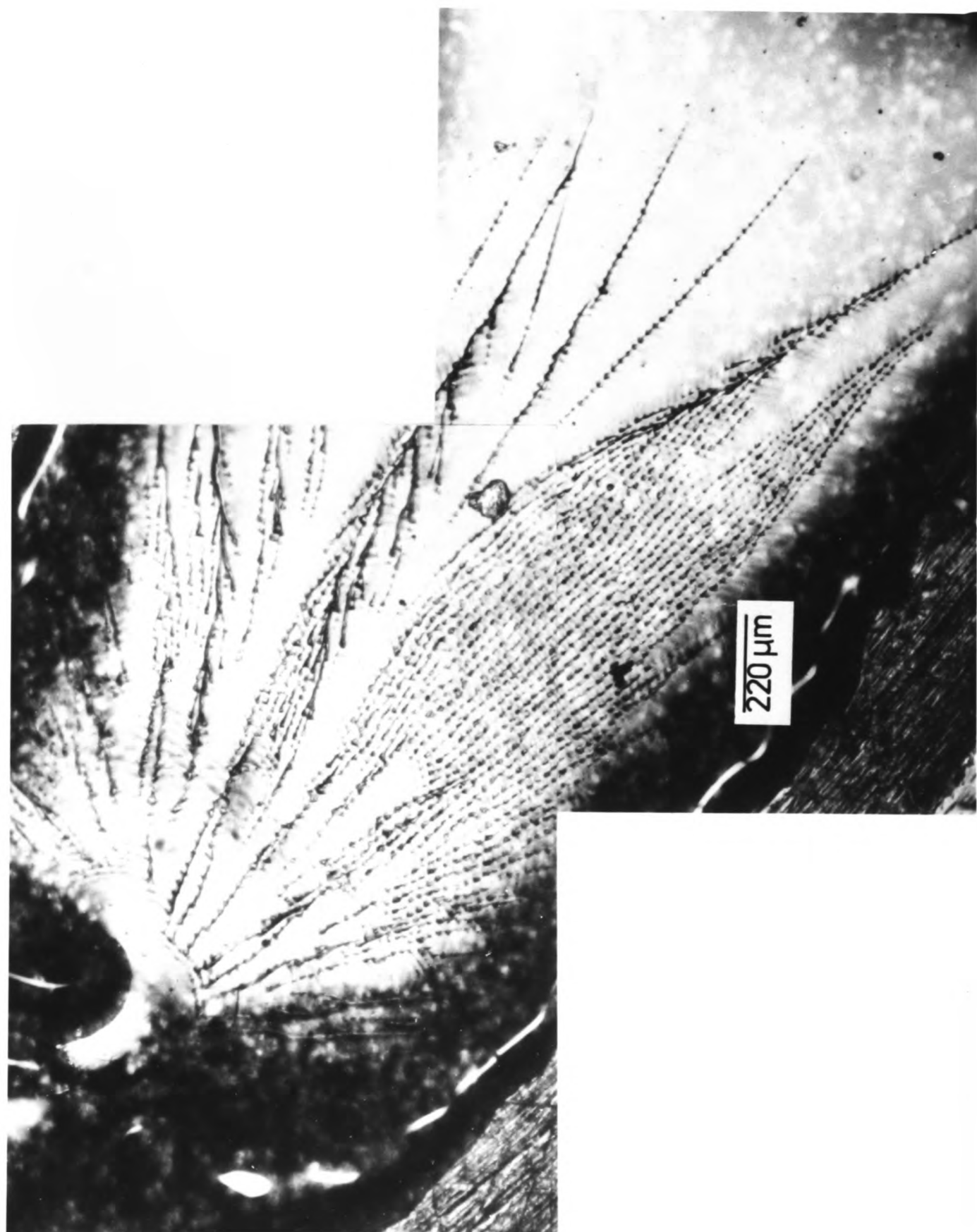
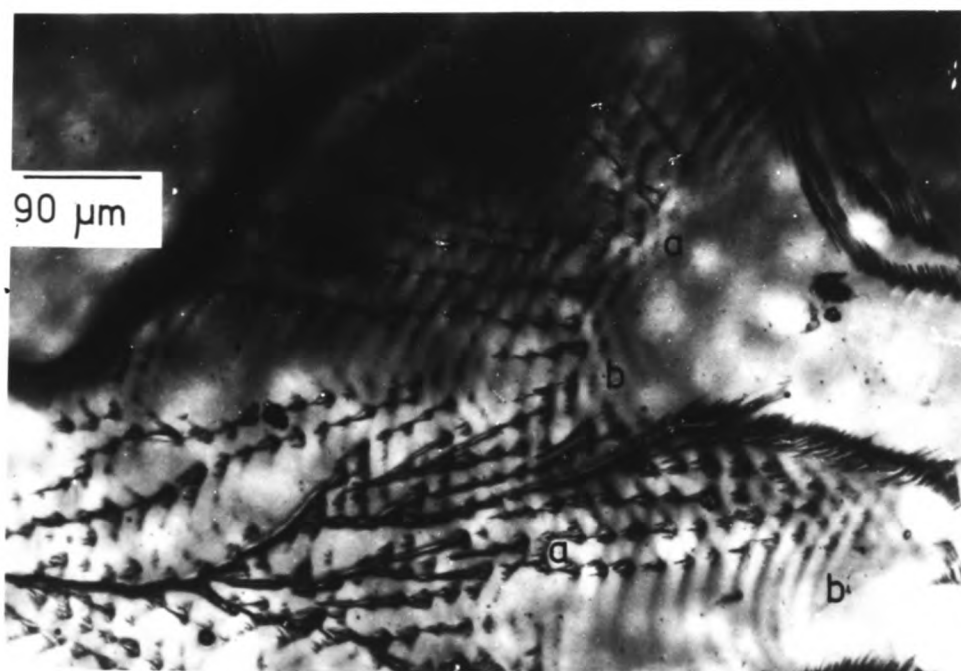
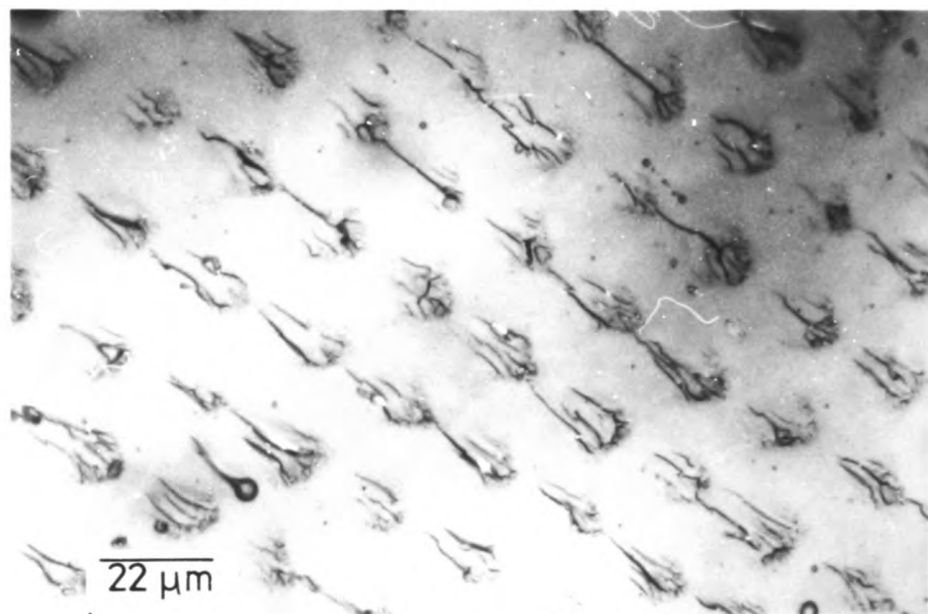
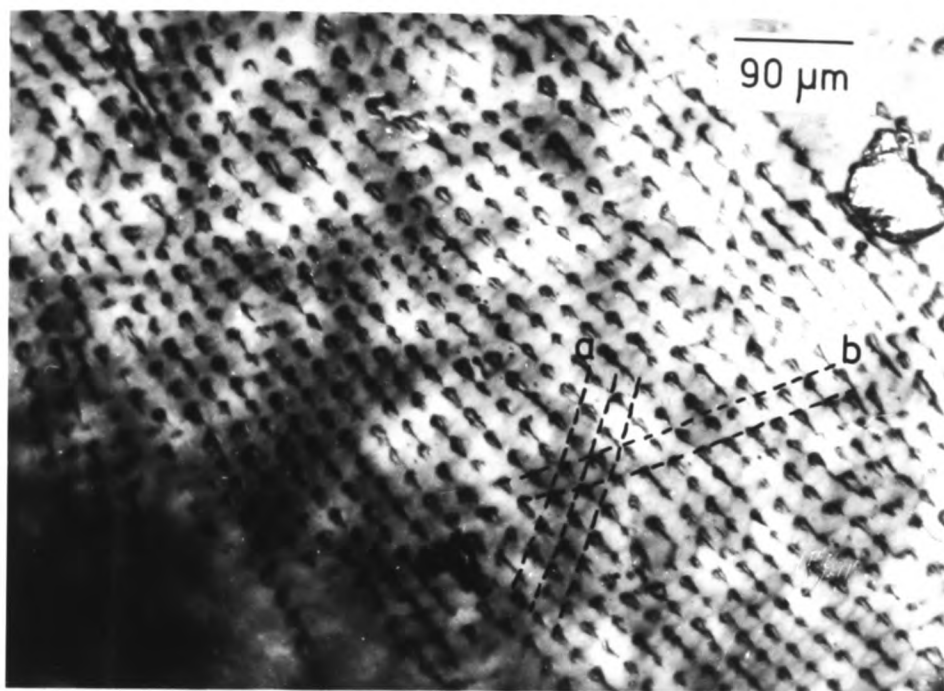


Figure 3.29

Examples of markings observed in areas of cohesive failure showing periodicity in two directions, illustrated by lines (a) and (b) superimposed on the photograph.

Figure 3.30

Points of intersection of stress waves can clearly be observed (a). Conventional Wallner markings appear in areas (b).



there is thus an energy barrier. Once this level is reached and the crack begins to move there is an energy excess, and the stress wave is produced by the sudden release of elastic energy.

- (iii) This stress wave travels faster than the fracture, and may be reflected from the surfaces of the specimen, causing it eventually to meet the fracture front. According to the direction of approach of the stress waves, they will momentarily both magnify and distort the stress distribution at the fracture front, with a possible deviation of the front from its original direction. This causes grooves or pits in the fracture surface, (Figures 3.28-3.30). Sometimes this deviation is periodic because a train of regularly spaced stress pulses interacts with the travelling fracture. These pulses could be caused by the propagation of the fracture, as described above.

The markings observed can be shown to occur at the intersections of two circular wave patterns, probably the first reflected stress wave from the top surface and the first from the bottom surface, as described in Figures 3.31 and 3.32.

Thus, it is clear that the problem of off-axis stress has been eliminated, and it can be seen from the numerical results for the stress to cause failure that much higher values are recorded when the specimen is subjected to stress perpendicular to the plane of the substrate.

The implications of the effects discussed earlier will be considered in greater detail when the mode and locus of failure are discussed in subsequent chapters. However, some preliminary observations may be made.

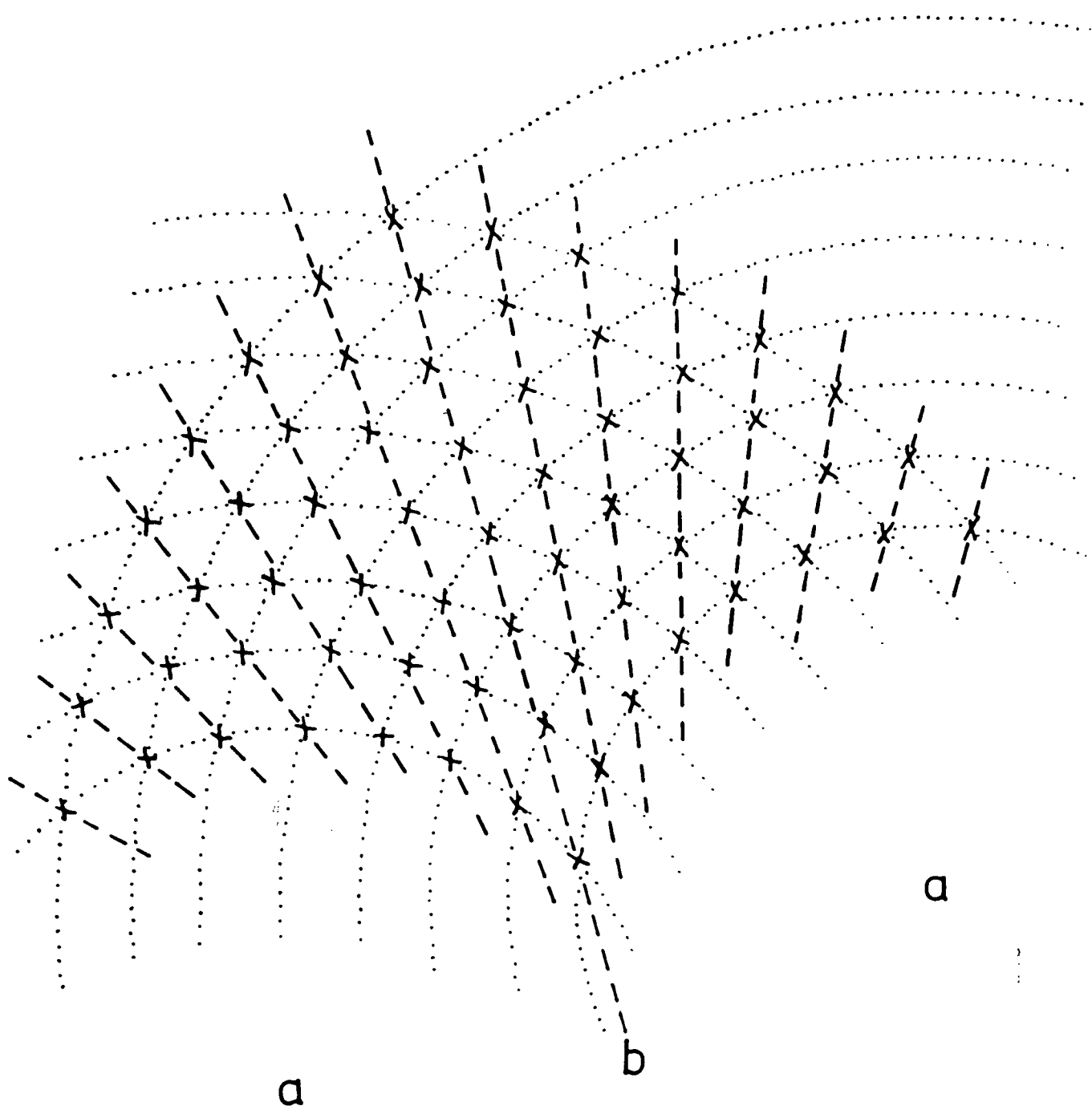
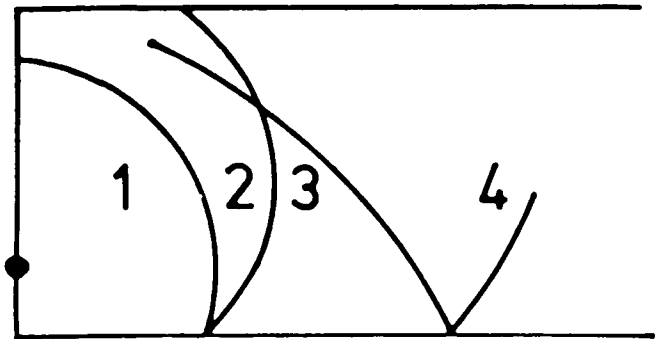
Many specimens exhibit cohesive and apparent adhesive failure occurring together, at a discrete value of failure stress. This suggests that the magnitudes of the adhesive forces at the interface,

Figure 3.31

Reflection of stress waves. (1) System concentric with fracture front. (2) First reflection from upper surface of specimen. (3) First reflection from lower surface. (4) Second reflection from upper surface [3].

Figure 3.32

Schematic representation of the formation of the observed markings. (a) Foci of periodic stress waves (.....). (b) Focus of surface markings (--x--x--).



and the cohesive forces within the film must be similar, or that the apparent adhesive failure is, in fact, related in some way to the cohesive mode of failure, and is not a separation of the film from the substrate at the interface.

The properties of this interface may be critical for the performance of the film, and in studying the locus of failure the interactions occurring at the interface will be considered.

Of the twelve sets of specimens tested seven showed a standard error in the measured values of stress to cause failure of less than 10%; two fell between 10% and 13%; and three between 13% and 19%. These compare very favourable with the results of May, Smith and Snow [27], who claim errors of 10%, and Zorll [33], who claims 10-15%, for similar tests. Errors in the region of 10-15% represent very good reproducibility compared with the results obtained by other methods of testing.

Thus, it appears that the requirements outlined in section 3.2 have been satisfied, and it just remains to solve the problem of the "Araldite" and the test will be simple to carry out, and relatively simple to interpret.

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C H A P T E R F O U R

MODE OF FAILURE

CHAPTER FOUR

MODE OF FAILURE

4.1 DISCUSSION OF THEORIES

Various theories explaining the mechanisms of adhesion have been discussed in Chapter 1, but a mechanism is now required to describe how a film fails under test. It was quite clear in which areas of the specimen the film had failed cohesively, leaving a visible layer of lacquer on the substrate and displaying the detailed surface markings described above. However, there were large regions described as areas of "apparent" adhesive failure. No lacquer could be detected on the substrate using an optical microscope, but more detailed study was required before any firm conclusions could be drawn.

The system is initially considered as a homogeneous lacquer film on a clean metallic substrate. Various authors have considered the statistical probability of a crack propagating only at the film/substrate interface, or only within the lacquer. McGill [10] is one of the latter group; he states categorically that adhesive failure never occurs, and that adhesion is solely due to the Van der Waals forces acting between the atoms in the two adhering surfaces, the strength of these interactions exceeding the strength of either of the materials involved. This idea will be considered in detail in Chapter 6.

McGill's argument develops in the following way: consider a rupture which initiates between a surface atom of the adherend (substrate) and the coating. There are three alternative directions for the extension of the crack - it may extend between the next pair of adherend and coating atoms, between two atoms of the adherend, or between two atoms of the coating. If each atom occupies a roughly cubical space there are three paths between adherend and adherend, and

three between coating and coating for each path between adherend and coating. If the probability of all paths occurring is equal, only once in seven instances will the crack progress between two different materials, while in six instances it will move away from the interface. Thus, the probability of a crack growing along the interface for a distance $(n+1)$ atoms is $(1/7)^n$; if $(n+1) = 7$, then the probability is below 1 in 10^5 . Also, if the strength of the interactions across the interface is greater than that of the interactions within either the coating or the adherend, then the probability of crack propagation between two unlike atoms is less than one in seven.

Bikerman [5] is usually credited with the original discussion of this theory, and others have developed it to consider weak boundary layers caused by inclusions or inhomogeneities at the interface. Sharpe [14], for example, considers contaminants on the metal surface, oxides or grease; variations in the molecular weight of the polymer; and the complexity of other compounds present, such as plasticisers. He also mentions that under certain circumstances orientation of the polymer may occur at the metal surface forming a boundary layer.

Another suggestion is that the strength of the forces attracting the first molecular "monolayer" of the polymer to the substrate causes an increase in the separation between this layer, and the next layer of the polymer film, thus decreasing the strength of the forces binding these two layers together. When an external stress is applied to the system failure will occur at the weakest point, which will be between the first monolayer, and the bulk of the film. Thus, a boundary layer of polymer remains on the substrate. However, there seems to be no reasonable explanation for this increase in layer separation, as the film acts as a single unit; there is no force preventing the successive layers of film from moving towards the substrate with the first "monolayer", and retaining the normal film structure.

Crocker [7] reviews the various theories, but observes that

"weak boundary layers (WBL) are undoubtedly common, but so is true adhesional failure"; while Huntsberger [9] regards the biaxial character of the residual stresses within most polymeric films attached to rigid substrates as such that it is almost certain that a crack will propagate to an interface whatever its initial position. Then both the shear and normal components of the internal stress will bias the propagation along the interface.

However, Good [8] gives a detailed critique of the WBL theory. He suggests that if the bond strength is represented by u , without specifying the nature of the media A and B, that the probability of the fracture continuing at the interface is

$$P(AB) = \exp\left(-\frac{u_{AB}}{kT}\right) / \left\{ \exp\left(-\frac{u_{AB}}{kT}\right) + \exp\left(-\frac{u_{AA}}{kT}\right) + \exp\left(-\frac{u_{BB}}{kT}\right) \right\}$$

which tends to unity if there are only dispersive forces acting across the interface, and ionic, covalent and metallic interactions within both phases. It is thus predicted that the crack will be almost unable to depart from the interface. Bikerman suggested that $u_{AA} > u_{AB} > u_{BB}$, when A and B are suitably defined, but Good states that if one phase is metallic and the other a covalent polymer then $u_{AA} > u_{BB} \gg u_{AB}$. A and B are still undefined, but presumably the implication of the statement is that the binding forces between the two media are much weaker than those within either one. This contradicts McGill's argument that the strength of the interactions across the interface exceeds the strength of the interactions in either of the individual materials.

Bair et al. [2] and Raevskii [13] also discuss the problem of the WBL, but the question still remains; in the system under test, does failure occur cleanly between the coating and the substrate, within the first layer of the homogeneous coating, or within a weak boundary layer at the interface? Some effort has been made to answer this question in the following sections.

4.2 SEM ANALYSIS

Bascom et al. [4], Birkett and Rooney [6], and Andrews and Kinloch [1] have discussed the possibilities of using various microscopic and spectroscopic techniques for studying the site of failure in coatings. The first, and most simple technique used in the present work was scanning electron microscopy (SEM).

The discs were removed from the "dollies" by a sharp blow, using a hammer and chisel; and the tested areas of the preliminary test specimens were punched from the reverse side of the plate using a 2cm punch in a fly-press. Each one was swabbed lightly with methanol, which does not affect the lacquer, and mounted on a stub for viewing in the microscope.

Specimens with a thick coating of lacquer remaining on the surface charged severely under the beam, but the areas which appeared to have failed in the adhesive mode did not charge at all. However, the presence of a fairly large steel specimen in the chamber affected the magnetic field of the objective lens, and images could not be obtained at a magnification greater than x5K, as the resolution deteriorated. Certain specimens were coated with a film of gold, to eliminate the charging and so increase the resolution. However, this could not be done to all specimens, as they were required for further, qualitative analytical tests.

Figure 4.1 shows the surface of an area of apparent adhesive failure, at four different values of magnification. The grooves produced by the surface abrasion are clearly visible, but no clear fragments of lacquer can be observed. These would appear white on a grey background, due to their different conducting properties from those of the substrate. This point is illustrated in Figure 4.2, which shows a small area on one specimen where a few fragments of lacquer remained on the surface; these were also visible under an optical microscope and the type of failure occurring at this point was characterised as cohesive.

Figure 4.1

Scanning electron micrographs of the surface of a specimen in an area of apparent adhesive failure.

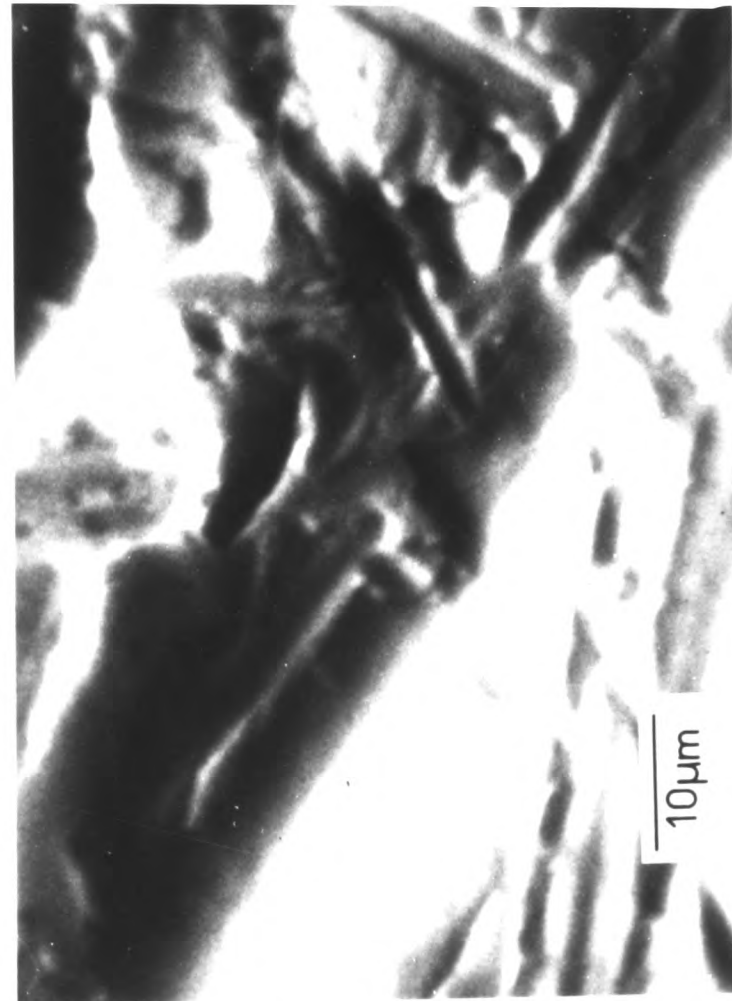
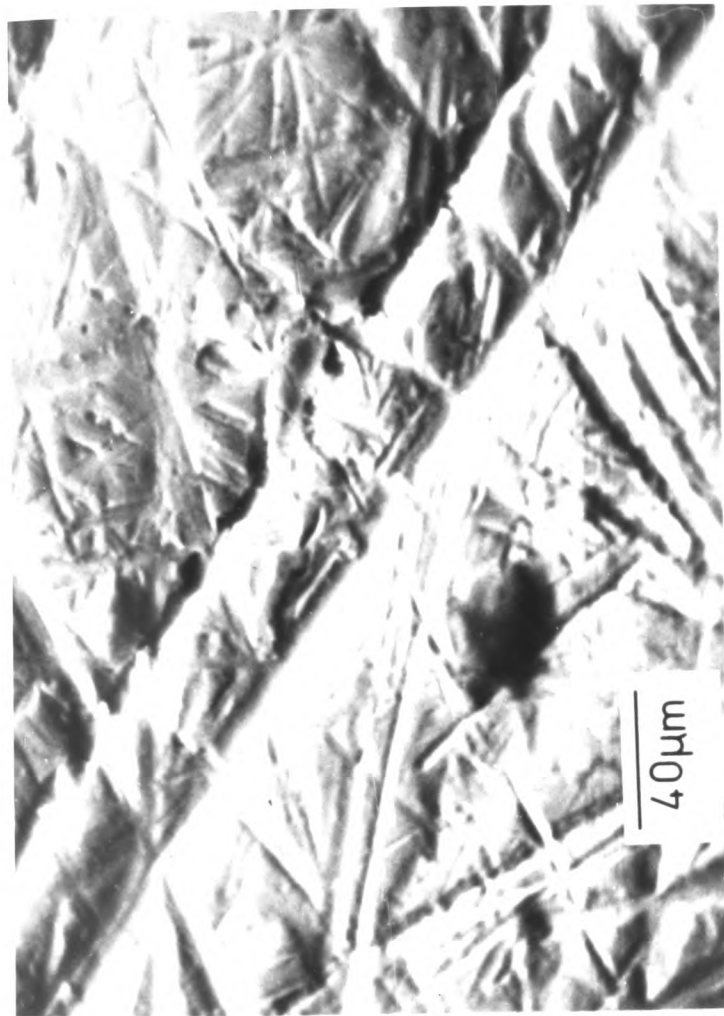
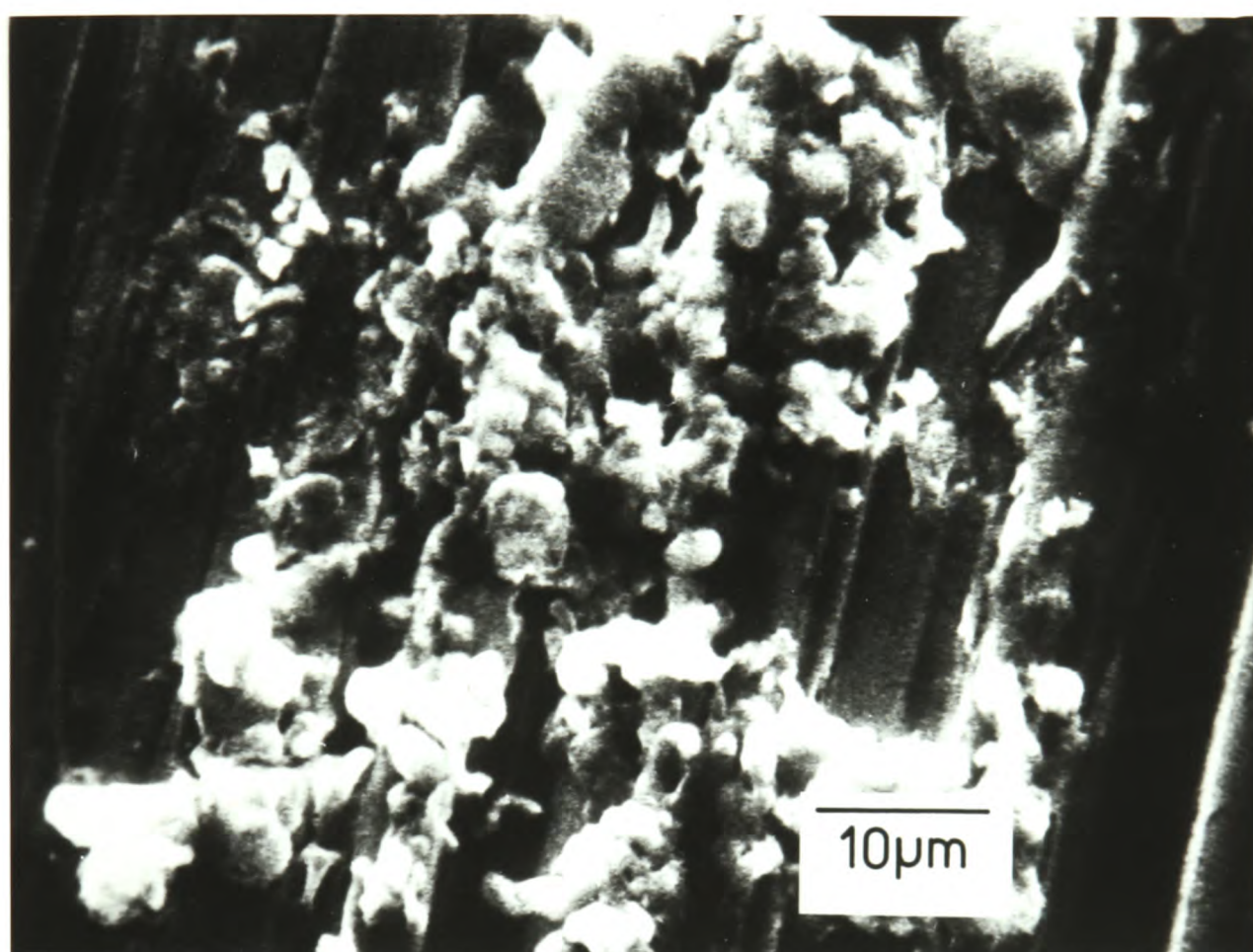


Figure 4.2

Scanning electron micrograph of an area where fragments of lacquer remained on the specimen surface.



The surface shown in Figure 4.1 appears to be continuous, and is either clean substrate, or the substrate with a continuous layer of lacquer which follows the contours of the substrate.

Figures 4.3 and 4.4 show two further areas of apparent adhesive failure, and may be compared with Figure 4.5 which shows an area of cleaned substrate which has not been coated. The substrate surface clearly has a different form from the tested surfaces. It is a much rougher surface, with angular features and re-entrant cavities. The tested surfaces are much smoother and regular. This suggests that either parts of the substrate have been removed by the lacquer, or more probably, that there is a layer of lacquer remaining on the substrate, filling the re-entrant cavities and following the surface contours (Figure 4.6).

Each specimen was studied using the EDAX (energy dispersive analysis of x-rays) attachment to the microscope, to investigate the elements present on the surface. An example of the type of spectrum obtained is shown in Figure 4.7, and examples of the peaks observed on the spectra of X-ray energy versus number of counts are as follows:

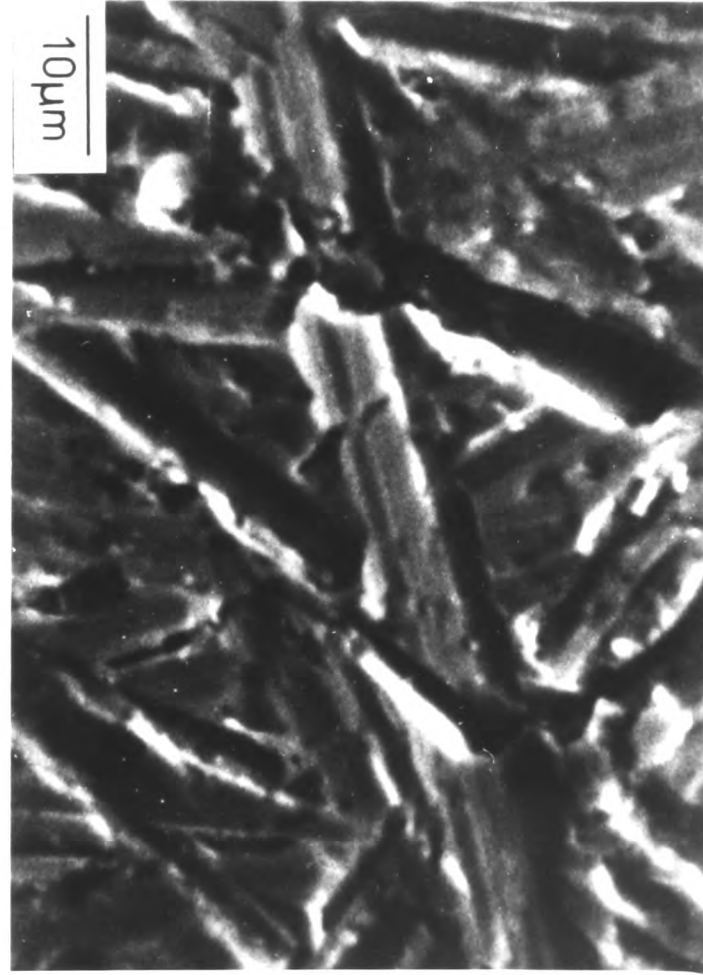
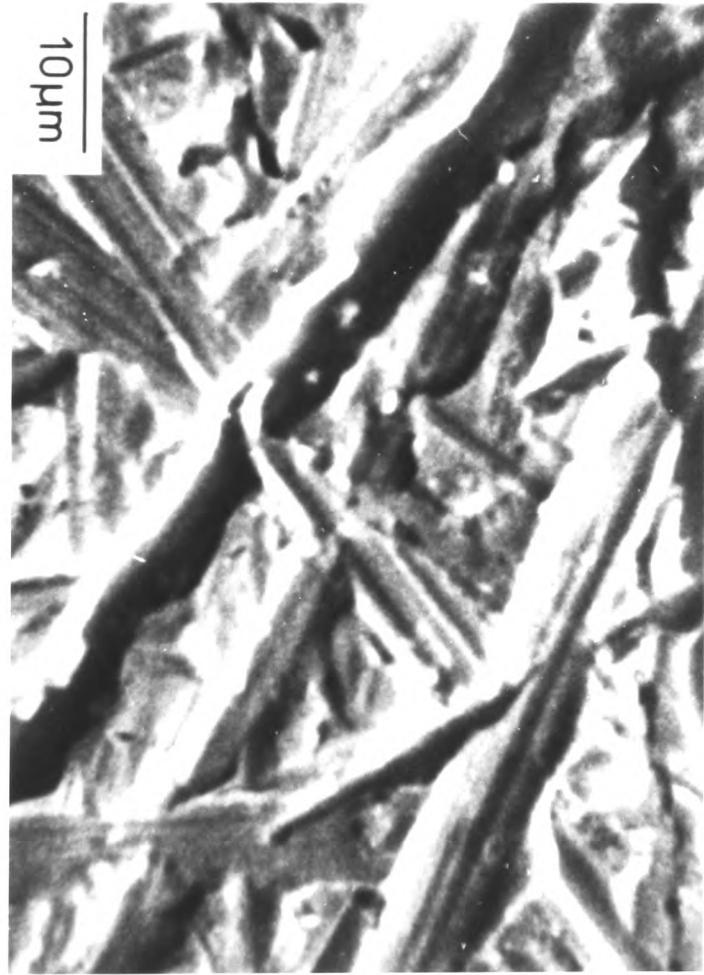
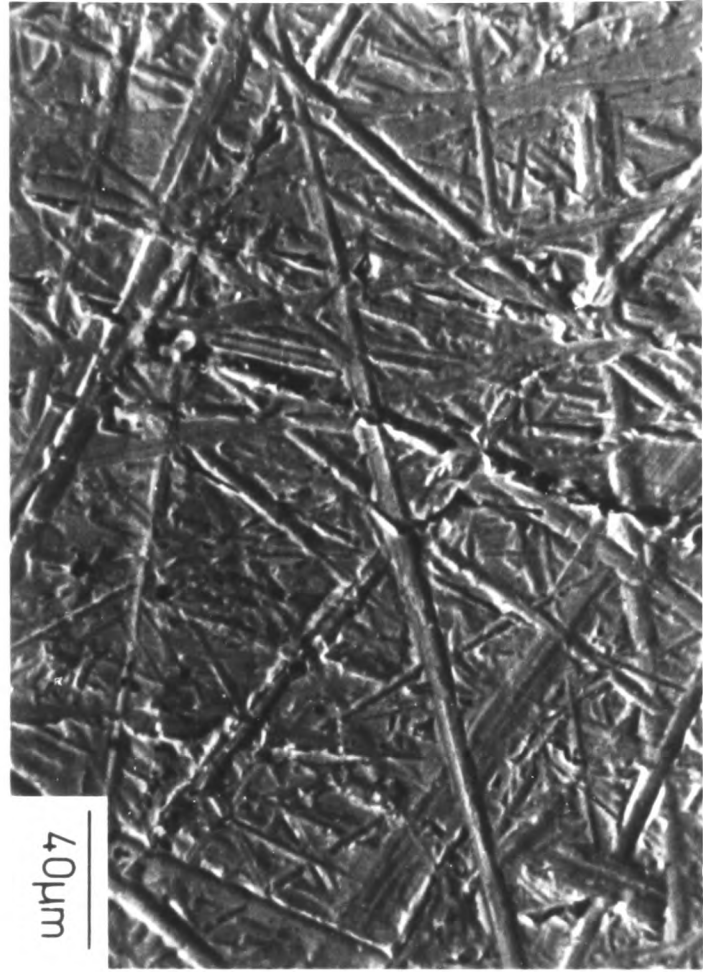
<u>Specimen</u>	<u>Peak eV</u>	<u>Element</u>	<u>Comment</u>
Cleaned substrate	7100	β Fe	
	6460	α Fe	Major peak
	5740	Mn	
	2080	P	Minor peak
Untested film	7040	β Fe	
	6380	α Fe	
	5760	Mn	
	2620	Cl	Major peak
	2000	P	Minor peak
Tested film - area of "adhesive" failure	7100	β Fe	
	6440	α Fe	Major peak
	5740	Mn	
	2700	Cl	
	2060	P	Minor peak

TABLE 4.1

Figure 4.3 } Scanning electron micrographs of the surface of a specimen
Figure 4.4 } in areas of apparent adhesive failure.

Figure 4.5

Scanning electron micrographs of the surface of a cleaned, mild steel substrate.



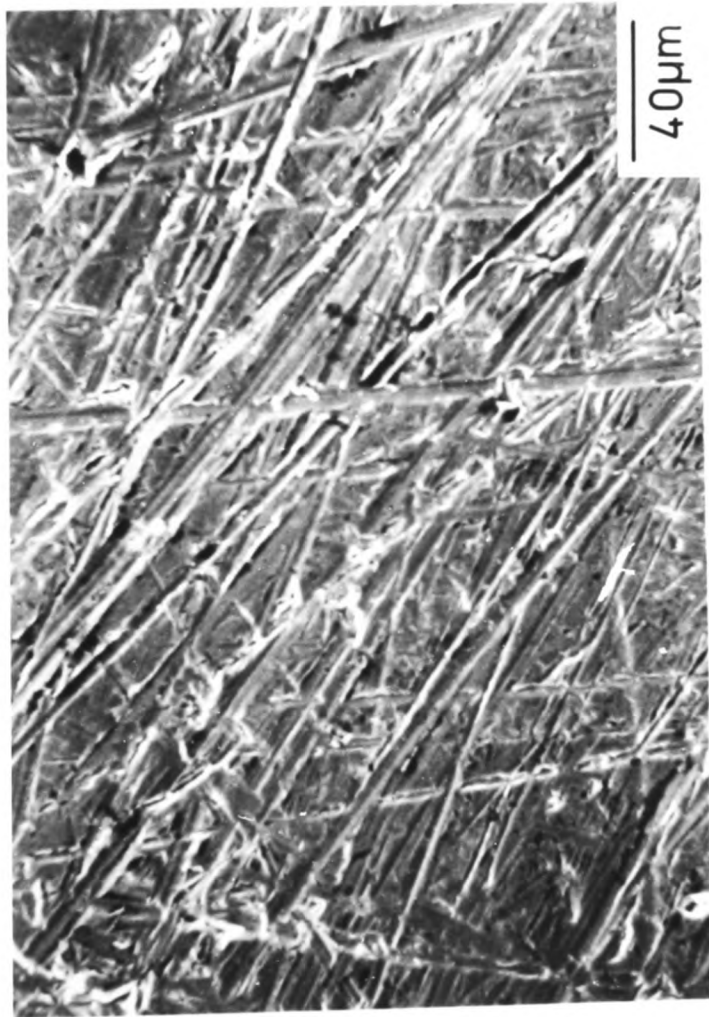
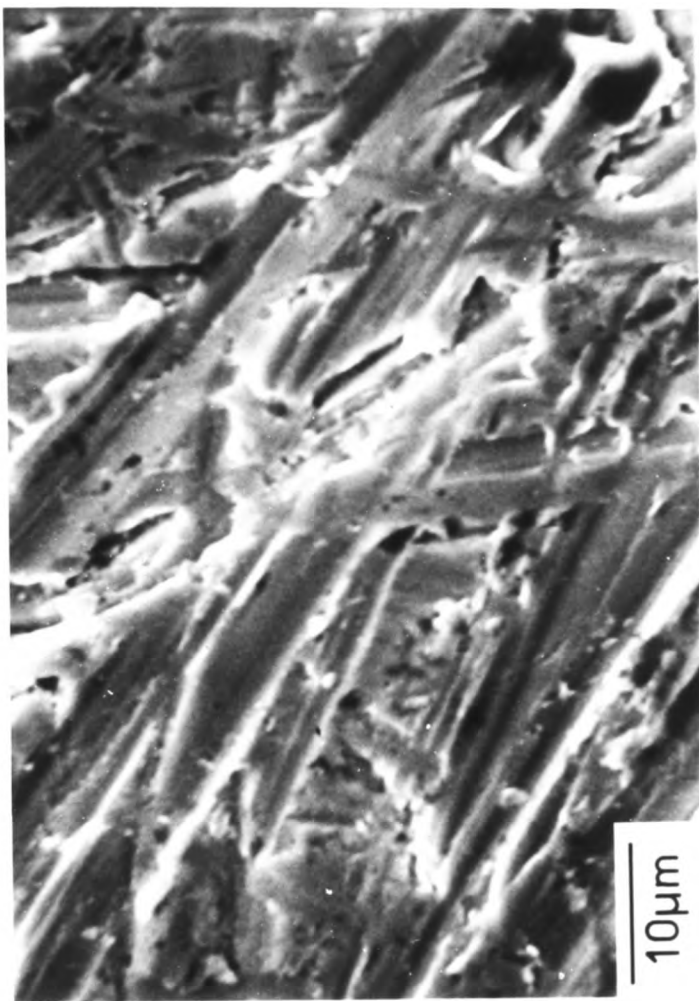


Figure 4.6

(a) Schematic representation of continuous lacquer film following surface contours and filling re-entrant cavities.

(b) Illustration of the effect of surface roughness and film thickness on the path within the lacquer of an incident beam of electrons. In many places the path length is greatly increased.

a.



b.

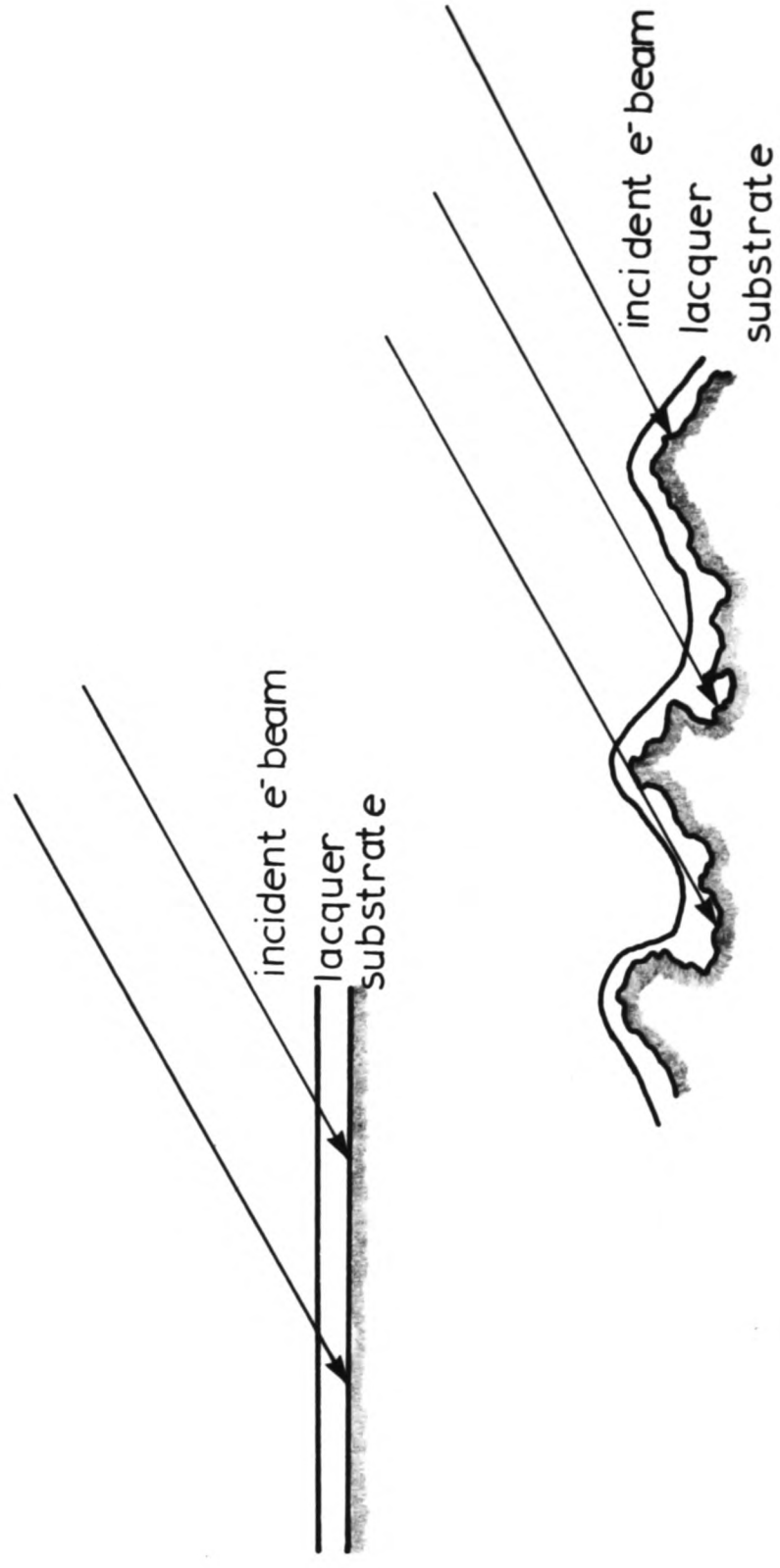
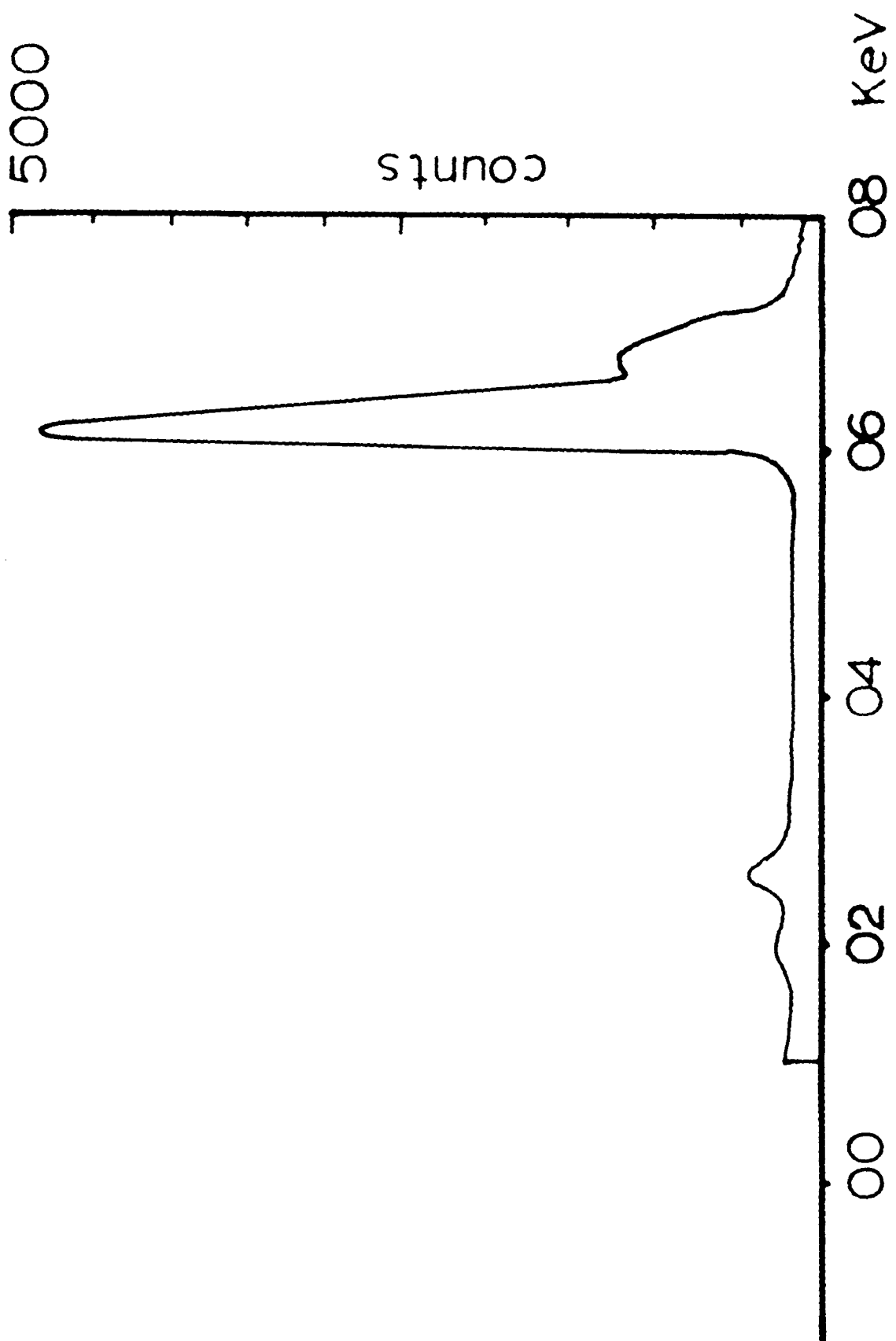


Figure 4.7

An example of the type of spectrum obtained using EDAX, showing small phosphorus and chlorine peaks, and larger iron α and β peaks.



Charging occurred in the case of the untested film, and the spectrum was obtained by focusing the beam to a spot on the surface of the specimen, rather than scanning an area. The diameter of the spot was of the order of $100\text{\AA}$, and the fact that small iron, manganese and phosphorous peaks appeared in the case of both the tested and untested film indicates that the beam penetrated the film, and excited X-rays from the substrate.

The characteristic energies for the X-rays recorded are normally quoted as:

βFe	7057 eV
αFe	6398 eV
Mn	5894 eV
Cl	2621 eV
P	2013 eV

Slight fluctuations occur in the recorded values due to fluctuations in the calibration of the EDAX display unit.

The major peak occurring in the spectrum obtained from the cleaned, mild steel substrate was the αFe peak, while that occurring in the spectrum from the untested lacquer was the chlorine peak. If the tested specimen had failed purely in the adhesive mode there would have been no lacquer remaining on the substrate, and hence the spectrum obtained would be that for a cleaned substrate. However, all such specimens exhibited a distinct, though small chlorine peak (Figure 4.7). This suggests that there is either a thin, continuous layer of lacquer remaining on the substrate in these areas, or that fragments of lacquer remain, for example locked into the re-entrant grooves on the surface. Figures 4.1, 4.3 and 4.4 showed no evidence of these fragments, and there was evidence of a continuous surface layer, as discussed earlier, but further investigation is required before any firm conclusions may be drawn.

4.3 ESCA RESULTS AND DISCUSSION

Specimens were prepared for study by the ESCA (electron spectroscopy for chemical analysis) technique. Strips were cut from the centre of each disc, 19.05mm long and 4mm wide, making sure that the total area of each specimen was of the required type - cleaned mild steel, untested lacquer, or an area of possible adhesive failure. They were washed in methanol and stored in a desiccator until tests could be carried out. A sample of "Alloprene" was also tested for purposes of comparison. This technique is used to study only the surface of the specimen, as the penetration depth is of the order of $30\text{\AA}$ in organic materials. It can give the relative atomic concentrations at the surface to a standard error of 10% [15].

Spectra were recorded on an AEI ES 200B ESCA spectrometer, and correction for sample charging effects was achieved by using the hydrocarbon signal at 285.0 eV binding energy as an energy reference. Line shape analysis was carried out using a DuPont 310 Analogue Curve Resolver. The spectra for all but the "Alloprene" specimen were recorded at electron take-off angles of 30° and 70° , the latter corresponding to grazing electron take-off, which thus enhances surface features. "Alloprene" was tested at the take-off angle giving the maximum intensity.

The results are summarised in Table 4.2, and will be considered under four headings:

- (i) "Alloprene"
- (ii) Substrate
- (iii) Untested lacquer
- (iv) Tested specimen
- (i) "Alloprene"

High resolution spectra were obtained for C_{1s} , Cl_{2p} and O_{1s} . The C_{1s} envelope was resolved into the components corresponding to $\underline{C}$ - Cl and carbon not attached to chlorine, their relative intensities of 70:30 (Table 4.2) corresponded closely to the theoretical values,

and the Cl_{2p}/C_{1s} intensity ratio was 1.95.

The theoretical O_{1s}/C_{1s} ratio was calculated from the approximate structural formula for "Alloprene" as $\sim 0.3\%$. However, the value observed was $\sim 6\%$, and this, with a small high binding energy tail which occurred in the C_{1s} spectrum suggested that the end-groups of the chains were oriented towards the surface of the material.

No.	Description	θ°	C_{1s} (total = 100%)				O_{1s}	Cl_{2p}		$Fe_{2p_{3/2}}$
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4*</u>		<u>1</u>	<u>2†</u>	
1	'Alloprene'	max			70.0	30.0	6.0	195.0	0	0
2	Mild Steel	30	5.5	4.5	14.5	75.5	62.0	0	0	~ 9.0
		70	5.0	2.0	16.0	77.0	46.5	0	0	< 9.0
3	Lacquer	30	4.0	8.5	32.0	55.5	23.5	76.5	0	0
		70	3.5	4.5	25.0	67.0	22.5	47.5	0	0
4	Tested	30	7.0	6.0	24.0	63.0	63.0	22.0	4.0	~ 7.5
		70	6.5	2.0	20.5	71.0	47.1	11.4	2.0	~ 6.0

* The components are as follows:-

- C_{1s} , 1 ~ 289.1 eV $C \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$
- 2 ~ 287.9 eV $C=O$
- 3 ~ 286.6 eV $C-O$ and $C-Cl$
- 4 ~ 285.0 eV hydrocarbon

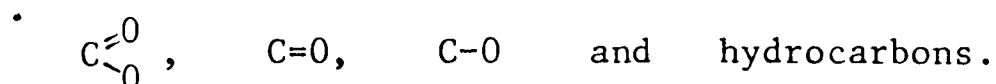
† The components are as follows:-

- $Cl_{2p_{3/2}}$ 1 ~ 200.3 eV $C-Cl$
- 2 ~ 198.3 eV 'Fe-Cl'

TABLE 4.2
Relative Signal Intensities ESCA

(ii) Substrate

Both O_{1s} and C_{1s} levels appeared on this spectrum and the high resolution spectrum at $\theta=30^\circ$ showed iron in its highest oxidation state, $Fe_{2p_{3/2}}$, with a binding energy of ~ 711.5 eV, and a low binding energy O_{1s} signal at ~ 530.6 eV which was associated with oxygen attached to iron. Four components of the C_{1s} spectrum were observed:



The spectral variation as a function of electron take-off angle indicated that at least some of the carbonaceous material was present as an overlayer; in going from $\theta=30^\circ$ to $\theta=70^\circ$ the Fe_{2p} peak was decreased, and C_{1s} at a binding energy of 285.0 eV increased. The contribution from the Fe-O signal in the O_{1s} spectrum was also lower at 70° , suggesting that this was below the carbonaceous layer.

This overlayer could have been produced during the specimen cleaning process, either just after abrasion, or just before analysis. If the latter occurred, then this layer should not be present between a film of lacquer and the substrate.

(iii) Untested lacquer

A theoretical value for the Cl_{2p}/C_{1s} intensity ratio was calculated for "Alloprene" and "Cereclor" as 1.96 and 0.80 respectively. Table 4.2 shows that the experimental value for the lacquer was 0.77, which was close to that for "Cereclor" and suggested that the plasticiser had segregated at the surface. This is consistent with the results of Whitehouse [17]. There was also a large O_{1s} signal, and components in the C_{1s} spectrum corresponding to the "Alloprene" end groups, which must have appeared through the "Cereclor" overlayer.

Hydrogen chloride was lost from the sample surface after prolonged exposure to X-rays, as evidenced by a decrease in the $\underline{C}$ -Cl and Cl_{2p} peaks, so little extra information could be gained from the $\theta=70^\circ$ spectra.

(iv) Tested specimen

Once again O_{1s} , C_{1s} and C_{2p} levels appeared in the spectra, and the presence of relatively large amounts of both oxygen and chlorine were confirmed by high resolution spectra at $\theta=30^\circ$. The spectra would arise from a combination of the surfaces of the substrate and any lacquer remaining on it, thus there were probably both $\underline{C}-Cl$ and $\underline{C}-O$ at ~ 286.6 eV. For this reason it was difficult to characterise the surface at the interface as similar to, or different from the surface of the untested film.

The Cl_{2p} spectrum showed evidence of chlorine attached to the metal, and the O_{1s} peak suggested evidence for a signal due to $Fe-\underline{O}$, with iron again present in its highest oxidation state.

Thus, the sample appeared to consist of an overlayer comprising of a mixture of a thin lacquer interface layer, and the oxidised carbon layer originally on the mild steel. The overlayer lay on a metal surface which was oxidised, and contained some chloride features.

Problems were encountered with the $\theta=70^\circ$ spectra similar to those for the untested lacquer sample.

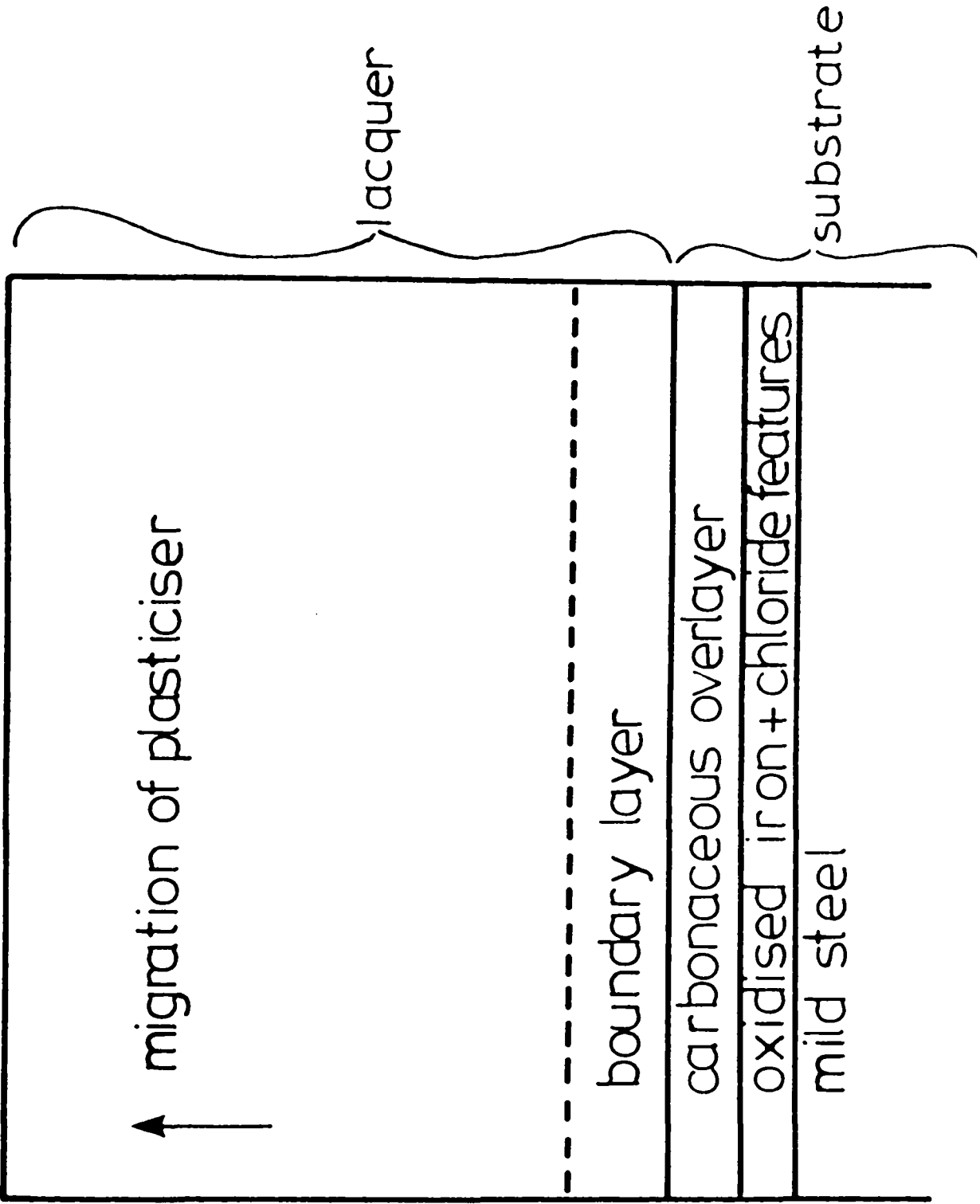
Figure 4.8 summarises these results.

Thus, the question is clearly answered, that the "apparent" adhesive failure is not, in fact, a clean separation at the interface, but is failure within a boundary layer. This layer has been predicted to be less than $25 \text{ \AA}$ thick [3], and further efforts to calculate this thickness have reinforced the evidence for the structure suggested in Figure 4.6. The thickness calculated from the data collected at a take-off angle of 70° was greater by a factor of two than the thickness calculated from the $\theta=30^\circ$ data. However, there were insufficient data available to calculate an absolute value for film thickness.

Although it has been shown that a film remains on the substrate after testing, it has not been completely characterised, so a further surface analytical technique was employed to investigate the chemical properties of this film.

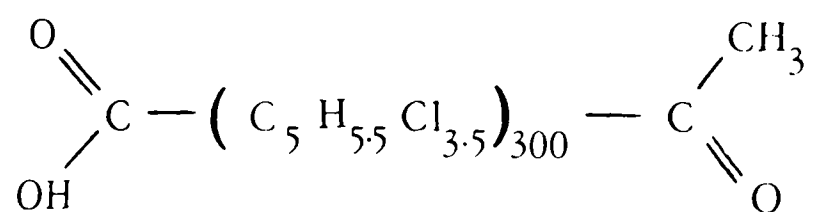
Figure 4.8

Summary of the results obtained using electron spectroscopy for chemical analysis (ESCA).



4.4 AUGER RESULTS AND DISCUSSION

"Alloprene" has a nominal chlorine content of $\sim 65\%$ by weight. Taking the structural formula as



the ratio of the number of carbon atoms present to the number of chlorine atoms is 1.43:1.

"Cereclor 42" is a chlorinated paraffin with a chlorine content of $\sim 42\%$ by weight, and a carbon chain length of 22-24. Thus the ratio of carbon to chlorine in "Cereclor 42" is 3.58:1.

The lacquer under test contains 70% "Alloprene" and 30% "Cereclor 42" by weight, and thus has a nominal carbon to chlorine ratio of 1.89:1, which is fairly close to that of pure "Alloprene". Changing the ratio of "Alloprene" to "Cereclor" to 65:35% by weight gives a carbon to chlorine ratio of 1.98:1, a change of 5%. In fact, it is the number per cent of chlorine which changes markedly from one sample to the other, the nominal carbon content remains around 32-36% of the atomic species present.

Auger analysis was used to investigate the variation of the carbon to chlorine ratio through the depth of the film, to detect any inhomogeneities developed within the film, on curing. This type of analysis samples only the surface of the specimen, to a depth of $\sim 30 \text{ \AA}$ for an organic specimen [15].

The specimens were prepared for examination by punching discs, 6mm in diameter, from the tested areas. These were washed in methanol and stored in a desiccator until required. As this method samples only the surface layers it is very sensitive to surface contamination: thus, the specimens were analysed as received, and then ion bombarded to

remove the surface layer and any contamination. A layer approximately 20-30 Å thick was removed in this way. Four specimens were prepared:

- (i) cleaned, abraded mild steel,
- (ii) untested lacquer ($\sim 100\mu\text{m}$ thick),
- (iii) lacquer failed in cohesion,
- (iv) specimen failed in boundary layer.

A silver standard was used to establish the relative sensitivity for each element $S_{x,\text{Ag}}$, where x is the element considered.

$$S_{x,\text{Ag}} = \frac{I_x^H}{K_x I_{\text{Ag}}^H}$$

where I_x^H , I_{Ag}^H are the peak-to-peak heights obtained from the handbook [12], and K_x is the scale factor. The concentration of element x is then

$$C_x = \frac{I_x}{S_{x,\text{Ag}} \cdot I_{\text{Ag}}}$$

where I_x is the peak-to-peak height of x on the spectrum, and I_{Ag} is the peak-to-peak height for the pure silver target.

However, when the relative concentrations of two elements are to be considered

$$\begin{aligned} \frac{C_x}{C_y} &= \frac{I_x}{S_{x,\text{Ag}} \cdot I_{\text{Ag}}} \cdot \frac{S_{y,\text{Ag}} \cdot I_{\text{Ag}}}{I_y} \\ &= \frac{I_x}{I_y} \cdot \frac{S_{y,\text{Ag}}}{S_{x,\text{Ag}}} \end{aligned}$$

and the silver standard is not required.

Severe charging occurred with the specimen of untested lacquer, and spectra could only be obtained from the as-received specimen with $E_p \sim 1$ KeV, where E_p is the energy of the incident beam. However, the most meaningful results were obtained from the specimens after ion bombardment, and with $E_p \sim 2.5$ KeV. These results will be detailed below,

while Table 4.3 summarises the results obtained from all the tests carried out.

<u>Conditions</u>	<u>Specimen</u>	$\frac{C_c}{C_{cl}}$	C_o	<u>Comment</u>
As-received $E_p \sim 1$ KeV Standard sensitivity 1mV	Untested lacquer	4.76		Corrected for charging
	Cohesive failure	3.57		Corrected for charging
	Boundary layer	2.22	5.57	
As-received $E_p \sim 2.5$ KeV Standard sensitivity 3mV	Mild Steel		2.48	
	Cohesive failure	9.13		Corrected for charging
	Boundary layer	2.05	1.84	
After bombardment $E_p \sim 2.5$ KeV Standard sensitivity 10mV	Mild Steel		0.59	
	Cohesive failure	3.85	0.21	
	Boundary layer	1.06	0.27	

TABLE 4.3
Results of Auger Analysis

Relative Sensitivities (from handbook)

$$S_{c,Ag} = 0.104$$

$$S_{cl,Ag} = 0.486$$

$$S_{o,Ag} = 0.95$$

$$I_{Ag} = 98$$

(i) Mild steel substrate (Figure 4.9)

$$I_c = 3$$

$$I_o = 54.9$$

$$\therefore \frac{C_c}{C_o} = \frac{3}{54.9} \times \frac{0.95}{0.104} = 0.50$$

(iii) Lacquer failed in cohesion (Figure 4.10)

$$I_{cl} = 170$$

$$I_c = 140$$

$$I_o = 20$$

$$\frac{C_c}{C_{cl}} = \frac{140}{170} \times \frac{0.486}{0.104} = 3.85$$

$$\frac{C_c}{C_o} = \frac{140}{20} \times \frac{0.95}{0.104} = 63.94$$

(iv) Boundary layer (Figure 4.11)

$$I_{cl} = 66$$

$$I_c = 15$$

$$I_o = 25$$

$$\frac{C_c}{C_{cl}} = \frac{15}{66} \times \frac{0.486}{0.104} = 1.06$$

$$\frac{C_c}{C_o} = \frac{15}{25} \times \frac{0.95}{0.104} = 5.48$$

Figure 4.9

Plot of Auger electron energy (E) versus $\frac{d}{dE} (N(E)dE)$, for the mild steel substrate. Incident beam energy ~ 2.5 keV, sensitivity 3mV. (N(E) is the number of electrons with energy E).

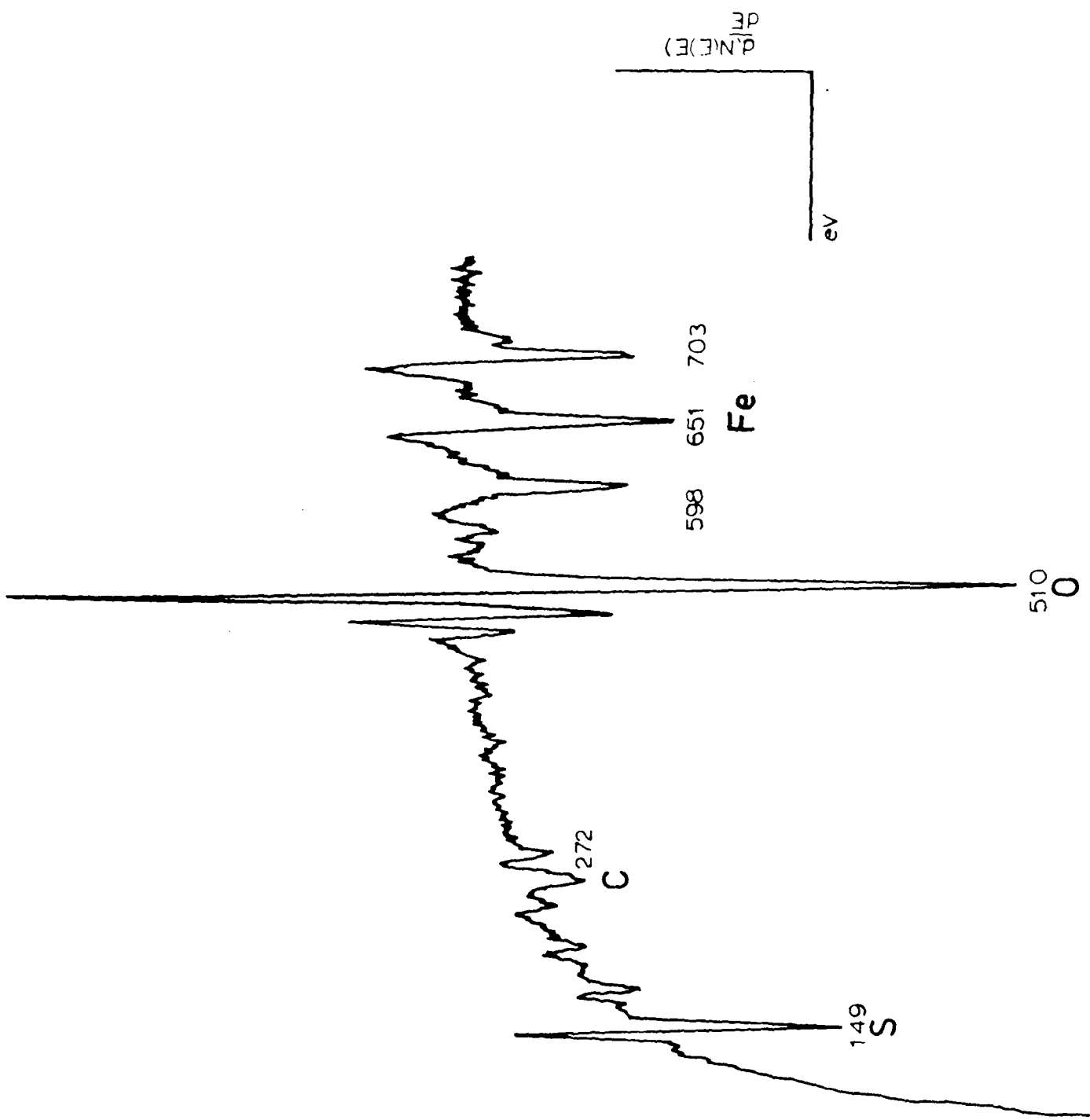
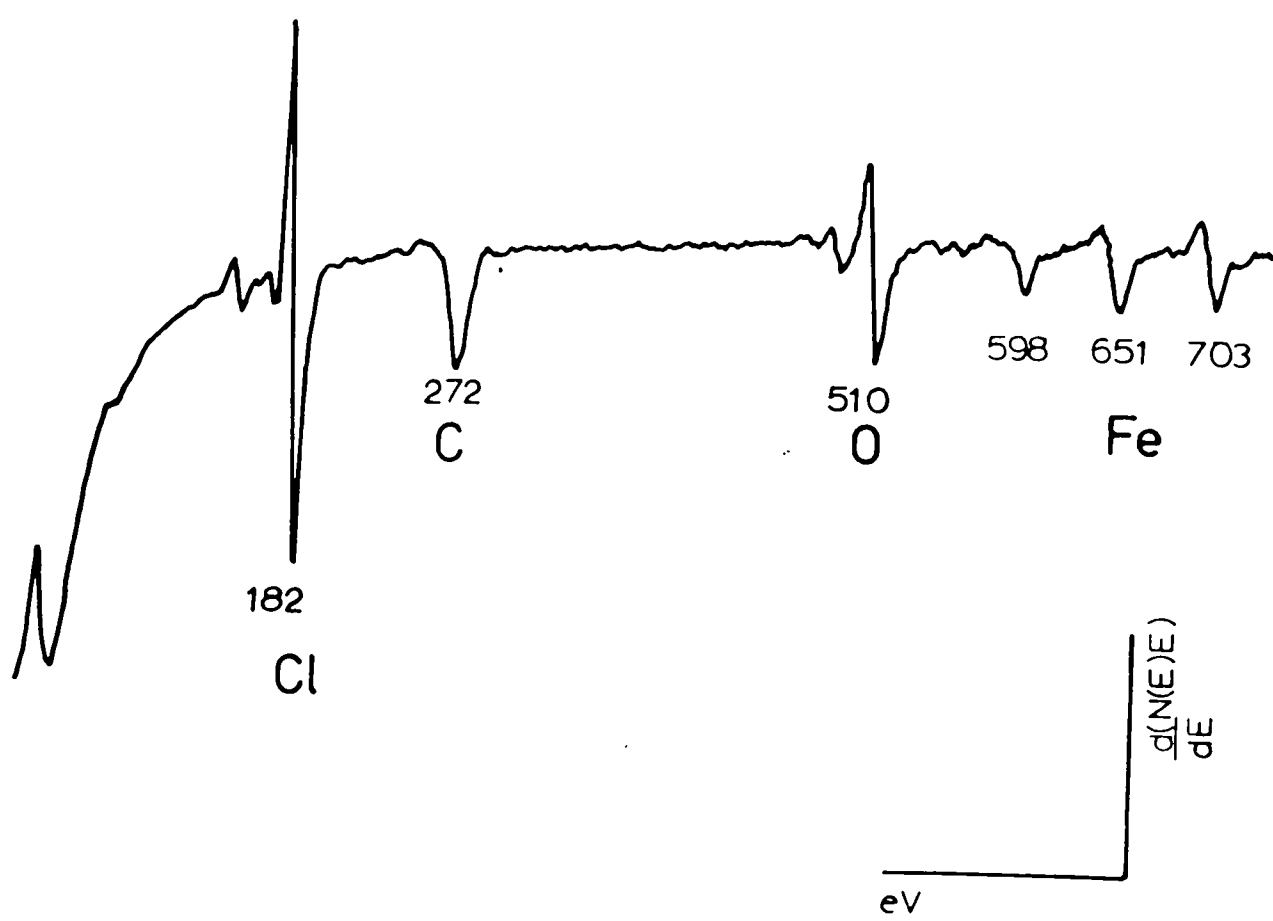
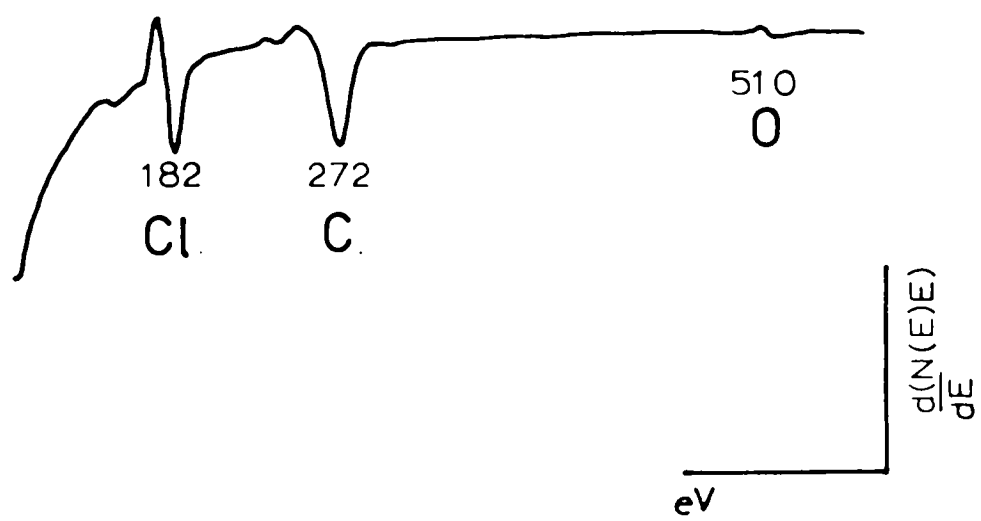


Figure 4.10

Plot of Auger electron energy (E) versus $\frac{d}{dE} (N(E)dE)$ for a lacquer which had failed cohesively. Incident beam energy ~ 2.5 keV, sensitivity 100 mV.

Figure 4.11

Plot of Auger electron energy (E) versus $\frac{d}{dE} (N(E)dE)$ for the weak boundary layer. Incident beam energy ~ 2.5 keV, sensitivity 10 mV.



It appeared that most of the contamination was removed by bombardment as the carbon content was almost eliminated from the silver standard, and significantly reduced in the mild steel specimen. The effect of contamination is observed as an increase in the numerical value of the carbon to chlorine ratio C_c/C_{cl} , and probably also the concentration of oxygen C_o .

Considering the results obtained after bombardment, the value of C_c/C_{cl} in the boundary layer is very low, and within the range of experimental error it may be compared with the value for pure "Alloprene" (1.43). This suggests that either the "Cereclor" migrated away from the interface during curing, leaving a layer of almost pure "Alloprene" here, or that there was an increased chlorine concentration due to the interaction of chlorine, or hydrogen chloride, from the polymer, with the substrate.

If there was a "plasticiser-free" layer at the interface this would probably be strong, but brittle; whereas molecules which were chemically bonded to the substrate would form a strong boundary layer and failure would occur between this layer and the body of the film. There was evidence for some type of interaction in the results of the ESCA work.

The value of C_c/C_{cl} towards the centre of the film is much higher, ~ 3.85 . This suggests a high concentration of plasticiser which may have migrated into the body of the film, although ESCA shows a high concentration of plasticiser at the surface of the film. This may be explained by the fact that ESCA was sampling the surface layers of the film, and cohesive failure occurred within this region, so the results are, in fact, not inconsistent.

Little useful information may be drawn from the results from the as-received specimens, as there is no measure of the level of contamination. However, it should be noted that the value of C_c/C_{cl} remains low at the interface, and if it is assumed that the level of contamination

does not vary greatly across the depth of the lacquer, the results obtained with $E_p \sim 1$ KeV suggest that the chlorine content increases with increasing depth into the film, measured from the top surface, reinforcing the ideas discussed above.

From the results obtained after bombardment the oxygen concentration appears to remain constant through the film, although it is higher than is predicted by the end-group concentration alone. The concentration is higher at the surface of the substrate due to the oxide of iron present here.

Thus it appears that the boundary layer is rich in chlorine, and that the plasticiser has indeed segregated to the outer surface of the film. This implies that the lower layers of the film must contain a higher percentage of "Alloprene" than the original lacquer. The evidence for any chemical interaction between the film and the substrate will be considered in the next chapter, but the implications of the results obtained by these techniques must now be examined as a whole.

4.5 DISCUSSION

Scanning electron microscopy suggested that the areas of apparent adhesive failure, on each substrate, in fact had a very thin layer of lacquer remaining on the surface, which followed the contours of the abraded substrate. This was reinforced by the results of the energy dispersive X-ray analysis (EDAX), which detected X-rays from chlorine atoms on these surfaces, which could only have originated in the lacquer.

Electron spectroscopy for chemical analysis (ESCA) revealed that this film was probably less than 25 Å thick, or of uneven thickness, and contained not only chlorine atoms attached to the polymer chain, but also chlorine which had reacted with the iron from the substrate. Finally, Auger analysis suggested that the film was indeed rich in chlorine, due, in part, to the migration of the plasticiser away from the interface.

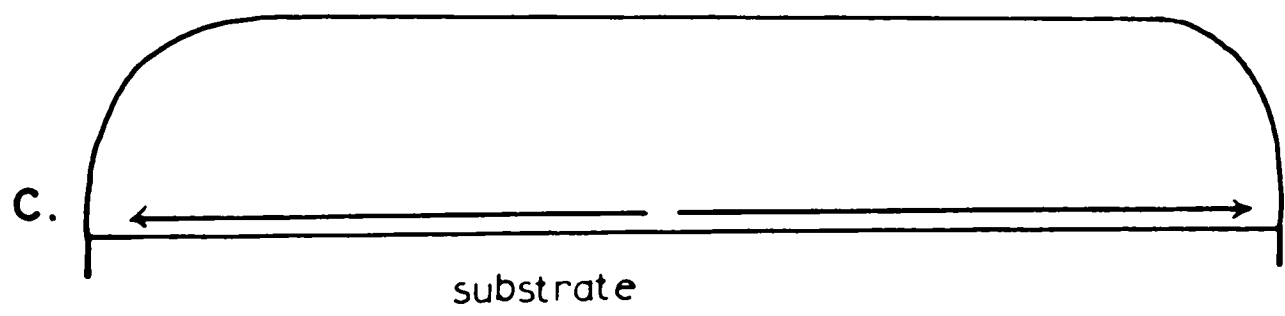
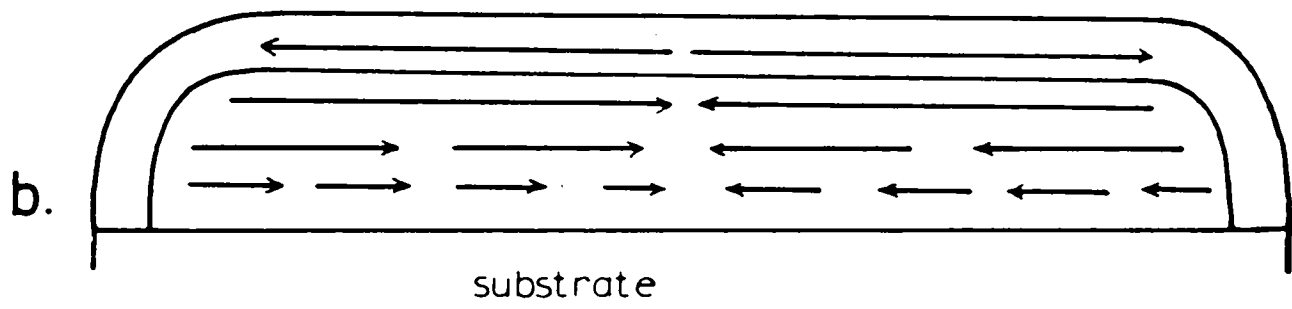
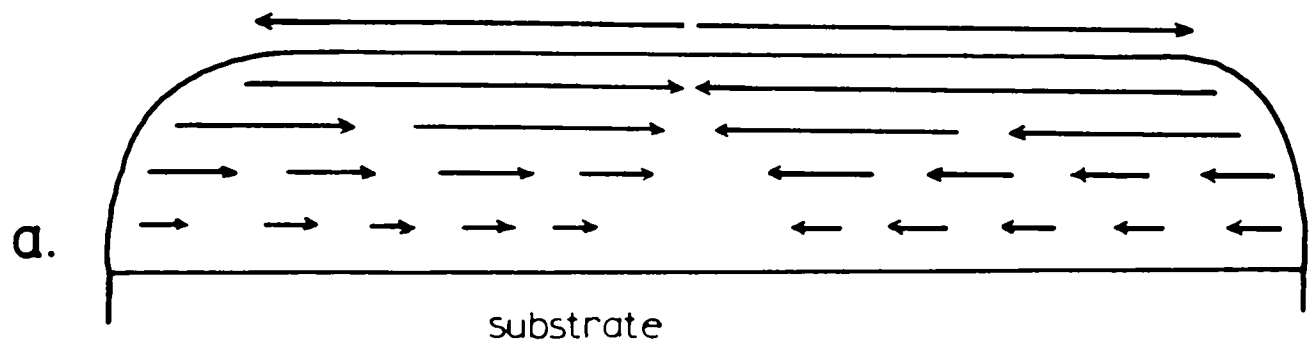
It is suggested that this migration takes place in the following way: as soon as the film is cast solvent begins to evaporate from the upper surface of the lacquer, and the film contracts vertically and horizontally due to the loss of volume (Figure 4.12). The surface is held in tension by the lacquer below, which has not yet contracted, and these lower layers suffer a compressive stress exerted by the surface layer. As the lower regions of the film are still mobile, and the plasticiser molecules are smaller, and more mobile than the binder, the former are squeezed upwards by the compressive stress exerted on the film, and to some extent relieve these stresses. This process continues as successive layers of the film lose solvent which diffuses upwards and out of the film; the excess plasticiser becomes locked into the upper layers of the film, as these cure, but plasticiser continues to move away from the substrate as regions deeper into the film lose solvent.

When the whole film has finally cured the interfacial region is depleted of plasticiser, and remains in tension, as there are no

Figure 4.12

Schematic representation of the mechanism causing plasticiser migration towards the lacquer/air interface. Arrows indicate direction of induced stress and their lengths signify the magnitude of the stress at each level in the coating.

- (a) Surface layers of film contract due to loss of solvent.
- (b) Successive layers of the film lose solvent, and cure.
- (c) The full thickness of the film cures, and the interfacial region between coating and substrate remains in tension.



mobile molecules left to relieve the stresses induced here by solvent loss. This is confirmed by a simple experiment in which a cured film is removed from its substrate by dissolving the latter in dilute hydrochloric acid. As the film dries it begins to curve, so that the upper surface becomes convex, implying that the lower surface has contracted, i.e. it is restored to the form it was in after curing.

In one such experiment the radius of curvature of the film was found to be $\sim 0.9 \pm 0.05\text{cm}$, which represented a decrease in the area of the lower surface of $\sim 4\%$. It has been calculated that plasticiser molecules occupy approximately 5.4% of the interfacial area of an homogeneous film, and these results may imply that about 74% of the plasticiser has migrated away from the interface.

However, several other factors must be taken into consideration:

- (1) The film tends to take up acid during the dissolution process, and the radius of curvature of the detached film gradually decreases as the film dries. However, it is difficult to estimate the final radius of curvature or to detect any permanent effects of the acid on the film;

- (2) no account has been taken of the change in area due to solvent loss. The dimension change will not be the same in the plane of the film as through its depth;

- (3) chemical interactions between the film and the substrate will affect the properties of the interfacial region.

Thus, the type of failure was characterised as weak boundary layer (WBL), the boundary layer consisting of "Alloprene" macromolecules strongly bound to the substrate, and a compound containing iron and chlorine.

It is suggested that the layer is formed in the following way; the "Alloprene"-rich region at the interface will be strong, but brittle and bound to the substrate by bonds which are much stronger than those occurring within the film itself (see Chapter 6). This layer is held

in tension by the substrate, and when a vertical stress is applied to the system small cracks will initiate and propagate most easily within this region due to the stress concentration occurring here, leaving a thin coating of lacquer on the substrate when total failure occurs.

It is also suggested that some degree of chain orientation may occur at the interface, decreasing the amount of chain entanglement within the boundary layer. It was observed in the previous chapter that for the higher grades of "Alloprene" the stress to failure was independent of the molecular weight of the polymer, that is to say independent of chain length. When failure occurs within a polymer of this type the only contribution to the failure stress which varies with molecular weight is the "entropy" or chain entanglement factor. Thus, the fact that the stress is independent of chain length suggests that the type of failure occurring does not involve the disentanglement of polymer chains.

It was noted that the lacquer prepared from R5 grade "Alloprene" required a much lower stress to cause failure than the other grades, and it is suggested that some other factor was important here, which has not, as yet, been identified.

The increase in stress to failure with film drying time is probably associated with the interaction of the film with the substrate. It is known that "Alloprene" tends to degrade when in contact with iron, and it is suggested that the chlorine atoms which were detected and which had reacted chemically with the substrate were released from the polymer chains by this degradation. A "rust"-coloured compound is formed at the interface, the amount of which increases with drying time, and it is thought that the presence of this compound somehow enhances the strength of the WBL. However, this degradation will be discussed fully in Chapter 5.

It is interesting to note that Meyer and Rose [11] state that in many cases failure is caused by a migration of certain chemical

components of the coating to the interface - which is the opposite of the effect discussed above - and Walker [16] records that in chlorinated-rubber based paints on steel the mode of failure was found to be cohesive.

References - Chapter Four

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C H A P T E R F I V E

INTERACTIONS BETWEEN THE LACQUER AND THE SUBSTRATE

CHAPTER FIVE

INTERACTIONS BETWEEN THE LACQUER AND THE SUBSTRATE

5.1 INTRODUCTION

Reference has been made in earlier chapters to the fact that chemical reactions may occur at the interface between the film and the substrate. The evidence for these reactions will now be discussed, and efforts made to establish their nature.

It is recognised that both "Alloprene" and "Cereclor" may degrade in the presence of iron [4], and it is generally accepted that an unpigmented lacquer composed of these two compounds, applied to a mild steel plate, and exposed to sunlight will discolour badly, turning very dark brown.

Two examples of discolouration were observed in the specimens prepared for tensile testing. Coated discs which were not included in a particular batch for testing were stored either in a closed wooden box, or on glass plates on the laboratory bench. Some specimens developed a "rust"-like discolouration which was continuous across the surface of the disc, other specimens developed a "cell"-like discolouration, as may be observed in Figure 5.1.

The former occurred most frequently in specimens stored on the laboratory bench, while the latter occurred more often in those stored in darkness, in the box. However, there were exceptions to this rule.

After specimens had been tested, as described in Chapter 3, they were stored in open wooden boxes. Lacquers which had shown no discolouration before bonding were in the same state after failure, but a "rust"-like discolouration soon developed on storage; on one occasion this appeared overnight. Once again, a few specimens developed the "cell"-like structure. These specimens had been stored in a dark

cupboard after testing, but some specimens stored with them developed continuous discolouration.

Areas of the specimen surface which had failed in the weak boundary layer rarely suffered any change on storage. Discolouration mainly occurred in areas of thick lacquer remaining on the substrate.

In the following sections the examination of these two types of discolouration will be discussed, and as far as possible at present, their nature described.

Figure 5.1

Examples of "cell"-like discolouration.



2.4 cm

5.2 EXAMINATION OF THE CONTINUOUS DISCOLOURATION

Discs coated in lacquer based on various grades of "Alloprene" were stored on the laboratory bench and their gradual discolouration observed. The most noticeable variation occurred between the rate of discolouration of a lacquer based on R20 grade "Alloprene", and that of the same lacquer having had hydrogen chloride gas passed through it before the film was cast. The latter discoloured very rapidly compared with the former sample. However, after three months storage all specimens were the same "rust"-like colour, and there was no perceptible change during a further month's storage. When a scored specimen was left in dilute hydrochloric acid overnight, the film was completely detached from the substrate, and was found to be translucent and the same "pale-sand" colour as a freshly cast film. The discolouration was therefore occurring at the lacquer/substrate interface.

One set of tested specimens had developed a continuous "rust-coloured" substance in a region where the film had failed in the weak boundary layer. Although there was a possibility that this was not typical of the usual discolouration it was decided to examine it more closely, and in fact, the tests which will be described below revealed that it was representative of the interfacial discolouration.

The tests which were carried out were as follows:

(a) ESCA

A strip of dimensions 19.06 x 4 mm was cut from the substrate using a jeweller's saw, washed in methanol and stored in a desiccator at atmospheric pressure to await examination. This was carried out as described in the previous chapter, when considering the mode of failure of the film.

It was found that the "rust" layer contained a higher concentration of chlorine and oxygen in the surface regions than did the weak boundary layer discussed in Chapter 4. The amount of this chlorine which was in the form of chloride ions was the same as in the previous specimen, and

the excess was combined with carbon.

The contribution due to oxygen is electrons in the spectrum was very complex, with a large component appearing at a high binding energy. This energy suggests that it may be associated with a metal carbonate feature, by analogy with the high electron binding energy of the singly bonded oxygens in organic carbonates, (in the region of 533-535 eV) [3]. Iron was also present in its highest oxidation state.

The signal intensities changed very slightly with angular variation, which demonstrates that the layer of "rust" is relatively thick; greater than 100 Å.

Thus, it appears that the layer could contain a ferric compound, a metal chloride, some form of metal carbonate and a compound containing C-Cl groups.

(b) Auger analysis

A disc 6mm in diameter was punched from a specimen similar to that used in the ESCA studies. It was washed in methanol and stored in a desiccator as before, until Auger analysis could be performed. When mounted in the analyser chamber the specimen was first bombarded with argon ions to remove any surface contamination.

Figure 5.2 shows the spectrum obtained from the specimen using an incident beam energy of 2.5 KeV, and sensitivity of 10mV. The relative concentrations of atomic species were calculated as described in Chapter 4, and the results were as follows:

$$C_{Cl}:C_C = 1.34$$

$$C_O:C_C = 0.59$$

$$C_{Cl}:C_O = 2.29$$

For comparison the corresponding results obtained from the weak boundary layer were:

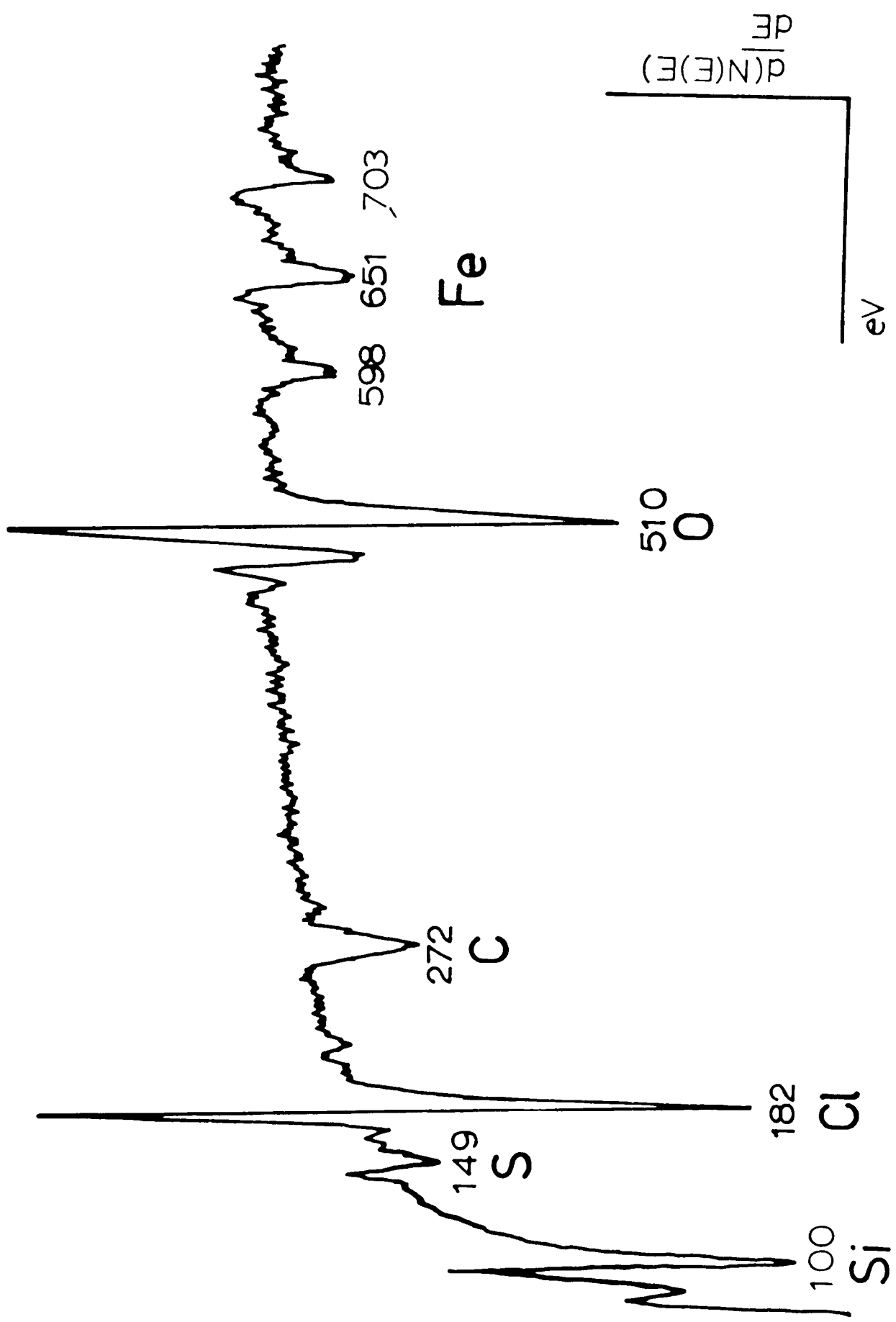
$$C_{Cl}:C_C = 0.94$$

$$C_O:C_C = 0.18$$

$$C_{Cl}:C_O = 5.10$$

Figure 5.2

Plot of Auger electron energy (E) versus $\frac{d}{dE}(N(E)dE)$ for a specimen of continuous discolouration. Incident beam energy ~ 2.5 keV. Sensitivity 3mV. (N(E) is the number of electrons with energy E.)



Clearly these results are consistent with those obtained using ESCA; the chlorine and oxygen contents have both increased relative to the carbon content, and the oxygen appears to have increased relative to the chlorine concentration.

Sulphur and silicon both appear on this spectrum, although neither was present in the weak boundary layer. The sulphur was a contaminant deriving from a fluorescent specimen also in the chamber, and the silicon remained as silicon carbide after the abrasion and washing of the substrate. This will be considered again below, but the relative concentrations of silicon and carbon at the surface were 2.35:1.

(c) TEM

Areas of film were removed from untested, discoloured discs using a scalpel, and taking care to include as much of the discolouration from the substrate as possible. Specimens were taken from lacquers based on several grades of "Alloprene", some of which had been stored for six months before the films were cast, and also from the hydrochlorinated lacquer.

A thin film of carbon was evaporated onto the lower side of the pieces of lacquer, i.e. the face covered in the "rust"-like deposit; this provided a thin, continuous, conducting film to support the deposit. The lacquer was dissolved away using toluene, and fragments of the remaining deposits were mounted on copper grids for examination in the transmission electron microscope.

Two different diffraction patterns were obtained from the lacquer which had been stored before the films were cast. The first (Figure 5.3a) derived from needle-shaped crystals (Figure 5.3b) which lay in the plane of the specimen, which was originally the plane of the mild steel substrate. These ranged in size from approximately $(0.1 \times 0.02)\mu\text{m}$ to $(3 \times 0.4)\mu\text{m}$. The plane spacings were calculated using the expression $Dd = 2\lambda L$, where D is the diameter of a particular ring in the diffraction

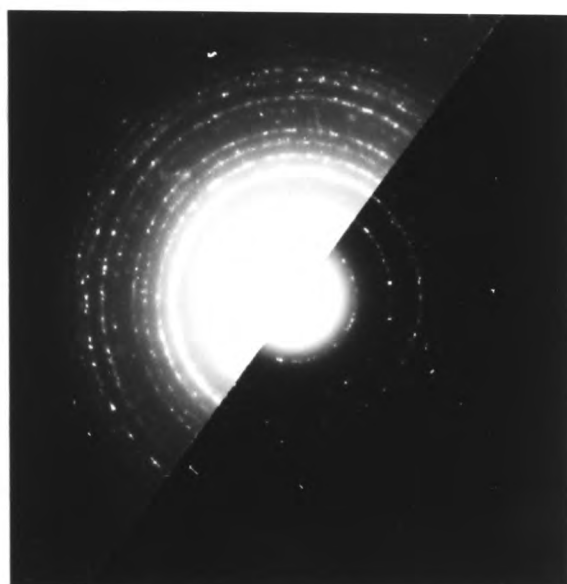
Figure 5.3a

Diffraction pattern obtained from crystals of β .FeO.OH.

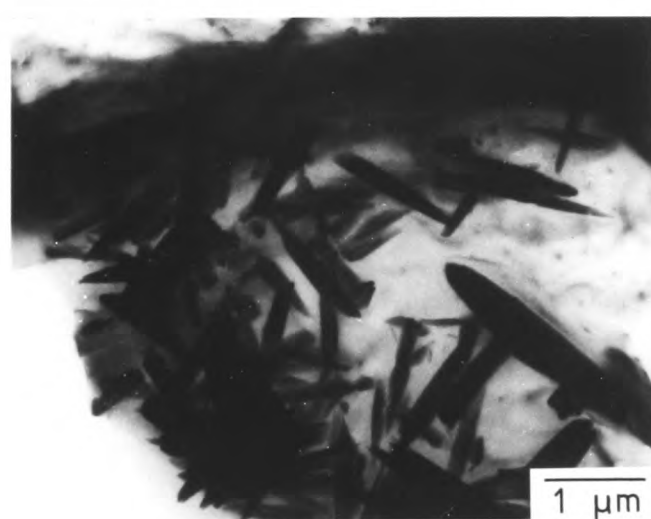
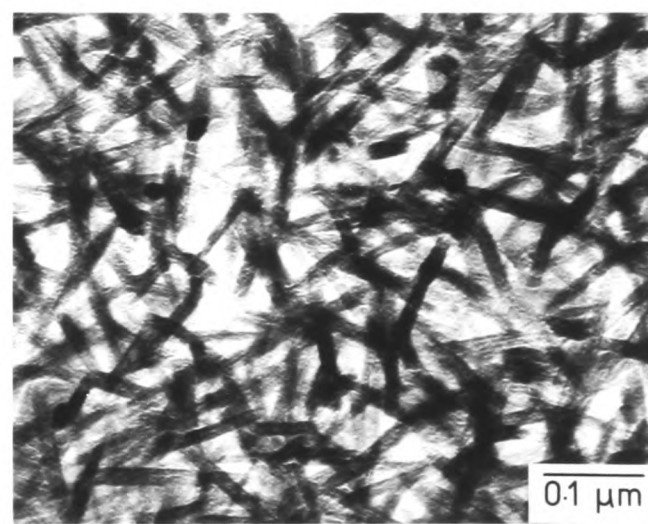
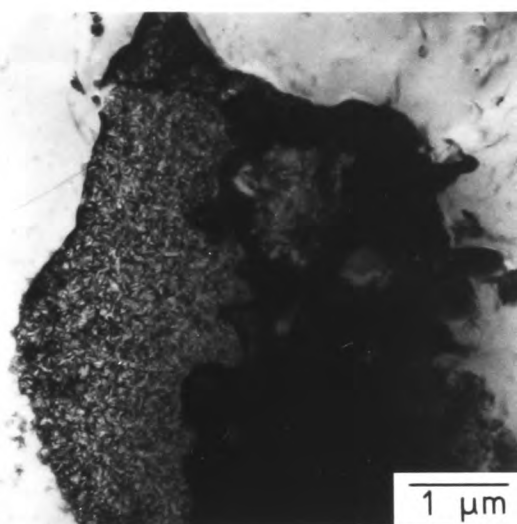
Figure 5.3b

Needle-shaped crystals of β .FeO.OH.

a.



b.



pattern; d the relevant plane spacing; λ the electron wavelength of 0.037 Å; and L the camera length, or distance from the specimen to the photographic plate, in this case L was evaluated graphically to be 71.67cm. The spacings calculated and relative intensities coincide with those given in the ASTM index [1] for β .FeO.OH, or akaganeite, they were as follows:

<u>Experimental</u>	<u>Theoretical</u>	<u>Relative Intensities</u>	<u>hkl</u>
Å	Å		
7.57 [*]	7.40	100	110
5.30	5.25	40	200
	3.70	10	220
3.31	3.311	100	310
2.58	2.616	40	400
2.53	2.543	80	211
	2.343	20	420
2.30 [*]	2.285	40	301
2.08 [*]	{ 2.097	20	321
	{ 2.064	20	510
1.96	1.944	60	411
	1.854	10	440
1.74	1.746	40	600
	1.719	10	501, 431
1.63 [*]	1.635	100	521
	{ 1.515	40	002
1.49	{ 1.497	20	611
	1.480	20	112, 710 ⁺
	1.459	10	640
1.43	1.438	80	541
1.36	1.374	40	730, 312

(* brightest rings)

β .FeO.OH has a tetragonal structure

The second diffraction pattern is shown in Figure 5.4a, and the type of area from which it is derived in Figure 5.4b. These appeared to be platelets which were single crystals lying in the plane of the

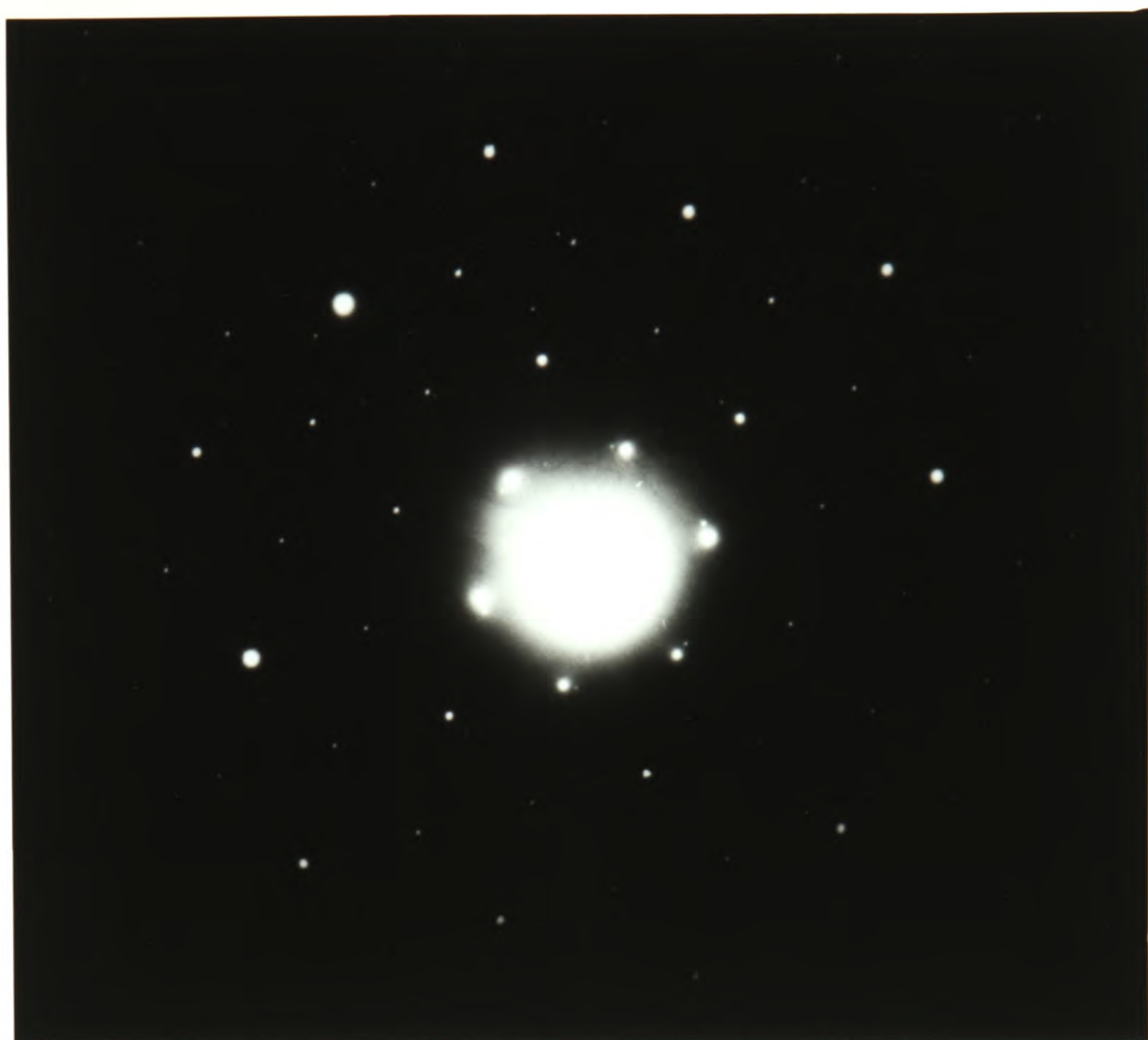
Figure 5.4a

Hexagonal spot diffraction pattern obtained from specimen of continuous discolouration.

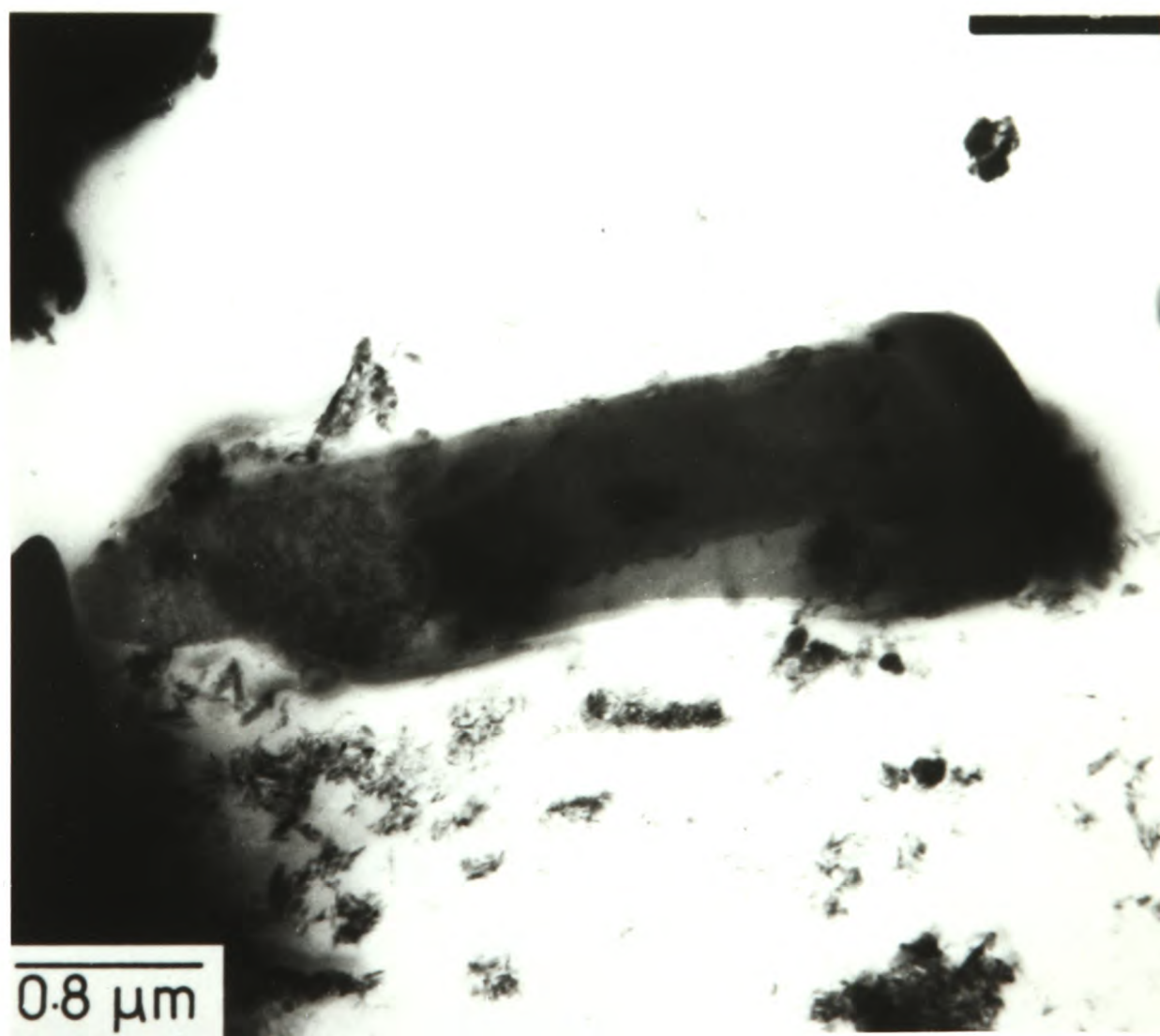
Figure 5.4b

Plate-like crystal from which (a) is obtained.

a.



b.



specimen. The hexagonal spot pattern corresponded with plane spacings as follows:

Experimental $\bar{A}$

4.49*

2.65

(2.55 clear spot, not on the hexagonal net)

2.23

1.71

1.52*

1.31

1.28

1.13

0.91

0.86

0.75

0.64

0.57 (* brightest spot)

However, these spacings do not coincide with any of those given in the ASTM index, so further investigations had to be made to attempt to identify the chemical elements present in the crystal.

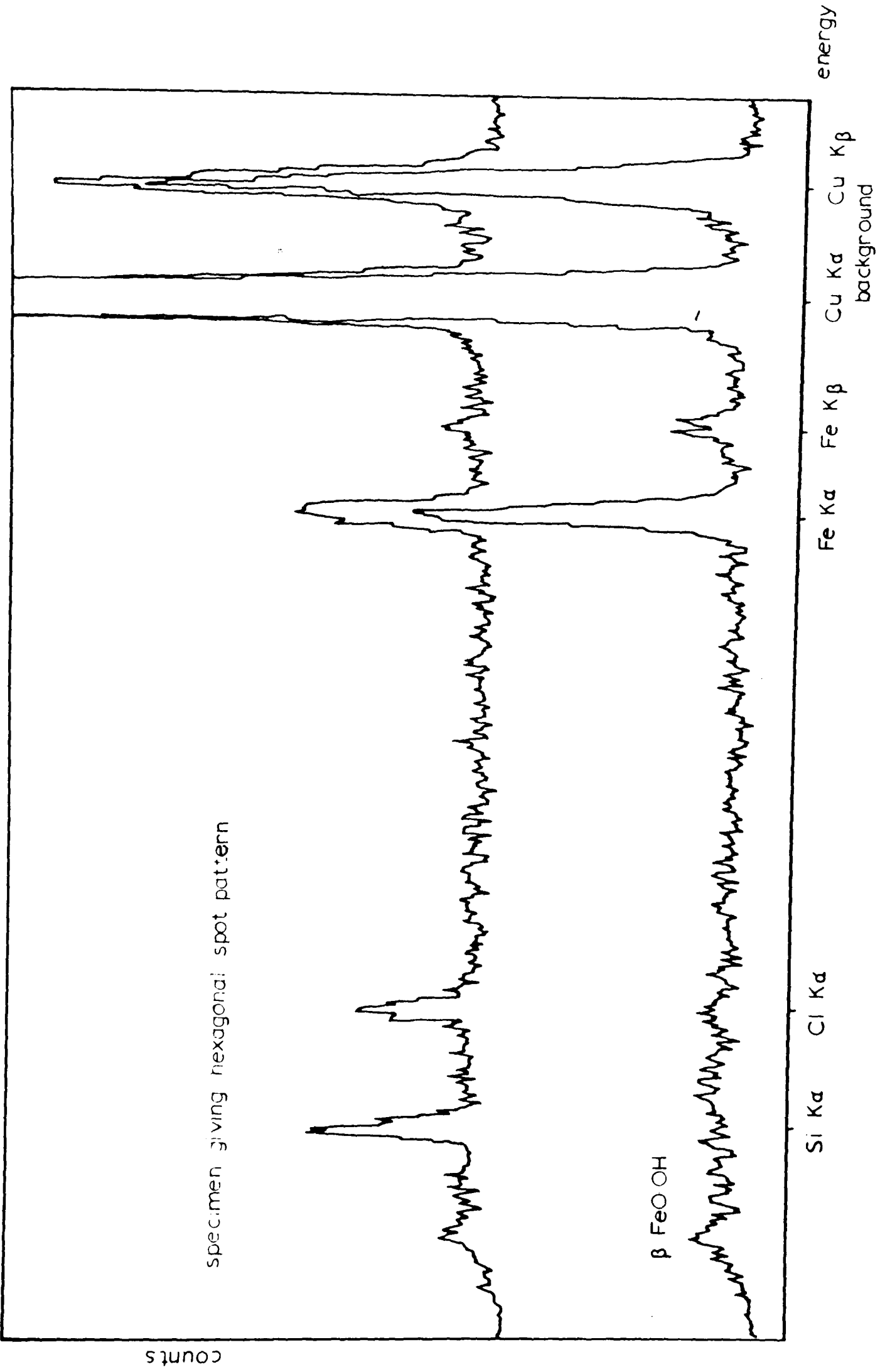
The specimens from the hydrochlorinated lacquer contained the same two compounds, but the platelets were much more abundant, and the specimens obtained from a lacquer which had not been stored appeared to contain only the β -FeO.OH.

(d) EDAX

The same specimens were examined using the energy dispersive analysis of X-rays technique, to identify the elements present by the X-rays emitted from them. Figure 5.5 shows a superposition of the EDAX plot obtained from both the β ferric oxide-hydroxide, and the unknown compound. The latter clearly contains silicon, iron and chlorine, although oxygen, hydrogen and carbon may be present but cannot be

Figure 5.5

Spectra obtained using EDAX for specimens of β -FeO.OH and the unidentified compound.



detected as their X-ray wavelengths are too long.

Thus, it appears that some chemical interaction is occurring between the lacquer, the iron of the substrate and silicon carbide remaining on the substrate surface after abrasion and cleaning. The small quantity of silicon present in mild steel (0.05% maximum by weight [5]) is too small to produce the comparatively large amount of this compound observed. The compound produced forms crystals in the region of $4\mu\text{m} \times 1\mu\text{m}$ in dimension, which are less than about $0.1\mu\text{m}$ in thickness. They lie in the plane of the film/substrate interface.

The quantity of this compound is increased by the presence of free hydrogen chloride in the film, as shown by its increased concentration in the specimen from the hydrochlorinated lacquer. It should be noted that the specimen from the stored lacquer also contained this compound, but in smaller quantities, and that from the fresh lacquer did not contain any. This implies that free hydrogen chloride may be produced by the decomposition of the lacquer on storage, as considered in earlier chapters.

Remy [6] records that although silicon carbide is extremely chemically resistant, at high temperatures it is attacked slightly by chlorine; however, Bailar *et al.* [2] record that chlorine attacks silicon carbide vigorously at 100°C , producing silicon tetrachloride and carbon.

Thus, it is possible that at room temperature, and in the unusual and confined environment at the lacquer/substrate interface, a reaction involving chlorine ions and silicon carbide may occur, at a fairly low rate. Although some compound other than silicon tetrachloride is formed, as the iron from the substrate is also involved in the reaction. The results of the investigation using ESCA suggest that this compound may contain chloride or carbonate features, and may not have a simple structure.

5.3 EXAMINATION OF "CELL STRUCTURE"

Figure 5.6 shows four discs which were stored in a closed wooden box for three months after coating. "Cell"-like discolouration had developed on these discs, and the surface of the film, which was originally smooth, after storage showed an unevenness similar to quilting, the surface being raised at points directly above the circumference of each "cell". The discolouration was dark brown around the edge of each "cell", and a lighter and less dense colour towards the centre, it was also most severe around the edge of each disc, and on further storage the number of "cells" increased until each disc was completely discoloured. This may be observed by reference back to Figure 5.1, where the discs in the left-hand column are most severely discoloured.

This discolouration was not removed when the lacquer was dissolved in toluene, and was once again occurring at the lacquer/metal interface.

(a) Optical and scanning electron microscopy

Cross-sections of the specimens were prepared in order to investigate the cause of the change in the contours of the film surface.

These were prepared in the following way:

- (i) Discs were cut on a milling machine in the direction perpendicular to the coated surface. The tool speed was 100 rpm with 2cm min^{-1} feed. About one-third of the diameter of each disc was cut away in steps of 0.076cm per cut, and finished with one cut of 0.013cm. Four discs were cut together, with a sheet of paper placed between each one to protect the lacquer, and the coated surfaces positioned towards the body of the machine.
- (ii) Two discs at a time were clamped in a special polishing vice (Figure 5.7), to minimise edge rolling during polishing, and the cut edges were then rubbed down on successively finer grades of carborundum paper, with cold water continuously flowing over them. (220, 320, 400, 600 grades.)
- (iii) The specimens were finally polished with $1\mu\text{m}$ Dialap diamond paste

Figure 5.6

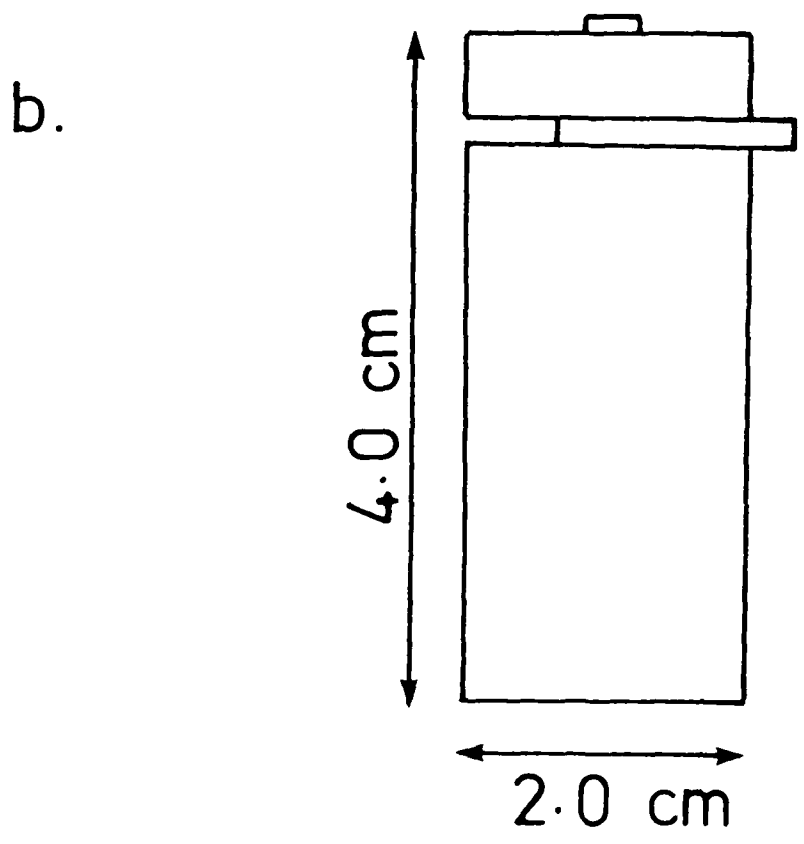
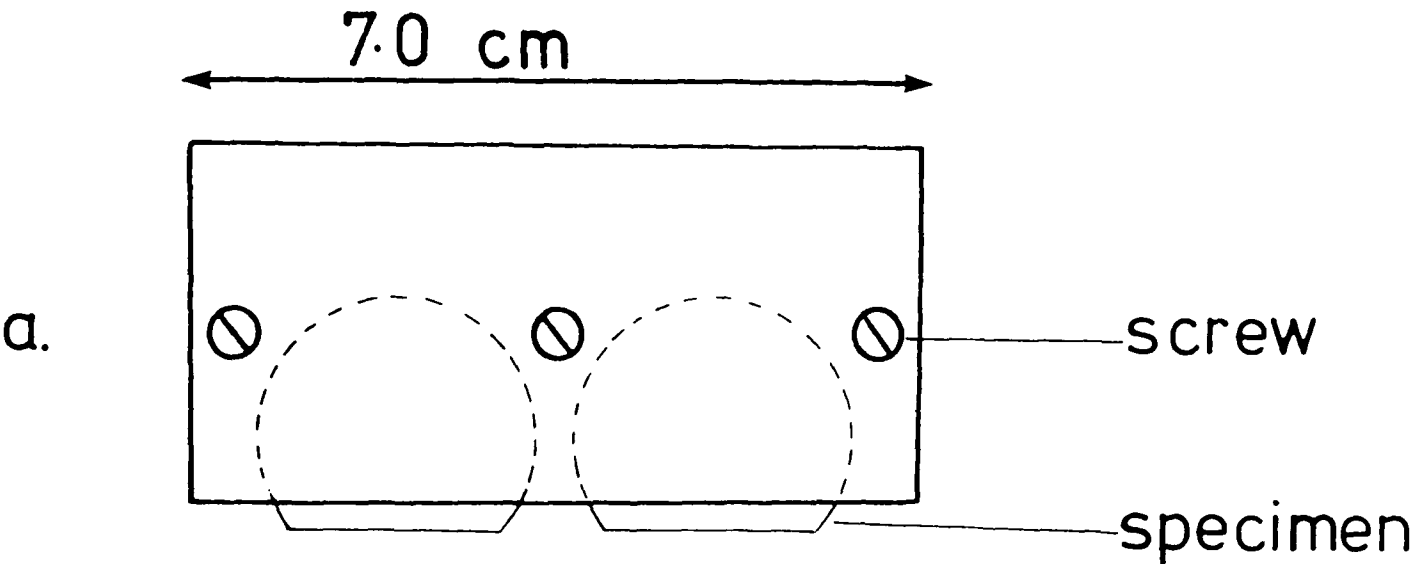
Examples of "cell"-like discolouration, showing the unevenness which develops in the surface of the film.

1.1 cm



Figure 5.7

Diagram of the polishing vice, designed to minimise edge rolling in the specimen during polishing. (a) Plan view. (b) Elevation.



on a rotating polishing wheel. Paraffin was used as a lubricant as it does not damage the lacquer.

- (iv) Finally the discs were washed in hot water and absolute alcohol, and stored in a desiccator at atmospheric pressure to await examination.

Figures 5.8a and b are optical micrographs of the interfacial region; Figure 5.8a shows the contours of the edge of the mild steel substrate and Figure 5.8b shows the "rust"-coloured compound in this region. The discolouration appears to extend into the lacquer, and there is no clear point where the compound ends and the lacquer begins, as there is in the case of the substrate in Figure 5.8a. Figure 5.9 is a scanning electron micrograph of an area of the interface where discolouration had not occurred.

A thin film of gold was evaporated onto the surface of the specimen before examination in the scanning electron microscope, to produce a conducting layer and prevent charging of the lacquer. Figure 5.10 shows scanning electron micrographs of two regions of the film, each at two magnifications. The edge of the substrate is indicated by the arrows, but a layer of encrustation may now be observed above this, which was not visible in the optical micrographs. However, there is no clear boundary to the lacquer region.

There appear to be large areas where there is no contact between the upper and lower regions of the interface. However, it is suggested that interaction products had, in fact, been carried away either by the polishing action or the washing process. Anything which was water soluble would be removed. If such large voids were present at the interface the failure stress of such systems would be much lower than for specimens which had not discoloured. However, from the tensile tests which were carried out on such specimens, this did not appear to be so. After testing, the surface of such a specimen contains pits (Figure 5.11), which were not observed in the regions of weak

Figure 5.8a

Optical micrograph of a cross-section through the specimen, showing the contours of the surface of the substrate.

Figure 5.8b

Optical micrograph showing the "rust"-coloured compound occurring in the region shown in (a) above.

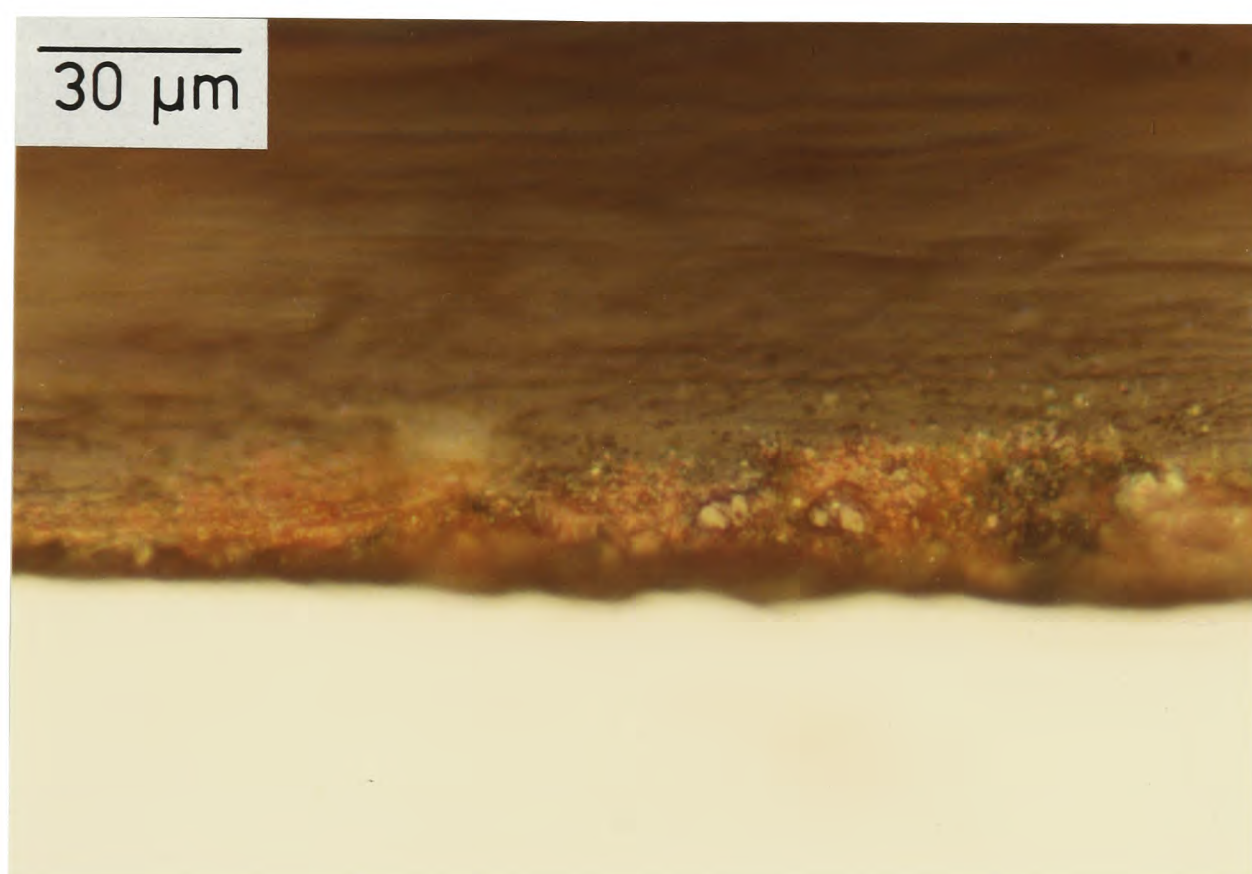
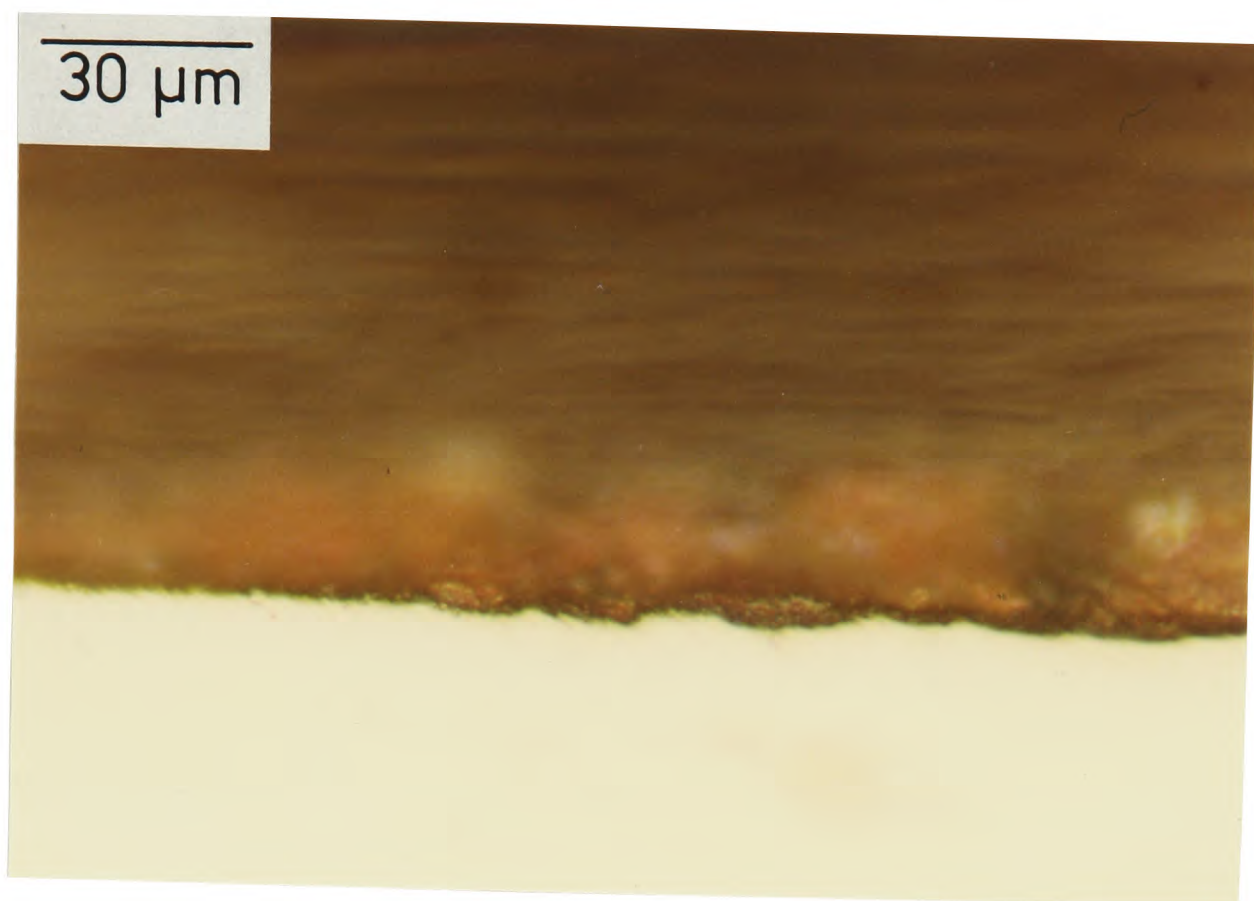


Figure 5.9

Scanning electron micrograph of a cross-section through the specimen in an area where discolouration had not occurred.

20 μm

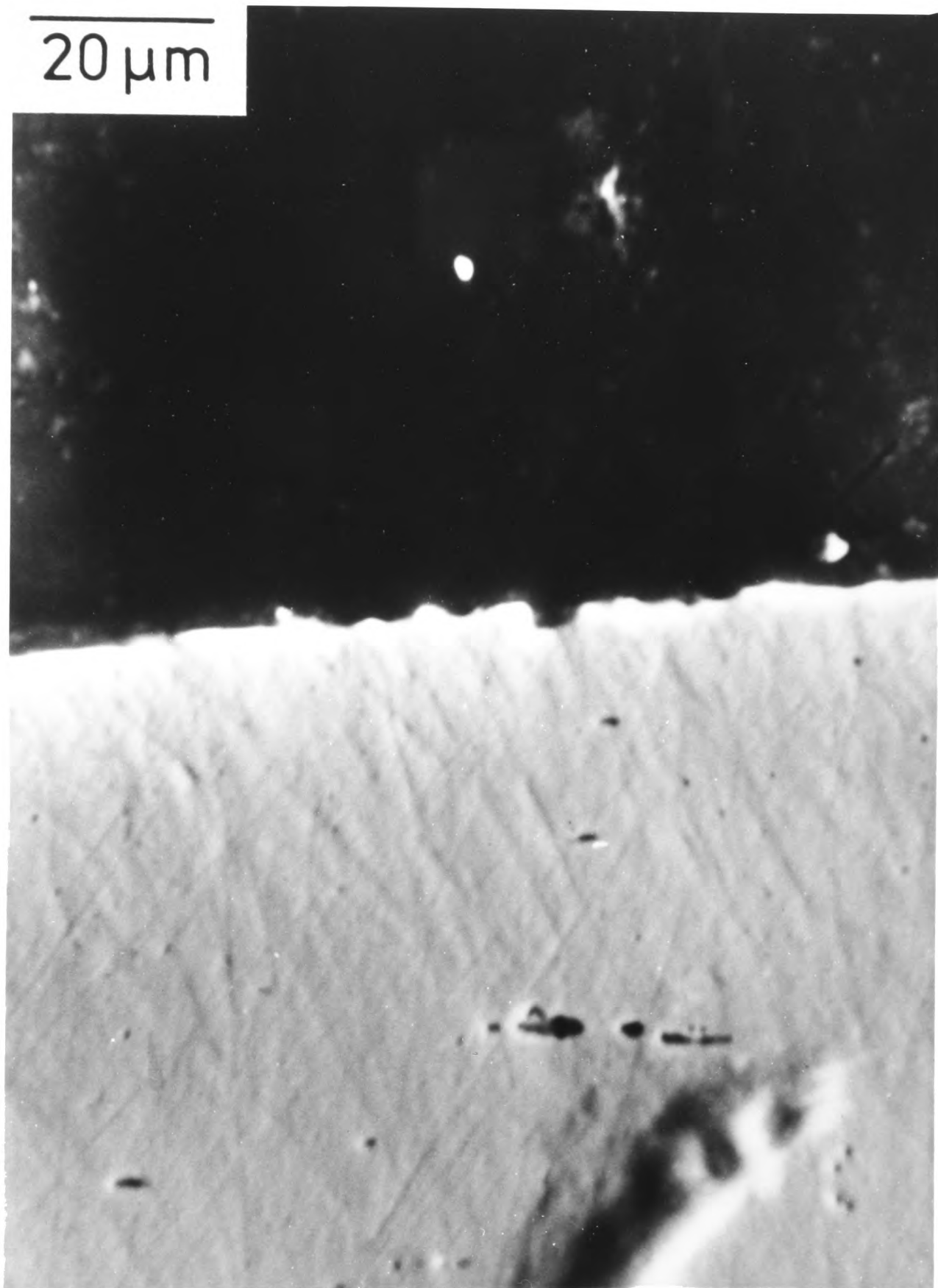


Figure 5.10

Scanning electron micrographs of two sections of the interfacial region. Arrows indicate the edge of the substrate.

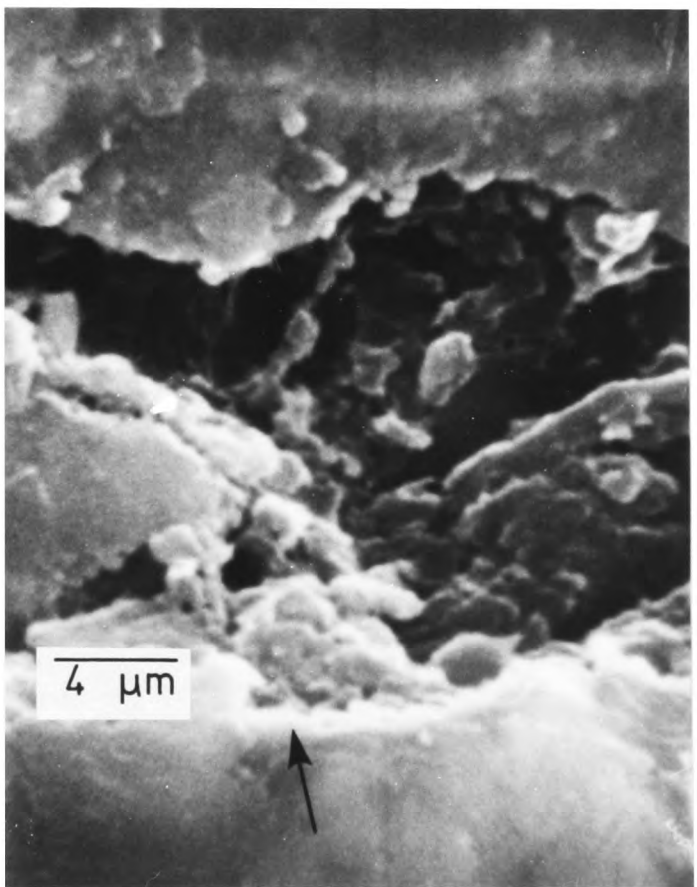
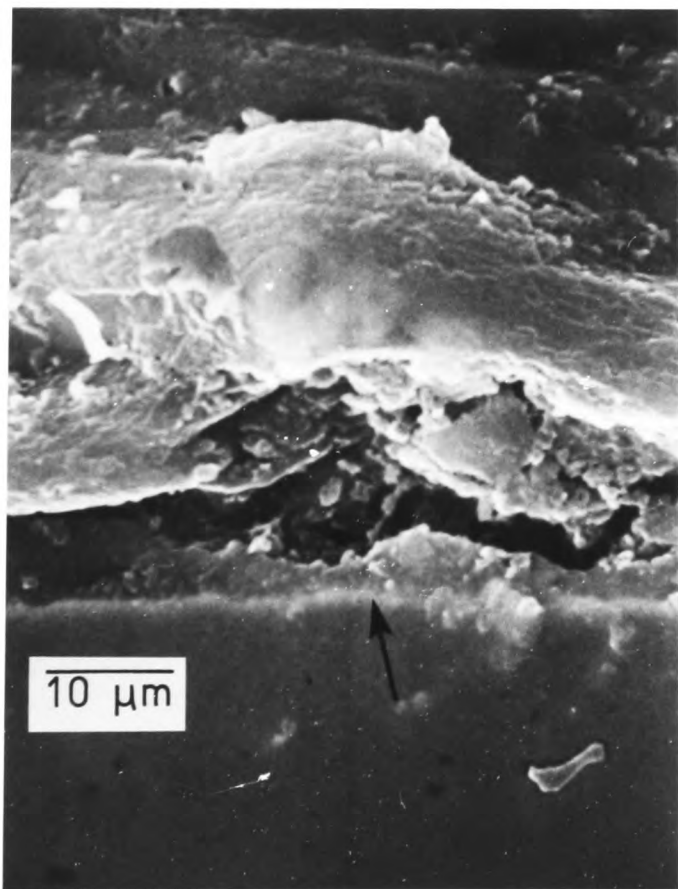
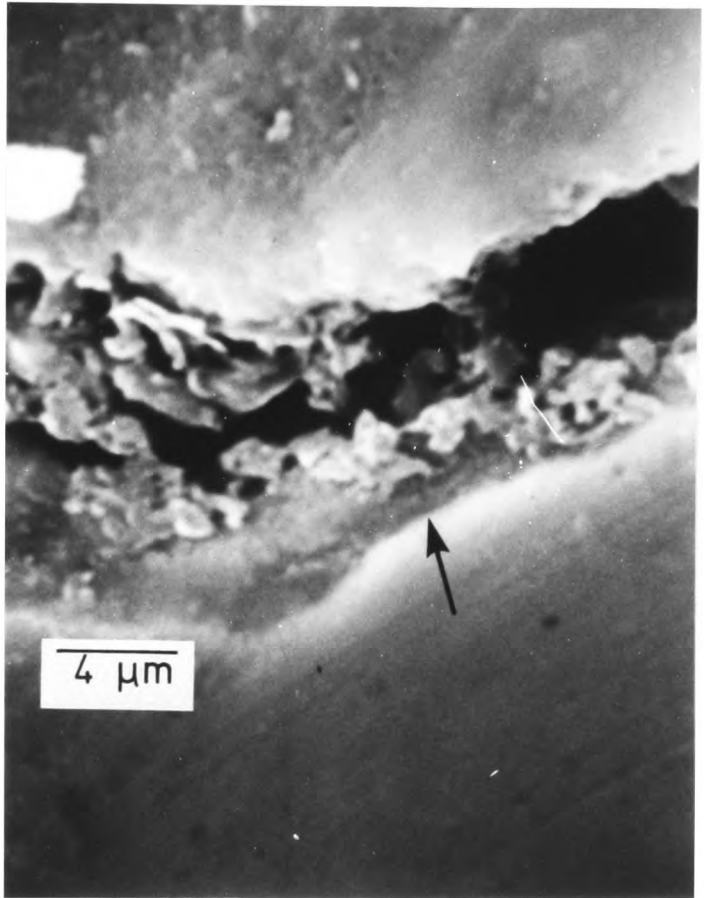
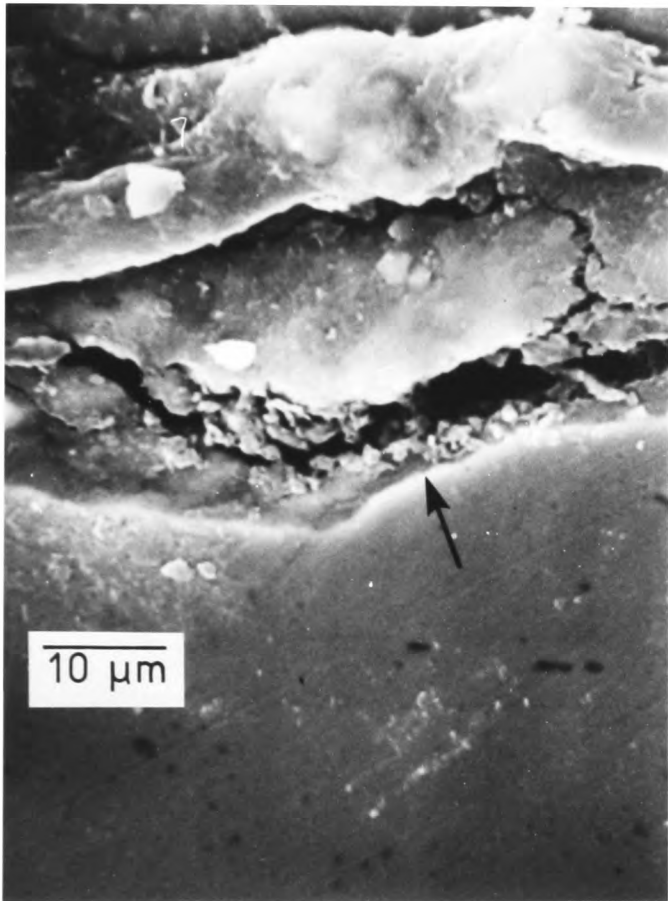
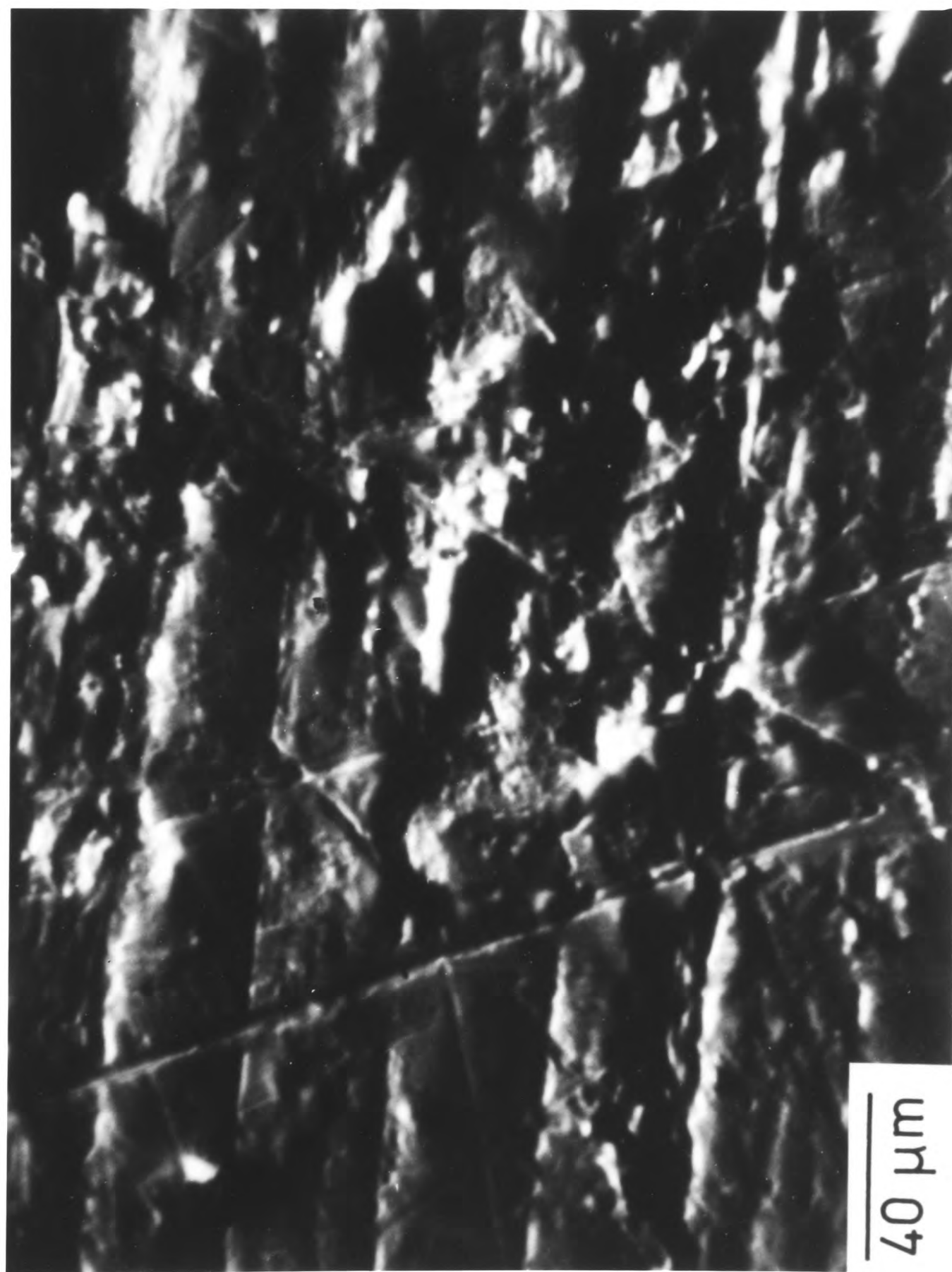


Figure 5.11

Scanning electron micrograph of the surface of a discoloured specimen after tensile testing.



40 μm

boundary layer failure of specimens which had not discoloured before bonding.

(b) TEM

Areas of lacquer were removed from the substrate using a scalpel, as described above; a carbon film was evaporated over the discoloured surface, and the lacquer dissolved away in toluene. Small pieces of the deposit were mounted on copper grids for examination in the electron microscope.

Once again the crystals of $\beta\text{-FeO.OH}$ were detected, and the platelets which gave a hexagonal, spot diffraction pattern. However, these were only present in small quantities. The dominant diffraction pattern is shown in Figure 5.12. This is a combination of the ring pattern shown in Figure 5.13, and a spot pattern. Both the patterns occasionally occurred alone, and Figures 5.14 and 5.15 show examples of the areas on the specimen from which each pattern derived. However, the patterns occurred most frequently together, and the plane spacings calculated from the diffraction patterns are:

<u>Experimental</u>	<u>Spot Pattern</u> Å	<u>Ring Pattern</u> Å
	2.73	2.59
	2.09	1.52
	1.65	
	1.56	
	1.44	
	1.18	
	1.02	
	0.91	
	0.84	
	0.77	

It has not been possible to identify either of these compounds, as their plane spacings do not coincide with any recorded in the ASTM index [1].

However, Figure 5.16 shows the EDAX plots obtained from each compound and it may be observed that the compound giving the ring pattern

contains at least iron, chlorine and a trace of silicon; while that giving the spot pattern does not contain chlorine or silicon, but does contain iron. Oxygen, hydrogen or carbon may also be present in either of them, but cannot be detected using this technique.

Figure 5.12

Dominant diffraction pattern
obtained from "cell"-like
discolouration

Figure 5.13

Ring pattern component of
5.12

Figure 5.14

Area of the specimen from
which the spot pattern in
5.12 is obtained.

Figure 5.15

Arrow indicates the area
of the specimen from which
the ring pattern in 5.13 is
obtained.

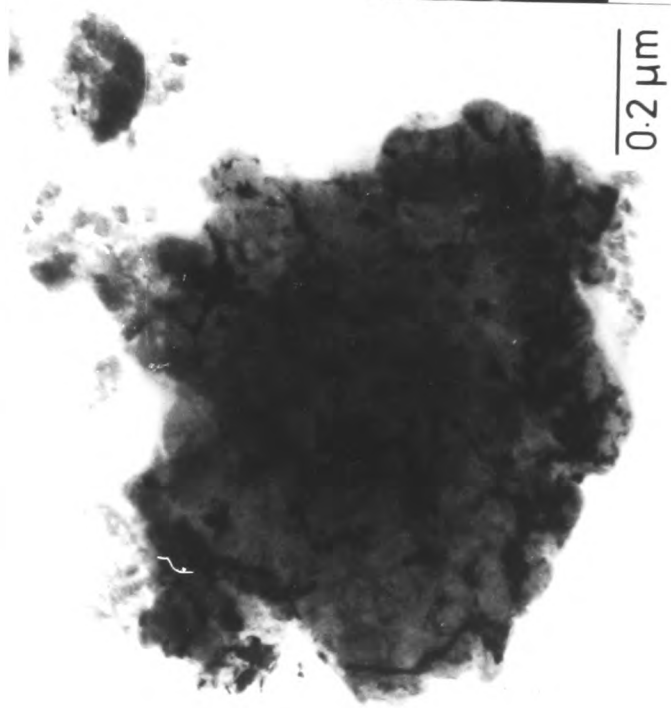
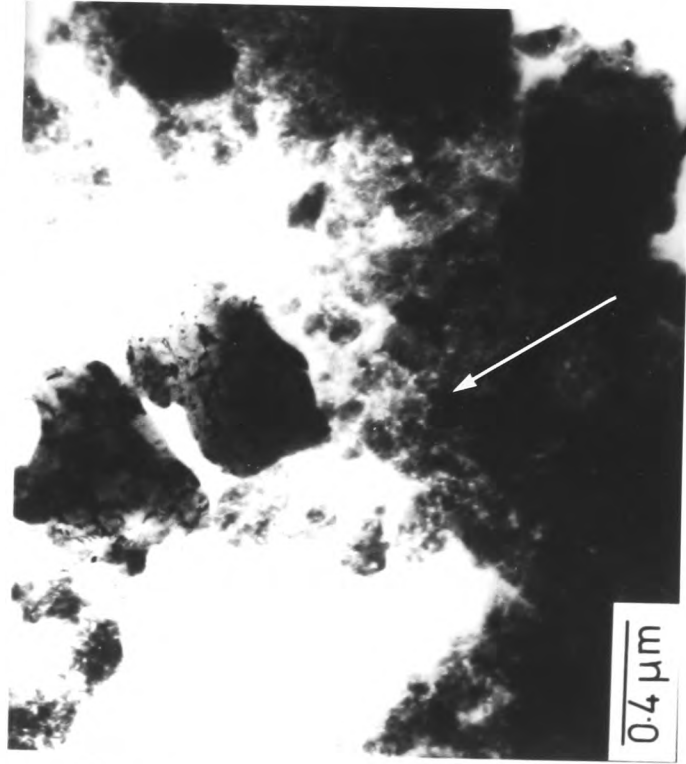
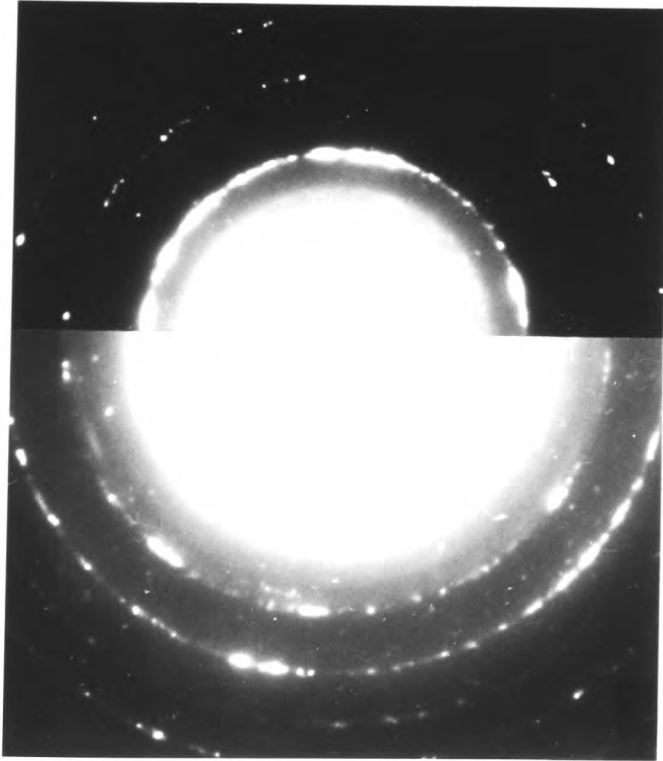
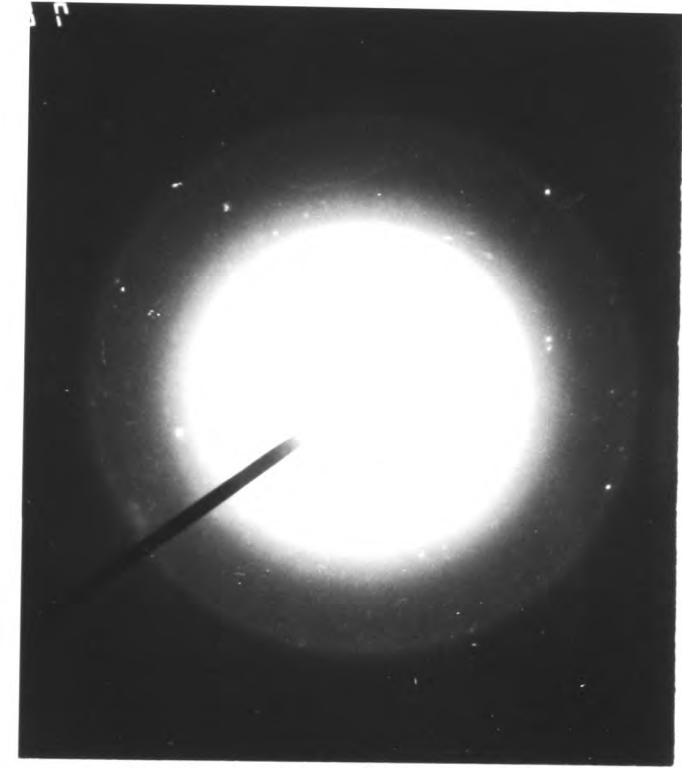
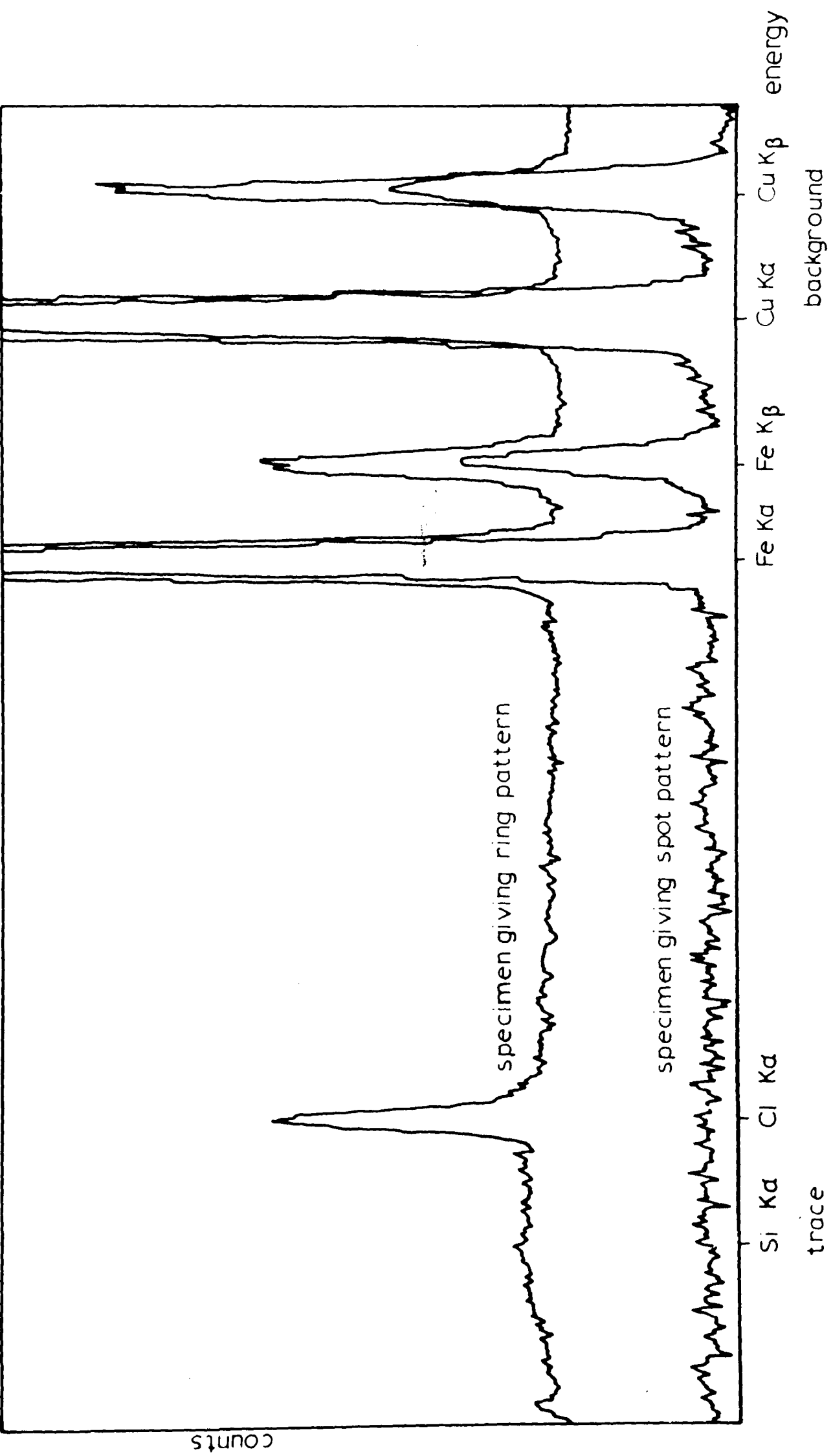


Figure 5.16

Spectra obtained using EDAX for compounds occurring in the "cell"-like discolouration.



5.4 DISCUSSION AND CONCLUSIONS

Some comparison may be drawn between the interactions discussed in this chapter, and filiform corrosion (FFC). Van der Berg *et al.* [7] describe it as a form of corrosion which occurs on both painted and unpainted metals, and is characterised by more or less constricted rust filaments with uni-directional growth from an active "head", which is continuously converted into an inactive "tail". They suggest that the corrosion mechanisms which cause FFC and general rusting of painted steel may have a lot in common.

In the "head" region of a filament stimulated by the presence of Cl^- ions Van der Berg *et al.* detected $\beta\text{-FeO.OH}$, which resulted from ferrous hydroxides being oxidised in the presence of the Cl^- ions. However, in the tail $\gamma\text{-FeO.OH}$ and $\alpha\text{-FeO.OH}$ were detected, which have not been found in the specimens discussed above.

Van der Berg *et al.* also found that under certain circumstances $\beta\text{-FeO.OH}$ reinforced the adhesion at the interface. This is consistent with the results obtained from tensile tests on aged films.

Another comparison which may be relevant is the formation of "Benard cells" in pigmented films. The mechanism of their formation is described in Figure 5.17. Small convection cells develop in the paint as it cures, or dries, which carry pigment particles upwards to the film/air interface. As the film becomes more viscous, and finally sets, the particles are held at the circumference of each cell. Thus, markings very similar to those observed in the "cell"-like discolouration are formed on the surface of the film. It is possible that a similar mechanism may be involved in the case of the unpigmented film; loose particles may be lifted from the substrate surface, into the film, but as the lacquer is fairly viscous when the film is cast they remain close to the interface. Here the conditions are such that some chemical interaction takes place between the film and the particles - whether fragments of the substrate material, or silicon carbide - thus

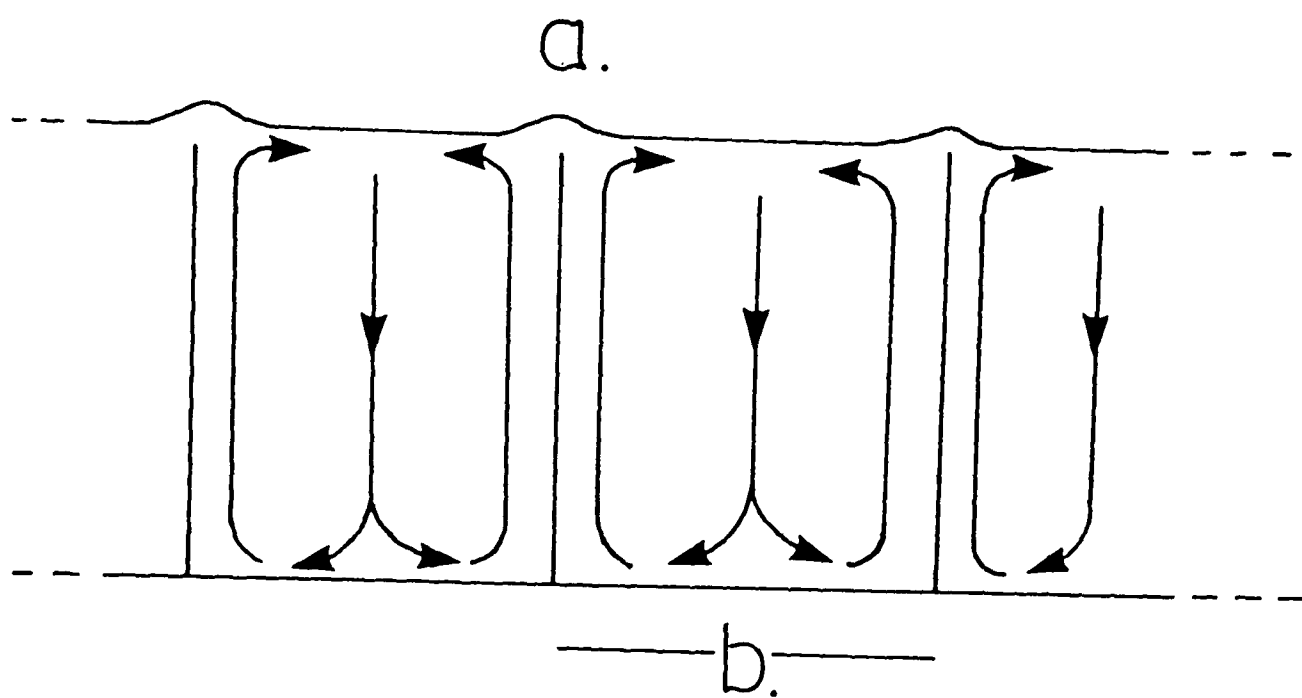


Figure 5.17

Schematic representation of the formation of "Benard Cells".
 (a) Unevenness of the surface occurring at the circumference of each cell, where pigment may be deposited. (b) Diameter of the cell. The arrows indicate the direction of motion within the convection cell.

forming a "cell"-like discolouration in the interfacial region. Several points have not yet been resolved, for example how the presence of excess hydrogen chloride in the lacquer accelerates the formation of the continuous film of discolouration, and in particular the compound which gives a hexagonal, spot diffraction pattern. Also, how the conditions of storage affect the interactions between the film and the substrate.

Although the structures of several of the compounds present do not match any of those given in the ASTM tables, it is possible that they may be compounds which normally have a particular crystal structure, but the unusual environment at the interface promotes the formation of different crystal structures, or even non-stoichiometric compounds.

It is clear that silicon carbide plays an important part in these reactions, which suggests that some other abrasive medium should be used. However, as it does not appear to have a destructive effect on the bonds between the film and the substrate this may not be necessary from a practical point of view.

Although these interactions have not been reported previously, it is likely that they also occur between pigmented films and a mild steel substrate, and their presence masked by the pigmentation.

References - Chapter Five

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CHAPTER SIX

THEORETICAL TREATMENT

C H A P T E R S I X

THEORETICAL TREATMENT

6.1 INTRODUCTION

In previous chapters it has been suggested that Van der Waals forces alone may be sufficient to provide the adhesive forces binding the lacquer to the steel substrate. The literature provides many expressions for calculating these forces when simple molecules are adhering to simple substrates, but no attempt has been made to apply such expressions to polymeric molecules on more complex substrates.

It was decided to investigate the possibility of making various approximations in order to obtain the magnitude of these secondary, physical or Van der Waals forces acting in the system under test, and to compare this with the experimental results obtained earlier, to make further deductions about the site of failure within the system.

Van der Waals forces may be divided into three components:

(a) Keesom force: this is an attractive force acting between two molecules possessing permanent dipoles, causing their mutual alignment - it is thus described as an orientation effect. The potential energy of this interaction is described by the expression

$$u_k = \frac{-2 \mu_1^2 \mu_2^2}{3kTR^6(4\pi\epsilon_0)^2}$$

(b) Debye force: one molecule possessing a permanent dipole induces a dipole in a second, non-polar molecule, thus producing an attractive potential described by the expression

$$u_D = \frac{-(\alpha_2 \mu_1^2 + \alpha_1 \mu_2^2)}{R^6(4\pi\epsilon_0)^2}$$

It is often described as the induction effect.

(c) London force: this is due to the random motion of the electrons within a molecule. Although the molecule may be non-polar in nature, it has an instantaneous dipole moment due to the motion of the electrons. This can interact with the instantaneous dipole moment which it induces in a second molecule resulting in an attractive potential between them. There are many expressions which have been used to describe this interaction, and those which will be considered in this discussion are presented in Table 6.1.

Although most of these formulae were originally devised for application to the problem of a spherically symmetric molecule adsorbed on a metal surface, it does not seem unreasonable to apply them to the case of polymeric macromolecules adhering to a metal surface. London himself said [14]:

"... for the long organic molecules it seems desirable to try to build up the Van der Waals attraction as a sum of single actions of parts of the molecule ... it seems quite plausible to build up in such a way the Van der Waals attraction of polyatomic molecules from single atomic interactions ..."

In order to calculate the attractive force exerted by a molecule on the metal surface, or on a second molecule, the formulae for the potential energy must be differentiated with respect to the separation, R .

The London force is often referred to as the "dispersion force", as the oscillator frequencies entering into the calculations involved are also those which enter into the theory of the dispersion of light. London [14] describes them as the "proper frequencies" of the electronic motion.

These forces are discussed in detail by London [14], Fowler [7] and Hinshelwood [9].

For the purposes of the calculation the film considered is composed of "Alloprene" R20 grade and "Cereclor 42" combined in the ratio 65:35 % w/w respectively, as the data supplied by ICI are relevant to this particular film composition.

For a non-polar polymeric film the only forces of attraction to a

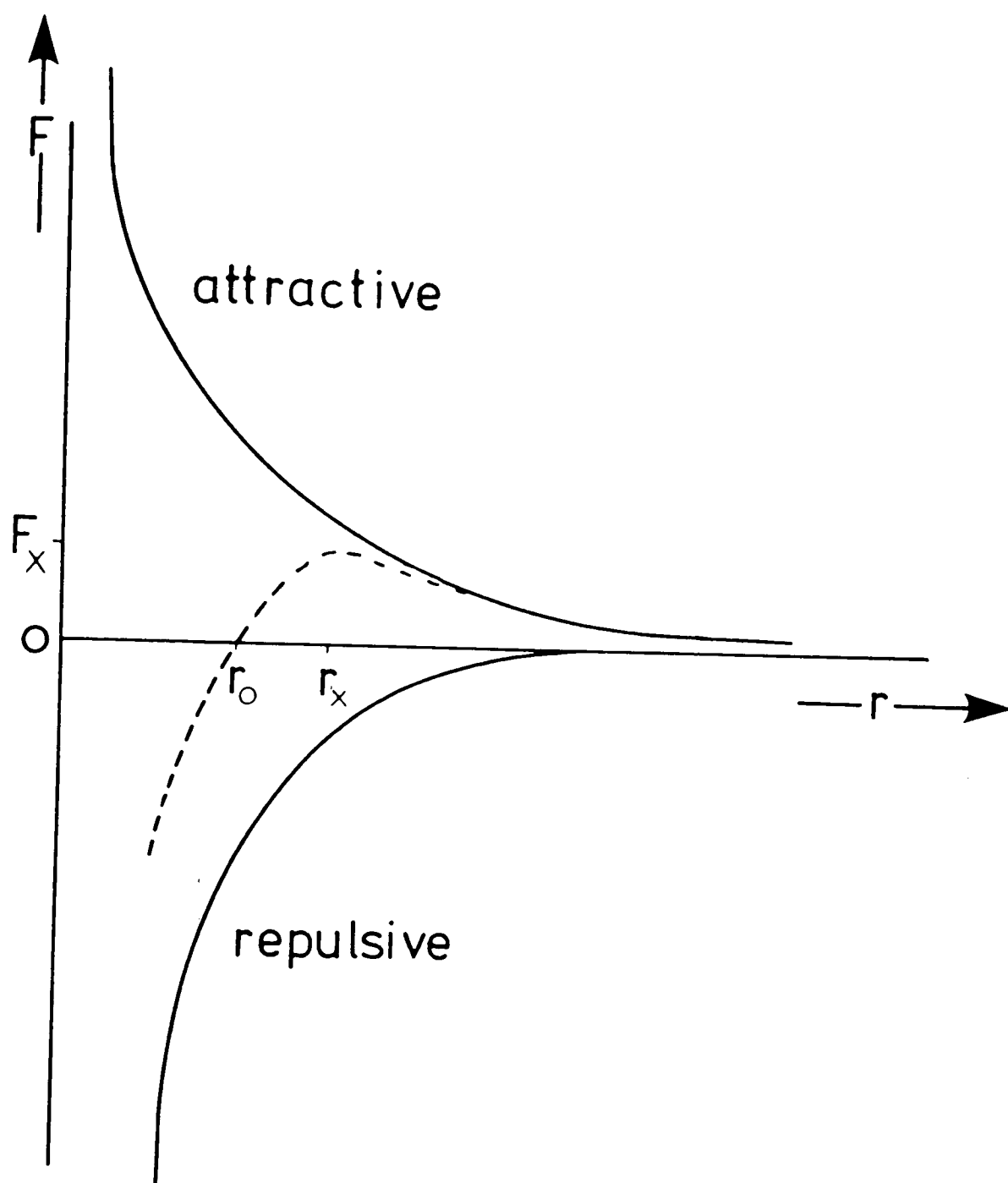
Author: Formula	Reference	Comment
(1) London: $U_L = \frac{-3I_1 I_2 \alpha_1 \alpha_2}{2(I_1 + I_2) R^6 (4\pi\epsilon_0)^2}$	[14]	It is assumed to be equal to $h\nu_0$; De Boer [5] states that $h\nu_0$ may be larger than I, and Pitzer [19] suggests that I should be increased by a factor of 2.25.
(2) London: $U_L = -\frac{3}{4} \frac{h\nu_0 \alpha^2}{R^6 (4\pi\epsilon_0)^2}$	[14]	$\nu_0 = e/(m\alpha)^{\frac{1}{2}}$. Only applicable to forces of cohesion. Derived by Fowler [7], Hinshelwood [9] and London [14].
(3) Prosen and Sachs: $U_L = \frac{-\alpha e^2 k_m^2 \ln(2k_m R)}{8\pi^2 R^2 (4\pi\epsilon_0)^2}$	[20]	$k_m^3 = 3\pi\rho$. Based on quantum mechanical perturbation theory. Derived for interactions between a molecule and metal surface. Cannot be applied to cohesion.
(4) Czyzak: $F_L = \frac{n_0^3 \alpha_1 I_1 I_2}{24 R^3 (I_1 + I_2) (4\pi\epsilon_0)}$	[3]	Based on a quantum mechanical calculation. F_L = force per unit area acting between a metal and a molecular layer on the surface. Once again $I \sim h\nu_0$.
(5) Margenau: $U_L = \frac{-3e\hbar\alpha_1 \alpha_2}{2R^6 M^{\frac{1}{2}} \left[\left(\frac{\alpha_1}{N_1}\right)^{\frac{1}{2}} + \left(\frac{\alpha_2}{N_2}\right)^{\frac{1}{2}} \right] (4\pi\epsilon_0)^2}$	[15]	Derived for a molecule on a metallic surface, may be adapted to calculate forces of cohesion.
(6) Slater and Kirkwood: $U_L = -\frac{1}{R^6} \frac{3eh}{8\pi(4\pi\epsilon_0)^2} \sqrt{\frac{N\alpha^2}{m}}$	[22]	Calculation based on quantum mechanical variation method. Formula quoted by London [14] and Margenau [15]. Only applicable to forces of cohesion, as it contains no information about a second atomic species.
(7) Lennard-Jones: $U_L = \frac{-mc^2\psi}{LR^3}$	[13]	Considered theory of mirror charges. Results obtained usually larger than expected. Discussed by Margenau and Pollard [16, 17], Bardeen [1] and Prosen, Sachs and Teller [21].

TABLE 6.1

Summary of formulae used to calculate the attractive London potential (U_L) between two molecules, or the London force per unit area (F_L) between a metal and a surface layer

Figure 6.1

Schematic representation of the force acting between two atoms (F), as a function of their separation (r). The dashed curve represents the sum of the attractive and repulsive interactions.



metal substrate are London forces. However, if a chlorine atom is substituted into the chain, then it will produce a C^+Cl^- dipole which will increase both the cohesive and adhesive interactions - bringing the Debye forces into effect. As metals do not possess dipole moments there can be no Keesom interactions between such a film and the substrate; however, within the film the C^+Cl^- dipoles can interact to produce an increase in the cohesive strength of the film.

Thus, in the system under consideration, the force of adhesion of the film to the substrate consists of London and Debye interactions; while the force of cohesion within the film consists of London, Debye and Keesom interactions.

It has been assumed that the substrate surface is purely metallic. As shown earlier, it is actually composed of ferric oxide, and a carbonaceous overlayer. This will be considered later when the theory has been developed, and the forces associated with a clean substrate have been evaluated.

It is no simple task to decide on a starting point for the calculations which follow. To quote Dekker [6]

"... there is no general, quantitative theory for (considering) dipolar solids ... therefore approximations have to be made in developing a theory which is applicable."

6.2 METHODS FOR CALCULATING THE ATTRACTIVE FORCES OF ADHESION AND COHESION

The film is composed simply of "Alloprene" and "Cereclor" in given proportions, and each polymer is itself composed of carbon, hydrogen and chlorine atoms combined together in known proportions. The structure of the film in terms of the orientation of the polymer chains cannot be specified, and it is assumed to be an homogeneous distribution of the three types of atom present.

Following London's suggestion [14] it is proposed to split up the macromolecule into smaller units, to find the energy involved in the interactions of each unit and combine these to give the energy associated with the interactions of a unit area of the film on the substrate, or in the case of the cohesive forces, on the film itself.

Two methods are proposed, and will be described below. Numerical calculations will then be carried out, and the results obtained from each theory will be compared and discussed.

(a) The "Average Element" Theory

This is basically a statistical approach to the problem, in which a theoretical model is constructed and numerical calculations based upon it, following ideas mentioned by De Boer [5].

Although the film is composed of two polymer species, each is made up of the same three atoms, carbon, hydrogen and chlorine, in known proportions. The model thus considers the film to be composed of a single polymer whose molecular weight is the average of those of "Alloprene" and "Cereclor", combined according to their relative abundance within the film. An "element" of this macromolecule is considered to be a section possessing properties which are the average of the properties of the H, C and Cl atoms, weighted according to their relative abundance in the film, and the number of "elements" per unit volume is equal to the total number of atoms per unit volume of the film.

Various additional data have to be calculated for this model, for example the value of the dielectric constant ϵ is known for the

film [10], and knowing the number of "average elements" per unit volume the value of α , the polarisability can be calculated. The distortion [18] or electronic [6] polarisability is calculated using a statistical combination of the values for H, C and Cl atoms, obtained from the literature [19]. This may possibly be justified by a quotation from Pitzer [19],

"... In calculations use single atoms rather than bonds, as location of atom centres is unambiguous, and the approximation of isotropic polarisability is better for an atom than a bond ... interactions between atoms have much less effect on the mean poarisability than on the anisotropy of the polarisability ... simple summation rules for the mean polarisability of a molecule, in terms of component atoms or bonds are sound to an approximation ..."

The value of the dipole moment, μ may be calculated for the element using the Clausius-Mossotti relationship [18], and the first ionisation potential and number of electrons in the outer shell are calculated statistically using the values for the H, C and Cl atoms [8].

Thus, the various expressions given earlier may be used for calculating the London and Debye forces acting between an average element of the film, and the steel substrate. It is assumed that these forces are only effective over a distance of one atomic diameter, so the values obtained must be multiplied by the number of average elements per unit area of the interface, i.e. by $n_0^{\frac{2}{3}}$ to find the attractive force per unit area.

The cohesive force per unit area is calculated in a similar way, but the Keesom force must be included here.

(b) The H/C/Cl theory

Although this would appear to be the most sound approach, and indeed the individual values calculated for the magnitude of the attractive force in a single interaction are possibly more accurate than in the previous theory, more problems are encountered when these individual interactions have to be combined to give the attractive forces per unit area.

As stated above, it is assumed that the film is an homogeneous distribution of C, H and Cl atoms, and the number of each atomic species per unit volume can be estimated. The values of distortion polarisability, α_0 for each atom were calculated, and agreed very closely with those available in the literature [19], and the values of I and N were also obtained from the literature [8].

The forces associated with the London and Debye interactions were calculated, to find the force acting between each individual atomic species and the substrate. These values were multiplied by the number of these particular atoms per unit area of the interface, and the results for the three species added to give the total attractive force per unit area.

The individual forces of cohesion were calculated in a similar way, including the Keesom contribution, but problems were encountered when these values had to be multiplied up and combined to give the total attractive force per unit area. The way in which this was done will be described in detail below.

In all calculations using equations (1), (4) and (5) in Table 6.1, for estimating the forces of adhesion, Kelvin's theory of image charges is assumed, so that $\mu_1 = \mu_2$ and $\alpha_1 = \alpha_2$, where subscript 1 represents the film, and 2 represents the substrate; as no values for polarisability and dipole moment are available for a steel substrate.

6.3 REPULSIVE INTERACTIONS

At the equilibrium separation of the atoms in question, r_o on the diagram in Figure 6.1, the attractive and repulsive forces between the atoms are equal, and the net force experienced is zero. However, as the interatomic separation is increased towards r_x the attractive force outweighs the repulsive force, and a maximum F_x is reached at separation r_x . F_x is defined as the force which must be applied to the bond in order to cause failure, the interatomic force decreases from this point as r increases, and the atoms may be separated.

Lennard-Jones [13] used the expression $u = -A/r^6 + B/r^{12}$ to describe the interatomic potential; $(-A/r^6)$ represents the attractive interaction, and (B/r^{12}) the repulsive interaction. A and B are constants.

The force,

$$F = \frac{du}{dr} = \frac{6A}{r^7} - \frac{12B}{r^{13}} = 0 \quad \text{at } r_o$$

$$\frac{dF}{dr} = -\frac{42A}{r^8} + \frac{12 \times 13B}{r^{14}} = 0 \quad \text{at } r_x$$

$$\therefore \frac{42A}{r_x^8} = \frac{12 \times 13B}{r_x^{14}}$$

$$\therefore r_x^6 = \frac{26B}{7A} \quad (1)$$

and

$$\frac{6A}{r_o^7} = \frac{12B}{r_o^{13}}$$

$$\therefore r_o^6 = \frac{2B}{A} \quad (2)$$

Thus, from (1) and (2)

$$r_o^6 = r_x^6 \frac{7}{13} \quad (3)$$

$$\begin{aligned}
 F_x &= \frac{6A}{r_x^7} - \frac{12B}{r_x^{13}} \\
 &= \frac{6A}{r_x^7} \left\{ 1 - \frac{12B}{r_x^{13}} \cdot \frac{r_x^7}{6A} \right\} \\
 &= \frac{6A}{r_x^7} \left\{ 1 - \frac{2B}{A r_x^6} \right\}
 \end{aligned}$$

But

$$\begin{aligned}
 \frac{2B}{A r_x^6} &= \frac{2B}{A} \frac{7A}{26B} && \text{from (1)} \\
 &= \frac{7}{13}
 \end{aligned}$$

$$\therefore F_x = \frac{6A}{r_x^7} \left\{ 1 - \frac{7}{13} \right\} = \frac{6A}{r_x^7} \frac{6}{13}$$

However,

$$r_o = r_x \left(\frac{7}{13} \right)^{\frac{1}{6}} \quad \text{from (3)}$$

$$\begin{aligned}
 \therefore F_x &= \frac{6A}{r_o^7} \left(\frac{7}{13} \right)^{\frac{7}{6}} \frac{6}{13} \\
 &= \frac{6A}{r_o^7} \times 0.224
 \end{aligned} \tag{4}$$

The attractive component of the interaction at equilibrium separation is $\left(\frac{6A}{r_o^7} \right)$, thus the force which must be applied to break the bond is 0.224 times this value.

London [14] used the Born and Mayer approximation $u = -A/r^6 + Be^{-r/\rho}$, and ρ was suggested to be approximately 0.345×10^{-10} m.

De Boer [5] found that in his work the experimental values he obtained were higher than those predicted by the above expressions, and

suggested that the equations used to calculate the force associated with the attractive London interactions should include terms proportional to r^{-8} and r^{-10} , instead of being truncated at terms of r^{-6} . This would produce an answer one-and-a-half times the original value, and would partly compensate for the repulsive interactions.

In the approximations carried out in this chapter the attractive component of the force at equilibrium separation will be evaluated, equivalent to $6A/r_o^7$, and multiplied by 0.224 to find the net force required to separate the atoms.

6.4 DATA NECESSARY FOR CARRYING OUT CALCULATIONS

The information already available is summarised below [10]:

Absolute density of "Alloprene R20"	$1.6 \times 10^3 \text{ kg m}^{-3}$
density of "Cereclor 42"	$1.16 \times 10^3 \text{ kg m}^{-3}$
density of combination	$1.414 \times 10^3 \text{ kg m}^{-3}$
Number molecular weight of "Alloprene R20"	57×10^3
molecular weight of "Cereclor 42"	570
Average molecular weight of film	37×10^3
Dielectric constant of film	3.9

The data which must be calculated for each individual model will now be considered.

The number of "average elements" per unit volume of the film is $6.26 \times 10^{28} \text{ m}^{-3}$, which gives a value of $n_o^{\frac{2}{3}}$ of $15.77 \times 10^{18} \text{ m}^{-2}$, and the atomicweight of this element is calculated to be 13.60. The values for I, N and α_o were calculated for the element using a statistical combination of the individual values for the H, C and Cl atoms, according to their relative abundance in the film, and are recorded in the Table 6.2.

The Clausis-Mossotti relationship [18] was used to calculate the total polarisability and dipole moment for the polymer film.

Using

$$\alpha = \frac{3\epsilon_o}{n_o} \frac{(\epsilon-1)}{(\epsilon+2)}$$

the value of α was calculated to be $2.08 \times 10^{-40} \text{ Fm}^2$. Assuming that the film is equivalent to a dilute solution of dipoles in a non-polar solvent, then

$$\frac{(\epsilon-1)}{(\epsilon+2)} \frac{3\epsilon_o}{n_o} = (\alpha_o + \frac{\mu^2}{3kT})$$

At a temperature of 300K the value of the dipole moment of the "average element" was found to be $1.05 \times 10^{-30} \text{ Cm}$. The dipole moments of the individual H, C and Cl atoms were assumed to be zero, as no data were available in the literature, but in calculations of the Debye and Keesom

forces for the H/C/Cl theory the magnitudes of the dipole moments of the H-C and Cl-C bonds were used; these are respectively $\underline{1.332 \times 10^{-30} \text{ Cm}}$ and $\underline{4.995 \times 10^{-30} \text{ Cm}}$ [12].

In the formula proposed by Prosen and Sachs [20] for the calculation of the London force, the electron density within the metal is required. The substrate is taken as being equivalent to iron, and it is assumed that there are two "free" electrons per atom [2]. The number of iron atoms per unit volume can easily be calculated from its density and atomic weight, and thus the electron density is calculated to be $\underline{\rho = 16.6 \times 10^{28} \text{ m}^{-3}}$.

The last value required is the equilibrium separation of the two atoms under consideration. The closest distance of approach at the interface is normally taken to be the sum of the radii of the molecules of the film and the metal atom. Thus, following Czyzak [4] and Kittel [12] the separation of the iron and chlorine atoms will be $\sim (1.26 + 1.81)\text{\AA} = 3.07\text{\AA}$. The separation of iron and carbon will be $\sim 2.25\text{\AA}$ and that of iron and hydrogen will be $\sim 1.79\text{\AA}$. This assumes that all atoms can come to their closest distance of approach. The average separation at the interface is $2.31\text{\AA}$, which is the separation considered in the "average element" theory, calculated from the contributions of each atomic species weighted according to their relative abundance at the interface.

<u>Property</u>	<u>Average Element</u>	<u>Hydrogen</u>	<u>Carbon</u>	<u>Chlorine</u>	<u>Units</u>
α_o	1.190×10^{-40}	4.671×10^{-41}	1.034×10^{-40}	2.536×10^{-40}	Fm^2
α	2.08×10^{-40}	-	-	-	Fm^2
μ	1.05×10^{-30}	-	-	-	C.m.
I	2.022×10^{-18}	2.179×10^{-18}	1.804×10^{-18}	2.084×10^{-18}	J
n_o	6.26×10^{28}	2.47×10^{28}	2.21×10^{28}	1.58×10^{28}	m^{-3}
$\frac{2}{n_o^3}$	15.77×10^{18}	8.48×10^{18}	7.88×10^{18}	6.30×10^{18}	m^{-2}
N	3.58	1	4	7	
w_A	13.60	1	12	35.5	
I	<u>Iron</u> 1.261×10^{-18}				J
N	2				
ρ	16.6×10^{28}				m^{-3}
μ	$\frac{\text{C-Cl}}{4.995 \times 10^{-30}}$ 1.332×10^{-30}	$\frac{\text{H-C}}{1.332 \times 10^{-30}}$			C.m.

TABLE 6.2
Data Necessary for Carrying out Numerical Calculations

The estimation of the atomic separation occurring within the film is more complicated, but will be described in detail below.

Consider atom A, the volume occupied by this atom in the film is V_0 , and the nearest-neighbour A atom distance is $2r = V_0^{\frac{1}{3}}$ (Figure 6.2a). If only the interaction with the nearest neighbouring A atom is strong, then the volume of film interacting with the atom is $V = \frac{4}{3}\pi(2r)^3$ or $V = \frac{4}{3}\pi V_0$.

For each A-A interaction broken during failure, half of the A/B, A/C interactions within volume V are also broken (Figure 6.2b). However, although the separation A-A is fixed at $2r$, the distances A-B and A-C cannot be fixed, and it is necessary to integrate the expressions for these interactions over the allowed separation.

Let N_B be the number of B atoms interacting with atom A. Let their closest distance of approach be the sum of their radii, and the furthest distance be $V_0^{\frac{1}{3}}$; these are represented by r_1 and r_2 respectively. Thus, the number of B atoms in the unit volume dV , surrounding atom A is $\frac{N_B dV}{\frac{4}{3}\pi(r_2^3 - r_1^3)}$. Thus, the total force

acting on atom A due to all the B atoms within the volume under consideration is
$$\int_{r_1}^{r_2} \int_0^{\pi/2} \int_0^{2\pi} \frac{N_B F(r) r^2 dr \sin\theta d\theta d\phi}{\frac{4}{3}\pi(r_2^3 - r_1^3)}$$

where $F(r)$ is the force acting between atoms A and B, at separation r ; this varies with r^{-7} in all the expressions which are applicable here.

Therefore the expression becomes

$$\frac{N_B 2\pi C}{\frac{4}{3}\pi(r_2^3 - r_1^3)} \int_{r_1}^{r_2} \frac{1}{r^5} dr = \frac{6N_B C}{16(r_2^3 - r_1^3)} \cdot \frac{1}{r^4} \Bigg|_{r_1}^{r_2}$$

where C represents the constant term in the expression for $F(r)$. This must be multiplied by the number of A atoms per unit area of the film to give the total force per unit area of the film due to A/B interactions.

A similar route must be followed to obtain the corresponding values for B/B, C/C, B/C and A/C interactions, taking care not to consider any interactions twice.

Figure 6.2a

Schematic representation of the model used for calculating inter-atomic distances within the film.

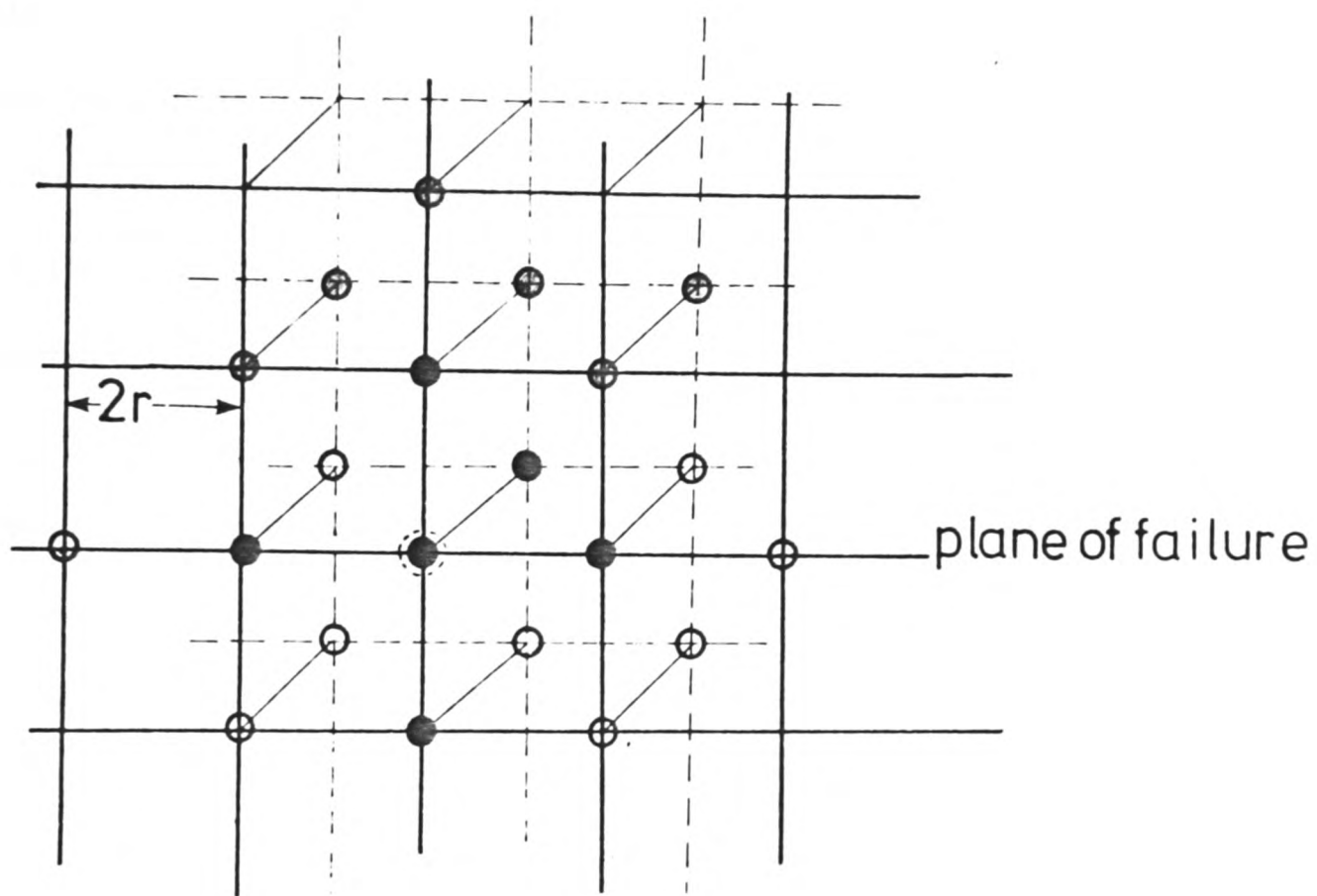
- ⊙ represents the 'A' atom under consideration,
- represent the nearest neighbour 'A' atoms,
- represent the second-nearest neighbour 'A' atoms which must be considered when failure occurs along the plane indicated.

Figure 6.2b

- ⊙ represents the 'A' atom under consideration,
- represent the 'B' atoms within the sphere of radius $2r$, and
- represent the 'C' atoms within the sphere.

(Not proportional to actual numbers present)

a.



b.

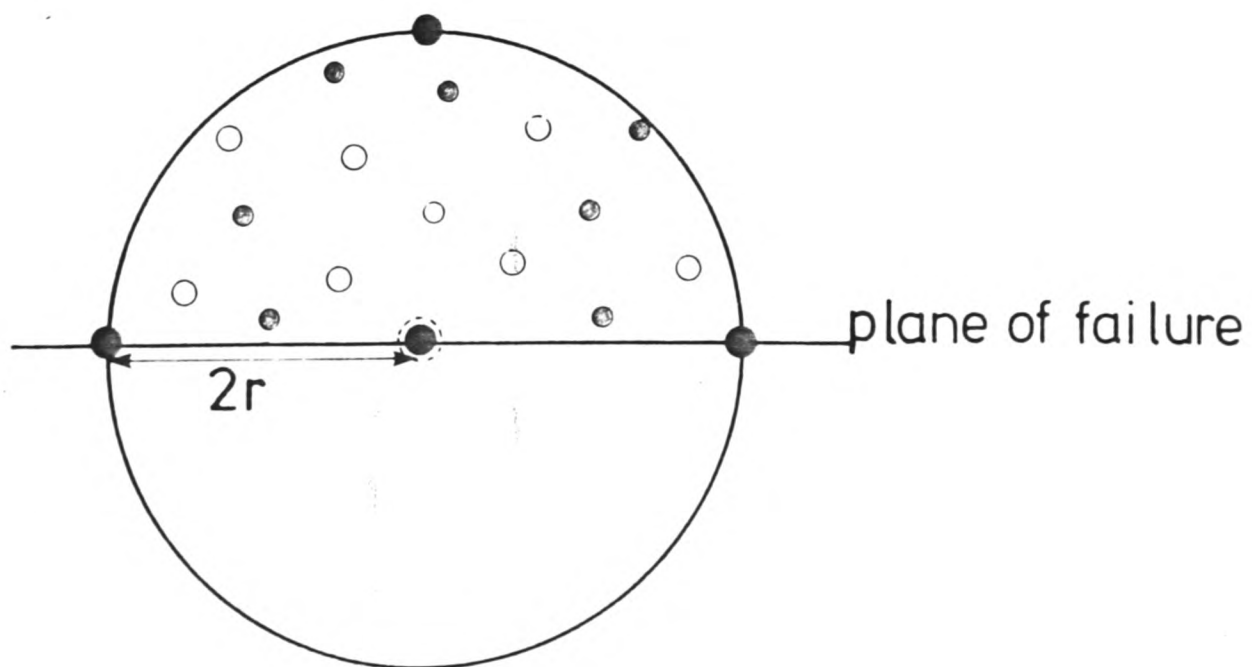


Table 6.3 summarises the values required for these calculations, when A, B and C are chlorine, carbon and hydrogen atoms.

However, a comparison was made between the actual film thickness, and the film thickness predicted by the weight of film present on each specimen. The result revealed an increase in the volume of the film by a factor of $\sim 70\%$. This implies that all interatomic separations discussed above should be increased by approximately 20%. Thus, the separation of Cl/Cl, H/H and C/C became $4.79 \text{ \AA}$, $4.12 \text{ \AA}$ and $4.27 \text{ \AA}$ respectively, and the average atomic separation becomes $3.02 \text{ \AA}$. These values are recorded in Table 6.3 under the symbol r_o .

In calculating the Debye forces for the H/C/Cl theory the interactions considered are between the H-C and C-Cl dipoles and individual H, C and Cl atoms. The number of H-C dipoles present depends on the number of H atoms per unit volume of the film, and similarly the number of C-Cl dipoles depends on the number of Cl atoms present. Thus, the number of H-C/H interactions broken in cohesive failure is equal to the number of H/H London interactions per unit area, which are broken; and the number of H-C/C and H-C/Cl interactions is equal to the number of H/C and H/Cl interactions broken, respectively.

Similarly, for the interactions of the C-Cl dipoles, the numbers of C-Cl/H, C-Cl/C and C-Cl/Cl interactions broken are equal to the numbers of Cl/H, Cl/C and Cl/Cl interactions which are broken, respectively.

The combination of these six different interactions gives the total attractive Debye force per unit area of the film.

The Keesom forces act only between two polar molecules, so the interactions considered are between H-C/H-C, C-Cl/C-Cl and C-Cl/H-C dipoles. The numbers of each of these individual interactions broken in cohesive failure is equal to the number of H/H, Cl/Cl and Cl/H interactions broken, respectively. This is based on the reasoning detailed above.

In the cases of both Debye and Keesom forces the separation of the

two interacting species must be considered as for the London interactions.

Table 6.4 gives the results of the calculations.

<u>Interaction</u>	<u>Number/Unit Area</u>	<u>Separation</u>
Fe/Cl	$6.30 \times 10^{18} \text{ m}^{-2}$	$3.07 \text{ \AA}$
Fe/C	$7.88 \times 10^{18} \text{ m}^{-2}$	$2.25 \text{ \AA}$
Fe/H	$8.48 \times 10^{18} \text{ m}^{-2}$	$1.79 \text{ \AA}$
Fe/Average Element	$15.77 \times 10^{18} \text{ m}^{-2}$	$2.31 \text{ \AA}$

TABLE 6.3a - Adhesion

Separation of Atoms and Abundance at Film/Substrate Interface

(i) Primary Interactions

<u>Interaction</u>	<u>$2r \text{ \AA}$</u>	<u>$\frac{4}{3}\pi V_o = V \text{ m}^3$</u>	<u>$r_o \text{ \AA}$</u>	<u>Interactions/Unit Area</u>
Cl/Cl	3.99	2.65×10^{-28}	4.79	$6.30 \times 10^{18} \text{ m}^{-2}$
H/H	3.43	1.70×10^{-28}	4.12	$8.48 \times 10^{18} \text{ m}^{-2}$
C/C	3.56	1.90×10^{-28}	4.27	$7.88 \times 10^{18} \text{ m}^{-2}$
Average Element	2.52		3.02	$15.77 \times 10^{18} \text{ m}^{-2}$

(ii) Secondary Interactions

<u>Interaction</u>	<u>N</u>	<u>$r_1 \text{ \AA}$</u>	<u>$r_2 \text{ \AA}$</u>	<u>Interactions/Unit Area</u>
H/Cl	6.56	2.34	4.79	$41.32 \times 10^{18} \text{ m}^{-2}$
C/Cl	5.86	2.80	4.79	$36.92 \times 10^{18} \text{ m}^{-2}$
H/C	4.68	1.52	4.27	$36.88 \times 10^{18} \text{ m}^{-2}$

TABLE 6.3b - Cohesion

Separation of Atoms and Abundance per Unit Area of the Film

<u>Expression</u>	<u>Interaction</u>	<u>Equilibrium Attractive Force N</u>	<u>Equilibrium Attractive Force/Unit Area</u>	<u>Nm⁻²</u>	<u>Total Net Force/Unit Area at Separation</u>		<u>Comment</u>
(4) Czyzak	Average Element H/Fe C/Fe Cl/Fe				<u>MNm⁻²</u>	<u>kgf cm⁻²</u>	
			6.51 x 10 ⁸		1.68 x 10 ²	1.71 x 10 ³	Pitzer's correction gives F=3.57x10 ³ kgf cm ⁻² .
			1.27 x 10 ⁸				
			1.18 x 10 ⁸				
(3) Prosen & Sachs	Average Element H/Fe C/Fe Cl/Fe		8.63 x 10 ⁷	3.31 x 10 ⁸	1.36 x 10 ²	1.39 x 10 ³	Pitzer's correction gives F=2.54x10 ³ kgf cm ⁻² .
		2.01 x 10 ⁻¹⁰	3.17 x 10 ⁹		7.32 x 10 ²	7.46 x 10 ³	
		8.22 x 10 ⁻¹¹	6.97 x 10 ⁸				
		1.06 x 10 ⁻¹⁰	8.35 x 10 ⁸	2.30 x 10 ⁹	5.77 x 10 ²	5.88 x 10 ³	
(1) London	Average Element H/Fe C/Fe Cl/Fe		7.69 x 10 ⁸				
		6.97 x 10 ⁻¹⁰	1.20 x 10 ¹⁰		2.71 x 10 ³	2.76 x 10 ⁴	Pitzer's correction gives F=6.19x10 ⁴ kgf cm ⁻² .
		2.15 x 10 ⁻¹⁰	1.82 x 10 ⁹				
		1.98 x 10 ⁻¹⁰	1.56 x 10 ⁹	4.28 x 10 ⁹	1.02 x 10 ³	1.04 x 10 ⁴	Pitzer's correction gives F=2.26x10 ⁴ kgf cm ⁻² .
(5) Margenau	Average Element H/Fe C/Fe Cl/Fe		9.01 x 10 ⁸				
		1.43 x 10 ⁻¹⁰	1.34 x 10 ¹⁰		3.02 x 10 ³	3.08 x 10 ⁴	
		8.49 x 10 ⁻¹⁰	3.31 x 10 ⁹				
		3.90 x 10 ⁻¹⁰	2.88 x 10 ⁹	7.31 x 10 ⁹	1.70 x 10 ³	1.73 x 10 ⁴	
Debye	Average Element H-C/Fe C-Cl/Fe		1.12 x 10 ⁹				
		6.35 x 10 ⁻¹²	1.00 x 10 ⁸				
		2.15 x 10 ⁻¹¹	1.82 x 10 ⁸				
		1.52 x 10 ⁻¹¹	9.58 x 10 ⁷	2.78 x 10 ⁸			

TABLE 6.4

(a) Results of Calculations Involving Adhesive Interactions

Expression	Interaction	Equilibrium Attractive Force/Interaction N	Equilibrium/ Attractive Force/Unit Area	$\frac{\text{Nm}^{-2}}$	Total Net Force/Unit Area at Separation		Comment
					$\frac{\text{MNm}^{-2}}$	$\frac{\text{kgf cm}^{-2}}{}$	
(6) Slater & Kirkwood	Average Element	1.60×10^{-10}	2.52×10^9	1.25×10^8	5.69×10^2	5.80×10^3	Incomplete, as only interactions between like atoms may be considered.
	H/H	1.02×10^{-12}	8.66×10^6				
	C/C	5.24×10^{-12}	4.14×10^7		0.93×10^2	0.95×10^3	
	Cl/Cl	1.19×10^{-11}	7.50×10^7				
(2) London	Average Element	8.44×10^{-11}	1.33×10^9	5.77×10^7	3.03×10^2	3.09×10^3	Incomplete, as only interactions between like atoms may be considered.
	H/H	1.02×10^{-12}	8.66×10^6				
	C/C	2.62×10^{-12}	2.06×10^7		0.77×10^2	0.79×10^3	
	Cl/Cl	4.50×10^{-12}	2.84×10^7				
(1) London	Average Element	1.39×10^{-10}	2.20×10^9	2.22×10^9	4.98×10^2	5.08×10^3	Pitzer's correction gives $F=1.14 \times 10^4 \text{ kgf cm}^{-2}$.
	H/H	8.59×10^{-13}	7.28×10^6				
	C/C	2.71×10^{-12}	2.14×10^7				
	Cl/Cl	8.43×10^{-12}	5.32×10^7		5.62×10^2	5.73×10^3	
	H/C		1.19×10^9				
	H/Cl		4.86×10^8				
(5) Margenau	Average Element	1.52×10^{-10}	2.40×10^9	3.18×10^9	5.43×10^2	5.54×10^3	Pitzer's correction gives $F=1.21 \times 10^4 \text{ kgf cm}^{-2}$.
	H/H	9.73×10^{-13}	8.26×10^6				
	C/C	4.99×10^{-12}	3.94×10^7				
	Cl/Cl	1.13×10^{-11}	7.12×10^7		7.77×10^2	7.92×10^3	
	H/C		1.73×10^9				
	H/Cl		5.98×10^8				
Debye	Average Element	9.73×10^{-13}	1.53×10^7	5.07×10^7			
	H-C/H	2.00×10^{-14}	1.70×10^5				
	H-C/C		3.06×10^6				
	H-C/Cl		1.15×10^7				
	C-Cl/H		2.98×10^7				
	C-Cl/C		2.82×10^6				
Keesom	Average Element	5.31×10^{-13}	3.36×10^6	2.37×10^8			
	H-C/H-C	4.16×10^{-13}	6.56×10^6				
	C-Cl/C-Cl	1.22×10^{-13}	1.03×10^6				
	H-C/C-Cl	8.40×10^{-12}	5.30×10^7				
			1.83×10^8				

TABLE 6.4
(b) Results of Calculations Involving Cohesive Interactions

6.5 COMPUTATION AND DISCUSSION

Column six of Table 6.4 details the results obtained for the total force, both attractive and repulsive, per unit area of the specimen at the condition defined above for bondfailure.

Before these results are discussed it should be noted that the experimental stresses to failure measured in the tests described in Chapter 3, were between about 4 and 15 MN m^{-2} , or 38 and 155 kg cm^{-2} , and that the maximum stress measured was $\sim 20 \text{ MN m}^{-2}$.

(i) Consider first the values given in Table 6.4a. The fourth and fifth columns detail the individual attractive forces per unit area of the interface, at equilibrium, and it may be observed that the expression of Czyzak gives values differing by less than a factor of two using either the "average element" or "H/C/C1" theory, as do the expressions of Prosen and Sachs, and Margenau. The expression of London gives values differing by just less than a factor of three, and in all cases the values derived using the "average element" theory are the largest. However, there is a variation of more than an order of magnitude between those obtained using Czyzak's and those obtained using Margenau's expression, which represent the opposite ends of the scale.

The Debye interactions contribute a significant amount to some values, the most being 46% of those from the Czyzak expression, using the "H/C/C1" theory, but the contribution in other cases varies between $\sim 1\%$ and 13% .

(ii) Considering the total net force per unit area, at separation, given in column six of the table; before Pitzer's correction is applied to the dispersion contribution, the values obtained using the "average element" and "H/C/C1" theories vary by factors of up to eighteen and thirteen respectively, across the range. When Pitzer's correction is applied this variation is reduced to factors of seventeen and nine respectively.

(iii) Table 6.4b details the results obtained when the cohesive interactions

are considered. Columns four and five give the individual attractive forces at equilibrium, per unit area of the film. The results obtained using the "average element" theory vary by less than a factor of two across the four values for the dispersion interaction. However, only two of the values obtained using the "H/C/C1" theory may be considered, as the Slater and Kirkwood, and London ('2') expressions do not allow interactions between unlike atoms to be considered, and so these results are incomplete. The two values which may be considered vary by a factor of just over 1.4, and are very similar to the results obtained using the former theory.

The Keesom and Debye interactions contribute less than 9% to the values obtained using the "H/C/C1" theory and less than 2% to those obtained using the "average element" theory.

(iv) Taking the values of the total net force per unit area of the film, given in the sixth and seventh columns, before Pitzer's correction is applied, there is a variation of less than a factor of three across all values, and when the correction is applied this only increases to a factor of four.

Reviewing the table as a whole, and disregarding Pitzer's correction, it may be seen that the cohesive interaction in the case of the "average element" theory is associated with a stress of the order of $3-5.7 \times 10^2 \text{ MN m}^{-2}$, while the adhesive interaction is associated with a stress of about $1.7-30 \times 10^2 \text{ MN m}^{-2}$. In the case of the "H/C/C1" theory the cohesive stress varies between 5.6×10^2 and $7.8 \times 10^2 \text{ MN m}^{-2}$, while the adhesive stress varies between 1.4×10^2 and $17 \times 10^2 \text{ MN m}^{-2}$. The results obtained using the London ('1') and Margenau formulae for both interactions suggest that the adhesive stress is indeed greater than the cohesive stress. In the case of the "average element" theory up to a factor of 5.5, and in the case of the "H/C/C1" theory up to a factor of 2.2

These two formulae are clearly the most useful of those considered,

as they are applicable to both adhesive and cohesive interactions, and, on the whole, give similar numerical values.

The results as a whole serve as a comparison between the two theories, the "average element" and the "H/C/Cl" theory, and the application of the various expressions for calculating the components of the Van der Waals interactions. It is interesting to note that the values of the cohesive stress are at the most a factor of forty greater than the maximum applied stress to cause failure in the WBL of the specimens tested, or when Pitzer's correction is applied this increases to a factor of sixty.

In the case of the dispersive type of cohesive interactions the "average element" theory appears to serve as a good approximation to the more complicated "H/C/Cl" theory, although it is not quite so useful in the case of the adhesive interaction, the values obtained being larger than those calculated using the other theory. The rule appears to be reversed for the Debye and Keesom interactions, and it serves as a good approximation for the adhesive stresses.

In the following section the investigation will be extended to consider interactions between second-nearest neighbouring, like atoms; the interactions of chain end-groups with the substrate, and the effects of surface contamination. Further refinements to the theories will also be considered.

6.6 EXTENSION OF INVESTIGATION

(a) Contribution of second nearest neighbouring cohesive interactions

In the "H/C/Cl" theory, the interactions occurring between two chlorine atoms are the strongest which occur between two like atoms; therefore, the cohesive interactions between second nearest neighbouring chlorine atoms were investigated, including the additional H/Cl and C/Cl interactions occurring within this volume. As C/H interactions make a large contribution to the total force per unit area the additional interactions of this type occurring in the region between first and second nearest neighbouring C/C interactions were included. As H/H and C/C interactions contribute only 1.5% of the total force they were not considered in this investigation.

Margenau's expression was used for calculating the force of each interaction, and each contribution was combined to obtain the attractive, cohesive force per unit area, at equilibrium. The results are shown in Table 6.5.

<u>Interaction</u>	<u>Additional Contribution MN m⁻²</u>	<u>Percentage Contribution to Values in Table 6.4</u>
Cl/Cl	31.7	44%
H/Cl	49.4	8%
C/Cl	119.4	16%
H/C	42.8	2.5%

TABLE 6.5

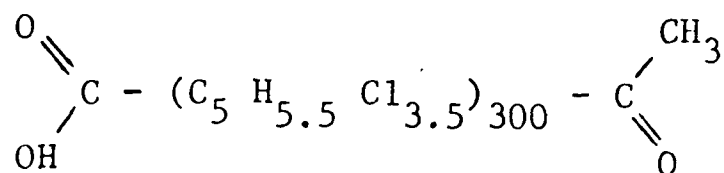
Additional contribution to attractive, cohesive force/unit area when considering interactions between second-nearest neighbours

The contribution of these additional interactions to total, attractive force per unit area, at equilibrium due to Cl/Cl, H/Cl, C/Cl and H/C interactions is only 7.8% of the original value, and it was thus considered to be permissible to neglect all interactions between second-nearest neighbouring like atoms.

It should be noted that the Cl/Cl contribution is made up from one interaction at $r = 9.58 \text{ \AA}$, four at $r = 8.30 \text{ \AA}$ and an angle of $35^\circ 15'$ (Figure 6.2a).

(b) End-group contribution

The structural formula of "Alloprene" is



The contribution of the interactions of the chain end-groups with the substrate, to the total adhesive interaction at the interface was considered, and their magnitude was compared with the total adhesive stress.

For the OH- group, polarisability $\alpha = 1.13 \times 10^{-40} \text{ Fm}^2$, ionisation potential $I = 2.11 \times 10^{-18} \text{ J}$, and the abundance at the interface $n_1 = 4.54 \times 10^{16} \text{ m}^{-2}$. The O= element has $\alpha = 9.36 \times 10^{-41} \text{ Fm}^2$; $I = 1.93 \times 10^{-18} \text{ J}$ and $n_2 = 9.08 \times 10^{16} \text{ m}^{-2}$. The separation between each end-group and the substrate was taken as the average separation discussed earlier, $R = 2.31 \times 10^{-10} \text{ m}$. All the above values were calculated from data available in Reference 8.

Expression (1) due to London was used to calculate the dispersive force per unit area due to the end-groups, as it requires fewer properties of the groups to be known than does Margenau's expression, and hence involves fewer approximations. Without Pitzer's correction the contribution due to the OH- groups was found to be 9.49 MN m^{-2} , and that due to O= was 12.60 MN m^{-2} . The total contribution was 0.18% of the force per unit area calculated using the "average element" theory, or 0.48% of the force calculated using the "H/C/Cl" theory.

The Debye interactions were also calculated, and were found to contribute only 0.47% of the Debye force per unit area calculated using the "average element" theory, or 0.17% of that force calculated using the "H/C/Cl" theory.

Although the individual London interactions of each end-group are of the same order of magnitude as those of H/Fe, C/Fe, Cl/Fe or even the "average element"/Fe; and in the case of the Debye forces of the same order of magnitude as "average element" interactions, the end-groups are much fewer in number at the interface than each individual species of atom, so their total contribution is smaller.

Thus, it is considered permissible to neglect the interactions involving chain end-groups.

(c) Contaminated Surface

Examination of the surface of a mild steel substrate using ESCA revealed that a layer of ferric oxide was present, together with carbonaceous contamination, and the substrate was not, in fact, clean metal. The nature of the carbonaceous layer could not be clearly defined, but an investigation was carried out to find the magnitude of the forces of adhesion between the lacquer and oxide layer, using the "average element" theory, and the London ('1') expression for calculating these forces.

The polarisability of the oxide molecules was calculated using the data available [8], and the Clausius-Mossotti equation; and the ionisation potential was calculated using London's approximation $I = h\nu_0 = \frac{he}{(m\alpha)^{\frac{1}{2}}}$. The values obtained were $\alpha = 2.66 \times 10^{-40} \text{ Fm}^2$; $I = 6.82 \times 10^{-18} \text{ J}$.

The separation between the elements of the film and the oxide molecules was taken as the separation in the "average element" theory, $R = 2.31 \times 10^{-10} \text{ m}$. If the substrate surface was completely covered with ferric oxide the dispersive force of adhesion, per unit area, at equilibrium would be $2.82 \times 10^4 \text{ MN m}^{-2}$. It must be noted that this is only an order-of-magnitude investigation, as many approximations have to be made in the calculation of polarisability and ionisation potential. However, the oxide gives a force per unit area which is of the same order of magnitude as that obtained for a clean substrate,

i.e. approximately 10^4 MN m^{-2} . Thus, the presence of the oxide layer does not seem to have a destructive effect on the adhesion of the coating to the substrate.

(d) Refinement of the Model

It has been suggested that instead of simply adding all the interactions occurring between an atom and all those surrounding it, the components of the interatomic forces, in a direction perpendicular to the plane of failure, should be considered. Figure 6.3a illustrates this. These components could then be added to give the total, perpendicular component of the attractive forces, which must be overcome to cause failure.

However, there are several complications which arise.

- (i) The exact positions of the atoms are not known, so some form of approximation has to be derived in order to allow for this. Simple integration over the allowed angles θ would seem to solve the problem.
- (ii) When a stress is applied to the system the atoms move towards the stress axis, and the angular distribution changes. More atoms are located at positions of large θ than in the unstressed system, and there is not an even angular distribution. Thus, simple angular integration is not the answer; a more complex summation is required. Also, the description of the angular distribution varies according to the magnitude of the applied stress, this should be fixed at some value close to the failure stress.
- (iii) As the angle subtended by a particular interatomic bond changes so does the separation of the atoms - (Figure 6.3b). If θ is increased to $(\theta+d\theta)$ the perpendicular component of the interatomic forces changes from $F(r)\sin\theta$ to $F(r')\sin(\theta+d\theta)$, where $r' = r\cos\theta/\cos(\theta+d\theta)$, which increases as $d\theta$ increases. Thus, as $F \propto r^{-7}$, the interatomic force decreases as the angle increases.

It would be possible to devise an expression for the perpendicular component of the interatomic forces acting between an atom and all those

surrounding it, and to find the magnitude of this when the system was stressed almost to failure. However, considering the approximations made earlier in this chapter, when the model of the atoms in the film was first constructed, it is suggested that this would be over-refining the model.

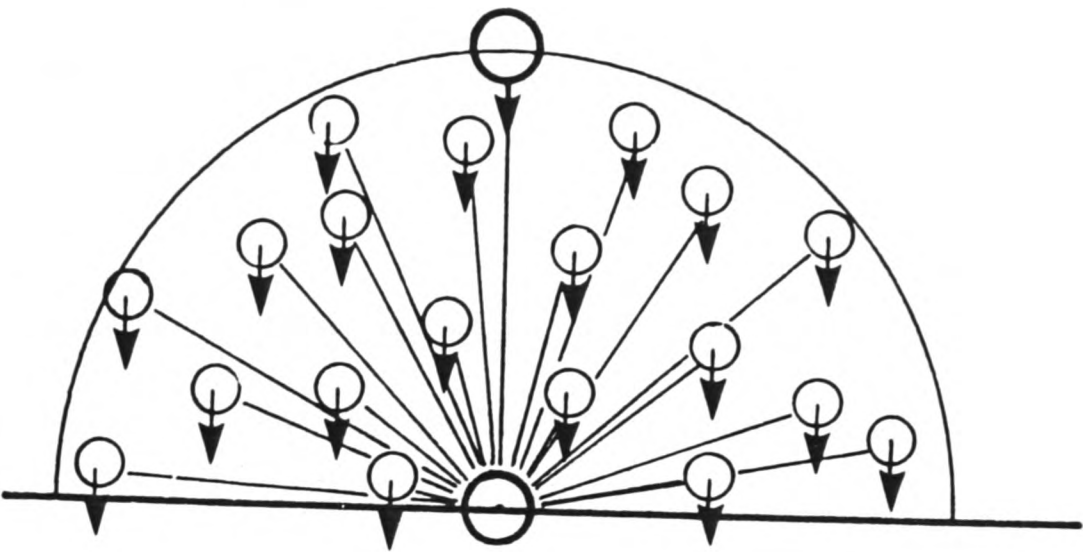
Figure 6.3a

Representation of the components of the interatomic forces acting in a direction perpendicular to the plane of failure. Arrows indicate the direction of these components.

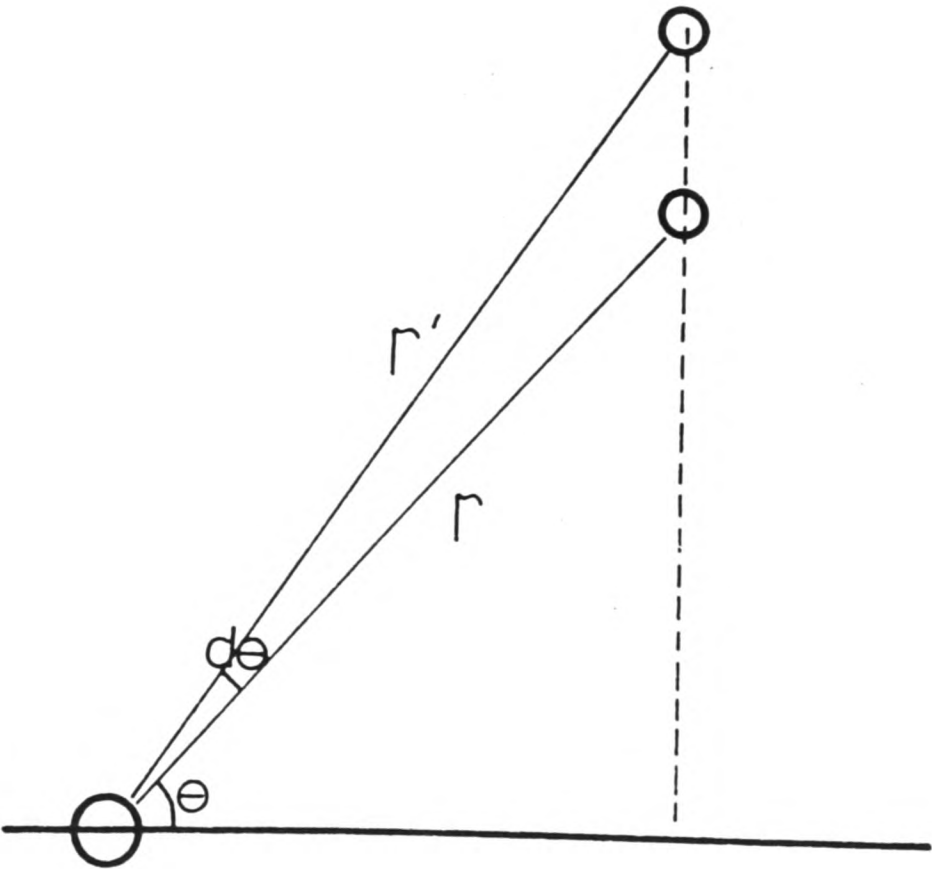
Figure 6.3b

Representation of the variation of interatomic separation, with bond angle.

ca.



b.



6.7 CONCLUSIONS

Reviewing the results obtained using the "average element" theory and the "H/C/Cl" theory, it appears that in the case of the total net force per unit area, at the point defined for the separation of the atomic layers in question, the former theory is particularly useful, as it is more simple to employ and yields almost the same values as the more complicated "H/C/Cl" theory, for both the adhesive and cohesive interactions.

Thus, the "average element" theory is useful as a quick and relatively simple method of investigating the magnitudes of interactions, but the "H/C/Cl" theory takes more of the variables of the system into account, and thus provides a more complete description of the properties of the film.

Clearly the Margenau and London ('1') expressions are most useful when calculating the strength of the cohesive interactions, as all combinations of atomic interaction may be included; it is also convenient to be able to use these two expressions for the adhesive interaction. As their results for the adhesive force per unit area are fairly consistent they would appear to be preferable to the expressions of Czyzak or Prosen and Sachs. However, the strength of the latter lies in the fact that it requires fewer approximations to be made in order to calculate the necessary properties of the film.

From the discussions of Section 6.6 it appears that the presence of an oxide film on the substrate surface makes little difference to the magnitude of the adhesive interaction at the interface; and the interactions of the chain end-groups with the substrate contribute only a small proportion of the total adhesive stress.

An ideal paint is formulated such that the cohesive strength of the film should be less than the strength of the adhesive interaction binding it to a particular substrate. "Alloprene" based paints have been proved to follow this particular requirement, and the calculations

discussed in this chapter reinforce this point. However, although experiments have shown that failure always occurs within the lacquer, close to the film/substrate interface, the stress required to cause failure is a factor of between fifteen and forty lower than the cohesive strength of the film calculated above. Using a simplified version of the Griffith crack criterion, mentioned in Chapter 3, this implies that a crack, or inclusion 0.07-0.5 μm in length could act as a stress concentrator and cause premature failure of the film. This could be pockets of atmospheric gases incorporated into the film during the preparation of the lacquer, small pockets of trapped solvent, or possibly small solid particles which were not dissolved in the lacquer.

The calculations discussed in this chapter give an insight into the physical properties of the lacquer, and the importance of the various atomic species. They also explore the usefulness of the various expressions for describing the London, or dispersion interactions, and compare the magnitudes of the London, Debye and Keesom forces effective in the system.

References - Chapter Six

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CHAPTER SEVEN

CONCLUSIONS

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7.1 CONCLUSIONS

A method has been developed for testing the strength of adhesive joints and applied to chlorinated-rubber based lacquers on mild steel; it is simple to employ and gives easily reproducible results. The test is of the direct pull-off type in which a butt joint is made by sandwiching a coated disc of steel between two mild steel cylinders of the same diameter. This is tested in tension, using a constant strain rate sufficiently high for failure to occur almost instantaneously across the coated area, but not so high that the specimen is impact tested.

Using this test method the response of the coating to various stresses may be determined, and the stress to cause failure of the specimen may be measured. Also, the mode of failure may be investigated by careful examination of the substrate and lacquer surfaces after test.

It was found that the coatings under test experienced elastic extension when a stress was applied, and that the maximum stress to cause failure was $\sim 20\text{MN m}^{-2}$. The effects of several variables of the system on the strength of the coating were investigated; these were film thickness, lacquer storage time, binder molecular weight and film drying time. It was found that coating strength was greater for thin films than for thick, and that the strength also increased with the duration of lacquer storage and film drying time.

It was deduced that during the preparation of the lacquer, small pockets of air were trapped in the solution, which were released very slowly on storage. These acted as stress concentrators in coatings prepared from fresh lacquer, thus causing premature failure, but were

released from the solution before films were cast using the stored lacquer.

The lacquer also degrades on storage, releasing hydrogen chloride into the solution, which reacts slowly with the substrate when a film is cast. The quantity of the compound formed at the interface increases during the film drying time, and is found to increase the strength of the coating in the interfacial region. The effect of the reduction in the residual solvent content of the film, and the change in the composition of the lacquer/substrate interface lead to an increase in the failure stress of films as the duration of their drying time is increased.

The stress to cause failure of the coating appears to be independent of the molecular weight of the binder when it is above about $15-20 \times 10^3$. This may be because some degree of chain orientation occurs at the interface, and failure does not involve any contribution due to chain entanglement. However, it may also be that the chain entanglement contribution is constant for binders above the critical molecular weight, and that it is below this value that variation occurs.

The mode of failure in most specimens was found to be a mixture of cohesive and weak boundary layer (WBL) failure. The boundary layer remaining on the surface of the substrate was probably continuous but uneven, and was rich in "Alloprene", as the plasticiser was found to migrate towards the upper surface of the coating. A mechanism has been proposed to describe this migration, based on the shrinkage stresses within the film. However, the fact that migration does occur suggests some degree of incompatibility between the binder and the plasticiser. True adhesive failure between the coating and the substrate did not occur in any specimens. A mechanism has also been proposed to describe the type of failure occurring, and the markings observed on the lacquer and substrate surfaces after failure had taken place.

Discolouration occurred at the lacquer/substrate interface when the upper surface of the specimen was exposed to the air. The nature

of this discolouration was found to depend upon the presence or absence of light where the specimens were stored, and on the storage of the lacquer before use. In one case a continuous "rust"-coloured layer was formed which was composed of crystalline β -FeO.OH in the case of unstored lacquer, and for the stored lacquer included a second crystalline compound probably resulting from the interaction of the degraded lacquer with both the substrate material and silicon carbide remaining from the substrate abrasion and cleaning routine. This compound has not yet been identified. The second type of discolouration was also "rust"-coloured but formed a "cell"-like structure at the interface. This was mainly composed of two compounds, one of which was produced by the interaction of the lacquer, silicon carbide and substrate material, and another which contained iron but no chlorine from the lacquer or silicon. Neither of these compounds has yet been identified.

The thickness of the discoloured layer was found to be $> 100 \text{ \AA}$, which was greater than that of the WBL.

Van der Waals interactions are recognised as contributing the major forces of adhesion between a polymer coating and a metal substrate, and are also the interactions causing interchain attraction within the polymer itself. Approximations were made in order to apply the expressions derived for calculating the Van der Waals forces between simple molecules adhering to metallic substrates, to the complex system under consideration. The theoretical contribution of these forces to the cohesive strength of the film was found to be less than their contribution to the strength of the adhesive bonds between the coating and the substrate. However, the cohesive strength may be enhanced by the breaking of some covalent bonds at failure, resulting from chain entanglement, and the magnitude of the adhesive force per apparent unit area of the lacquer/substrate interface may be enhanced by the effects of surface roughness and the associated increase in real surface area.

However, the magnitude of the numerical values obtained for the

forces in this system were within the range expected after consideration of the experimental values of the stress to cause failure of a specimen. This suggests that the approximations made are valid when an order of magnitude calculation is required, and that the Van der Waals forces alone are indeed sufficient to cause the adhesion of the lacquer to the substrate.

Although the work was carried out on lacquers it has relevance to pigmented films, or paints, and their use as coatings for mild steel, but in this case the system is complicated by the presence and nature of the pigment.

7.2 SUGGESTIONS FOR FURTHER WORK

The work described here has covered several aspects of the interactions between chlorinated-rubber based coatings and mild steel substrates, and also changes occurring within the coatings themselves. Many of these aspects could themselves be areas for additional fruitful research. Suggested areas are outlined below.

- (i) The nature of the dependence of failure stress of supported films on binder molecular weight, by studying the composition of the WBL remaining on the substrate after testing, and any chain orientation occurring within this layer. The latter may be investigated using infra-red spectroscopy, as discussed by Willis & Zichy [1].
- (ii) Degradation of paints and lacquers on storage, and their subsequent interaction with the substrate. The nature of the interaction products and the factors affecting their formation may be investigated using chemical and X-ray analytical techniques, when specimens have been prepared under carefully controlled conditions.
- (iii) The cause and affects of plasticiser migration in paints and lacquers, and the subsequent formation of the WBL. Internal reflection infra-red spectroscopy [1], Auger electron analysis and ESCA may be used to study the variation of composition with depth through the film, and films may be cast on various, deformable substrates to investigate the affect of shrinkage stresses on the development of such inhomogeneities.
- (iv) The extension of the theoretical work to consider the variation of failure stress with strain within the specimen. This has been mentioned briefly in Chapter 6 when considering the possibility of evaluating the components of interatomic force in the direction of the applied stress. Although the modification was considered inappropriate to the present work, in the context of a more elaborate theoretical calculation it would be important.
- (v) Investigation of the application of the thermodynamic approach in

evaluating the magnitudes of adhesive interactions between the coating and the substrate. The value of the thermodynamic work of adhesion, W_A , could be calculated when the mechanism of adhesion involved only the formation of interfacial secondary bonds; this could be compared with the experimental value of the intrinsic adhesive failure energy, θ_o , to evaluate the contribution of other mechanisms of adhesion to the total bond strength.

(vi) Some preliminary work has been carried out to investigate the effects of various corrosive atmospheres on the properties of the coating/substrate interface. Although no conclusions may yet be drawn from these investigations it is clearly important to evaluate the change in failure stress and chemical composition of the interfacial region after exposure to different environmental conditions.

References - Chapter Seven

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Appendix - Trade Names

Alloprene R20, chlorinated cis-polyisoprene: ICI Ltd., Mond Division

Araldite, epoxy resin and hardener: Ciba-Geigy (UK) Ltd.

Cereclor 42, a chlorinated paraffin: ICI Ltd., Mond Division

Elcometer, bench-top tensile testing device: Elcometer Ltd.

Pyrene, manufactured steel plates: Pyrene Ltd.

Solvesso, aromatic hydrocarbon solvent: Esso Petroleum Co.