SURFACE COATING
DETERIORATION STUDIES

by

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SUMMARY

This project is concerned with the deterioration of surface coatings as a result of weathering and exposure to a pollutant gas (in this case nitric oxide). Poly(vinyl chloride) (PVC) plastisol surface coatings have been exposed to natural and artificial weathering and a comparison of the effects of these two types of weathering has been made by use of various analytical techniques. These techniques have each been assessed as to their value in providing information regarding changes taking place in the coatings during ageing, and include, goniophotometry, micropenetrometry, surface energy measurements, weight loss measurements, thermal analysis and scanning electron microscopy. The results of each of these studies have then been combined to show the changes undergone by PVC plastisol surface coatings during ageing and to show the effects which additives to the coatings have on their behaviour and in particular the effects of plasticiser, pigment and uv and thermal stabilisers.

Finally a preliminary study of the interaction between five commercial polymers and nitric oxide has been carried out, the polymers being polypropylene, cellulose acetate butyrate, polystyrene, polyethylene terephthalate and polycarbonate. Each of the samples was examined using infra-red spectroscopy in the transmission mode.

Index Terms

Goniophotometry

Micro-indentation or Recovery/Time Analysis

Scanning Electron Microscopy

Surface Energy Measurements

Poly (Vinyl Chloride) Surface Coatings - Natural and Artificial weathering of

Nitric Oxide - interaction with polymers

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CHAPTER I

INTRODUCTION

1.1 General Introduction

The work described in the following chapters was undertaken to study the effect of both natural and artificial weathering on PVC plastisol surface coatings and follows on from previous work carried out in this department.[1] The surface coatings used were of three different formulations, the first was PVC plastisol alone, the second was PVC plastisol with added pigment and the third was PVC plastisol with added pigment together with u.v. and thermal stabilisers. These were chosen so that the effect of the additive on the ageing characteristics of the PVC plastisol coatings could be assessed. This initial chapter will therefore be an introduction to the project and to the techniques used to study the changes brought about in the PVC plastisol surface coatings due to ageing.

1.2 Statement of Objectives

This project was begun with four objectives in mind. Firstly to assess the suitability of various analytical techniques to measure the changes brought about in the surface coating by ageing. Analytical techniques were used to assess changes taking place both in the bulk and at the surface of the coating. Secondly to compare the artificial weathering techniques used in this study with natural weathering. Samples of the PVC plastisol surface coatings had been previously exposed to natural weathering at the Building Research Station's exposure site for periods up to 2 years[1] and so it was possible to compare these samples with those exposed to artificial weathering techniques for periods up to 10,000 hours. By comparing the results gained from these two exposures it was hoped that it would be possible to determine how effective the weatherometer was in reproducing natural weathering conditions.

The third objective was to assess how effective the components of natural weather are in causing degradation to PVC plastisol surface coatings when taken in isolation. To achieve this objective the surface coatings were exposed to uv radiation alone and to thermal radiation in a humid atmosphere. At the end of these exposures it should be possible to say what contribution uv and thermal radiation make to the overall degradation of the coatings.

The last objective was to find out what effect the pigment and uv and thermal stabiliser had on the ageing characteristics of the PVC plastisol coatings. For this reason the three formulations chosen for use in this work were exposed simultaneously in all of the exposure tests. They were also a purpose formulated range of coatings which are of a simpler formula than commercial coatings.

1.3 Surface Coatings

The most common types of polymer encountered in everyday life are surface coatings seen as paints and varnishes on our surroundings. In this role they have a dual functionality to protect the underlying substrate from attack by external factors such as weather and to appear attractive and pleasing to the eye. This second function is thought to be fulfilled if a paint retains its colour and gloss after exposure to external factors. To be a successful surface coating therefore a polymer must be able to withstand attack from external forces and not be degraded by them.

This study sets out to examine the ageing characteristics of one type of paint film and to measure the effect of added pigment and uv and thermal stabiliser upon the expected lifetime of that paint film. The surface coating offers a model in which not only can the degradative processes of the system as a whole be studied but also the degradation processes particular to the polymer PVC can be studied. Surface analytical techniques would be expected to provide the most valuable results in a study of this kind because of the large surface to bulk ratio of a surface coating and the majority of analytical techniques which have been used in this study fall into this category. A number of different techniques have been used to monitor the changes taking place in the coating during ageing both at the surface and in the bulk of the coating and it is hoped that the results provided by each of the individual techniques can then be assessed to give an overall picture of degradation for the coating.

1.4 Weathering Techniques

Natural weather is a very complex phenomenon made up of various factors which have been summarised by previous workers[2-5]. The most significant of these factors are generally considered to be those associated with radiation, temperature, oxygen, other harmful (eg industrial) atmospheric gases, water, micro-organisms, dust and wind (etc). Of these, the ultraviolet component of natural radiation (ie sunlight) is probably the most potent single factor in the degradation of surface coatings, although its combination with the infra-red (ie heat) component and/or water is believed to be more potent still.

Another feature of natural weathering is the great seasonal variations that occur in the intensity of both thermal and uv radiation and because of this it may seem doubtful that reproducible results could ever be obtained from outdoor weathering exposures. Indeed, to quote Rosendahl[6] "A researcher, who was so over cautious to expose a test series not only once but several times over, had to find out that even in the ideal climate of Florida with exposures started in different years, but the same time of year, the durabilities found varied by as much as a factor of two". Other workers however have observed that weathering conditions both in the UK, and elsewhere, when taken over the year as a whole, tend to level out[4], although marked variations may be observed in the weathering response of similar materials exposed at the same site over shorter seasonal periods of time during (a) spring and summer, and (b) autumn and winter.[7-9]

Some conflict therefore exists between different workers as to the reliability and reproducibility of natural weathering exposures and it would obviously be advantageous if a method of weathering could be found that could give both reliable and reproducible results. The weatherometer or artificial weathering machine was designed for this purpose and one objective of this study is to find if it has successfully achieved this.

A further disadvantage of natural weathering is the length of time involved in exposure tests. With artificial weathering techniques this time can be reduced by approximately three-quarters. Continuing consumer demands for new colours and improved durability performance make it impossible to wait for lengthy outdoor tests and so the speed of the weatherometer in producing reproducible results is another distinct advantage.

1.4.1 Natural Weathering

Weathering has been defined by Stager[2] as the effects of all technoclimatic, mechanical, physical, chemical and electrical influences which, under operating conditions and by their collective effect on the surface and in the interior lead through irreversible processes to final deterioration. The most significant factors to which a coating is exposed during natural weathering are generally considered[2-5] to be those associated with radiation, temperature, oxygen, other harmful gases, water, micro-organisms, dust and wind. The ultra-violet component of sunlight is believed to be the single most harmful factor in degrading surface coatings but when in combination with other natural weathering factors its effect is more potent still. However, while some factors may be more important than others in natural weathering it is important to realise that a surface coating will be exposed to the complicated balance of all these factors and it is all of these factors together with their complex interactions which govern the behaviour of a paint film.

It would be very difficult to reproduce this delicate balance artificially but because of the time constraint on natural weathering it is valuable to be able to create suitable artificial weathering techniques. With regard to this it is interesting to note that natural weathering studies themselves usually have some element of acceleration inherent in them[4] as the samples are positioned in such a way that they receive the maximum amount of solar radiation.

1.4.2 Artificial Weathering

As more photochemically stable organic binders have been developed for use in paint films in recent years so the useful life of paint films has been extended. This in turn has led to the necessity for accelerated weathering exposure tests to assess the durability of these coatings. Artificial weathering tests which have so far been devised can be divided into three categories.

(1) Those involving exposure to just one or two of the factors comprising natural weathering. This type of accelerated weathering has been utilised in this project in the case of the exposure of surface coatings to uv radiation and to thermal radiation in a humid atmosphere. It is useful in assessing the contribution made by these factors to the overall picture of deterioration although it cannot be thought of as simulation of natural weathering.

(2) Those in which the samples under test are exposed to a repeating cycle of simulated natural weathering conditions. The weathering elements used in this type of exposure are usually intensified as compared with natural weathering but not to the extent that they are in (1) above. The BS3900 Part F3 artificial weathering apparatus falls within this category and was the device used for the artificial weathering of the samples in this project.

(3) The last category of artificial weathering techniques devised is that where accelerated natural weathering is carried out at tropical sites such as Florida[10]. Deterioration of surface coatings at such a site is accelerated compared to other locations because of Florida's unique conditions of intense sunlight, high humidity and moderate rainfall coupled with a minimal seasonal effect. Other sites used for accelerated natural weathering include Arizona[11], Pretoria and Durban[12], the prevailing weather patterns at these sites tend to be well documented along with performance data for a range of previously exposed materials.

It is also possible to accelerate natural weathering by concentrating sunlight onto the surface coating by means of a system of mirrors in conjunction with an equatorial mount (used for maintaining the sample perpendicular to the sun's rays). The two types of apparatus developed for this purpose are both located in Phoenix, Arizona and are designated EMMA[13] (Equatorial Mount with Mirrors for Acceleration) and EMMAQUA[11,14] the latter incorporating a water spray.

Each type of artificial weathering has its limitations when trying to reproduce natural weathering and all of the methods described above have their own disadvantages. The first method described is only a means of elucidating the particular ageing effects of one or more deteriorative weathering factors, the second type of acceleration does try to simulate natural weathering as a whole but because of the delicate balance between so many forces it can never totally reproduce the effects of natural weathering. A large number of artificial weathering machines have been produced in recent years[15-19] all with this aim and differing essentially only in the type of radiation used and the facilities available to control the various elements of their respective operating cycles. One of the major problems facing the designers of artificial weathering machines is the existence of considerable variation in natural environments together with the unique pattern of weathering at each site.

Reproducibility of natural sunlight is another problem and the choice of a suitable ultra-violet light source has been one of the foremost topics under discussion[20]. The suitability of a given light source is judged on the extent to which the spectral wavelength distribution of the light emitted "matches" that of natural sunlight. On this basis the xenon-arc lamp is regarded as offering closer correspondance with sunlight than any other artificial source[4,21,22].

The last type of artificial weathering, accelerated natural weathering can be considered to approximate most closely to natural weathering conditions and this method of exposure is therefore preferred by many researchers, although with new improved coatings produced today it is still necessary to expose samples for periods up to 2 years.

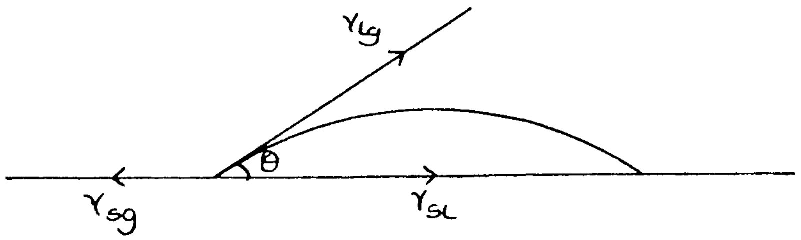
1.5 Analytical Techniques

The range of analytical techniques available for the study of the deterioration processes in surface coatings can be divided into two broad groups, firstly those which monitor changes in the surface of a coating and secondly those which monitor changes in the bulk properties of a coating. Techniques which monitor surface changes are more appropriate in a study of surface coatings because of the large surface to bulk ratio of the samples. In this study however some techniques which measure bulk changes have been used so that these changes when taken in conjunction with surface changes can be used to give an overall picture of the deterioration and degradation taking place within the polymer.

1.5.1 Surface Energetics

Under the broad heading of "surface energetics" are included those energy factors commonly associated with the processes of wetting, spreading and adhesion[23-27] of (a) a given coating when freshly applied to a substrate, and (b) a given liquid in contact with the formed coating surface. In the context of weathering the wettability of the coating surface by water, is of particular relevance, whether it be in the form of rain or dew droplets. Water is, of course, well-known as one of the more potent deteriorative weathering factors[28], especially in synergistic combination with radiation. Therefore the extent to which surface moisture adheres to (ie wets) a given paint film during exposure will have a direct bearing upon the paints' weathering performance. A technique which can be used to determine the surface energy of a coating involves the measurement of the contact angle which a given liquid makes with the coating. This is a very useful technique and as well as giving the surface energy of a solid, yields information regarding the surface roughness and heterogeneity of a coating. Thomas Young was the first person to link together the contact angle and surface energetics[29,30] in 1905 and then in 1878 J Willard Gibbs published the basic thermodynamics of wetting[31]. Uncertain experimental values however led to conflict over theoretical interpretations and so no further advances were made in this field until techniques for measuring reproducible contact angles were developed. Gibbs theory had predicted that for any given system there would be one and only one stable contact angle but with the development of improved techniques this was found not to be so and one of the fundamental characteristics of wetting is the ability of a liquid drop to form a continuum of different stable contact angles between two extremes on a solid surface[32]. Solman gave this phenomena the name of 'hysteresis'[33].

A free liquid drop on a solid surface will take the shape which minimises the free energy of the system and this shape is a result of the balance between the cohesive forces in the liquid and the adhesive forces between the solid and the liquid.



Young's equation[29,30] states that minimising the free energy of the system requires the minimisation of the sum

$$\gamma_{lg} A_{lg} + \gamma_{sg} A_{sg} + \gamma_{sl} A_{sl}$$

where γ is the surface or interfacial tension

A is the area

lg refers to the liquid-gas interface

sg refers to the solid-gas interface

and sl refers to the solid-liquid interface.

For a plane, homogeneous, non-deformable surface minimisation of the above equation yields

$$\gamma_{lg} \cos \theta = \gamma_{sg} - \gamma_{sl}$$

This is an idealised situation where there is only one equilibrium contact angle for a given system, in reality this is not the case and for a liquid-solid system it is possible to measure a number of stable contact angles. Two of these angles are relatively reproducible and are the largest and smallest of the stable angles. The smallest is known as the receding contact angle and the largest as the advancing contact angle, this is because the smallest is usually measured by pulling back the periphery of a drop over a drop and the largest by advancing the periphery of a drop over the surface. The difference between these two angles is called the hysteresis.

As stated earlier measurement of contact angles can give information about the roughness of a surface and this has been quantified by Wenzel[34,35]. For rough areas there are two areas the apparent area A^1 of a plane having the same macroscopic dimensions and the true area A taking into account the peaks and valleys of the surface. Wenzel defined the ratio r or roughness factor as

$$r = \frac{A}{A^1}$$

Replacing A by rA^1 in the equation

$$\gamma_{lg} A_{lg} + \gamma_{sg} A_{sg} + \gamma_{sl} A_{sl}$$

and minimising we get Wenzel's equation

$$\cos \hat{\theta} = r \cos \theta_0$$

$\hat{\theta}$ is the observed contact angle on a surface having an intrinsic contact angle of θ_0. Although a contact angle of $\hat{\theta}$ minimises the free energy of the system techniques of measurement are such that this angle is seldom measured.

Surface rugosities can act as capillaries in the surface of a coating and there is a critical roughness above which a liquid will spread spontaneously over the surface[36,37]. This is possible when $r = \frac{1}{\cos \theta}$. It has been shown that the roughening of a surface increases the advancing contact angle and decreases the receding contact angle until r = 1.2-1.4 when the advancing contact angle also begins to decrease[38,39].

Many authors have stressed that contact angles and drop shapes depend very strongly on anisotropy in the surface[41]. A drop placed on a surface grooved in one direction will tend to elongate in the direction of the grooves and in this case the contact angle will depend upon the position where the angle is measured. This is caused because the energy barriers are higher across the grooves than along them and the drop will elongate in the direction of the lowest energy barriers. Objectors to Wenzel's theory state that contact angles are determined solely by the nature of the surface at the periphery of a drop and that the average roughness of the entire surface should not be used to describe the effect at any isolated point on the surface. Wenzel's theory is therefore useful when dealing with uniformly rough surfaces but not useful if a surface is non-uniformly rough.

1.5.2 Measurement of Contact Angles

In general when measuring contact angles the limitations on accuracy are not related to the measuring techniques used but due to the reproducibility of the surfaces being studied. There are a number of different methods which can be used for measuring contact angles and providing suitable precautions are taken there is good agreement between the results produced by each method.

1.5.2.1 Drop or Bubble Method

This is the most commonly used method of measuring a contact angle which is determined by constructing a tangent to the profile of a liquid drop on a surface at the point of contact either by using a projected image of the drop or a photograph[41,42]. The contact angle may also be measured directly using a telescope fitted with a goniometer eyepiece[43,44]. The advantage of this type of measurement is that it employs simple instruments, only small volumes of liquid are required and the control of temperature and the vapour phase is easily achieved by enclosing the drop and the surface in a thermostated cell with viewing windows. Contact angles can be determined to within 1° using this method although for very small angles (less than 10°) and large angles (greater than 160°) the uncertainty is greater due to the difficulty in locating the point of contact between the solid and the liquid and constructing a tangent to the drop profile.

The contact angle of a sessile drop can also be measured directly by determining the angle at which light from a point source is reflected from the drop surface at the point of contact[45,46] with the solid. This eliminates the drawing of a tangent to the profile of the drop and requires no lenses or other optical equipment, the disadvantages however are that measurement is restricted to angles less than 90° and that a requirement is the elimination of unwanted reflections. The drop cannot therefore be enclosed in a thermostated cell and so contact angles in a controlled environment cannot be conveniently measured.

A further way of determining the angle made by a liquid drop in contact with a surface is by measurement of its dimensions. For a very small droplet the distorting effect due to gravity is negligible and the drop can be considered to be a segment of a sphere, the contact angle θ can therefore be calculated from the drop height h and the diameter of its base d using the equation[47]

$$\tan\frac{\theta}{2} = \frac{2h}{d}$$

1.5.2.2 Vertical Rod Method

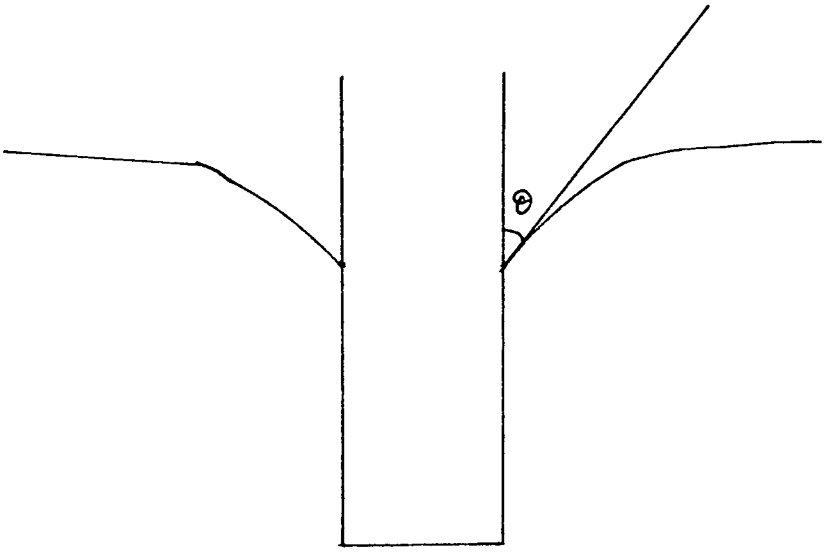


Figure 1 Vertical-Rod Method

Contact angles can be measured directly on a vertical rod or plate partially immersed in a liquid[48] using a telescope fitted with a goniometer eyepiece. Advancing and receding angles can be determined simply by immersing and withdrawing the rod in the liquid. It is necessary to use a rod of thickness greater than 50 μ because if a thin rod is used the radius of curvature of the liquid profile near such a rod is about equal to the radius of the rod and it is almost impossible to draw a tangent even when using high magnification[49]. This method is particularly useful when using viscous liquids to form contact angles because the time taken to attain a static contact angle is short.

1.5.2.3 Tensiometric Methods

The Wilhelmy Plate method[50] for determining the surface tension of a liquid involves measuring the force exerted on a thin wettable plate when brought into contact with a liquid. When the contact angle on the plate is not zero, this force is given by

$$W = p\gamma_{lg} \cos \theta - V\rho g$$

where p = perimeter of the plate

V = volume of liquid displaced by the plate

ρ = density of the liquid.

If the density of the liquid is known the contact angle θ can be determined using this equation. The term $p\gamma_{lg} \cos \theta$ is equal to the weight of liquid supported by the plate.

1.6 Colour and Gloss

The most obvious properties of surface coatings are their colour and gloss[51-54] and so it is not surprising that most attempts to characterise polymer surfaces have been made in this field. The colour and gloss of a surface is caused by the action of rays from a light source which fall upon the surface and is also dependant upon the position and shape of the surface. When assessing the glossiness of a surface we also make an assumption about the texture of the surface and this is assisted by a sense of touch which gives an impression of the surface rugosity and hardness.

1.6.1 Gloss

The term 'gloss' is used to describe the result of a visual appraisal of a surface. No precise definition of such a complex phenomenon is possible although various attempts[55-57] have been made to define it and its various angular qualities

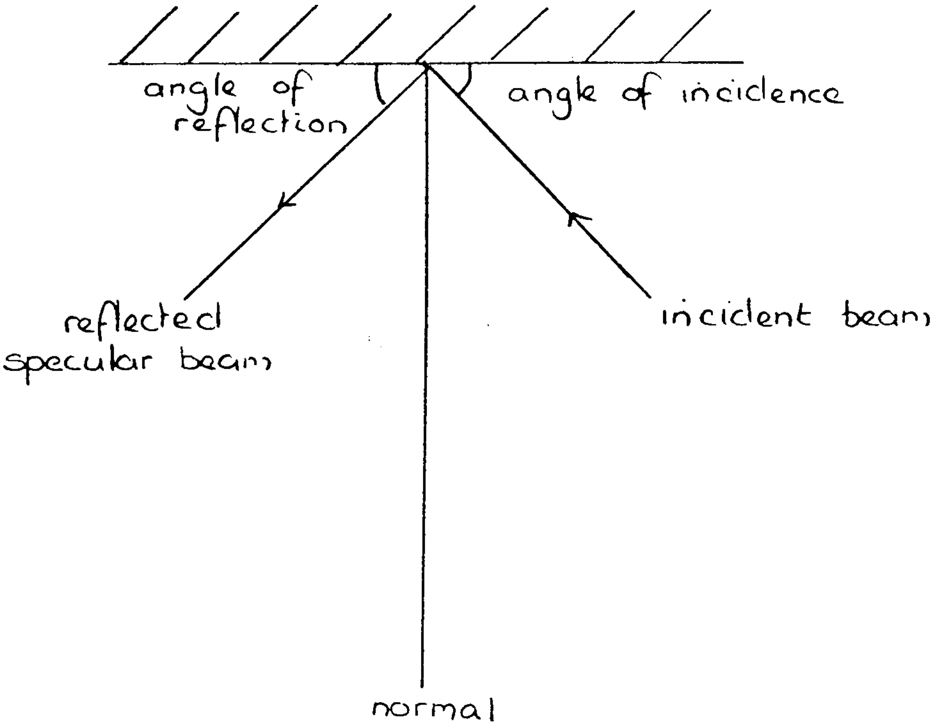


Figure 2 Reflectance phenomena - Definition of Terms

Figure 2 defines some of the terms used to describe the rays from a light source being deflected by a surface coating.

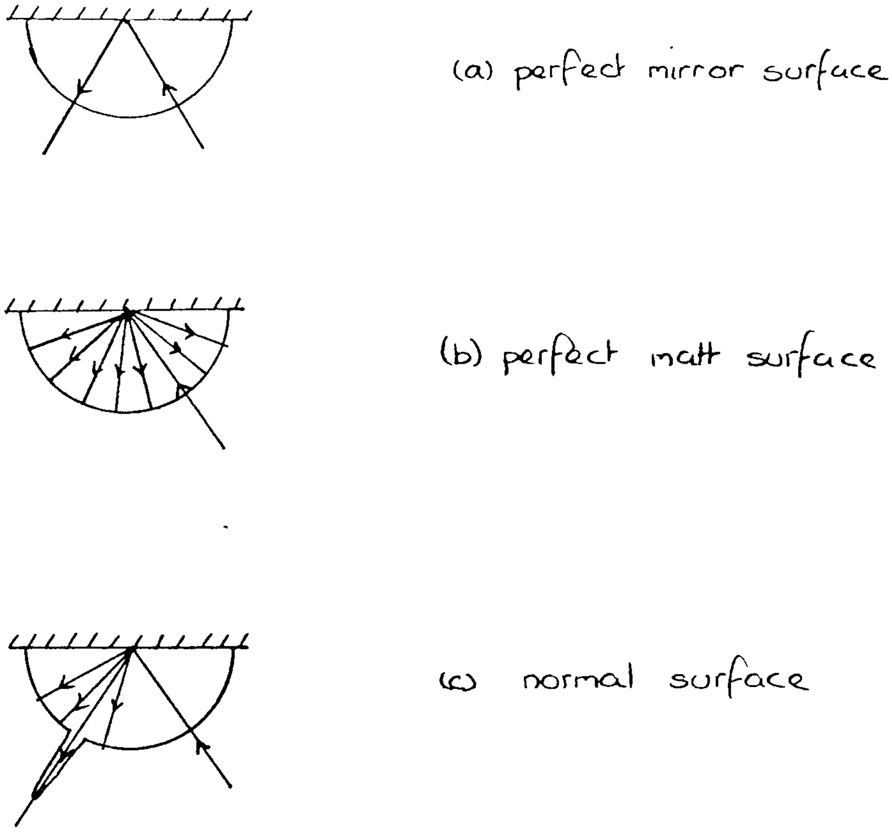


Figure 3 Spatial distribution of light reflected from various types of surface

There are three types of surface which can be described, a perfect mirror surface, a perfect matt surface or a normal surface. A perfect mirror surface as shown in (a) above is defined as 'a plane surface which reflects all incident light unidirectionally at an angle equal to the angle of incidence', this is called 'specular' reflection. Surfaces which act as near perfect mirrors reflecting over 90% of all incident light are plane polished surfaces of silver and ordinary silver backed mirrors.

A perfect matt surface, as shown in (b) above can best be described as a surface which reflects incident light equally in all directions. In practice perfectly matt surfaces are very rare with barium sulphate and smoked magnesium oxide surfaces providing the closest approximation. The normal type of surface encountered is shown as (c) above and is one which reflects incident light in all directions but with the predominance of reflections being at the specular angle. The percentage of incident light reflected at the specular angle depends on the surface with high gloss surfaces having a high specular reflection and semi-gloss surfaces having a lower specular reflection.

When making an assessment of the characteristics of a surface an individual forms an impression based upon the sharpness and contrast of images reflected to the eye from the surface and the diffuse reflectance of the film. Harrison[55-57] after extensive studies in which the ability of individual observers to rank a range of surfaces according to gloss was compared with instrumental measurements concluded that the gloss of a surface is not a simple physical property but a psychological Gestalt, that is an appraisal of the physical situation taken as a whole. He writes "gloss is not a single simple sensation but a complex of at least three simpler sensations. These were found to be, sharpness of mirror image, variations in the brightness of a surface when viewed at different angles and the parallactic effect in which we seem to be looking at one surface through another. Gloss is a combination of all three but not in fixed proportions".

The types of instrument which can be used to measure the gloss of a surface can be conveniently divided into two groups, namely gloss meters and goniophotometers and both of these groups are discussed here.

1.6.1.1 Gloss Meters

The 'specular gloss-meter' or 'reflectometer' is the simplest of the gloss measuring devices and is basically a reflection photometer.

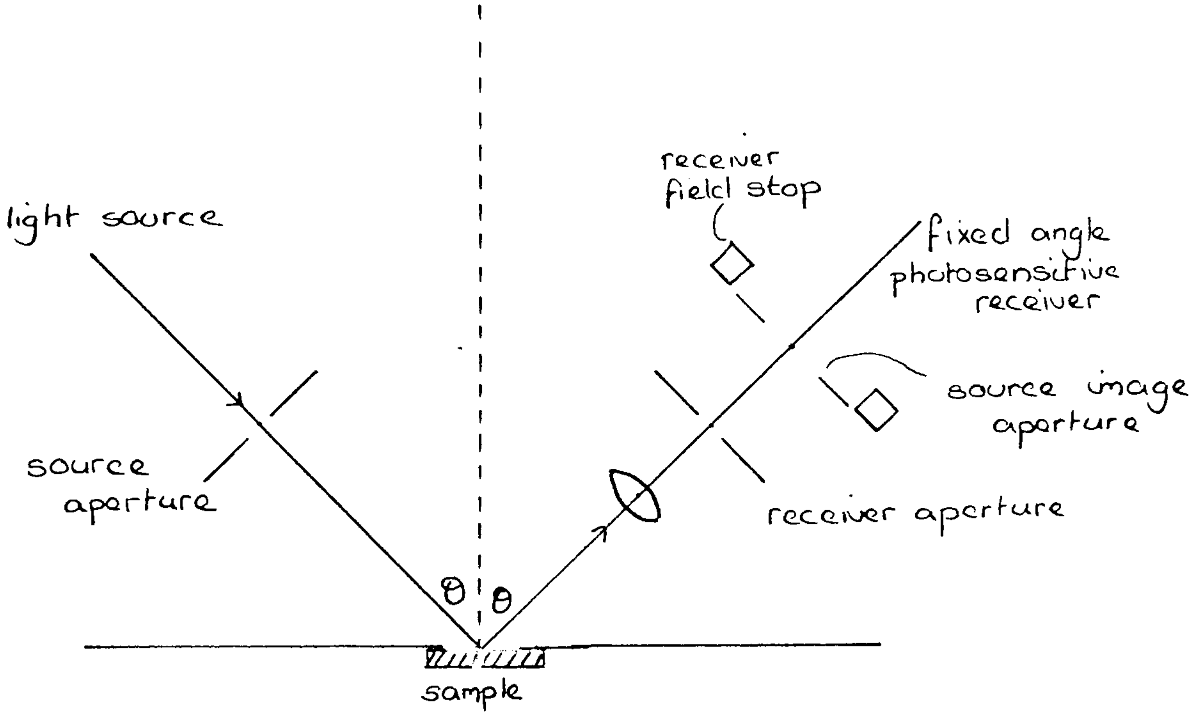


Figure 4 General Layout of a Specular Gloss-Meter

This instrument consists of three main parts, an incandescent light source, a part for the surface of the specimen and a photosensitive receiver. These three components are in fixed positions relative to each other such that the light reflected from the specimen surface is received at the specular angle, ie at an angle equal to the angle of incidence. Readings taken from the instrument are then related to that of a polished black tile or glass which is assigned an arbitary 'gloss value' of one hundred units for all angles of the incident and the reflected light. The choice of specular angle depends upon the type of surface being examined and the angle most commonly chosen for paint films of intermediate gloss is 60^{0}. It has been found however that for high gloss values 20^{0} specular geometry gives better resolution and for low gloss values a specular angle of 85^{0} is preferred. The main disadvantage of the specular gloss-meter is the general lack of agreement between gloss readings obtained from different laboratories and hence the lack of reproducibility in results. This seems to be due to poor standardisation and maintenance of instruments and so despite these drawbacks specular gloss-meters are widely used in industry because of their simplicity and ease and speed of analysis[58-63]. They only measure the light reflected at the specular angle however and not the angular distribution of the reflected light. An instrument in which the photosensitive receiving device is movable is therefore required to measure this angular distribution.

1.6.1.2 Goniophotometer

A goniophotometer is such an instrument and is capable of measuring the intensity of light reflected from a given surface as a function of viewing angle. The basic layout of a goniophotometer is shown in Figure 5.

Goniophotometry is the most informative and precise technique for measuring the gloss of a surface and it is capable of giving more than the gloss characterisation of a surface and so is very useful in studying the deterioration of polymer surfaces. The earliest known goniophotometer was in 1762 devised by Bouguer[64] in an attempt to corroborate Lambert's (cosine) law for uniform diffusers but despite being known for so long it has only been in recent years that the true potential of this type of instrument for gloss measurement has been

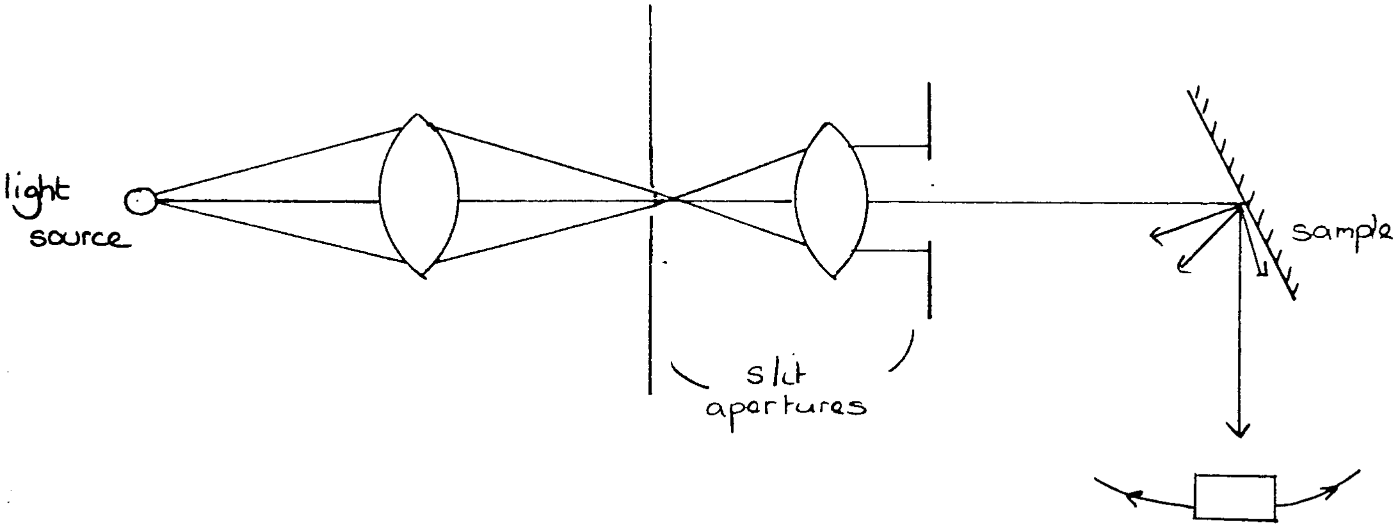


Figure 5 General layout of a goniophotometer

realised. In 1966 Hoffman and Kosbahn[65] described a relatively simple design of goniophotometer limited to three angles of incidence (30°, 45° and 60°) and using a convergent beam with an angle of convergance of about 8°. This has the advantage of obviating the need for a collimator on the viewing side and enabling an inexpensive photocell to be used. The instrument was also equipped with an automatic curve plotting facility.

In the same year a new commercial instrument the GP2 was described by Heinzloof of the Carl Zeiss Company[66] and although manual in operation the GP2 has found widespread use in practice because it combines accuracy of measurement with an optical system limited to the essential elements. Other developments in the field of instrumentation have been concerned with the modification of existing instruments. Carr has described an automated version of the Zeiss GP2 goniophotometer[67], Colling et al the modification of a Unicam SP500 spectrophotometer[68] and Loof the modification of the Zeiss DMC25 spectrophotometer[66] all for goniophotometric use. Billmeyer and Davidson[69,70] and Quinney and Tighe[71] have both described the modification and use of the Brice-Phoenix Light Scattering Photometer as a goniophotometer. The last three named instruments are strictly speaking spectrogoniophotometers as they are capable of measuring reflectance as a function of wavelength as well as of angle. Although few surfaces are goniochromatic that is the colour changes with geometry of illumination or viewing angle or both, it is a phenomenon which is well recognised and it is with this that Billmeyer's work has been principally concerned[69,72-75]. Other workers have used goniophotometers for studying the effects of surface defects and pigmentation[68,76-79].

Typical examples of goniophotometric curves are shown in Figure 6. These show that for a surface of high gloss most of the reflected rays are at the specular angle while for a surface of low gloss there is a more even spatial distribution of reflected rays. There are several ways of combining the experimentally determined values to yield a conveniently handled quantity which may then be compared with subjective gloss assessments. It is usual however to study three quantities the intensities of the specular (I_s) and diffuse (I_d) reflections in conjunction with the peak width at half-height ($W_{\frac{1}{2}}$). These quantities have been shown to correlate with`empirically judged image sharpness and contrast

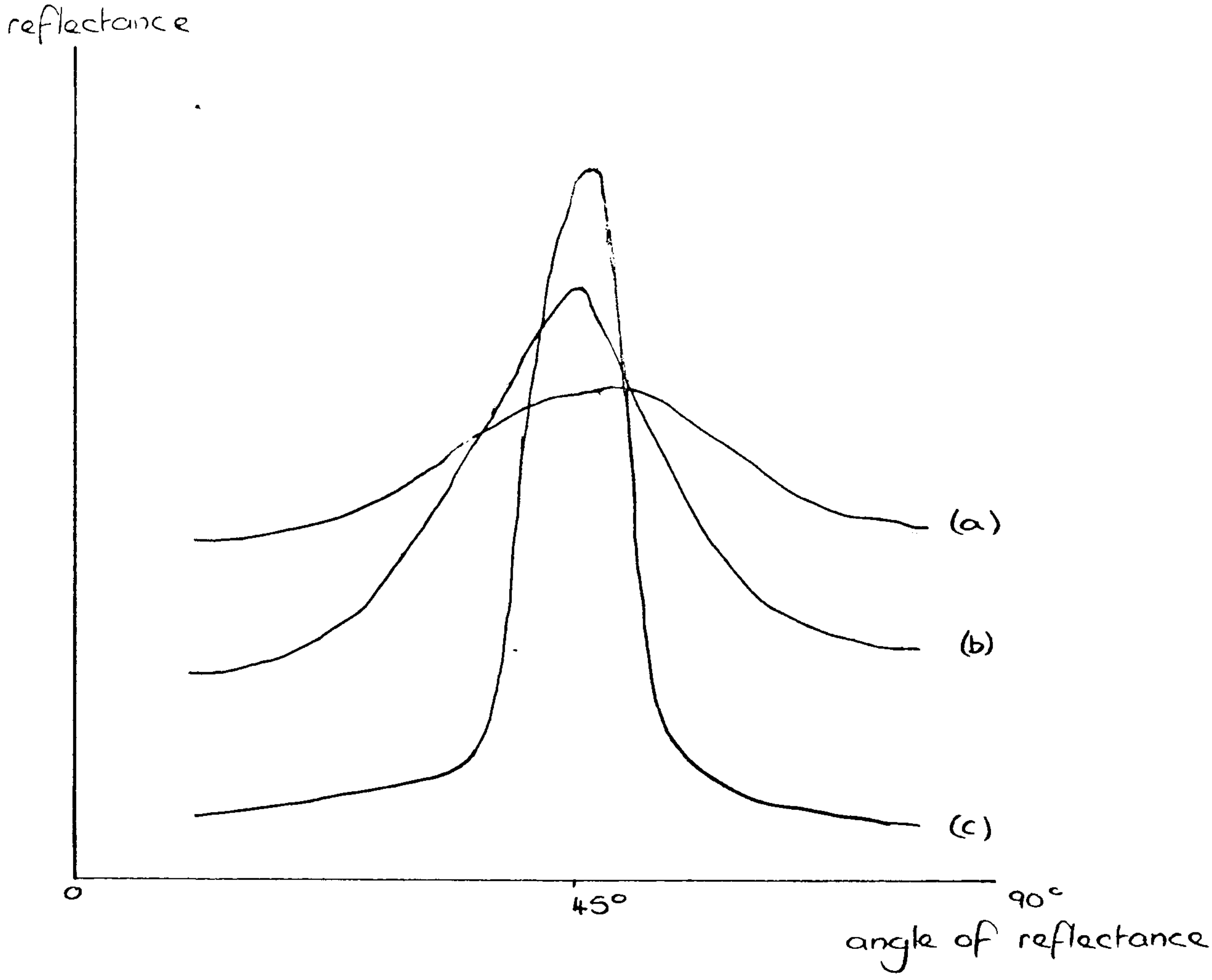


Figure 6 Typical goniophotometric curves for
a - low gloss surface
b - medium gloss surface
c - high gloss surface

and lustre to a greater extent than have simple photometer reflectance values.

1.6.1.3 Contrast Gloss Meters

The 'Contrast Gloss Meter' is an alternative to the 'Specular Gloss Meter' and it attempts to accommodate the visual evaluation that a human observer makes of the distinctness of an image observed at the sample surface rather than the intensity of the reflected light. The principle of this type of instrument involves the use of the sample as a mirror reflector and the degree of contrast at border lines between dark and light fields is then assessed. Contrast gloss-meters have been designed in which the fineness of detail that can be seen by specular reflection at a fixed angle is estimated or in which a pattern can be reflected specularly at various angles and the angle closest to normal to the sample surface at which the pattern can be seen is taken as a measure of gloss[80]. Although evaluation of the gloss of a surface with this type of instrument is in principle related to a specific model of subjective gloss assessment the fact that human evaluation is also involved makes the standardisation of such devices difficult. The most important features of contrast glossmeters are their extended range of applicability to surfaces in the medium and low range of reflectance and the fact that they have provided support for the view that gloss should be linked with the sharpness of an image as perceived by an observer[81,82].

1.6.2 Colour

The colour of a polymer surface is not as relevant as the gloss as the colour is largely attributable to pigments that are added to polymers for decorative and/or protective purposes in coatings. The perception of the colour of a surface is a sensation arising from the manner in which light incident upon the surface is reflected into the eyes of an observer. The colour is characterised by the spectral distribution of the reflected light within the visible range of the electromagnetic spectrum. The radiation from a surface that gives rise to the perception of colour is called a colour stimulus being the agent that stimulates the eye to produce the visual perception of colour[83,84]. Such stimuli can be registered and measured by physical instruments but the perception of colour can only be experienced by a living creature. The instruments which have been developed over the years for colour measurement can be considered as two main types, visual and photoelectric colorimeters.

1.6.2.1 Visual Colorimeters

Visual colorimeters use the human eye as a light receiver and are based on either additive or subtractive colour mixing. The additive type involve the matching up of the colour of the surface under examination; as seen in half of the field of view from under a specified type of white light illumination, with that obtainable by mixing variable amounts of red, blue and green light as observed in the other half of the field of view. Red, blue and green are chosen because they are defined by the International Commission on Illumination as the primary colour stimuli and it is from their relative intensities that the CIE system tristimulus values are derived and taken as the specification of the colour. The subtractive type of visual colorimeter in contrast involves colour matching of the sample surface with light reflected from a white background in front of which three series of variable-strength filter glasses are introduced.

Results obtained from visual colorimeters however suffer from a lack of accuracy and reproducibility because of the human element of assessment involved and because of this photoelectric colorimeters are more favoured by industry.

1.6.2.2 Photoelectric Colorimeters

Two main types of photoelectric instrumentation exist for colour measurement and these are namely (reflection) spectrophotometer and tristimulus colorimeters. The spectrophotometer measures the variation in intensity of surface reflectance as a function of the wavelength of the reflected light. The amount of light reflected from a coloured sample is measured at each wavelength as a percentage of that reflected from a standard white surface. Variations in instrumental design however, particularly with respect to the geometry of the optical system, inevitably give rise to differences in the results obtained and so a given reflectance measurement is often, to an extent, characteristic of the instrument as well as the sample.

Photoelectric tristimulus colorimeters[85,86] are instruments which evaluate directly the CIE system tristimulus values of a coloured sample. The main difference between these instruments and a spectrophotometer is that whereas in a spectrophotometer the monochromatic light is obtained by means of prisms or gratings, in tristimulus colorimeters only three narrow bands of light are used corresponding to the three primary colour stimuli, red, blue and green light. While the values these instruments give are only approximate, and can in some regions differ widely from the correct values, they are popular because they are quick and easy to use and much cheaper than spectrophotometers. They tend to be unsuitable for absolute measurements but useful in the measurement of colour differences.

1.7 Scanning Electron Microscopy

Surface microscopy is a valuable analytical tool for studying surface coatings and especially for studying changes which occur during ageing. The simplest form of surface microscopy is optical microscopy but this is of only limited use in studying the ageing characteristics of surface coatings because of its low power of resolution and very small depth of focus. This, combined with, in the case of pigmented samples the light scattering effects, means that the fine structure of a surface is very difficult to determine with any accuracy.

The electron microscope however is a very valuable technique when applied to the detailed analysis of surface coatings. It is a technique of great importance in studying surfaces and their inner structures[87-93] and in particular the changes which occur in a surface coating during ageing[89-91,93-97]. It enables the changes which occur during the early stages of weathering to be followed, changes which otherwise would not be noted, either visually or with an optical microscope. A disadvantage of electron microscopy is the care and time which is required for the preparation of samples for analysis, but even this has been to a large extent overcome with the introduction of the scanning electron microscope. The latter instrument has a second important advantage over the electron microscope and that is its exceptional depth of focus and range of magnification (x20 - x50,000) which enable it to produce micrographs of great clarity showing the three-dimensional topography of surfaces. The scanning electron microscope is therefore the most powerful and versatile instrument currently available for the direct observation of surface coatings[98-100] and changes in them which take place during ageing[99,100].

The cost of a scanning electron microscope precludes it from ever becoming a routine analytical tool in most laboratories and so many companies in industry instead of buying their own instrument are tending to finance the use of a scanning electron microscope owned by the larger research groups and by universities.

1.8 Infra-red Spectroscopy

Infra-red spectroscopy is a very convenient means of determining the chemical composition of organic coatings and transmission infra-red spectroscopy can be successfully used to follow changes brought about by ageing in thin transparent polymer films[101]. For thicker opaque coatings however this is not practical because of the sample's high absorbance characteristics. A way of applying infra-red spectroscopy to pigmented coatings was therefore required and a technique was developed to fulfill this need, namely internal reflection spectroscopy (IRS) also known as attenuated total reflectance (ATR).

The use of the infra-red spectrophotometer in the internal reflection mode was introduced about twenty years ago[102,103] and has since been applied to the analysis of paint films and plastics. An adequate description of internal reflectance phenomena can be based on Newton's "Opticks" first published in 1717[104].

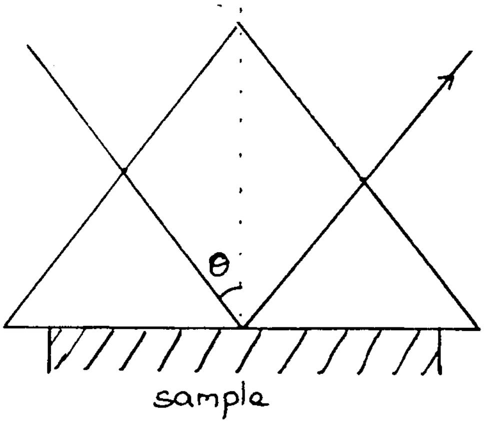


Figure 7 Single Internal Reflection Effect in MIRS

When a light beam is directed towards one face of a refractive prism as shown in Figure 7 it will be totally reflected if the angle of incidence θ is greater than the critical angle. It can be easily demonstrated that this totally reflected beam penetrates the space beyond the back face before returning through the prism and it can be shown that the amplitude of this beam decreases exponentially with distance from the back surface and is therefore called the 'evanescent' wave. When a sample is placed against the back surface of the prism this evanescent wave undergoes selective attenuation which is related to the infra-red activity of the sample. A plot of wavelength against transmittance then yields a spectrum similar to that of regular transmission spectroscopy. The depth of penetration of the evanescent wave is defined by Harrick[105] as:

$$d_p = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}^2)^{0.5}}$$

where λ_1 is the wavelength of the light in the refractive prism, θ is the angle of incidence and n_{21} is the ratio of the refractive indices of the optical element n_1 and of the sample n_2. The value of d_p is one of the factors which determine the strength of absorption in the spectra and the above relationship shows that the depth of penetration increases with wavelength. As the scan moves from 4000 to 250 wavenumber cm^{-1} the depth of penetration typically increases from 0.75 to 15 µm, this wavelength dependance therefore produces some distortion in IRS peaks as compared with transmission spectra. The depth of penetration decreases as the angle of incidence increases and so the angle of incidence can be used to control the depth of penetration. This is useful when studying effects, such as, weathering, plasticiser migration and multilayered films. The depth of penetration also increases as n_{21} tends to unity but as the index of refraction of the refractive prism must be greater than that of the sample to obtain undistorted spectra KRS-5 (thallium bromide-iodide) is usually used as a reflector and so the ratio of n_{21} is seldom varied in practice.

A second effect that distorts the bands in the spectra and displaces them to longer wavelengths is the change in sample refractive index that the instrument sees as it passes through an absorption band. Dispersion effects occur in both transmission and reflection spectroscopy but in the former case the beam angle is constant and the effect is not noticed.

Dispersion is the effective increase in the refractive index of a material as the frequency of the source light increases. From this discussion it can be seen that it is necessary when obtaining spectra to make a compromise between peak height and peak distortion. To obtain a satisfactory IRS spectra it is also necessary that the sample should be in intimate contact with the back face of the refractive prism. An IRS scan obtained in this way is then generally similar enough to a regular transmission scan to permit a direct comparison to be made.

Internal reflection spectroscopy does have several advantages over transmission spectroscopy and these are 1) IRS can be easily applied to a wide range of solids and liquids (using a special liquid cell), 2) the ease with which samples can be prepared for analysis, 3) films do not produce interference fringes, 4) the spectra are independent of the sample thickness, 5) IRS can be used to study surface reactions as the beam penetrates to a depth of only a few microns and 6) the sample is not destroyed as in the case of organic and inorganic powders handled as mulls for transmission spectroscopy. The main disadvantage of IRS as compared with transmission spectroscopy is the lower quality of the spectra obtained, especially in the case of rough or inflexible surfaces.

Internal reflection spectroscopy is therefore a very useful tool for studying surface coatings and the effects of ageing upon their surfaces, as well as more specific phenomena such as plasticiser migration, cure reactions and weathering effects.

1.9 Weight Loss Measurements

When one considers that it is often in terms of the time taken for a certain percentage weight loss to occur that the effective service lifetime of a paint film has been expressed, it is surprising to find that the measurement of weight loss on quantitative basis is a relatively recent technique for studying paint film deterioration[114]. The reason for this is possibly that for a long time workers had serious reservations regarding the accuracy of weight loss measurements mainly on account of the fact that the expected weight losses from paint films in general would be so small in comparison with the total weight of the film and its substrate. Additionally there were the problems associated with accompanying change in the weight of the substrate, dirt pick-up by the coating surface, and also seasonal weather variations, inherent in outdoor exposure, to be taken into account. Since the early 1960's, however, many of the procedural problems have been overcome by the design of more stringent test methods and the advent of more accurate weighing instrumentation. The most usual test procedure[115] involves the application of the paint film to a weather resistant substrate, such as, stainless steel, followed, after ageing, by careful washing of the coating surface in order to remove loose particulate matter, and thorough drying before determining the weight loss. This type of procedural control has led in more recent years to a more quantitative approach being taken to the weight loss analysis of paint films on ageing[114,116-120].

It is probably true to say that weight loss measurements have been most popularly applied to the study of erosion rates[114,116-120]. This has resulted in ample evidence appearing in the literature to suggest that the erosion rate is, in fact, a specific film property and should be considered as such in assessing the durability of a paint system[116], on the other hand, there is little evidence to suggest that erosion is directly related to other film properties such as gloss retention, except in a very general sense, yet, despite this, the study of erosion rates has come to be regarded as a useful quantitative means, in its own right, of following film degradation. Furthermore, erosion rate data has also been observed, in certain cases to provide useful correlations between the results of natural and accelerated weathering[119,121]. Of additional interest, in connection with accelerated weathering, is the contention by Berg et al[119] that weight loss measurements taken over the first several hundred hours of exposure are sufficient to characterise the likely performance of most paint films in practice. However, other workers[115] have suggested that it may be necessary to allow for a steady rate of weight loss to be reached before meaningful data can be obtained, although this undoubtedly reduces the early predictive ability of the test. In a more recent article, Whiteley and Rothwell[10] support the view that although weight losses need to be interpreted with caution in the early stages of weathering, if a steady rate is subsequently attained they can be extrapolated almost to a definite lifetime. In this way, an upper ageing limit can then be readily set with respect to the time taken for a given fraction of the film weight or thickness to be lost, assuming, of course, that only a general erosion of the surface takes place without any disastrous failure by, for example, cracking or checking.

Weight loss measurements have also been used extensively for assessing the "chalking" tendencies of pigmented paint films[121,115,122], notably those incorporating titanium dioxide pigments. On the other hand, a number of workers have also been able by means of weight loss analysis, to demonstrate the protective action of rutile-type titanium dioxide pigmentation on the paint system during exposure[120,123]. However, whilst the role of titanium dioxide pigments in paint systems may have attracted most attention up to now, Ritter[116] points out that the role of any paint ingredient can, in fact, be studied by the weight loss/ erosion rate technique.

1.10 Bulk Techniques

Commercial surface coatings are most readily thought of in terms of their aesthetic appeal and, subsequently, most readily assessed in terms of the retention of their surface properties, it is obviously important to realise that modern-day coatings are very much engineering materials which are expected to meet a range of bulk property requirements as well. However, it is probably fair to say that, if only because of the large surface area to bulk ratio which characterises surface coatings, bulk property analytical techniques have often tended to be somewhat less predictive on their own than surface techniques of the likely in-service performance of a given paint film on weathering. Nonetheless, bulk analysis forms an essential part of any overall testing program on the strength of which a new coating material might gain commercial acceptance. Methods used for mechanical testing and thermal analysis will now be discussed in more detail.

1.10.1 Mechanical Testing

The mechanical testing of surface coatings[100] includes the measurement of properties such as hardness, tensile strength, extensibility (elongation), flexibility, adhesion and abrasion resistance. The use of this type of test for predicting coating performance[107] has been applied for some time now to both detached and substrate-supported films, since it was first observed that significant changes in the mechanical properties of paint films occurred during both natural and artificial weathering. This was a clear indication that actinic radiation was penetrating at least part way into the film in order to effect the bulk interior changes to which the mechanical properties were related.

Of the various mechanical properties mentioned, hardness has certainly been one of the most popular chosen for measurement. Hardness, like gloss, tends to be a conceptual property insofar as it means different things to different people and is measured in different ways. However, a general working definition of hardness, based on practical concepts, simply states that "hardness is a resistance to indentation or scratching" although the latter part of this definition presents more problems than it solves. Consequently, it has been the measurement of indentation hardness that has proved most attractive and which, with the more recent advent of the microindentation technique, has been developed to the stage where the "state of this particular art" compares very favourably with any of the previously described surface techniques. An example of a microindentation instrument which is now in commercial use is the ICI Pneumatic Microindentation Apparatus developed by Monk and Wright[108] in 1965, since which time this particular instrument, in common with its related types, has been applied very effectively to the study of the properties and ageing characteristics of surface coatings[10,109,110].

1.10.2 Thermal Analysis

The application of thermal methods of analysis to the characterisation and ageing study of organic coatings materials has also been shown[111,112] to yield useful information which can often be correlated with corresponding mechanical test data. Perhaps the single most important ageing parameter which is obtainable from analysis is the glass transition temperature (Tg)[113], variations in which can be brought about by a range of physical and chemical effects such as plasticiser loss and cross-linking or chain scission within the polymer matrix. Determination of the Tg is generally carried out on unsupported coating samples by means of following the temperature dependence of a suitable physical or thermodynamic property such as refractive index, density, specific volume, torsional shear/Young's modulus or enthalpy. Variation in this latter property - enthalpy - with temperature, as measured by differential scanning calorimetry (DSC), is currently the most popular method which, in addition to the Tg, can also provide useful indications of the softening point and decomposition temperature of the test material.

In addition to DSC, however, other techniques such as thermogravimetric analysis (TGA), for compositional and thermal stability studies, and thermal mechanical analysis (TMA), for monitoring bulk property changes, are also widely used. TMA, in particular, is useful in that it overcomes the need to prepare free (ie detached) films for testing purposes; analysis in this latter case involves the determination of the displacement profile of a penetration probe on a substrate-supported film over a programmed temperature range.

CHAPTER II

2.1 Experimental Techniques and Procedures

This chapter deals with the various experimental techniques employed during the course of this work and can be conveniently divided into three sections:-

1 Surface coatings systems studied - including details of formulation and preparation.

2 Ageing environments - details of both the natural and artificial weathering environments are given.

3 Analytical techniques - the procedures used in this study are described.

2.2 Surface Coating Systems Studied

A range of experimental poly(vinyl chloride) plastisol coatings have been studied in the course of this work and the formulation of each of these coatings is given in Tables 1 and 2.

The complete formulations 8 + 8', differing only in plasticiser content, are intended to represent the basic framework of a commercial PVC plastisol coating manufactured and marketed by Vinatex Ltd, Havant, Hants who kindly prepared these coatings as shown. The complete formulation was then broken down into plasticised PVC alone and plasticised PVC plus pigment and it is hoped that by doing this the roles played by the various components of the coating during ageing could be assessed.

It was necessary to incorporate a small amount of thermal stabiliser into all the formulations initially for processing purposes. In the case of those coatings which were to be considered as containing no

TABLE 1

List of PVC Plastisol Coatings Studied

Formulation Number	Formulation Description
1	Plasticised PVC clear
5	Plasticised PVC + pigment
8	Plasticised PVC + pigment + uv and thermal stabilisers

TABLE 2

Details of PVC Plastisol Coatings Studied

Formulation number	Formulation Details				
	PVC resin	Plasticiser	Pigment	uv stabiliser	thermal* stabiliser
1	100	80	-	-	0.5
5	100	80	15	-	0.5
8	100	80	15	0.5	1.5
1'	100	50	-	-	0.5
5'	100	50	15	--	0.5
8'	100	50	15	0.5	1.5

*See Note on Page 35

thermal stabiliser after processing then only that amount of thermal stabiliser was added which it was estimated would be consumed during processing.

2.2.1 Preparation of Plastisol Coatings

The range of coatings described in Tables 1 and 2 was prepared using an eight litre high-speed Papenmier Mixer and they were then applied to each of the following substrates. (See Appendix I for detail of preparation techniques).

2.2.1.1 Glass panels. These were both primed (by dip-coating with British Steel Corporation's coil coat primer and curing at 225°C for 30 sec) and unprimed. These were suitable for analytical techniques requiring a flat substrate, also the coatings could be easily peeled off the unprimed glass substrate and used for gel content measurements and multiple internal reflection spectroscopy.

2.2.1.2 Aluminium panels. Again these were both primed as previously described and unprimed after pre-treatment with a thermo-setting epoxy resin coating. These samples were especially suitable for micro-indentation studies.

2.2.1.3 Stainless steel panels. These were primed as previously described and were used for weight-loss measurements where ageing resistance of the substrate is necessary.

Wherever possible the PVC plastisol coatings were machine-coated onto the various substrates to a film thickness of 0.008" using the ICI Automatic Film Applicator, before being cured for 90 seconds at

225°C. This was however impracticable for the glass substrates and for the less plasticised series of coatings due to rheological reasons. In these cases the samples were hand-coated to a film thickness of 0.007"-0.009" using a bar applicator, before being placed firstly in an oven for 10 minutes at 120°C and then cured for 60 seconds at 225°C.

The finished plastisol coatings were all glossy in appearance and relatively soft in surface texture.

2.2.2 Formulation of raw materials

The components that go to make up the PVC plastisol coatings used in this study can now be described more fully.

2.2.2.1 Poly(vinyl chloride) resin

The PVC resin used in the preparation of these plastisol coatings is a suspension polymer manufactured by Bush, Beach and Segner Bailey and marketed under the trade-name of 'Vinnol P-70'.

2.2.2.2 Plasticiser

The plasticiser used is an especially pure grade of di-iso-octyl phthalate (DIOP) manufactured by Albright and Wilson Ltd. Its varied level of addition constitutes the difference between the two series of coatings studied. The higher plasticiser content (80 pph of resin) of Series I confers an ease of coatability, whereas the lower content (50 pph of resin) of Series II is more in line with the level incorporated into commercial PVC plastisol coatings.

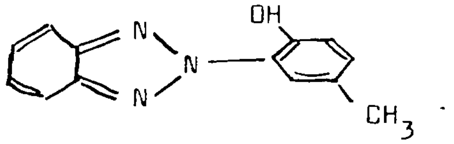
2.2.2.3 Pigment

The pigment chosen is a white, rutile titanium dioxide grade

(Tioxide R-CR3, British Titan Products Co Ltd) which it is claimed has outstanding chalk resistance[115,124]. It is particularly well suited for use in exterior plasticised coil coatings as it combines extremely high opacity and gloss with durability at low pigment volume concentrations[124].

2.2.2.4 Ultra-violet stabiliser

This is 2-(2'-hydroxy-5'-methyl phenyl) benzotriazole (I) marketed by Ciba Geigy Ltd under the trade name of 'Tinuvin P'.

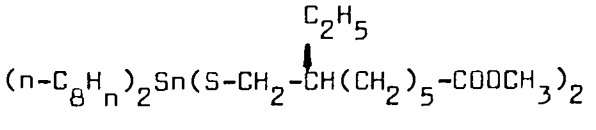


(I)

Its stabilising action is classed as being that of a 'uv-absorber'[125] or 'screening agent'.

2.2.2.5 Thermal Stabiliser

The thermal stabiliser used in these coatings is an organotin compound di-n-actyl-tin-bis-2-ethylheptyl mercaptoacetate (II) manufactured by Albright and Wilson Ltd, and marketed under the trade-name 'Mellite 831D'. Its powerful stabilising action of PVC is achieved mainly via its rapid 'fixation' of evolved hydrogen chloride gas, which would otherwise catalyse further chemical breakdown of the polymer[125,126].



$$(n\text{-}C_8H_n)_2Sn(S\text{-}CH_2\text{-}\overset{C_2H_5}{CH}(CH_2)_5\text{-}COOCH_3)_2$$

(II)

The coatings described here are designed to study their ageing characteristics and while they can be regarded as being related to commercial systems they are not directly comparable with them. In addition to the components mentioned present-day commercial plastisol coatings also contain filler resins, solvents designed for high speed coil coating production and multi-component plasticiser systems.

2.3 Ageing Environments

The types of ageing environment used in this study fall into two distinct categories (i) natural weathering and (ii) artificial weathering. The artificial weathering studies can then be sub-divided into three further groups, (i) artificial weathering machine, (ii) uv ageing cabinet and (iii) thermal and humidity ageing. (See Appendix II for detail of ultra-violet light sources).

2.3.1 Natural Weathering

The natural weathering exposures described in this work were carried out at the Building Research Station's exposure site. This is a semi-urban site being relatively clean with the concentration of particulate matter in the surrounding atmosphere being low. The samples were mounted onto exposure racks inclined at 45° and facing south. These standard conditions (ASTM D1435) ensure that for temperate climates such as the UK the test specimens receive the maximum amount of solar exposure throughout the year and that drainage of rain-water from the sample surface is facilitated[127]. It has been suggested[4] that inclining the samples to obtain the maximum amount of solar exposure does in itself introduce an element of acceleration to the outdoor weathering test. This acceleration effect has been estimated as being of the order of 20% over the first two years exposure for rigid PVC plastics and varies for different polymer systems.

2.3.2 Artificial Weathering

The artificial weathering techniques used in this study can be regarded as two types, firstly using the BS 3900 Part F3 artificial weathering machine and secondly those using similar apparatus designed to expose the samples to just one or two aspects of weathering such as uv or thermal ageing. These various artificial weathering techniques were chosen because of their likely value in aiding the interpretation of the ageing characteristics of the test samples.

2.3.2.1 Artificial Weathering Machine BS 3900 Part F3 Artificial Weathering Machine:-

This test method was originally developed[128] as an artificial weathering cycle capable of inducing, in a range of alkyd and oleoresinous paint films, changes which could be satisfactorily correlated with those arising from natural weathering at various sites in the UK. The weathering cycle is still used mainly for testing alkyd based paints but it has also been applied to a wider range of paint systems with varying degrees of success. One limitation of the BS weathering cycle is that it is found to be relatively slow when compared with other artificial weathering cycles. Approximately 2000 hours of exposure are necessary to induce changes comparable with two years natural weathering in the UK.

The BS 3900 Part F3 weathering apparatus consists essentially of an enclosed carbon arc light source atomised water spray and cooling fan (see figure 8). The particular machine utilised in this work was that which is located at the Building Research Establishment's Princes Risborough Laboratory, Aylesbury, Bucks. Sampling of the test panels was carried out initially at 500 hour and then later at 1000 hour intervals.

2.3.2.2 UV Exposure Cabinet

The cabinet used in this work is illustrated in Plate 1 and was supplied by Laboratory Thermal Equipment, Greenfield, Nr Oldham, Lancs, and consists of a battery of 28 fluorescent tubes, each 2 feet in

Plate 1 - The uv Exposure Cabinet

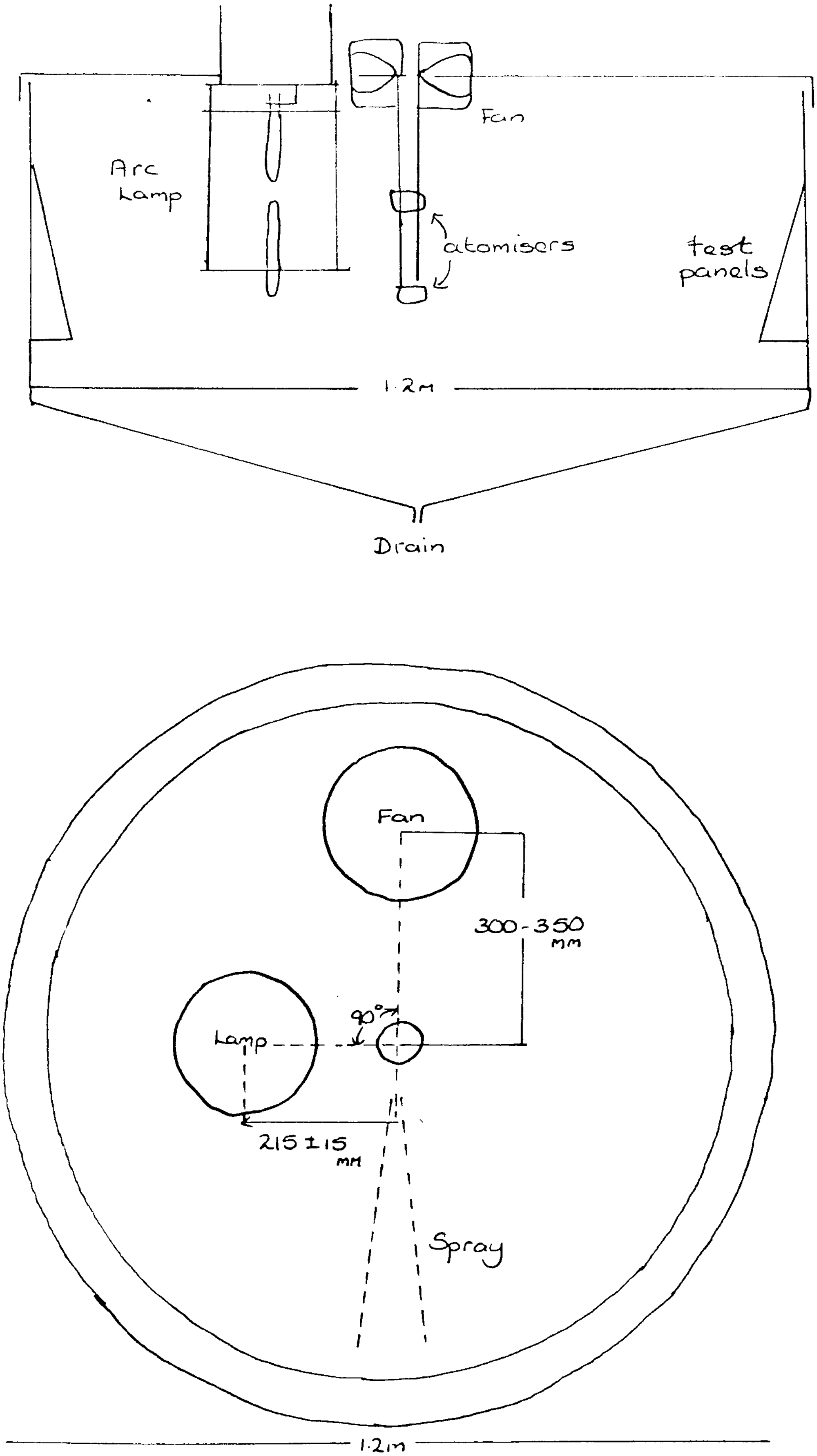


Figure 8 - Design layout of the BS 3900 F3 Artificial Weathering Apparatus

length, set in a circular arrangement around and 10 cm away from a rotating sample support frame. The collection of tubes comprised a symmetrically arranged 3:1 combination of two slightly differing types (a) 21 'Actinic Blue' (20 watt, Phillipps (GB) 20W/05) lamps and (b) 7 'Sunlamps' 120 watt Westinghouse (USA) FS20). The spectral output of this tube combination and arrangement has been found to produce a reasonable match for solar radiation. An advantage of this type of system over a single lamp source is that the tubes can be progressively renewed four tubes (3 'Actinic Blue' and 1 sunlamp) every 85 hours thus providing and maintaining a source of almost constant radiation intensity.

The test samples used in this exposure were mounted on the rotating drum opposite the central portions of the irradiating lamps, thus ensuring that all of the samples received as constant an intensity of radiation as possible. The samples were then tested at 500 hour intervals.

2.3.2.3 Environmental Test Chamber

The environmental test chamber as supplied by Montford Instruments Ltd London, is illustrated in Plate 2 and consists essentially of an oven cavity (30 x 30 x 32 cm) incorporating a heating unit and an air circulating fan. This apparatus has a very precise temperature control accurate to ± 0.1°C throughout the oven cavity and variable from -50°C to 500°C. Additionally the oven can be programmed to cycle between two temperatures and to hold the extreme temperatures for a set length of time. For this work the chamber was programmed to cycle between 30°C and 70°C and to hold each of these temperatures for three hours. Coding was facilitated by carbon dioxide and a

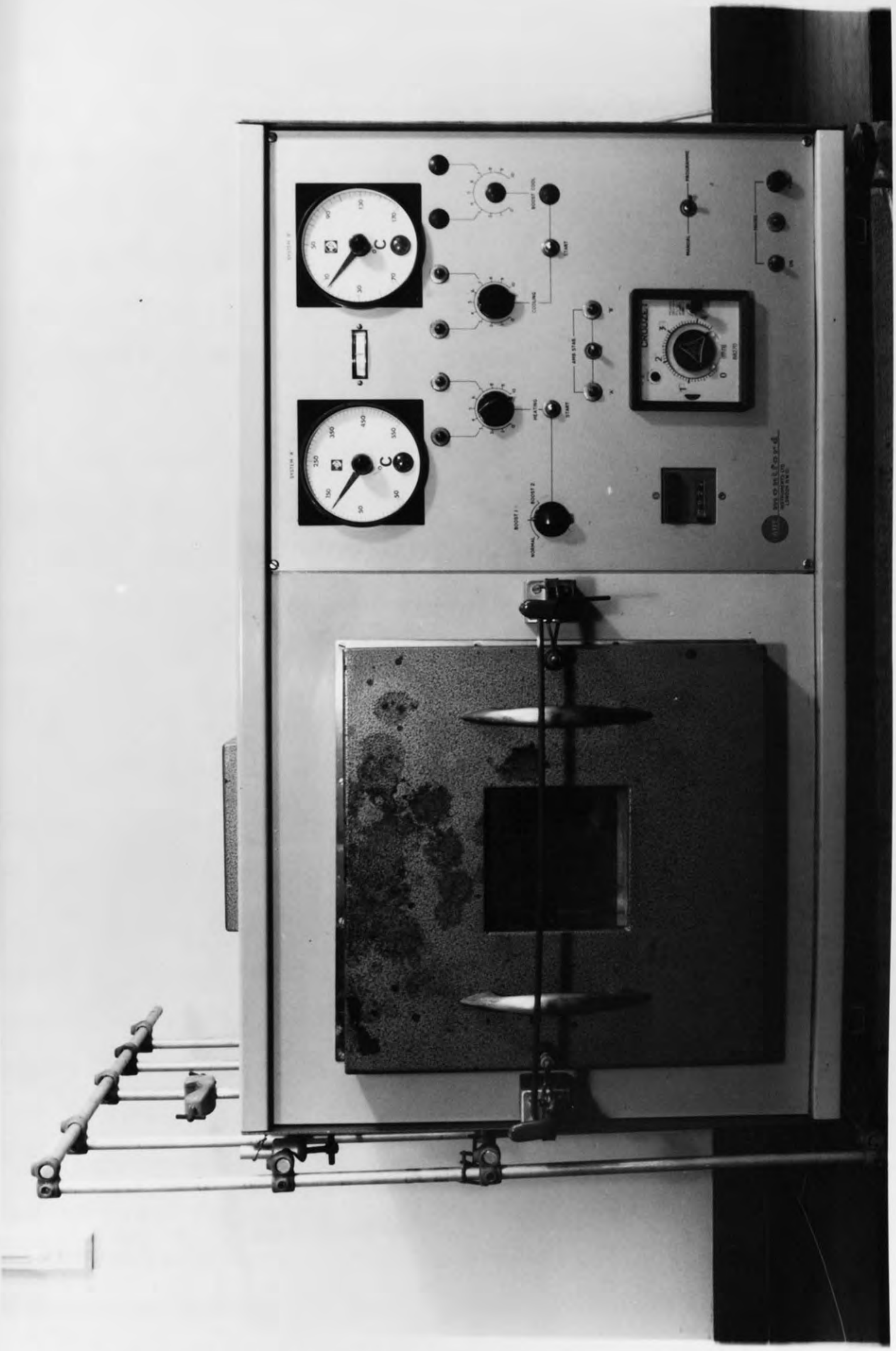


Plate 2 - The Environmental Test Chamber

complete cycle took approximately 10 hours.

The test samples were suspended in a sealed vessel above water to create a humid atmosphere. The samples were removed for testing every 500 hours.

2.4 Characterisation Techniques

The analytical techniques which were employed during the course of this work are now discussed.

2.4.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy proved to be a valuable technique for viewing the changes taking place in the topography of the polymer surface during ageing. Microscopic changes thus visible in the surface can then be related to changes in other properties due to ageing.

The scanning electron microscope used in this work was the Stereoscan Mark 2A instrument produced and marketed by Cambridge Scientific Instruments Ltd and illustrated in Plate 3. The basic principles of its operation, Figure 9, can be briefly summarised as follows. A beam of electrons emerges from the electron gun under the influence of an accelerating voltage of from 1 to 30 kv and this is then focussed by a series of electromagnetic condenser lenses into a small spot on the specimen surface. The incident electrons are partly reflected and partly absorbed, with some re-emission of low energy secondary electrons. The reflected primaries or the emitted secondaries are then collected by a scintillator, with the strength of the signal received being dependant upon the surface topography at the point at which the electron beam impinges on the specimen. By applying a scanning motion to the electron

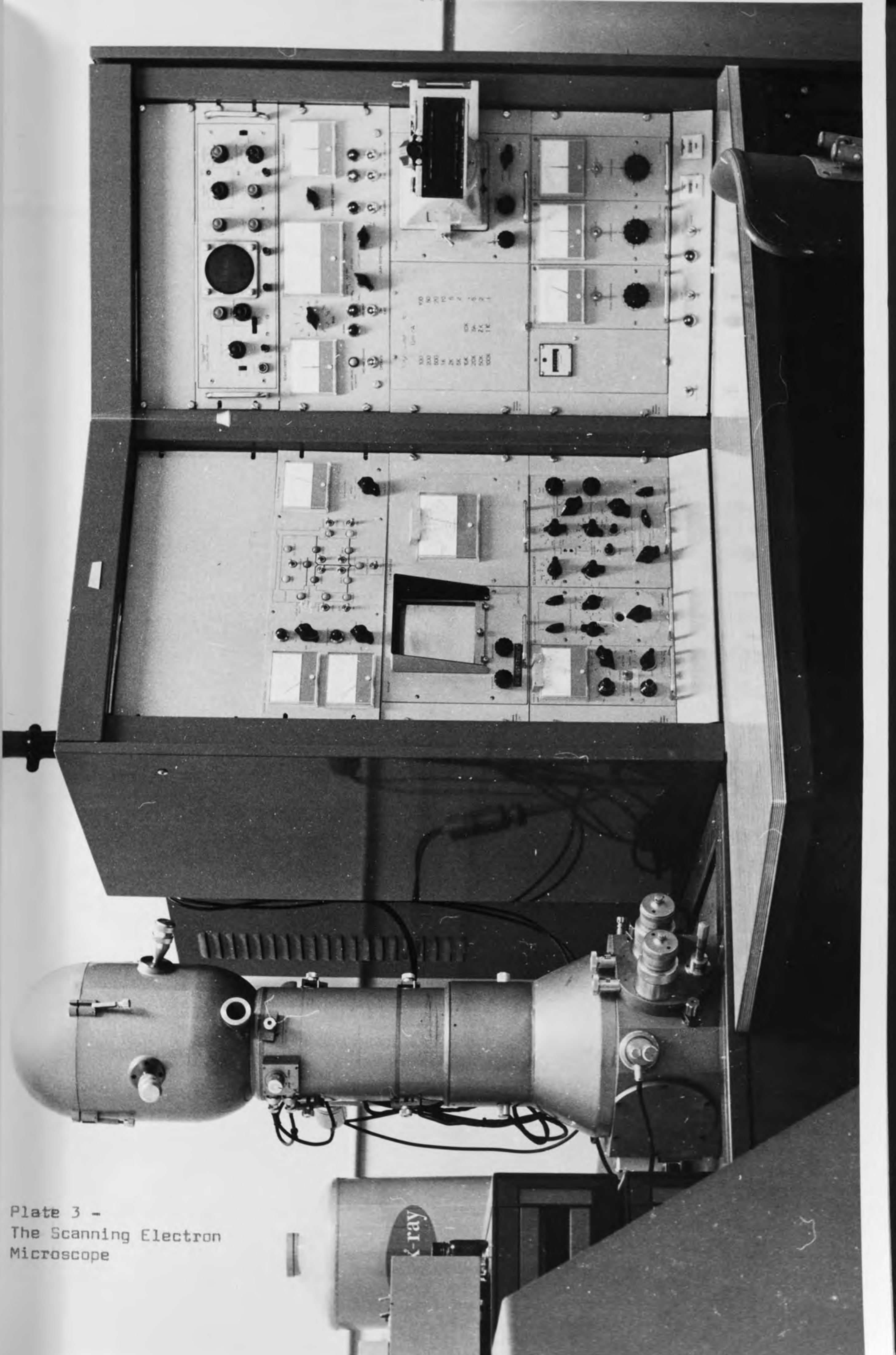


Plate 3 -
The Scanning Electron
Microscope

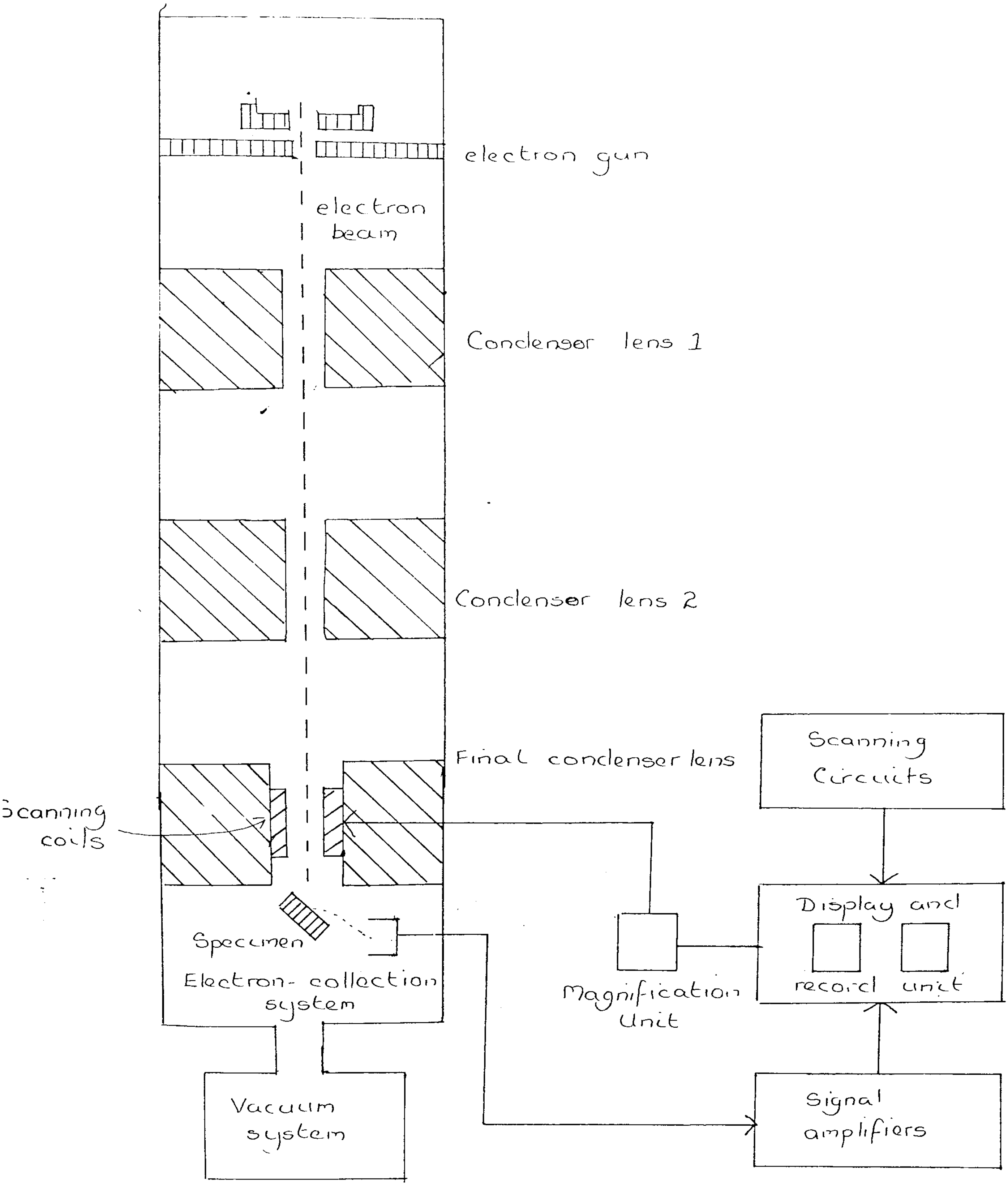


Figure 9 - Schematic representation of the basic principles of operation of the Stereoscan Mark 2A Scanning Electron Microscope

Figure 10 - Spectrum of an uncontaminated KRS-5 reflector plate

beam, using the scanning coils, the signal strength varies with the amplified signal being displayed photographically on a cathode ray tube using a synchronous scanning motion on the tube display. Magnification is changed by altering the amplitude of the scan on the specimen.

Samples for SEM analysis were mounted onto a small circular aluminium stub (1 cm diameter) with up to five samples on each stub in recognisable shapes. The surfaces were then covered with an electrically conducting layer as required for SEM analysis.

2.4.2 Multiple Internal Reflectance Spectroscopy (MIRS)

MIRS was employed in this work in an attempt to study the chemical changes taking place during ageing at the surface of the coatings.

A Perkin-Elmer Model 297 Infrared Spectrophotometer was used for the study and this was fitted with a Model 9T Single Beam Multiple Internal Reflectron Attachment[129] supplied by Wiltec Scientific Instruments Ltd, London, as illustrated in Plate 4. The internal reflectron element used in this attachment is a 45° KRS-5 2 mm reflector plate composed of a thallium bromide/thallium iodide eutectic mixture. A KRS-5 crystal is chosen in preference to either a Ge or ZnSe crystal because it yields the best spectra for the widest variety of samples and also it is less brittle than the other crystals, flowing under mechanical pressure.

To obtain a spectrum the KRS-5 plate was first carefully cleaned using ethanol and then dried and polished using a soft felt cloth stretched over a plane glass plate. This was repeated until a spectrum of the crystal alone showed it to be free from contamination as shown in Figure 10. The sample to be tested was then cut to the shape of the

Plate 4 - Multiple Internal Reflectance spectroscopy (MIRS) apparatus

crystal on both sides (only one side if the sample was very strongly absorbing) and mounted into the sample holder. This was then placed usually in the 45° angle of incidence slot in the MIRS attachment and the attachment was placed in the sample beam of the spectrophotometer. After trying 30°, 45° and 60° angles of incidence (illustrated in Plate 5) the 45° angle of incidence was found to give the best spectra for most samples. The mirror reflectors of the attachment were then optically aligned and the reference beam attenuation was carried out to balance the spectrophotometer for its energy loss in the sample beam.

The spectra were then recorded using either the three minute or more usually the 10 minute scan mode.

2.4.3 Energetics

Studies under the more general heading of 'surface energetics' were most conveniently carried out by means of contact angle measurements. Two different liquids were chosen, in this case water and methylene iodide, and the contact angle which they made with the coating surface was measured. Water and methylene iodide were chosen because of their ease of purification and the different polar and dispersive contributions which they make to their respective surface tensions.

The contact angles that each of these liquids made with the coating surface were measured using a sessile drop technique as illustrated in Plate 6[130,131]. All contact angles measured in this way are taken to be equilibrium advancing contact angles (see Figure 11) as distinct from dynamic advancing and receding angles.

Other data can then be calculated from these measurements, firstly the

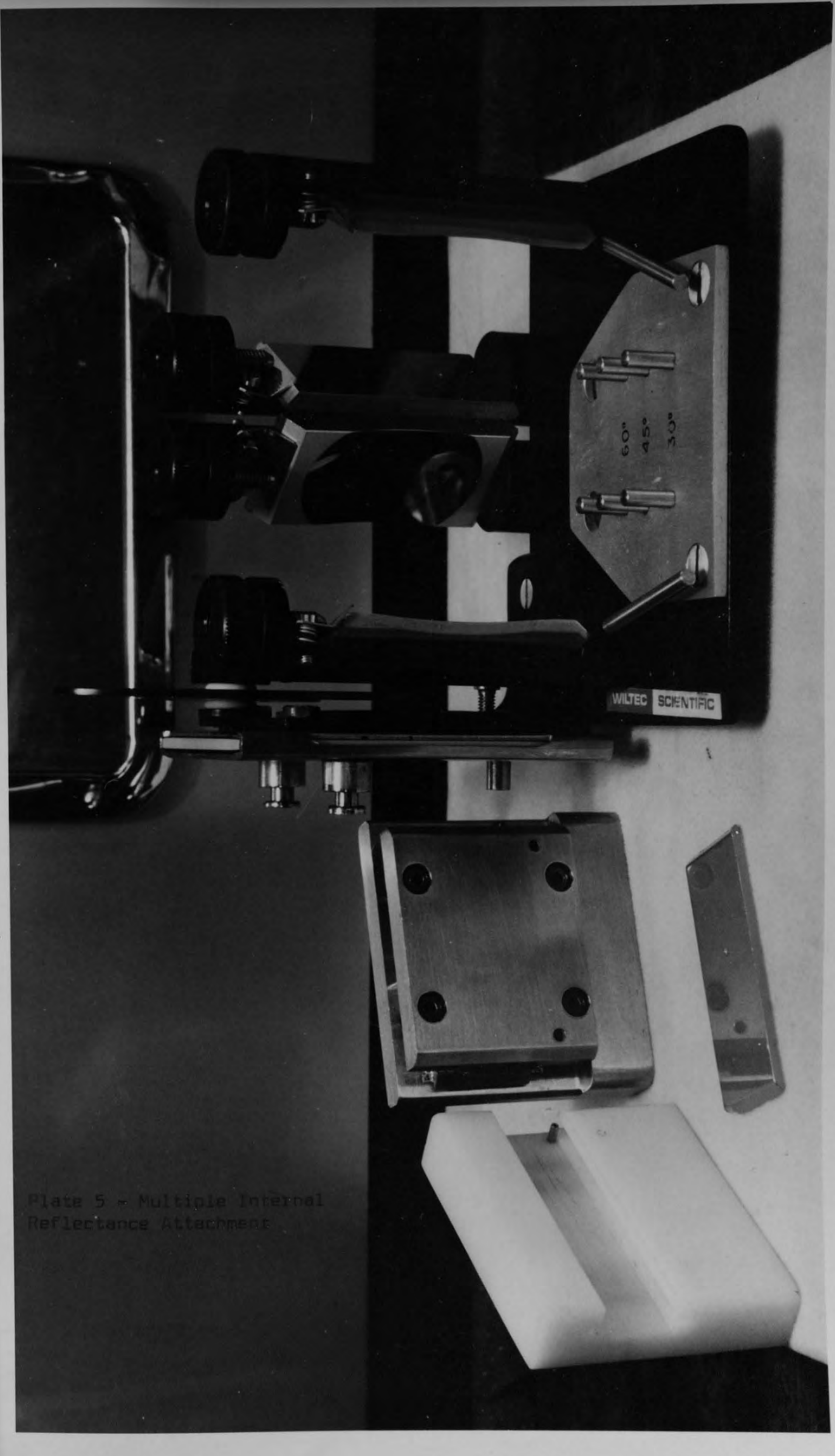


Plate 5 - Multiple Internal Reflectance Attachment

Plate 6 - Sessile Drop Technique for measuring contact angles using a Goniophotometric eyepiece

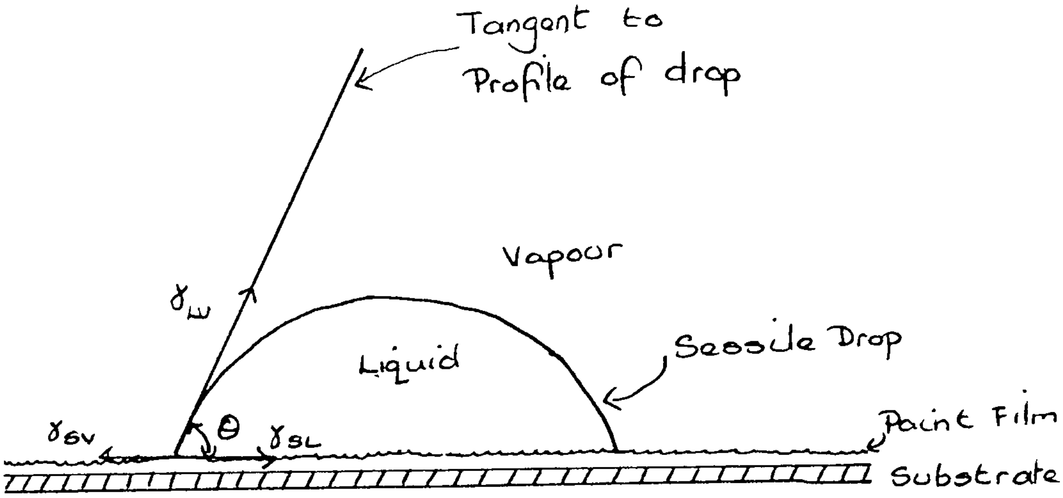


Figure 11 The profile of a sessile drop resting on a paint surface

critical surface tension (γ_c) of coating surface can be calculated and secondly the coatings surface free energy[23,131-139] together with its polar and dispersive components can be found (where γ_c is defined as the surface tension of that liquid which just completely wets the solid surface). It is to obtain the surface free energy of the solid phase that contact angles made by two different liquids are obtained. Water and methylene iodide are usually chosen for this because of their widely differing polar and dispersive components of surface tension. Changes in these components should theoretically yield information about the changes in polarity at the surface brought about by ageing. The surface free energy - its components were obtained by using the

Owens and Wendt equation.

There are however some experimental difficulties with this technique, firstly contact angle measurements are extremely sensitive to any surface contamination and so consequently all samples have to be very carefully cleaned and dried before any measurements are possible. Secondly contact angles are also affected by surface roughness and in an ageing study this is a significant factor and makes their accurate measurement more difficult.

This second effect has been quantified by Wenzel and he has developed a relationship between the macroscopic surface roughness factor (r) and the measured contact angles for rough (θ') and ideally smooth (θ) surfaces

$$r = \frac{\cos\theta'}{\cos\theta}$$

Theoretically then this technique should provide valuable information regarding changes in polarity and rugosity of the surface during ageing.

2.4.4 Goniophotometry

This is the most informative and precise technique available for the measurement of the gloss of a surface and was the main analytical technique used throughout this project. The goniophotometer used in the present study is a converted Brice-Phoenix light-scattering photometer illustrated in Plate 7, which is in many ways ideally suited for this type of work. Strictly this instrument should be called a spectro-goniophotometer as it is capable of measuring reflectance as a function of wavelength as well as of incident and reflected angle.

The essential features of the high performance goniophotometer obtained by modification of the Brice-Phoenix light-scattering photometer

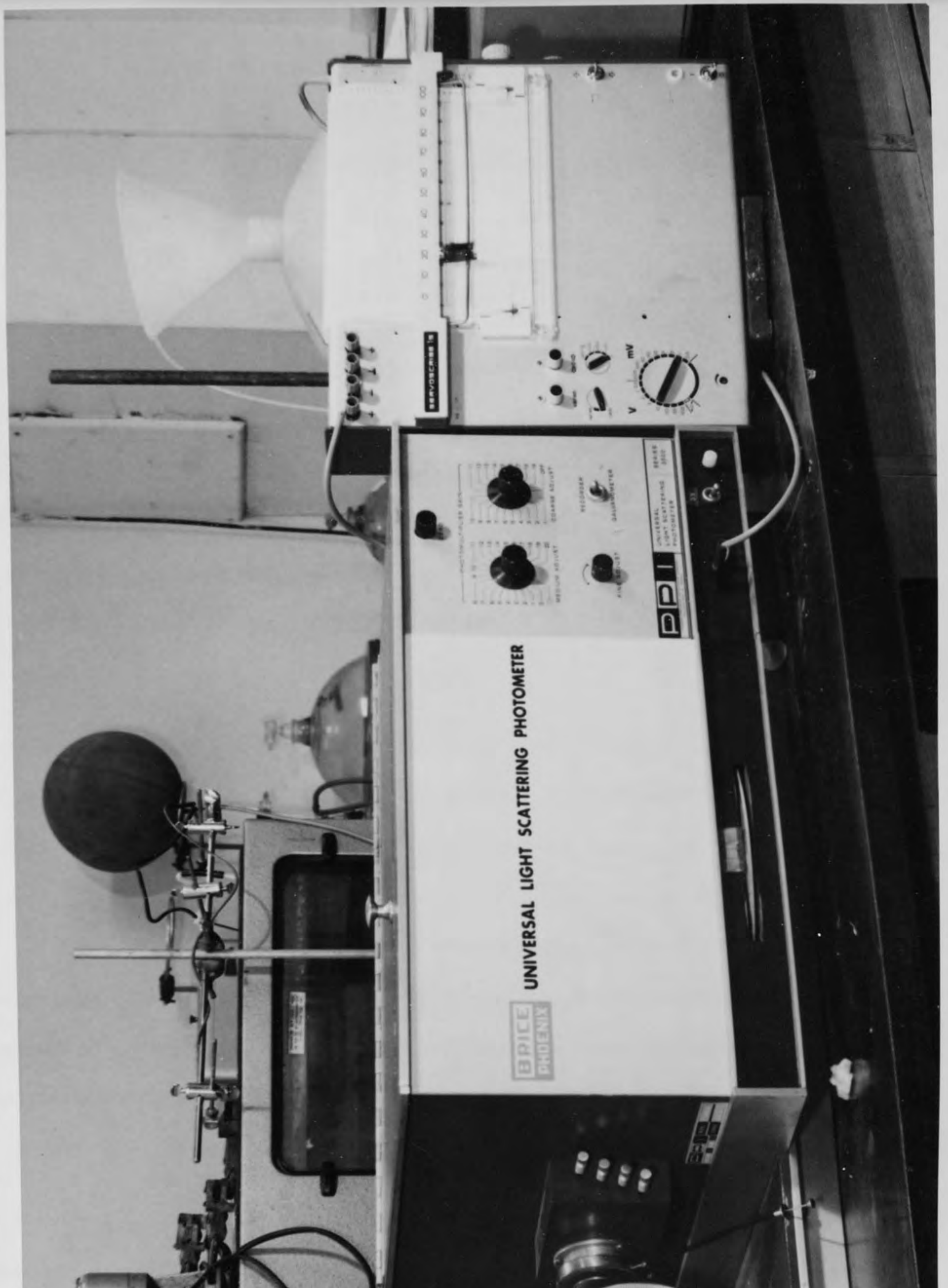


Plate 7 - The Automated Goniophotometer

(Series 2000) are shown in Figure 12.

A light beam from the lamp A passes through a preselected wavelength filter (B) and shutter unit (C) into a collimating tube (E), incorporating a removable polariser and slit aperture (F) the width of which may be varied. The light impinges on the sample mounted at (G) and is thereby reflected, scattered or transmitted, its intensity being measured as a function of the scattering angle by a photocell (H). The intensity of the light beam is controlled by a series of neutral filters (D). The photocell which may be rotated through an angle of 270° has a removable analyser and variable slit aperture (I). The signal from the photocell is amplified and registered on a galvanometer or chart recorder.

The specimen mount has a brass base, calibrated at 15° intervals illustrated in Plate 8, which is located positively on the specimen table (g) and which is designed in its normal use to take a glass cell with a square base. The specimen holder which can be rotated through 360° fits onto this base and will take any optically flat specimen up to a maximum thickness of 2 mm. The mount was coated with matt black paint to prevent any stray light reflections from it reaching the photocell In this study both the pigmented and unpigmented coatings studied were mounted onto an aluminium substrate.

The ability to reduce the size of the incident beam is limited principally by the sensitivity of the instrument but a 1 mm radius circular beam gives adequate sensitivity and enables small areas of the polymer surface to be examined. In studies where the sample must be successively examined (eg in ageing studies) then an alignment mark on the mount and sample support facilitates reproducible mounting of the specimen.

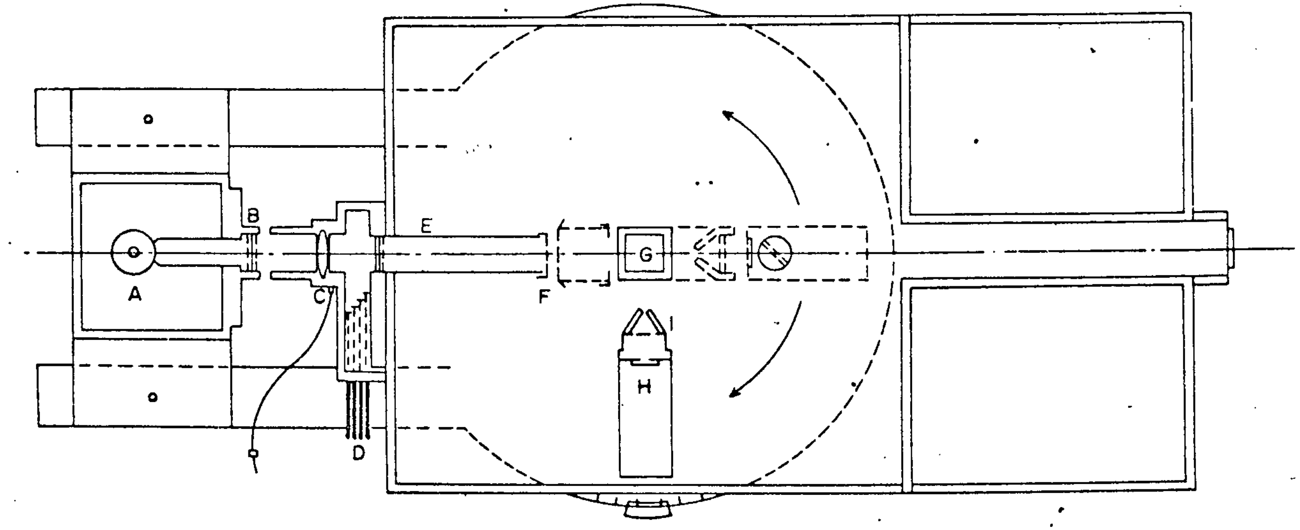


Figure 12 - Essential features of the goniophotometer

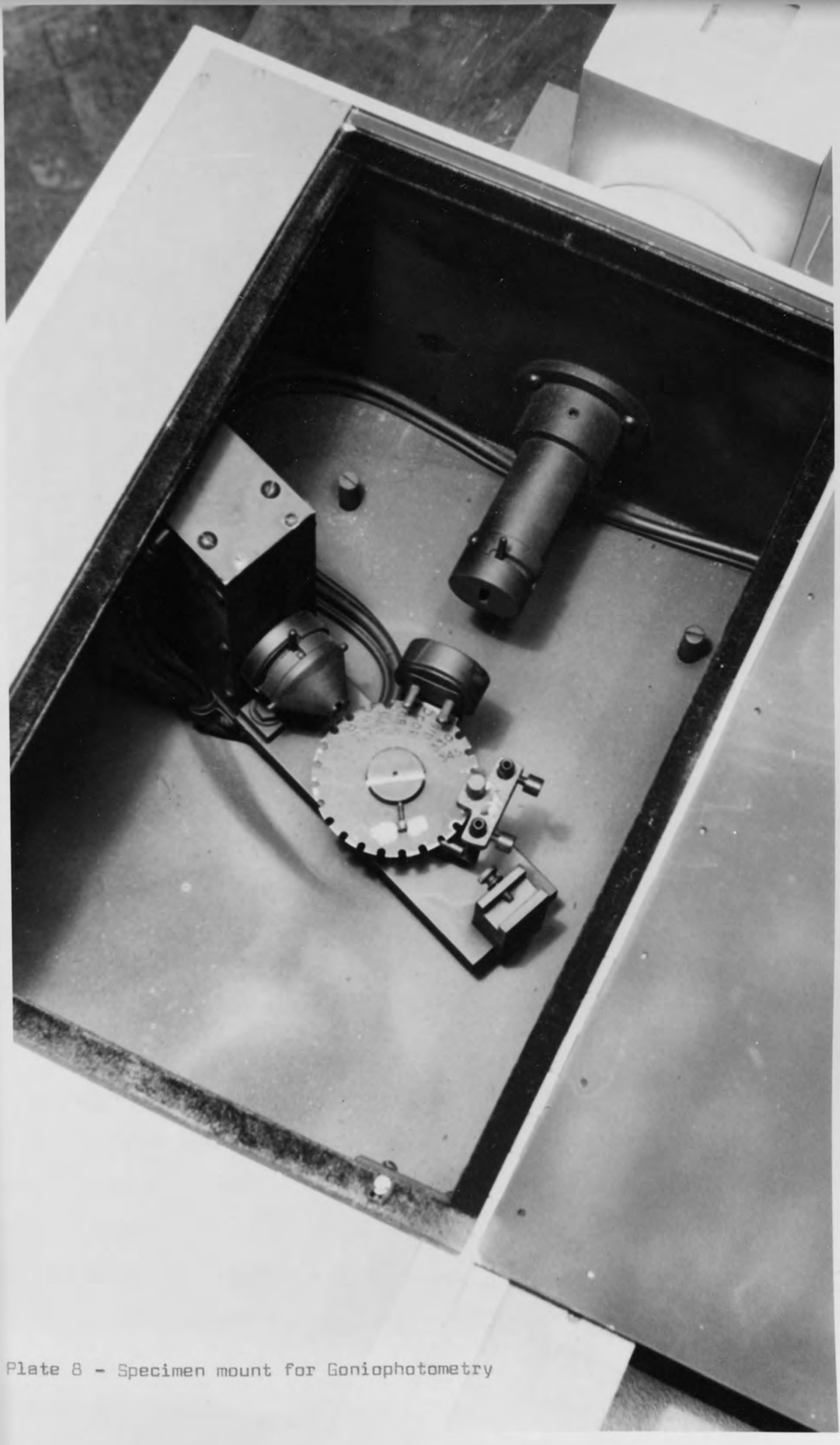


Plate 8 - Specimen mount for Goniophotometry

A typical curve obtained from the goniophotometer is shown in Figure 13 and a summary of the terms used in the interpretation of goniophotometric data is given.

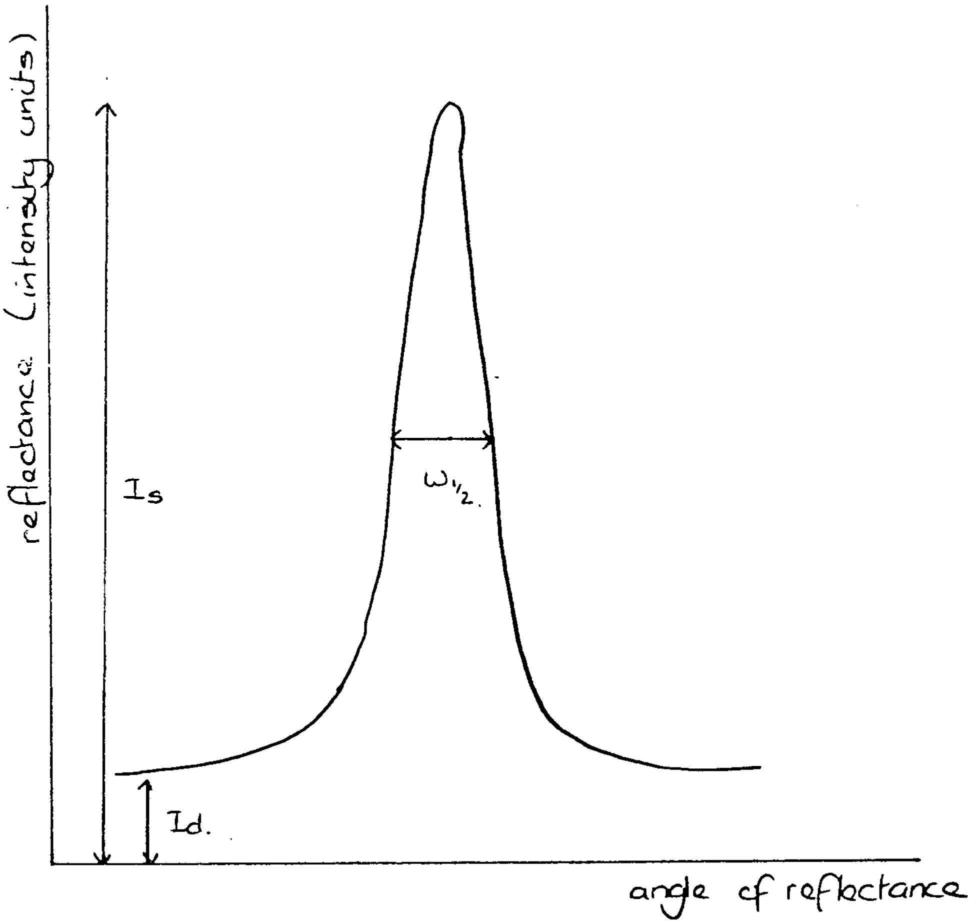


Figure 13 A typical goniophotometric curve

1 Specular reflectance (I_s - intensity units)

This is defined as the maximum angular reflectance from the sample, which occurs at or near to an angle equal to the angle of incidence of the illuminating light. It is the specular component of a surface's overall gloss that a gloss meter measures, and it also corresponds to the visually perceived brightness of an image observed on reflection at the sample surface.

2 Specular angle (degrees)

This is the angle at which specular reflectance occurs, which for a perfect mirror surface will be an angle equal to the angle of incidence. In most cases however surfaces are imperfect and so there will be a slight difference between the specular angle and the angle of incidence.

3 Angular Displacement (degrees)

This is the difference between the angle of incidence of the illuminating light and the specular angle.

4 Diffuse reflectance (I_d - intensity units)

In this work the diffuse reflectance (I_d) is taken to be the reflectance which occurs at an angle of reflection of 0^o ie along the normal to the sample surface. This represents the background reflectance which is seen visually by an observer as 'haze' which impairs the sharpness of the image definition. In theory diffuse reflectance is all reflection which occurs at an angle other than the specular angle.

5 Peak height (I_s-I_d, intensity units)

The goniophotometric peak-height represents the component of a sample's reflectivity which occurs in the specular region and which despite being superimposed on a background of diffuse reflection lends itself to the surface's mirror imaging capability.

6 Peak width at half-height ($W_{\frac{1}{2}}$, degrees)

This provides a measure of the extent to which a surface spatially distributes around the specular angle light which is incident upon it. In visual terms the specular reflectance and peak height are related to the brightness of an image viewed at the surface, whereas the sharpness of an image is related to the peak width.

7 Gloss factor (GF, intensity units/degrees)

This is obtained by dividing the peak height by its width at half its height

$$GF = \frac{I_s - I_d}{W_{\frac{1}{2}}}$$

The gloss factor therefore encompasses both the brightness and sharpness of the image producing capability of a surface in one term. It is therefore the most meaningful goniophotometric parameter in terms of its potential correlation with visual gloss ratings.

The effect of surface defects upon goniophotometric data

When a high-gloss paint is weathered the initial change in goniophotometric data is a reduction in specular reflectance and a lowering of the peak-height. This is seen visually as a dulling of the surface. This effect can be attributed to the formation of microscopically small defects at the surface of the film whose size are smaller than the wavelength of the incident light. These micro-defects reduce I_s by removing energy from the incident light beam by means of diffraction and/or Mie-type scattering processes. The surfaces specular reflectance and peak height continue to decrease as more of these micro-defects occur at the surface of the film.

Eventually however these defects reach a size larger than that of the wavelength of the incident light and at this stage they become known as macro-defects. These macro-defects are now capable of causing angular divergance of the reflected beam and this shows itself visually as a loss in sharpness of an image seen at the surface of the film. At this stage the peak-width begins to increase and the overall shape of the goniophotometric peak changes from a sharp triangular shape to a broader curved profile.

The ageing deterioration process continues until the film can be seen visibly to be degraded with the imperfections increasing in size and number, by this stage the film will have outlived its usefulness.

2.4.5 Weight Loss Measurements

Weight-loss measurements were carried out on PVC plastisol coatings, both naturally and artificially weathered, which were coated onto weather-resistant stainless steel substrates. The weighings were carried out on an analytical balance accurate to four decimal places. The weight changes were then expressed as an overall percentage weight change. Previous to any weighing the samples were very carefully and gently cleaned under running water to remove all traces of loose debris from the surface. This was very necessary for the outdoor exposures, especially since the coatings are relatively soft and so tend to harbour debris on their surface. Weight-loss measurements thus enabled a close check to be maintained on the loss of plastisol from a coating by volatilisation and leaching from the surface.

2.4.6 Thermal Analysis

The thermal analysis of the PVC plastisol coatings was carried out to determine any shift in their glass transition temperature on ageing. The instrument which was used for this work was a Perkin-Elmer DSC-2 Differential Scanning Calorimeter fitted with a liquid nitrogen sub-ambient accessory, illustrated in Plate 9.

The test samples were heated under a helium atmosphere over a temperature range 160-350^{0}K at a rate of 20^{0}/min and the thermograms were recorded. A sample's glass transition temperature was seen as a step-wise change in the recorded base-line, the temperature at which this occurred being taken as that temperature at which the change in heat capacity of the sample was at its mid-point.

Plate 9 - The Perkin-Elmer DSC-2 Differential Scanning Calorimeter with

2.4.7 Micro-indentation - Recovery/Time Analysis

A micro-indentation technique was employed as a means of mechanical testing of the samples. The instrument used was an ICI Pneumatic micro-penetrometer illustrated in Plates 10 and 11, which provided an automatic record of, initially, the indentation (μm), followed on removal of the indentor load, by the sample recovery profile over 1 min. The coatings used in this test were coated onto aluminium sheets and then circular discs were cut out after ageing. An indentor of radius 0.132 cm was used and an indentation time of 1 min. Because of the extremely soft nature of the coatings a smaller indentor was unable to register the small changes that occurred in hardness during ageing.

The mechanical properties of a material can be determined by examining the deformation of a specimen responding to a defined stress and in the case of a spherical indentor, the relationship between the load applied to the indentor, the radius of the indentor and the depth of the indentation, in terms of the modulus of a perfectly elastic material, as derived by Hertz[140] is

$$\frac{E}{1-w^2} = \frac{3}{4} \times \frac{mg}{r^{0.5}h^{1.5}}$$

where E = Young's modulus of the specimen

w = Poisson's ratio

m = load applied

r = radius of the indentor

h = depth of indentation

and g = gravitational constant

The depth of indentation therefore is an indication of the hardness of a paint film. The greater the hardness of the sample, the lower will

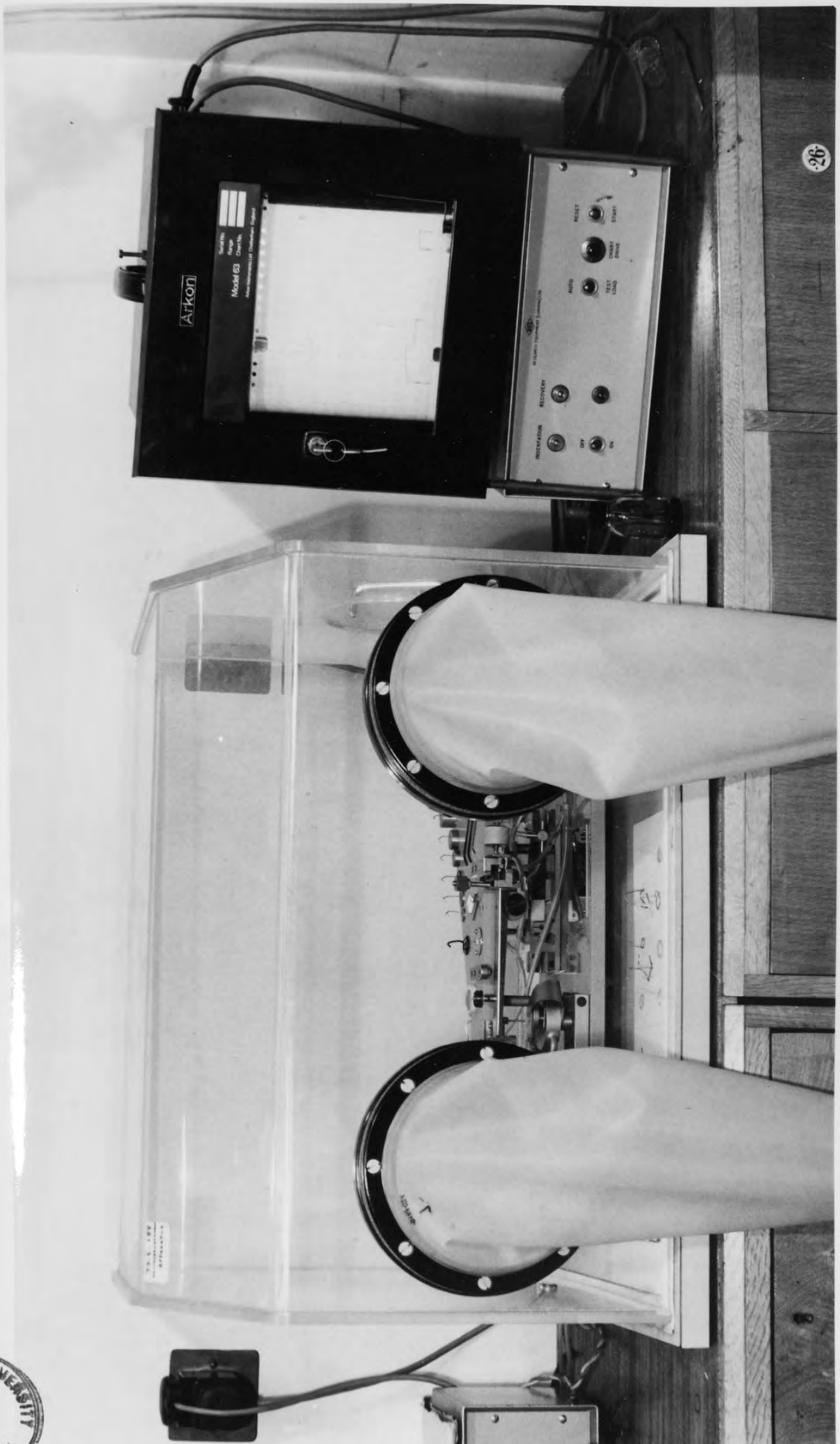


Plate 10. ICI Pneumatic Micro Penetrometer

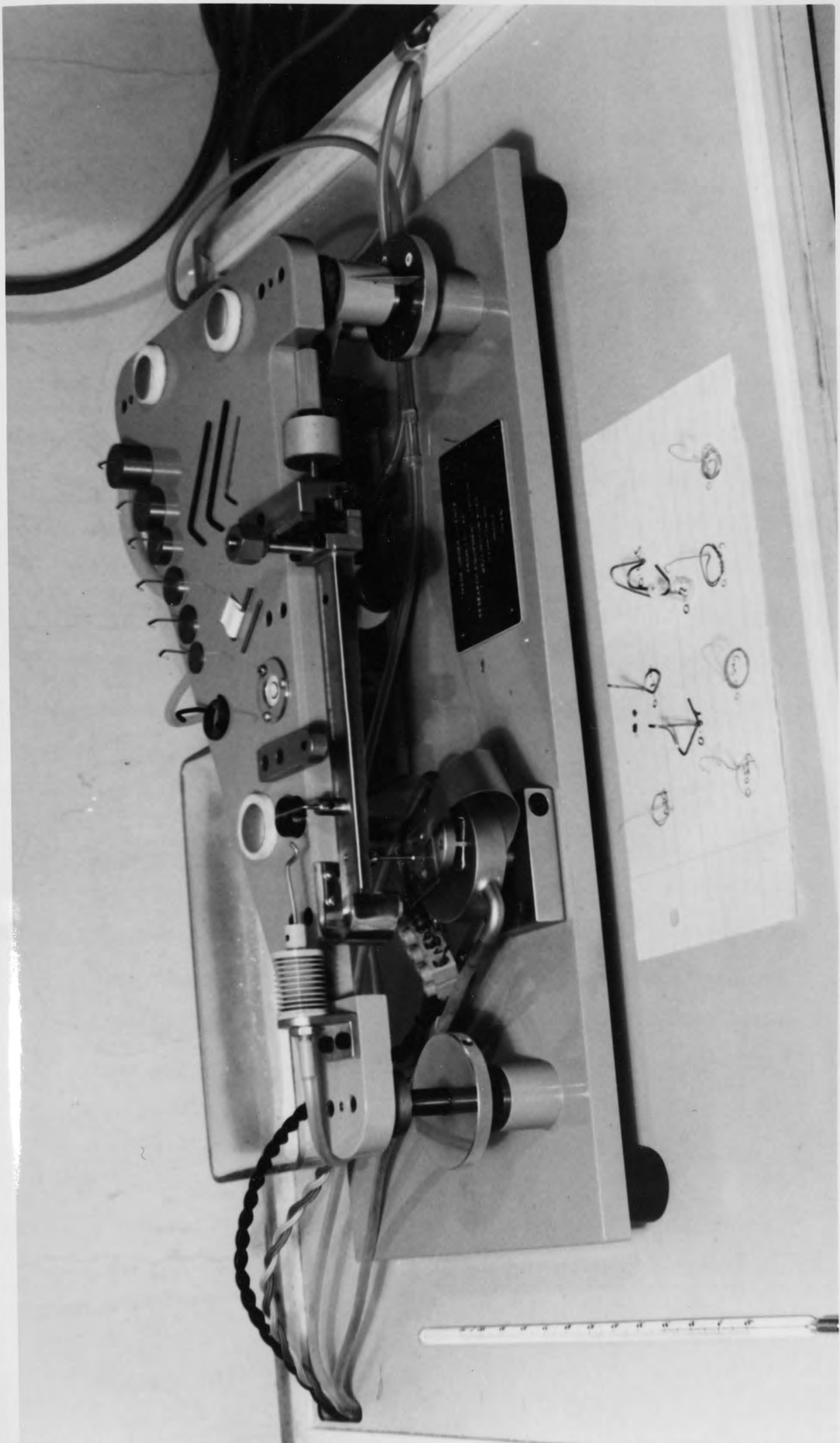


Plate 11 - A detailed view of the ICI Pneumatic Micro-Penetrometer

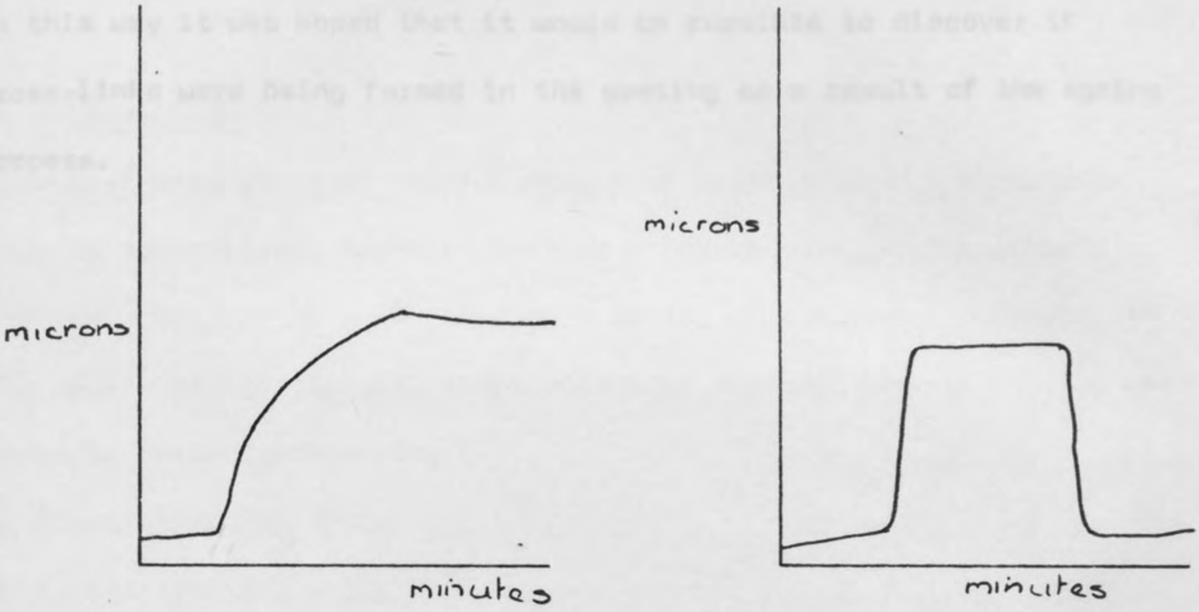
be the depth of indentation obtained with a given load and therefore the greater will be the value of $\frac{E}{1-\omega^2}$. For the purpose of this work the value of ω - (Poisson's ratio) can be considered as a constant so that a plot of $\frac{E}{1-\omega^2}$ against length of exposure can be used to show the ageing characteristics of the paint film.

Mean indentation results were obtained from at least three determinations for each load and a minimum of three loads were used on each sample. A value for $\frac{E}{1-\omega^2}$ was then calculated for each load and an average was taken to obtain the final result. The shape of the indentation and recovery curves obtained from the samples can also be used to give useful information regarding the behaviour of the coatings on ageing. Figure 14 shows four indentation and recovery profiles which are typical for the four different paint compositions, plastic, rubbery, visco-elastic and glossy. The indentation/recovery profile can therefore be used to help determine the rheological state of the samples at ambient temperature.

2.4.8 Gel Content

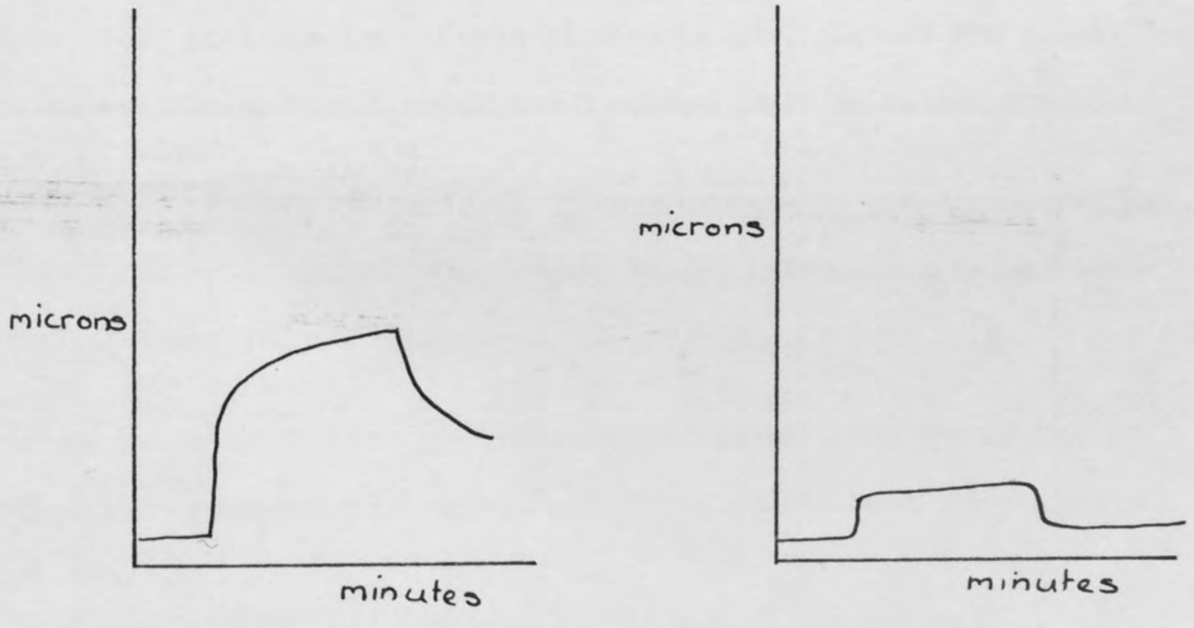
Gel content measurements were taken in the hope that they would provide information about the number of cross-links formed in the coating during ageing. Measurements were carried out on the naturally weathered PVC plastisol coatings of lower plasticiser content. These had been coated onto a glass substrate without primer and so were easily removed for analysis.

The determination was carried out as follows: - 0.5 g of polymer was placed in a flask and 50 ml of methylene dichloride was added to it. This was then refluxed for 15 min before being filtered to remove the dissolved uncrosslinked polymer solution. The gel which remained was



(a) Plastic

(b) rubbery



(c) visco-elastic

(d) glassy

Figure 14 - Typical Indentation and Recovery Profiles for different surface coatings

then dried to constant weight and the gel content was calculated as a percentage of the total weight of coating.

In this way it was hoped that it would be possible to discover if cross-links were being formed in the coating as a result of the ageing process.

CHAPTER III

EXPOSURE OF PVC PLASTISOL SURFACE COATINGS TO NATURAL WEATHERING

3.1 Introduction

The natural weathering of the PVC Plastisol Surface Coatings was conducted at the Building Research Station exposure site, as previously described, Chapter II p 40. For each series of coatings, differing in their levels of plasticiser, three different formulations of coating were exposed to natural weathering

(1) Plasticised PVC alone

(2) Plasticised PVC + pigment

(3) Plasticised PVC + pigment + uv and thermal stabilisers.

The more highly plasticised Series I coatings were exposed for periods up to 30 months in length and the less plasticised Series II coatings for periods up to 18 months in length. It was hoped that by exposing each of these coatings the effects of plasticiser, pigment and stabilisers upon the weathering behaviour of the coatings could be established.

The analytical techniques employed in this study were, goniophotometry, contact angle measurements, micro-indentation, weight-loss measurements thermal analysis and gel content.

It should be noted that the goniophotometric results for the Series I coatings were obtained by R Molley and are described here for comparison only.

3.2 Garston exposure

Natural weathering of the Series I surface coatings was commenced during the summer while that of the Series II surface coatings was commenced during the winter months. The different starting times should therefore provide some insight into the effects of seasonal variations in the weather upon the surface coatings. really?

3.3 Goniophotometry

Goniophotometric analyses were carried out using the automated instrument previously described and employing multi-chromatic (ie unfiltered) mercury light illumination at an angle of incidence to the sample surface of 50°. For the analysis of the PVC plastisol series I coatings the 'wide beam' was used for illumination whereas for the series II coatings the 'narrow beam' was used. This was because in the case of the less plasticised series of coatings (series II) the coating was applied to the aluminium substrate by hand and brushmarks were detectable on the surface. The results obtained by using the 'wide beam' for illumination would have been distorted by these marks and so the 'narrow beam' was chosen.

As previously mentioned the goniophotometric results for the first series of coatings were obtained by R Molloy and are reported in his PhD thesis. The results are briefly summarised here, figures 15,16. The three coatings

(1) plasticised PVC
(2) plasticised PVC + pigment
(3) plasticised PVC + pigment + uv and thermal stabilisers

were all exposed for periods up to 17 months in length and significant changes in reflectance were observed over this period for each of the coatings. During the first two months of exposure varied changes occurred in the reflectance of the samples and these were attributable to the equilibration effects dependant upon the initial state of the coating surfaces. After this time however there was a marked decrease in the specular reflectance of all the samples followed by an increase after 6 months weathering in the case of the pigmented formulations and 9 months in the case of the unpigmented formulation. The increase in specular reflectance for each of the samples was however shortlived and was followed by further periods of deterioration. In the case of the two pigmented coatings the rate of deterioration falls after 12 months weathering in contrast to the rate of deterioration of the unpigmented coating which continues to fall rapidly. In the latter case, at the end of the 17 month exposure period, the surface was seen to be extensively degraded with small, dark brown spots liberally covering the entire surface area. The two pigmented coatings on the other hand were still intact and not noticeably discoloured.

The changes in diffuse reflectance during the 17 month exposure period are seen to be relatively insignificant, compared to the change in specular reflectance, showing little change. The changes in peak width at half-height ($w_{\frac{1}{2}}$), figure 16, also show little change over the exposure period for the pigmented coating. For the unpigmented coating however after 9 months weathering $w_{\frac{1}{2}}$ begins to increase rapidly coinciding with the deterioration in specular reflectance after the same length of time. The plot of gloss factor against exposure time is seen to be little different from the plot of specular reflectance against exposure time and this indicates that specular reflectance is predominant in determining the gloss factor. The diffuse reflectance contributes little towards the overall gloss factor changes as does peak width at half-height except in the last 8 months of the exposure of the unpigmented coating.

The second series of PVC plastisol coatings, with the lower plasticiser

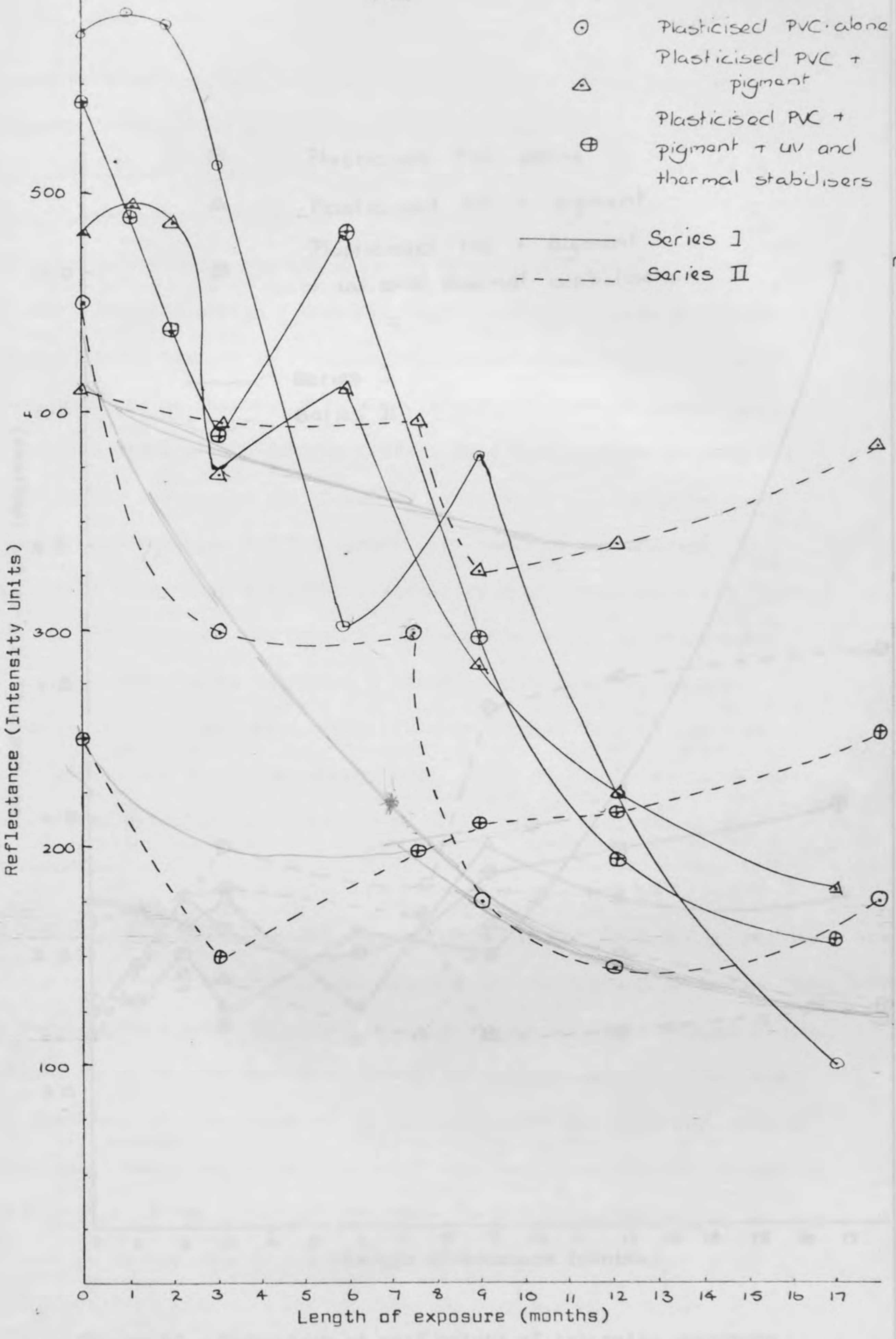


Figure 15 - Specular reflectance of naturally weathered PVC plastisol coatings

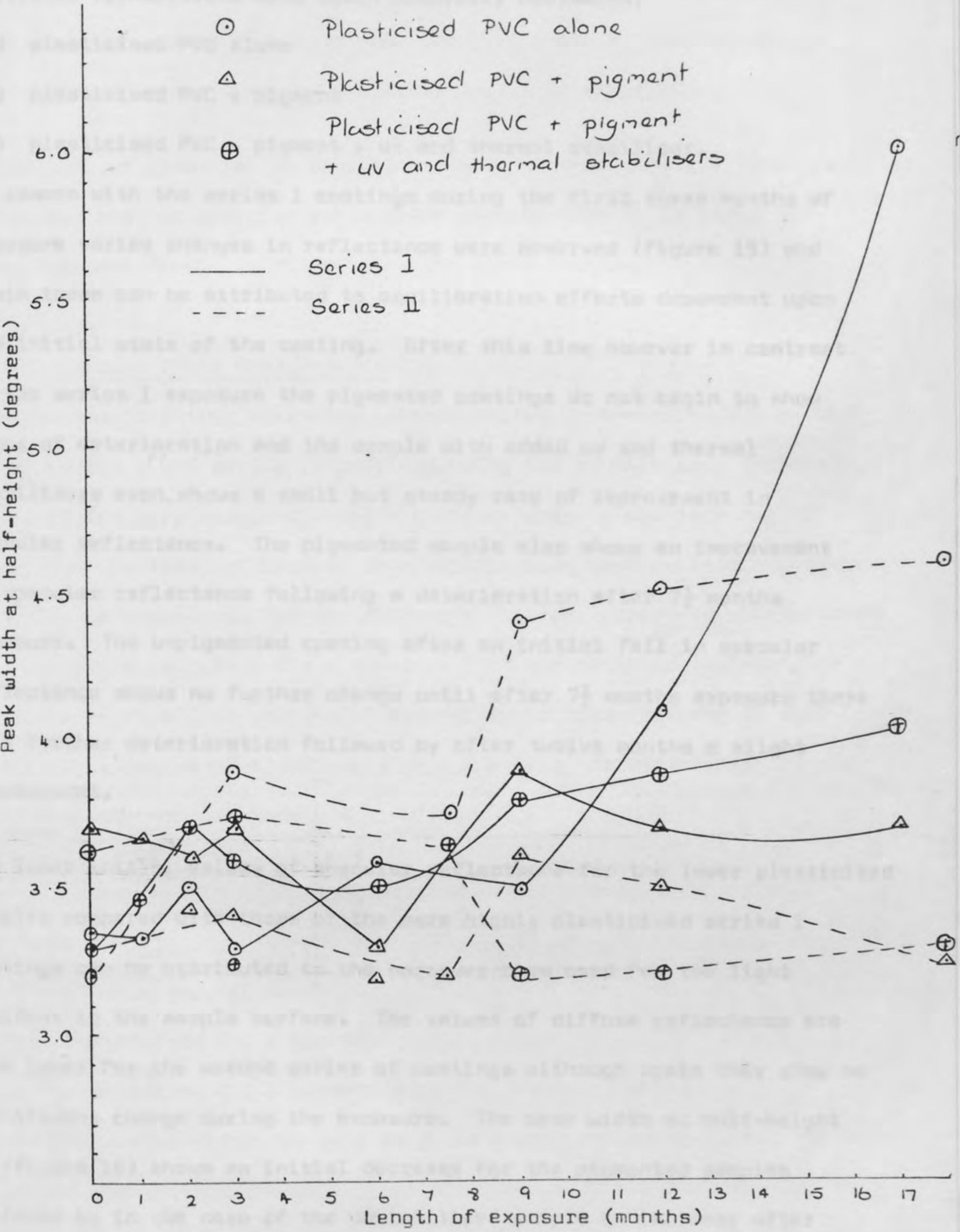


Figure 16 - Peak-width at half height of naturally weathered PVC plastisol coatings

content were also exposed outdoors for a period of 18 months. Three different formulations were again naturally weathered,

(1) plasticised PVC alone

(2) plasticised PVC + pigment

(3) plasticised PVC + pigment + uv and thermal stabiliser.

In common with the series I coatings during the first three months of exposure varied changes in reflectance were observed (figure 15) and again these can be attributed to equilibration effects dependant upon the initial state of the coating. After this time however in contrast to the series I exposure the pigmented coatings do not begin to show signs of deterioration and the sample with added uv and thermal stabilisers even shows a small but steady rate of improvement in specular reflectance. The pigmented sample also shows an improvement in specular reflectance following a deterioration after 7½ months exposure. The unpigmented coating after an initial fall in specular reflectance shows no further change until after 7½ months exposure there is a further deterioration followed by after twelve months a slight improvement.

The lower initial values of specular reflectance for the lower plasticised samples compared with those of the more highly plasticised series I coatings can be attributed to the narrower beam used for the light incident to the sample surface. The values of diffuse reflectance are also lower for the second series of coatings although again they show no significant change during the exposure. The peak width at half-height $w_{\frac{1}{2}}$ (figure 16) shows an initial decrease for the pigmented samples followed by in the case of the unstabilised sample an increase after 7½ months corresponding to the decrease in specular reflectance, followed again by a further decrease. The stabilised coating in contrast shows a sharp fall in $w_{\frac{1}{2}}$ after 7½ months followed by no further change. The unpigmented sample shows an initial increase in $w_{\frac{1}{2}}$ followed by a period of stability up to 7½ months when there is again an increase in $w_{\frac{1}{2}}$ followed by after 9 months a further period of stability.

The plot of gloss factor against exposure time (figure 17) again closely follows that of specular reflectance showing that I_s is again the predominant factor in determining the gloss factor.

3.4 Contact Angle Measurements

Measurements of the advancing contact angles were carried out on both the series I and series II coatings using the sessile drop technique. The angles were measured using a goniophotometric eyepiece and an average was taken of several determinations on each surface. Contact angles were measured for two different liquids, water and diiodomethane, in order to calculate the dispersive (γ_d) and polar (γ_p) components of the surface free energy. A second liquid diiodomethane is used because using water alone would only indicate the wettability of the surface by hydrogen-bondable liquids.

Three formulations of surface coating were again studied for each series

(1) Plasticised PVC alone

(2) Plasticised PVC + pigment

(3) Plasticised PVC + pigment + uv and thermal stabiliser

the two series differing only in their levels of plasticiser. The higher plasticised series of coatings (series I) had been exposed to natural weather for periods up to 30 months in length and the less plasticised series of coatings (series II) for periods up to 18 months in length. As can be seen from the water contact angle of the pigmented

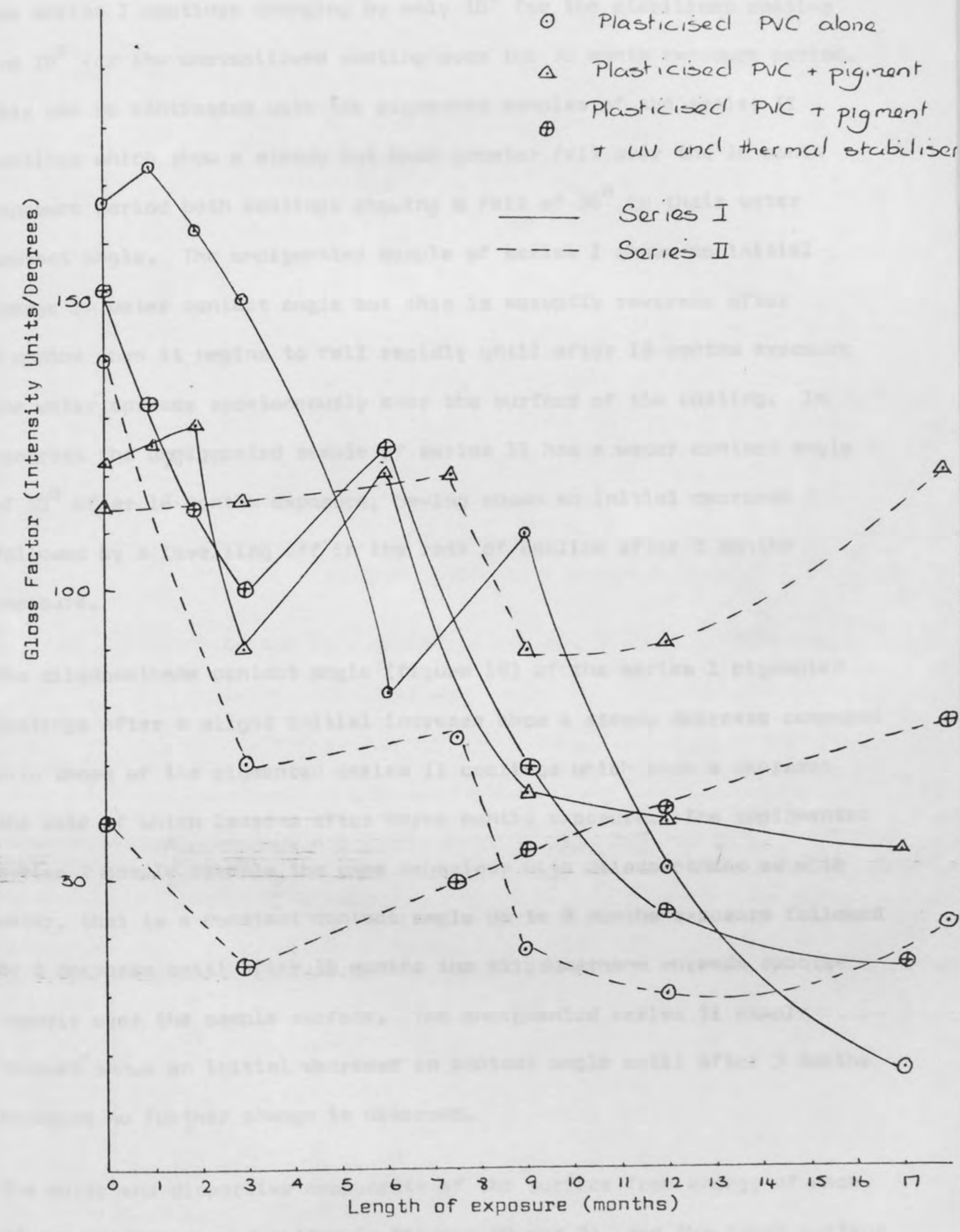
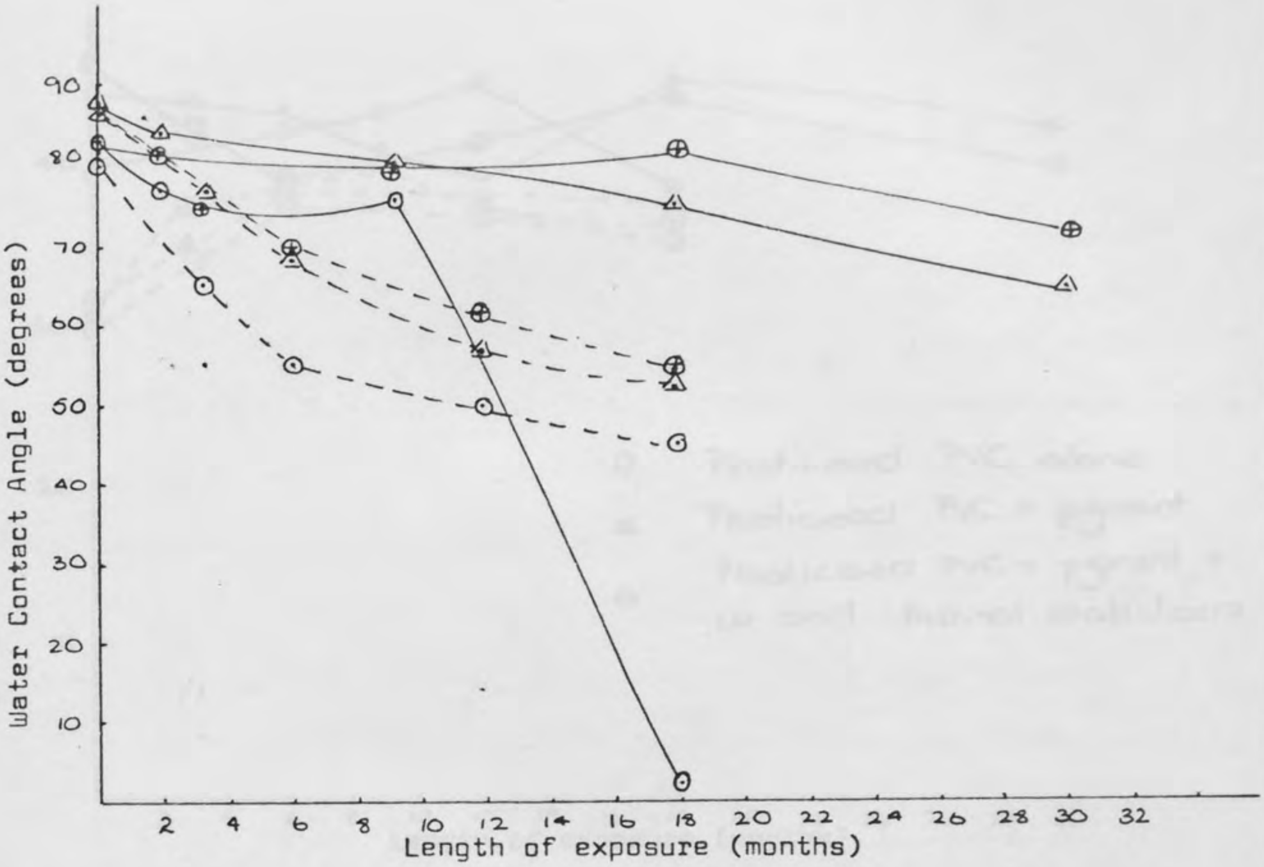


Figure 17 - Gloss Factor of naturally weathered PVC plastisol coatings

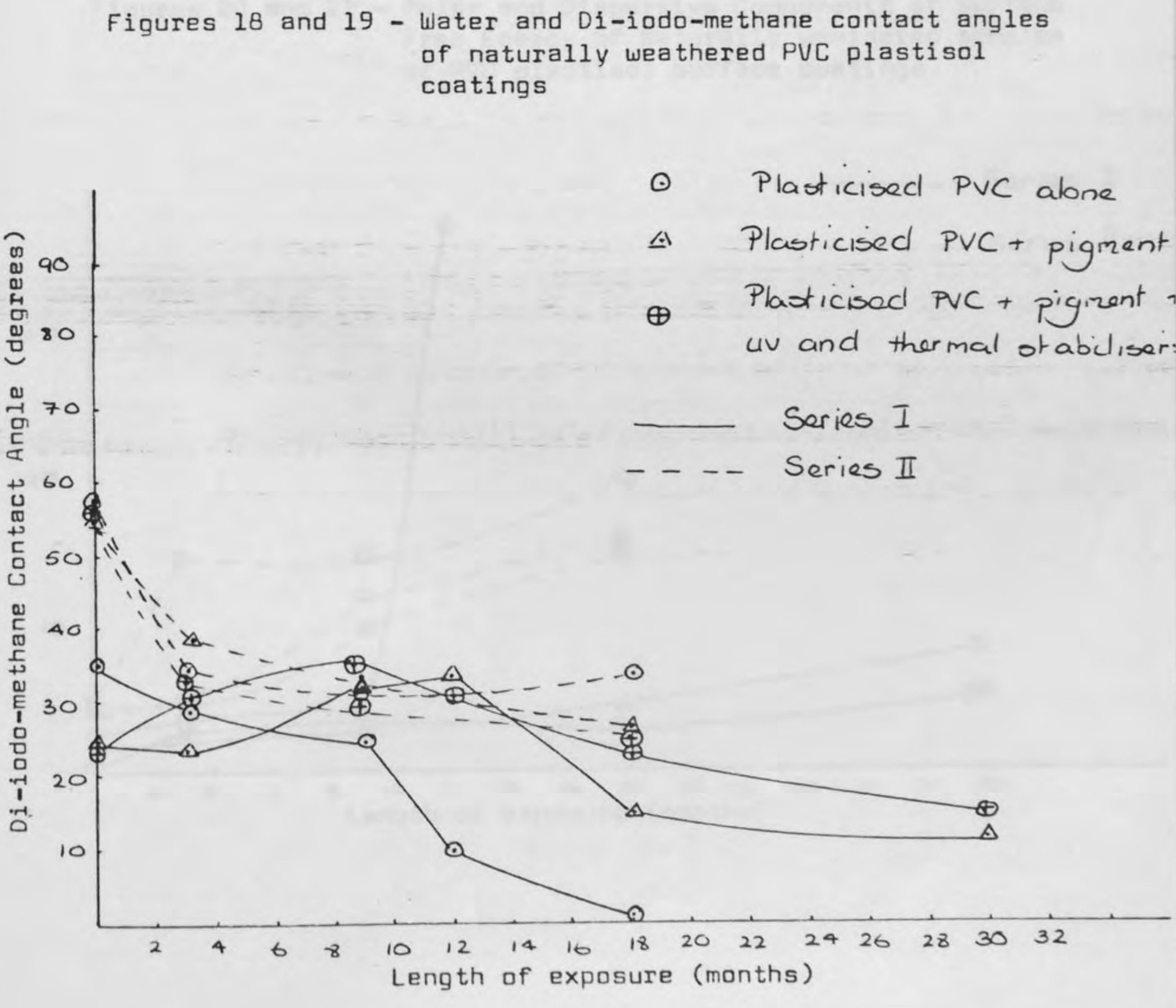
coatings (figure 18) show a gradual decrease with time in the case of the series I coatings changing by only 10^{0} for the stabilised coating and 18^{0} for the unstabilised coating over the 30 month exposure period. This can be contrasted with the pigmented samples of the series II coatings which show a steady but much greater fall over the 18 month exposure period both coatings showing a fall of 30^{0} in their water contact angle. The unpigmented sample of series I shows no initial change in water contact angle but this is abruptly reversed after 9 months when it begins to fall rapidly until after 18 months exposure the water spreads spontaneously over the surface of the coating. In contrast the unpigmented sample of series II has a water contact angle of 50^{0} after 18 months exposure, having shown an initial decrease followed by a levelling off in the rate of decline after 5 months exposure.

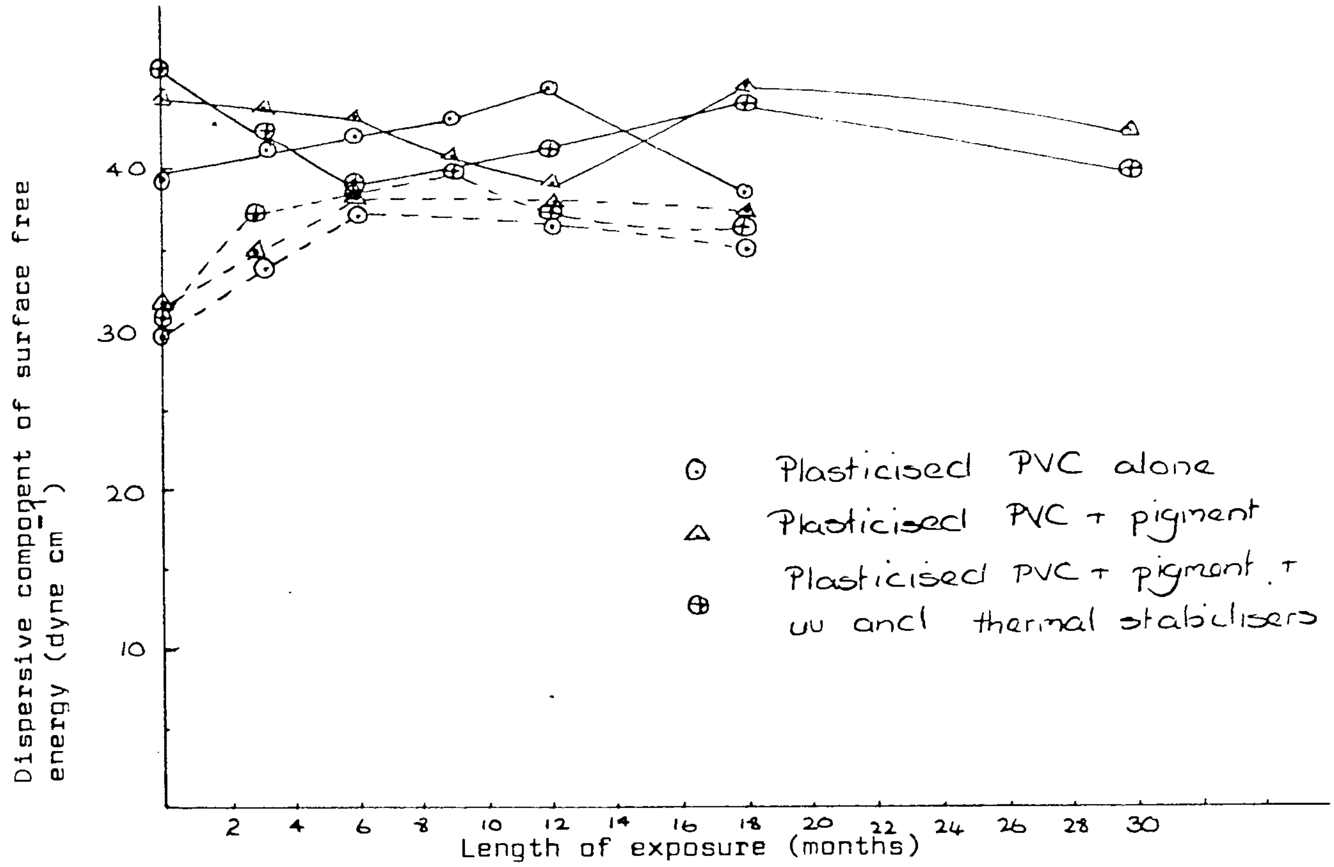
The diiodomethane contact angle (figure 19) of the series I pigmented coatings after a slight initial increase show a steady decrease compared with those of the pigmented series II coatings which show a decrease the rate of which lessens after three months exposure. The unpigmented series I sample reveals the same behaviour with diiodomethane as with water, that is a constant contact angle up to 9 months exposure followed by a decrease until after 18 months the diiodomethane spreads spontaneously over the sample surface. The unpigmented series II sample however shows an initial decrease in contact angle until after 3 months exposure no further change is observed.

The polar and dispersive components of the surface free energy of each of the coatings are detailed in figures 20 and 21, and the total surface free energy is shown in figure 22. As can be seen, the surface free

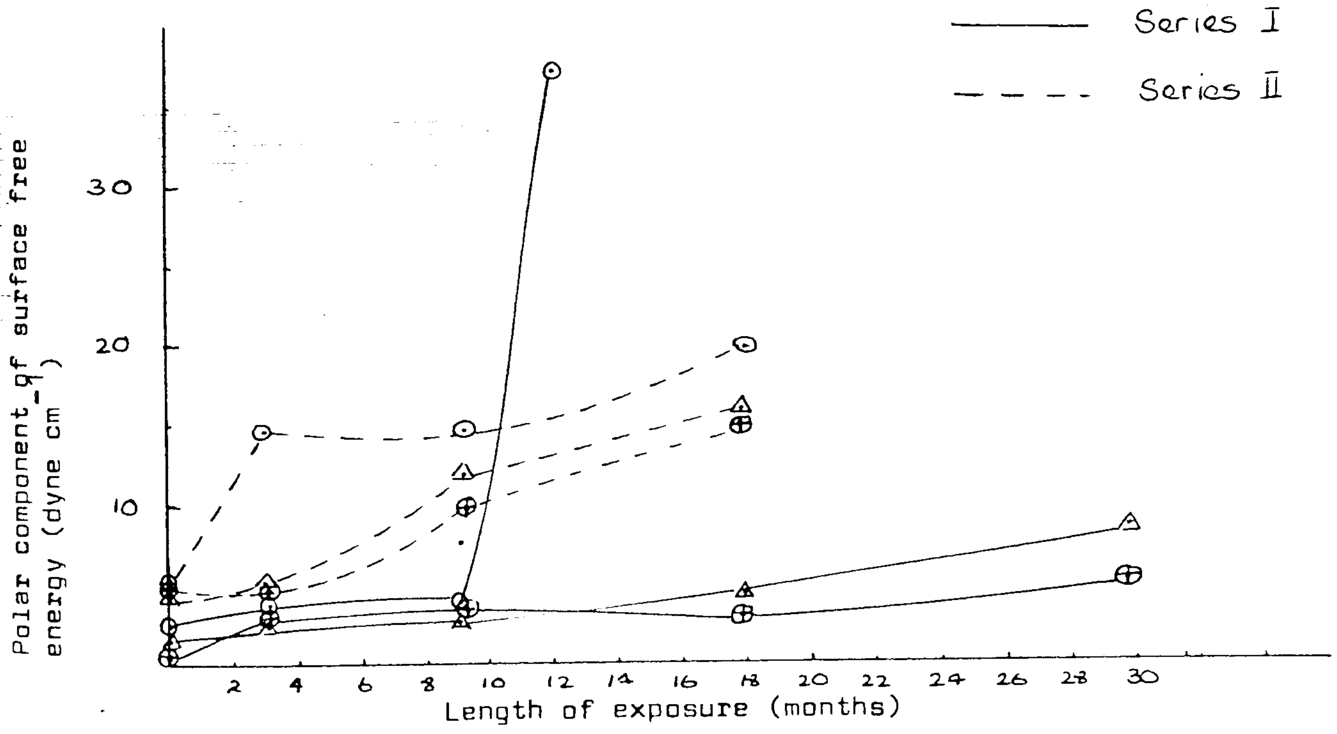


Figures 18 and 19 - Water and Di-iodo-methane contact angles of naturally weathered PVC plastisol coatings





Figures 20 and 21 - Polar and Dispersive Components of Surface Free Energy of Naturally weathered samples of PVC plastisol surface coatings



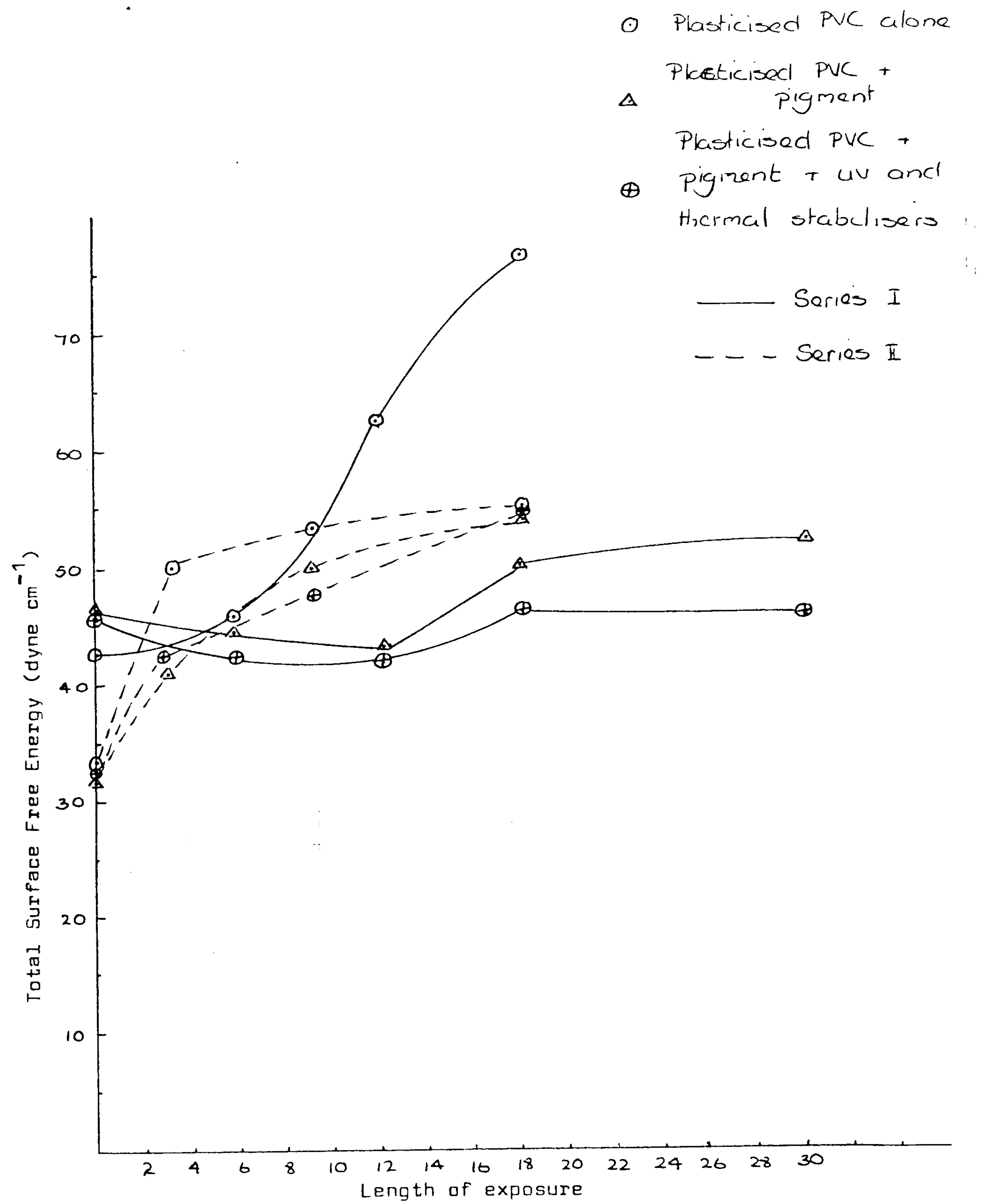


Figure 22 - Total Surface Free Energy of Naturally Weathered PVC Plastisol Surface Coatings

energies of the pigmented coatings of series I fall slightly in the first 12 months of the exposure to natural weather due to the sharp fall in polar component of the surface free energy compared with the slight rise in the dispersive component. This trend is however reversed after 12 months when both pigmented coatings show an increase in surface free energy (less pronounced in the case of the stabilised coating) followed after 18 months by no further change. The stabilised coating also shows no change in surface free energy between the 6 and 12 month exposure periods. This is due to the increase in the polar component of the surface free energy counter-balancing the fall in the dispersive component. In this case the total surface free energy masks the underlying trends of the polar and dispersive components. Similarly after 18 months weathering the lack of apparent change in the surface free energy is again due to the opposing polar and dispersive effects. This time however the polar component of surface free energy is falling while the dispersive component increases at the same rate. The unpigmented Series I surface coating shows a steady increase in surface free energy for the first 9 months of the exposure, after which time the increase becomes very marked reaching a value of 72.5 dyne cm^{-1} after 18 months exposure. It is at this time that the liquids used for the determination of surface free energy spread spontaneously over the coating. As can be seen from figures 21+22 the dramatic rise in surface free energy is due mainly to the large increase in the dispersive component compared with the lesser fall in the polar component of surface free energy.

The surface coatings of series II have much lower total surface free energies initially compared with those of series I due to the lower values of the polar component. The dispersive component of surface free energy exhibits similar behaviour for both the unpigmented and pigmented series II coatings, that is an initial increase in dispersive free energy during the first 3 months of exposure followed by only a slight increase in the remaining 15 months of the exposure. The dispersive energy of the unpigmented sample in fact falls slightly towards the end of the exposure period. The polar energy of the pigmented coatings in contrast rises steadily throughout the exposure. That of the unpigmented coating however behaves in a similar way to its dispersive component of surface free energy, that is rising sharply during the first 3 months of exposure and then rising only slightly during the remaining 15 months of natural weathering. These trends are further illustrated by the changes in total surface free energy exhibited by the coatings during their 18 months exposure to natural weathering as shown by figure 22.

The results for surface free energy measurements should be considered in the light of corresponding literature data relating to rigid (unplasticised) PVC[141].

H_2O contact angle - 87^0

CH_2I_2 contact angle - 36^0

γ_d - 40 dynes cm^{-2}

γ_p - 1.5 dynes cm^{-2}

As can be seen from these figures the main difference from the initial values obtained in this work is the CH_2I_2 contact angle for the Series II surface coatings. This is much higher in the case of the plasticised samples and is also reflected in the lower value of the dispersive component of the surface free energy. It seems apparent therefore that the differences noted here between these results and those for rigid PVC may be ascribable to the effect at the coating surface of the aromatic and aliphatic hydrocarbon groups as opposed to the ester groups of the diisooctylphthalate plasticiser.

The differences and the changes in the surface free energy of the coatings will be further discussed in Chapter VI in the light of information obtained by using various other analytical techniques.

3.5 Thermal Analysis

Thermal analysis of the naturally weathered samples was carried out using a differential scanning calorimeter to measure their glass transition temperatures as previously described. The results forthe unpigmented series I coatings were obtained by R Molloy[1] and are described in his PhD thesis. Glass transition temperatures of both pigmented and unpigmented samples of series II were obtained during the course of this work and the results are shown in Table 3 along with those obtained by R Molloy[1]. In all cases the values shown are the mean Tg of several determinations.

As can be seen from Table 3 the glass transition temperatures of the unpigmented coatings show little change during the first 12 months of natural weathering, but then rise sharply. The unpigmented PVC plastisol coatings of series II have higher glass transition temperatures than those of series I as would be expected due to the lower plasticiser content of the series II coatings. The addition of pigment to the samples does not affect the initial glass transition temperature but does appear to give the coatings more resistance to weathering as there is no change in the glass transition temperature of the pigmented coatings throughout the exposure. This evidence correlates with the visual appearance of the samples after 18 months outdoor exposure with the pigmented samples appearing to be intact compared with the unpigmented

TABLE 3

Variation in Glass Transition Temperature ($Tg^{o}C$) on Natural Weathering of Series I PVC Clear and Pigmented Plastisol Coatings

EXPOSURE TIME		0	1	2	3	6	9	12	17	27
Plasticised PVC (alone)	I	-41	-39	-39	-43	-37	-34	-34	-8	+23
Tg(^{o}C)	II	1	-	-	-16	-	-12	-12		
Plasticised PVC + pigment	I	-43	-	-	-	-	-	-45	-	-40
$Tg^{o}C$	II	-20	-	-	-	-21	-	-	-18	-

sample which is beginning to show signs of degradation.

3.6 Weight Loss

Weight loss measurements were taken in the hope that they would provide valuable information regarding the loss of plasticiser from the sample surface during weathering by for example volatilisation and leaching. However as reported in R Molloy's PhD thesis[1] the results given by the series I coatings (higher plasticiser content) were invalidated by the tendency of the samples to retain trace amounts of dirt both on and in their surfaces. The second series of coatings with their lower plasticiser content did not exhibit the same tendency to retain dirt in their surface and the overall percentage weight changes shown by them are seen in Figure 23. This reveals a steady but different rate of weight loss throughout the exposure by the two pigmented coatings, the stabilised coating showing a greater rate of weight loss than the unstabilised. The unpigmented coating in contrast shows a slight initial gain in weight followed by a steady loss which increases sharply after 8 months before resuming its former rate of loss after 9 months. The unpigmented coating shows the greatest loss in weight by the end of the exposure.

3.7 Micro-indentation - Recovery/Time Analysis

A spherical indentor was used in this study to obtain the deformation of each of the samples under various loads, from 1 g to 16 g depending upon the rigidity of the sample. The deformations for three different loads were obtained for each sample and for each load at several different points on the sample surface. Young's modulus of elasticity was then calculated for each sample using the Hertz equation

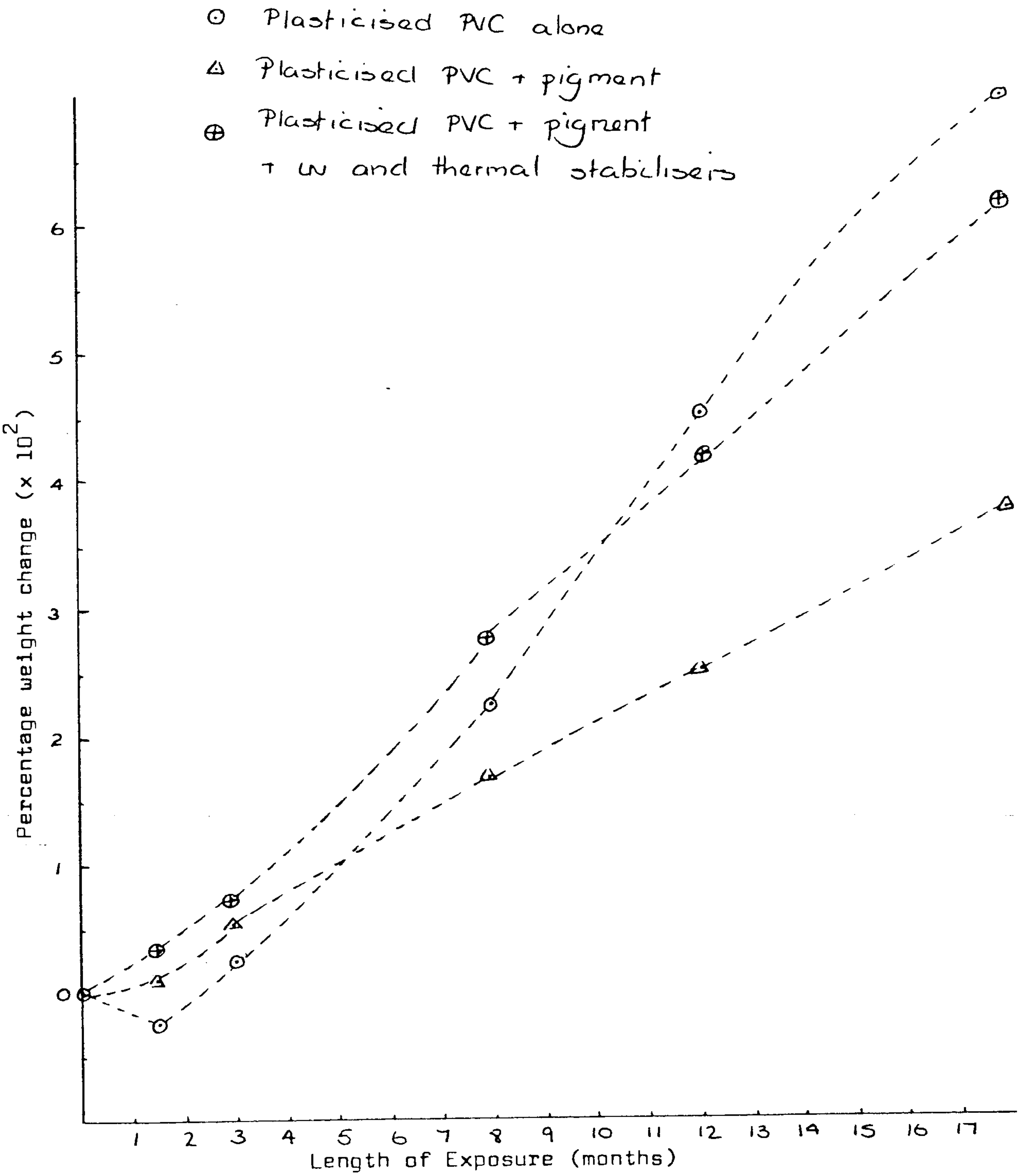


Figure 23 - Weight loss shown by naturally weathered PVC plastisol surface coatings

$$\frac{E}{1-\upsilon^2} = \frac{3}{4}\,\frac{mg}{r^{\frac{1}{2}}h^{3/2}}$$

where E = Young's modulus of elasticity

υ = Poisson's ratio for the material

m = load

g = gravitational acceleration

r = radius of the spherical indentor

h = depth of indentation

In each case the depth of indentation was taken as the depth between the indentation and the recovery. Figure 24 shows a plot of $E/_{1-\upsilon^2}$ against length of exposure for each of the samples. As can be seen the different levels of plasticiser in the two series of coatings has not made a great difference to their elasticity with the more highly plasticised coatings of series I appearing to be only slightly less rigid than the less plasticised series II coatings. Throughout the exposure the only sample which appears to undergo any significant change is the unpigmented coating from the second series of samples (lower plasticiser content). This after a drop in rigidity during the first 6 months of exposure becomes increasinly more rigid until by the end of the outdoor exposure Young's modulus for the sample has increased significantly. It is interesting therefore to compare the initial indentation-recovery profile of this sample with the profile obtained after 18 months exposure to natural weathering, these are shown in Figure 25.

The indentation-recovery profiles were both obtained using a load of 4 g. In both cases there is insufficient recovery time for the sample to recover completely after the load has been removed but in the case of the unexposed sample both the indentation and recovery are greater

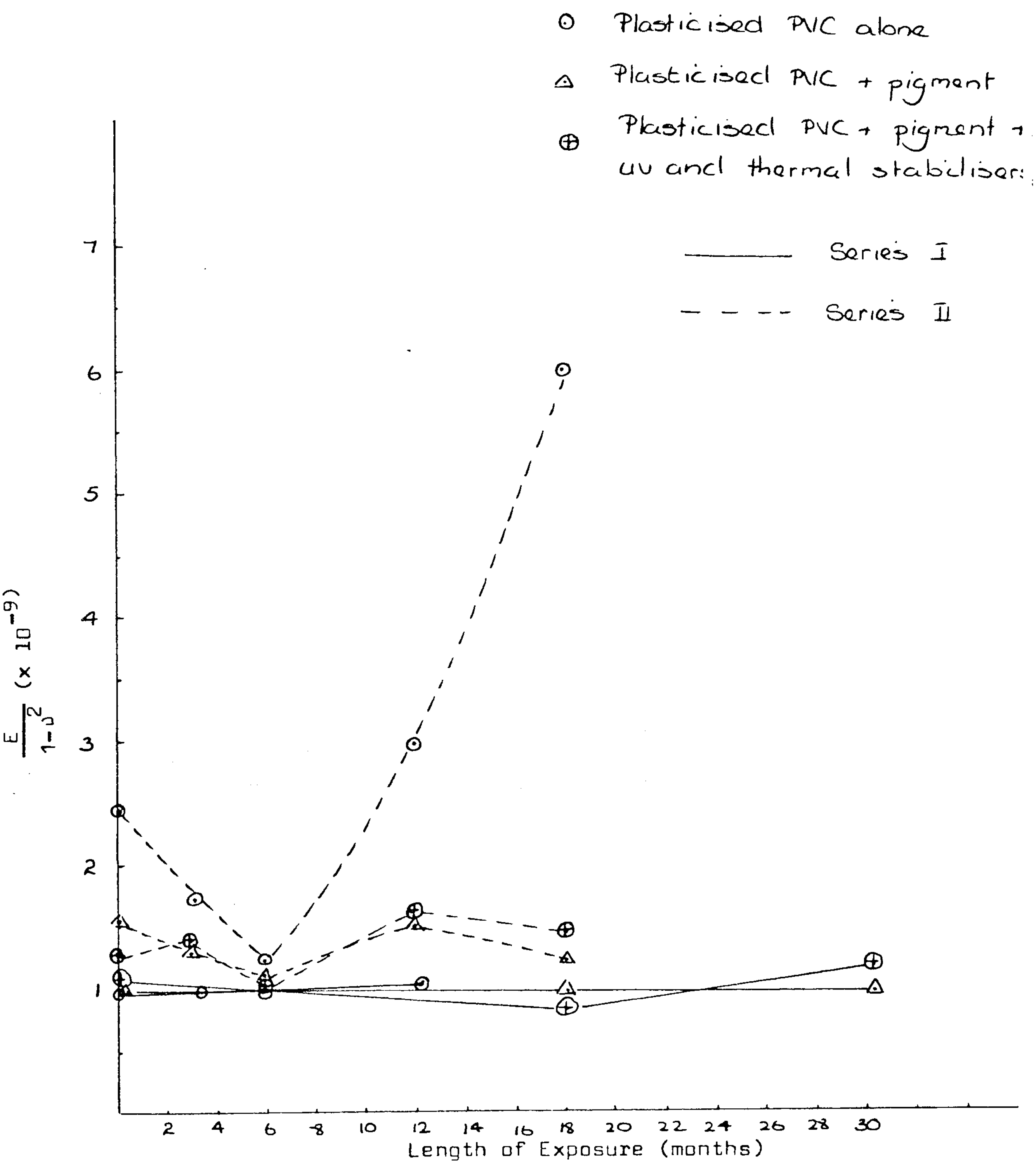
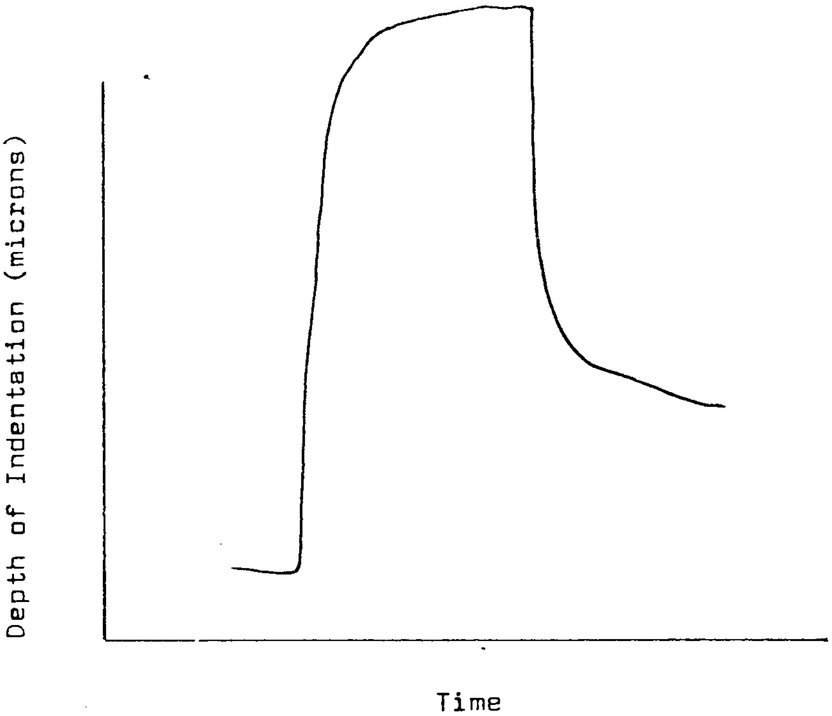
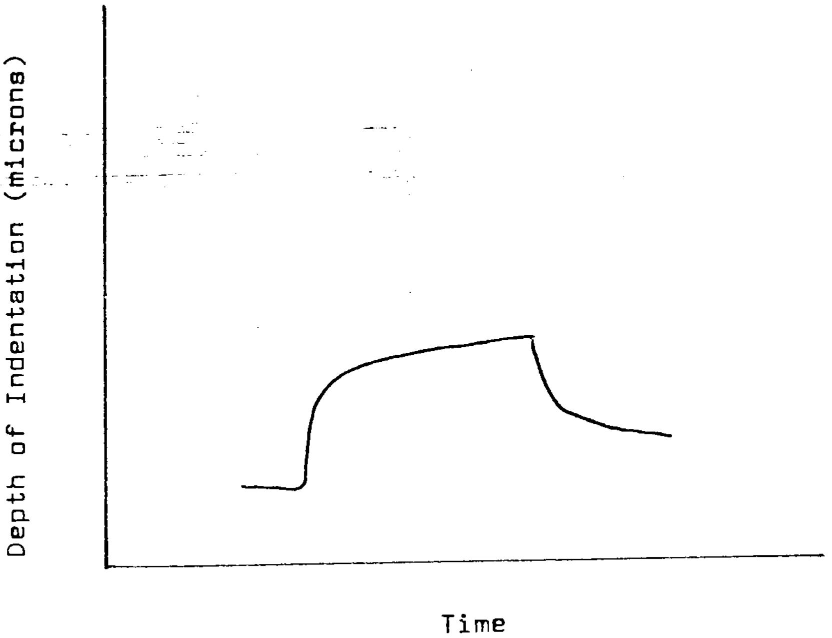


Figure 24 - Changes in rigidity shown by naturally weathered PVC plastisol surface coatings



(a) Before exposure to natural weathering



(b) After 18 months exposure to natural weathering

Figure 25 - Micro-indentation/Recovery Profiles for a Naturally Weathered unpigmented PVC plastisol surface coating (series II)

than for the sample exposed to natural weather for 18 months. This reflects the increasing rigidity of the samples and confirms the visual appraisal of the surface which is becoming degraded and covered with small brown spots and 18 months exposure.

The failure of any of the remaining samples to show any significant changes in rigidity during the exposure is probably due to the relatively soft nature of the coatings so that considerable changes with the coatings would have to take place before they became measureable. The results obtained also show that the low level of pigmentation used in these samples has little or no rigidifying effect upon them.

3.8 Gel Content

The gel contents of the series I coatings which had been naturally weathered for periods up to 29½ months in length were measured. The method of determining the gel content is described in Chapter II, page 69. The coatings used in this determination had been coated onto a glass substrate without primer and so were easily removed. The results of the determination are shown in Figure 26, a plot of gel content against exposure time. The gel content is calculated as a percentage of the total weight of the coating.

During the exposure the gel content of the two pigmented coatings does not change appreciably but remains about 30% of the total weight of the coatings. A change is seen however in the gel content of the unpigmented coating with a fall after 9-12 months exposure to natural weathering. This evidence would therefore suggest that the PVC plastisol surface coating is not forming cross-links as a result of the ageing process.

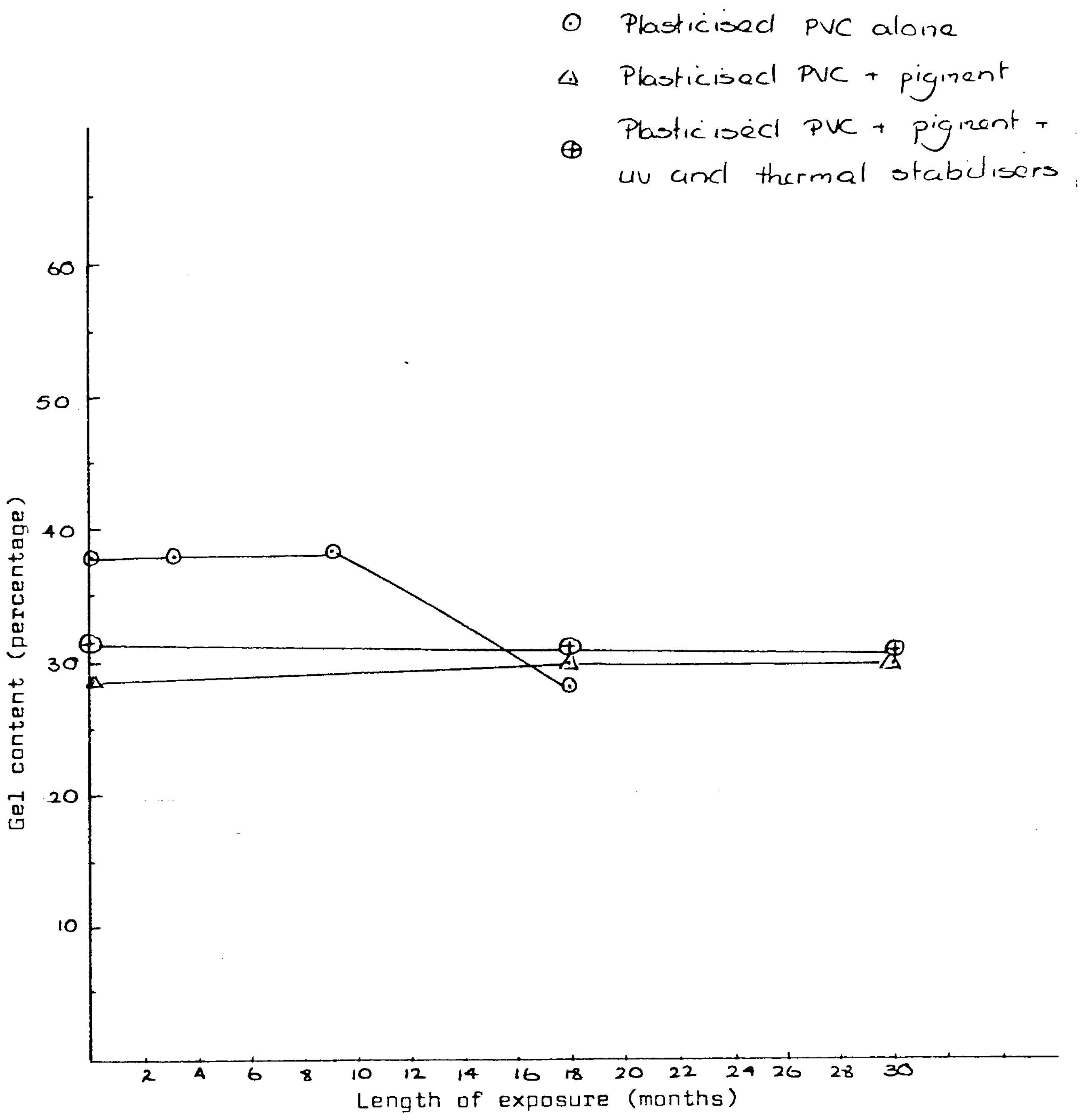


Figure 26 - Gel content of naturally weathered PVC plastisol surface coatings

The next two chapters of this work will describe comparable results obtained for corresponding artificially weathered samples after which the combined results of these three chapters will be discussed.

CHAPTER IV

THE ARTIFICIAL WEATHERING OF POLY (VINYL CHLORIDE) PLASTISOL SURFACE COATINGS USING THE BS3900 PART F3 WEATHEROMETER

4.1 Introduction

The previous chapter looked at the natural weathering of PVC plastisol surface coatings, and to complement those results the artificial weathering of the same series I and series II coatings will be studied in this chapter. The coatings which were artificially weathered were of the same formulation as those naturally weathered, that is:

(1) plasticised PVC alone

(2) plasticised PVC + pigment

(3) plasticised PVC + pigment + uv and thermal stabilisers.

Again samples from the series I and series II coatings were used differing only in their level of plasticiser. Each of the coatings was exposed to artificial weather in the BS 3900 Part F3 artificial weathering apparatus for periods up to 10,000 hours in length for the Series I coatings (more highly plasticised) and for periods up to 4,000 hours in length for the series II coatings.

Analysis of the coatings was carried out by means of goniophotometry, micro-indentation, contact angle measurements, scanning electron microscopy and weight loss measurements.

4.2 Goniophotometry

The goniophotometric results discussed in this chapter were all obtained using the converted Brice-Phoenix light scattering photometer previously described (Chapter II page 56). In the case of the Series II coatings a narrower beam of incident light was selected to impinge upon the sample because of the irregular brush marks in the surface of the coating. It was felt that the use of a wider beam, such as that used for the series I coatings, could distort the results obtained.

A plot of specular reflectance against exposure time for each of the series of coatings can be seen in figure 27. The values of specular reflectance for corresponding formulations of each series of coatings cannot be directly compared because in the case of the series I coatings a wider beam was used for the incident light. The overall trends shown by each series of coatings however can be compared. Considering first the series I coatings, (more highly plasticised 80 pphr), all three formulations of surface coating show a similar pattern of behaviour, that is an initial sharp fall in specular reflectance followed by a lesser rate of fall. Superimposed upon this lessening specular reflectance is a cyclic pattern of behaviour showing periods of greater and lesser decreases in specular reflectance. The length of this cycle varies for each of the coating being over a longer period of time for the pigmented coatings than for the unpigmented coating. At the end of the 10,000 hour exposure it is interesting to note that both the pigmented and unpigmented coatings have a specular reflectance of about 75 intensity units despite the fact that visually the unpigmented sample appears to be more extensively degraded.

The series II PVC plastisol surface coatings were exposed for periods up to 4,000 hours in length and as can be seen from figure 27 the specular reflectance of each of the coatings did not drop appreciably during this time. Again each of the samples exhibited cyclic patterns of behaviour showing alternating periods of recovery and deterioration. The length of the cycles are in these cases less than in the case of the corresponding series I coatings. As previously mentioned the lower values of specular

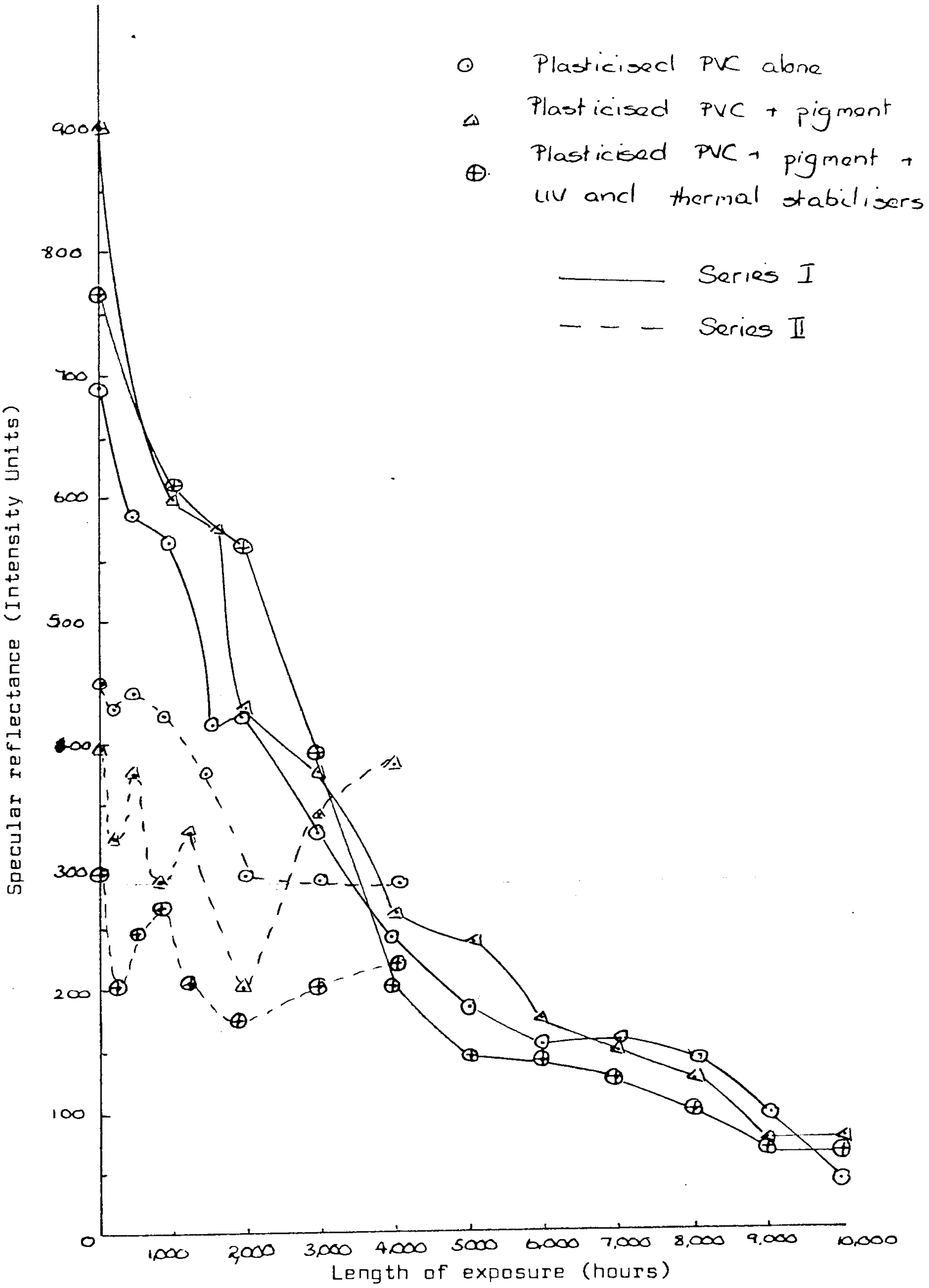


Figure 27 - Specular reflectance of artificially weathered PVC plastisol coatings

reflectance exhibited initially by the series II coatings, compared with the corresponding series I coatings, are due to the incident light forming a narrower beam on the series II PVC plastisol coatings.

The variations shown in diffuse reflectance shown by each of the coatings throughout the exposure are insignificant when compared with the much greater changes in specular reflectance. The changes in peak width at half-height are more significant particularly for the more highly plasticised coatings however as shown by figure 28. Each of the series I coatings shows an increase in $W_{\frac{1}{2}}$ throughout the 10,000 hour accelerated weathering exposure. Each of the coatings has an initial $W_{\frac{1}{2}}$ value of 3.5 and after 10,000 hours exposure they each have a $W_{\frac{1}{2}}$ value of approximately 6.2 suggesting that macro deformations of the same order are taking place in the surface of each of the coatings. The behaviour of each of the coatings throughout the exposure differs however with a cyclic pattern of behaviour again being superimposed upon the general trend of an increase in $W_{\frac{1}{2}}$. This pattern of successive improvements and deteriorations in the peak width at half-height is most pronounced for the two unstabilised coatings but is still present for the stabilised coating although each cycle covers a longer time period. This pattern of behaviour is due to the formation of macro-defects in the surface of the coating being gradually smoothed away as they increase in size before further macro defects are formed which again increase the peak-width at half-height. Figure 29 shows how the shape of the goniophotometric curves obtained from the samples at stages throughout the exposure changes reflecting both the loss of gloss and formation of macro-defects in the surface. This shows how the unpigmented coating of the more highly plasticised series of coatings shows a loss of gloss and increase in macro-defect formation towards the end of the exposure.

As can be seen the series II coatings

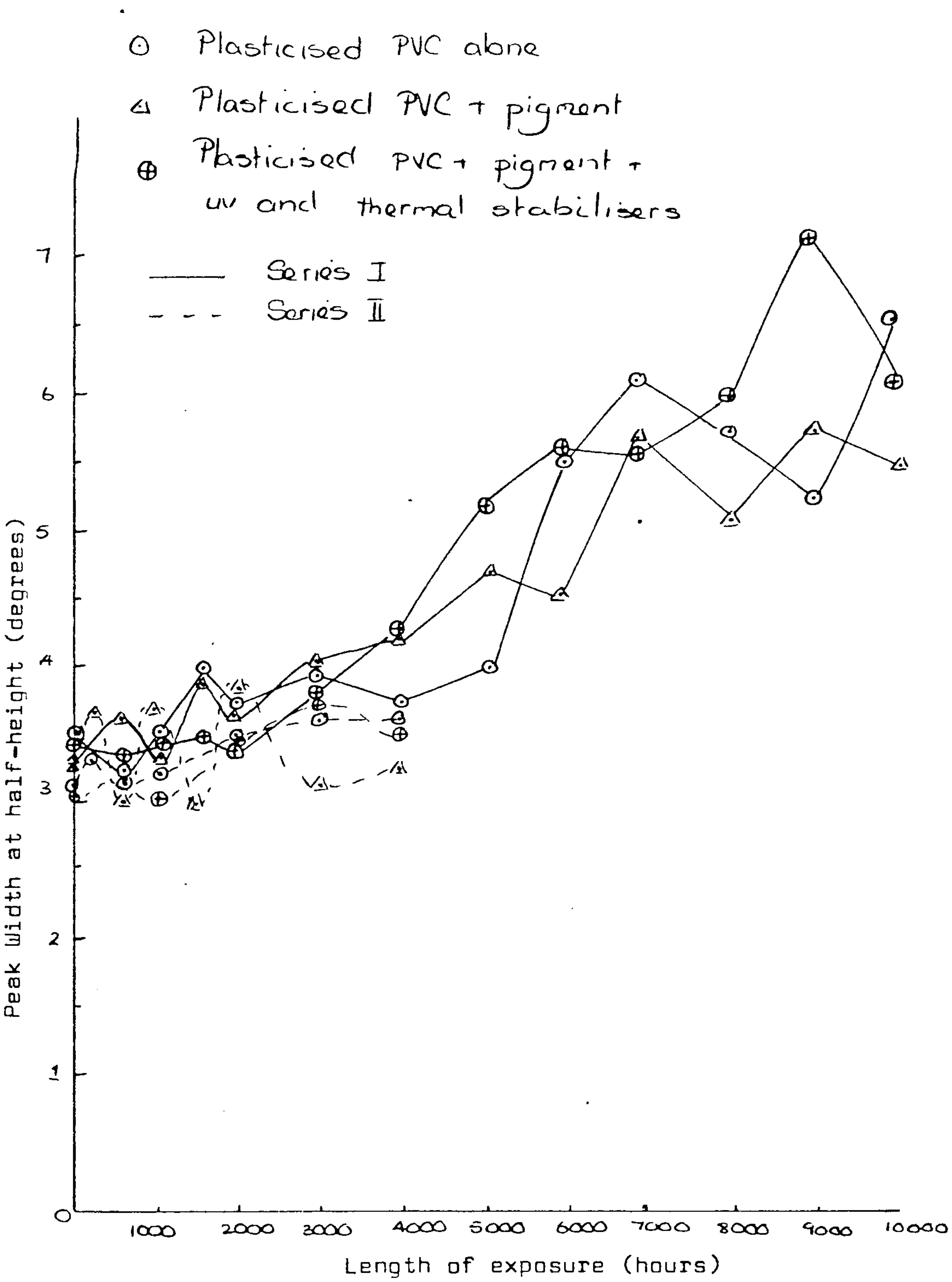
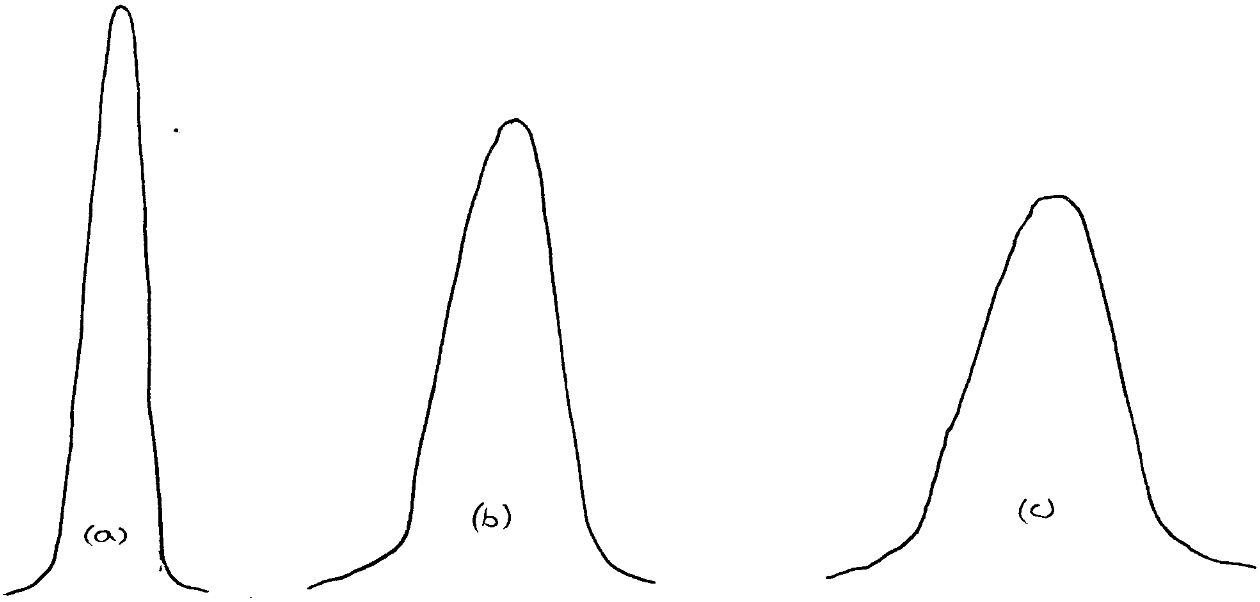


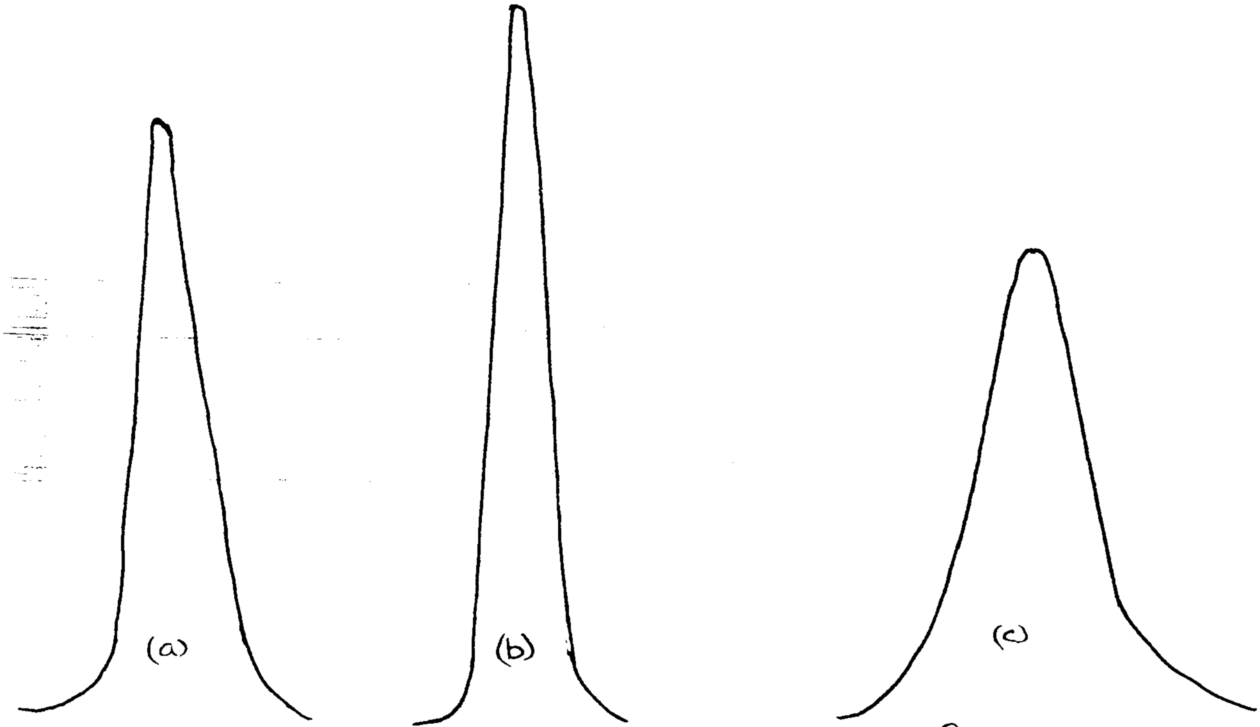
Figure 28 - Peak-Width at half-height of artificially weathered PVC plastisol coatings

exhibited a cyclic behaviour during the exposure with regard to peak width at half-height with the values after 4,000 hours being only slightly higher than the initial values. This cyclic behaviour is most pronounced for the pigmented coating whose cycle is the shortest and the one with the greatest variation in $W_{\frac{1}{2}}$ between the peak and trough heights. The cycles in the cases of the unpigmented and the stabilised coatings are less pronounced and stretch over a longer period of time. The goniophotometric curves obtained from the pigmented sample after 1000, 1500 and 2000 hours respectively are shown in figure 29 and reveal clearly the changing peak width at half-height. If the exposure of the series II coatings had been allowed to continue for 10,000 hours as was that of the series I coatings then it is probable that the more dramatic changes in $W_{\frac{1}{2}}$ exhibited by the series I coatings would also have been exhibited by the series II coatings.

A plot of gloss factor against exposure time for each of the coatings is shown in figure 30. Comparing this with figure 27 a plot of specular reflectance against exposure time it can be seen that the two plots for each coating are very similar. This shows that the predominant factor in the gloss factor is the specular reflectance of the coating and that the peak width at half-height is a lesser contributing factor. The gloss factors of each of the series I coatings show a fall in value throughout the exposure, the final values being less than 5% of their initial values. Turning now to consider the gloss factors of the series II coatings it can be seen that after 4,000 hours exposure the stabilised coating has lost only 30% of its gloss factor while the unstabilised pigmented coating has a gloss factor equivalent to its initial gloss despite having had intermediate falls in gloss by as much as 67%. The cyclic fluctuations in gloss factor are particularly pronounced for



Unpigmented coating of Series I after (a) 4,000 hours
(b) 7,000 hours
(c) 10,000 hours



Pigmented coating of Series II after (a) 1,000 hours
(b) 1,500 hours
(c) 2,000 hours

Figure 29 - Goniophotometric curves obtained from PVC plastisol surface coatings after exposure to artificial weathering

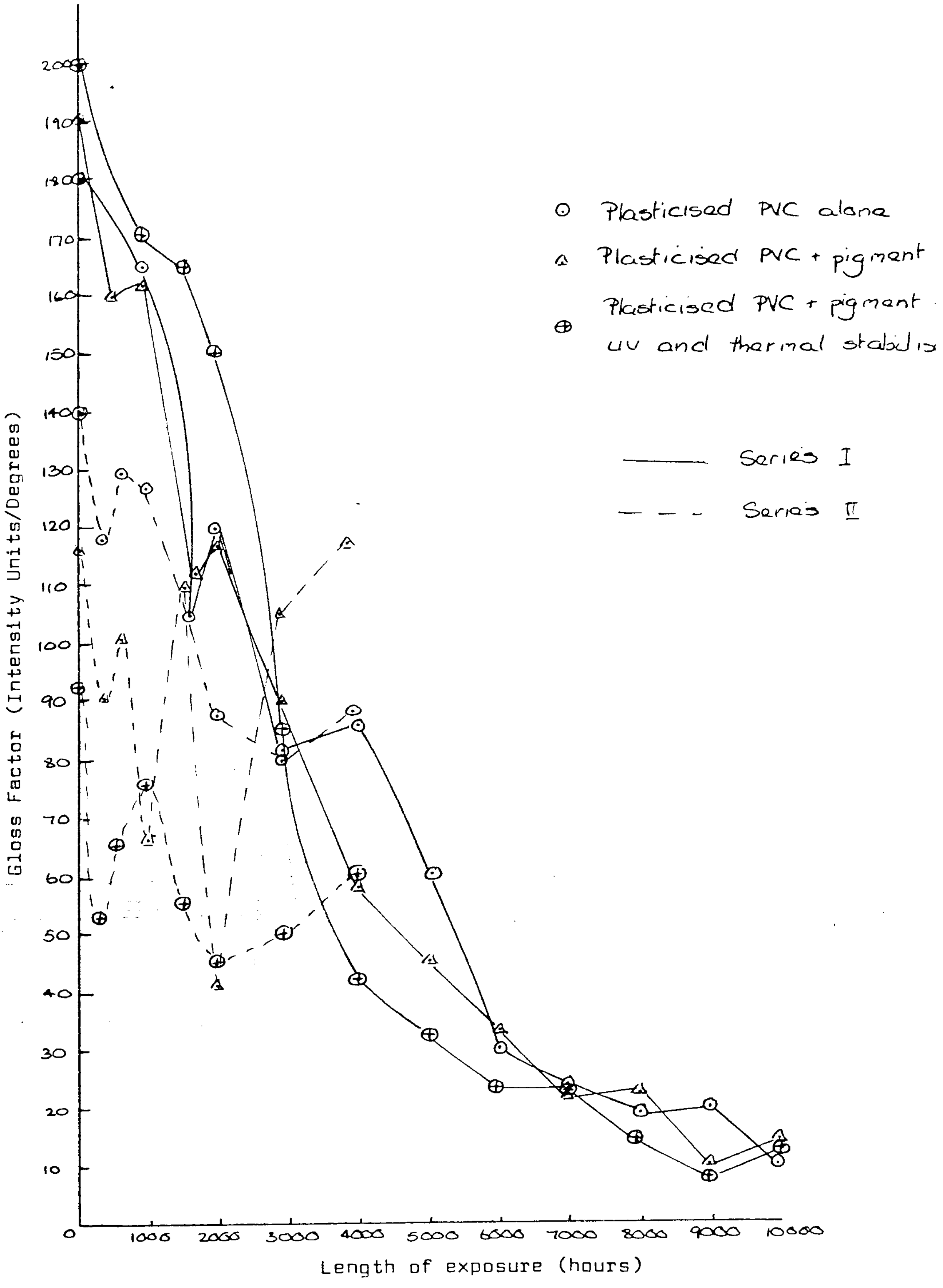


Figure 30 - Gloss factor of artificially weathered PVC plastisol coatings

this pigmented unstabilised coating but do occur to lesser degree in the other coatings. The unpigmented coating shows a 40% loss of gloss factor at the end of 4,000 hours exposure to artificial weathering. In this case the recovery phase of each cycle causes a much lower increase in gloss factor compared with the decrease in gloss factor shown in the downward phase of each cycle. It is interesting to note that after 4,000 hours the gloss factors of the series I coatings (with a higher plasticiser content) had each fallen to less than 50% of their initial values, and that these values are comparable with the gloss factor values of the series II coatings after 4000 hours exposure. The more highly plasticised series of coatings having much higher initial gloss factor values.

4.3 Micro-indentation

All the recovery-time analysis results discussed here were obtained using an ICI Pneumatic micro-penetrometer with a spherical indentor of radius 0.132 cm. For each sample recovery profiles were obtained from three different loads at several points on the sample surface. The height between indentation and recovery was used in each case to calculate Young's modulus using the Hertz equation

$$\frac{E}{1-\nu^2} = \frac{3}{4}\,\frac{mg}{r^{\frac{1}{2}}h^{\frac{3}{2}}} \qquad \text{(see chapter III pp 90)}$$

Figure 31 shows a plot of $\frac{E}{1-\nu^2}$ against exposure time and as ν , Poissons ratio, is constant the curves can be treated as a plot of Young's modulus against exposure time displaced along the y axis by a constant factor of $(1-\nu^2)$. None of the more highly plasticised series I coatings show any change in rigidity until 5,000 hours of exposure to artificial weathering has elapsed. After this length of time each of the samples shows an

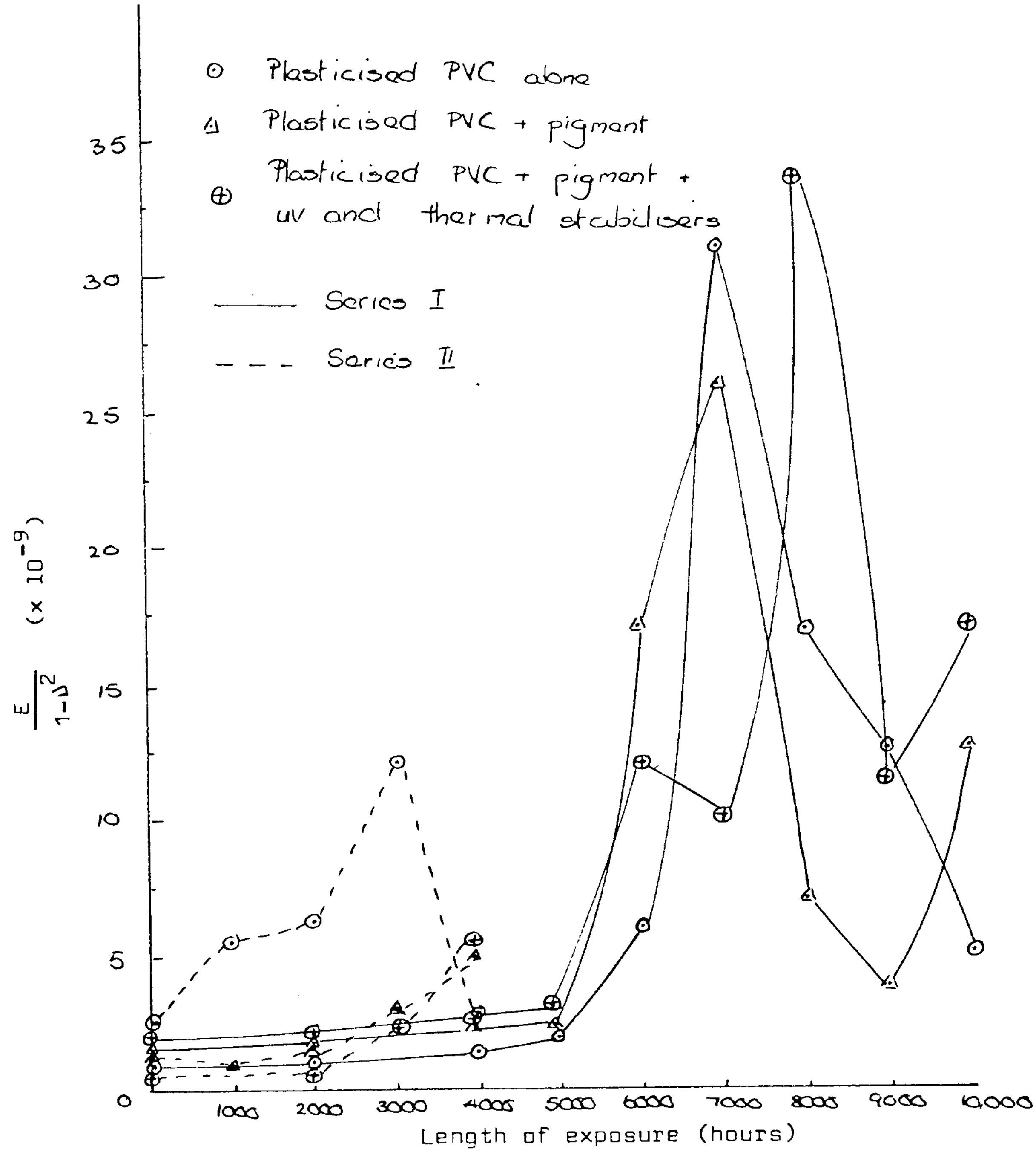


Figure 31 - Indention/Recovery Time Analysis for artificially weathered PVC plastisol coatings

increase in Young's modulus and therefore in rigidity, followed by, after varying lengths of time, a fall in Young's modulus. A cyclic pattern of behaviour is again revealed by each of surface coatings as the value of Young's modulus successively increases and decreases. This is less pronounced in the case of the unpigmented coating, the value of the modulus being stabilised rather than increasing at the end of the cycle. It is likely that the extremely soft nature of the coatings prevent any changes taking place in the first 5,000 hours of exposure being analysed. It is not until after this length of time that the surfaces become rigid enough for changes to be discernible. The lower level of plasticiser in the series II coatings does however allow earlier changes to be observed. The pigmented coatings show a slight increase in Young's modulus throughout the 4,000 hour exposure but it is the unpigmented PVC plastisol coating which shows the largest change in modulus. An initial rise in modulus is followed by a period of stability before a sharp rise leads to a maximum and then an even sharper fall in modulus to, after 4,000 hours of artificial weathering, a value of Young's modulus similar to the initial value.

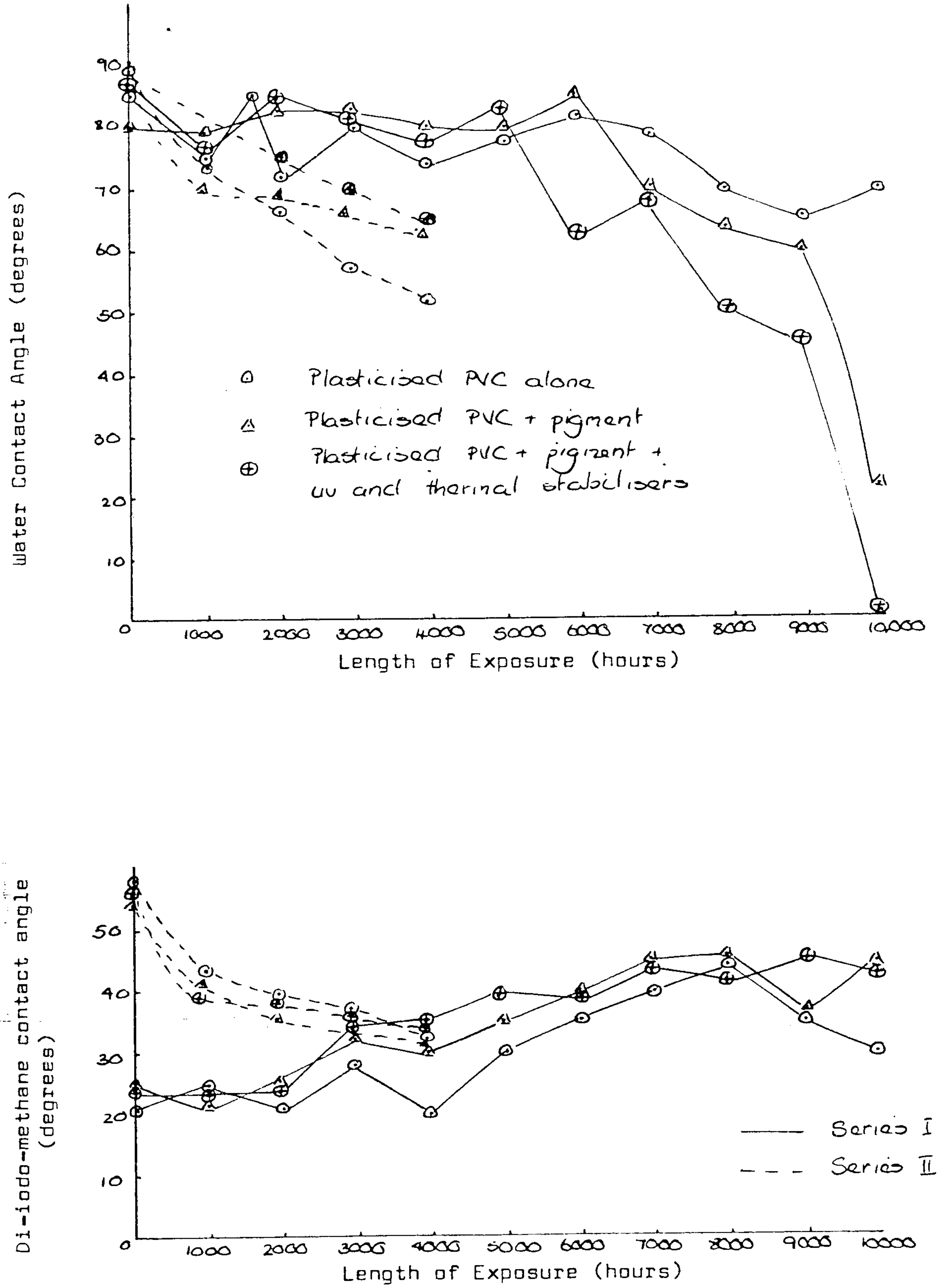
It is interesting to note that the pigment added to some of the surface coatings does not appear to have had a rigidifying effect and that despite the lower level of plasticiser in the series II coatings they do not appear to be appreciably more rigid initially.

4.4 Surface Energetics

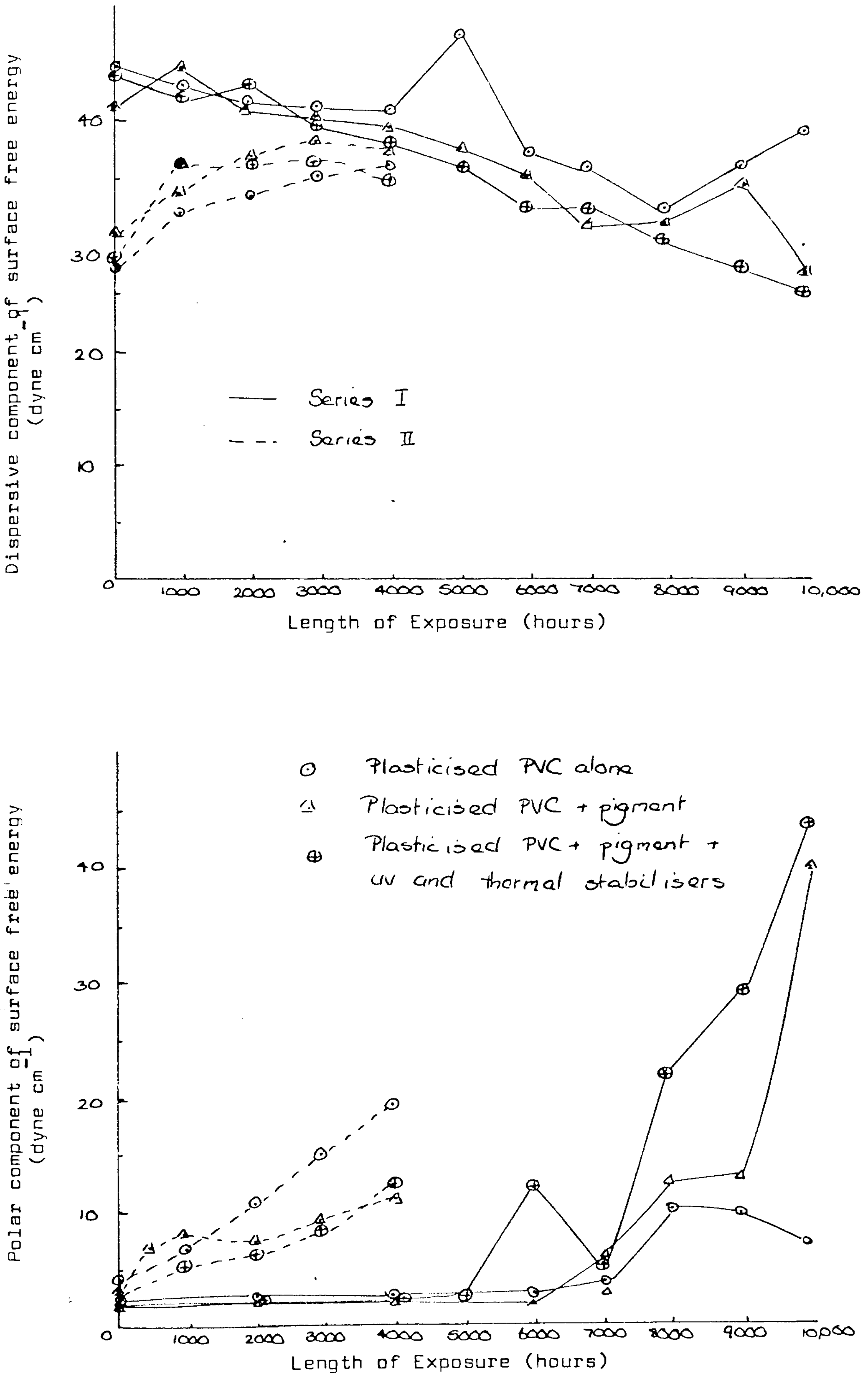
Contact angle measurements were made using a sessile drop technique and all contact angles measured were taken to be equilibrium advancing contact angles. The measurements were made using a goniophotometric eyepiece which gives accuracy to $\pm 2^{\circ}$. Five plots are shown for each surface coating, these being water contact angle, di-iodo-methane contact angle, dispersive component of surface free energy, polar component of surface free energy and total surface free energy all against exposure time, in figures 32-36 respectively.

As can be seen from figure 32 the water contact angles of the series I and series II coatings are initially all between 80° and 90° showing that the differing levels of plasticiser in the coatings does not have any measureable effect on the water contact angle. Considering first the pigmented coatings of series I it can be seen from figure 32 that there is little change in water contact angle during the first 5,000 hours of exposure to artificial weathering. This is then followed by a steady increase in their wettability by water until, in the case of the stabilised coating, after 10,000 hours spontaneous spreading of the water over the surface occurs. In the case of the pigmented series II coatings a small increase in wettability by water is observed during the 4,000 hour exposure. The unpigmented samples of the two series however show differing patterns of behaviour, the more highly plasticised series I coating showing little change in water wettability throughout the 10,000 hours, while the series II coating shows a steady increase in wettability throughout its 4,000 hour exposure.

The wettability of each of the PVC plastisol surface coatings by di-iodo-methane is shown in figure 33 and as can be seen in this case the level of plasticiser has affected the behaviour of the coatings. The more highly plasticised series I coatings are initially more wettable by di-iodo-methane, than are the less plasticised series II coatings, as shown by the lower contact angles. After 4,000 hours exposure to artificial weathering however the more highly plasticised coatings are only slightly more wettable by di-iodo-methane than their less plasticised series II



Figures 32 and 33 - Water and Di-iodo-methane contact angles of artificially weathered PVC plastisol coatings



Figures 34 and 35 - Dispersive and Polar components of surface free energy of artificially weathered PVC plastisol coatings

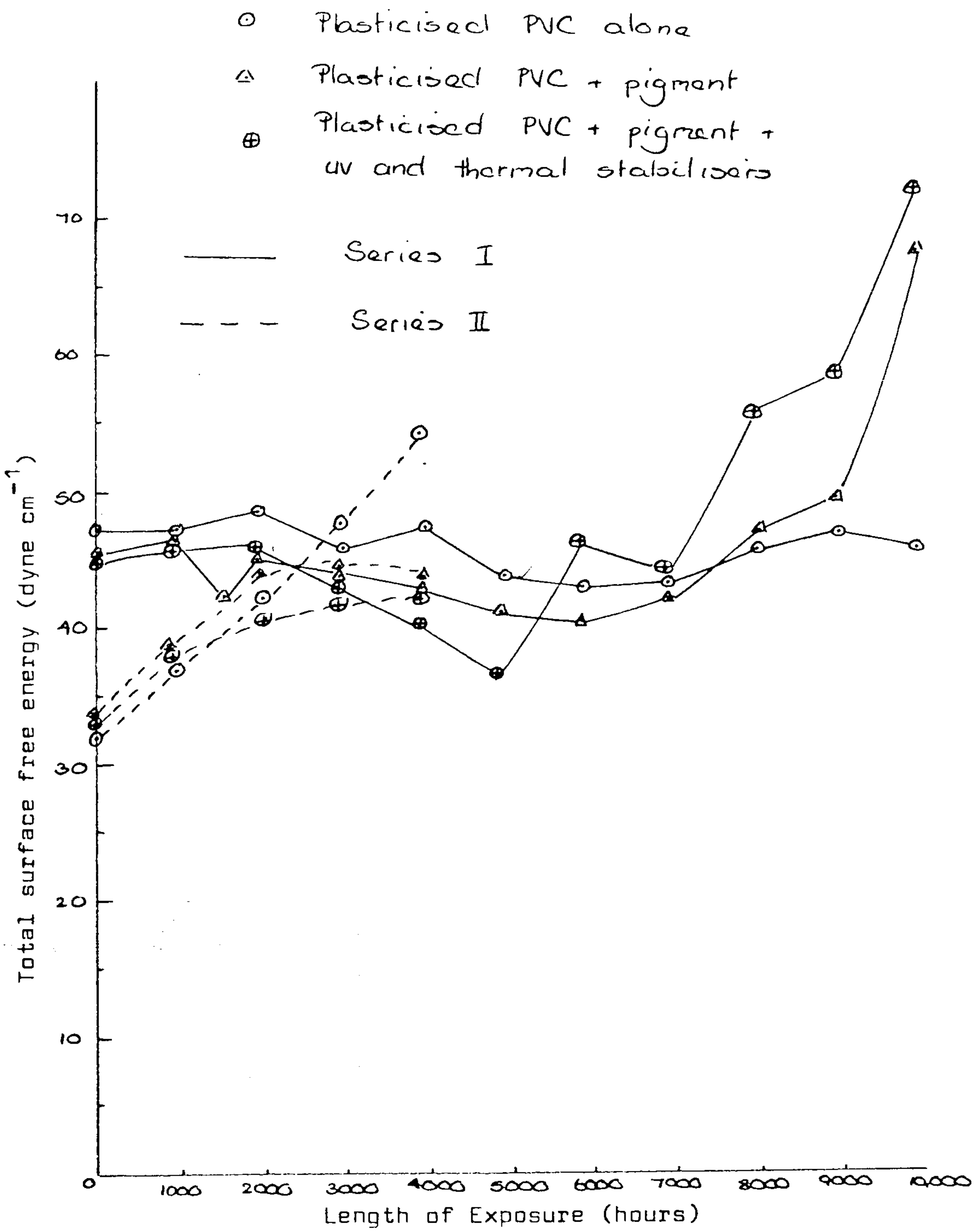


Figure 36 - Total surface free energy of artificially weathered PVC plastisol coatings

counterparts. The di-iodo-methane contact angles of the series II coatings fall initially until after 2,000 hours exposure to artificial weathering the wettability of the coatings by di-iodo-methane achieves a stable value. In contrast the wettability by di-iodo-methane of the more highly plasticised series I coatings gradually decreases until after 6,000 hours exposure to artificial weathering no further increase in contact angle is seen.

The results obtained for both water and di-iodo-methane should be considered in the light of corresponding results for rigid (unplasticised) PVC which are:

H_2O contact angle - 87^o
CH_2I_2 contact angle - 36^o
γ_d - 40 dynes cm^{-2}
γ_p - 1.5 dynes cm^{-2}

From these it can be seen that the addition of plasticiser to the coatings primarily effects the di-iodo-methane contact angles and that it has little effect upon the water contact angles. It also appears that the addition of pigment to the coatings has little effect upon either the water or di-iodo-methane contact angles.

The changes which occur in the surface free energies of the coatings resulting from the exposure to artificial weathering are now discussed. The results obtained are shown in figure 36. The total surface free energies of the series II coatings are initially lower than those of the series I coatings because of the lower components of dispersive free energy. The polar components of surface free energy are initially insignificant for all the coatings having values of between 1 and 4 dynes cm^{-1}. The surface free energies of the series II coatings show a gradual rise throughout the 4,000 hours until at the end of this time they have free energies comparable with their series I counterparts. For these coatings the gradual increase is attributable to a gradual increase in both the polar and dispersive components of surface free energy during the exposure. The more highly plasticised series I coatings show, in contrast, an initial fall in surface free energy during the first 5,000-6,000 hours of exposure to artificial weathering. This is followed in the case of the pigmented coatings by a sharp increase in free energy. This behaviour is attributable to a small but steady decrease in the dispersive component of surface free energy coupled with after 6,000 hours exposure a sudden increase in the polar component. The unpigmented coating does not show this increase in surface free energy towards the end of the exposure but shows a stabilising of the surface free energy. Again a cyclic pattern of behaviour is superimposed upon the overall trend of the series I coatings' behaviour the length of the cycle varying from 2,000 hours for the stabilised coating to 5,000 hours for the unpigmented coating.

4.5 Scanning Electron Microscopy

Scanning electron microscopy of artificially weathered samples was carried out using the Stereoscan Mark 2A instrument previously described. Stereoscan micrographs were obtained for each of the coatings during the final stages of exposure, that is after 4,000 hours for the series II coatings and from 6,000 to 10,000 hours for the series I coatings. Magnifications ranging from x200 to x1000 were employed to obtain the micrographs shown in Plates 12 to 32. The length of exposure and magnification are given alongside each micrograph.

On comparing the series I micrographs it is noticeable that the surface of the unpigmented coating is more pitted and marked after 6,000 hours exposure than is that of the corresponding pigmented sample after the same length of time. Traces of debris can be seen adhering to the unpigmented coating which is itself showing signs of breakdown. After a further 1,000 hours exposure to artificial weathering the surface takes on a more pitted appearance, the pits being surrounded by areas in which the coating has not yet been eroded. This situation is reversed after 8,000 hours however with the areas of deep erosion having spread to surround islands of less eroded surface. After 9,000 hours exposure to artificial weathering the surface coating can be observed to be breaking down completely the end result of which is observed after 10,000 hours as a break in the coating through which the substrate is revealed. This cracking and breaking down of the surface confirms the visual appearance of the surface coating which after this length of time is discoloured and covered with small brown specks.

The pigmented coatings also show deformations in their surfaces after 10,000 hours exposure but not to the same extent as the unpigmented sample. Both the stabilised and the unstabilised coating show a network of ridges across the surface, those in the stabilised coating being arranged in an haphazard manner. In the unstabilised coating however the ridges radiate from a number of pit marks which cover the surface and one of which can be seen in the micrograph. These marks appear to contain some debris which is embedded in the surface accelerating the rate of degradation.

The series II coatings show less uniform changes across their surfaces during the 4,000 hour exposure and as can be seen from the micrograph degradation of the surfaces is taking place in small isolated areas and not over the entire surface as in the case of the series I coatings. The pigmented coatings show deformations in their surfaces only under

MICROGRAPHS OF ARTIFICIALLY WEATHERED SAMPLES
OF SERIES I PVC PLASTISOL SURFACE COATINGS

Plate 12 - Plasticised PVC alone after 6,000 hours, magnification x200

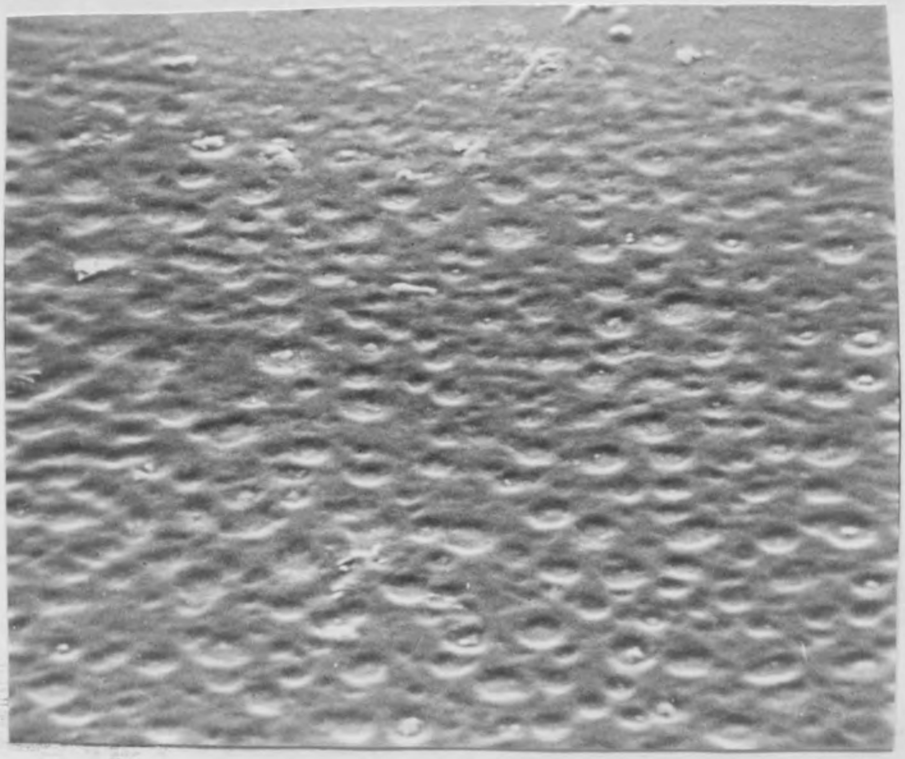


Plate 13 - Plasticised PVC alone after 7,000 hours, magnification x200

Plate 14 - Plasticised PVC alone after 8,000 hours, magnification x410

Plate 15 - Plasticised PVC alone after 9000 hours, magnification x1000

Plate 16 - Plasticised PVC alone after 10,000 hours, magnification x190

Plate 17 - Plasticised PVC alone after 10,000 hours, magnification x460

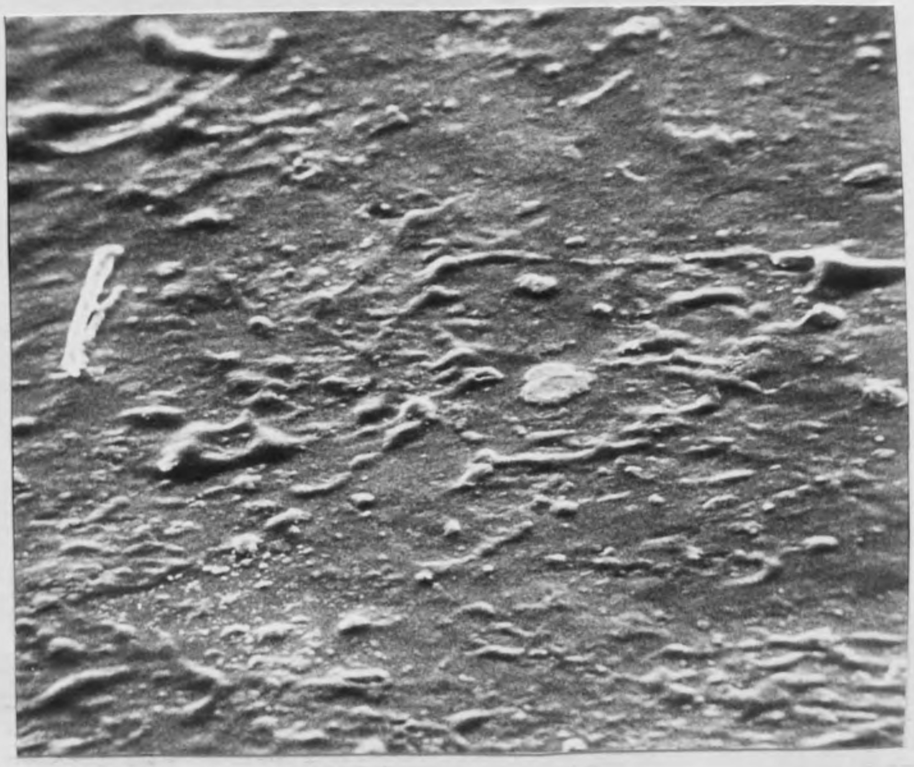
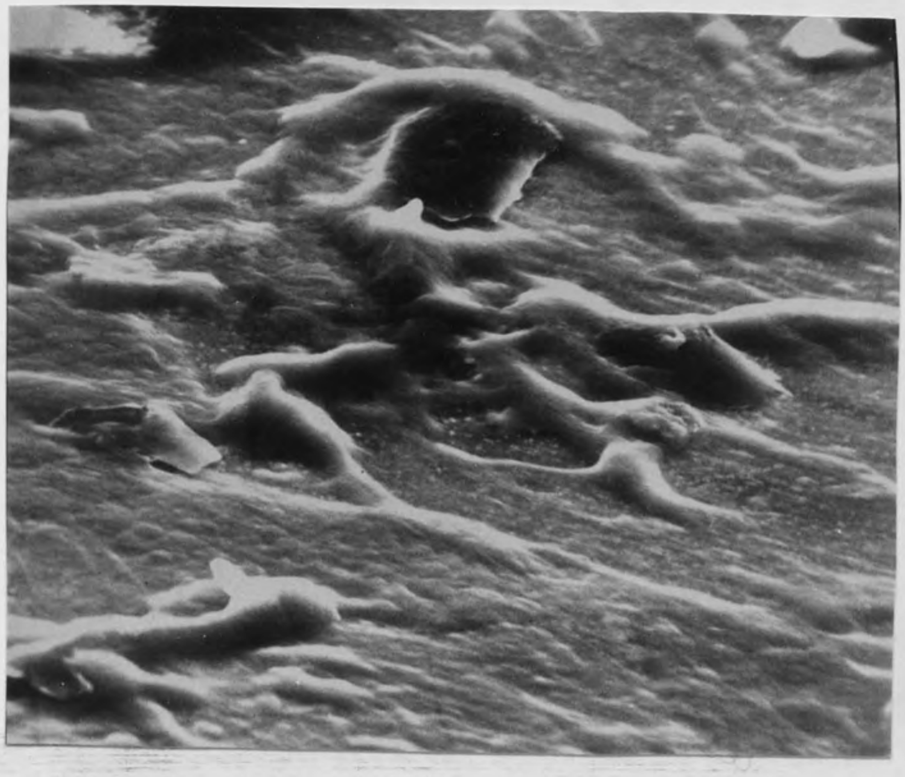


Plate 18 - Plasticised PVC alone after 10,000 hours, magnification x215



late 19 - Plasticised PVC + pigment after 6,000 hours, magnification x950

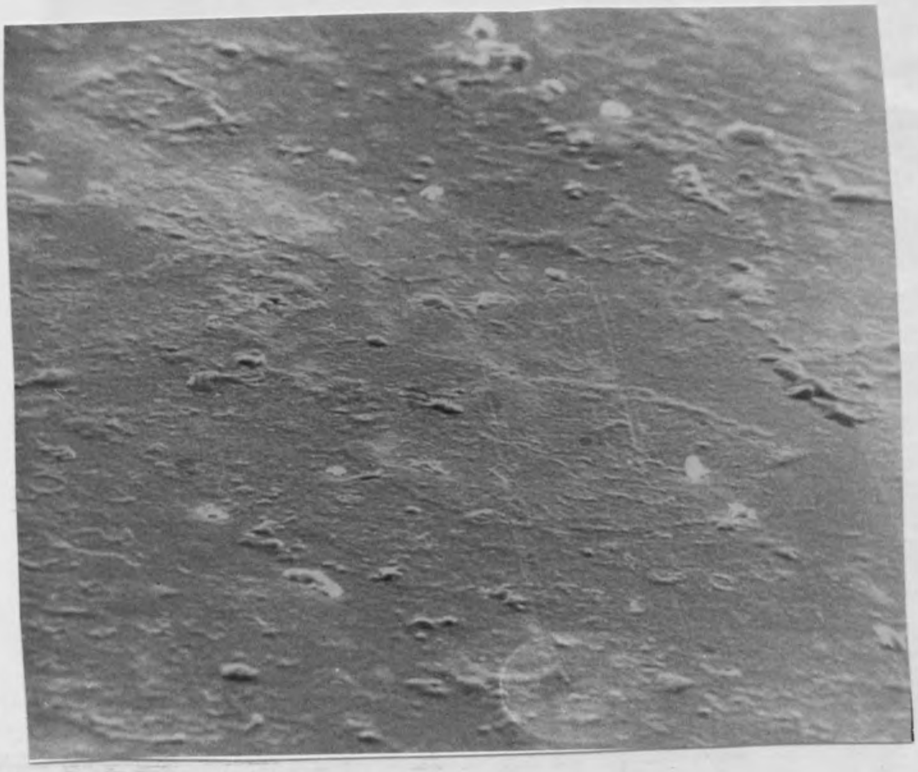
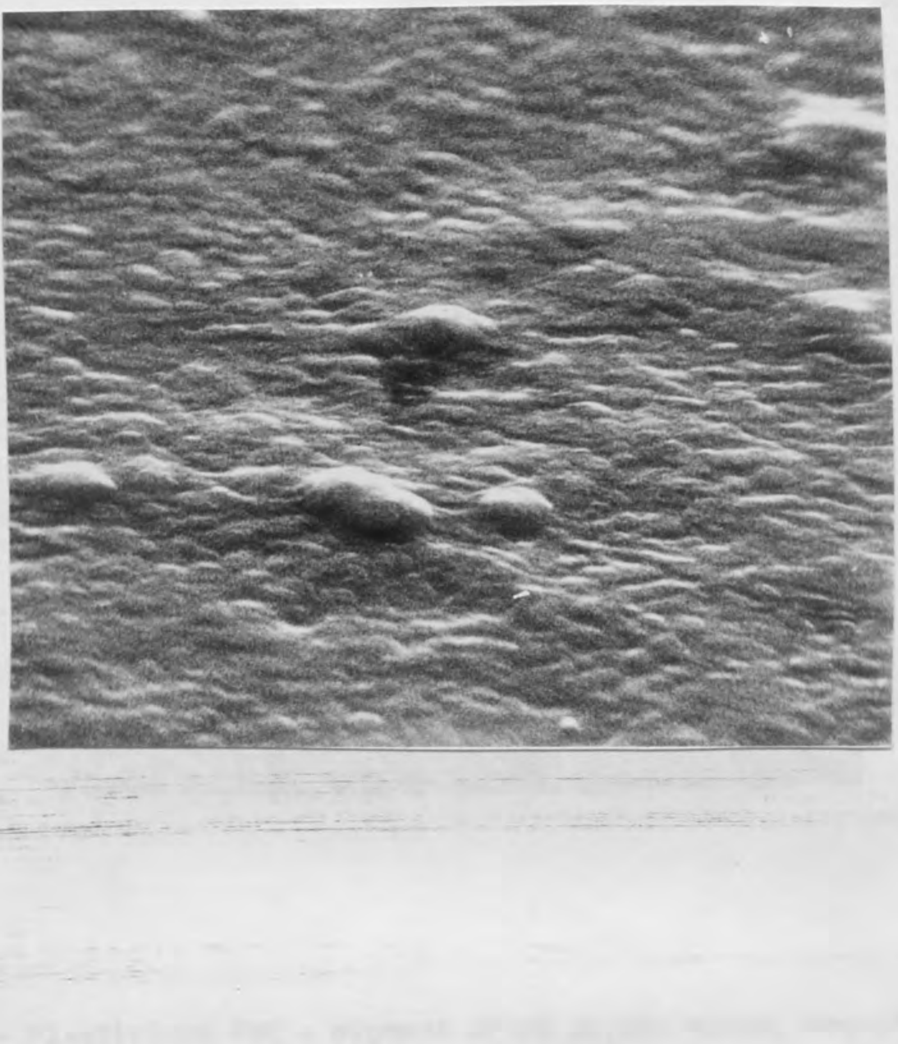


Plate 20 - Plasticised PVC + pigment after 6,000 hours, magnification x190



late 21 - Plasticised PVC + pigment after 8,000 hours, magnification x1,450

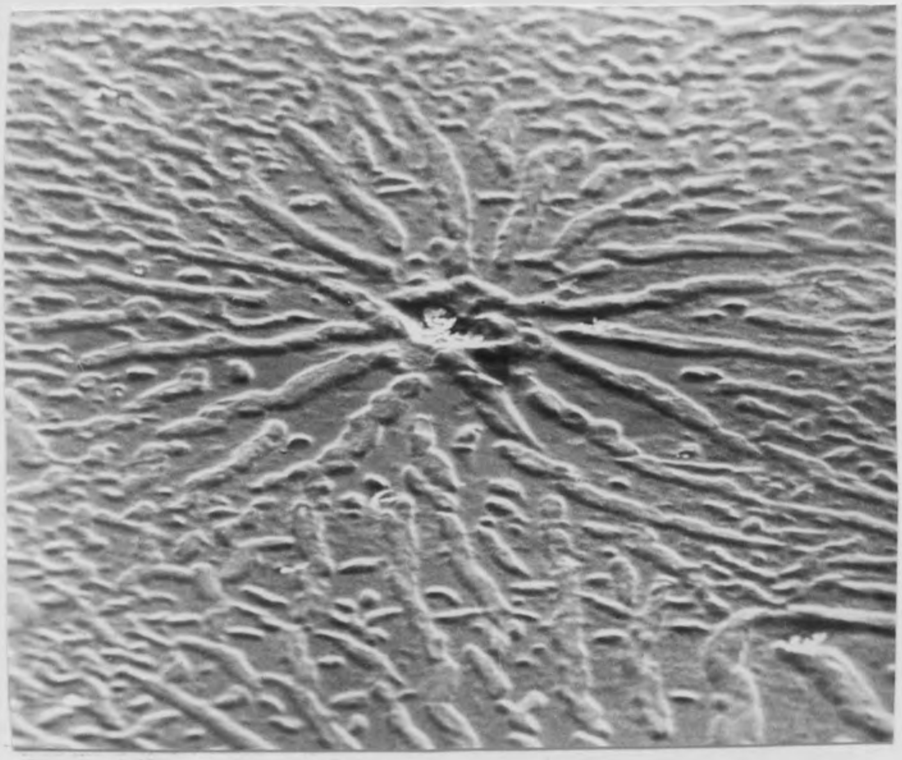
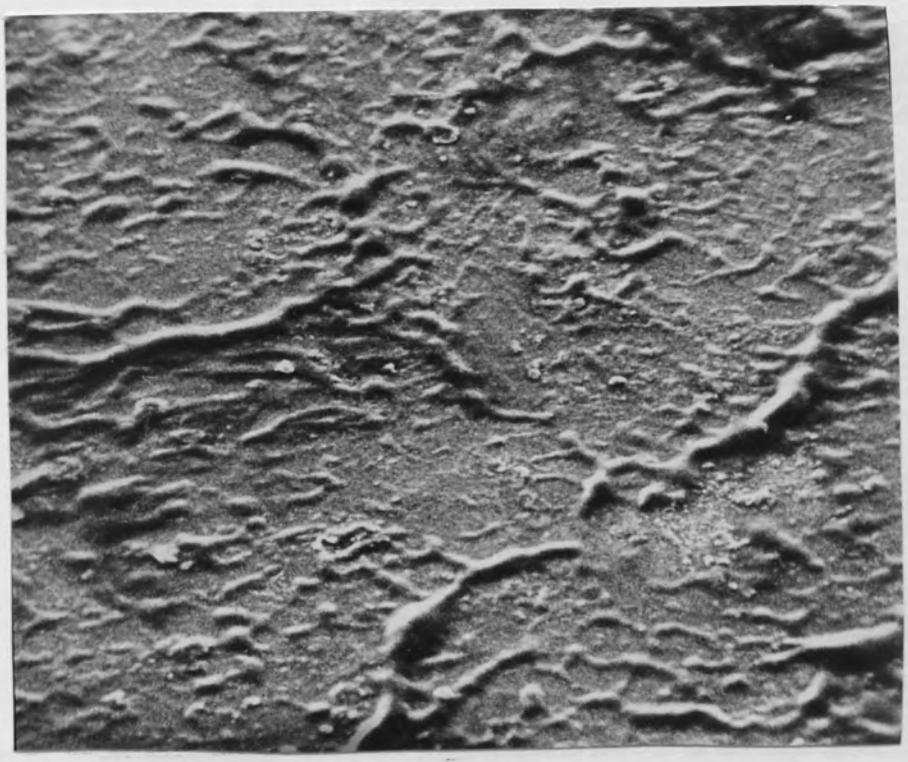


Plate 22 - Plasticised PVC + pigment after 10,000 hours, magnification x200



late 23 - Plasticised PVC + pigment after 10,000 hours, magnification x225

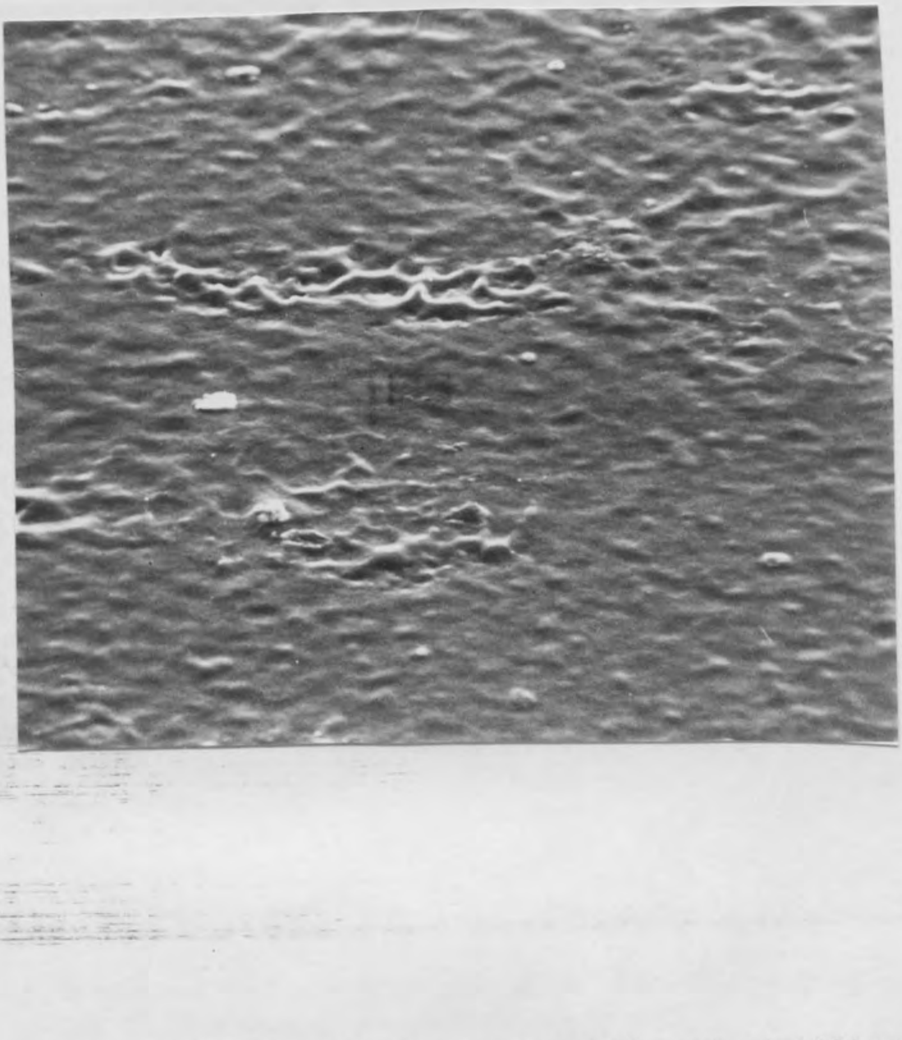


Plate 24 - Plasticised PVC + pigment + uv and thermal stabilisers after 7,000 hours, magnification x190

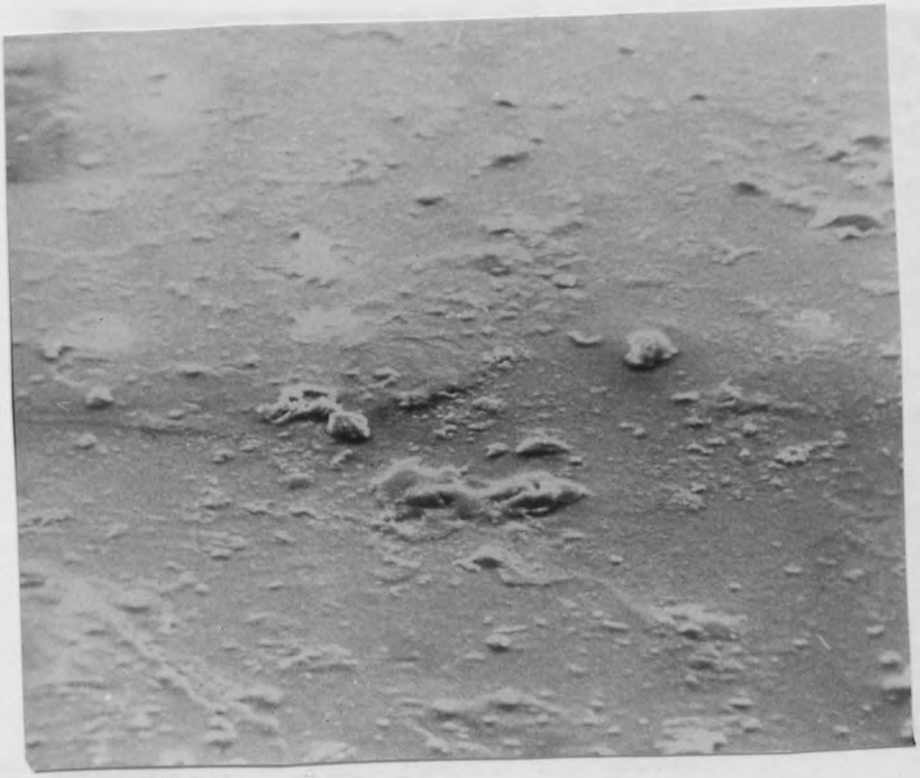


Plate 25 - Plasticised PVC + pigment + uv and thermal stabilisers after 9,000 hours, magnification x240

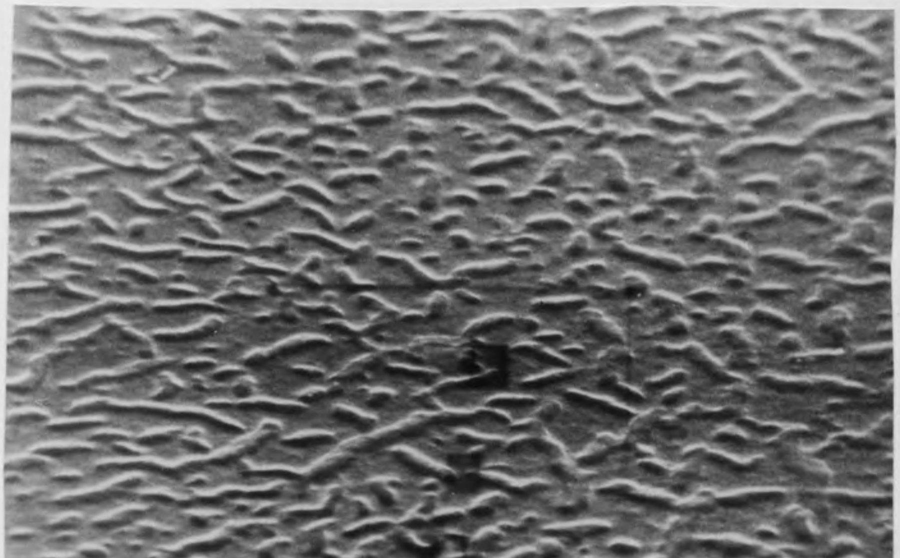


Plate 26 - Plasticised PVC + pigment + uv and thermal stabilisers, after 10,000 hours, magnification x240

MICROGRAPHS OF ARTIFICIALLY WEATHERED SAMPLES OF SERIES II PVC PLASTISOL SURFACE COATINGS

late 27 - Plasticised PVC alone after 4,000 hours, magnification x90

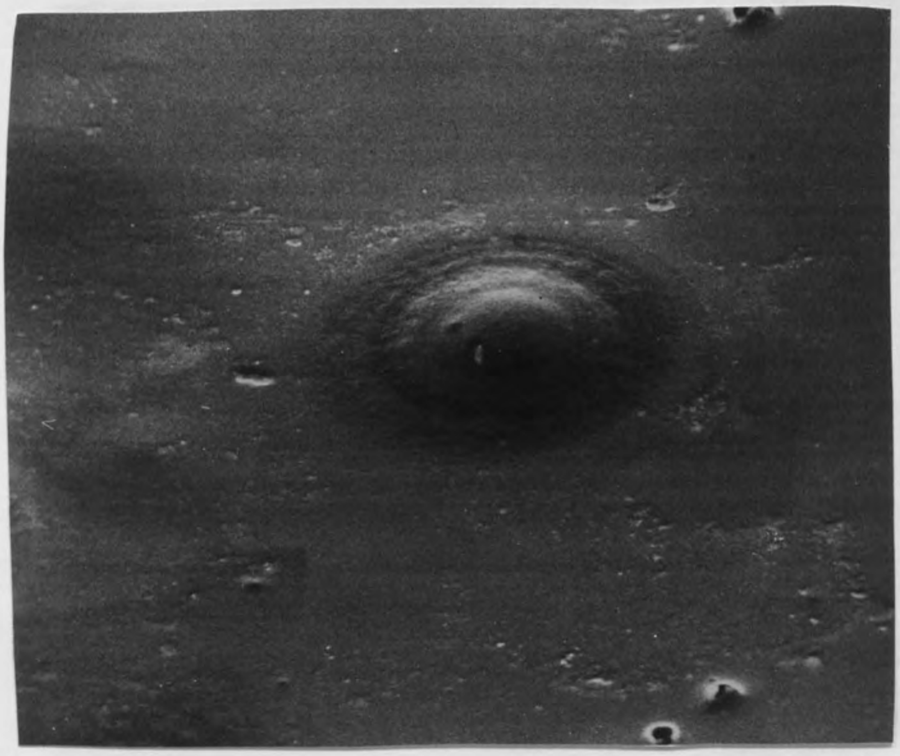


Plate 28 - Plasticised PVC alone after 4,000 hours, magnification x190

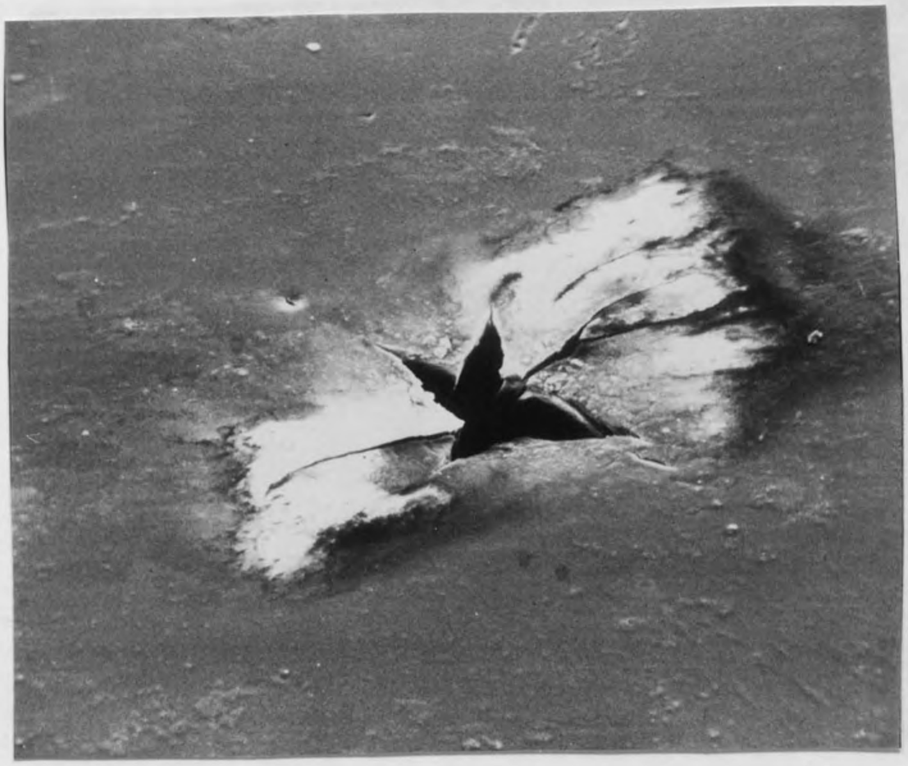


Plate 29 - Plasticised PVC alone after 4,000 hours, magnification x200

Plate 30 - Plasticised PVC alone after 4,000 hours, magnification x190

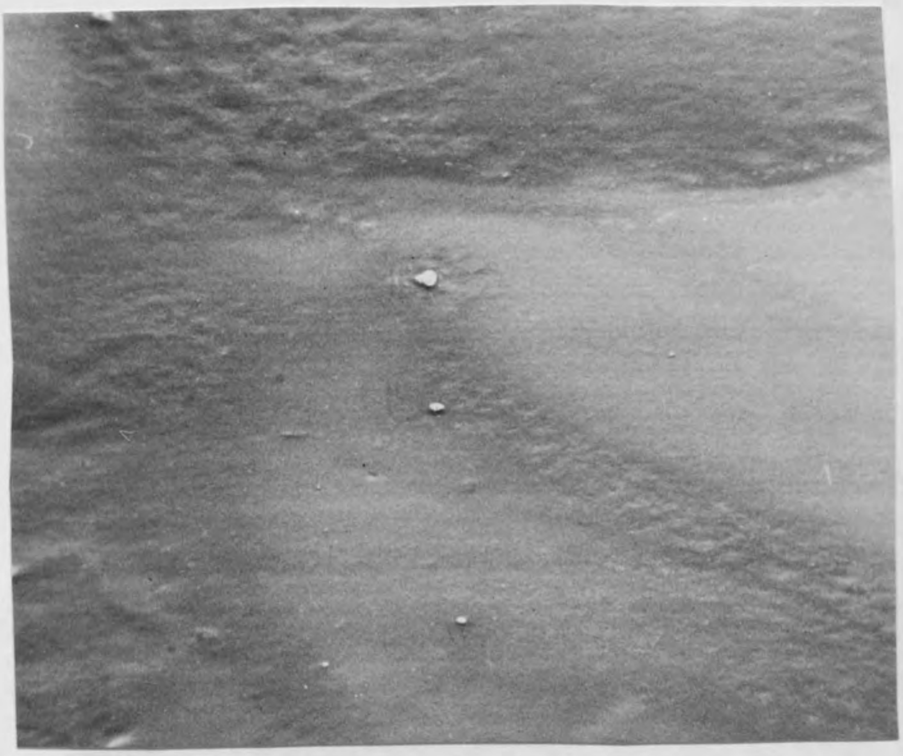


Plate 31 - Plasticised PVC + pigment after 4,000 hours, magnification x980

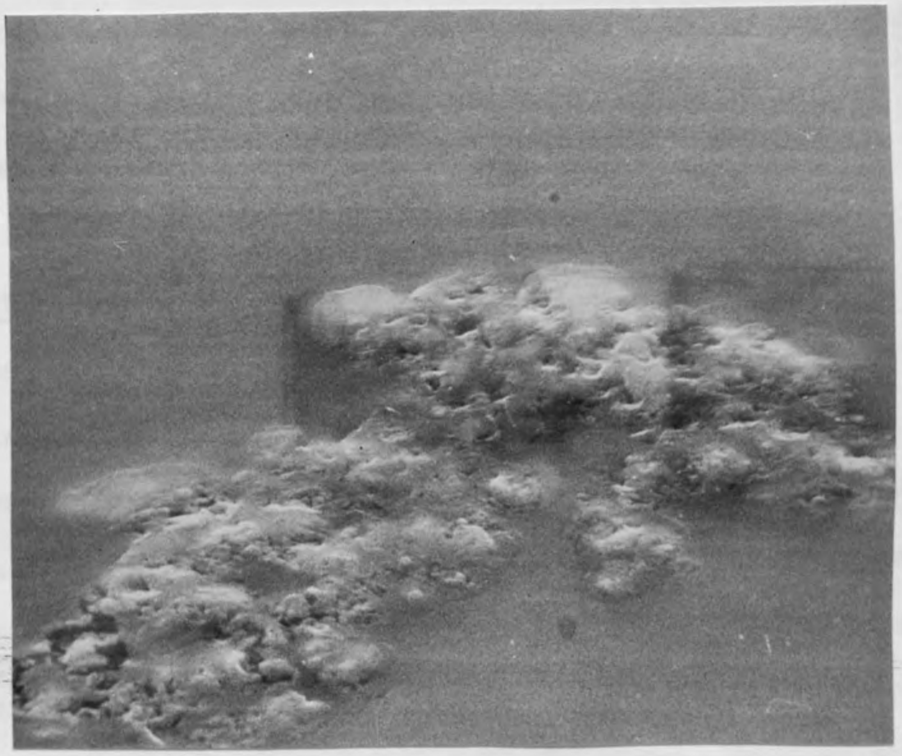


Plate 32 - Plasticised PVC + pigment + uv and thermal stabilisers after 4,000 hours, magnification x1,100

high magnifications showing that as yet they have not undergone extensive degradation. The unpigmented coating in contrast shows signs of severe isolated breakdown with a much lower magnification. In this case the surface of the coating appears to bubble from beneath before the surface of the bubble is lost leaving a breach in the coating exposing the substrate beneath. The stages in this 'bubble' development can be clearly observed in the micrographs. It is interesting to note that the areas of surface between these defects remain relatively unaffected by artificial weathering unlike that of the more highly plasticised series I unpigmented coating which shows extensive degradation over the whole surface. The defects in the series II coatings are not at this stage readily discernible to the naked eye.

4.6 Weight Loss

Weight loss measurements were taken, as previously stated, with the aim of providing information regarding the loss of plasticiser from the sample surface during exposure to artificial weathering. As noted however in Chapter III, p 88, the soft nature of the series I coatings rendered them unsuitable for this type of analysis and so only results for the series II coatings are reported here. A plot of percentage weight change against exposure time is shown in figure 37. Each of the coatings showed a weight loss from the outset of the exposure with the rate of loss appearing to stabilise for each coating after approximately 1,500 hours exposure to artificial weathering. The unpigmented coating showed the greatest loss of weight during the exposure as would be expected. It was not expected however that the stabilised coating would show a greater weight loss than the unstabilised coating as is the case. These results tend to confirm the idea that the addition of pigment to the coatings has a greater stabilising effect than does the addition of the thermal and uv stabilisers.

accuracy.

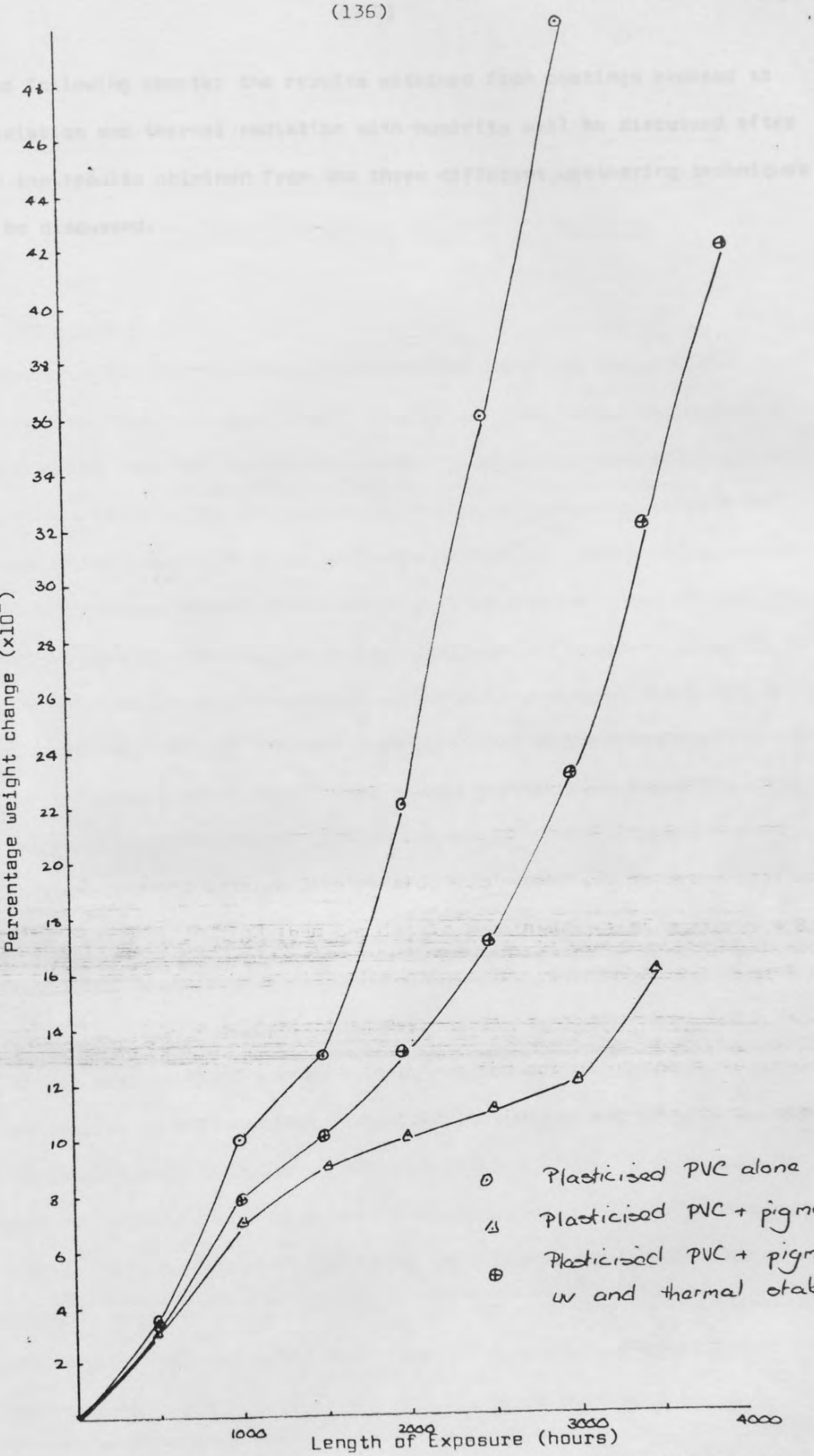


Figure 37 - Weight loss of artificially weathered PVC plastisol surface coatings

In the following chapter the results obtained from coatings exposed to uv radiation and thermal radiation with humidity will be discussed after which the results obtained from the three different weathering techniques will be discussed.

CHAPTER V

THE ARTIFICIAL WEATHERING OF POLY(VINYL CHLORIDE) PLASTISOL SURFACE COATINGS BY EXPOSURE TO ULTRA-VIOLET RADIATION AND TO THERMAL RADIATION IN THE PRESENCE OF HUMIDITY

5.1 Introduction

The previous two chapters have discussed the result of exposing PVC plastisol surface coatings to both natural and artificial weathering and following that two aspects of weather have been chosen and isolated for further study. The reason for the choice of these two aspects of weather is that they are potentially two of the most degradative features of natural weathering and it was hoped that by analysing the effect each of them have, individually, on surface coatings, it would be possible to use the information to help unravel the complex processes which are taking place during the natural weathering of plastisol surface coatings.

The three coatings of series II were chosen for this exposure, that is:

(a) plasticised PVC alone

(b) plasticised PVC + pigment

(c) plasticised PVC + pigment + thermal and uv stabilisers.

The aspects of weather selected were ultra-violet radiation and thermal radiation in the presence of humidity as it was felt that these were two of the most powerful degradative agents present in weather. Exposure of the samples to ultra-violet radiation was carried out in a uv Exposure Cabinet supplied by Laboratory Thermal Equipment, this is described in Chapter II, page 41. The exposure to thermal radiation is also described in Chapter II, page 44 and in this case the environmental test chamber was supplied by Montford Instruments Ltd. The samples exposed to ultra-violet radiation were analysed using techniques of goniophotometry, micro-pentrometry and surface energetics, these samples were exposed to ultra-violet radiation for a total of 5,000 hours. The samples exposed to thermal radiation were exposed for only 1,000 hours in total and these were analysed using goniophotometry alone.

5.2 Exposure of PVC Plastisol Surface Coatings to Ultra-Violet Radiation

5.2.1 Goniophotometry

After exposure to ultra-violet radiation the glossiness of the coatings was measured using a Brice-Phoenix light-scattering photometer which had been modified to measure reflectance as a function of viewing angle. A narrow beam of incident light was used in each case because each of the coatings were from the series II formulations and as previously mentioned the brush marks present on the surface could cause a distortion of the results if a wider beam was used. Plots of specular reflectance, peak-width at half-height and gloss factor are shown in figures 38-40. The most striking feature is the cyclic pattern of behaviour displayed by the unpigmented coating, and to a lesser extent by the pigmented coatings. This cyclic behaviour is however superimposed upon a trend of falling specular reflectance. For each of the coatings the specular reflectance is highest before exposure to uv radiation with the unpigmented coating reflecting most light at the specular angle. The pigmented coatings also lose their gloss more quickly than the clear coating, their specular reflectance at the end of the exposure being only 20% of that initially, compared with 45% for the unpigmented coating. The peak-width at half-height of the clear coating also shows less marked changes during the 5,000 hour exposure, compared with those of the pigmented coatings, with only a slight increase in value. The pigmented coatings in contrast both show marked increases in peak-width during the exposure, the stabilised coating after 3,000 hours and the unstabilised coating after 4,000 hours. It is interesting to compare these

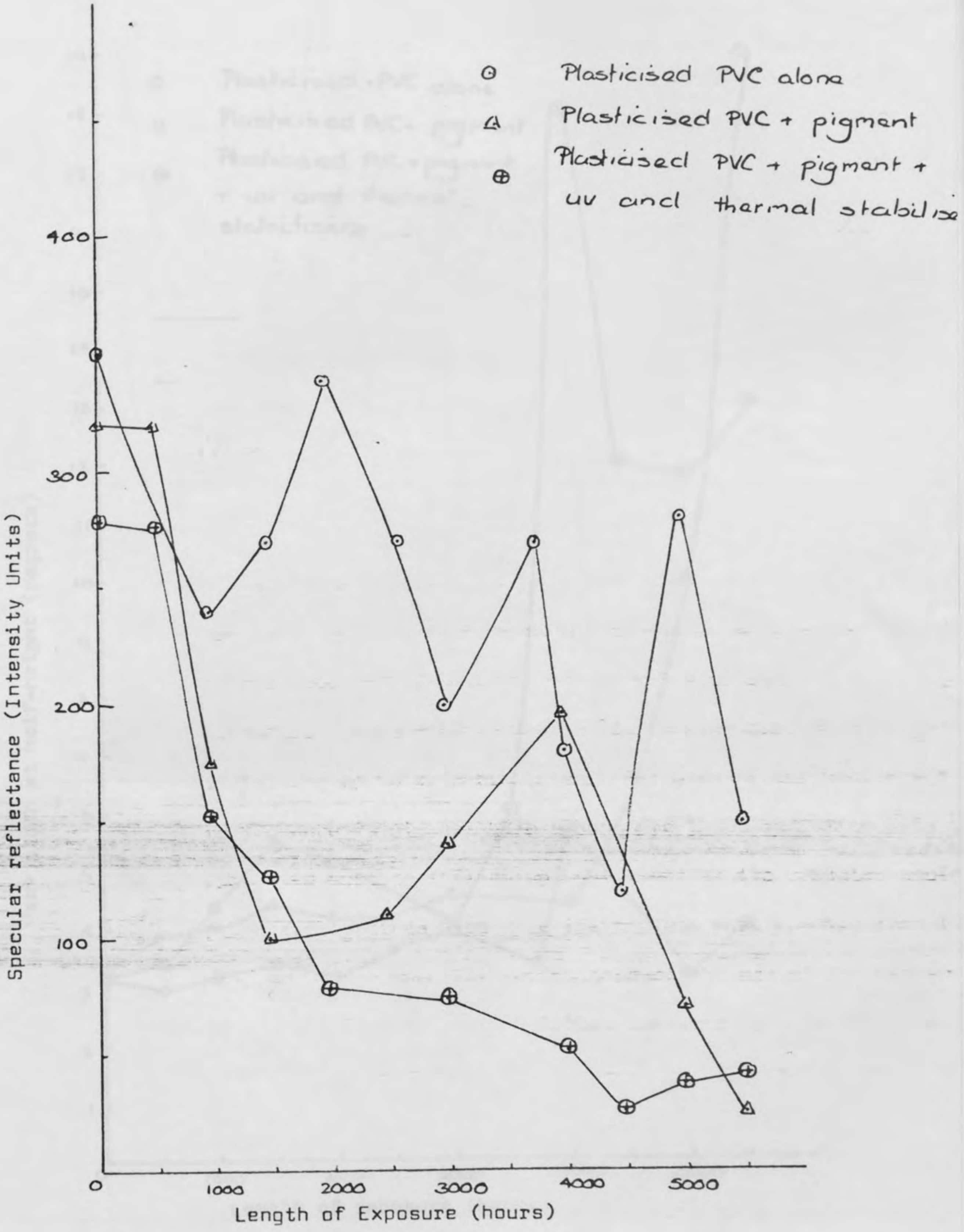


Figure 38 - Specular reflectance of PVC plastisol coatings after exposure to uv radiation

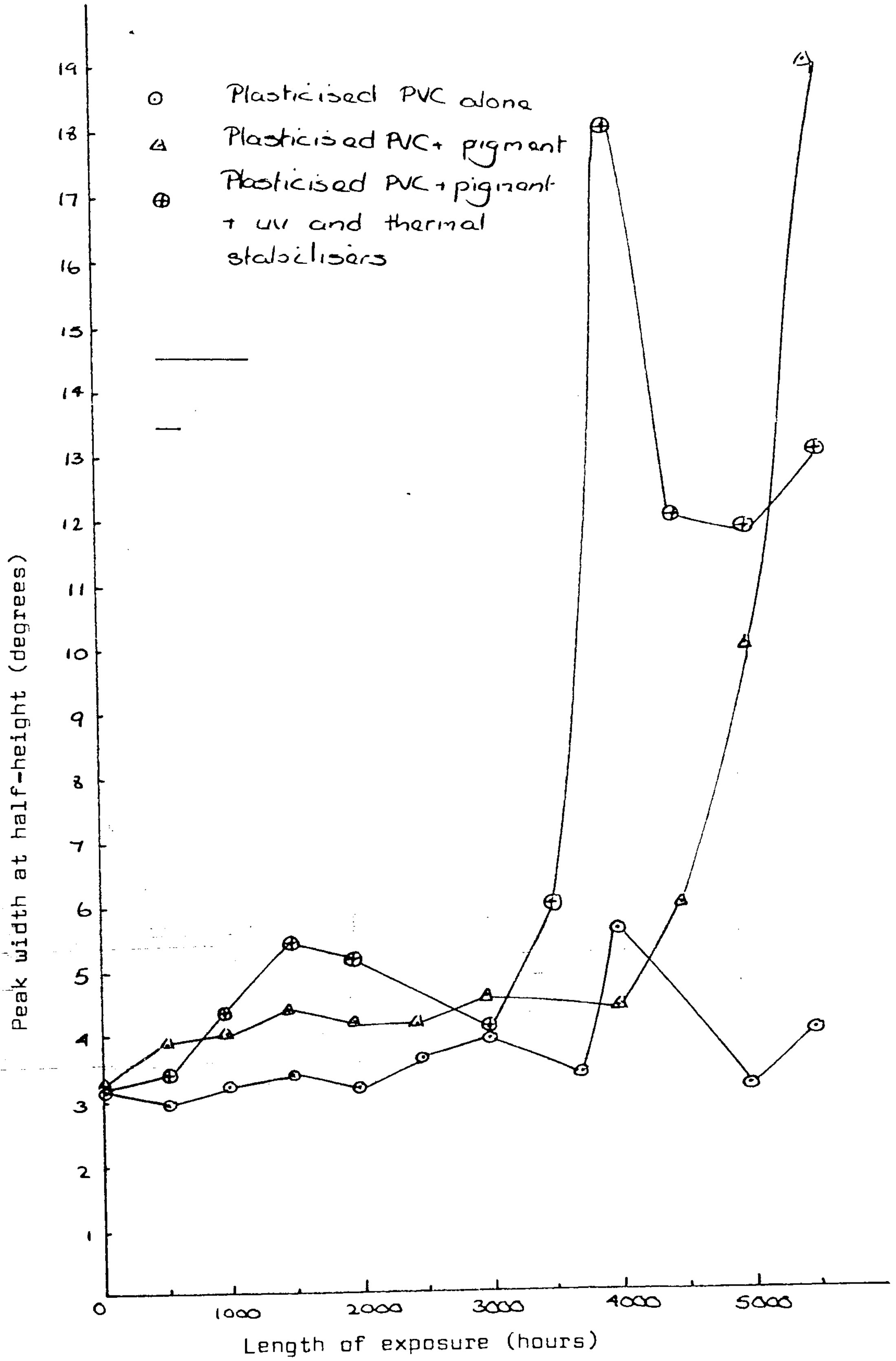


Figure 39 - Peak width at half-height of PVC plastisol coatings exposed to uv radiation

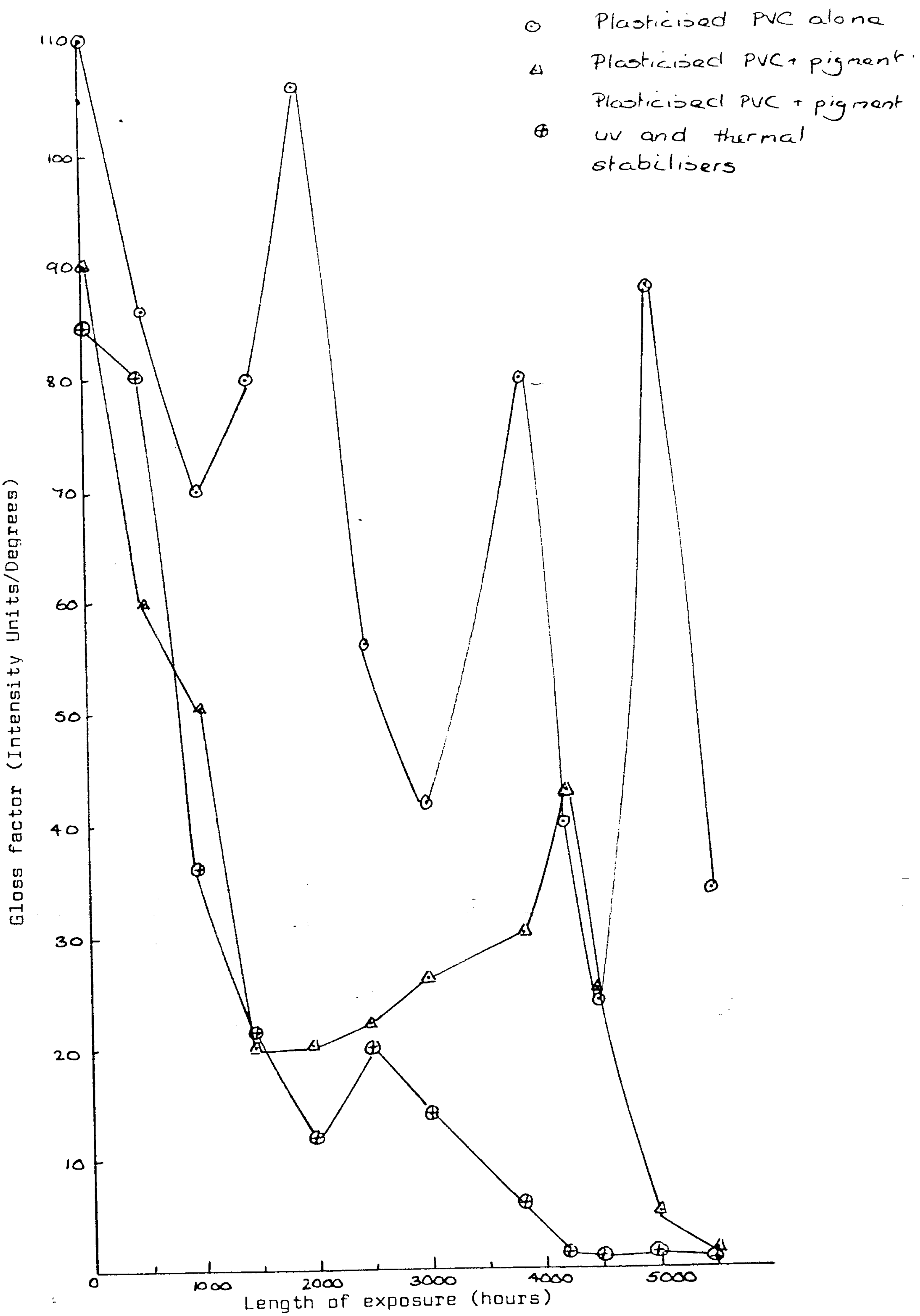


Figure 40 - Gloss Factor of PVC plastisol coatings after exposure to uv radiation

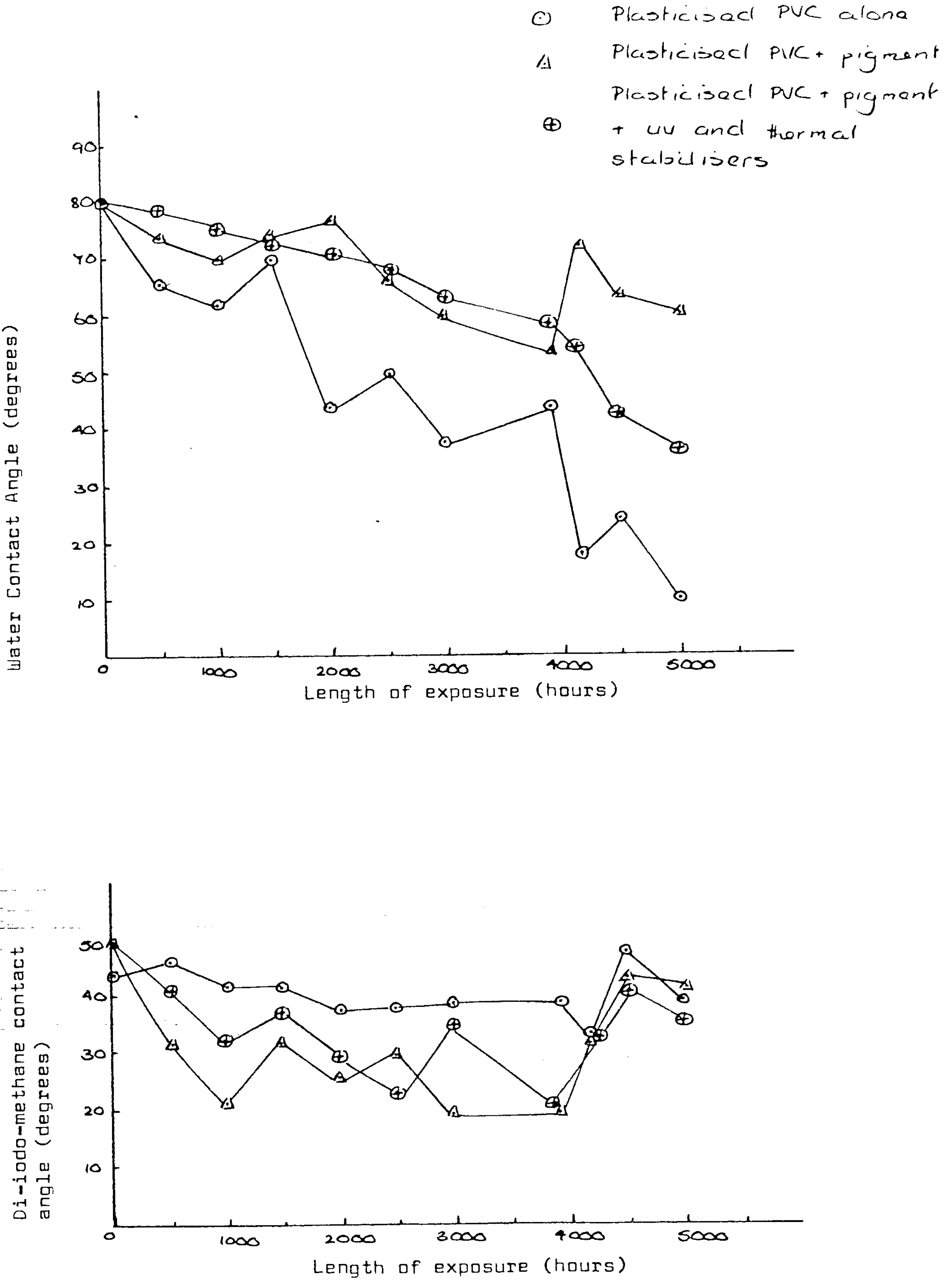
results with those of the specular reflectance for the same coatings when it can be seen that the initial sharp fall in specular reflectance is accompanied by a stable peak-width at half-height and that the sharp increase in peak-width occurs when the coatings have lost most of their glossiness. The loss of gloss is not therefore associated with the formation of macro-defects in the surface which would cause an increase in peak-width.

The plot of gloss factor against exposure time again shows that the predominant factor is specular reflectance and that peak-width at half-height has a less marked effect upon gloss factor. It can be seen that the unpigmented coating has a higher gloss at the outset of the exposure and that it retains its gloss better than the other two coatings.

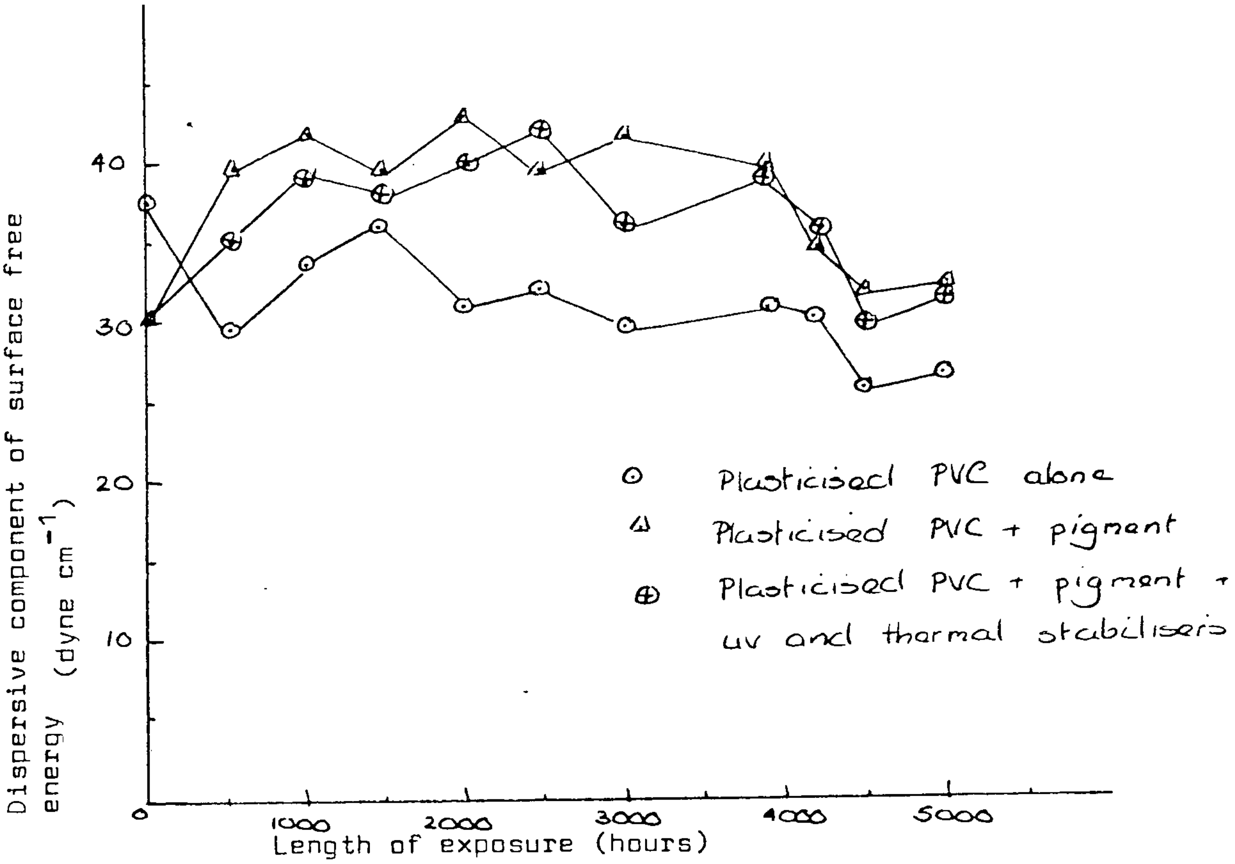
5.2.2 Contact Angle Studies

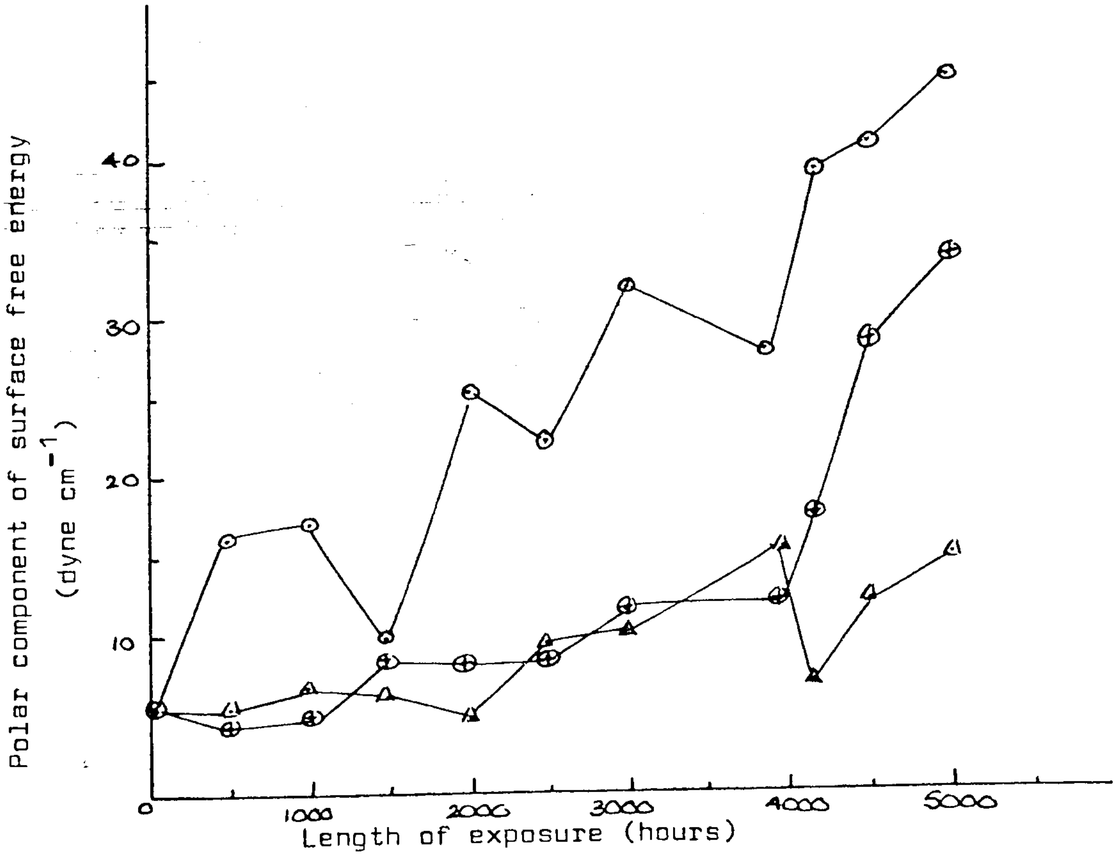
Water and Di-iodo-methane contact angles were measured for each of the coatings using the sessile drop technique. The advancing contact angles were measured using a goniophotometric eyepiece and for each surface an average was taken of several determinations on that surface. Plots of water contact angle, di-iodo-methane contact angle, polar component of surface free energy, dispersive component of surface free energy and surface free energy, all against exposure time are shown in figures 41-45. Again the most striking feature in each of the plots is the cyclic pattern of behaviour displayed by coatings with successive increases and decreases in surface free energy. Other trends upon which this behaviour is superimposed will now be discussed.

Initially the water contact angles have the same values for each of the three coatings and in each case the value of the water contact angle falls during the exposure to uv radiation showing an increase in



Figures 41 and 42 - Water and di-iodo-methane contact angles of PVC plastisol coatings after exposure to uv radiation





Figures 43 and 44 - Dispersive and Polar components of surface free energy of PVC plastisol coatings after exposure to uv radiation

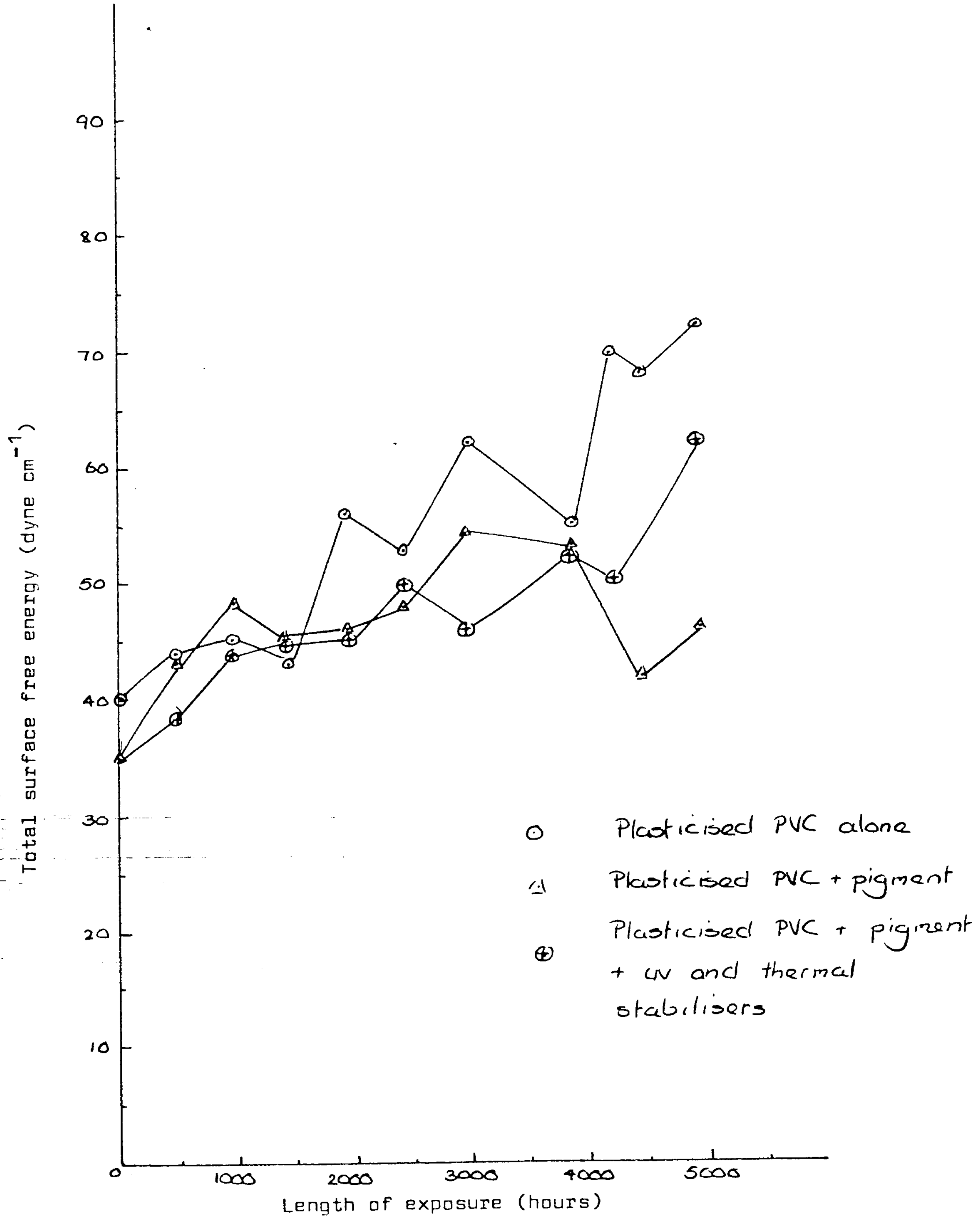


Figure 45 - Total surface free energy of PVC plastisol coatings after exposure to uv radiation

wettability by water. The unpigmented coating being more wettable than the two pigmented coatings at the end of the exposure period. The wettability of each of the coatings by di-iodo-methane is only slightly more at the end of the exposure than at the start although for the pigmented coatings it does vary during the exposure. For these coatings the di-iodo-methane contact angle falls to around 28° during the first 1,000 hours exposure to ultra-violet radiation and remains at this value until after 4,000 hours when it rises again to near the original value showing first an increase in wettability followed by a decrease.

This behaviour is reflected by the surface free energy of the coatings which in each case shows a gradual increase throughout the exposure, the unpigmented coating showing the largest increase in surface free energy. This increase is, in the case of the clear coating, dominated by the large increase in the polar component of surface free energy, the dispersive component falling slightly during the exposure. For the pigmented coatings however both polar and dispersive components of surface free energy rise during the first 4,000 hours of the exposure to ultra-violet radiation after which the polar component increases and the dispersive component decreases leading to an overall increase in surface free energy during this period of time.

5.2.3 Micro-indentation

As described in Chapter III, p 88 a spherical indentor of radius 0.132 cm was used in this study under various loads. Several determinations were made at different loads. Young's modulus of elasticity was then calculated for each of the coatings using the equation:

$$\frac{E}{1-\nu^2} = \frac{3}{4}\,\frac{mg}{r^{\frac{1}{2}}h^{3/2}}$$

A plot of $^{E}/_{1-\nu^2}$ against exposure time is shown in figure 46 for each of the coatings. Initially the unpigmented coating is more rigid than the two pigmented coatings whose rigidity does not change appreciably during the first 4,000 hours of exposure to ultra-violet radiation. After this time however the rigidity of the stabilised coating begins to rise rapidly until after 5,000 hours exposure it is the most rigid of the three coatings. The unstabilised pigmented coating in contrast continues to show little variation in rigidity during the final 1,000 hours of the exposure. The rigidity of the unpigmented coating rises gradually during the first 3,000 hours of the exposure before showing a more rapid increase during the final 2,000 hours exposure to ultra-violet radiation. Again it can be seen that superimposed upon these general trends is a cyclic pattern of behaviour, more pronounced for the unpigmented coating but still discernible in the behaviour of the pigmented coatings.

5.3 Exposure of PVC Plastisol Surface Coatings to Thermal Radiation in the presence of Humidity

As previously mentioned in this chapter each of the three coatings, unpigmented, pigmented and pigmented with the addition of uv and thermal stabilisers were exposed to thermal radiation in the presence of humidity for a total of 1,000 hours. This exposure was carried out towards the end of the study of PVC plastisol surface coatings and with each 1,000 hour exposure taking 6 weeks there was insufficient time available to prolong this exposure. The samples exposed to thermal radiation were studied using a goniophotometer with a narrow beam of incident light. The results are shown in tables 4-6. As can be seen the gloss factor of each of the coatings rises during the first 500 hours of the exposure before falling in the case of the pigmented coating and continuing to rise in the case of the unpigmented coating. In the absence of a longer

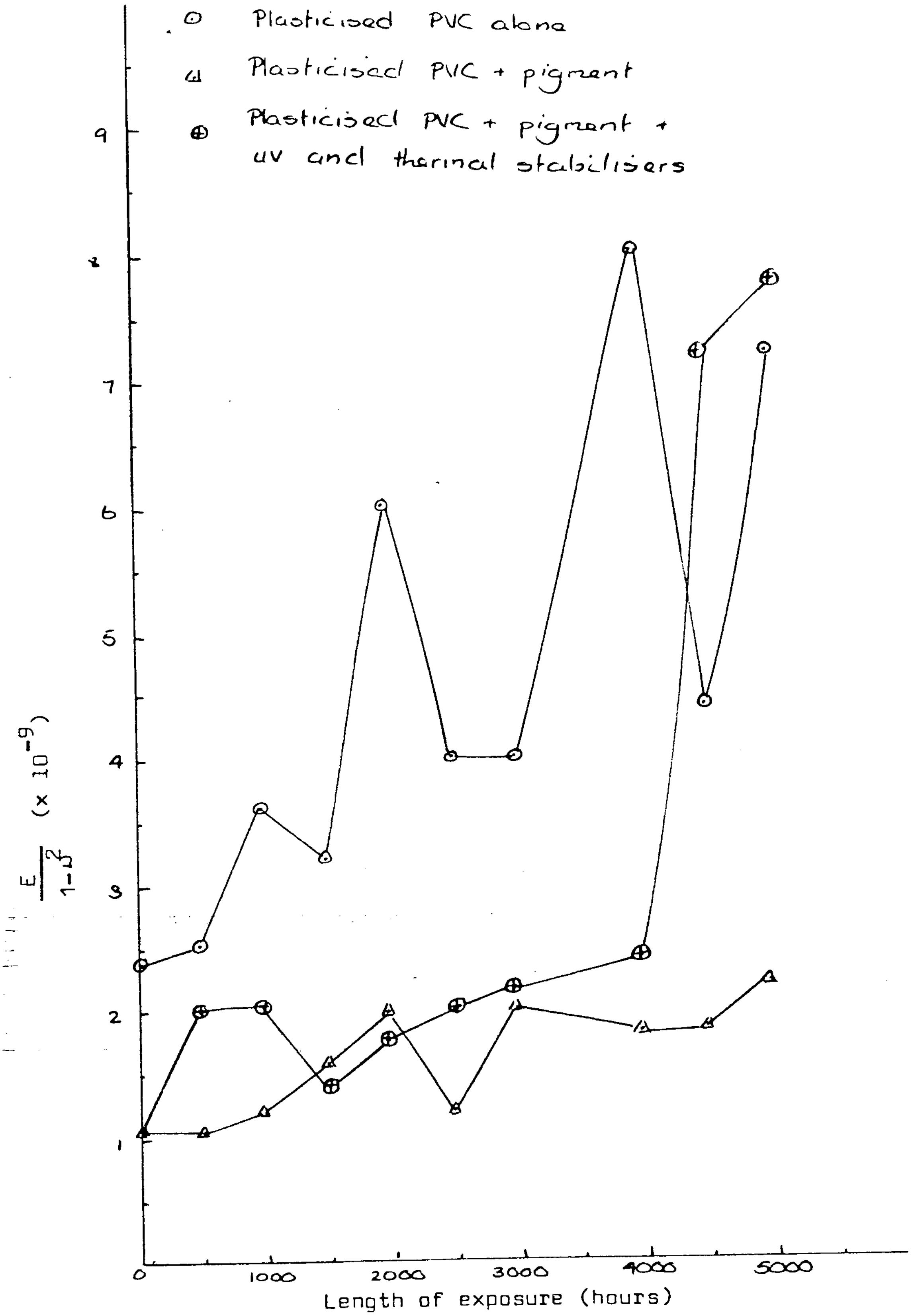


Figure 46 - Rigidity of PVC plastisol surface coatings after exposure to uv radiation

exposure time it is impossible to know whether these results represent genuine trends in the coatings' behaviour or whether they represent the initial 'settling down' period of the coating before genuine patterns of behaviour become discernible.

THE EXPOSURE OF PVC PLASTISOL SURFACE COATINGS TO THERMAL RADIATION IN THE PRESENCE OF HUMIDITY

TABLE 4

PVC Plastisol Surface Coating

Length of Exposure	I_s	I_d	$W_{\frac{1}{2}}$	GF
Control	148.3	11.8	4.5	29.6
500 hours	190.4	10.5	4.1	43.4
1000 hours	160.2	9.5	2.9	51.3

TABLE 5

PVC Plastisol Surface Coating + Pigment

Length of Exposure	I_s	I_d	$W_{\frac{1}{2}}$	GF
Control	320.1	16.1	4.4	68.8
500 hours	426.1	16.5	3.1	132
1000 hours	367	15.9	3.2	111

TABLE 6

PVC Plastisol Surface Coating + Pigment + uv and Thermal Stabilisers

Length of Exposure	I_s	I_d	$W_{\frac{1}{2}}$	GF
Control	121.2	17.7	3.0	34.6
500 hours	264.2	17.3	3.2	77.6
1000 hours	154.7	15.5	3.4	40.8

I_s - Specular Reflectance

I_d - Diffuse Reflectance

$W_{\frac{1}{2}}$ - Peak width at half-height

GF - Gloss Factor

CHAPTER VI

DISCUSSION

In the previous three chapters the results of exposing PVC plastisol coatings to both natural and artificial weathering have been presented and in this chapter they will be brought together for discussion. The various aspects of weathering behaviour which have been highlighted will, it is hoped, when they are brought together characterise the obviously complex mechanism of coating deterioration.

It is convenient to break down the discussion into stages because of the many and varied aspects of the work and so the discussion will be based on the following sequence of considerations.

(a) general impressions of the overall mode of plastisol deterioration and the extent to which the analytical techniques used have been able to follow the various property changes occurring during weathering.

(b) the principal features of natural weathering.

(c) the principal features of artificial weathering.

(d) comparison of artificial and natural weathering performance.

(e) apparent effect of the various additives incorporated into the coatings, including, the effect of the different levels of plasticiser.

The overall impression gained from the weathering of plastisol coatings is that it consists essentially of a relatively uniform erosion of the soft coating surface superimposed upon which are more serious forms of localised film breakdown taking place. In both the naturally and artificially weathered samples the overall erosion pattern seems to be governed by the successive formation/dismission of Micro-irregularities of the surface, as viewed by the goniophotometer. Initially these appear to be the only irregularities formed but as the exposure progresses macro-defect formation becomes apparent, the prime manifestation of which in natural weathering is flaking. This impression is confirmed by a visual appreciation of the surface which shows, particularly in the unpigmented coatings, the formation of brown spots on the surface, initially at isolated points, progressively covering more of the surface. Goniophotometry is therefore able to show the way in which the coating is being eroded at the surface as the successive roughening/smoothing actions are taking place superimposed upon which in the later stages of the exposures are the formation of macro-defects seen visually as brown spots. Scanning Electron Microscopy should therefore be able to confirm the evidence of defect formation given by goniophotometry.

SEM can be used to view the whole of the surface of the coating after exposure to weathering magnifying if necessary each point of the surface in turn. It is able to show the increasing deterioration as the surface coating breaks down, initially only in isolated areas and then over the whole surface. It is also able to show in the case of the unpigmented coating of the lower plasticised series how although most of the surface remains intact severe breakdown is taking place in a few isolated areas. In this case it is a more revealing technique than goniophotometry which can only give an overall impression of much larger areas of the surface and hence shows only a general loss of gloss over the entire surface and does not detect the breakdown of the film which is taking place in isolated areas. SEM, then, is a very useful technique for observing in depth changes taking place in the appearance of the coating which are not visible to the naked eye.

The two techniques already mentioned reveal changes which are taking place in the physical appearance of the coatings but do not give any clue as to the chemical changes taking place. To give an insight into this change the surface free energy of each of the coatings was measured throughout each of the exposures. The wettability of the surface by each of the two liquids chosen, one of which is subject to London dispersion force interactions (di-iodo-methane) and the other of which is subject to polar interactions (water), shows, as the exposure progresses, how the wettability of the surface by each of these very different liquids is changing. A second stage in this analysis is to calculate the polar and dispersive components of surface free energy and hence show how the balance between polar and non-polar groups at the surface of the coating is changing throughout the exposure. In all cases it can be seen that the polar component of surface free energy is increasing throughout the exposure and therefore gives a valuable insight into the types of functional groups which are migrating to the surface of the polymer during ageing. Contact angle measurements are then a useful tool in helping to analyse the chemical changes taking place at the surface of the coating during ageing.

As yet we have discussed only the changes taking place at the surface of the coating and the remainder of the analysis techniques which were employed were designed to help define changes taking place in the bulk of the coating. Micro-indentation measurements were taken in the hope that they would show changes taking place in the hardness of the coating during the ageing process. The coatings were expected to become harder and more brittle on ageing as a result of loss of plasticiser and cross-linking occurring and hence it was thought that micro-indentation would prove to be an ideal technique to follow these changes. In the event, however, this was not as successful as had been hoped as due to the extremely soft nature of the series I coatings no significant changes were discernible in the naturally weathered samples throughout the exposure and it was not until after 6,000 hours that any changes were observed in the hardness of the artificially weathered samples. In the case of the less plasticised series II coatings it was only in the unpigmented coating that changes in hardness during the early stages of the exposures could be detected and it was only in the latter stages of the exposures that discernible changes in the hardness of the pigmented coatings could be observed. Micro-indentation can therefore be a useful technique in observing the effect of bulk changes taking place in surface coatings during the later stages of any exposure but cannot be used to assess the sensitive changes which are taking place during the initial stages. It should be noted that although an indentor with a relatively large radius was used in this study with an even larger radius indentor it may have been possible to detect smaller changes which must have been taking place within the coating.

Thermal analysis was used as a further, and hopefully, more sensitive means of discerning the rate of plasticiser loss and rate of cross-linking taking place within the coating. The method chosen was to measure the glass transition temperature of the coatings and as has been seen this was successful in showing that the glass transition temperature of the pigmented coatings did not change on ageing while those of the unpigmented coatings increased significantly. The glass transition temperature is the temperature at which the sample changes from a glassy to a plastic state and so in this study the unpigmented samples have clearly lost some of their plasticity during the exposure, a change which occurs in both the series I and series II coatings after exposure to 12 months natural weathering.

In addition to these measurements the weight-loss of the samples was determined to show if the increase in glass transition temperature could be related to loss of plasticiser at the surface or if there was a further underlying cause. The problem with this technique was the tendency of the naturally weathered samples to harbour foreign particles due to the soft nature of the coatings. This meant that each of the samples had to be very carefully washed and dried before weighing to remove as much extraneous matter as possible. A problem therefore exists in obtaining accurate results although in this case the results obtained were very useful in pin-pointing the fact that the increases in glass transition temperature could not be due to plasticiser loss alone.

The final technique used was to measure the gel content of the naturally weathered series I coatings. The disadvantages of this technique were firstly that the sample is destroyed by the analysis and so cannot be further analysed and secondly that only samples applied to the substrate without the aid of primer were suitable for analysis due to the problem of removing the primer from the sample. The latter of these was a particular problem to this project as the majority of the coatings were applied using a primer and also they were required for other types of analysis.

In summary then all of the techniques employed in this work have been useful in characterising the changes taking place in plastisol coatings during ageing to a greater or lesser degree and have between them yielded information regarding changes occurring on the surface and in the bulk of the coatings. Drawing together all these results, therefore, it should be possible to determine the exact nature of these changes.

As mentioned previously the natural weathering exposures of the two series of coatings were started at different times of the year with the exposure of the more highly plasticised coatings being initiated in the summer and that of the lower plasticised coatings in the winter. It has been previously suggested that the summer months are generally the most deteriorative period for plastisol surface coatings due to their susceptibility to solar radiation. If this is the case then the results of the two exposures should reflect these variations with the most deteriorative periods in each exposure occurring after different lengths of time. The results however did not support this theory strongly. The series I coatings showed decreasing gloss trend during the initial summer months of exposure and although the series II coatings (less plasticised) also showed a tendency to lose glossiness during the summer months, the same tendency was shown at the beginning of the exposure during the winter months. It appears then that the initial loss of gloss may be due rather to a settling down of the surface rather than the timing of the exposure. The micro-indentation results do suggest that, at least in the case of the less plasticised coatings seasonal variations may have some affect upon the weathering behaviour of the coatings as they begin to show a slight increase in hardness after 6 months exposure, ie at the beginning of the summer months. This is not conclusive however as the more highly plasticised coatings were too soft to discern any changes which may have taken place during the initial stages of ageing and so it is difficult to say if the increasing hardness is due to the greater deteriorative effect of the summer months, the fact that the coatings had been weathered for 6 months and were beginning to show the cumulative effect of these months of ageing or a combination of these. Surface energy measurements do not support the view of seasonal variations in the strength of degradation, with the changes in surface free energy appearing to bear no relation to the time of year in either exposure. Weight loss measurements also seem to be unrelated to the season, the weight being lost steadily throughout the exposure.

It appears therefore from this evidence that while the effect of solar radiation (uv) is the single most important factor in the weathering of plastisol coatings, the range of weathering factor as a whole is equally important due to the soft nature of the coatings.

The artificially weathered samples show the same overall pattern of behaviour as the naturally weathered samples with a loss of gloss occurring throughout the exposure and with a periodicity showing successive deteriorations and improvements. Comparing the results obtained from the weatherometer exposures and those obtained from the exposures to uv alone it can be seen that in the initial stages of exposure the results obtained from the uv exposure mirror those obtained from the weatherometer exposure, reproducing the changes in specular reflectance. The successive improvement/deterioration in gloss is also apparent although the cycle length differs for the two exposures. The surface energies and hardness of the plastisol coatings are also found to mirror those of the artificially weathered samples during the first 3000-4000 hours of the exposure to uv alone,showing that the main feature of artificial weathering and the most degradative aspect is, as would be expected, the ultra-violet radiation. After 3-4000 hours exposure to uv alone however the plastisol coatings begin to show signs of increased degradation when compared with the artificially weathered samples. One particularly noticeable difference is the goniophotometric peak width at half-height,which increases dramatically in the case of the pigmented coatings. This increase suggests that the formation of macro defects is taking place at the surface of the coatings and so causing the incident light to be reflected over a wide range of angles. The formation of macro-defects,it is thought should lead to a roughening of the coating surface and this should be reflected in the contact angle measurements obtained, as increasing surface rugosity is reflected by decreasing contact angle measurements. In the case of the plastisol coatings however this is not found to be so as the results do not indicate a sudden increase in spreading by either water or di-iodo-methane after this length of time. It appears therefore that the reason for the plastisol surface gaining a 'matt' finish is due not to macro-defect formation but to some other change taking place at the surface. The only difference in change of hardness is shown by the pigmented stabilised sample which after 4000 hours exposure to uv alone shows an increase in hardness again suggesting that some change in the composition of the coating is taking place. It appears, then, that uv is the main factor in artificial weathering which brings about the degradation of plastisol coatings and that when exposed to uv alone the same type of deterioration of the coatings is experienced but that in the latter case the degradation is accelerated to a greater degree. This would be expected because in the case of the weatherometer the samples are periodically cooled while being exposed to uv and are also not irradiated for 1 hour in every 24 hours. The uv exposed samples are however irradiated for all 24 hours and are not subjected to cooling and so are at an above ambient temperature. As mentioned previously the effect of the elevated temperature was not established due to a lack of time.

As mentioned previously the BS 3900 Part F3 Artificial Weathering Machine takes approximately 2000 hours to induce changes comparable with 2 years natural weathering in the UK. After 1500 hours therefore the artificially weathered samples should have shown the same weathering characteristics as the naturally weathered samples after 18 months. Goniophotometrically speaking the less plasticised samples show during the first 18 months and

1500 hours respectively the same periodicity with the length of each cycle corresponding to equivalent time periods within each of the exposures. Although the pattern of behaviour is the same, the end result is not and as can be seen a greater loss of gloss is induced in the naturally weathered samples after 18 months than in the artificially weathered samples after 1500 hours. The unpigmented sample also shows a greater increase in peak width at half-height after 18 months suggesting that the naturally weathered sample is more prone to macro-defect formation than its artificially weathered counterpart. In terms of the hardness of the samples both the naturally and artificially weathered samples show a change in hardness, with in both cases, only the unpigmented sample showing a significant hardening. The BS 3900 Part F3 Artificial Weathering Machine can therefore induce the same changes in the bulk of the plastisol coating as can natural weathering. In terms of the surface of the coating however although the weatherometer can reproduce the cyclic pattern of behaviour of the coatings it cannot reproduce the complex balance of changes taking place. This is further shown by the surface energy measurements, where those obtained from the artificially weathered samples do not correspond to those obtained from the naturally weathered samples. By the end of the 18 months exposure the plastisol coatings are more wettable by water, showing that the surfaces have increased in polarity compared with the artificially weathered samples after 1500 hours.

It appears therefore that while the artificial weathering machine employed in this work can reproduce changes taking place in the bulk of the coating it cannot reproduce the delicate changes taking place at the surface. One reason for this could be the above ambient temperature which the artificially weathered samples experience within the weatherometer.

The increased temperature allows the plasticiser to flow over the surface more easily and hence has a 'mending' effect on the surface. This theory is supported by the surface free energy measurements which show an increase in surface polarity of the naturally weathered samples when compared with the artificially weathered samples over the surface of which the less polar plasticiser can more easily spread.

An interesting point is that the artificially weathered samples show a greater weight loss over an equivalent time period than do the naturally weathered samples suggesting that either, there is a greater loss of plasticiser from the surface of the artificially weathered samples, accelerated by the higher temperature, or that the naturally weathered samples are retaining particles of dirt from the atmosphere within their soft surfaces so disguising the true rate of weight loss. The latter cause could also help to explain the differences in surface behaviour of the artificially and naturally weathered plastisol coatings in that the weatherometer cannot hope to reproduce the more physically erosive aspects of natural weathering. Naturally abrasive particles in the atmosphere can become embedded in the surface of the coating and so lead to the formation of macro-defects and a consequent lowering of the gloss factor of the samples.

Turning now to the effect which the various additives have on the stability of PVC, it has been noted previously that PVC alone is not an inherently weather resistant material and derives most of its properties in this respect from its skilful formulation[142] although this degree of instability may be aggravated by the presence of plasticisers and other additives which are themselves prone to degradation[143]. It is not surprising therefore to find that plasticised PVC alone is not itself a stable material and that after 18 months exposure to natural weathering has deteriorated to such an extent that it is of no further importance as a coating. The more highly plasticised coatings show a greater loss of gloss during their exposures to weathering underlining the fact that a higher plasticiser content increases the photosensitisation of the coating and hence its instability. Estevez[4] has claimed that optimum weatherability is obtained when the plasticiser content is between 40 and 50% although Darby and Graham[144] have put this figure at roughly 35 pph for plasticised PVC film, submitting that, at lower levels of plasticisation the life of the film is considerably shortened on account of the lower mobility of the stabilisers used in the composition; the rate of migration of the stabilisers to the surface not being considered to be high enough to offset the damage caused by photodegradation which other workers have shown to be very much a surface reaction[145-147]. At higher than optimum levels of plasticiser however the advantage gained from efficient stabiliser mobility begins to be outweighed by the increasing photosensitisation of the film by its increasing carbonylic content. The greater increase in surface polarity shown by the lower plasticised series of coatings is due to the more polar PVC appearing at the surface of the plastisol coating compared with, in the case of the more highly plasticised coatings, the DIOP plasticiser which shows a balance between dispersive and polar forces at the surface due to the effect of the aromatic and aliphatic hydrocarbon groups opposed to the ester groups.

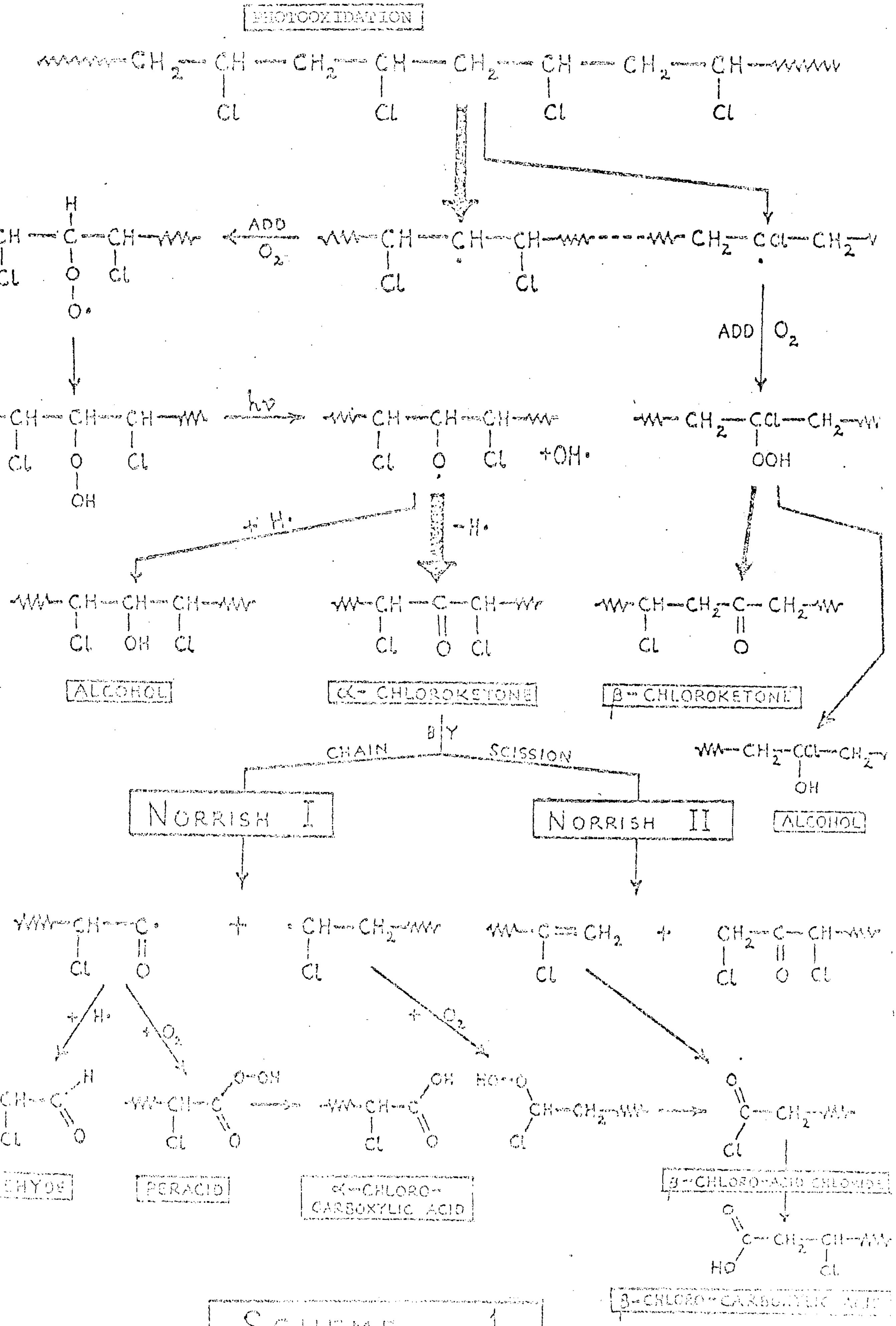
The greater increase in Tg shown by the less plasticised unpigmented coating is again a consequence of the differing levels of plasticiser with the lower level of plasticiser allowing the polymer chains more contact and hence a greater chance of forming cross-links than is the case for the more highly plasticised coating where the presence of plasticiser tends to keep the polymer chains apart. The more highly plasticised coatings therefore are more likely to be prone to chain scission reactions and not cross-linking, this view is enforced by the gel content measurements which show no increase throughout the exposure.

As noted previously the presence of plasticiser also has a surface mending effect on the surface coating especially at elevated temperatures at which it can flow more easily over the surface of the coating.

Continuing with other additives it appears from this study that the pigment is the singly most effective stabilising agent contained within the coating. Its stabilising action is well known as being that of a uv absorber, although at higher levels than employed in this work it can give rise to a variety of degradation processes[148] including a role as oxidation catalyst in the photolysis of the binder[149,150] and the tendency to cause chalking[151,154]. In fact in the plastisol samples studied here the low level of pigment appeared to give the coatings greater protection against weathering than did the added uv and thermal stabilisers. This is seen most clearly in the case of the more highly plasticised coatings which were exposed to natural weathering where after 18 months the unpigmented coating had broken up to such an extent as to no longer be of practical use as a coating whereas the pigmented coatings were still intact and serviceable.

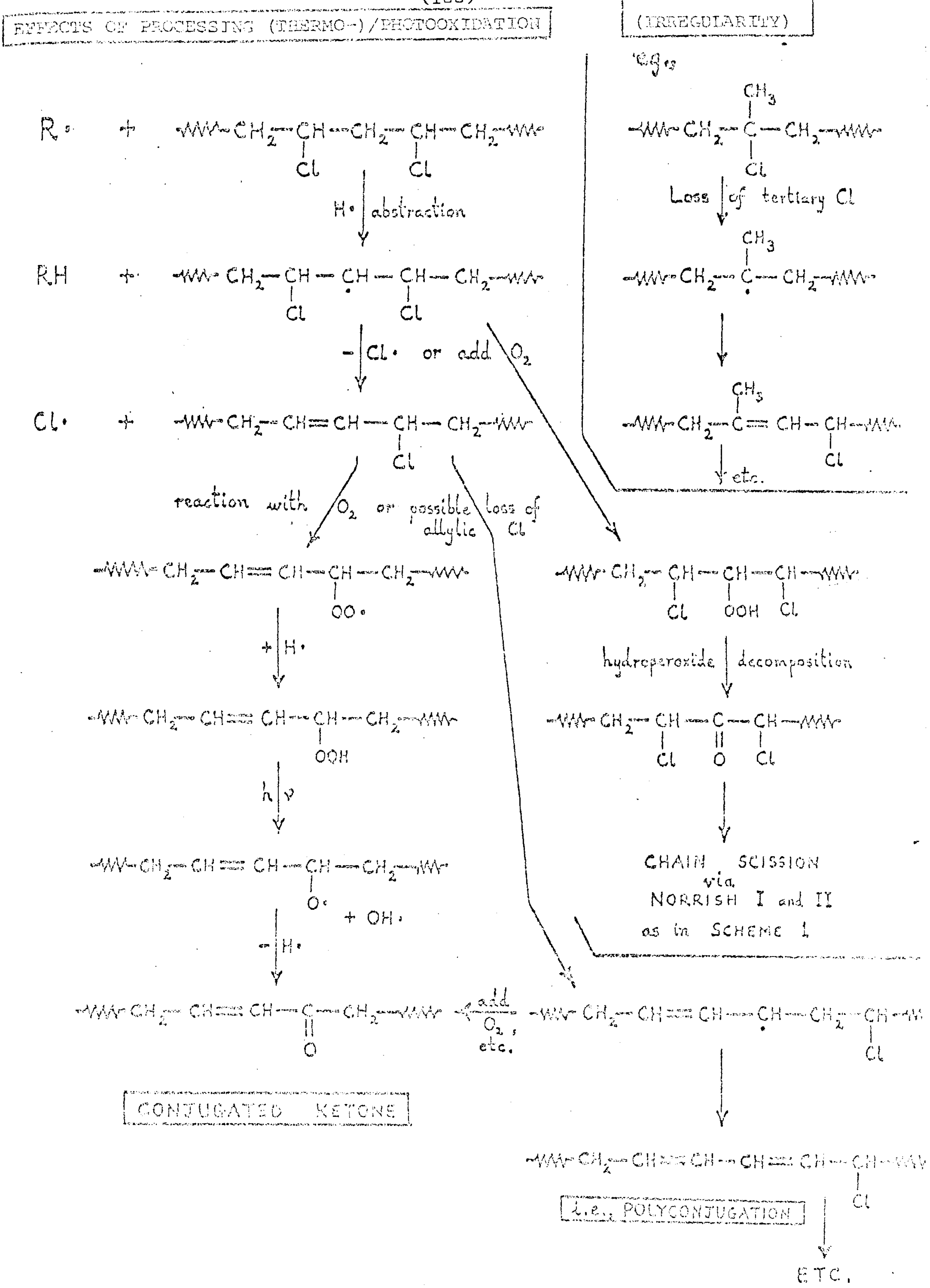
The overall impression gained from the exposure of PVC plastisol coatings to weathering, both natural and artificial, therefore is one of gradual breakdown throughout the exposure. As has been seen micro-defect formation occurs initially at the surface leading to a fall in gloss, followed by the formation of macro-defects and the onset of flaking as clearly shown by micrographs obtained by the use of scanning electron microscopy. The micrographs also show that the formation of defects and increasing roughness of the surface is further concentrated into isolated areas by the PVC itself, PVC being well-known for its ability to autosensitise its own further decomposition. At the same time as these surface changes are occurring the added plasticiser is also taking part in further deterioration as it is gradually migrating to the surface of the polymer and there being lost to the atmosphere. This change is seen by the loss of weight of the coating and also by the increasing polarity of the surface as more PVC becomes apparent in the uppermost layer of the coating. The loss of plasticiser also contributes to the increasing rigidity and rise in glass transition temperature shown by the unpigmented coating by the end of the exposure. Measurement of the gel content showed no perceptible increase suggesting that cross-linking reactions are not playing an important part in the degradation, this probably because the presence of plasticiser tends to keep the polymer chains apart so that chain scission reactions are more likely. The plastisol coatings do not show any appreciable change in colour until towards the end of the exposure and so double bond formation, also, does not play an important role in the degradation process initially.

A large amount of research has gone into the study of the photodegradation of PVC[155-160] and yet it is still not fully understood and appears to be a complex, interdependent 'balance' of various types of reactions whose relative rates determine their respective contributions to the overall reaction. Two schemes which have been put forward are shown on the next pages [161,162]. Scheme 1 depicts the photooxidation of PVC as a predominantly chain scission process leading, ultimately, to the formation of carboxylic acid groups. Although the precise mechanism of this process is uncertain the fact that more than one carboxylic acid is formed suggests that there are two alternate modes of photolysis



SCHEME 1

Current theories on the photooxidation of PVC.



SCHEME 2

Current theories on the photooxidation of processed PVC.

(Norrish I and II) of the intermediate α-chloroketone, whose apparent prevalence over the β-chloro adduct supports the growing view in favour of initial methylenic, as opposed to chloromethylenic, hydrogen abstraction. The chain scission process is also found to be auto-accelerating, presumably due to the photosensitising effect of the initially formed carbonyl groups.

Scheme II is concerned with the thermal/photooxidative degradation of PVC, that has been processed prior to ageing. The ageing process introduces other highly photosensitised (eg allylic) structures into the polymer chain which then tend to increase the subsequent rate of photooxidation. Additionally, a conjugative condition exists in the polymer whereby the dehydrochlorination suffered during processing can continue during irradiation, although this is probably of secondary importance now to reaction with oxygen as evidenced by the appearance of conjugated ketones in the degradation products.

PVC is an inherently unstable coatings material and relies for its stability in this role on its additives and the careful way in which it is formulated, the characterisation of its mode of breakdown is therefore important in the search for new and better ways of stabilising it against attack from weathering.

CHAPTER VII

A PRELIMINARY INVESTIGATION INTO THE INTERACTION OF NITRIC OXIDE WITH POLYMER SURFACES

7.1 Introduction

The previous sections of this work have dealt with the effects of natural and artificial weathering upon poly vinyl chloride plastisol coatings, the artificial weathering sections being mainly concerned with the effects of heat, light and humidity. In reality however there are other pollutants in the atmosphere which play an important part in the degradation of polymers and examples of these gases are ozone, sulphur dioxide, carbon monoxide and the oxides of nitrogen and it is with the latter of these that the final section of this work is concerned. The effect of nitric oxide on different commercial polymer coatings has been studied in the presence of ultra-violet light and also the effect of uv alone.

As an introduction to the subject the following sections will deal with the effect of ultra-violet radiation and nitric oxide on polymers and will also consider commercial polymer materials. The remainder of the chapter will discuss the experimental aspects of the work and the results obtained.

7.1.1 Photodegradation of Polymers

The word 'photodegradation' describes two main types of degradation process initiated by light, when the reaction takes place in the absence of oxygen the process is described as 'photolysis' and in the presence of air or oxygen the process is described as 'photo-oxidation'. The amount of energy supplied to the sample to bring about photodegradation depends on the wavelength and intensity of the radiation used and the degree of penetration into the sample. The term 'photodegradation' generally implies the use of ultra-violet radiation and it is that definition which will be used throughout this work.

The photolytic degradation of polymers consists usually of three or four basic steps which will now be further described[163].

(1) Absorption of the Incident Radiation

If the polymer is to absorb directly it must have a strong absorption band in the region of the wavelength of light used. A carbonyl group has this property and so any carbonyl containing polymers would be expected to undergo photolytic degradation fairly readily. An added sensitiser (such as benzophenone) or an impurity (eg traces of residual solvent) might also absorb the light and a transfer of energy to the polymer might then occur.

(2) Homolysis of the Polymer Molecule

Heterolytic bond scission to give ionic species is not encountered in this type of degradation but homolysis to give radicals may occur preferentially at one type of bond or more commonly at different sites. The mode of homolysis is influenced by the energy of the incident light and therefore because the carbon-hydrogen bond energy is significantly higher than that of either the carbon-carbon or carbon-oxygen bond, it is not susceptible to 365 nm radiation. C-H bond scission may, however, sometimes occur with radiation under 254 nm.

(3) Chain Scission

Chain scission may occur by rupture of one of the backbone C-C bonds or indirectly as a consequence of homolysis elsewhere in the polymer molecule. Chain scission is revealed by a fall in molecular weight of the sample.

(4) Cross-linking

Cross-linking is often observed as a sequel to homolysis and is ndicated by a rise in molecular weight and the formation of an insoluble gel. This situation however is in many cases complicated by the simultaneous occurrence of scission and cross-linking.

7.1.2 Commercial Polymer Materials

Polymers which are currently used commercially can be divided into three groups depending upon their resistance to photodegradation and these are: (1) highly photostable polymers which are used without photostabiliser added, eg poly(tetrafluoro-ethylene), poly(methyl methacrylate). (2) moderately photostable polymers that can be used without photostabiliser, eg poly(ethylene terephthalate), polycarbonates, and (3) poorly photostable polymers which need extensive stabilisation for outdoor uses, eg polyolefins, poly(vinyl chloride), polystyrene, nylons, rubbers and cellulose.

The definition of long-term photostability of polymers and polymeric materials differs depending on their application. In the packaging industry for instance 'long-term properties' means 1-4 years. Gradual photodegradation after their use decreases the litter problem and is therefore beneficial. In the building and machine industries however long-term properties of 10-40 years are required. In some cases therefore it may be important to increase the rate of photodegradation reactions but most industries do require polymers with a low rate of photodegradation and the commercial interest in degradable plastics has decreased in recent years.

Considering the structure of common polymers, they contain mostly C-C, C-H, C-O, C-N and C-CL bonds and should not absorb light of longer wavelengths than 190 nm, ie they should not be photodegradable by visible light. Uv spectroscopy measurements however show that most commercial polymers have increased absorption due to the presence of internal and external impurities. External impurities found in commercial polymers are things such as (1) impurities formed during the manufacture of monomers, (2) impurities from the polymerisation process, eg initiator residues, emulsifiers and solvents, and (3) impurities from the processing and storage of polymers. Production of polymers always occurs in contact with different metals which are used for reactors and other machinery parts and as a result of this organic and inorganic salts are formed which may be responsible for further degradation of the polymer[164].

Internal impurities are due to the formation of different chromophoric groups, when polymerisation occurs in the presence of air (oxygen) and even in an inert atmosphere and parts of the initiator added are built into polymer chains. Additives used commercially in the processing of polymers into plastics or rubber materials may also be a source of internal impurities as new compounds are formed and some fragments of additives are permanently built into the polymer chain.

Commercial polymers then are highly complex materials which may undergo varying reactions in the presence of uv light partly dependant upon the processes by which the polymer has been prepared.

7.1.3 Nitric Oxide

Nitric Oxide (NO) exists in the atmosphere and is found there as a result of either industrial processes or as a result of the solar-initiated photo-dissociation of nitrogen dioxide (NO_2) which is the principal light absorbing species present in smog.

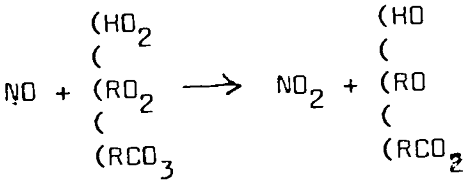
$$NO_2 + h\nu \xrightarrow[(295\text{-}430\ nm)]{} NO + O$$

However, although efficiently photodissociated in this, the primary photochemical act, nitrogen dioxide is then somewhat paradoxically, ultimately reformed in highly complex photo-oxidation processes at a much faster rate than it was initially destroyed[165], the net effect being a very rapid conversion of NO back to NO_2 which, in smog, occurs by three major paths, as shown below:

(i) reaction with ozone: $NO + O_3 \longrightarrow NO_2 + O_2$

(ii) thermal oxidation by molecular oxygen: $2NO + O_2 \longrightarrow 2NO_2$

(iii) reaction with radicals:



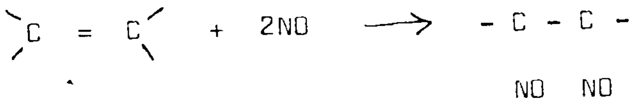
$$NO + \left(\begin{array}{l} HO_2 \\ RO_2 \\ RCO_3 \end{array} \right. \longrightarrow NO_2 + \left(\begin{array}{l} HO \\ RO \\ RCO_2 \end{array} \right.$$

The net result of all this is that nitric oxide (NO) exists quite stably in the atmosphere in intrinsically small concentrations dependant upon the exact nature of the outdoor location. However, although again depending largely on the nature of the site, this nitric oxide concentration can vary quite significantly on a diurnal basis, particularly in the vicinity of conurbations[166] and dense traffic areas[167].

7.1.4 The Interaction of Nitric Oxide with Polymers

When one comes to consider the actual interaction of nitric oxide with polymers, however, it is found that there are relatively few reports in the literature which clear mechanistically with this particular aspect. This is true of this type of study in general which, is surprising considering the amount of 'bad publicity' which gaseous atmospheric pollutants have long received in respect of their observed deteriorative effect on paint films. However, these latter studies have invariably been only concerned with the visualisation of surface effects rather than the nature of their chemistry. Of the mechanistic studies that have been undertaken in this field, undoubtedly the most notable are those due to Jellinek and co-workers[168,169] concerning the reaction of nitrogen dioxide (NO_2) with hydrocarbon polymers, and to Ogihara et al[170,171], in their examination of the oxidation reaction of polyethylene by NO_2. As regards polymer interaction with nitric oxide (NO), however, literature reports are confined to what appear to be relatively less detailed investigations[172,173], two of these being concerned with poly(vinyl chloride) thermal decomposition.

The nature of the particular interaction between nitric oxide (NO) and thermally degrading/degraded PVC has revealed some extremely interesting features of their reactivities. Firstly Geddes[173] has observed how samples of PVC powder, when heated in a stream of NO at 150°C and pressed into films for absorption spectroscopy, remained colourless for over 60 minutes as in the case of a thermally stabilised sample. In addition to this, on leaving a deep red discoloured sample of PVC, which had previously been degraded for 95 minutes at 150°C, in an atmosphere of NO at room temperature, it was found to be noticeably less discoloured after 10 minutes, pale yellow after 500 minutes and practically colourless after 1500 minutes, its absorption spectrum strongly resembling that of PVC heated for 85 minutes at 150°C in NO. This 'bleaching' action of NO indicated that, even at room temperature, it was capable of effecting a considerable reduction in polymer conjugation. From this, Geddes postulated that, although the apparently stabilising influence of NO could be a result of the inhibition of the radical-chain dehydrochlorination, the fact that NO could decolourise degraded PVC at room temperature was more in keeping with an addition reaction of the type:-



$$\gt C = C \lt + 2NO \longrightarrow -\underset{NO}{C}-\underset{NO}{C}-$$

This latter proposal was later supported by Mladenov and Slavov[172] who observed that when PVC was heated in NO an accelerated dehydrochlorination occurred, the rate of which appeared proportional to the NO concentration. Furthermore it was suggested that not only the NO present in the system but also chlorine conceivably formed by the reaction,

$$2NO + 2HCL \longrightarrow N_2O + H_2O + CL_2$$

could enter into combination reactions with the degrading PVC. In this way chlorination of C = C double bonds in the polymer, as a follow up to dehydrochlorination, could paradoxically lead to an improvement in the polymer's subsequent thermal stability.

Ogihara[170,171] has studied the oxidative degradation of polyethylene in a nitrogen dioxide (NO) atmosphere by means of infra-red spectroscopy. The analysis of the infra-red spectra obtained showed the formation of nitro, nitrite ester, nitrate ester, carbonyl and hydroxyl groups as a result of heating the polyethylene in nitrogen dioxide. In the early stages of the reaction nitro and nitrite ester groups were formed by the addition of NO_2, which has an odd electron structure and may therefore be expected to combine readily with radicals, to the activated position of polyethylene. Nitrate ester, carbonyl and hydroxyl groups were then formed in a secondary stage as the decomposition products of the nitro and nitrite ester groups. The suggested mechanism for the reaction is shown below:

$$RH \xrightarrow{\text{activated}} \dot{R} + \dot{H}$$

In the early stages:

$\dot{R} + \dot{N}O_2 \longrightarrow RNO_2$ nitro group

$\dot{R} + \dot{O}NO \longrightarrow RONO$ nitrite ester group

Secondary stages:

$RONO \longrightarrow R\dot{O} + \dot{N}O$ O-N fission

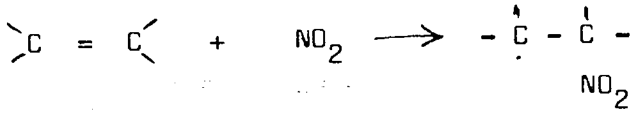
$R\dot{O} + \dot{N}O_2 \longrightarrow RONO_2$ nitrate ester group

$$\left.\begin{array}{l} R'CH_2\dot{O} \longrightarrow R'CHO + \dot{H} \\ R''R'''CH\dot{O} \longrightarrow R''R'''CO + \dot{H} \\ R''R'''CH\dot{O} \longrightarrow R''CHO + \dot{R}''' \end{array}\right) \text{carbonyl group}$$

$R\dot{O} + \dot{H} \longrightarrow ROH$ hydroxyl group

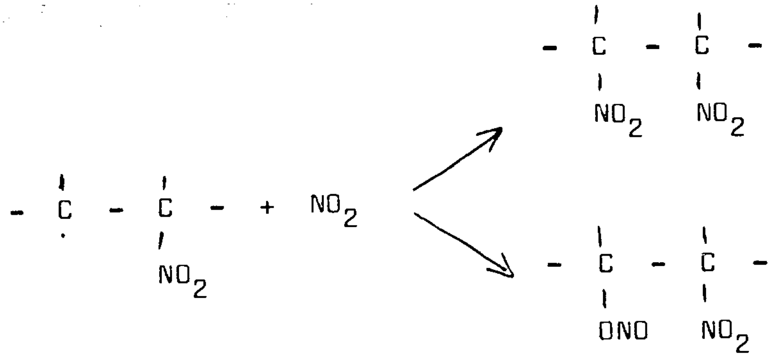
$RONO_2 \longrightarrow R\dot{O} + \dot{N}O_2$

The initial reaction site in polyethylene was found to be the double bond with which nitrogen dioxide can then react abstracting a hydrogen molecule and forming a radical. Gray and Yoffe proposed the following mechanism for this reaction



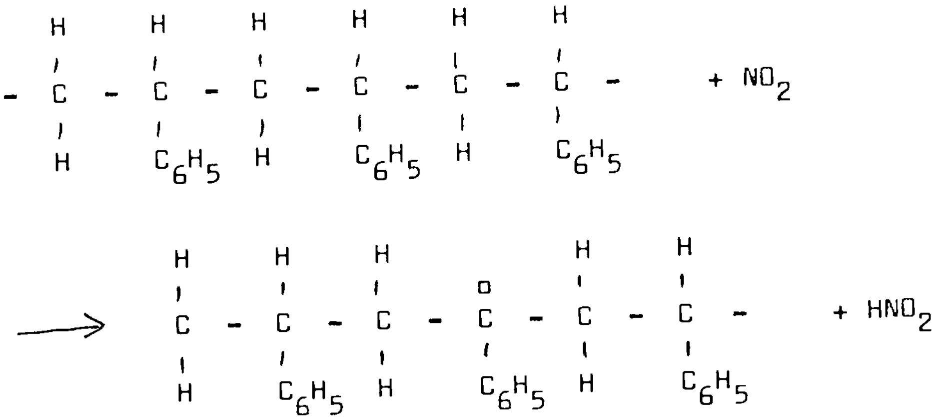
$$>C=C< + NO_2 \longrightarrow -\dot{C}-\underset{NO_2}{C}-$$

A further NO_2 molecule can then react with this product forming dinitro and nitro-nitrite compounds.



$$-\dot{C}-\underset{NO_2}{C}- + NO_2 \longrightarrow \begin{cases} -\underset{NO_2}{C}-\underset{NO_2}{C}- \\ -\underset{ONO}{C}-\underset{NO_2}{C}- \end{cases}$$

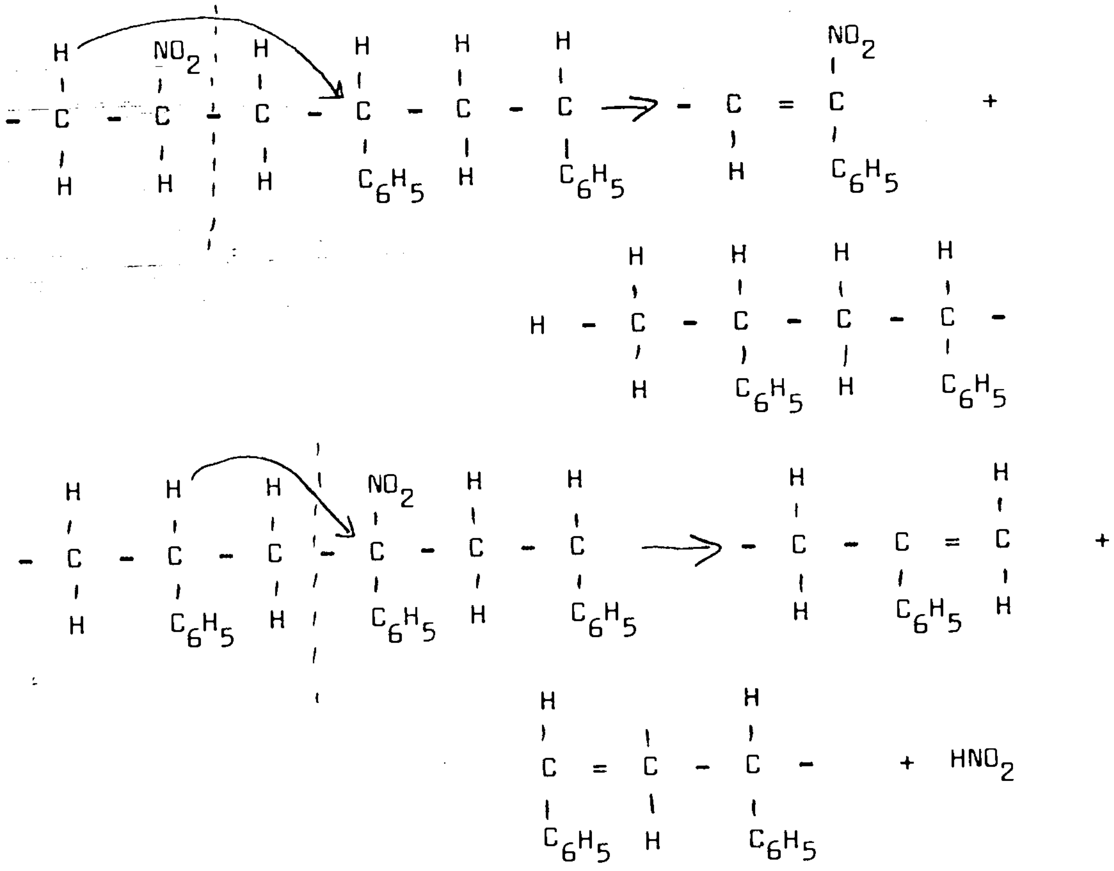
Jellinek and Toyoshima[168] have studied the reaction of NO_2 with polystyrene and found that it reacts in a similar way to polyethylene. Nitrogen dioxide initially reacts with an α-hydrogen on the polystyrene backbone to form a polymer radical with which additional nitrogen dioxide molecules can react to form nitro and nitrite groups.



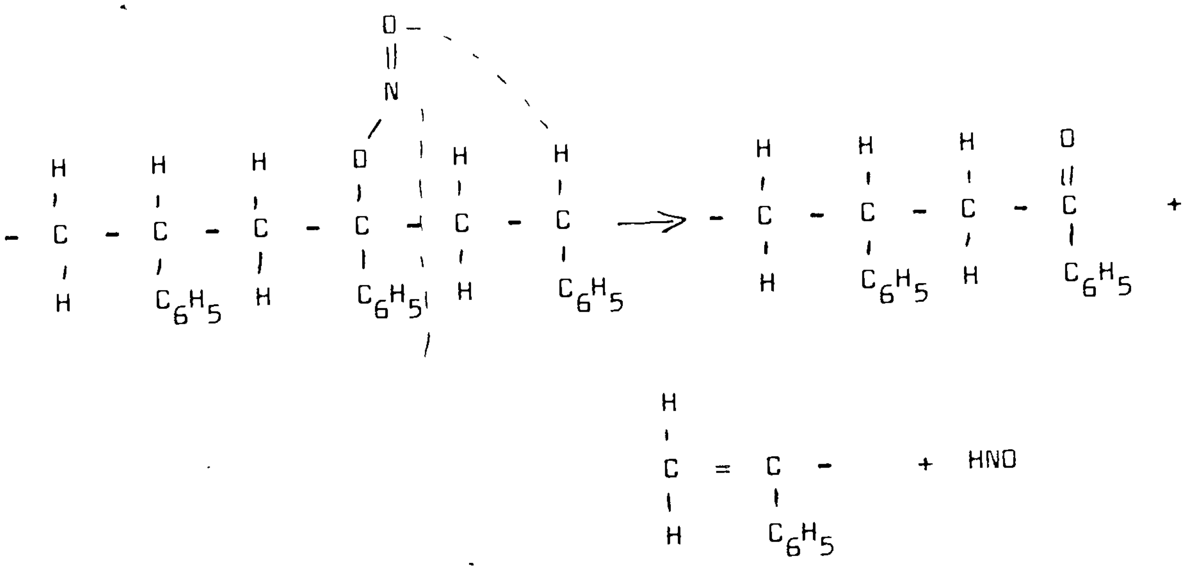
$R\cdot + NO_2 \longrightarrow RNO_2$

$R\cdot + NO_2 \longrightarrow RONO$

Jellinek has then speculated that chain scission reactions may then occur at both low and high temperatures, the mechanism for low temperature chain scission reactions is given below.



or for the nitrite



2HNO → $H_2N_2O_2$

At higher temperatures a depropagation reaction may occur leading to the formation of monomer and nitrated monomer.

7.2 Experimental Aspects

Five types of polymer film were chosen for this study, these being polypropylene, cellulose acetate butyrate, polystyrene, polycarbonate and polyester. These were chosen because of their varying chemical structures and because they were clear and relatively thin films which could be easily analysed by infra-red spectroscopy in the transmission mode. Each of the films is a commercially available product, the suppliers being detailed in Table 5 . This work is intended as a preliminary investigation into the effect of nitric oxide and ultra-violet light on different polymers both individually in the case of uv and simultaneously. The polymer films examined, method of exposure and analytical technique are now described in more detail.

TABLE 5

SUPPLIERS OF POLYMER FILMS

Polymer Film	Supplied by
Polypropylene	ICI Plastics Division Welwyn Garden City, Herts
Cellulose Acetate Butyrate	May & Baker Ltd Dagenham, Essex
Polystyrene	Sidaplax NV Gentbrugge, Belgium
Polycarbonate	Bayer, Germany Distributed by May & Baker Ltd Dagenham, Essex
Polyester (Polyethylene teraphthalate)	ICI Plastics Division Welwyn Garden City, Herts

7.2.1 Polymer Films

7.2.1.1 Polypropylene

The polypropylene film was supplied by ICI Plastics Division and is manufactured under the tradename of 'Propafilm O'. Propafilm O is an uncoated polypropylene film of high clarity and tensile strength which is relatively impermeable.

The film also shows excellent chemical resistance, and together this combination of properties makes it ideal for use as a packaging material which is its main application. A film of 15 micron thickness was used for this study[174].

7.2.1.2 Cellulose Acetate Butyrate

The cellulose acetate butyrate (CAB) film employed for this study is manufactured commercially by May and Baker Ltd under the name of 'Cabulite'. Cabulite is an outstanding material for thermoforming and outdoor use and amongst its many varied uses are advertising and display units, lighting, specialist glazing material, and drawing materials. It is resistant to attack by both acids and alkalis. A film of 0.5 mm thickness was used for this study.

7.2.1.3 Polystyrene

The polystyrene film used for this work was 100 micron thick and produced by Sidaplex NV, Belgium, under the tradename of 'Polyflex[111]. The film is a biaxially orientated clear polystyrene with a high surface finish. Typical applications for which the film is used include, thermoforming (vacuum or pressure) of containers, sterile packaging, graphic arts, photographic applications, overhead projection transparencies, display signs, document protectors, folded boxes and copying systems. The film is not recommended for outdoor use due to degradation although it is very resistant to alkalis and resistant to all but very strong acids.

7.2.1.4 Polycarbonate

'Makrofol KG' a polycarbonate film produced by Bayer Germany and distributed by May and Baker Ltd, Essex was employed for this work. A film of 2 micron thickness was used, a film whose main application is as a flame-retardant electrical insulating film. It is used for coil insulation, capacitor wrapping and wherever an electrical insulating film with increased fire safety is required. Its most important properties therefore are its resistance to heat and electricity. It is resistant to attack by dilute acids, saturated aliphatic and cycloaliphatic hydrocarbons and alcohols. Makrafol is destroyed by alkaline solutions, ammonia and amines[175].

7.2.1.5 Polyester

A polyester film manufactured by ICI Plastics Division under the trade-name of 'Melinex' was used for this work. Type 'S' Melinex of 12 micron thickness was found to be most suitable as 'Melinex' film is slightly hazy in its thicker forms. 'Melinex' is reported to have outstanding strength, durability and dimensional stability, together with low water absorption and a good resistance to chemical attack. It is also a good electrical insulant and in its thinner gauges possesses a good clarity. 'Type S' is a general purpose film with a wide range of applications[176].

7.2.2 Ageing Techniques

The samples were exposed to nitric oxide and to ultraviolet light so that the combined and individual effects of NO and UV could be studied under identical conditions. This involved the use of a sealed system, due to the toxic nature of nitric oxide (figure 47). The system consisted of two glass vessels, one of which was connected to allow a free flow of gas through it (see figure 47) and both of these vessels were then placed in a large box. An ultra-violet light source was then placed above the opening of the box, the box was necessary in order to ensure that the vessels were irradiated only by the uv light source. The glass vessels were manufactured from 'Pyrex' glass and were 33.5 cm high and 6 cm in diameter with a sealable lid. One of the lids was modified so that two tubes could be connected to it, one for the inflow of gas and the other for the outflow. As ultra-violet light of wavelength less than 340 mu is cut out by the glass the ultra-violet light source used produced radiation of a higher wavelength than this. Each of the samples

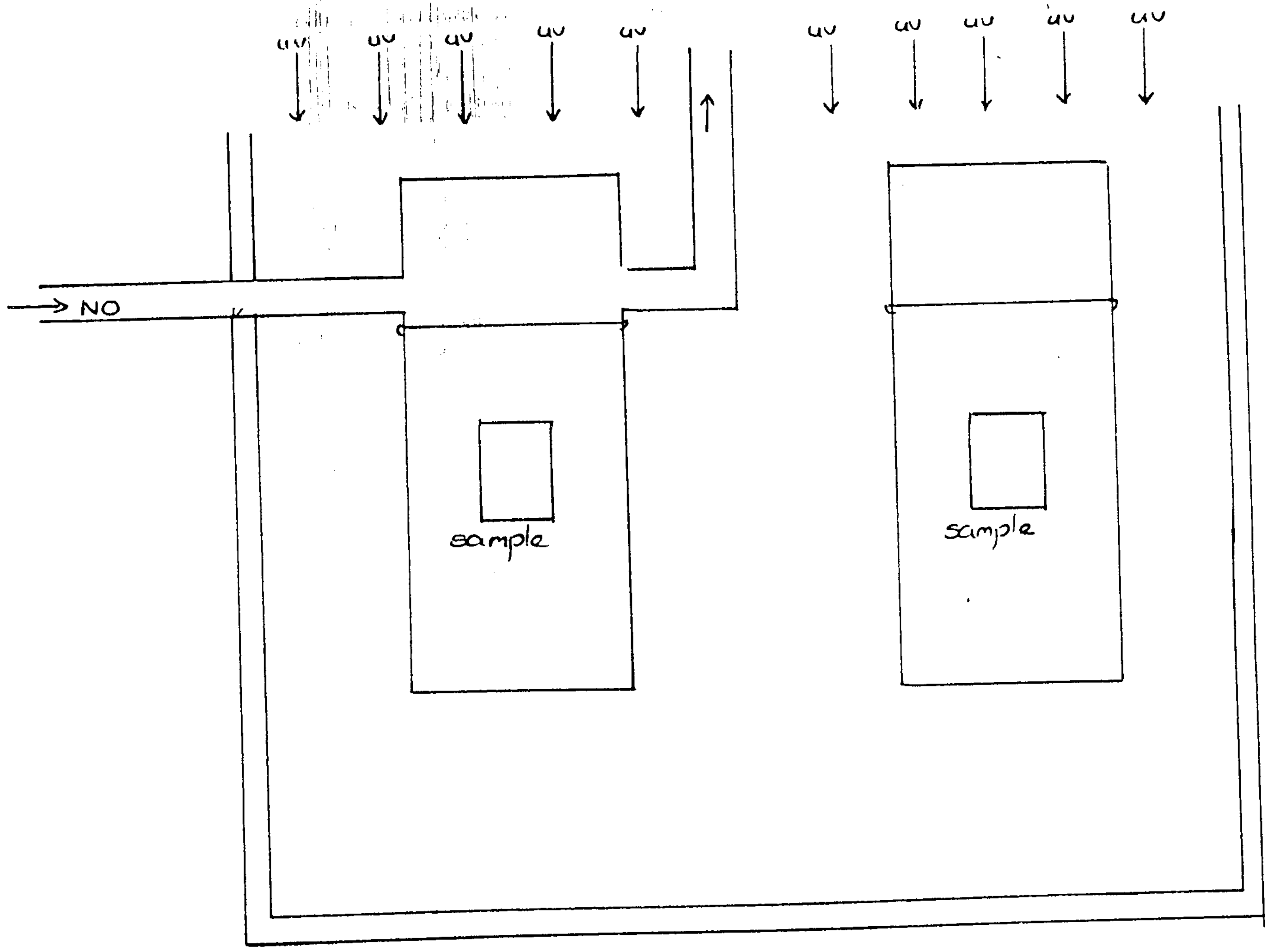


Figure 47 - System for the Reaction of uv and NO with Polymer Surfaces

was suspended inside the vessel from a wire frame during the exposure to NO and uv. The containers were then sealed and placed inside a well ventilated fume cupboard. Nitric oxide was then flushed through the system until all traces of reddish brown gas disappeared, this was nitrogen dioxide formed by nitric oxide reacting with the oxygen in the system. The inlet and outlet tubes were then sealed and the ultra-violet lamp was switched on, the system was then left for 2 hours before being thoroughly flushed through with nitrogen to remove all traces of nitric oxide. The samples were then left overnight before being removed as a safety measure to ensure that all remaining traces of nitric oxide had reacted with oxygen in the atmosphere. After being removed the samples were analysed using an infra-red spectrometer, to measure any changes which had taken place during the exposures to NO and uv.

The nitric oxide used was supplied by BDH Chemicals Ltd, as being 99.6% pure.

7.2.3 Analytical Techniques

Each of the films employed in this study was chosen for its clarity and hence the ease with which it could be analysed using an infra-red spectrometer in the transmission mode. In the transmission mode infra-red spectroscopy is the most convenient means of gaining information relating to the chemical composition of organic coatings systems, its main disadvantage being that it can only be used for relatively thin, transparent polymer films. In these films the appearance or disappearance of functional groups on ageing can be followed directly. Transmission spectroscopy has another advantage as an analytical technique in that the sample remains unaffected by analysis and therefore can be used repeatedly.

All infra-red spectra shown in this work were obtained using a Perkin-Elmer grating infra-red spectrophotometer Model 257, the spectra were in the region 4000 cm^{-1} to 600 cm^{-1}.

The infra-red spectra of each sample was obtained before exposure to NO and uv and then again when the sample had been exposed to uv and NO for 2 hours as previously described.

7.3 Results

The infra-red spectra of each of the samples before and after exposure to NO and uv are shown in figures 48-59. The polypropylene, polycarbonate and polyethylene teraphthalate films were each exposed to uv alone for 2 hours, to uv for 2 hours followed by NO for 2 hours and to uv and NO for 3 hours. In the two former exposures the samples were left standing in an atmosphere of nitrogen on completion of the exposure whereas in the latter exposure they were left to stand in air after completion of the exposure test. The polystyrene film was included in only the former 2 tests and the cellulose acetate butyrate film in the latter exposure only. The results obtained for each of the films will now be discussed in more detail.

7.3.1 Polypropylene

As can be seen from figures 48-50 there is no apparent change in the 'Propafilm' after exposure to both uv and uv and NO. This confirms the visual appearance of the film which showed no change in colour or clarity after the exposures. In contrast to these results however the spectra of the polypropylene film obtained after exposure to NO for 3 hours followed by air overnight does show small differences from the spectra obtained before the exposure. A shift in wavelength at which the sample

Figure 48 - Infra-red spectra of polypropylene before and after exposure to uv radiation

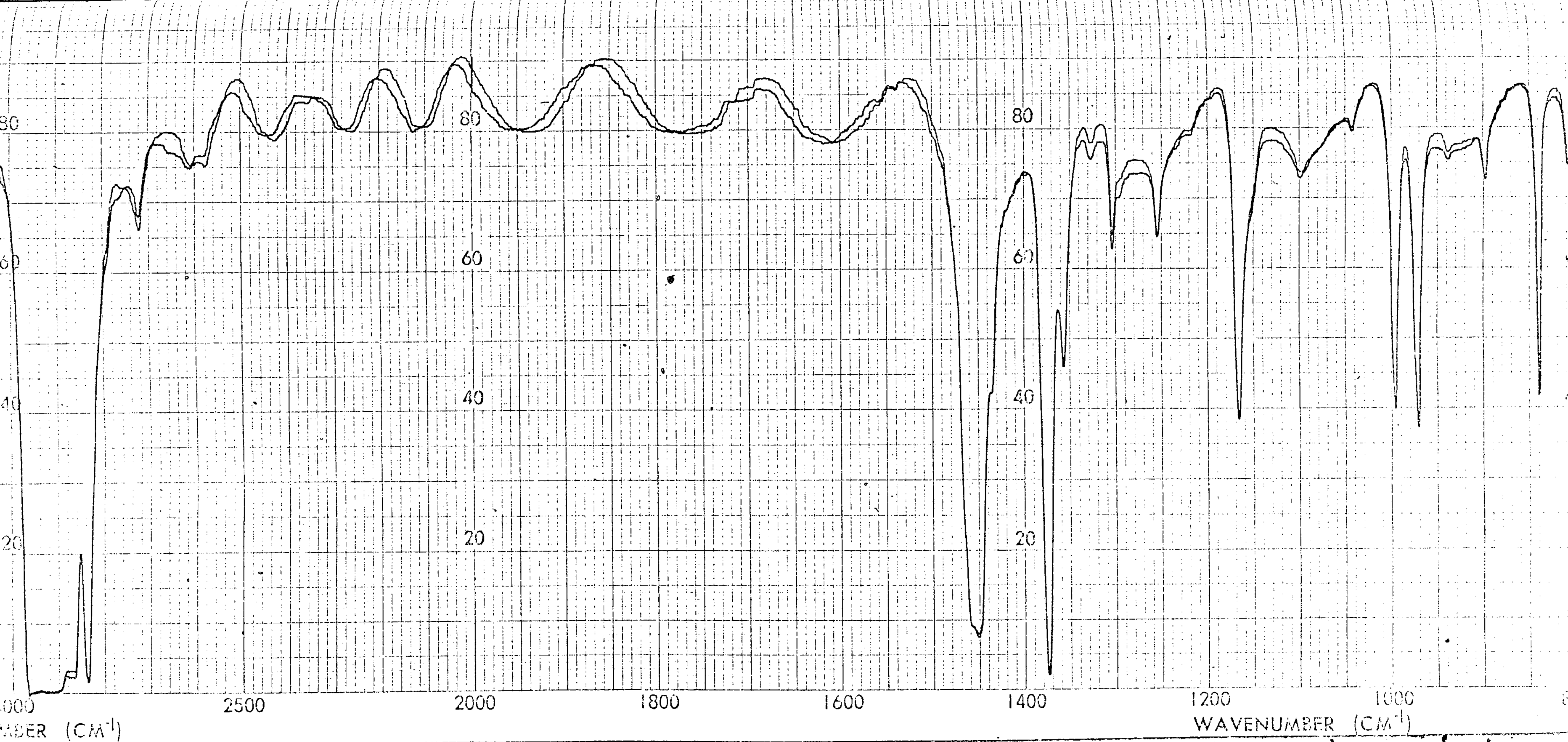


Figure 49. - Infra-red spectra of polypropylene before and after exposure to uv radiation and NO

Figure 50.- Infra-red spectra of polypropylene before and after exposure to uv radiation and NO, having been left to stand in air

absorbed infra-red radiation in the region 1500-2500 cm^{-1} can be observed after exposure to NO, the shift being towards higher wavelength absorbance. A change in the relative strengths of the peaks at 1,100 and 1,040 cm^{-1} is also seen. These peaks are both due to additives in the polypropylene film about which little is known. No change in the physical appearance of the sample could be detected after exposure to NO and air.

These results suggest that the polypropylene film used in this exposure is resistant to attack by both ultra-violet radiation and nitric oxide in the short term but that it may be susceptible to attack by nitric oxide if air is also allowed into the reaction vessel. The vital factor would therefore appear to be the presence of air and more especially the presence of oxygen. Nitrogen can be disregarded because when in the second exposure the vessel was flushed through with nitrogen there was no apparent change in the polypropylene film.

7.3.2 Cellulose Acetate Butyrate

As previously mentioned the spectra of CAB was obtained only after it had been exposed to uv followed by NO for 3 hours and stood in an air atmosphere overnight. The spectra of samples of CAB exposed to uv and to uv and NO were not recorded. After exposure to NO the CAB film was examined visually and was found to have changed in appearance with the clear transparent film having been yellowed by the exposure to NO. This suggested that the film had undergone some structural change during the experiment and it was hoped that by comparing the spectra obtained before and after the exposure it would be possible to evaluate the changes which had taken place. The spectra are shown in figure 51 and as can be seen although there is a change in the degree of absorption by the sample the position of the absorption bonds has not changed. The weaker absorbance

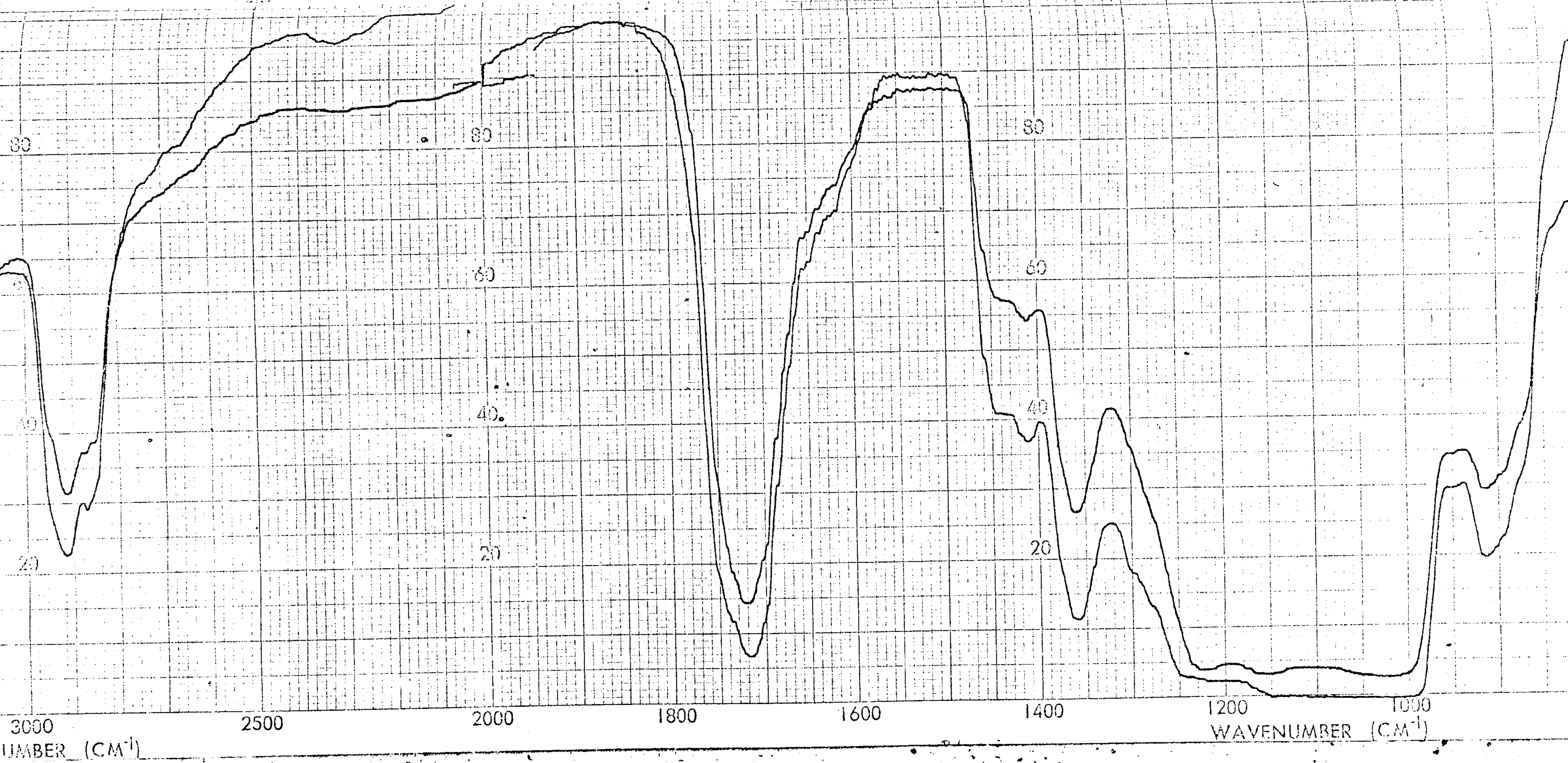


Figure 51 - Infra-red spectra of CAB before and after exposure to uv radiation and NO_2 having been left to stand in air

bands shown by the sample after exposure to NO are probably attributable to the yellowing of the sample during the exposure to NO. The reasons for the colour change in the CAB sample during the experiment cannot therefore be deduced from the infra-red spectra.

7.3.3 Polystyrene

Samples of 'Polyflex 110' were exposed to uv both in the presence of and in an atmosphere excluding NO. The infra-red spectra of the polystyrene film obtained both before and after these exposures are shown in figures 52 and 53. As can be seen from figure 52 there are changes in the infra-red spectra of polystyrene after exposure to uv radiation alone, the changes occurring in the relative strengths of the peaks at 1540 cm^{-1}, 1660 cm^{-1} and 1745 cm^{-1}. It is reasonable therefore to suppose that the ultra-violet radiation has initiated a structural change in the polymer. A structural change which then enables the nitric oxide to react readily with the polystyrene film. The infra-red spectra of the polystyrene film after exposure to uv and NO is shown in figure 53 and significant changes in the absorbance pattern of the polystyrene can be observed if the spectra is compared with that obtained before the sample was exposed to either uv or NO. These changes include the appearance of several new peaks in the spectrum at 1840, 1710, 1625, 1560 and 870 cm^{-1} due to the reaction of polystyrene with NO. Several peaks have also been lost from the spectrum including those at 1774, 1415, 1247 and 1112 cm^{-1}. Other changes include a slight downward shift in the wavelength of the absorbance peaks at longer wavelengths (2000-2500 cm^{-1}) and a change in the relative strengths of a number of other peaks.

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This evidence suggests therefore that polystyrene is susceptible to attack by both ultra-violet radiation and nitric oxide, the ultra-violet

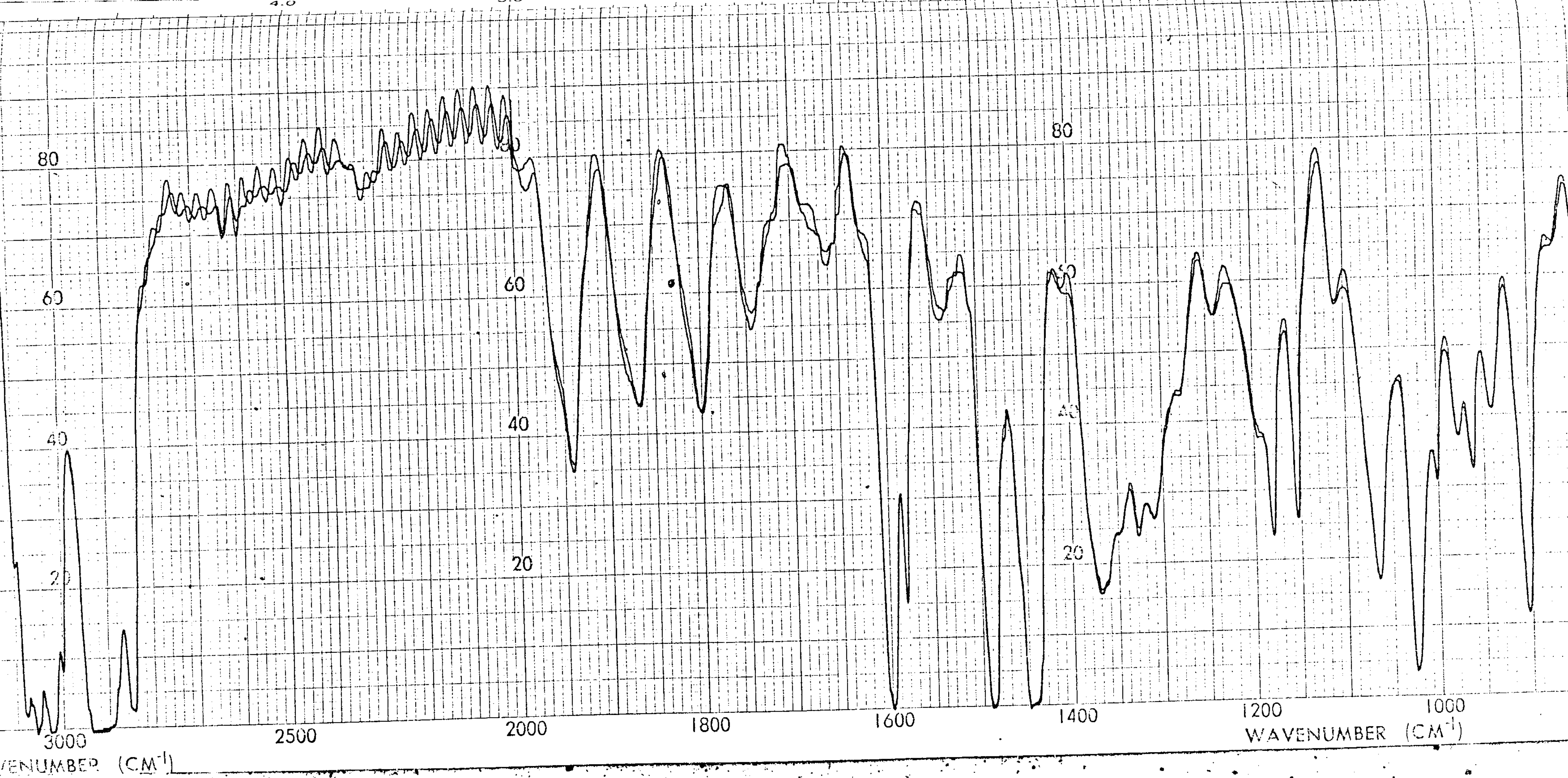


Figure 52 - Infra-red spectra of polystyrene before and after exposure to uv radiation

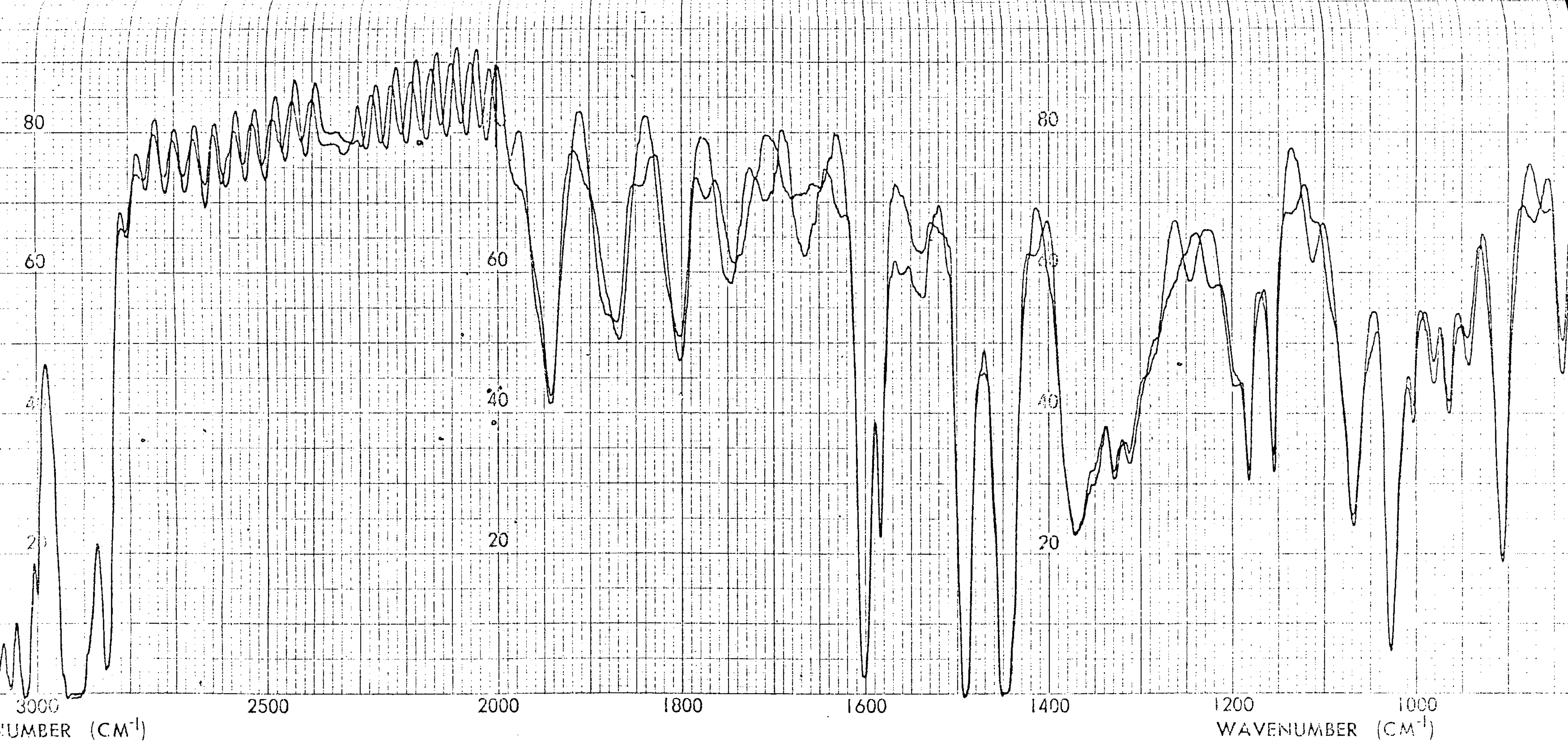


Figure 53 - Infra-red spectra of polystyrene before and after exposure to uv radiation and NO

radiation probably acting as an initiator to the attack by nitric oxide. No change in the physical appearance of the samples was observed throughout the exposure.

7.3.4 Polycarbonate

'Makrofol KG' was exposed to uv alone and to uv and NO, the samples in the former exposure being left to stand in a nitrogen atmosphere after the nitric oxide had been flushed out of the system and the sample from the latter exposure being left in an air atmosphere. Spectra obtained from each sample before and after the exposures are shown in figures 54-56. From figure 54 it can be seen that the exposure to ultra-violet radiation appears to have had little affect upon the polycarbonate sample with only a slight change in the relative intensities of some peaks. This evidence is consistent with that obtained by visual examination of the sample, which showed no change in the physical appearance of the sample. A change in the polycarbonate sample can however be seen on exposure to uv and NO as shown in figure 55. The main change in the infra-red spectrum of the polycarbonate sample after exposure to uv and NO is the appearance of a new absorbance band at 1664 cm^{-1} and the increase in strength of the absorbance peak at 1650 cm^{-1}. Both of these absorbances characterise the reaction of 'Makrofol KG' with nitric oxide. No change was noted in the physical appearance of the sample in contrast to the yellowing of the polycarbonate sample noted after exposure to NO followed by exposure to air. The spectra obtained from the sample after this exposure are shown in figure 56. Only the relevant parts of the spectrum were recorded in the latter case. After the infra-red spectrum had been taken the sample was placed in a dessicator which was then evacuuated for 24 hours. This was to remove any nitric oxide dissolved within the sample before the spectrum was retaken. As can be seen by the reduction in strength of the

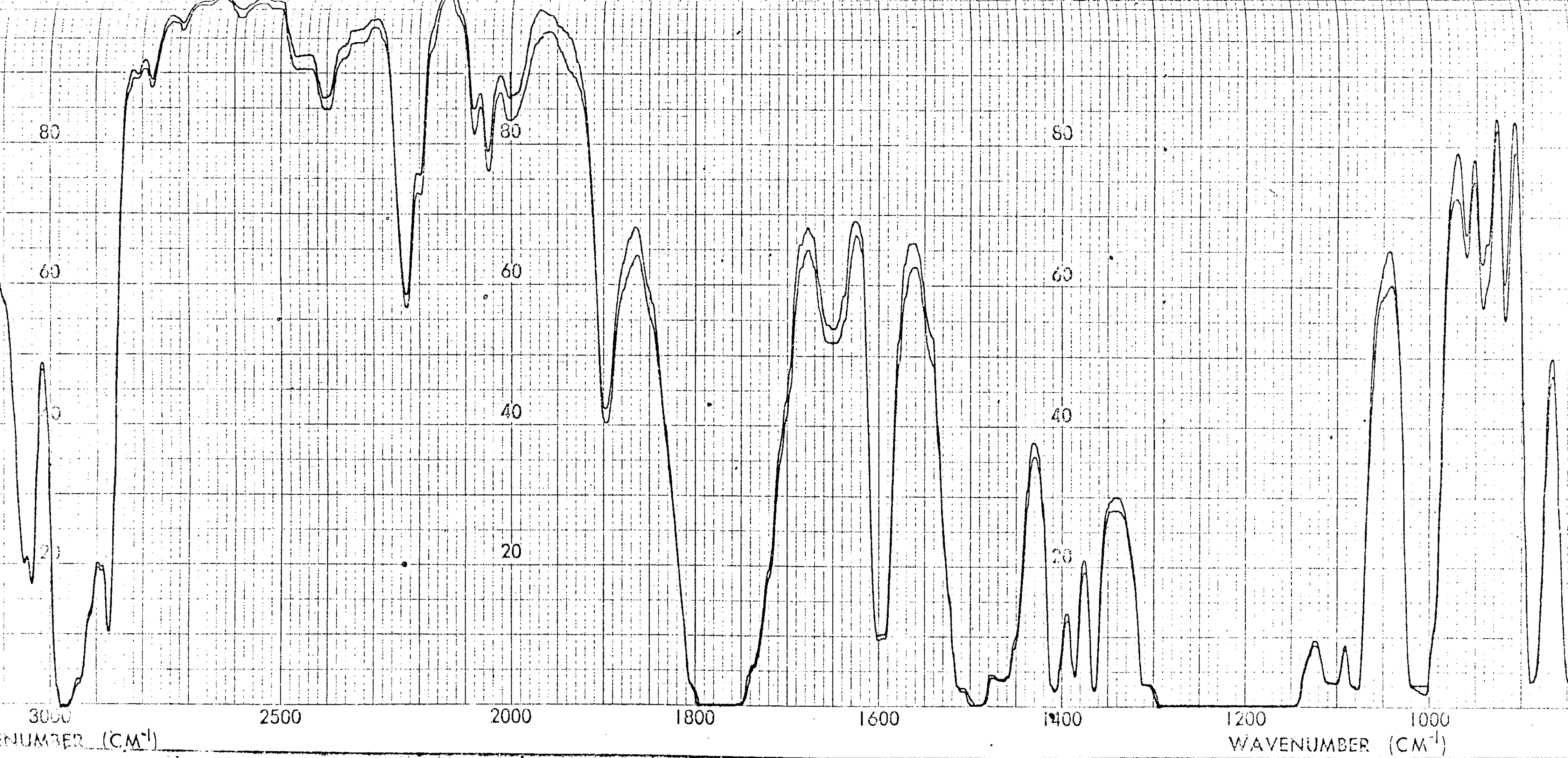


Figure 54 – Infra-red spectra of polycarbonate before and after exposure to uv radiation

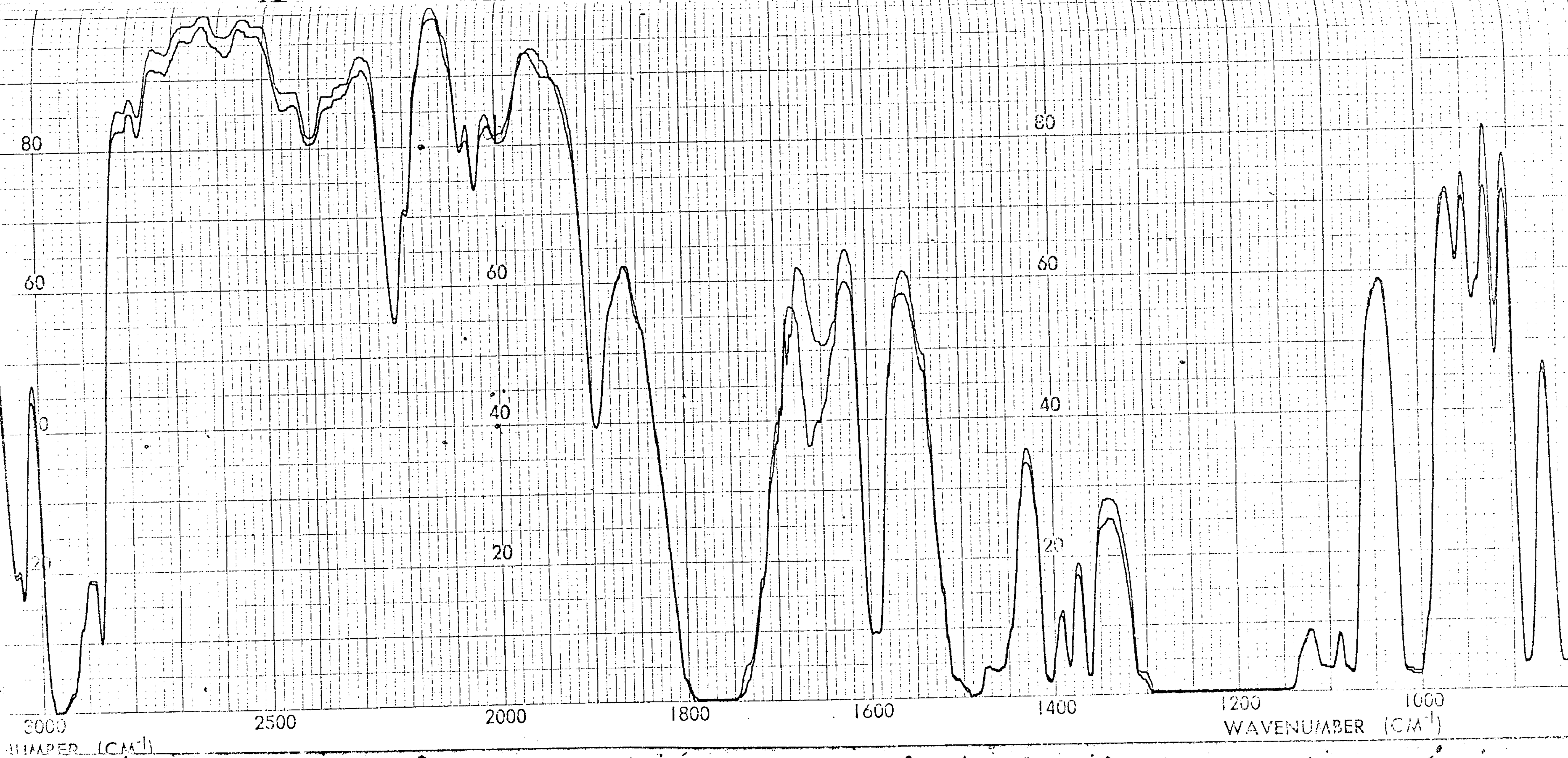


Figure 55 - Infra-red spectra of polycarbonate before and after exposure to uv radiation and NO

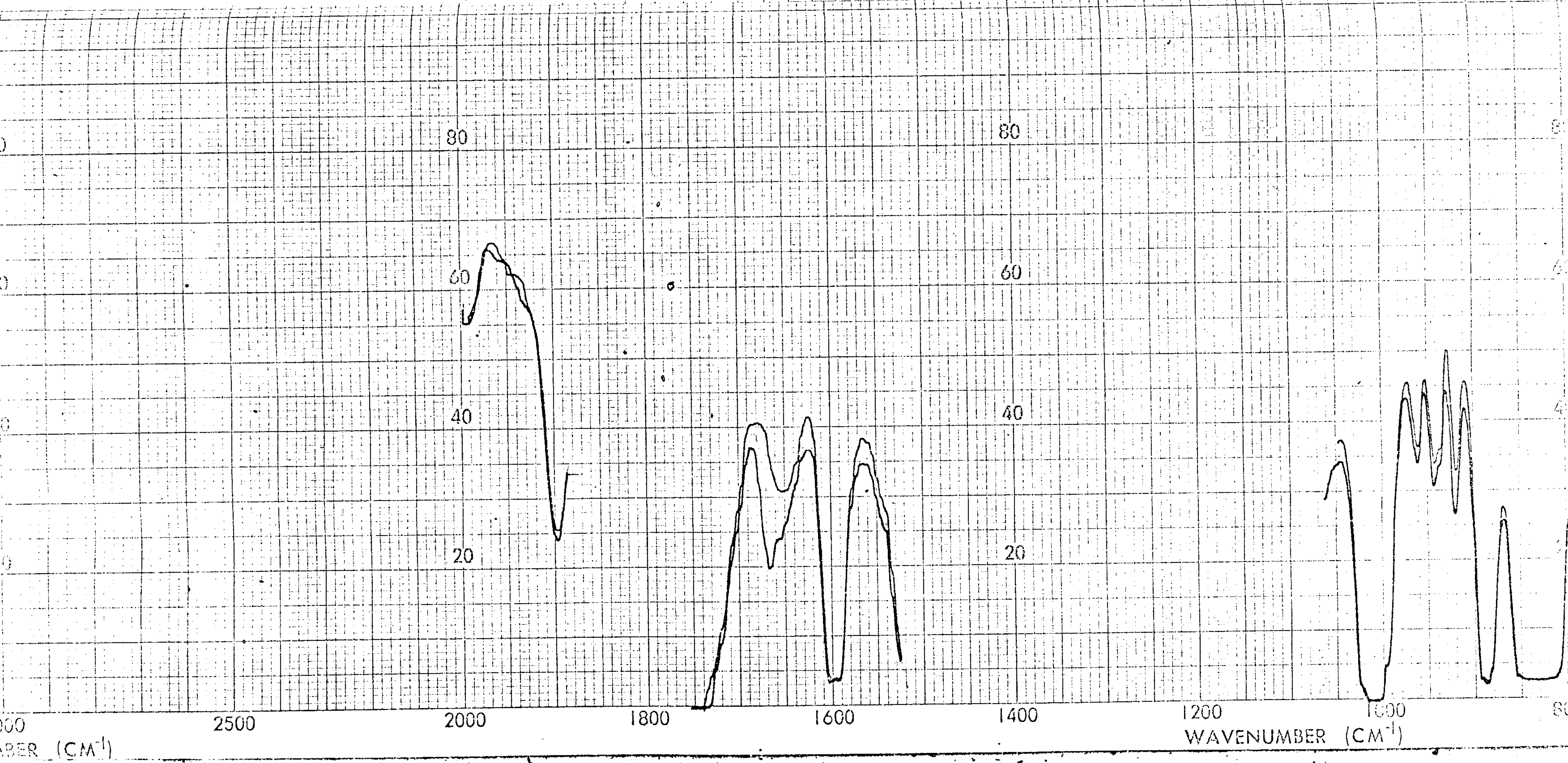


Figure 56 – Infra-red spectra of polycarbonate before and after exposure to uv radiation and NO, having been left to stand in air

absorbance at 1650-1665 cm^{-1} some nitric oxide was dissolved within the sample, the absorbance however is not due entirely to dissolved nitric oxide.

7.3.5 Polyethylene Terephthalate

'Melinex' film was exposed in the same way as the other films to uv alone and to uv and NO, the spectra obtained as a result of these exposures being shown in figures 57-59. On exposure to uv alone (figure 57) a slight shift in the wavelength of absorbance at the longer wavelength end of the spectrum can be seen, the shift being towards absorbance at a higher wavelength, a small change in the relative strength of some peaks can also be observed. Figure 58 shows that the exposure to uv and NO has no apparent affect upon the structure of the polyethylene terephthalate sample the spectra before and after the exposure being identical. After exposure to NO followed by exposure to air the spectrum (figure 59) obtained shows very similar changes to those observed after exposure to uv alone with a change in the relative intensities of some peaks and a shift in the wavelength at which others absorb. No change was seen in the physical appearance of the samples after any of the exposures.

It would appear therefore that no reaction took place between the 'Melinex' film and nitric oxide during the limited time for which the two were brought into contact.

The results of each of these exposures will be discussed more fully in the following section.

7.4 Discussion

There are two distinct areas of this work which may be considered and these are firstly the effect of uv radiation on polymer films and secondly

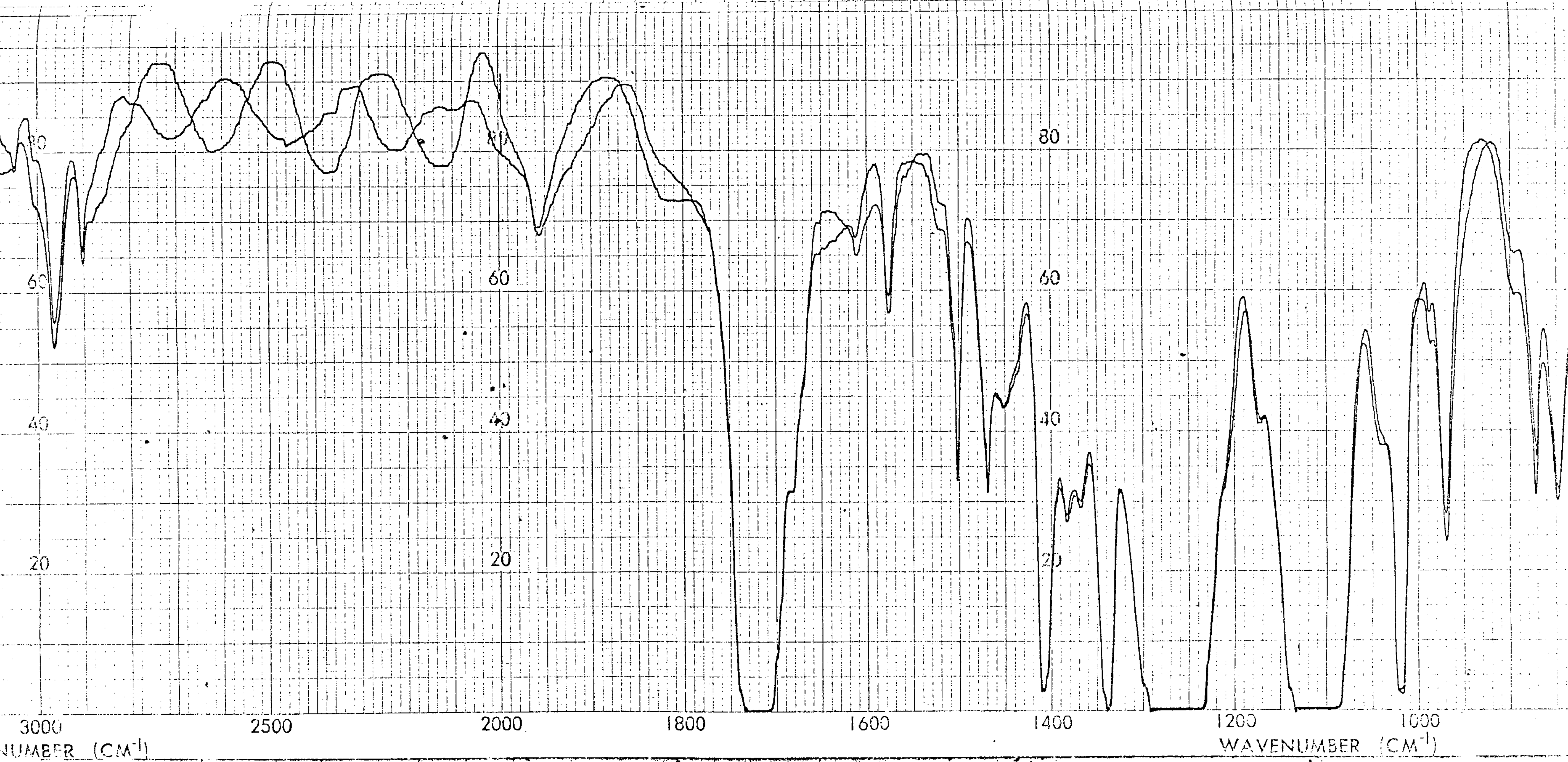


Figure 57 - Infra-red spectra of polyethylene terephthalate before and after exposure to uv radiation

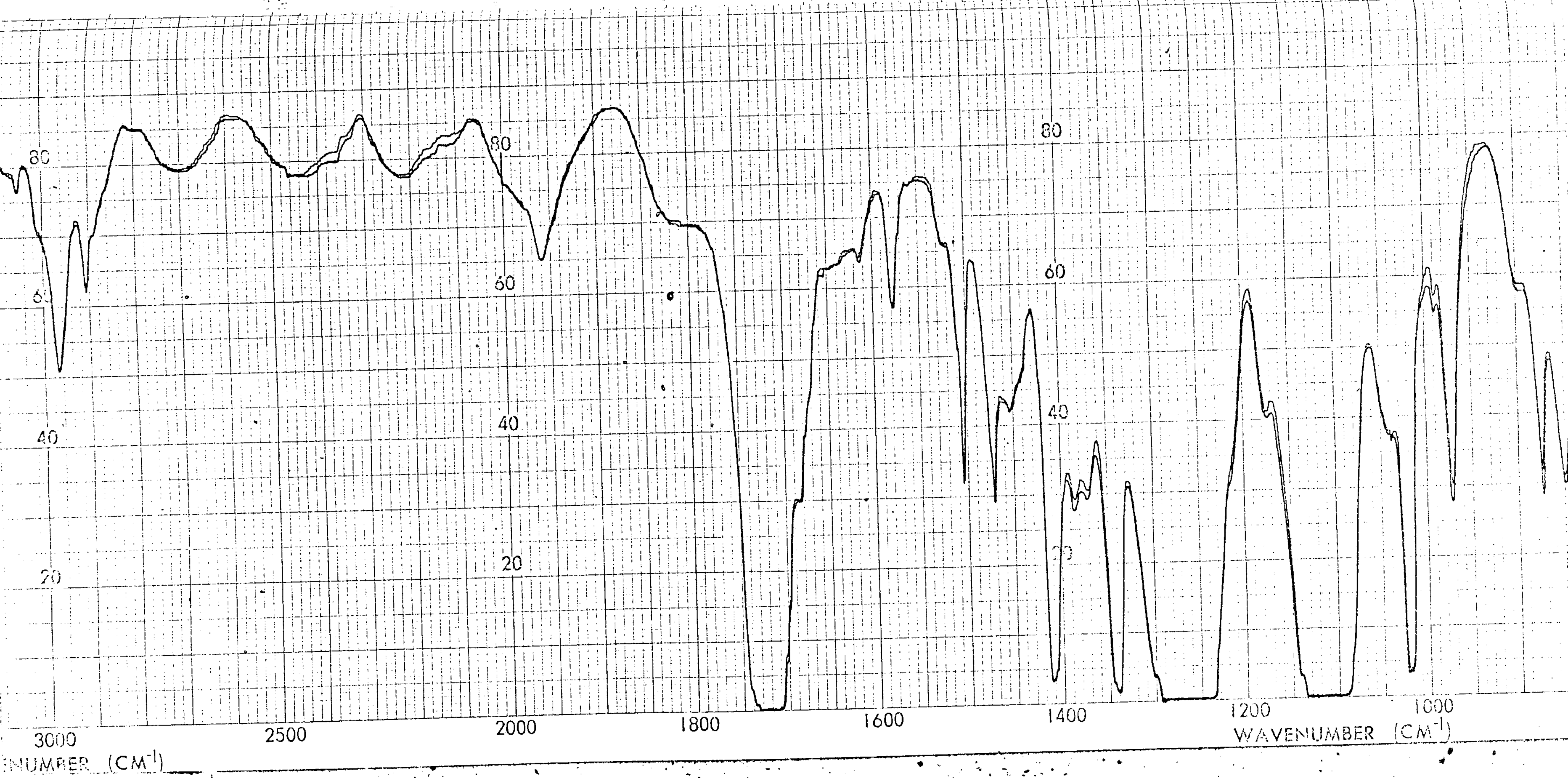


Figure 58 - Infra-red spectra of polyethylene terephthalate before and after exposure to uv radiation and NO

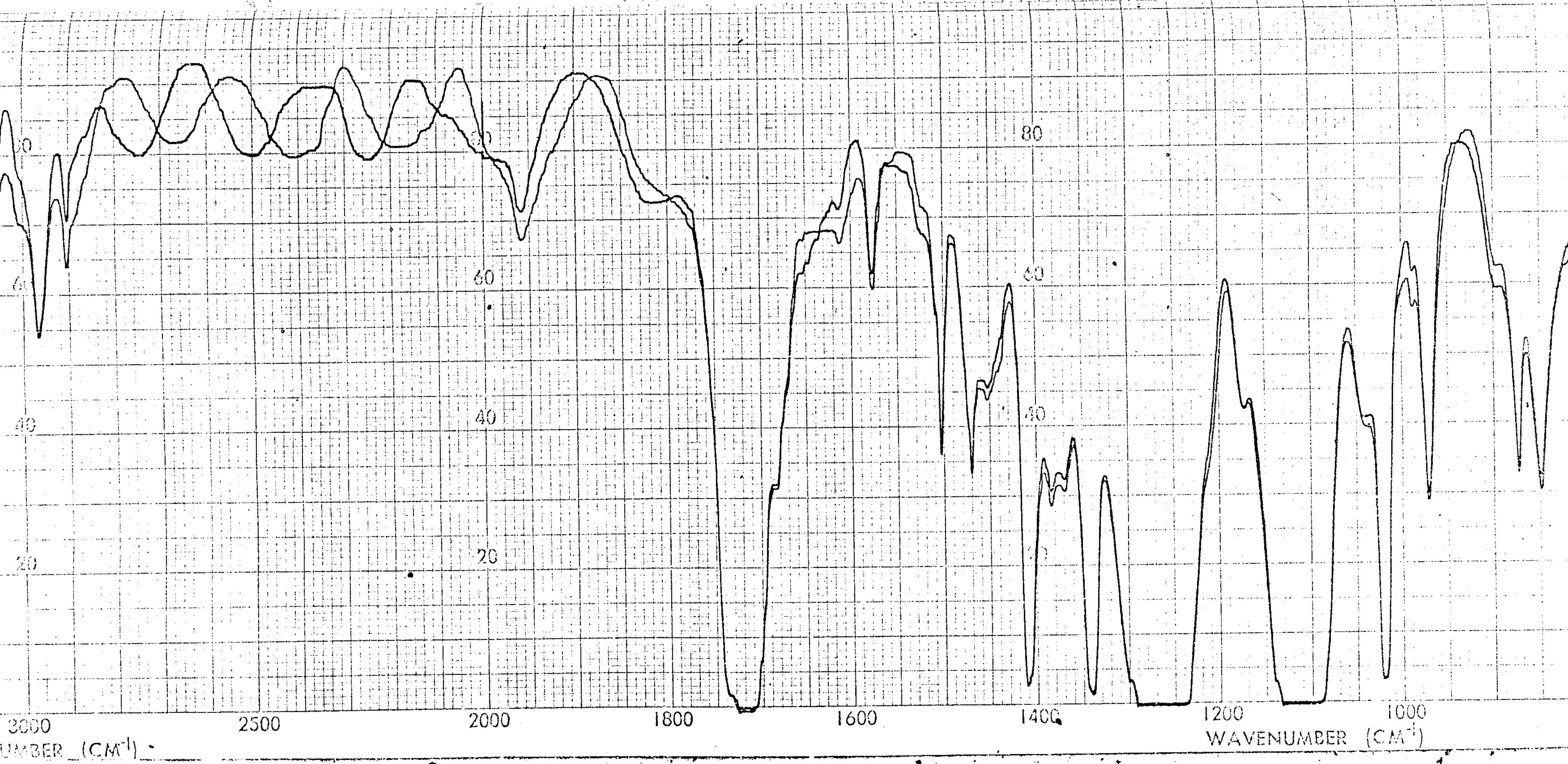


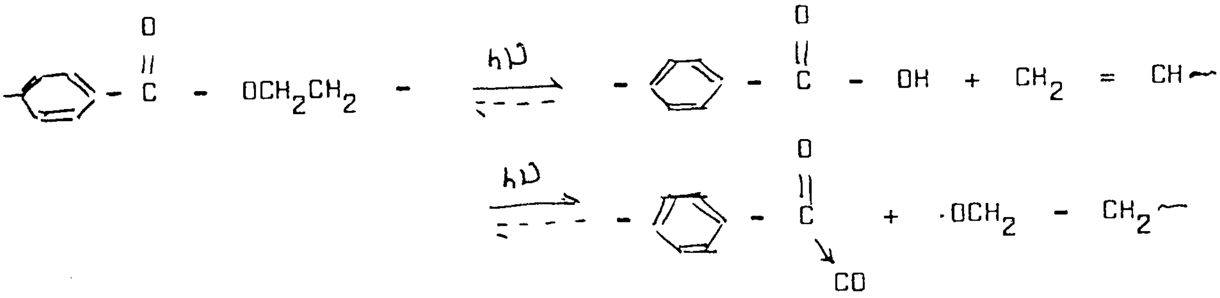
Figure 59 - Infra-red spectra of polyethylene terephthalate before and after exposure to uv radiation and NO, having been left to stand in air

the effect of nitric oxide and uv radiation on polymer films. These two areas were treated as separate stages of the work experimentally with the exposure of the samples to uv radiation preceeding the exposures to nitric oxide as it was felt that the photodegradation reactions initiated by uv radiation would encourage the subsequent reaction with nitric oxide. The work will then be discussed in this way.

7.4.1 Photodegradation

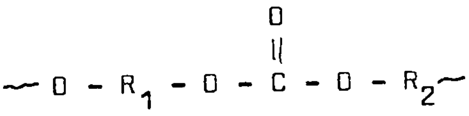
Each of the five polymer samples was exposed initially to uv radiation alone for two reasons, firstly so that the effect of the uv radiation of the sample could be determined and secondly, in an attempt to mirror the effect of sunlight on the sample prior to the introduction of nitric oxide to the system. The results of the exposure of the samples to uv alone will be discussed here. As shown by the results previously described ,of the four polymers whose spectra were measured after exposure to uv alone polypropylene showed no change in absorbance of infra-red radiation and the other three samples showed only small shifts in the wavelength of absorbance and small changes in the relative strengths of some peaks. It appears therefore from these results that none of the polymers used were extensively degraded by exposure to uv degradation. Two possible explanations of this are either that the changes taking place within the polymer are of such a nature as to be not detected by infra-red spectrometry (eg masked by other peaks) or that there are no changes taking place within the polymer. The latter possibility is the likely explanation in the case of the polypropylene film as subsequent exposure to NO also produced no visible changes in either the polymer film itself or the infra-red spectra of the polymer. The poly(ethylene teraphthalate) and polycarbonate films would be expected to show signs of degradation in the presence of uv, of the type previously reported by McNeill and Wiles[163,177].

As previously described in order for a polymer to be affected by uv it is necessary for a uv absorbing chromophore to be present in the polymer. In the case of poly(ethylene terephthalate) it is well-known that the ester carbonyl group is the significant chromophore for uv absorption and so the primary processes involved in the photodegradation process have been stated as



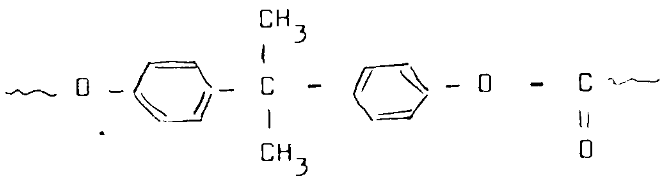
Neither of these processes is photo-oxidative so that two of the three primary products from PET (COOH, CO and CO_2) are produced directly by photolysis. It should also be noted that the poly(ethylene terephthalate) film employed for this work, 'Melinex', is used commercially as a packaging material and so would be expected to contain additives to inhibit the photodegradation process.

Little information is available as to the formulation of the polycarbonate film 'Makrofol KG' used for this work. Polycarbonate has the general formula -

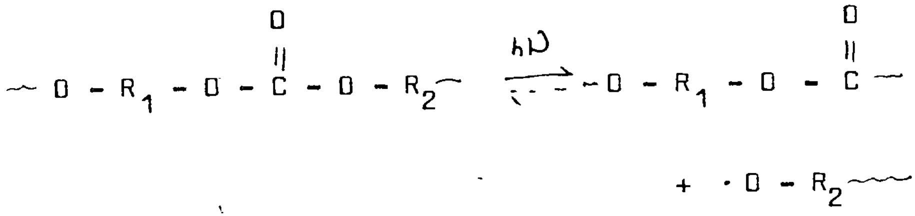


$$\sim O - R_1 - O - \overset{\overset{\displaystyle O}{\|}}{C} - O - R_2 \sim$$

where R_1 and R_2 may be aliphatic or aromatic groups and in the case of Makrofol KG it is probable that it has the structure



as this is the only commercially significant polycarbonate. Since polycarbonate also contains a carbonyl group however it should be degradable by uv radiation in the same manner as poly(ethylene terephthalate)



$$\sim O - R_1 - O - \overset{\overset{O}{\|}}{C} - O - R_2 \sim \xrightarrow{h\nu} \sim O - R_1 - O - \overset{\overset{O}{\|}}{C} \sim \; + \; \cdot O - R_2 \sim\sim$$

This photodegradation of polycarbonate may then lead to the later reaction of the degraded polymer with NO which will be discussed in the next section.

Pure polypropylene and polystyrene would not be expected to be degraded by uv radiation because they contain no chromophores which absorb in the uv region of the spectrum. However in the commercial samples that were used there are traces of impurities left from the processing which the films have undergone and these do contain chromophoric groups which absorb uv light. As mentioned previously the energy which they absorb may then be passed onto the polymer leading to chain scission reactions.

$$\sim CH_2 - CHX \sim \rightarrow \sim \dot{C}H_2 + \dot{C}HX \sim$$

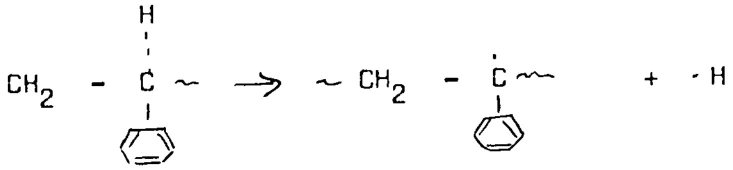
or

$$\sim CH_2 - CHX - CH_2 \sim \rightarrow \sim CH_2 - \dot{C}X - CH_2 \sim + \dot{H}$$

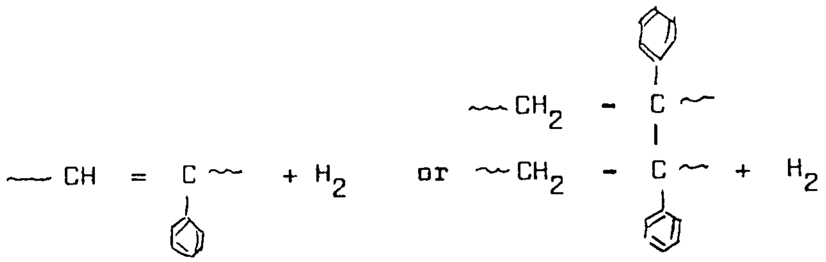
(unstable)

$$\rightarrow \dot{C}HX + CH_2 = CX - CH_2 \sim$$

The photolysis of polystyrene has been studied by Grassie and Weir[178] and they have shown that the characteristics of vacuum photolysis are gas evolution in small quantities, development of insolubility and discolouration. They have suggested that C-H bond scission is the homolytic reaction induced by uv light centred on the weakest C-H bond present, that is, the tertiary H atoms α to the aromatic ring.



The highly reactive H radical can then abstract a further H atom from the polymer or an adjacent polymer leading in the first case to conjugation and in the second to the cross-linking of the two polymers.



Both the polypropylene and polystyrene films used here are available commercially for packaging purposes and so again would be expected to contain additives which inhibit the process of photodegradation. The additives in 'Propafilm' are effective in this purpose as these results show, the film appearing to be totally unaffected by short exposure to uv radiation. The polystyrene sample however 'Polyflex' although showing little change in the pattern of its infra-red absorption does appear to have been degraded as shown by its reaction with nitric oxide.

In conclusion the polypropylene film manufactured by ICI Plastics Division appears to be the only one totally unaffected by exposure to uv radiation. Each of the other films appears to have degraded to some degree by the exposure to uv radiation; although the evidence obtained from infra-red spectrometry was not conclusive in this respect. The mechanisms by which the polymers may degrade have been outlined in this section and will be further used to explain their varying reactions with nitric oxide. Finally it must be emphasised that the exposure to uv radiation was of only a short duration (2 hours) and that each of these polymer films is used commercially as a packaging material and would therefore be expected to contain additives which inhibit photodegradation reactions from taking place. A longer exposure to uv may therefore have shown more definitive changes in the polymers.

7.4.2 Reaction with Nitric Oxide

All of the five polymer films studied were exposed to nitric oxide gas after being irradiated by uv for 2 hours previously. It was hoped that the initial exposure to uv would cause the polymers to degrade forming radicals with which the nitric oxide could then readily react. This situation would then mirror the real-life situation when polymers are exposed to sunlight and to nitric oxide which is present in small quantities in the atmosphere.

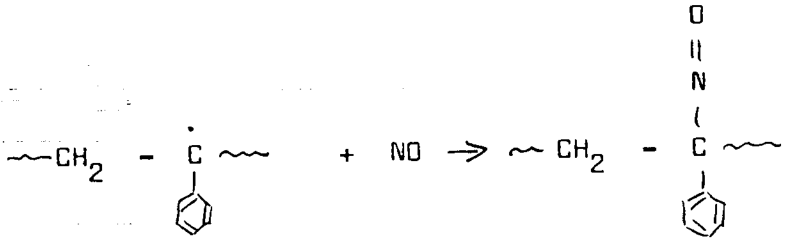
Of the five samples only polystyrene and polycarbonate showed any significant changes in the infra-red spectra obtained before and after exposure to NO. Polypropylene showed no change at all in the absence of air and only a small change in the relative strengths of some peaks in the presence of air. The peaks concerned were shown to be due to additives in the polypropylene film and so could not be identified. The uv stabilisers present in the polymer were found to be very effective in preventing photodegradation occurring within the polymer and therefore in preventing subsequent attack by nitric oxide.

Cellulose Acetate Butyrate was exposed initially to uv and then to NO followed by a period standing in air. Again no changes were discernible in the infra-red absorption pattern but in this case the clear sample was yellowed at the end of the exposure suggesting that some conjugation had occurred within the polymer. CAB contains a chromophoric group which can absorb energy from uv irradiation, in the form of the C = O group, and would therefore be expected to be susceptible to photodegradation. The discolouration observed here suggests that some chain scission has taken place followed by the subsequent abstraction of a further H atom to form a double bond within the film, thus leading to the yellowing of the film. There is, however, no evidence of a further reaction with nitric oxide taking place.

Poly(ethylene terephthalate) showed no visible or spectral signs of reaction with nitric oxide in the absence of air and only a slight change in infra-red absorption after exposure to both NO and air. In the latter case the changes observed mirrored those observed when the film was exposed to uv alone suggesting that the changes were caused by uv irradiation and that the nitric oxide did not react with the resultant material. From figure 59 however it is possible to argue that a peak is beginning to form at 1640 cm^{-1} and that this is due to the reaction of irradiated poly(ethylene terephthalate) with nitric oxide. This peak could be attributable to the stretching of a C = N bond in the polymer with any other changes taking place being masked by the PET spectrum itself. If this is the case then the additives in the poly(ethylene terephthalate) film used to inhibit photodegradation have succeeded in inhibiting most photodegradation enabling the nitric oxide to react with only the small proportion of radicals formed.

Polycarbonate is shown to react strongly with nitric oxide both in the presence and absence of air with the changed spectra in figures 55 and 56 showing the formation of new peaks in the 1665 cm^{-1} region of the spectrum indicative of oxime formation. The presence of oxygen therefore has no discernible effect upon the reaction. Reaction of polycarbonate with nitric oxide has been noted previously[179] and in this case the same polycarbonate film as used in this work was not previously exposed to uv irradiation. This therefore suggests that uv is unnecessary to initiate the reaction of polycarbonate with nitric oxide.

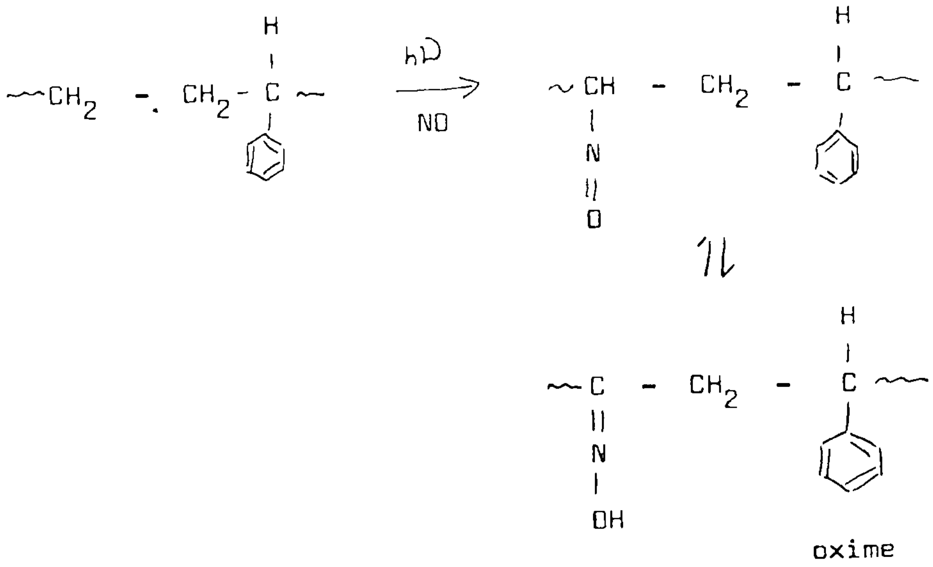
Previous work has shown that nitric oxide shows a high permeability to polycarbonate a fact born out by figure 56 which shows that after standing overnight in a vacuum the strength of the peak at 1665 cm^{-1} lessened as dissolved NO was removed from the polymer. The polystyrene film is also shown to react strongly with nitric oxide with significant changes in the infra-red spectra of the film after exposure to NO. In this case the degradation is most probably initiated by exposure to uv which causes chain scission to take place within the polymer chain as previously described. The radical which is formed may then be susceptible to attack by nitric oxide as shown



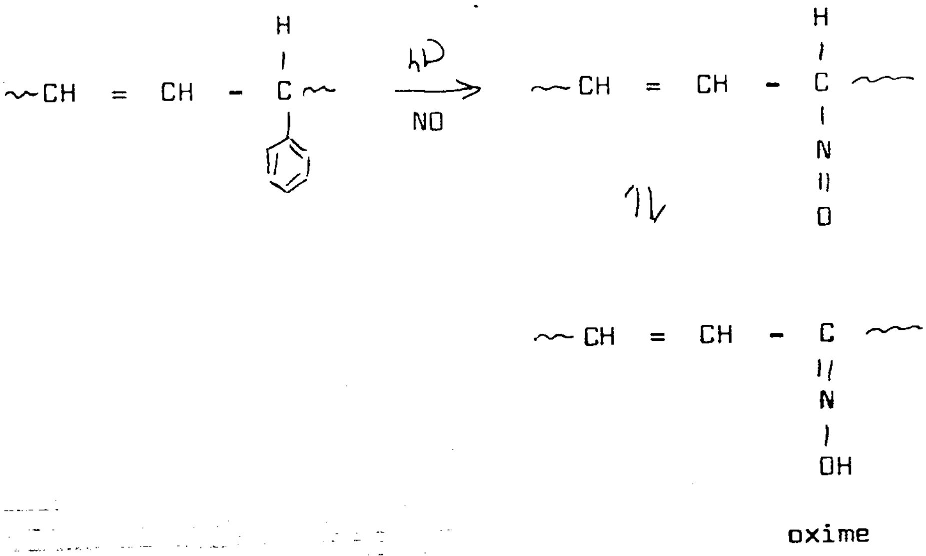
forming a nitroso group.

If any irregularities are present in the chain then other products may result from the degradation process, some of which are shown below.

(1)



(2)



In both of these cases the resulting product is an oxime. Spectral evidence seen in figure 53 supports the formation of both nitroso (-N=O) and oxime (=N-OH) groups in the polymer with the C=N stretching band of the oxime appearing at 1625 cm^{-1} in the spectrum and the accompanying N=O stretching absorbance of the nitroso group in the 1550 cm^{-1} region of the spectrum.

7.5 Conclusions

Perhaps the most surprising result found is the remarkable resistance shown to photodegradation by the 'Propafilm', this observation being in contrast to the results obtained by previous workers where polypropylene has been found to be readily photo-degradable and readily reactive with nitric oxide. The particular polypropylene film studied here however is reported[174] as being highly crystalline and as most degradation occurs in the amorphous regions of the polymer it is not perhaps so surprising to find the film so unreactive. Each of the other polymers has been degraded by uv to a greater or lesser degree with the 'Melinex' film probably being the next least affected. This is not quite so surprising since poly(ethylene terephthalate) is below its Tg at room temperature and in consequence is a 'stiff' polymer. In these so-called 'stiff' polymers there is a much greater likelihood of reforming a cleaved bond (radical-radical reformation) than in for example polypropylene which at room temperature is above its Tg and hence contains relatively mobile polymer chains[177]. In addition the quantum efficiency for the formation of products by bond breaking reactions is much higher for plastics containing more flexible polymer chains than for those with less flexible polymer chains. Melinex however would still have been expected to be photodegraded more readily due to the presence of a uv absorbing chromophore in the polymer. The stability of these two polymers therefore must be attributable to the uv stabilisers added to them to prolong their commercial life and usefulness.

Polycarbonate and polystyrene were both degraded by nitric oxide although the degradation took place by different mechanisms, the reaction with polystyrene being initiated by uv irradiation and the reaction with polycarbonate requiring no initiation. It has been noted previously that nitric oxide shows a high permeability to polycarbonate[179] due to the polarity of the polymer, nitric oxide is therefore able to react with the bulk of the polymer and not just at the surface as is the case with the polymers less permeable by nitric oxide. In both cases however the major outcome of the reactions appears to be the formation of oxime groups in the polymer.

Finally it must again be emphasised that all of the polymer films studied in this section of the work are commercially available products and as such contain many additives which may themselves contribute to the polymers' characteristics. The nature of these additives is unknown and therefore their effect upon the photodegradation of the polymers and subsequent attack by nitric oxide cannot be analysed. It can however be said that the interactions of nitric oxide and uv with polymers is also likely to be a complex balance of a number of different, yet inter-dependant, processes of varying importance of which only a few have been investigated in this work. It is obvious therefore that there is a considerable amount of further work to be done in this area before any definite conclusions can be drawn as to the way in which nitric oxide and uv react with these polymers.

CHAPTER VIII

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

In conclusion it may be said that perhaps the most surprising aspect of this work is the apparent cyclic pattern of behaviour which the coatings exhibited on exposure to both natural and artificial weathering. This may have been due to experimental variability in the results but this explanation seems unlikely when the number of samples from which measurements were obtained is taken into account. Another consideration is the nature of the surface coatings themselves, unique two component systems of polymer and plasticiser. In a naturally weathered system of this type the greatest deterioration would be expected in the summer months due to the increased amount of ultra-violet radiation received by the samples. In the winter months however little erosion would be expected due to the lower level of ultra-violet radiation and the surface mending effect of the plasticiser. It is therefore a complex system and further investigation into the weathering behaviour of the coatings is required to assess the experimental variability of the results. Finally as the conclusion to this thesis the following observations have been made:

(1) Three types of weathering have been employed in this work, natural, artificial and uv and one of the objectives of the work was to assess their ability to reproduce natural weathering. The BS 3900 Part F3 Artificial Weathering Machine has been seen to be unable to reproduce the effects of natural weathering upon PVC plastisol surface coatings although it does appear to have brought about the same general trends in the weathering of the samples.

The weatherometer therefore is a useful tool for assessing the lifetime and general behaviour of PVC plastisol coatings on ageing but could not be used to determine the precise changes brought about by natural weathering.

The uv cabinet was also able to reproduce the same general trends in the weathering of the samples suggesting that the most degradative aspect of natural weathering is the exposure to ultraviolet radiation, although more work needs to be carried out to confirm this view.

(2) Each of the analytical techniques in this work has been assessed in terms of its usefulness in providing evidence of the nature of the degradation processes taking place in the surface coating.

Goniophotometry proved to be a very valuable technique in characterising surfaces and also a technique which gives highly reproducible results. While goniophotometry is able to characterise the complete sample surface, scanning electron microscopy was able to pinpoint processes.taking place at isolated areas on the sample surface which were not discernable by the naked eye.

Surface energy measurement was another useful technique which was to give an insight into the type of migration taking place towards the surface of the coatings. Weight loss measurements, thermal analysis and gel content measurements did not in themselves give information which could be used directly to characterise the behaviour of the coatings but did provide supportive evidence to be used in conjunction with other techniques.

Micro-indentation studies were disappointing in that the coatings were very soft which made changes in rigidity hard to discern and measurements difficult to reproduce.

In conclusion then each of the analytical techniques used provided more or less valuable information as to the degradation processes taking place in PVC plastisol coatings and these results when assimilated were able to characterise the behaviour of PVC plastisol coatings when exposed to weathering.

(3) The uv and thermal stabiliser added to the plastisol coatings did not appear to have a significant effect upon the resistance of the coatings to weathering unlike the added pigment which gave considerable stability to the coatings. The plasticiser also played an important part in the resistance of the coatings to weathering.

With these conclusions in mind the following areas are suggested as areas in which further work could be usefully carried out.

(1) Following the very brief study in this work of the effect of thermal radiation on the plastisol coatings, it would obviously be of benefit to continue this work and to analyse the effect of both thermal radiation and humidity on the coatings to establish the part played by these two factors in the degradation of the coatings.

(2) As yet only the effect of uv and thermal stabilisers and pigment have been investigated and this represents only a very simple paint formulation so using this work as a basis progressively more complex formulations could be made up to establish the most efficient way of stabilising PVC plastisol coatings.

(3) The mechanism for the degradation of PVC is still under debate

and this is an area in which further work could be most usefully carried out to determine how the degradation takes place and hence give insight into how it could be best prevented.

(4) Having established suitable methods of analysing the breakdown of plastisol PVC coatings the scope of the work could be further extended to other surface coatings, to find hoe they react to the stresses of artificial weathering. The Artificial Weathering Machine having been established as a successful reproducer of natural weathering could be put to great use and benefit in this area, so obviating the need for lengthy outdoor exposures.

(5) Finally turning to the exposure of various polymers to nitric oxide, this work has only been intended as a preliminary investigation into the effects of nitric oxide and so considerably more work remains in this area. No effort has been made to establish how the nitric oxide reacts with the polymer and whether a surface or bulk reaction takes place and so this could be a useful starting point. Surface energetics measurements could be used to determine changes taking place at the surface of the coating.

This work could be extended to the PVC plastisol coatings to find how they react to nitric oxide which is a well-known pollutant to which coatings are exposed, and for all coatings it could be extended to cover other pollutants found in the atmosphere (eg SO_2, CO) to discover the effects they have on coatings, if any.

APPENDIX 1

Preparation of samples for analysis.

The PVC plastisol coatings used in this study were all prepared by Vinatex Ltd. and were applied to three different substrates, glass, aluminium and stainless steel, the different techniques for which each of these were used are given below.

(a) Glass panels - The coatings were applied to six inch square glass panels without a primer so that they could be easily removed and used for gel content measurements. Each coating was applied to several sheets of glass and each of these was exposed at the Building Research Station's site. Two samples were taken of each coating for each point in time at which examination and characterisation of the samples was to be carried out. These samples were then used for thermal analysis and gel content measurements. For thermal analysis two or three small circular samples, approx. ¼" dia. were punched from each coating after they had been detached from the glass panels and these were then analysed using the 'Differential Scanning Colerimeter'. Gel content measurements were then carried out on two samples and an average of the two results taken. The samples were washed gently under running water before being analysed to remove any traces of dirt from the surface.

(b) Aluminium panels. - The coatings were applied to six inch square panels which had previously been primed. Duplicate panels of each coating were exposed at each of the different exposure sites and at each point in time that examination and characterisation of the coatings was carried out a one inch circular sample was punched from each of the panels. Analysis of these samples was then carried out as described below:-

(1) Goniophotometry - Each sample was gently cleaned under running water to remove excess dirt from the surface and dried overnight in a dessicator before being subjected to goniophotometric analysis. The gloss factor at three points on the surface of each sample was then determined and an average of the values taken.

(2) Surface Energetics - The samples were prepared in the same way as for goniophotometry and in this case were also cleaned and dried between measuring water and di-iodo-methane contact angles. For each liquid between three and six contact angles were measured on each sample before an average value was obtained.

(3) Micro-indentation - The samples for analysis by micro-indentation were not cleaned again before use and for each sample indentation measurements were taken from at least three different points on the surface with at least three different loads.

(4) Scanning Electron Microscopy - From each circular sample upto four smaller samples were cut for analysis by SEM. Each of these smaller samples were then prepared as described for goniophotometry, mounted onto a small circular aluminium stub and covered with an electrically conducting layer. Each coating was then viewed using the scanning electron microscope and specific characteristic defects of the surface were looked for. These defects were then observed more closely and photographed.

The coatings applied to the aluminium panels were each analysed in the above sequence, SEM being the last technique used because it destroyed the samples making further analysis impossible.

(c) Stainless steel panels - The coatings were applied to six inch x two inch steel panels which had been previously primed and again duplicate panels of each coating were exposed at the Building Research Station's site. Each panel was carefully cleaned using a gentle brush under running water before being dried in a dessicator and weighed.

APPENDIX 11

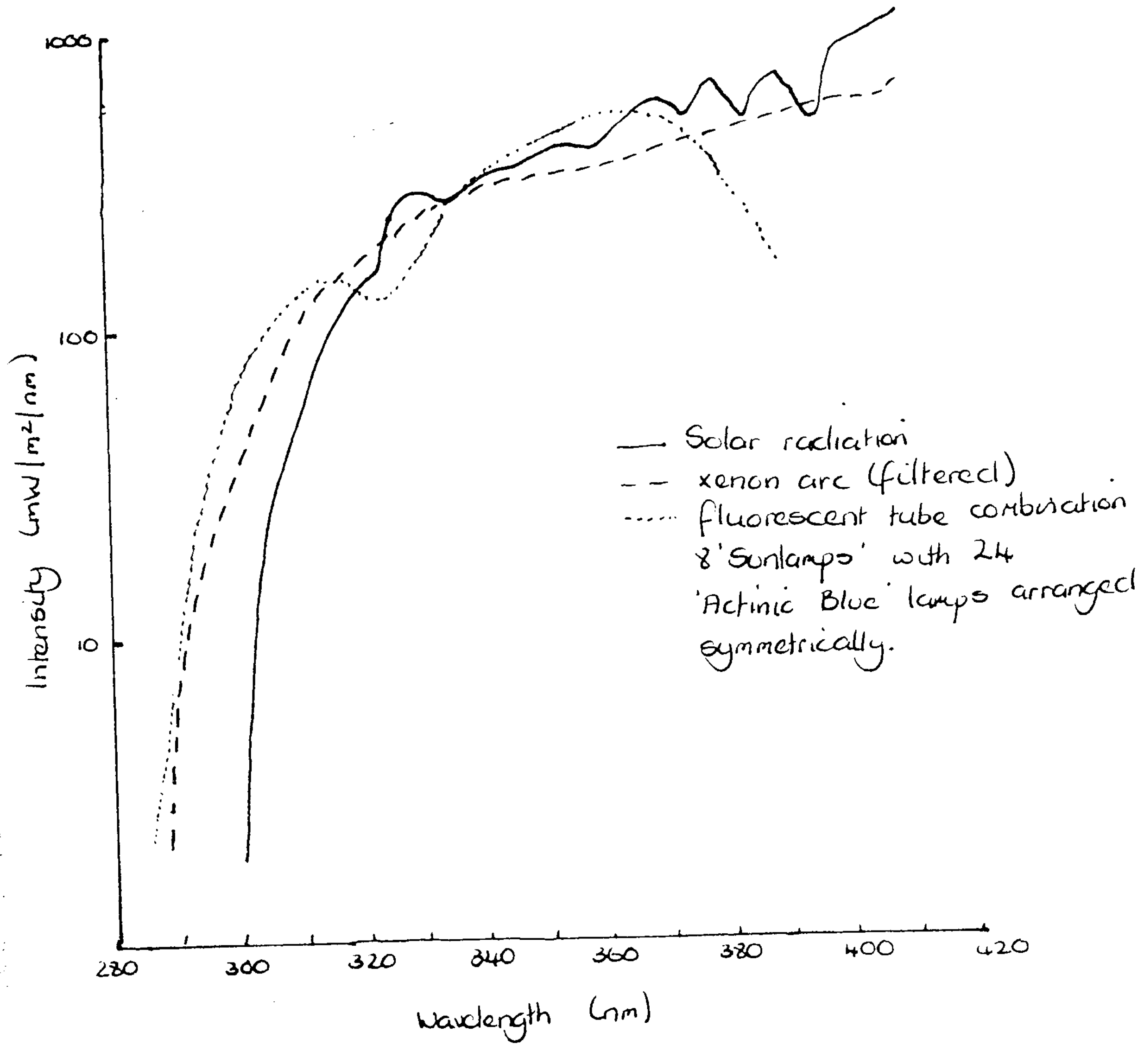
Ultra Violet Light Sources.

Four different sources of ultra-violet light have been employed during the course of this work, and these are, for the weathering of the PVC plastisol coatings, sunlight, the BS 3900 part F3 Artificial Weathering Machine and the uv cabinet. For the work concerning exposure of polymer films to uv and nitric oxide a single uv lamp was used.

The spectral distribution of light from each of these sources differs and a plot of wavelength vs intensity for the first three of these sources is given on page 218.

These differing sources of uv light also mean that the temperature at which the samples are irradiated differs, that in the uv cabinet being in the order of 35°C and that in the artificial weathering machine 45°C with a surface temperature of the samples approaching 50°C.

The lamp used for the exposure of polymer films to the ultraviolet light and the nitric oxide was a mercury vapour discharge lamp in a quartz arc tube. The arc tube was enclosed in an outer bulb of black glass which absorbs all radiation other than that in the long wave uv of predominantly 365 nanometres, little visible light is emitted.



Spectral distribution of uv light sources compared to sunlight.

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