REFLECTANCE AND RELATED STUDIES
OF THE
WEATHERING OF SURFACE COATINGS

by

Robert Molloy

A thesis submitted for the degree of
Doctor of Philosophy
of the University of Aston in Birmingham

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SUMMARY

This project is concerned with the way in which a selected combination of analytical techniques can be applied to the study of the various ageing processes which occur in surface coatings during exposure. Particular emphasis in this respect is placed on the development and application of the goniophotometric technique to the quantitative characterisation of reflectance changes brought about by weathering - a usage which appears not to have been previously exploited to any notable extent. In conjunction with goniophotometry, a variety of other techniques are also used, notably scanning electron microscopy, multiple internal reflection spectroscopy and surface roughness measurement, with their respective data being correlated as far as possible.

The actual coatings materials examined in this way comprise, in the first part, a range of commercial paints chosen to represent a cross-section of those currently available. Their ageing study is then followed by a more detailed investigation into the weathering mechanism of a particular class of coatings - namely, those based on poly (vinyl chloride) (PVC) - including the roles played by the various additives present in the system.

Finally, in addition to both the natural and artificial weathering tests which have been conducted at various outdoor sites and under various conditions, an adjunctive case study of the interaction of PVC with nitric oxide is also described.

INDEX TERMS:

goniophotometry;
scanning electron microscopy;
multiple internal reflection spectroscopy;
surface roughness measurement (profilometry);
poly (vinyl chloride) surface coatings - natural and
    artificial weathering of, interaction with nitric
    oxide.

To my grandparents

The work described in this thesis was carried out between October 1972 and September 1975 in the Department of Chemistry of the University of Aston in Birmingham.

It has been done independently and has not been submitted for any other degree.

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Robert Molloy

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The Intellect: "Apparently there is colour, apparently sweetness, apparently bitterness, actually there are only atoms and the void".

The Senses: "Poor Intellect, do you hope to defeat us, while from us you borrow your very evidence. Your victory is in fact your defeat".

DEMOCRITUS (c. 420 B.C.)

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CHAPTER I

INTRODUCTION

CHAPTER I

INTRODUCTION

I.1 General Introduction

Surface coatings, it can be said, fulfil two main functions; firstly, as a form of protection against external attack on the underlying surface (i.e., substrate) and, secondly, as a means of decoration in order to give the surface an aesthetically attractive appearance. In certain applications, such as those associated with interior domestic surfaces (e.g., walls, floors, furniture, etc.), the surface coating should additionally be able to satisfy certain hygienic requirements such as resistance towards the "harbouring" of dirt, bacteria and other impurities. Consequently, any study which is devoted in some way to the development of a basic understanding of the factors involved in the many and varied processes by which surface coatings degrade, must have an obvious commercial significance.

In a classical sense, such studies, of course, ought necessarily to precede any form of preventative measure which may be taken in order to offset deterioration of the surface coating. However, it is probably true to say that it is only during the relatively recent part of surface coatings history that fundamental scientific research has been seriously undertaken by the industry. Indeed, for a considerable length of time after the initial introductions, in the 1920s and 30s, of many of the earlier synthetic film-forming polymers (i.e., binders) for use in surface coatings, "rule of thumb" or practical experience at various stages of enlightenment, sufficed to achieve the expected standards. However, the science of surface coatings eventually came to be borne out of the existing technology and it is the careful application of this science which, today, leads to the development and production of modern surface coatings with dependable performance at economic prices.

Thus, it is very largely from within the realms of the science of surface coatings, as opposed to the technology, that this project finds its roots, although it is hoped that the stage to which it has been taken will interest the technologist in industry from where the problem originated and where some of the findings can realise their commercial significance.

From a commercial standpoint, of course, the value and importance of a detailed study such as this will tend to be assessed, ultimately, in terms of the eventual contribution which the results make towards satisfying some of the more readily conceived commercial needs. In this respect, obvious objectives must include, for example, establishing a basis upon which the expected "lifetime" of a particular paint in a particular application may be predicted and, following on from this, facilitating the choice of paint for its intended use. In conjunction with these broadly-based requirements, there are also to be considered the more specific problems associated with improving the individual ageing performance of the actual film-forming polymer (binder) in a given paint system. In theory, this latter consideration ought to be primarily concerned with stabilising the polymer against those ageing processes by which it has been found to degrade. However, in industrial practice, this somewhat classical approach towards increasing the paint's weathering resistance has often tended in the past to become superceded to some extent by what has been commonly regarded, with some justification, as skilful formulation by the paint technologist. Consequently, this technology-orientated code of practice has recently been seen to be changing with the realisation in industry, particularly among the larger paint manufacturers, that more importance needs to be attached to the fundamental, scientific principles which govern the polymer's, and hence the paint film's, response to ageing. Certainly, this trend is currently all the more requisite in view of the increasingly high demands that are made of modern surface coatings.

However, despite what, at times, can appear to be a somewhat unsystematic inclusion of "stabilising additives", it can nevertheless be argued that the role of polymers as binders in surface coatings systems as a whole still essentially provides a particularly stern test of their singular, inherent weatherability in service. Consequently, when regarded in this light, the surface coating system, in its narrower context, affords the research worker an interesting model in which to study not only the degradative processes attributable to the "system" as a whole but also those which are particular to the polymer. Furthermore, because of the large surface area to bulk ratio in paint films, it is reasonable to expect that changes in the surface characteristics of the paint on ageing will provide a great deal of valuable information concerning the various degradation processes operational in service.

Thus, having recognised (a) the value and importance of an "in-depth" study of the ageing and weathering of surface coatings, and (b) the inherent qualifications that paint films possess regarding their potentiality as highly informative model systems, the actual feasibility of such a study now requires consideration. In order to be able to assess the performance characteristics of paint films reliably, two main problems appear to exist. Firstly, there is the need for suitable analytical techniques which are capable of monitoring (quantitatively, wherever possible) the multifarious types of changes which occur in paint films during ageing. Additionally, it would be hoped that these techniques, whilst differing individually in terms of the specific information which they each provide, would nevertheless prove to be to some extent complementary in a collective sense. This analytical requirement is probably all the more relevant in view of the conspicuous lack of availability to the paint industry of such instrumentation, most notably in the case of gloss measurement. The second major problem envisaged in this type of study is concerned more with experimental design than actual analysis and is related to the use of artificial weathering techniques alongside those of natural weathering. Whilst artificial methods of ageing can never hope to reproduce the extremely delicate and complex "balance" of deteriorative factors involved in natural weathering(1), they must be considered in view of the length of time which natural weathering experiments take to run. However, correlations between the results of artificial and natural weathering tests, as a means of predicting the performance of a given paint in service, have often tended in the past to be somewhat unsystematic. This has frequently meant that the effectiveness of subsequent modifications to the paint's formulation have invariably proved difficult to assess within the context of an artificial weathering experiment. Indeed, it is probably true to say that until a quick and reliable method of predicting performance is established, new paints will continue to be accepted with caution by the industry. Consequently, it is with this view in mind that the choice and/or design of artificial weathering experiments should warrant careful consideration and evaluation, before the temptation presents itself to indulge in an unjustified over-interpretation of their results.

I.2 Initial Statement of Objectives

On the basis of the foregoing introductory remarks, it seems appropriate, even at this early stage, to try to summarise those objectives which would appear to be of most obvious importance at the outset of a project such as this. However, as yet, this initial "statement of intent" can only really be relatively broadly-based until such time as the "state of play" allows those aspects of the programme's finer structure to be elaborated upon. Nevertheless, the main interests of the present study can be visualised as being directed towards the following aims:-

1) the evaluation of those existing, established analytical techniques which can be envisaged at this stage as being potentially useful in the study of surface coatings' deterioration. At the same time, their all-round applicability to a range of surface coatings systems and/or their particular suitability to one or more systems can be gauged;

2) the development of newer, more novel techniques, especially in those areas of analysis where particular needs exist, such as in the field of quantitative gloss characterisation;

3) the assessment of, and comparison between, the natural weathering performances of a cross-section of the most commercially important paint systems, as characterised by the techniques from (1) and (2) above;

4) a closer, more detailed study of one particular class of paint system in the hope of elucidating the mechanism of binder (and hence paint film) breakdown. By this means, a closer examination can also be made of the way in which the "environmental balance" of prevailing physical and chemical climatic factors might be expected to influence the subsequent weathering pattern. Additionally, the role of the various types of additives (e.g., pigments, stabilisers, etc.) within the paint system as a whole during ageing require evaluation in order to be able to effect formulation improvements scientifically. However, this latter objective can only be realised via the study of a suitably "purpose-formulated" range of coatings which are rather more simplistic and experimental (in the sense of being non-commercial) in nature; and

5) a comparison and correlation, wherever possible, between the natural weathering results obtained in (3) and (4) above and the corresponding results obtained from selected artificial weathering tests on the same materials. It will also be relevant to note how widely applicable each of the various artificial weathering environments are to the various paint systems studied in terms of the correlative ageing responses which they are each capable of inducing.

Thus, it is within the framework of these objectives that this project is initially viewed. Furthermore, these aims are considered to be sufficiently broad in definition as to allow for ample programme flexibility should the need for this requirement arise.

Therefore, having outlined the prospective scope of this study, its various aspects can now be described in somewhat greater detail.

I.3 Factors Comprising Natural Weather

The definition of what is meant by the term "weathering" has recently been reviewed(2). One example of its meaning has been provided by Stager(3) who has defined weathering 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". Whilst this is a fairly rigorous definition, others have been put forward which define aspects relating to the use of polymeric materials in specific applications.

The factors which comprise natural weather or the factors to which a material is exposed during natural weathering have also been summarised by previous workers(3-6) and various of their effects described(4). The most significant of these factors are generally considered to be those associated with radiation, temperature, oxygen, other harmful (e.g., industrial) atmospheric gases, water, micro-organisms, dust and wind (etc.). Of these, the ultraviolet component of natural radiation (i.e., sunlight) is probably the most potent single factor of degradation, although its combination with the infra-red (i.e., heat) component and/or water is believed to be more potent still. However, although it may be true to say that certain elements of an environment, in which a material such as a paint film finds service, may prove to be more deteriorative than others, it is far more important to realise that it is invariably the sum total of all of the prevailing weathering factors, including their many complex interactions, which governs the paint's ensuing performance.

Indeed, when considering the inherent complexity of natural weather together with the particular uncertainties of the British climate, it might perhaps seem doubtful that standardised conditions could ever be expected. However, previous workers have observed that weathering conditions both in the U.K. and elsewhere, when taken over the year as a whole, tend to level out - to quote Estevez(5), "It is worth emphasising that the deterioration (on exposure to natural weathering) is remarkably reproducible, that is, the material exposed under the same conditions will show the same deterioration. It is, of course, this fact that makes the subject worthy of scientific or technical attention, but it is, in its way, quite surprising to find how the varied factors that constitute weathering, acting, it would seem, almost erratically, nevertheless produce the same result year after year in a manner that, within limitations, is predictable". On the other hand, marked variations in weathering response have been observed(7-9) in the case of similar materials exposed at the same site over shorter, seasonal periods of, say, six months, (a) during spring and summer, and (b) during autumn and winter.

For many practical purposes, however, natural weathering exposure tests are too lengthy and so the need for suitable artificial weathering tests arises. (It is relevant to note here that, strictly speaking, natural weathering exposure has, itself, an element of acceleration(5), by virtue of the fact that the test samples are invariably mounted in such a way as to receive the maximum amount of solar radiation).

I.4 Artificial Weathering Tests

With the advent in recent years of more photochemically stable organic binders for use in paint films, accelerated determination of weatherability has grown in importance. The artificial weathering tests that have been devised so far can be divided into three main types, namely:-

a) those involving exposure to, perhaps, just one or two intensified weathering factors, such as in the case of thermal ageing in an oven or ultraviolet irradiation in a UV-cabinet,

b) those in which the samples under test are exposed to a repeating cycle of simulated weathering conditions in a machine running continuously for twenty four hours a day. Again, certain of the elements of this exposure will tend to be relatively intensified compared with those occurring in natural weathering, although usually not to the extent as in (a) above; and finally

c) accelerated natural weathering at a tropical outdoor site such as in Florida in the U.S.A.(10). Paint film deterioration is accelerated here compared to most other locations because of Florida's unique conditions of intense sunlight, high humidity and moderate rainfall coupled with a minimum seasonal effect. Other geographical locations at which weathering sites for this type of outdoor exposure are to be found include Arizona in the U.S.A.(11) and Pretoria and Durban in South Africa(12). Additionally, the prevailing weather patterns at these various sites are generally well documented along with previous performance data for a range of materials.

Another interesting approach to accelerated outdoor weathering involves the concentration of natural sunlight into the sample area by means of a system of mirrors (for increasing the intensity of the sun's radiation) in conjunction with an equatorial mount (for maintaining the samples perpendicular to the sun's rays), the samples being air-cooled. The two types of apparatus which have been 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), differing only in that the latter additionally incorporates a water spray.

However, each of these three types of artificial weathering test has its obvious limitations when it comes to correlating their results with those of natural weathering. Type (a), for instance, is not so much a weathering test as a means of elucidating the particular ageing effects of one or more known deteriorative weathering factors; yet, it has been claimed(15) that simple ultraviolet irradiation of gloss finishes in a UV-cabinet has induced degradation which correlates well with outdoor weathering. On the other hand, however, type (b) does at least constitute an attempt on the part of the research worker to simulate natural weathering conditions as a whole, even though the inherent complexity of the latter undoubtedly precludes this. Nevertheless, it has been with this aim in mind that a number of artificial weathering machines have been developed in recent years, differing essentially in the type of radiation used and the facilities available to control the various elements of their respective operating cycles. Amongst the equipment currently available are the Atlas Weather-Ometer(16), Dew Cycle(17), Xenotest(18), Climatest(19) and

BS 3900 Part F3(20) artificial weathering machines. Comparative assessments of these(21) as well as other(1, 22, 23) instruments have been reported in the literature in which varying degrees of applicability to the prediction of natural weathering performance have been claimed for the methods described. However, it is with respect to this predictive capacity that each of these artificial weathering machines share a common, yet fundamental, shortcoming - namely, their intrinsic inability to reproduce satisfactorily the complex balance of deteriorative factors which comprise a given natural weathering environment. This problem is, of course, accentuated by the existence of considerable variation in natural environments together with the unique pattern of synergistic effects which are operational at each site. Indeed, it is often the irreproducibility of the latter in artificial weathering machines which is the prime cause of the disproportionate acceleration of degradative mechanisms which may, in reality, be relatively unimportant in natural weathering.

However, apart from the design, control and flexibility (wherever possible) of the actual weathering cycle, the design feature of artificial weathering machines which has, perhaps, attracted most attention has been the choice of a suitable ultraviolet light source(24) for irradiation of the samples under test. Suitability, in this respect, must be judged on the extent to which the spectral wavelength distribution of the light emitted "matches" that of natural sunlight. Consequently, it is on this basis that the xenon-arc lamp is currently regarded as offering closer correspondence with sunlight than any other artificial source(5, 25, 26) (although, even so, there are still certain limitations in its use such as the tendency for its spectral distribution to change and also for its light intensity to diminish during ageing of the lamp(27)). It has, therefore, been mainly due to the favourable results obtained with the xenon-arc lamp that the Xenotest(18) apparatus has gained in popularity over recent years. On the other hand, possibly the most successful "cycle" of operation has been that of the Dew Cycle apparatus. This has been especially so in the United States where it was developed(17), despite the many changes in type and design of cycle that have been and continue to be made in weathering machines(28). And yet, the Dew Cycle's widespread use has, almost predictably, invited sufficient criticism over its ten years' history for it to have been recently re-evaluated(29) with a view to possible modification.

Consequently, it is in view of their inherent deficiencies that the status of artificial weathering machines still remains somewhat uncertain. This impression is readily gained from the literature in which a variety of contrasting opinions are expressed regarding the extent to which, if at all, correlation exists between artificial and natural weathering. However, there is little doubt that some degree of correlation can be obtained when specific conditions such as machine type, natural weathering location, paint type and rating method are pre-selected. Indeed, Estevez(5) emphasises that the degree of acceleration obtained in an artificial test depends upon, and is therefore subsequently descriptive of, both the particular weathering machine used and the particular nature of the material exposed. He goes on to recommend that as extensive and, yet as specific a knowledge as possible of both the outdoor and the particular artificial weathering responses should form the basis of any correlative judgement. The real difficulty, therefore, appears to lie in the evaluation of new materials (e.g., new binders) for which no previous natural weathering experience exists. In these cases, the role of the artificial weathering test is essentially restricted to providing information regarding the relative effects of formulation changes, a role, incidentally, which it has long been considered to fulfil most usefully.

Finally, the last of the three main types of artificial weathering test mentioned previously, i.e., type (c), accelerated natural weathering, can reasonably be considered to approximate closest to natural (i.e., non-tropical) weathering conditions when compared with the previous types (a) and (b). Whilst its accelerating nature necessarily implies a similar "imbalance" of naturally-occurring deteriorative factors, this "imbalance" is less serious than in the case of the various mechanical devices described previously. This has lead to a number of workers preferring accelerated natural weathering to the use of type (b) weathering machines on the grounds of reliability and despite its relatively lesser accessibility. However, although Florida, for example, requires shorter testing times than most locations, it is now being found that many of today's modern finishes are requiring at least two years' exposure there for definitive testing. Hence, the emphasis has shifted a little recently towards the utilisation of the EMMA and, more especially, the EMMAQUA equatorial mount. Ageing studies involving the latter have shown it to correlate well with exposures in hot, sunny climates such as in Arizona(11) and Florida(30), but much less so with more temperate climates such as in the U.K.(21).

Thus, although there is still an ever-increasing need for the development of newer, artificial weathering techniques which can be "programmed" to simulate more closely a given set of natural weathering conditions, the difficulties involved in achieving this may now be more clearly appreciated. Whilst existing methods may suffice, in certain cases, for the evaluation of minor modifications to existing, well-characterised materials, improved methods are constantly being required for the rapid and commercially-important assessment of the likely durabilities of newer, more stable polymers. However, this current hope is by no means a despairing one, especially in view of the deeper understanding which has been gained over recent years concerning the complexity of natural weather coupled with the increasing sophistication of artificial weathering test equipment.

I.5 Analytical Techniques

The full range of analytical techniques now available for use in the study of surface coatings' deterioration is just about as wide and varied as the range of ageing effects which are being followed. These techniques can, however, be conveniently divided into two main types, namely, (1) those which are associated specifically with monitoring surface changes, and (2) those which are more concerned with changes in the bulk properties of the coating. Of these two types, obviously the surface techniques will be particularly appropriate in a study of paint film deterioration. In addition, they can be considered to be further sub-divided into predominantly optical, physical and chemical methods. On the other hand, changes in bulk (e.g., mechanical) properties, in the case of most coatings' applications, tend to be somewhat less informative on their own of the ageing processes involved. This, however, is not surprising in view of the large surface area to bulk ratio which characterises surface coatings. Nevertheless, the different type of additional information which can be gained from bulk techniques frequently proves to be of great value when considered in conjunction with that relating to surface phenomena. Indeed, it is worth emphasising that it is through this sort of collective consideration, of the total amount of data made available by the various methods of analysis, that the potentially most informative combination of techniques can be deduced for monitoring the ageing response of a particular material to a given environment.

The most important of the many analytical techniques used to date in the characterisation of surface coatings are now reviewed, with particular reference to aspects of gloss and its measurement.

I.5.1 Surface Techniques

I.5.1.1 Optical Methods

I.5.1.1(a) Gloss

Gloss, together with colour, represent the two most important features of a surface coating with respect to its visual appearance (31-34). In this context, gloss is a subjective phenomenon which, historically, has proved difficult to define in precise terms. Harrison's (35 - 37) study of the subject lead him to conclude that the gloss of a surface was not a simple physical property, nor was it a property independent of the observer and his surroundings. Indeed, gloss, as such, could be considered to be something of a psychological Gestalt, in as much as it was an appraisal of a physical situation taken as a whole. Nevertheless, despite the inherent complexity of gloss, which has so far precluded the evaluation of its total visual impression, various attempts have been made to define it and various of its angular quantities. For example, to quote Harrison(36): "Gloss is not a single sensation, but a complex of at least three simpler sensations. These were found to be: sharpness of mirror image, variations in the brightness of the 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". On the other hand, Hunter(38, 39) had previously set out to define six types of gloss based on his observations, whilst other workers(40, 41) have also reported their own impressions. However, a more modern rendition of what is meant by the gloss of a surface has recently been put forward by the International Commission on Illumination (CIE) who formally define it as follows(195):

> "Gloss (of a surface): Directionally selective reflecting properties responsible for the degree to which reflected highlights or the images of objects may be seen as superimposed on the surface".

Generally, however, gloss can be regarded as a complex phenomenon associated with the physical nature of a surface and the way in which it affects the spatial distribution of reflected light. The fact that the fundamental laws governing the reflection of light have been known for a very long time, coupled with the amount of general agreement which was found to exist amongst earlier workers when describing the various factors which affect gloss, formed the basis upon which gloss assessments were initially made. Indeed, over the years, numerous systems have been designed for the purpose of gloss measurement; a situation which appears to be symptomatic of the uncertainty which still exists concerning the best method by which to obtain meaningful results which can be correlated with those obtained by visual assessment. A comprehensive review and classification of these systems has recently been made by König(42). From these various systems, three main types have emerged, each of which is represented by its own selection of instruments. These three types are now briefly described.

I.5.1.1(a)(i) Specular Gloss-Meters

The so-called "specular gloss-meter" (also commonly referred to as a "reflectometer") is basically a reflection photometer and is, perhaps, the simplest form of gloss measuring device developed over the years. It consists essentially of three main parts; namely, an incandescent light source, a port 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, i.e., 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 arbitrary "gloss value" of one hundred units for all angles of the incident and the reflected light. The general layout of a specular gloss-meter is shown in Figure 1(a); variations between different instruments being mainly concerned with the geometry of the illuminating and viewing conditions.

It is now forty years ago since the first photoelectric specular gloss-meter was described by Hunter(43). This work lead shortly afterwards to the adoption by the American Society for

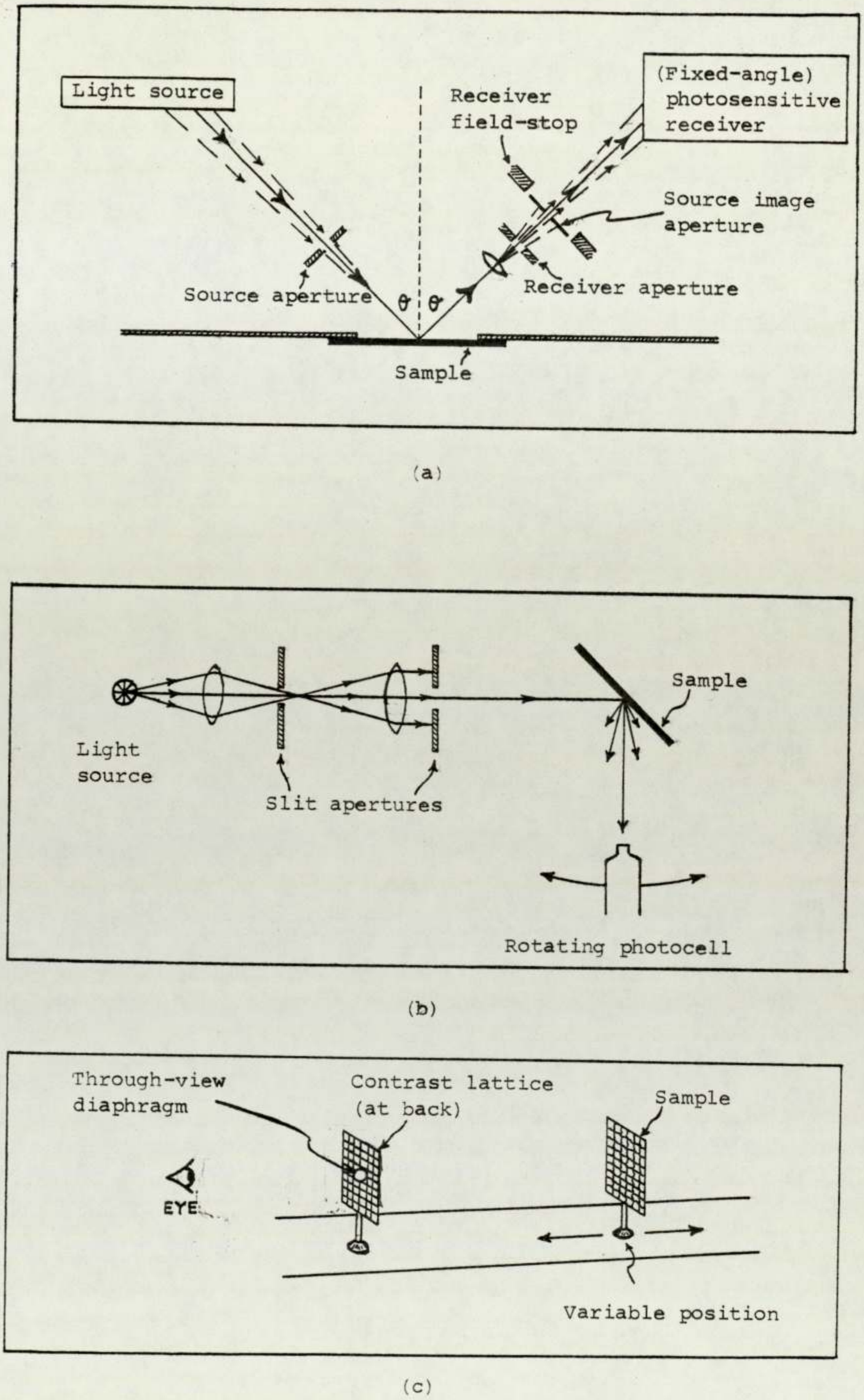


FIGURE 1 - General layout of (a) a specular gloss-meter,
(b) a goniophotometer, and ,
(c) a contrast gloss-meter.

Testing Materials (ASTM) in 1939 of the ASTM D523-53T Tentative Method of Test for Specular Gloss. Further work by Hunter(44) showed that a specular angle of 60° appeared to be the most generally useful condition for the examination of paint films of intermediate gloss, although the 45° gloss-meter has also been claimed(45) to be capable of grading samples in reasonable agreement with visual assessments for a wide range of surfaces. For particularly high gloss values (i.e., over 70), however, 20° specular geometry was found to give better resolution, whereas for low gloss values (i.e., below 30), 85° geometry was more appropriate. Indeed, it was during the course of this instrumental development that a great deal of work went into the choice of dimensions and tolerances for the source and receiver apertures(46); this was in order that any error contributed by them be limited to a maximum of one gloss unit at any point on the scale, even when measured on different instruments(47). However, a more recent round robin survey by Johnson(48) revealed a general lack of agreement between gloss readings obtained from different laboratories using the specular gloss-meter system, attributable mainly to poor standardisation and maintenance of the instrumentation. Consequently, this obviously unsatisfactory state of affairs was to lead shortly afterwards to the setting up, on an international basis, of a programme of close co-operation, between the various members of a selectively appointed task group, aimed at standardising specular gloss-meter (reflectometer) systems for the evaluation of various degrees of gloss. One of the major outcomes of this collaborative study, according to a recent article by Zorll(109), was that the various members (i.e., 20°, 60° and 85°) of the gloss-meter "family" were each evaluated in terms of their particular applicability (i.e., reliability and closeness of agreement with subjective visual gloss assessment) to specific levels of gloss. These findings are currently being written into the already existing International Organisation for Standardisation document (ISO 2813) in which the international standardisation of the 60° reflectometer is described. Hence, for the time being, it can be said that with ISO 2813, an international standard is available which meets most practical needs, certainly in industry at least.

Despite their apparent shortcomings, in terms of both the accuracy and reproducibility of their results (48, 55), the very considerable amount of attention which the design and use of specular gloss-meters (49 - 54) have nevertheless attracted over the years reflects, to a large extent, the value placed on their favourable aspects such as their intrinsic simplicity and ease and speed of analysis. However, although specular gloss-meters are still widely used, especially in industry, the fact remains that the total visual impression of gloss is characterised, not just by the specular reflection, but by the angular distribution of the reflected light. Consequently, an instrument is called for in which the photosensitive receiving device (i.e., photocell) is movable in order to be able to measure this angular distribution. Such an instrument is called a "goniophotometer".

I.5.1.1(a)(ii) Goniophotometers

The term "goniophotometer", describing, as it does, any instrument capable of measuring the intensity of light reflected from a given surface as a function of viewing angle, is to be much preferred to the relatively meaningless term "gloss-meter". The basic layout of a goniophotometer is shown in Figure 1(b) where it can be compared with that of the specular gloss-meter (Figure 1(a)).

The basic technique of goniophotometry, however, is by no means new. Indeed, the earliest known goniophotometer can be dated back as far as 1762, having been devised by Bouguer(196) in an attempt to corroborate Lambert's (cosine) law for uniform diffusers (i.e., matt reflectors) by experimental evidence. Consequently, in view of its long history, it is somewhat surprising that further reference to goniophotometers should have taken as long as until the early part of this century to reappear in the literature, and, even then, only in isolated reports(110, 197, 198). And yet if this is surprising, it is quite unaccountable as to why it has only been in recent years that the true potential of this type of system for gloss characterisation has been fully realised. It is, therefore, not surprising that this realisation should have subsequently stimulated a great deal of activity in this instrumental sector, both in terms of system design and data evaluation. A review of the more important recent developments in goniophotometers up to 1971 has been made by Zorll(34), although further notable advancements have taken place since then.

However, it has really only been over the past decade or so that reports of relatively high performance goniophotometers, by present day standards, have appeared in the literature. For instance, a goniophotometer system that combined high accuracy of measurement, as well as automatic data plotting, with an otherwise relatively uncomplicated design was described by Hoffman and Kosbahn(56) in 1966. In the same year, a new commercial instrument, the Zeiss GP 2 goniophotometer, was described by Loof(57). Although only manual in operation, the GP 2 has nevertheless since found widespread use in practice, mainly because it corresponds to the need for an instrument that provides for a compromise between sufficient accuracy of measurement and restriction to only the most important optical elements. Further instrumental developments attributable to Veiel(58) and Karagueuzoglou and Poisson(83) were reported shortly afterwards, in between which, in 1968, a paper appeared in which Colling et. al.(59) set out to describe the modification of an already existing piece of analytical instrumentation for goniophotometric purposes. The instrument in question was a Unicam SP500 spectrophotometer which could be easily adapted for use as what would essentially be a "spectrogoniophotometer", i.e., a goniophotometer with added (secondary) provision for studying the spectral modification of goniophotometric data(60). This apparatus was shown by the authors to have been successfully applied to an investigation into the relationship between the gloss of a paint film and the nature of its surface defects. At about the same time as this, further developments in spectrogoniophotometers were being made, notably by Billmeyer and his co-workers(61, 62) in the U.S.A. Once again, advantage was taken of the availability of an existing piece of alternative instrumentation, in this case a Brice-Phoenix light-scattering photometer(63), which could be suitably modified for spectrogoniophotometric use. The construction and performance of the instrument was discussed(62) with particular reference to the properties of typical goniochromatic(60) samples. More recent related studies(64 - 67) by Billmeyer, which have been concerned with the prediction of colour and reflectance of paint films from theory, have involved the use of the Zeiss DMC 25 recording spectrophotometer for which a goniophotometric attachment had been previously described(68).

Whilst activities in the field of instrumental design have continued elsewhere(69 - 71, 134), the most recent developments in the U.K., however, have been those reported by Carr(72), concerning automation of the Zeiss GP 2 goniophotometer for use in measuring both the specular reflection and the haze of paint and ink films, Edwards(73), in describing the design and operation of a simple high resolution "laser gonioreflectometer", and finally Quinney and Tighe(74), in their goniophotometric studies of film deterioration processes. The latter study, which is to some extent precursory to this present work, is particularly significant in view of the notable lack, if not absence, of previous application of the goniophotometric technique to the study of paint film deterioration. Most of the previous workers mentioned have tended to restrict their use of goniophotometry to the basic gloss characterisation of and comparison between different types of surfaces. Other workers, however, have studied the effects of various changes within a given paint system on its gloss but not, apparently, the effects of weathering. For example, Colling et. al.(59) have studied the effects of surface defects (brought about by various methods of application) and pigment volume concentration on gloss, whilst Guillaume(75) has used the Zeiss GP 2 goniophotometer for critical pigment volume concentration determination. Other workers, meanwhile, have applied the goniophotometric technique to the assessment of such film properties as degree of pigment dispersion(76, 77) and surface microtexture(78). However, the apparent lack of interest shown in the use of goniophotometry in ageing studies is still somewhat surprising considering the particular suitability which such a sensitive technique as this would be expected to have for following even the most subtle ageing effects.

Finally, having obtained them, the question arises as to what is the best way to interpret goniophotometric curves$^{(41, 79)}$, typical examples of which are shown in Figure 2 for various levels of gloss. There are several possible ways of combining the experimentally determined values to yield a conveniently handled quantity which may be then compared with subjective gloss assessments. However, it has become commonplace to consider three quantities in particular, namely, 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 by Hausstühl and Hamann$^{(80)}$ to correlate much more readily than simple photometer reflectance values with empirically judged image sharpness and contrast, and surface lustre. This has been confirmed independently by Hartmann$^{(81)}$, although Kosbahn$^{(82)}$ prefers a slightly different presentation of goniophotometric results in abridged form. It is obvious from this, therefore, that, although an ASTM Recommended Practice for goniophotometry does exist$^{(199)}$, a much wider common agreement will need to be reached regarding the interpretation of goniophotometric data, in addition to instrumental design, before goniophotometers can be standardised in the way that specular gloss-meters have been recently$^{(109)}$.

Following on from specular gloss-meters and goniophotometers, the third main type of gloss measuring device is the so-called "contrast gloss-meter".

I.5.1.1(a)(iii) Contrast Gloss-Meters

Whereas specular gloss-meters and goniophotometers are designed primarily with purely optical aspects in mind, contrast

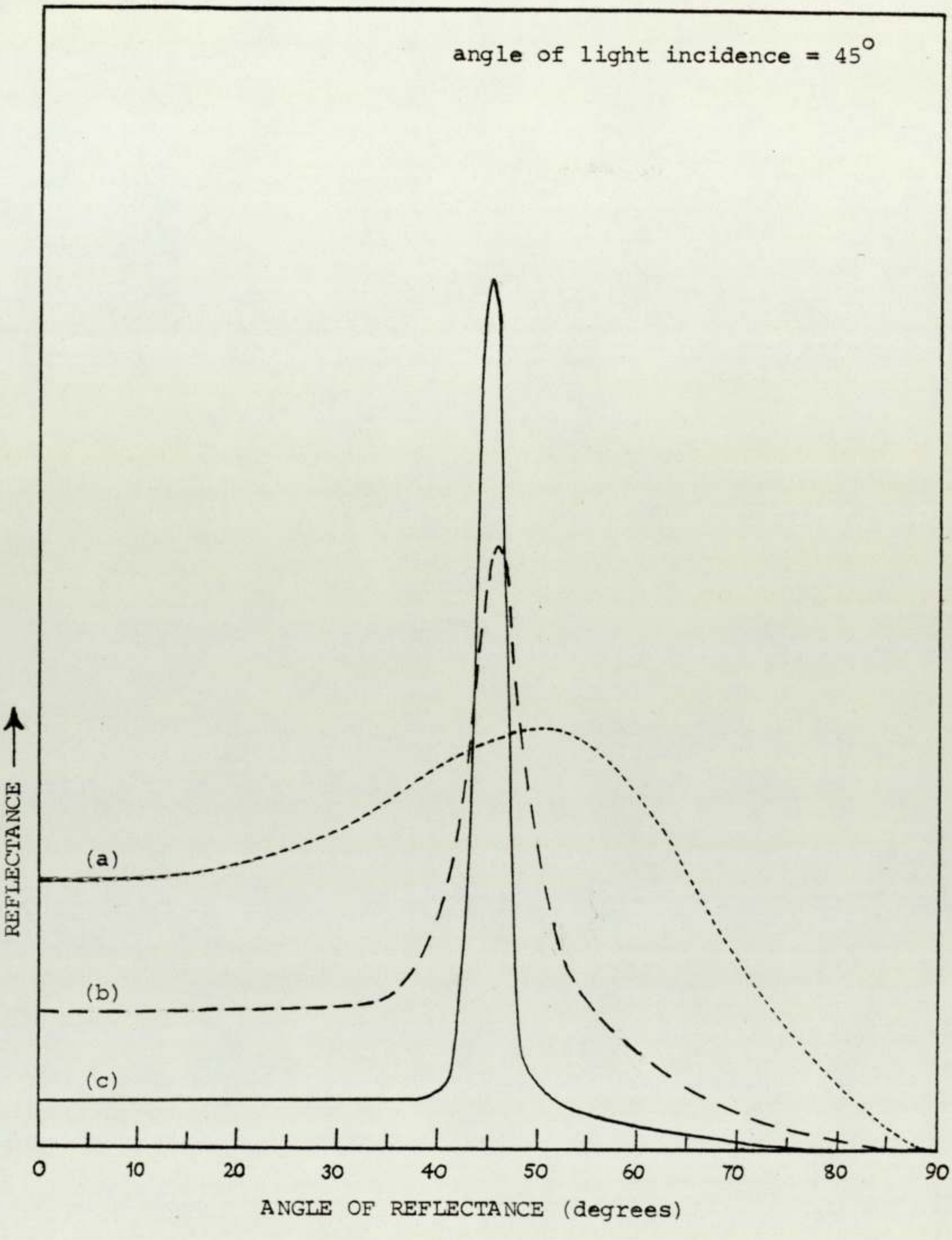


FIGURE 2 - Typical goniophotometric curves for (a) low, (b) medium, and (c) high gloss surfaces.

gloss-meters, on the other hand, are more concerned with the visual evaluation that a human observer makes regarding the distinctness of an image observed at the sample surface. This evaluation is made by means of "analysing" the degree of contrast at border lines between bright and dark fields when viewed using the sample surface as a mirror reflector. 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 the normal to the sample surface at which the pattern can be seen is taken as a measure of the gloss(84) (see Figure 1(c)). Although evaluation of the gloss of a surface with this type of instrument can be seen to be closely related to a specific mode of visual gloss assessment, the fact that human evaluation is also involved inevitably introduces some degree of observer error which, in turn, makes the standardisation of such devices difficult. More recently, however, a system proposed by Hunter(85) demonstrates that human factors of influence can be completely eliminated. Due to the inherent simplicity of their arrangement, various versions of "contrast gloss-meters" are found to exist. One device, which was later to be developed commercially, was reported by Goodier(86) as being particularly applicable to the testing of high gloss finishes, as encountered in the automotive industry. A different type of contrast gloss-meter was later described by Freier(87). Whilst this latter device was also mainly applicable in the range of medium to high gloss, it must be said that, in general, the main feature of contrast gloss-meters, when compared to their specular counterparts, is their extended range of applicability(88) towards the domain of medium and matt gloss.

Finally, the general concept that gloss should be linked with the sharpness of an image, as perceived by an observer, has been expressed. These studies were carried out by Bohmann(89), who was also able to provide experimental evidence for the relationships derived in using a modified Randel gloss-meter(88).

Despite the considerable advancements that have been made in the field of gloss measurement, a completely satisfactory solution to the problem of measuring gloss objectively is still wanting, in particular if it is required that the instrumentally obtained value or values shall agree with the subjective judgement of gloss arrived at by visual examination. However, it should be borne in mind that there are some aspects of visual gloss assessment which, as yet, are not and, maybe, in some cases, cannot be represented satisfactorily in any instrumental system of gloss measurement yet devised. For instance, a human observer makes use of both eyes to evaluate a glossy surface and, furthermore, the eyes move fairly arbitrarily during visual inspection. Aspects such as these enter the realm of the psychologist from where it must appear almost unimaginable that the required level of instrumental sophistication could be reached whereby even such non-technical phenomena could be duplicated in an analytical device. Indeed, even if such a device could exist that possessed all the features of human observation, it would probably be so sophisticated as to render it impracticable, as well as economically unviable, as a routine instrument for simple field tests.

Following on from this review of gloss and its measurement, we now come to the other visual impression by which we characterise a given surface - namely, its colour.

I.5.1.1(b) Colour

The perception of the colour of a given surface, like its gloss previously, is a sensation arising from the manner in which light incident upon the surface is reflected into the eyes of the beholder. However, whereas the gloss is characterised by the spatial distribution of this reflected light, the colour is characterised by its spectral distribution (within the visible range of the electromagnetic spectrum, see Figure 3(a)). The radiation from the viewed surface which gives rise to colour perception is called a colour stimulus which, when received by the retina, results in the transmission of impulses along the optic nerve to the sight centre in the brain, which produces the visual perception of colour(90, 94) (and similarly with the gloss). Whilst such stimuli can be registered and measured by instrumental means, the actual (psychological) perception of colour to which they give rise remains a unique sensation which can only be experienced by a living being. The study of a perception as such, without reference to either what is known or believed of its physical or physiological causes, is termed phenomenology. Rather than enter into any detail here regarding the more phenomenological aspects of colour, together with its systematisation, the reader is referred instead to standard texts(31 - 33, 91, 92) which adequately describe this part of the subject.

Of greater interest and relevance, however, to a practical study of, say, colour changes (as opposed to characterisation) in surface coatings on ageing, is the physical measurement of the stimuli which give rise to the total visual perception of colour. The colour stimulus is determined by the composition of the light with which the

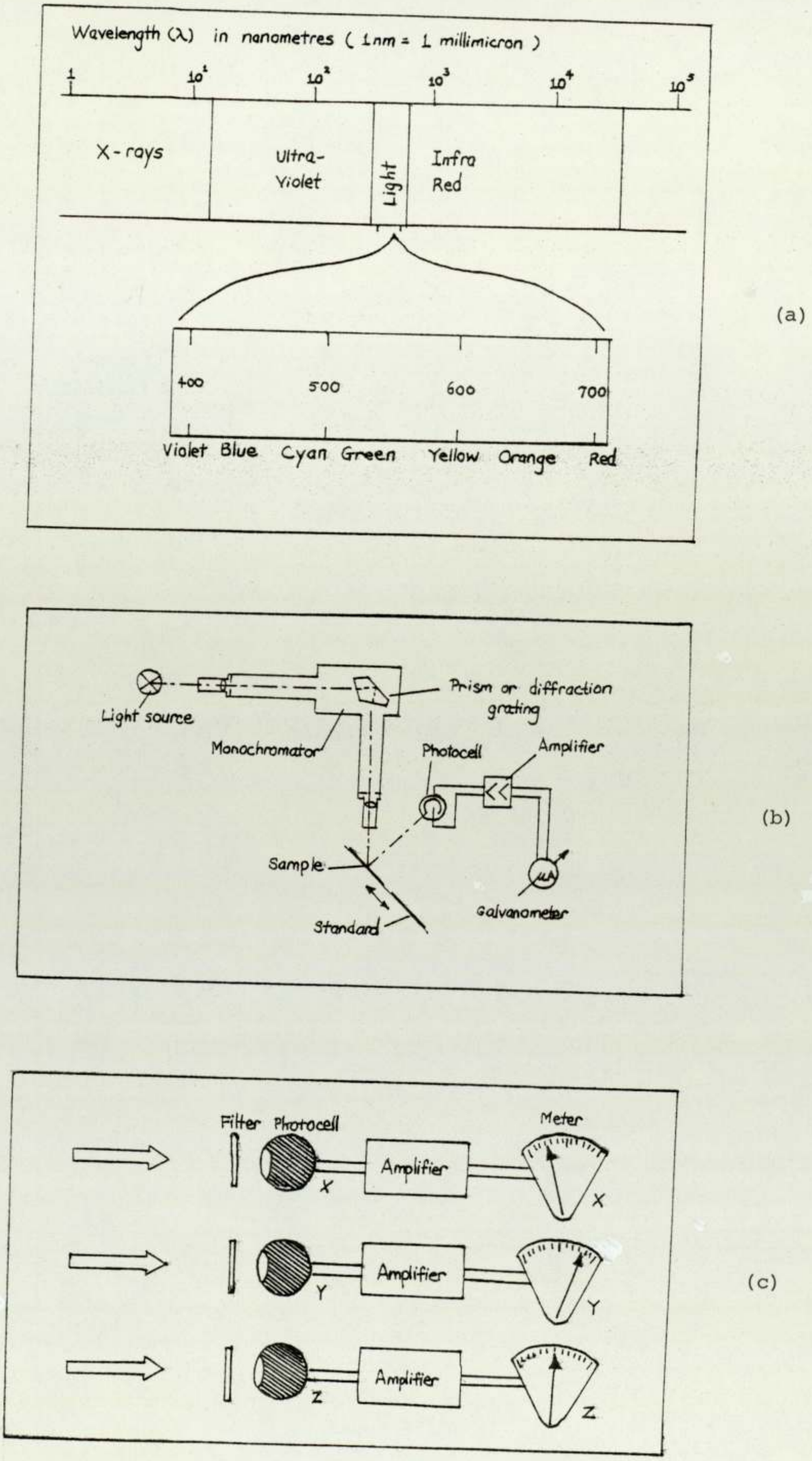


FIGURE 3 - Colour Measurement : (a) the visible range of the electromagnetic spectrum, and general layout of (b) a spectrophotometer, and (c) a tristimulus colorimeter .

surface is illuminated, and by that part of the incident light which is reflected by the surface, i.e., by the reflection or remittance spectrum of the surface. In certain cases, the angle of illumination and/or viewing can also affect the colour perceived from a given surface. The instruments that have been developed over the years for use in colour measurement can be considered to be of two main types - namely, visual and photoelectric colorimeters.

I.5.1.1(b)(i) Visual Colorimeters

Visual colorimeters, in which the light receiver is the human eye, are based on either additive or subtractive colour mixing. The additive types, which include Maxwell's disc and Guild's, Wright's and Donaldson's colorimeters, 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. The significance of using the three spectral colours, red, blue and green, is derived from the fact that they have been defined by the International Commission on Illumination (abb., CIE in reference to the French name, Commission Internationale de l'Éclairage) as the primary colour stimuli, and it is from their relative intensities that the so-called CIE system <u>tristimulus</u> values are derived and taken as the specification of the colour. Additionally, it can be noted here that the rods in the retina are believed to have stimulation thresholds in three primary spectral regions, although their exact position and form is still very much a subject for discussion(92).

In contrast to the additive type of colour mixing, instruments operating according to the subtractive principle involve colour matching of the sample surface with light reflected by a white background, in front of which three series of variable-strength filter glasses are introduced. One of the most common instruments based on this design is the Lovibond Tintometer which has previously enjoyed fairly widespread use in the paint industry. In a more recent modified form, it is possible to convert the filter readings to the previously mentioned CIE co-ordinates.

However, visual colorimeters in general suffer from the expected error susceptibility that any element of human assessment invariably introduces. Consequently, visual colorimeters have tended to lose much of their importance in colour control in industry in favour of photoelectric colorimeters.

I.5.1.1(b)(ii) Photoelectric Colorimeters

There are currently two main types of photoelectric instrumentation in use in colour measurement; these are (reflection) spectrophotometers and tristimulus colorimeters.

Firstly, the spectrophotometer, which has long been the basic tool for fundamental research in colorimetry, is an instrument which measures the variation in intensity of surface reflectance as a function of the wavelength of the reflected light. In this way, it can be seen to be analogous to the goniophotometer in gloss measurement. Many such spectrophotometers are available, most of which are now fully automated, including some with digital-computing accessories for conversion of spectrogram data to CIE co-ordinates (which would otherwise be a tedious operation). A typical instrumental layout is shown in Figure 3(b) in which it can be seen how 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. However, it should be stated that, as with gloss measuring devices, variations in instrumental design, particularly with respect to the geometry of the optical system, inevitably give rise to differences in the results obtained. This is especially so in cases where extreme precision is required, such that a given reflectance measurement is often found to be, to some extent, characteristic of the instrument from which it was taken.

However, whilst the reflection spectrogram is characteristic for a given coloured surface, it is difficult to form from it a mental picture of the colour, even after considerable experience. Equally difficult, of course, is the interpretation of colour differences corresponding to a pair of spectra. This is why the spectrogram data is generally computed to give the corresponding CIE system co-ordinates which, it is believed, afford a slightly better, more definitive colour specification. Indeed, it has been with this concept in mind that the second and more recent "generation" of photoelectric instrumentation, namely the tristimulus colorimeters, has been developed.

The photoelectric tristimulus colorimeters (91, 92) are instruments that evaluate directly the so-called CIE system tristimulus values of a given coloured specimen. A simplified representation of the principle upon which this type of instrument works is shown schematically in Figure 3(c). The main difference between this type of colorimeter and the spectrophotometer described previously is that, whereas in the latter the monochromatic light is obtained by means of prisms or diffraction gratings, in tristimulus colorimeters only three narrow bands of light are used, corresponding to the three primary colour stimuli - red, blue and green light. Consequently, an abridged spectrogram is obtained in effect which, more relevantly, describes the appearance of a given colour directly in terms of its primary colour content (according to the CIE system). Additionally, tristimulus colorimeters are quick and easy to use, and tend to be more robust and much cheaper than spectrophotometers. These advantages, which go a long way towards explaining the current overriding popularity of tristimulus colorimeters relative to other types of colour measuring instrumentation, have tended to outweigh the fact that the values which they give are more or less approximate values, which may in the case of some instruments show wide differences from the correct values in some regions. Hence, they have tended in the past to be regarded as unsuitable for absolute measurements but very useful in a number of other ways, particularly in the measurement of colour differences.

However, many of the shortcomings in colour instrumentation are currently being met by recent technological advances in this field. Indeed, as described recently by McLaren(93), sophisticated equipment is now available which can put figures to colour differences that the eye takes in its stride. McLaren highlights three developments, in particular, which are likely to have a marked impact in the field of colour measurement. Firstly, there is the recent revolution in the design of colorimeters which, by the use of modern electronic techniques incorporating integrated circuitry and digital display, are able to combine reliability with speed of use and reasonable cost. Secondly, current work on colour difference measurement can be expected to result in objective methods of specifying tolerances which will be more reliable than the subjective judgement of a single expert colourist. And thirdly, powerful digital computers are now available, also at reasonable cost, which can be linked to spectrophotometers and colorimeters so that the complex mathematics of colour match prediction and colour difference calculation can be easily carried out.

Thus, the instrumental measurement of colour is demonstrably further advanced than that of gloss, mainly by virtue of the fact that the various stimuli which give rise to the overall visual perception of the colour of a surface are currently more clearly understood than those pertaining to its gloss. Consequently, the level of sophistication of colour measuring instrumentation has also tended to increase concomitantly with the theory and in further advance of that for gloss measurement. Indeed, this state of affairs still prevails and, as can be gauged from just some of the more recent publications which have appeared in the literature relating to the theory(94 - 100) and measurement(62, 93, 96 - 108) of colour, will probably continue to do so until such time as the eye's sensitivity to changes in gloss can be evaluated as far as its sensitivity to colour changes has been.

I.5.1.1(c) Microscopy of Surfaces

Surface microscopy, over recent years, has proved to be a valuable analytical tool for use by the paint chemist in the study of surface coatings and, more especially, changes which occur in them during ageing. The unique, albeit qualitative, type of information which can be obtained from surface microscopy can often prove to be of immense value in providing a direct insight into the nature of the various defects which may be present in a given surface.

However, the simplest form of surface microscopy, optical (or light) microscopy, has proved to be of strictly limited value in its application to the study of irregular surfaces such as those commonly encountered in paint films. The intrinsically low resolving power and very small depth of focus achievable with the optical microscope, coupled, in the case of pigmented specimens, with their inevitable subsurface light scattering effects, has meant that the fine structure of a given surface has proved extremely difficult, if not impossible, to determine with any accuracy using this instrument. Consequently, when the optical microscope became superseded, in terms of performance, by its more illustrious successor, the electron microscope, attention quickly turned to what could be additionally achieved using this latter instrument.

In this respect, electron microscopy, when applied to the in-detail analysis of surfaces, has, indeed, proved over the years to be the powerful viewing technique which the surface coatings research worker had been looking for in order to lend credibility to his impressions of the actual physical appearance of a given surface. For the study of the surface(111 - 115) and inner structure(111 - 114, 116, 117) of paint films, as well as for following changes during ageing (113 - 115, 117 - 121), electron microscopy came to be, as it still remains, of considerable importance. Of particular significance at the time of its early usage was the provision it made for enabling even the most subtle initial changes in a given paint film on ageing to be readily observed. In this way, valuable information regarding the mechanism of film breakdown could be obtained much earlier in the paint's exposure history than had previously been possible by visual inspection or optical microscopy. Furthermore, the electron microscopy of both naturally and artificially weathered surfaces was able to show quite clearly that loss in gloss could be associated with an increase in surface roughness(118 - 120). However, Wilska(122) has pointed out that, although loss in gloss is almost invariably related to film deterioration, exceptional cases do exist where gloss measurements of weathered surfaces may be misleading if compared unequivocally with corresponding electron micrographs; more damaged surfaces, for instance, having occasionally been found to give higher gloss readings.

Despite the fact that electron microscopy is, by no means, a routine technique, it has obviously had much to offer its users over the years in the field of surface characterisation. Yet, it is not without its procedural difficulties, particularly with respect to sample preparation. Indeed, both the preparation of surface replicas(112) for surface topography and ultramicrotomed sections(123) for bulk structural studies are often troublesome operations, made even more difficult by the general fragility of surface irregularities and the large particle diameters of some pigments respectively. However, difficulties of this nature are now avoided by the use of the scanning electron microscope(124), perhaps better known as the Stereoscan, which, in recent years, has effectively taken over from where the electron microscope left off. In addition to the relative ease of sample preparation, scanning electron microscopy has another particularly important advantage over electron microscopy, namely the exceptional depth of focus which can be achieved instrumentally. Consequently, the Stereoscan has been able to produce micrographs of unprecedented clarity showing the three-dimensional topography of all types of surfaces. Furthermore, the Stereoscan can be used to great advantage over a wide range of magnifications (from about 20x up to 50000x) that encompasses both that of the optical and electron microscopes. Hence, just as the electron microscope quickly gained recognition for its usefulness in surface analysis, so the scanning electron microscope has since gained acceptance as the most powerful and versatile viewing instrument currently available for the direct observation of coatings' surfaces(125 - 127) and changes which take place within them during ageing(126, 127).

However, as with the electron microscope, the basic cost of the equipment precludes the Stereoscan from ever becoming a routine instrument which the majority of paint companies in the surface coatings industry could afford. Nevertheless, there appears to be a current trend for paint research departments to find, from within their budget, sufficient funds to finance their use of a Stereoscan by contractual agreement with, for example, university and larger industrial research departments.

I.5.1.1(d) Interferometry

Interferometry, which nominally embraces all forms of interferometric techniques, is another useful means of detecting small changes in surfaces. Of particular interest here, however, is interference microscopy which has been shown by previous workers to be of value in not only helping to "fingerprint" irregular surfaces(59, 128 - 130) but, more especially, in accurately assessing decreases in film thickness(131, 132) brought about by ageing. The technique itself, in common with all other interferometric methods, is based on the phenomenon of interference fringes which are formed when an optical flat is placed either next to or on the sample (nonflat) surface. These interference fringes can be thought of as "profile lines" of the sample surface and are extremely sensitive to small variations in film thickness. Changes in film thickness arising from ageing can also be determined via a spectroscopic(133) as well as microscopic interferometric technique, although the former is only suitable for thin clear films on reflecting substrates.

However, in comparison with the more direct microscopic techniques previously described, interference microscopy, and indeed interferometry in general, has not been widely used to follow film degradation since, as deterioration increases, the interference fringes become more diffuse and tend to merge with the background.

I.5.1.2 Physical Methods

I.5.1.2(a) Surface Roughness

The assessment of the surface roughness of a given coating material is of particular relevance in view of the effects which surface irregularities are known to have on a number of surface properties, although especially on gloss. Indeed, it is usually within the context of gloss evaluation that surface roughness studies are undertaken.

Strictly speaking, surface roughness studies can be considered to fall into two distinct categories. On the one hand, there are those methods which yield predominantly qualitative information, such as surface microscopy(51, 113, 114, 118) and interferometry(59, 129) as described previously. Although their respective data almost exclusively relates to the nature rather than size of surface defects, it can, in suitable form, also be treated in a semi-quantitative manner(59). However, it is the second category which is concerned with the actual quantitative size measurement of surface roughness irregularities. This is commonly achieved by means of an instrumental technique involving the movement of a point probe over the surface which then effectively traces out it rugosity, computing, in the process, the average height of the roughness irregularities. This type of technique has been used successfully by a number of workers(78, 135 - 139), both for simply characterising coatings surfaces, usually in relation to their gloss, and also as a means in itself of monitoring the effects of outdoor weathering(139).

More recent developments in this field, however, have seen the application of ray deflection mapping and schlieren optics to the quantitative characterisation of paint surfaces(140). When applied to surface measurements, the principle of both techniques is the measurement of the change in angle of deflection of a reflected ray of light which is caused by a change in the surface slope; where the two techniques differ lies in how this measurement is made. In this way, ray deflection mapping(140), although used to measure surface profiles, has been found to be particularly suited to the quantitative study of levelling. For example, it may be used to measure the slope and amplitude of ridges in an unlevelled surface, and for following the flow-out of freshly applied coatings. The schlieren technique(140, 141), however, by virtue of its potentially greater spatial resolution, has been developed for the visualisation of surface defects and for their quantitative estimation. Furthermore, by the use of opaque and coloured transparent schlieren stops, different facets of surface structure can also be revealed.

This recent application of ray deflection mapping and schlieren optics to surface characterisation has, to a certain extent, overcome one or two of the deficiencies inherent in the techniques previously mentioned. For example, the tracer point technique, whilst being capable of producing very accurate surface profile measurements, only allows for a relatively limited probe travel, thus prompting the averaging of several readings. This, of course, also renders it unsuitable for following the dynamics of levelling and flow-out. Similarly, optical interference methods, whilst precise in measurement, are generally not so easy to use and also tend to be less amenable to precise interpretation when compared with the ray deflection mapping and schlieren methods. Therefore, with respect to the future utilisation of these two latter techniques, it would seem reasonable to expect that their demonstrably high sensitivity and precision, harnessed, as it is, within relatively simple instrumentation, will, indeed, prove extremely useful in, say, the research and quality control laboratories of manufacturers concerned with high quality surface finishes.

I.5.1.2(b) Surface Energetics

Under the broad heading of "surface energetics" are included those energy factors commonly associated with the processes of wetting, spreading, and adhesion(142 -146) of (a) a given coating when freshly applied to a substrate, and (b) a given liquid in contact with the formed coating surface. However, although a lack of or loss of adhesion between coating and substrate frequently occurs before and after weathering respectively, often resulting in a lifting off of the film (ref. (a) above), it is usually in connection with the more subtle changes in the coating surface (ref. (b) above) that ageing studies are concerned. Of particular relevance within the context of natural weathering is the wettability of the coating surface by water, whether in the form of rain or dew droplets. Water, of course, is well known as being one of the more potent deteriorative weathering factors(166), especially in synergistic combination with radiation. Hence, the extent to which surface moisture adheres to (i.e., wets) a given paint film during exposure will undoubtedly have a direct bearing on the paint's weathering performance. A measure of wettability is most easily and conveniently obtained by measuring the contact angle(147) which a given liquid, in this context - water, makes with the coating surface. Additionally, other relevant parameters such as the critical surface tension and surface free energy can be derived from contact angle data. Furthermore, it is well known by now that changes in the contact angle and, hence, wettability of a coating surface can generally be ascribed to changes in surface energy(148), (e.g., polarity) and/or surface roughness(149 - 152). Consequently, the potential usefulness of this type of information to an ageing study, in which surface changes of this nature are the norm, can be readily appreciated.

Summarily, it is still true to say that contact angle measurement remains a relatively specialist technique, with its practitioners, by and large, tending not to be surface coatings workers. However, this situation could well change soon as the potential usefulness of this technique, especially when used in conjunction with other techniques, becomes more widely recognised by those workers actively engaged in ageing studies of surface coatings.

I.5.1.2(c) Ellipsometry

Ellipsometry(153), essentially, is a technique for measuring the thickness of films on substrates(121, 153, 154). This is achieved by means of determining the ellipticity, after reflection from a surface, of light which is initially plane polarised. For absorbing materials, therefore, such as pigmented paint films, the limit of the depth from which information is available obviously depends on the penetration of the incident electromagnetic radiation. At the other extreme, the sensitivity of the technique is now such that the presence on a surface of a very thin film or superimposed layer of material, of only a few ångströms thickness, can easily be detected and the real part of the refractive index of an absorbing medium determined with great accuracy. This latter aspect enables the growth of corrosion films on a surface to be investigated and ellipsometry has, indeed, been extensively used in such studies(155). However, the technique has not, as yet, been applied to the estimation of oxidised or otherwise degraded surface layers in weathered paint films due to the incorporate, as opposed to superimposed, nature of these surface layers which tend to be formed via chemically interactive rather than physically adsorptive processes. Thus, unless such a surface layer detracts significantly from the (assumed) initially isotropic and homogeneous nature of the unaged surface, the ellipsometric technique will be effectively insensitive to its presence.

Consequently, the application of ellipsometry to the study of paint films has so far been confined to the accurate determination of film thickness and changes that occur in them on ageing. In this respect, the technique offers itself as an attractive alternative to interferometry (121), with the added advantages that, in addition to its greater sensitivity, its data does not become more diffuse as ageing deterioration increases.

I.5.1.2(d) Weight Loss Measurements

When one considers that, for many years now, it has often been in terms of the time taken for a certain percentage (typically, 50%) weight loss to occur that the effective service lifetime of a paint film has been expressed, it is somewhat surprising to find that the measurement of weight loss on a quantitative basis is a relatively recent technique for studying paint film deterioration. This is particularly the case in the U.S.A. (156), more so than in the U.K., and possibly stems from the fact that, for a long time, workers in this field 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. Then, in addition to this, there were the problems associated with accompanying change in 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. However, since the early 1960s, 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(163), now in common practice, 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 (e.g., "chalk", dirt, etc.), and thorough drying before, finally, 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(156 - 161).

It is probably true to say that weight loss measurements have been most popularly applied to the study of erosion rates(156 - 161). 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(157). 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(160, 162). Of additional interest, in connection with accelerated weathering, is the contention by Berg et. al.(160) 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(163) 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 readily be set with respect to the time taken for a given fraction (typically, a half) 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.

Finally, weight loss measurements have also been used extensively for assessing the "chalking" tendencies of pigmented paint films(162 - 164), 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(161, 165). However, whilst the role of titanium dioxide pigments in paint systems may have attracted most attention up to now, Ritter(157) points out that the role of any paint ingredient can, in fact, be studied by the weight loss/erosion rate technique.

I.5.1.3 Chemical Methods

I.5.1.3(a) Infrared Spectroscopy

Infrared spectroscopy, as such, represents the most convenient source of information relating to the chemical composition of organic coatings systems. However, in its conventional, i.e., transmission, mode, it can only be used for relatively thin, transparent polymer films, in which the appearance or disappearance of functional groups on ageing can be followed either directly or by using differential techniques(178). When it comes to the study of opaque materials, however, such as pigmented paint films, transmission infrared spectroscopy is rendered unserviceable by the sample's high absorbance characteristics. Consequently, a much-needed extension of the basic infrared technique came to be required in order to be able to apply the technique to the chemical analysis of complete paint films. This requirement was met with the development of a suitably modified form of infrared spectroscopy - namely, internal reflection spectroscopy (IRS), also commonly referred to as attenuated total reflectance (ATR). (NOTE: The more recent name "internal reflection spectroscopy" conforms to the American Standards definition in ASTM E 131 (1966). The original name, "attenuated total reflectance", which is still frequently used, was coined by Fahrenfort(167) - one of the pioneers of the original analytical method).

I.5.1.3(a)(i) Internal Reflection Spectroscopy

The use of the infrared spectrophotometer in the internal reflection mode was introduced around the start of the last decade(167, 168). Since then, several reports have appeared in the literature describing its various applications to the analysis of paints, plastics and rubbers, as recently reviewed(169, 177). Additionally, the general background theory of internal reflection spectroscopy (IRS) has been well covered by Wilks et. al.(170 - 173), while the more mathematical aspects have been developed by Harrick(174). (With regard to the theory of internal reflectance, it is, indeed, interesting to note here that an adequate description of its related phenomena can, in fact, be based on Newton's "Opticks"(182), first published in 1717).

The main disadvantage of IRS, as compared with regular transmission infrared spectroscopy, lies in the lower quality spectra which are invariably obtained, especially in the case of roughened or inflexible surfaces. Nonetheless, IRS spectra are generally similar enough to transmission spectra to permit direct comparisons to be made even though they may not match exactly. However, the shortcomings of IRS are considerably outweighed by its many advantages(174) over the transmission method, the main ones being, (1) applicability to a wide variety of materials, (2) relative ease of sample preparation, (3) absence of spectral waveform distortion arising from interference effects from within the sample, (4) the spectra are independent of sample thickness, and (5) IRS can be used to study surface reactions. This last utility (5) is made possible be virtue of the fact that, in IRS, the infrared beam only penetrates the sample to an effective depth of the order of a few microns, thus rendering the technique especially suitable to the surface analysis of the effects of ageing on paint films. Furthermore, IRS spectral data is considered to be more amenable than transmission data to quantitative treatment via the "absorbance ratio" method(175), often giving better, i.e., less variable, results with fewer calculations. This type of IRS study has, in fact, been applied to the oxidative polymerisation of drying oil films(176).

It can be concluded, therefore, that, although not what one might regard as a particularly powerful technique, IRS is nevertheless an extremely useful one for studying coating surfaces. Importantly, it can also be applied to a study of the effects of ageing on a surface, as well as to more specific surface phenomena such as plasticiser or solvent migration, curing rates, surface contamination and the nature of the chemical bonding forces at the surface.

I.5.1.3(a)(ii) Infrared Specular Reflectance

Infrared specular reflectance (175) can be considered to be closely related to IRS procedurally, differing mainly in that the incident infrared beam is reflected directly from the sample surface without the need for an intervening internally reflecting prism as in IRS. The specular reflectance method has been compared with other (179) infrared techniques, including IRS, and is described as having certain advantages in particular applications. For example, it has been found to be particularly useful for obtaining the infrared spectra of highly reflective coatings, or of coatings on highly reflective substrates.

I.5.1.3(b) Modern Metallographic Techniques

Under the general heading of "modern metallographic techniques" (207) are included those structure-determining micrographic techniques which, since their development, have become the backbone of metallurgy. However, the term "metallography" has since come to embrace the study of polymers, ceramics and inorganic substances as well as metals, and might now be more aptly called "materiallography". Those of its techniques which have either already proved, or can be expected to prove, particularly amenable to a study such as this of paint film surfaces are now briefly reviewed.

I.5.1.3(b)(i) Energy Dispersive X-ray Analysis (EDXA)/Electron Probe Microanalysis (EPM)

Energy dispersive X-ray analysis (EDXA) (208) is rapidly becoming a valued technique for determining the elemental composition of paint surfaces as, indeed, it is for all types of surface. The basic technique consists of focussing a beam of electrons on the sample whereupon X-rays, characteristic of each element present in the surface, are emitted and subsequently analysed according to their energy.

However, it has mainly been in conjunction with the scanning electron microscope (SEM) that the EDXA spectrometer has been used (209 - 212), in order that the viewing system may aid selection of specific sample areas for elemental analysis. Conversely, the elemental analysis is also very helpful in interpreting SEM results, especially in differentiating between particles of different composition.

When the SEM is operated in this X-ray spectroscopic mode, its function can be likened to that of an electron probe microanalyser, both instruments making use of scanning and also giving rise to the same electron interactions with the sample surface in generating characteristic X-rays. The main difference between electron probe microanalysis (EPM) (213 - 215) and the SEM/EDXA technique lies in their respective points of emphasis; the EPM is first and foremost an elemental analyser, employing a much higher-energy electron beam so as to generate a higher intensity X-ray emission, whereas the SEM/EDXA system is essentially a microscope with an analysing facility. Additionally, whereas, in SEM/EDXA, the emitted X-rays are analysed according to their energy, they are analysed in EPM according to their wavelength. Hence, the EPM can be described as a wavelength dispersive X-ray analyser with a viewing facility.

Finally, it can be predicted that both of these related techniques should gain in prominence as potentially powerful tools for the analysis and characterisation of coatings and resins, in the way that they already have, of course, for metal surfaces.

I.5.1.3(b)(ii) Electron Spectroscopy for Chemical Analysis (ESCA)

Electron spectroscopy for chemical analysis (ESCA), also commonly referred to as X-ray photoelectron spectroscopy (XPS), is another extremely useful technique which has been developed in recent years for the chemical structure analysis of surfaces. It was actually around 1967 that Siegbahn and co-workers(270) demonstrated the general usefulness for chemical structure analysis of kinetic-energy spectroscopy of the electrons ejected from the inner shells of atoms irradiated with X-rays. Since then, however, interest in ESCA has grown rapidly as reflected in the recent development of commercial instruments and the appearance in the literature of several reviews of the theory and applications of the technique(271 - 275).

The basic difference between ESCA and the EDXA and EPM techniques described previously is that whereas in the latter two cases the principle is one of electron bombardment/X-ray analysis, in ESCA this situation is reversed with the sample under examination being bombarded by monoenergetic X-rays of known energy and the ejected electrons (photo-electrons) analysed with respect to their kinetic energy. The kinetic energies of the photo-electrons produced are equal to the X-ray energy minus the binding energy of core electrons and are, therefore, a function of (a) the element in the sample being irradiated, and (b) the chemical environment or oxidation state of the element(276, 277). In this way, ESCA has proved useful for the analysis of surface layers of from 5 - 100 Ångstroms thickness, a depth beyond which photoelectrons tend to be either self-absorbed by the sample or lose part of their kinetic energy and consequently contribute only to the spectral background.

Finally, ESCA data tends to be still only semi-quantitative in nature at present with the maximum sensitivity of the instrumentation still somewhat lower than that of, say, the electron microprobe. In addition, as a relatively large area of the sample is irradiated in ESCA, the technique is not suitable for mapping out the distribution of an element in the specimen surface, as can be done by either EDXA or EPM. However, despite these shortcomings, the fact that ESCA yields information concerning not only the elements present in the surface but also their functional group involvement (i.e., chemical environment) has not precluded the more recent recognition of its particular applicability to the important study of the chemical group changes occurring in the surfaces of paint films on ageing.

I.5.1.3(b)(iii) X-ray Fluorescence Spectroscopy

As its name suggests, X-ray fluorescence spectroscopy (XFS)(278) also employs an X-ray beam stimulus, in common with ESCA, in order to excite fluorescent radiation characteristic of each element detected in turn as being present in the sample surface. However, compared with ESCA, XFS provides for a more accurate analysis which, coupled with the relative simplicity of the process, has lead to its adoption as a standard technique in inorganic chemistry and in some types of metallurgical analysis. Its later use in the study of protective coatings(279) was one of the more logical extensions of its range of application, although it is probably true to say that the techniques previously mentioned have tended to gain preference over it in this particular role.

However, the informational value of X-ray fluorescence analysis has more recently been extended by the use of "soft" (i.e., longer wavelength) X-rays which enable elemental analyses to be made down as far as atomic number five and to a surface depth of about 1 micron. In this way, soft X-ray spectroscopy(151), when combined with ESCA data, provides a useful means of estimating the composition profile of a given surface.

I.5.1.3(b)(iv) Auger Electron Spectroscopy

In Auger electron spectroscopy, the sample surface is irradiated with a beam of electrons with energies of up to 3kV. At these relatively low energies, a large number of excited atoms lose their excess energy through the emission of characteristic Auger electrons rather than through emission of characteristic X-rays - a phenomenon which was first observed experimentally by the French physicist Auger in 1923. Because the energy of Auger electrons is characteristic for a given atom undergoing irradiation, the various elements present in a surface can therefore be identified by their Auger electron spectra. Additionally, since the chemical environment of an atom causes shifts in the energies of Auger electrons produced, some information regarding the bonding state of the element can also be obtained by this method(280). However, the depth of the analysed layer in Auger spectroscopy tends to be very shallow, i.e., of the order of 10 - 50 Ångstroms, and, compared with, say, the EDXA and EPM techniques described previously, the resolution is much lower. Nevertheless, the use of the Auger method for coatings analysis has recently been described (281) although, at the present time, this technique is still applied more successfully to the study of metal surfaces(282) than to polymers.

I.5.1.3(b)(v) Additional Techniques

Finally, in addition to the metallographic techniques previously described, there are one or two other related techniques which, although not yet of any prominence in the field of surface coatings' analysis, may well eventually promote polymer surface studies. Of these, the most notable are(207, 278) :-

(i) secondary-ion mass spectroscopy,
(ii) ion neutralisation spectroscopy,
(iii) combined field emission and field-ion microscopy, and ,
(iv) low-energy electron diffraction (LEED).

The first three of these techniques each have potential in the field of surface chemical analysis although they still require considerable development in order to become practicable in this respect. Low-energy electron diffraction (LEED), on the other hand, has already been shown(283), for metal surfaces, to be capable of usefully integrating its surface structure determining capability with a surface chemical analysis technique of the type described in this section, thus forming a powerful surface structure-composition characterising combination.

I.5.1.3(c) Other Analytical Methods

Although spectroscopic techniques, and in particular the infrared methods - whilst, at the same time, not discounting ultraviolet and visible spectroscopy - have undoubtedly predominated in the study of the chemical changes occurring during the ageing of paint films, other more "classical" analytical methods have also been utilised in certain cases. For example, gas chromatography, either on its own or in its more powerful combination with mass spectroscopy, has been readily applied to the study of degradation products, particularly those formed at higher temperatures. In addition, paper and column chromatography as well as gel permeation chromatography (GPC)(284) have been applied to the study of soluble polymers, during the ageing of which the occurrence of radical processes can be monitored by means of electron spin resonance (ESR). Furthermore, wide-band nuclear magnetic resonance (NMR) spectroscopy has also been found to be amenable to the study of the soluble components within a paint film as well as to network formation.

However, these analytical techniques are most easily and usefully applied to the examination of volatile products formed on photo-(285) or thermodegradation of paint films. Despite the general preference still shown for infrared spectroscopy(286) in such studies, gas chromatography(287, 288) has also proved to be particularly useful in this respect. Other additional product volatilisation/analysis techniques which are usually more concerned with the identification/characterisation of paint films rather than with an ageing study are pyrolysis-gas chromatography (PGC) and, more recently, laser-vaporisation analysis. This interesting latter technique involves the vaporisation of a minute amount of a paint film by means of a short, high-intensity pulse of laser radiation, the vaporised products then being analysed either spectroscopically or chromatographically in order to identify the chemical composition of the paint. Furthermore, this method could well prove to be of further use in monitoring chemical changes as part of a weathering investigation.

Finally, a brief mention also needs to be made here of the methods of chemical analysis which are available even though they have not been extensively applied to ageing studies on account of the general insolubility of paint films unless first saponified. However, various functional end-groups formed during the course of degradation can be determined where they are either ionisable or transformable into ionisable groups(289). Commonly, it is the carboxyl functionality which is determined, whether it be directly or after carboxylation of, for example, a paint sample's hydroxyl functionality(286, 289). However, in the case of paints based on polyesters, poly (vinyl chloride) and certain other polymers, carbonyl groups are formed at the surface during ageing which can be determined by reaction with diamines, typically N, N- dimethyl - p - phenylenediamine, since the resultant coloured condensation products are suitable for quantitative colorimetric measurement(290). Alternatively and additionally, the residual amine can also be determined spectrophotometrically in the reagent solution.

Thus, having now concluded this section on "Surface Techniques" with this coverage of the various chemical methods of analysis which are available, let us now turn our attention to those analytical techniques which are concerned with monitoring changes in the various bulk properties of paint films on ageing.

I.5.2 Bulk Techniques

Although 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 programme on the strength of which a new coating material might gain commercial acceptance.

The actual test methods which have been used to monitor changes in the bulk properties of paint films on ageing can be categorised under the following headings:-

(i) mechanical testing,
(ii) electrical methods, and,
(iii) thermal analysis.

The individual analytical techniques which fall into these separate categories will now be discussed collectively under these three headings.

I.5.2.1 Mechanical Testing

The mechanical testing of surface coatings(291) 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(292) 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 previously mentioned, hardness has certainly been one of the most popular chosen for measurement. Hardness, like gloss previously, 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(293) 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, 294, 295).

In addition to indentation hardness testing, however, stress/strain measurements have also been widely used as a means of following weathering deterioration and predicting the exterior durability of paint films. Whether they are expressed in their combined relational curve form or in the form of their basic mechanical property parameters of tensile strength(296 - 299) and extensibility (elongation)(10, 299 - 301) versus time of exposure, stress/strain measurements have been found to be capable of providing satisfactory predictions of long-term durability. However, as Elm stated in 1967, "Stress/strain investigations, as they are being conducted, ordinarily cannot contribute more than a relatively small segment of the whole fundamental property pattern which determines the service quality and durability of a coating". Indeed, it is generally acknowledged that the absolute levels of stress/strain properties of organic coatings is not too critical with respect to performance, this being particularly true of tensile strength. Indeed, very low levels of tensile strength are quite adequate to hold a film together. Similarly, in the case of elongation, although a certain amount is required in order that the coating can conform to dimensional changes of the substrate, higher capabilities in excess of this basic requirement do not add materially to performance. Other mechanical property parameters which have also been studied by various workers include internal stress(302 - 304) and creep compliance(305), in terms of their relation to weatherability, and, in the case of unsupported films, torsion modulus and logarithmic decrement by dynamic mechanical testing using the torsion pendulum(306).

Finally, the obviously important aspect of the adhesion of a given coating to its substrate has also received considerable attention with the result that many methods for the determination of this property now exist(291, 303), most of which though are not very accurate and do not allow for comparisons to be made between coatings. However, as the exact nature of the interfacial contact between coating and substrate becomes more clearly understood with regard to its effect on initial wetting and, hence, subsequent adhesion, so the theory and practice associated with the determination of adhesion will likely continue to advance. Likewise, flexibility(291, 307) and abrasion resistance(291) testing procedures have also become more systematic in recent years in their approach to predicting the long-term serviceabilities of surface coatings.

I.5.2.2 Electrical Methods

Although the electrical properties of polymers(308) in general have been well studied, literature reports of the diagnostic value of their related test methods in monitoring the effects of weathering in plastics and protective coatings are relatively few and far between. Of the insulating property parameters which have been used to assess ageing deterioration, measurements have commonly been of changes in electrical resistivity(309), dielectric constant and power factor(310). However, Shaw and Twiss(311) have also shown that ultraviolet irradiation of organic coatings decreases the electrical impedance and increases the loss tangent. It was concluded that the impedance method was capable of detecting breakdown in a coating long before visible signs occurred, as well as being able to show up non-uniformity in film thickness and the presence of "pinhole" defects. Similar findings to these have also been reported by Sato(312, 313). Additionally, electrical capacitance

(314, 315) as well as electrochemical(316, 317) methods have also been described for determining the anticorrosive properties and ageing characteristics of paint coatings.

I.5.2.3 Thermal Analysis

The application of thermal methods of analysis to the characterisation and ageing study of organic coatings materials has also been shown(318, 319) 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 thermal analysis is the glass transition temperature (T_g)(303), 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 T_g 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 T_g, 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 (i.e., detached) films for testing purposes; analysis in this latter case involving the determination of the displacement profile of a penetration probe on a substrate-supported film over a programmed temperature range.

Thus, having considered the various bulk techniques which are available to the coatings chemist, this section on analytical methods can now be concluded by affording a brief mention of what can best be referred to as "paint trade techniques".

I.5.3 Paint Trade Techniques

Under this general heading can be included those test methods employed in the coatings industry more for quality control and product evaluation than for purely research purposes. These, what can be regarded more as, development testing procedures tend to be more widespread in the industrial, rather than domestic, coatings sector where paints are invariably tailor-made to meet fairly rigorous, in-service, customer requirements. These paint trade testing procedures are fundamentally much simpler than the majority of those techniques previously described and are more technological than scientific in terms of their design and the interpretation of their results. Examples of just a few of the more common of these tests are as follows (291) :-

(a) salt-spray test/rust creep

(b) humidity test

(c) steam resistance

(d) blister box

(e) water/solvent immersion

(f) bend test

(g) pencil hardness

(h) scratch test/mar resistance

(i) crosshatch adhesion tape test

(j) stain resistance

(k) cold/gas check test

(l) scrub resistance/washability

(m) chemical resistance

(n) falling weight impact test.

From this list, it can be seen that certain of these tests are primarily concerned with particular in-service performances of industrial finishes and bear little relation to their would-be outdoor (i.e., natural weathering) durabilities. In such cases, the question of whether test performance meets specific customer requirements can be likened, in many respects, to the accelerated/natural weathering correlation and often calls for the judgement of an experienced paint technologist.

Thus, this section dealing with "Analytical Techniques" has served to show the great range and diversity of the test methods now available for both characterising and assessing the ageing characteristics of paint coatings. Whilst the techniques described in this chapter represent the most important of those in current use, there are still many more which have not been mentioned. In addition to the development of new and improved test methods, it is, perhaps even more importantly, now being realised how urgently the paint industry needs to master a number of important concepts while products continue their rapid pace of development. This state of affairs has prompted the recent publication of an up-dated treatise on the methods of characterisation of coatings (320) which explores the scientific frontier that has developed since the appearance of Mattellio's treatise (321) some thirty years ago.

CHAPTER II

EXPERIMENTAL ASPECTS

- THEORY AND PRACTICE

CHAPTER II

EXPERIMENTAL ASPECTS - THEORY AND PRACTICE

II.1 Introduction

In this chapter, the various experimental aspects of the present study are described in detail under the following three sub-headings:-

i) surface coatings systems studied - including details of formulation, preparation and application wherever possible,

ii) ageing environments - pertaining to both natural and artificial weathering tests, and including any relevant details of site control where applicable, and,

iii) analytical techniques - i.e., those techniques actually utilised during the course of the present work.

II.2 Surface Coatings Systems Studied

The various surface coating systems studied during the course of the present study can themselves be divided into two distinct groups, namely - 1) commercial coatings, and 2) experimental coatings.

II.2.1 Commercial Coatings

The complete range of commercial coatings systems studied are listed in Table 1 together with their known formulation details.

	BINDER-TYPE	PIGMENT(S)	$\frac{\text{PIGMENT}}{\text{BINDER}}$ RATIO	COLOUR	TYPE OF FINISH	SOURCE*
1	68% linseed oil/ pentaerythritol/phthalic alkyd	Rutile titanium dioxide (maximum chalk resistance)	0.8	White	Gloss	L
2	Vinyl toluene - modified alkyd	Mainly rutile titanium dioxide	-	Brown	Gloss	C
3	Polyurethane alkyd	Mainly rutile titanium dioxide	-	White	Gloss	C
4	Epoxy/polyamine, (1:0.75)	Rutile titanium dioxide	0.57	White	Gloss	L
5	Chlorinated rubber, thixotropic	Rutile titanium dioxide, china clay	1.4	White	Semi-gloss	L
6	Poly(vinyl chloride) organosol, plasticised	Not known	-	White	Matt	CC
7	Poly(vinylidene fluoride)/ acrylate**	Not known	-	Various	Semi-gloss	CC

* L = Laboratory prepared from commercial raw materials

C = Commercial product

CC = Commercial applied coating

** Set of ten differently coloured coatings on chromate-primed aluminium (approx. 20 μm. film thickness); trade name: "Kynar"

TABLE 1

RANGE OF COMMERCIAL COATINGS STUDIED, WITH DETAILS OF FORMULATION

Samples of each of these coatings, which had all initially been machine-coated on to an aluminium substrate, were supplied by the Organic Materials Division of the Building Research Station (BRS) in the form of small panels or punched discs; the samples, as supplied, had already undergone periods of up to two years natural weathering at the BRS semi-rural exposure site, or up to 4000 hours artificial weathering (BS 3900 Part F3), and, with the exception of the poly(vinylidene fluoride) coatings, had previously been well characterised by BRS workers (10) with respect to changes in certain of their mechanical properties.

II.2.2 Experimental Coatings

The range of experimental coatings systems which were studied consisted of two parallel series of poly(vinyl chloride) (PVC) plastisol coatings, differing only in their respective levels of plasticisation. Each series was comprised of the same eight formulations listed in Table 2 and detailed in Table 3. The "complete" formulation, i.e., no. 8, is intended to represent the basic framework of a commercial PVC plasticised coating manufactured and marketed by Vinatex Ltd., Havant, Hants., who kindly prepared these study materials according to the design specifications laid down in Tables 2 and 3. Consequently, it can be seen from Table 2 how this "complete" formulation has been broken down in such a way as to enable appropriate formulation sequences to be easily and conveniently selected from across the series. In this way, individual (and combined) roles played during ageing by particular component(s) of the coating system as a whole may be studied.

FORMULATION NUMBER	FORMULATION DESCRIPTION
1	Plasticised PVC clear
2	Plasticised PVC + uv stabiliser
3	Plasticised PVC + thermal stabiliser
4	Plasticised PVC + uv and thermal stabilisers
5	Plasticised PVC + pigment
6	Plasticised PVC + pigment + uv stabiliser
7	Plasticised PVC + pigment + thermal stabiliser
8	Plasticised PVC + pigment + uv and thermal stabilisers

TABLE 2: LIST OF PVC PLASTISOL COATINGS STUDIED

Formulation Number	FORMULATION DETAILS (in p.p.h. of resin)				
	PVC resin	Plasticiser, Series I (II)	Pigment	uv stabiliser	Thermal* stabiliser
1	100	80 (50)	-	-	0.5
2	100	80 (50)	-	0.5	0.5
3	100	80 (50)	-	-	1.5
4	100	80 (50)	-	0.5	1.5
5	100	80 (50)	15	-	0.5
6	100	80 (50)	15	0.5	0.5
7	100	80 (50)	15	-	1.5
8	100	80 (50)	15	0.5	1.5

(* see NOTE on page 71).

TABLE 3: DETAILS OF PVC PLASTISOL COATINGS STUDIED

II.2.2.1 Plastisol Coatings Preparation

The range of PVC plastisol formulations described in Tables 2 and 3 were prepared using an eight litre, high speed Papenmier Mixer. The coatings were then applied to each of the following substrates (which were specifically chosen on the grounds of their individual suitabilities for particular testing methods, as also indicated below):

i) optical glass panels - both primed (by dip-coating with British Steel Corporation's coil coat primer and curing at 225°C for 30 secs.) and unprimed; (especially suitable for goniophotometry and other techniques requiring optical planarity of the substrate),

ii) aluminium panels - both primed (as in (i) previously) and unprimed after pre-treatment with a thermosetting epoxy resin coating; (especially suitable for mechanical property test methods such as microindentation-recovery/ time analysis; the unprimed panels additionally allow for stripping off of the coating for unsupported film tests), and finally,

iii) stainless steel panels - primed (as in (i) previously) only; (especially suitable for weight loss measurements where ageing-resistance of the substrate is demanded).

Wherever possible, the plastisols were machine-coated on to these various substrates to a film thickness of 0.008 inches using the I.C.I. Automatic Film Applicator, before being cured for 90 secs. at 225°C. However, in the cases in which this could not be achieved satisfactorily, i.e., (a) with the glass panels, and (b) with the four pigmented formulations of Series II (see Table 3), for rheological reasons, the samples were hand-coated to a film thickness of 0.007 - 0.009 inches using a bar applicator, before being firstly placed in an oven for 10 mins, at 120°C., and then cured for 60 secs. at 225°C. Finally, the finished plastisol coatings were all glossy in appearance and relatively soft in surface texture:

hardness of Series I coatings = 55 - 58° Shore A Hardness,
hardness of Series II coatings = 80 - 82° Shore A Hardness.

NOTE: a certain amount of thermal stabiliser was necessarily incorporated initially into all formulations for processing purposes. However, in the case of formulation nos. 1, 2, 5 and 6, which were to be regarded after processing as containing, effectively, no thermal stabiliser, only that amount (i.e., 0.5 p.p.h. of resin - see Table 3) of stabiliser was added which, it was estimated, would just about be consumed during processing. In spite of this, trace amounts of thermal stabiliser could still possibly remain in those coatings formulations which are subsequently regarded after processing as being thermal stabiliser-free.

II.2.2.2 Formulation Raw Materials

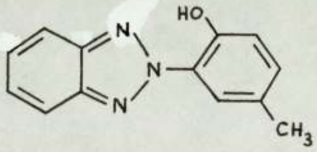
The various formulation ingredients referred to in type in Tables 2 and 3 can now be identified more precisely and described in terms of the information available about them:-

(a) the poly(vinyl chloride) (PVC) resin used in the preparation of these plastisol coatings is a suspension polymer manufactured by Bush, Beech and Segner Bailey, and marketed under the trade name of "Vinnol P-70",

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

(c) the pigment chosen is a white, rutile titanium dioxide grade (Tioxide R-CR3, British Titan Products Co. Ltd.) which is claimed to have outstanding chalk resistance (163, 180). It is particularly suited for use in exterior plastisol coil coatings, combining extremely high opacity and gloss with durability at low pigment volume concentrations (180),

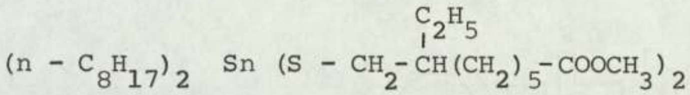
(d) the ultraviolet stabiliser is 2-(2'-hydroxy-5'-methylphenyl) benzotriazole (I) which is marketed by Ciba-Geigy Ltd. under



(I)

the trade name of "Tinuvin P". Its stabilising action is classed as being that of a "uv-absorber" or "screening agent" (181), and finally,

(e) the thermal stabiliser used in the coatings is an organotin compound — di-n-octyl-tin-bis-2-ethylheptyl mercaptoacetate, (II) — trade name "Mellite 831D" (Albright & Wilson Ltd.). Its powerful stabilising action on PVC is achieved mainly via its rapid "fixation" of evolved hydrogen chloride gas, which would otherwise catalyse further chemical breakdown of the polymer (181, 202).



$$(n-C_8H_{17})_2\ Sn\ (S-CH_2-\overset{\overset{C_2H_5}{|}}{C}H(CH_2)_5-COOCH_3)_2$$

(II)

In summary, the PVC plastisol coatings which have been described here are intentionally designed along simple lines in order to facilitate the study of their ageing characteristics. Whilst they can genuinely be regarded as being related to commercial systems, they are not, however, intended as being directly comparable with them; in addition to the formulation components previously mentioned, present day commercial plastisol coatings also contain other important ingredients such as filler resins, solvents designed for high speed coil coating production, as well as multi-component plasticiser systems in their now elaborate compositions.

Indeed, the inherent complexity of modern coatings formulations in general, serves to illustrate that, by no stretch of the imagination, can paint systems still be regarded as being essentially just resin/pigment mixtures, assuming of course that they ever could.

II.3 Ageing Environments

The many various ageing environments in which surface coatings materials are exposed for testing purposes clearly fall into two distinct categories - namely, those relating to (i) natural weathering, and (ii) artificial weathering. These two types have already been described in the previous chapter (see sections I.3 and I.4 respectively) in which the major factors governing their correlative capability were also discussed.

The various natural and artificial weathering environments actually utilised during the course of this study are now described in somewhat greater detail, commenting also on the reasons for their choice.

II.3.1 Natural Weathering

Natural weathering, during the course of the present work, was conducted at the following three outdoor sites which, as will become apparent, differed not only in location but, more significantly, in the nature of their respective environments:

II.3.1.1 at the Building Research Station

The Building Research Station (BRS) exposure site, as illustrated in Plate 1, has until fairly recently been described(10) as a semi-rural site. However, with the advent of a nearby motorway, it is probably now more accurately described as being semi-urban in its environment. The site, itself, however, is relatively clean in the sense that the concentration of particulate matter in the surrounding atmosphere is low; it is also well organised by the Building Research Station who maintain records of local meteorological data for site documentation purposes (as recommended, for example, in American Standards, ASTM D1435).

PLATE 1 - View of the Building Research Station exposure site, showing (A) exact location of sample rack in relation to (B) the solar radiation detectors.

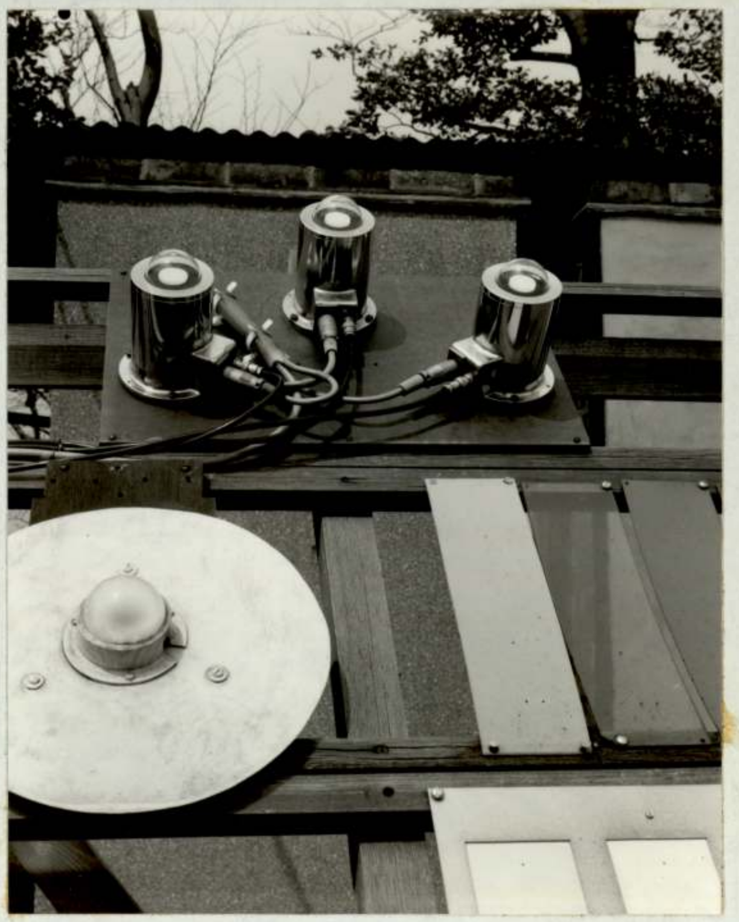


PLATE 2 - Solar radiation monitoring at the Building Research Station exposure site, showing the Monteith Solar Radiation Detector (bottom left) and the (above) set of three BRE UV sensors.

However, a particularly important feature of the site's documentation is the on-site facility which exists for solar radiation monitoring. This is currently carried out by means of two separate detector systems differing, not only in design, but also in terms of the specific data which they provide, and yet which, to a certain extent, complement each other. The first of these two systems, and the one which provided the data for this study, is the Monteith Solar Radiation Detector (Plate 2, bottom left) which prints out a continuous record of the total amount of solar radiation energy received by samples undergoing natural weathering. The second detector system, on the other hand, is currently comprised of a set of three sensing devices, also shown in Plate 2 (top), which, in combination, selectively monitor the ultraviolet component of solar radiation within three discrete narrow wavebands (centred around 315, 350 and 400 nm.) in the 300 - 400 nm. wavelength range of the solar spectral distribution(186) (see Figure 4(a)). The basic unit for this latter system is the Building Research Establishment's own recently developed ultraviolet sensor(183); although the prototype to this device was, in fact, described(184) back in 1968, it has only been since its more recent improvement(183), however, that actual commercial production(185) of the present version has been undertaken.

Hence, the current BRE uv sensor, along with the Monteith solar radiation detector previously mentioned, each provide a valuable means of converting the linear time scale of a given natural weathering exposure period, together with its intrinsic seasonal variations, to a linear energy scale. Indeed, this is often considered to be a more relevant way of expressing exposure data since solar radiation, and in particular its uv component, is invariably the most potent single

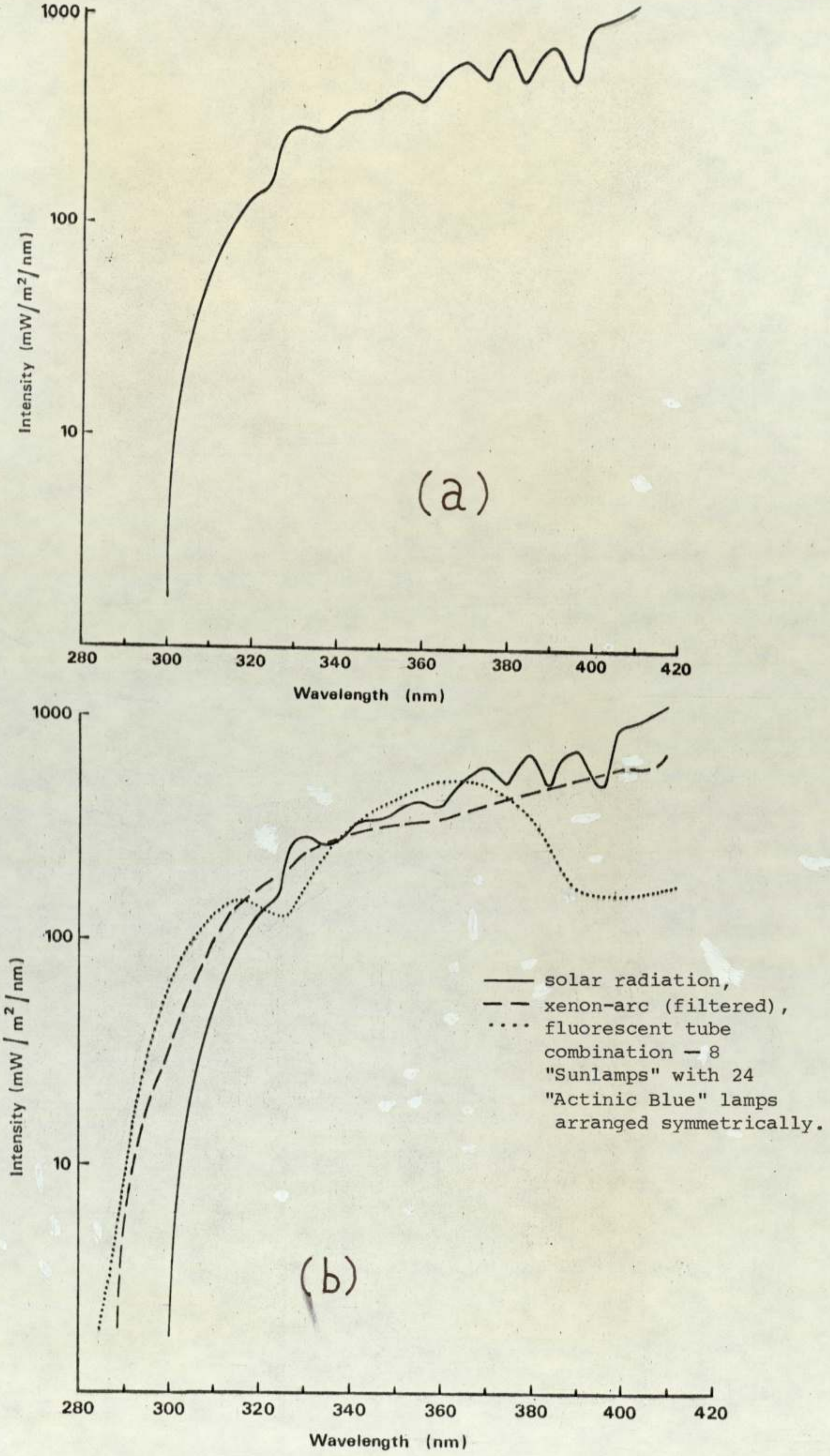


FIGURE 4 - Spectral power distributions relating to:-
(a) solar radiation(186), and,
(b) two UV sources compared with sunlight(9, 194).

factor involved in the outdoor weathering deterioration of paint films. However, it is probably truer to say that energy-based results, when considered in conjunction with corresponding time-based data, allow for a more meaningful interpretation to be made of a paint's overall weathering behaviour.

In addition to this, of course, the performance monitoring of natural weathering samples with respect to energy of exposure permits more direct correlations to be made, wherever possible, with corresponding results obtained from artificial weathering machines. As described previously in section I.4, the operating cycles of these machines are invariably centred around the seemingly all-important simulation of solar radiation, again, particularly of its uv component, by suitably designed lamps of known energy output. Consequently, natural and artificial weathering exposures can be equated on energy terms, and differences in sample response taken as being characteristic of the combined effects of the remaining weathering factors which comprise their respective environments.

However, with the BRE uv-sensor and, to a lesser extent, the Monteith solar radiation detector still relative newcomers to the field of radiation measurement, most commercial exposure stations monitor and record the total energy received by outdoor test samples by means of an Eppley pyrheliometer (187) (see Plate 3, (a), (b) and (c)). The use of this instrument has been widely reported(188 - 190), both in its early form(188) and in its progressively improved forms(189, 190), one of the more recent versions(190) of which is equipped with filters in order to measure the energies arising from those shorter (i.e., uv) wavelengths of radiation which are known to be particularly destructive to paint

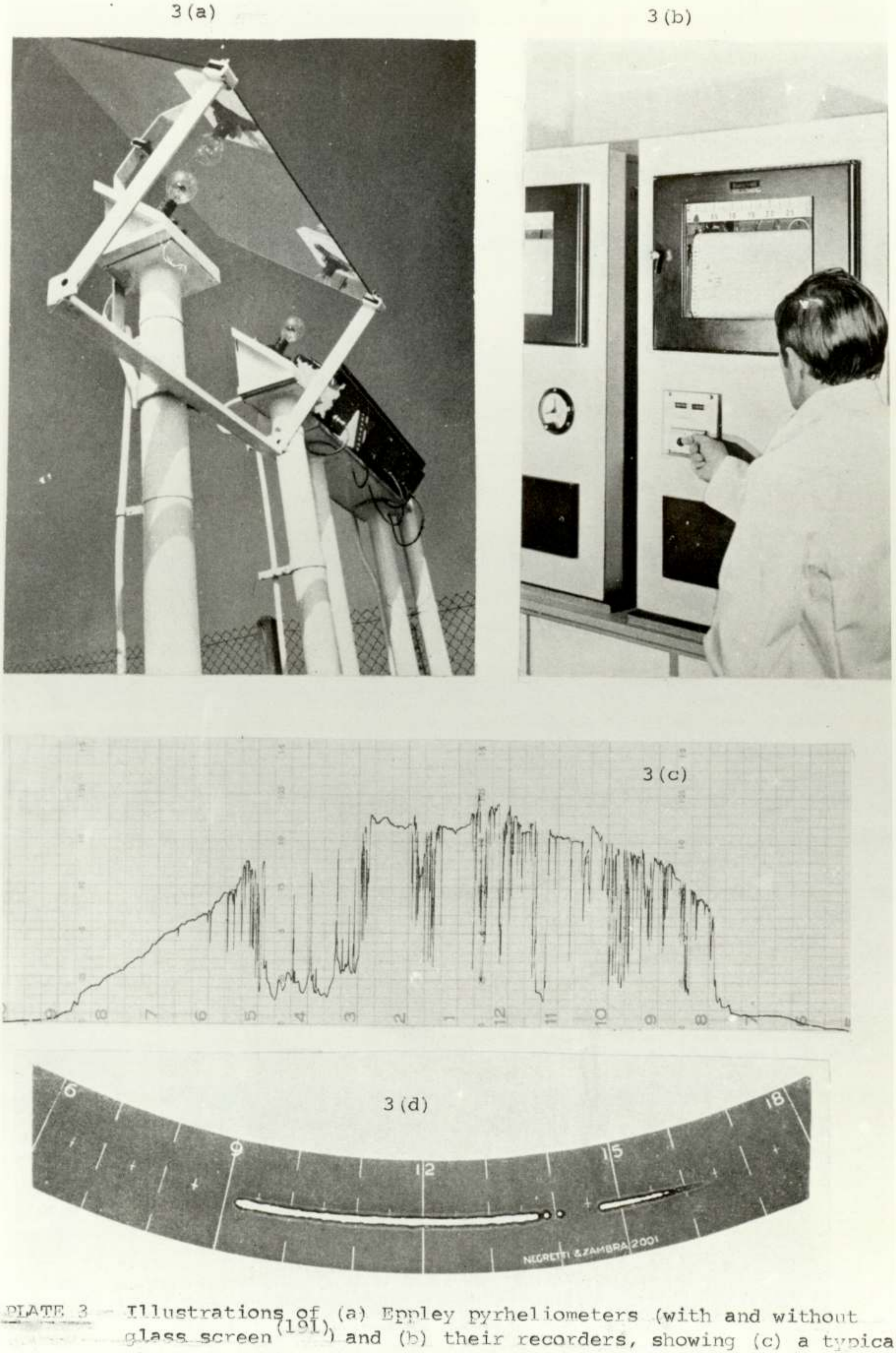


PLATE 3 - Illustrations of (a) Eppley pyrheliometers (with and without glass screen(191)) and (b) their recorders, showing (c) a typical chart recording of the total solar energy received on a February day;

(d) sunshine duration on an October day as recorded by the Campbell-Stokes instrument(191).

films. This latter facility, which, of course, is the important design feature of the BRE uv sensor, is of particular value in cases where the actinic radiation wavelengths, i.e., those wavelengths actually effective in causing degradation, are specifically known for the system under study.

At the time of its introduction, the Eppley pyrheliometer represented a considerable advancement from existing instruments, such as the Campbell-Stokes sunshine recorder (191) which was only capable of measuring the time during which the sun was shining brightly (see Plate 3(d)); no indication of the total amount of sunlight was possible in this latter case, although even with instruments in which it was. the actual uv content only comprised around 5% of the total energy reading, the other 95% being in the less deteriorative visible and infrared ranges of the solar spectrum.

Hence, the value and importance of solar radiation monitoring to this present ageing study is obvious, especially in view of the fact that direct comparisons are to be made between corresponding natural and artificial weathering data for the range of coatings systems previously described in section II.2. A graphical representation of data obtained from the Monteith detector is shown in Figure 5 for the period from June 1973 - October 1975. The total solar radiation "count", as printed out by the instrument's recording system, is transformed by a simple conversion factor into energy units of watt hours per unit area, typically, $mW.hr./m^2$.; this can be compared with the "Langley" (defined (189) as 1 $g.cal./cm^2$. or 3.69 $BTU's/ft^2$.) which is the energy unit most widely used in pyrheliometry for measuring the amount and intensity of solar radiation.

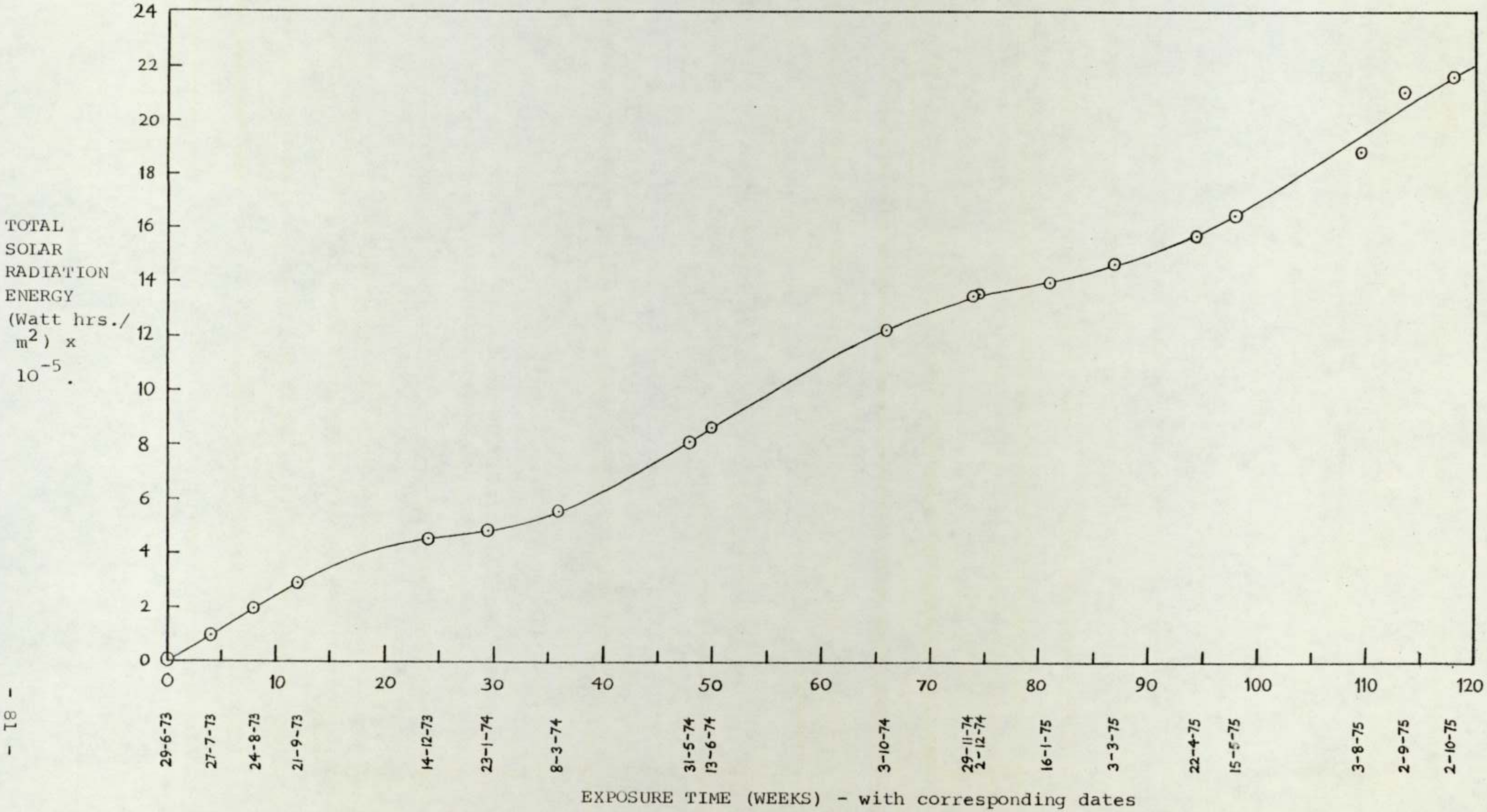


FIGURE 5 - Total solar radiation energy data from the Monteith detector, covering the period June 1973 - October 197

The exact location, on the BRS exposure site, of the solar radiation detectors, in relation to where test samples were placed, is indicated on Plate 1. The samples, themselves, were mounted on to exposure racks inclined at 45° and facing south. These standard conditions (see ASTM D 1435) ensure that, for temperate climates such as in the U.K., the test specimens receive the maximum amount of solar exposure throughout the year and that drainage of rain-water from the specimen surfaces is facilitated(2). In conclusion, it is therefore interesting to note that the maximisation of solar exposure in this way has, itself, been suggested(5) as introducing an element of acceleration to the outdoor weathering test. This effect which, for rigid PVC plastics, has been estimated as being of the order of a 20% acceleration over the first two years exposure, apparently varies for different polymer systems.

II.3.1.2 at the University of Aston in Birmingham

Natural weathering at Aston University was carried out at an elevated site on the roof of the main university building (see Plate 4, (a) and (b)). Apart from its obvious convenience in terms of its location at the place of study, this site was chosen as being representative of a more industrialised environment. As such, its effect on the weathering response of samples exposed there could usefully be compared with corresponding results obtained from similar samples exposed at the BRS site. Although the university roof site is not documented in the way in which the BRS exposure site is, it is nevertheless situated in a well-controlled area which is not shaded in any way and which is free from any localised emissions. Indeed, its well-exposed position provides for efficient ventilation and air

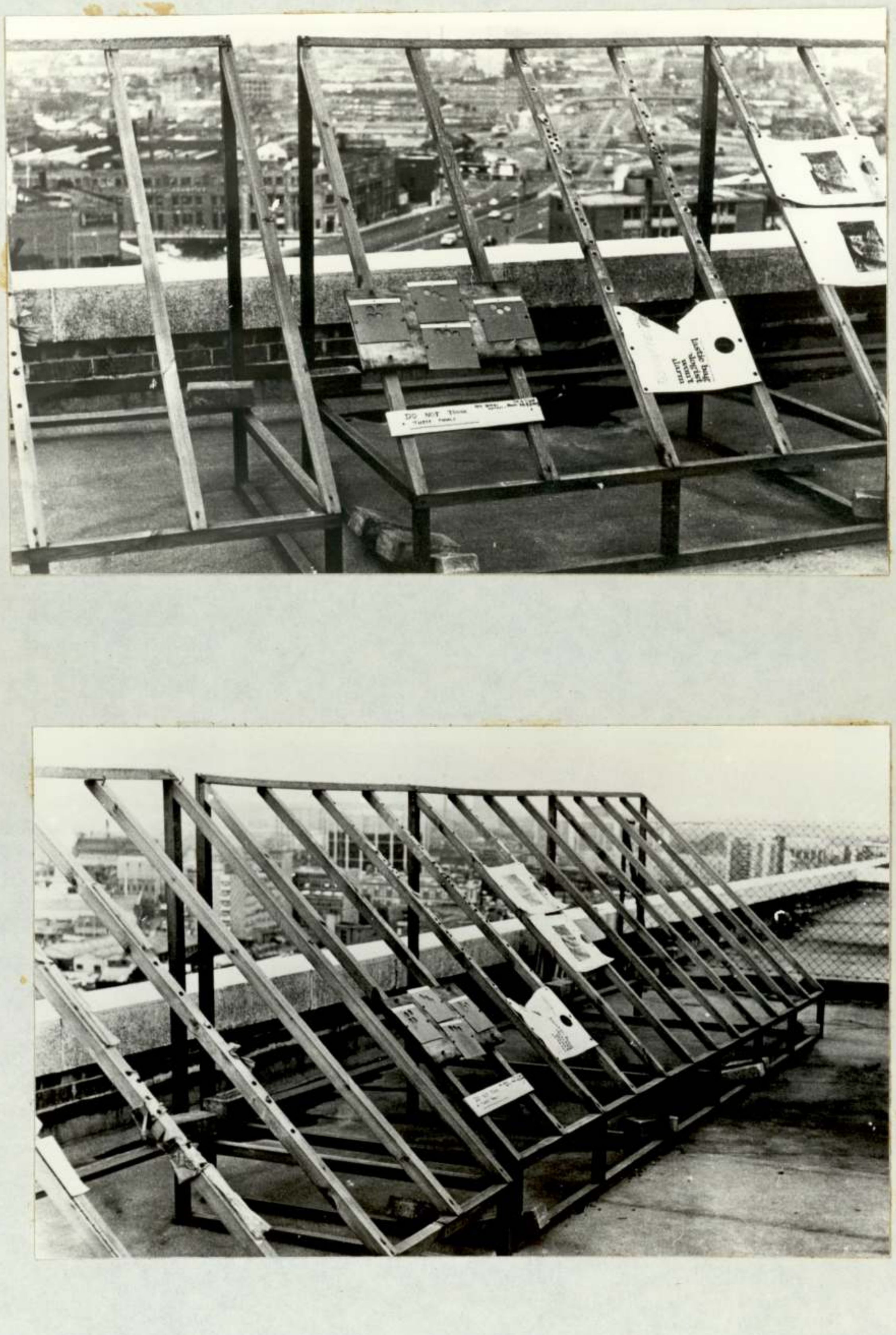


PLATE 4 - Views of the Aston University roof exposure site.

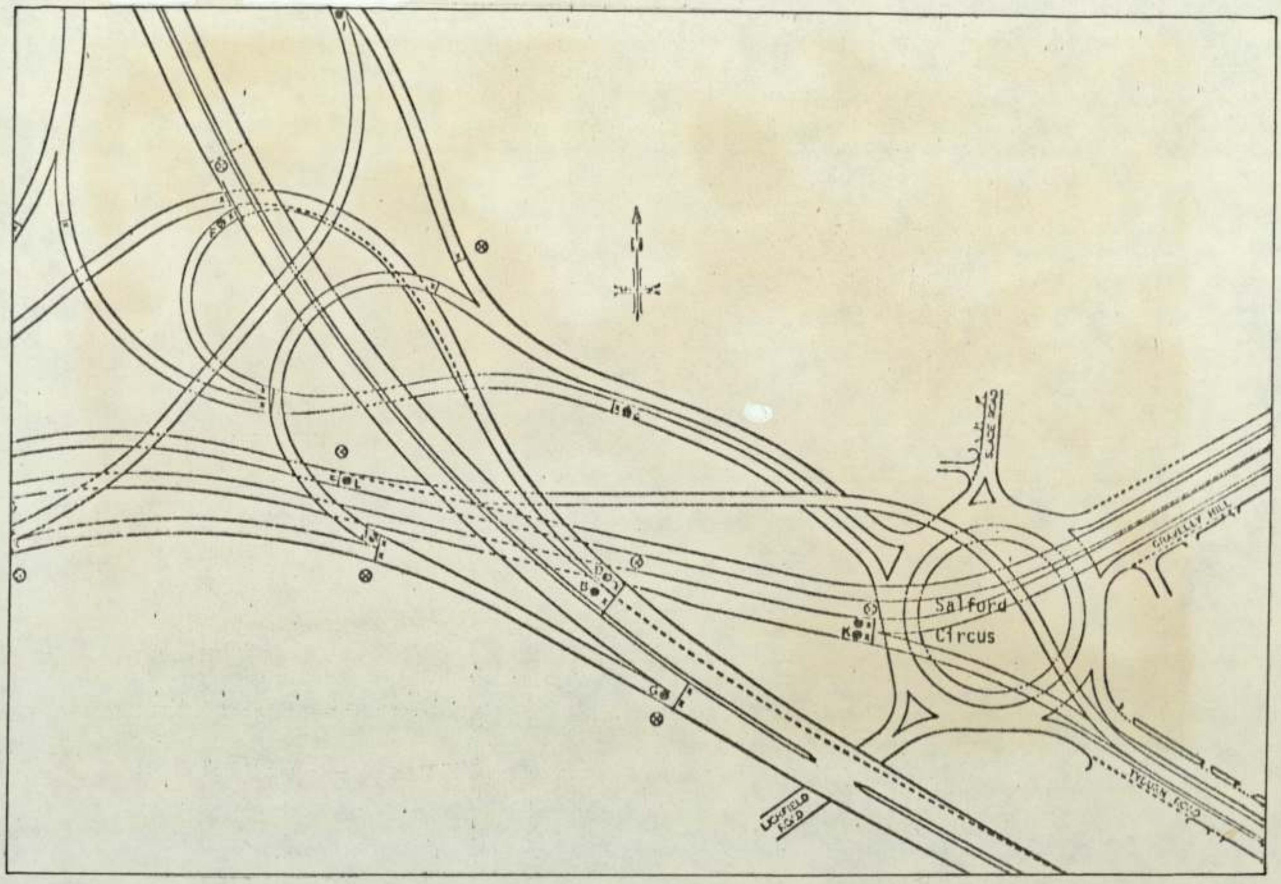
circulation within the vicinity of the exposure rack, which probably explains why the site is surprisingly clean considering its industrial surroundings.

This type of "industrial" exposure, of course, subjects the samples under test to the potentially deleterious effects of the various gaseous pollutants which are invariably more abundant in industrial atmospheres, such as ozone and oxides of nitrogen and sulphur. Additionally, and oppositely, however, there is the protective effect of industrial atmospheric haze, in filtering out shorter wavelength ultraviolet solar radiation, to be considered.

Hence, it is hoped that, by comparison of university roof and BRS exposures, valuable information can be obtained relating to the important bearing which the nature of the outdoor site undoubtedly has on weathering performance.

II.3.1.3 at the Gravelly Hill motorway link in Birmingham

At Gravelly Hill in Birmingham, about two miles north of the city centre and Aston University, is situated the Midlands motorway link (see Figure 6(a)), reputedly the most concentrated traffic interchange in Europe. The motor vehicle generated pollution, both in the form of atmospheric gases and airborne particulates, is continually being monitored at various sites (see Figure 6(b)) in this vicinity by other workers[(192)] at this University. It is at one of these sites, Salford Circus, that PVC plastisol coatings from this study were exposed concurrently with similar samples at the BRS and University roof exposure sites. However, it must be emphasised that this



6(a)

6(b)

FIGURE 6 - Diagrams[192] of (a) the Midlands motorway link; and
(b) the location of air pollution monitoring sites in its vicinity.

particular outdoor exposure test was intended as being more of a case study in itself rather than an experiment in parallel with the BRS and University roof exposures. In any case, the very nature of this Gravelly Hill exposure site precludes valid weathering comparisons from being drawn on account of the fact that the site is sheltered to a certain extent by adjacent overarching roadways. Nevertheless, this somewhat unique weathering location, documented, as it is, with respect to its high level of atmospheric pollution, provides a similarly unique opportunity for studying the various deteriorative effects which this type of environment may have on PVC plastisol surface coatings.

Finally, and of likely further interest, will be the way in which the results from this study compare, if at all, with those of planned artificial weathering tests in the presence of nitric oxide in nitrogen (NO/N_2) gas mixtures (see section II.3.2.4); nitric oxide, of course, being one of the principal pollutants discharged into the atmosphere by diesel and petrol-propelled vehicles.

II.3.2 Artificial Weathering

The artificial weathering techniques employed during the course of this project can be regarded as being of two types; firstly, that which involves the use of the BS 3900 Part F3 artificial weathering machine and, secondly, the remainder which involve simpler ageing apparatus designed around just one or two intensified weathering factors, such as uv and thermal ageing cabinets. These various artificial weathering methods are now described in more detail, having each been chosen on the grounds of (a) their considered suitability to the materials under test, and/or (b) their likely value in aiding the interpretation of certain aspects of natural weathering behaviour.

II.3.2.1 BS 3900 Part F3 Artificial Weathering Machine

The BS 3900 Part F3 artificial weathering test method was originally drawn up as a result of some earlier work(193) carried out by the "Joint Services Research and Development Committee on Paints and Varnishes". This work was centred around the development of an artificial weathering cycle which was 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 U.K. Consequently, the BS cycle, having been designed along these lines, subsequently became the accepted test method in this country for assessing the natural weathering durability of, in particular, alkyd-based paint films in temperate climates such as ours.

However, although this is probably still its most popular usage, the BS weathering cycle has, since its inception, been applied to a much wider range of paint systems, with varying degrees of success(21). Its chief correlative limitations have been found to be when it is either applied to the study of high durability paints, or paints exposed in hot, sunny climates. Additionally, when compared with other artificial weathering cycles(21), the BS cycle is found to be relatively slow, with 12 weeks (i.e., approx. 2000 hours) exposure suggested as being necessary to induce changes comparable with two years natural weathering in the U.K. Indeed, purely on an energy of exposure basis, 2000 hours exposure to the BS cycle would, in fact, only subject test specimens to an approximately equivalent amount of radiation to that received, on average, over a period of just one year's natural weathering in this country (as calculated from solar radiation data obtained from the Monteith detector).

The actual layout of the BS 3900 Part F3 artificial weathering apparatus is shown in Plate 5/Figure 7 followed, in Table 4, by details of its design specification and operating cycle. It can be seen to consist essentially of an enclosed carbon arc light source, atomised water spray and cooling fan. The temperature inside the apparatus during operation, however, is not specified, although it is recommended that the temperature of the room in which it is situated be maintained at 20±2°C. The particular BS 3900 machine utilised in this work was that which is located at the Building Research Establishment's Princes Risborough Laboratory (Aylesbury, Buck.). Sampling of test panels was carried out at intervals of (typically) 250 hours during the early stages of exposure, lengthening later on to 500 hour intervals in appropriate cases.

Finally, it is worth noting that, until recently, there has been no adequate means of characterising or monitoring the radiation received at the surface of samples exposed in artificial weathering machines, apart from spectrometric measurements of the output from single lamps(186). Consequently, it has been with this in mind that workers at the Building Research Establishment have recently developed a miniature, self-contained uv integrating recorder for this purpose(194), based on the BRE uv sensor(183) (previously described in section II.3.1.1) to which it is intended to be complementary. However, in its present form, this uv recorder is designed specifically for use in two particular artificial weathering machines, namely, the "Xenotest 450"(18) and the Frigistor "Climatest"(19), although, presumably, its range of

PLATE 5 - The BS 3900 Part F3 artificial weathering apparatus.

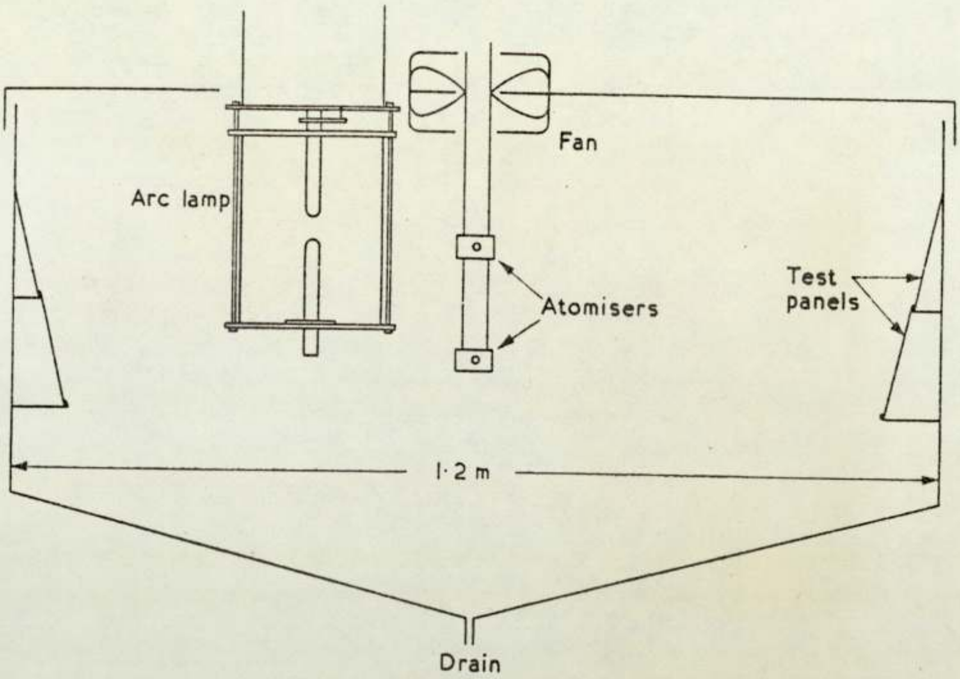
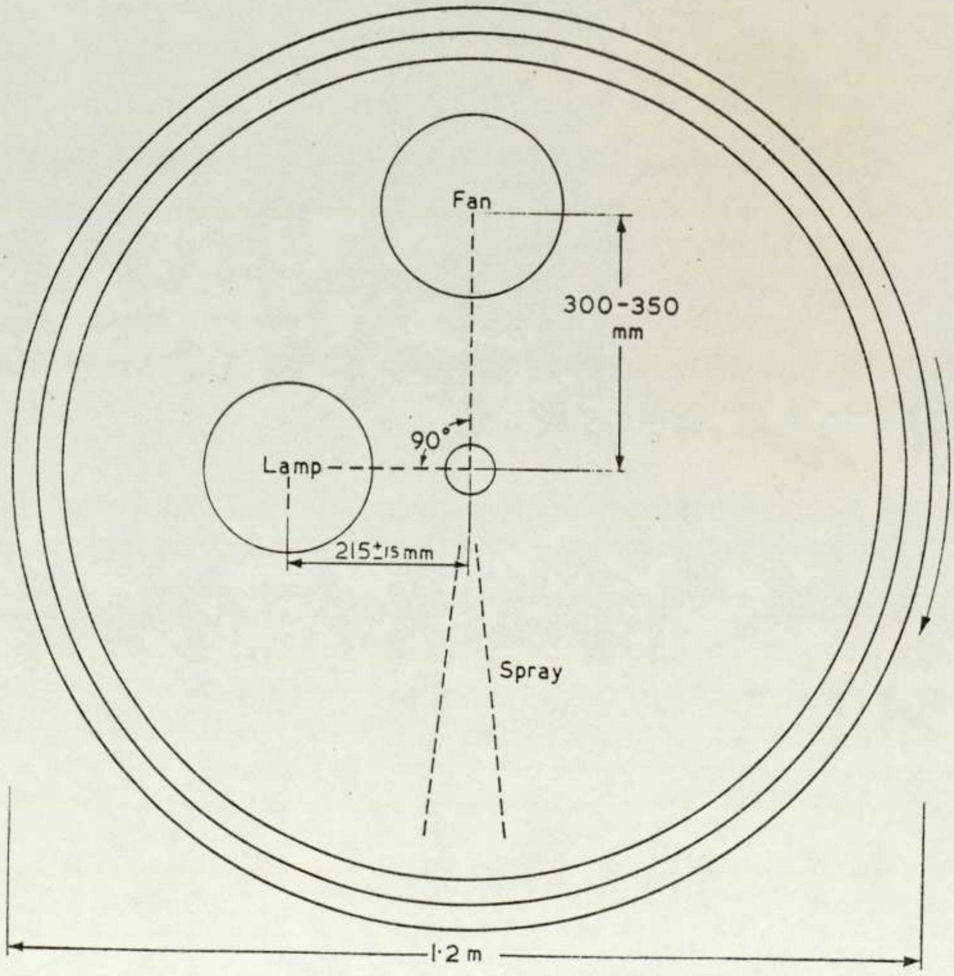


Diagram of artificial weathering apparatus



Plan view of artificial weathering apparatus

FIGURE 7 - Design Layout of the BS 3900 Part F3 Artificial Weathering Apparatus

DESIGN SPECIFICATIONS	24-HOUR OPERATING CYCLE
Radiation Source: 1600 Watt DC enclosed carbon arc; borosilicate filter mounted off centre, arc to panel distance 35 to 80 cm.; Drum: diam. 120 cm., rotating at 1 rev./20 min.; Water Spray: 90° before nearest approach to carbon arc.	4 hrs. radiation + water spray + fan off 2 hrs. radiation + water off + fan cooling 10 hrs. radiation + water spray + fan off 2 hrs. radiation + water off + fan cooling 5 hrs. radiation + water spray + fan off 1 hr. - cycle stopped for cleaning, etc.

TABLE 4

DESIGN SPECIFICATIONS AND OPERATING CYCLE FOR THE BS 3900 PART F3 ARTIFICIAL WEATHERING APPARATUS(20).

applicability will eventually be made more universal so as to include other machine types.

II.3.2.2 UV Exposure Cabinet

The uv exposure cabinet used during the course of this study is illustrated in Plate 6. The cabinet (supplied by Laboratory Thermal Equipment, Greenfield, near Oldham, Lancs.) consists of a battery of 28 fluorescent tubes, each 2 feet in length, set in circular arrangement around, and 10 cm. away from, a rotating sample support frame. The collection of tubes is, itself, comprised of a symmetrically arranged 3:1 combination of two slightly differing types, viz., (a) 21 "Actinic Blue" (20 Watt, Philips (GB) 20W/05) lamps, and (b) 7 "Sunlamps" (20 Watt, Westinghouse (USA) FS20); the spectral output of this particular tube combination and arrangement has been found(194) to produce a reasonable, although still far from perfect, match for solar radiation (see Figure 4(b)). However, despite the fact that single lamp sources, such as the xenon-arc lamp, can provide closer reproductions of solar radiation, as shown in Figure 4(b), multiple source systems such as this, based on fluorescent tubes, do have one useful advantage over a single source in that the tubes may be progressively renewed, one or more at a time, thus providing and maintaining a source of almost constant radiation intensity. In the case of the uv cabinet described here, a unit of four tubes (three Actinic Blue lamps plus one Sunlamp) is renewed every 85 hours for this purpose.

Additionally, test samples relating to this study which were exposed in the uv cabinet were positioned opposite the central portions of the irradiating lamps, this being a further measure to ensure that

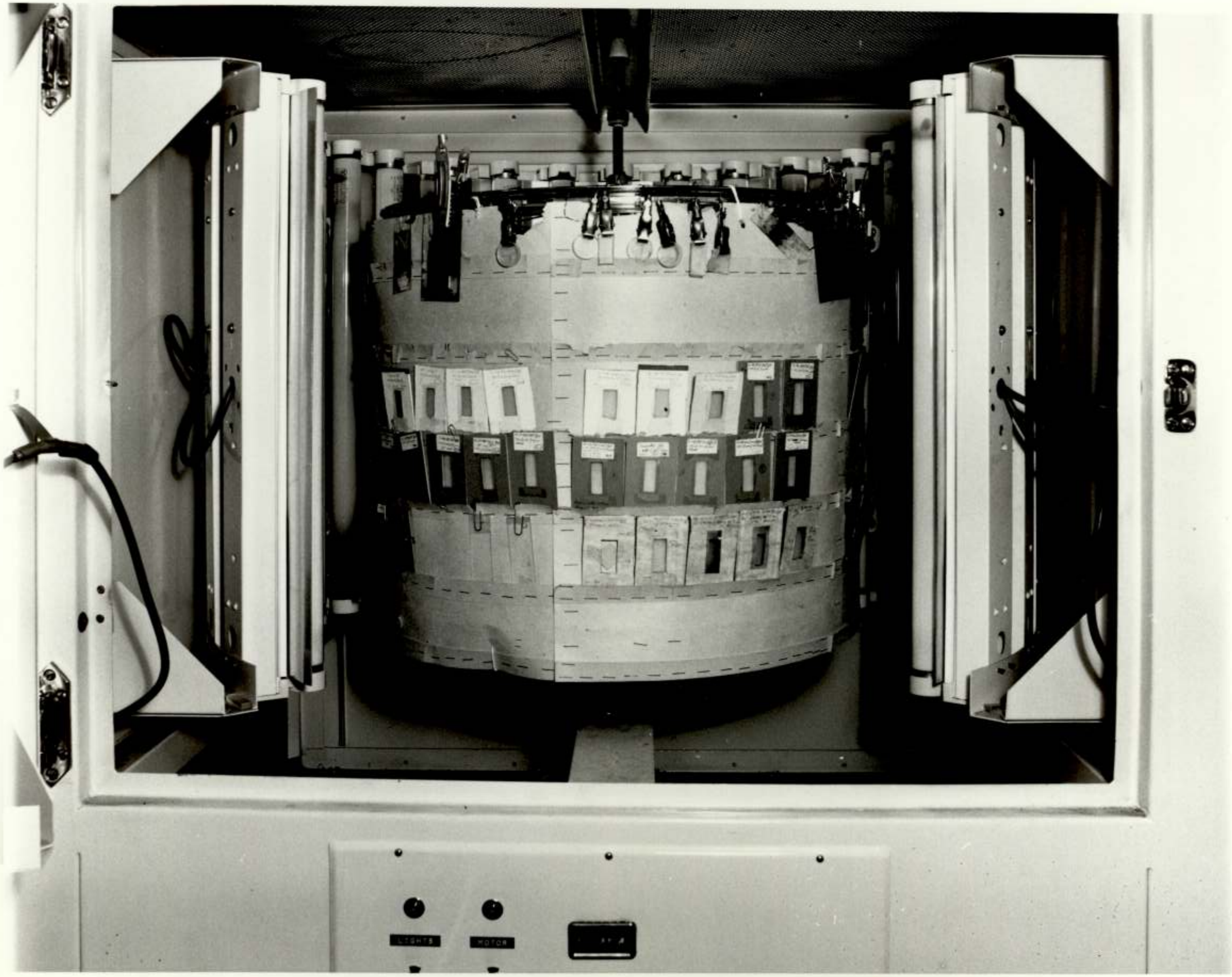


PLATE 6 - The UV exposure cabinet.

the samples all received as constant an intensity of irradiation as possible. Testing intervals between successive sample analyses tended to vary between 50 hrs., during the early stages of exposure, and, typically, 100 hrs. once a seemingly steady ageing pattern had been established; however, this obviously depended to a large extent on the nature of the particular coating material under examination. Finally, in addition to this photo-oxidative mode of ageing, photodegradative studies (of the PVC plastisol coatings) in both nitrogen and nitric oxide/nitrogen atmospheres were also made, as will be described in section II.3.2.4.

II.3.2.3 Thermal Ageing Apparatus

Two separate pieces of apparatus were made use of during the course of this work for thermal ageing purposes, the main one of which consisted of an environmental test chamber, while the other was basically a simple vacuum drying apparatus. These are now described in more detail:

II.3.2.3(a) Environmental Test Chamber

The environmental test chamber (Montford Instruments Ltd., London, N.W.10) is illustrated in Plate 7 and consists essentially of an oven cavity (30 x 30 x 32 cm.) incorporating a heating unit and an air circulating fan. The main feature of this apparatus for the purpose of this work is its very precise temperature control, accurate to within ±0.1°C throughout the oven cavity and variable over the temperature range of -50 to 500°C. Additionally, temperature cycles could be programmed, although this particular facility was not actually utilised here.

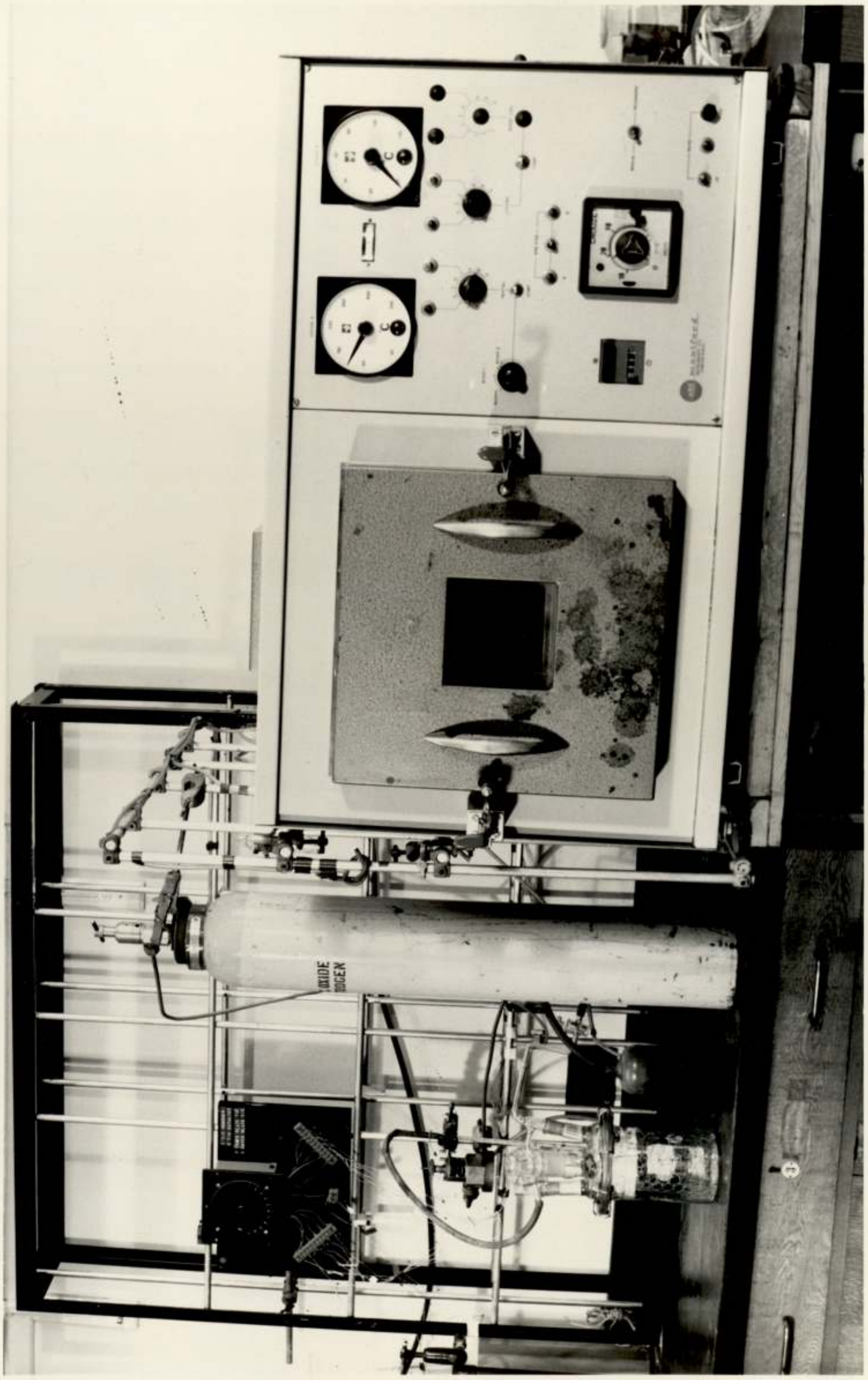


PLATE 7 - The environmental test chamber.

Thermal ageing experiments using the test chamber were conducted solely on the PVC plastisol coatings previously described, in controlled atmospheres of either nitrogen or nitric oxide in nitrogen (see section II.3.2.4 following). However, due to the fact that air could not be completely excluded from the oven cavity, sample exposures were found to be most successfully carried out in a self-contained Pyrex glass vessel which was conveniently housed in the oven cavity (see Plate 8). Test specimens were mounted vertically in this glass vessel on a wire-netting support as shown, with the circulating nitrogen or nitric oxide/nitrogen atmosphere in their midst ensuring that any volatiles emitted from the samples during ageing were quickly purged from the vessel and the ageing atmosphere renewed.

Finally, coatings materials exposed in the test chamber in this way were aged for periods of up to 60 hours, with analyses of them being carried out, initially, at 5 hourly intervals, increasing later to, perhaps, every 10 or 15 hours.

II.3.2.3(b) Vacuum Drying Apparatus

The vacuum drying apparatus (Gallenkamp) depicted in Figure 8 was, in fact, the thermal environment used for carrying out preliminary thermal ageing studies prior to the availability of the environmental test chamber previously described. However, although the drying pistol, as it is known, was obviously inferior to the test chamber as regards temperature control, etc., it nevertheless proved adequate for the purpose of characterising the behavioural pattern of plastisol coatings on thermal ageing in either air, nitrogen or under vacuum. Finally, whilst ageing temperatures were again around $100^{o}C$

PLATE 8 - Glass vessel used for housing thermal ageing test samples, housed, itself, in the oven cavity of the environmental test chamber.

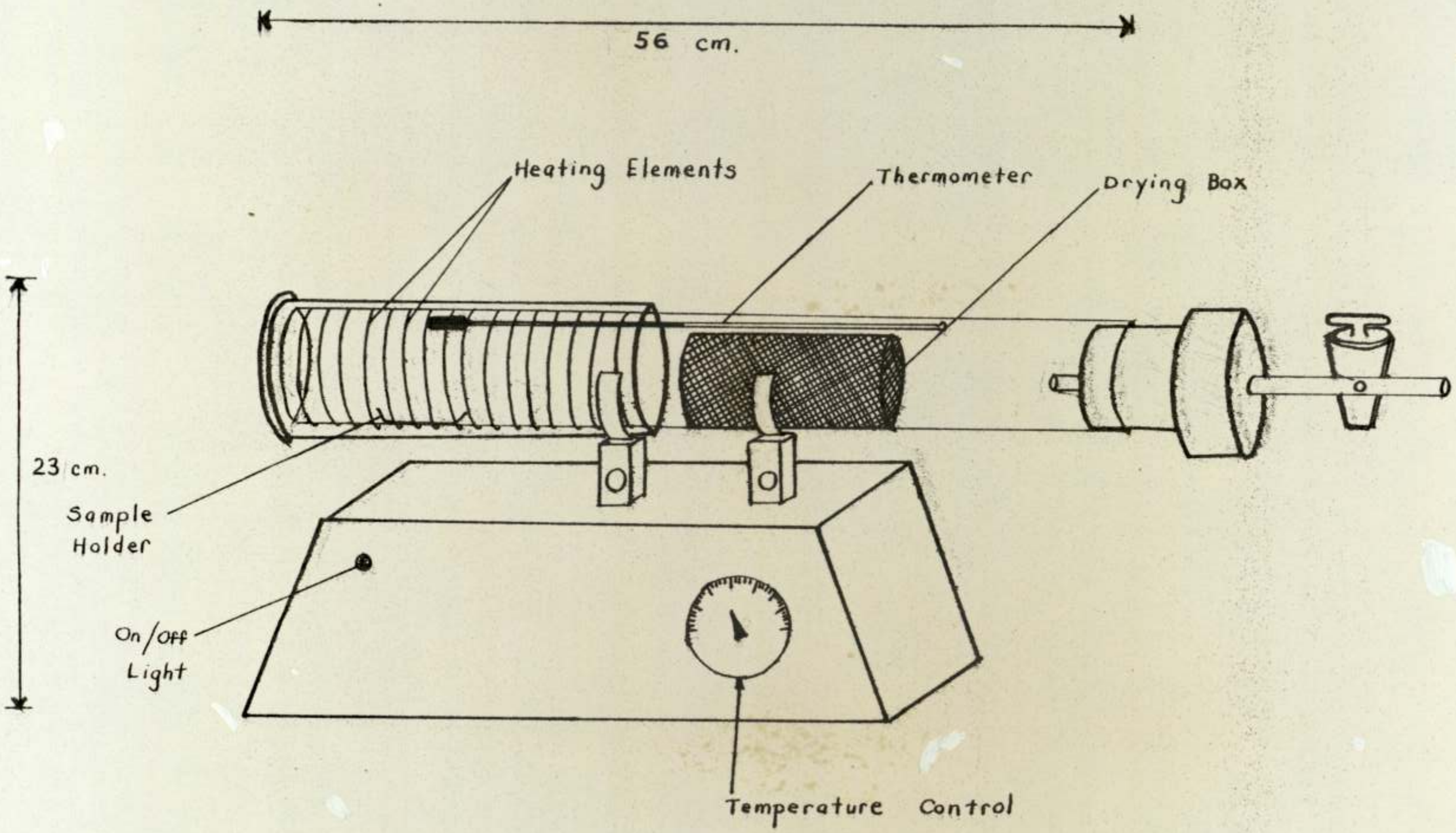


FIGURE 8 - The vacuum drying apparatus used for thermal ageing .

in common with subsequent test chamber experiments, actual exposure times were somewhat longer, reaching up to 140 hours.

II.3.2.4 Nitric Oxide Studies

The study of the effect(s) of nitric oxide (NO), as a potentially reactive constituent of an ageing environment, on exposed surface coatings provides an interesting case study which, additionally, bears some relation, albeit limited, to a natural weathering situation in an area of particularly high air pollution(192). For the purpose of these studies, gaseous mixtures of nitric oxide in nitrogen (NO/N_2: British Oxygen Co. Ltd., London, S.W.19) at various concentrations (see Table 5 overleaf) were kindly supplied by the Emission Control Research Laboratory of the British Leyland Motor Corporation (Jaguar Cars Ltd.), Coventry.

Ageing studies in the presence of a NO/N_2 atmosphere were carried out exclusively on the PVC plastisol coatings (PVC having previously been reported(200, 201) as being reactive towards nitric oxide) in both the thermal (see Plate 8 previously) and photochemical (uv) environments. In the latter case, a purpose-built quartz glass vessel was specially designed to enable the uv irradiation of test samples in the presence of selected ageing atmospheres. This quartz glass exposure vessel is illustrated in Plate 9 in its clamped position in the uv cabinet, showing how test specimens were mounted inside it.

Because of the extremely rapid, near-complete oxidation of nitric oxide in the presence of air, both the thermal and uv exposure

Cylinder Code No.	NOMINAL CONCENTRATION (ppm NO in N_2)	ACTUAL CONCENTRATION* (ppm NO in N_2)
F 76739	250	300
K 16591	500	488
F 73844	2500	2380
K 15696	3300	3140

(* as measured by the BLMC Emission Control Research Laboratory)

TABLE 5

RANGE OF NITRIC OXIDE/NITROGEN GAS MIXTURE CONCENTRATIONS

PLATE 9 - Quartz glass ageing vessel for UV irradiation/gas exposure tests (shown mounted in UV cabinet).

glass vessels needed to be purged thoroughly with dry, oxygen-free nitrogen prior to filling with nitric oxide/nitrogen. In the case of thermal ageing experiments, a steady NO/N_2 gas flow of approximately 0.1 - 0.2 $l.min^{-1}$. was maintained throughout exposure, whereas, for irradiation in the uv cabinet, a closed system had to be employed between testing intervals. These ageing tests were each conducted over similar exposure times and, in the case of thermal ageing, at identical temperatures to those employed in their corresponding experiments under inert nitrogen atmospheres.

Finally, the highly toxic nature of nitric oxide gas demanded the strict observance of all necessary safety precautions. Efficient removal of nitric oxide (and any other oxides of nitrogen present) from all quantities of NO/N_2 gas deployed in ageing experiments was achieved by passage through an alkaline potassium manganate absorbing solution (203). Additionally, an electronic "Leak-Seeker" device (Analytical Instruments Ltd., Cambridge) was used to check all gas-carrying equipment for leakages, as well as monitor the surrounding laboratory working area for any harmful gas build-up.

II.4 Analytical Techniques

From the wide range of analytical techniques which have already been mentioned in the previous chapter, those of them which were actually used during the course of this work are now described and details of their underlying theory given where relevant to the text. Although goniophotometry is the main one of these methods, its own description is, in fact, left until last so as to lead directly and conveniently into the following Chapter 3 in which modifications to the existing instrumentation are described as forming part of this current project.

II.4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM), as a direct means of visualising the surface topography of paint films, proved to be an extremely valuable and powerful viewing technique for following the ageing deterioration of surface coatings. In this way, microscopic changes in surface appearance could be usefully related to visually perceivable changes in gloss, as well as other effects, brought about by ageing.

The scanning electron microscope which was actually used in this work was the Stereoscan Mark 2A instrument, produced and marketed by Cambridge Scientific Instruments Ltd., and illustrated in Plate 10. The basic principles of its operation, as represented schematically in 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 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 dependent upon the surface topography at the point at which the electron beam impinges on the specimen. By applying a scanning motion to the electron 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 merely by altering the amplitude of the scan on the specimen.

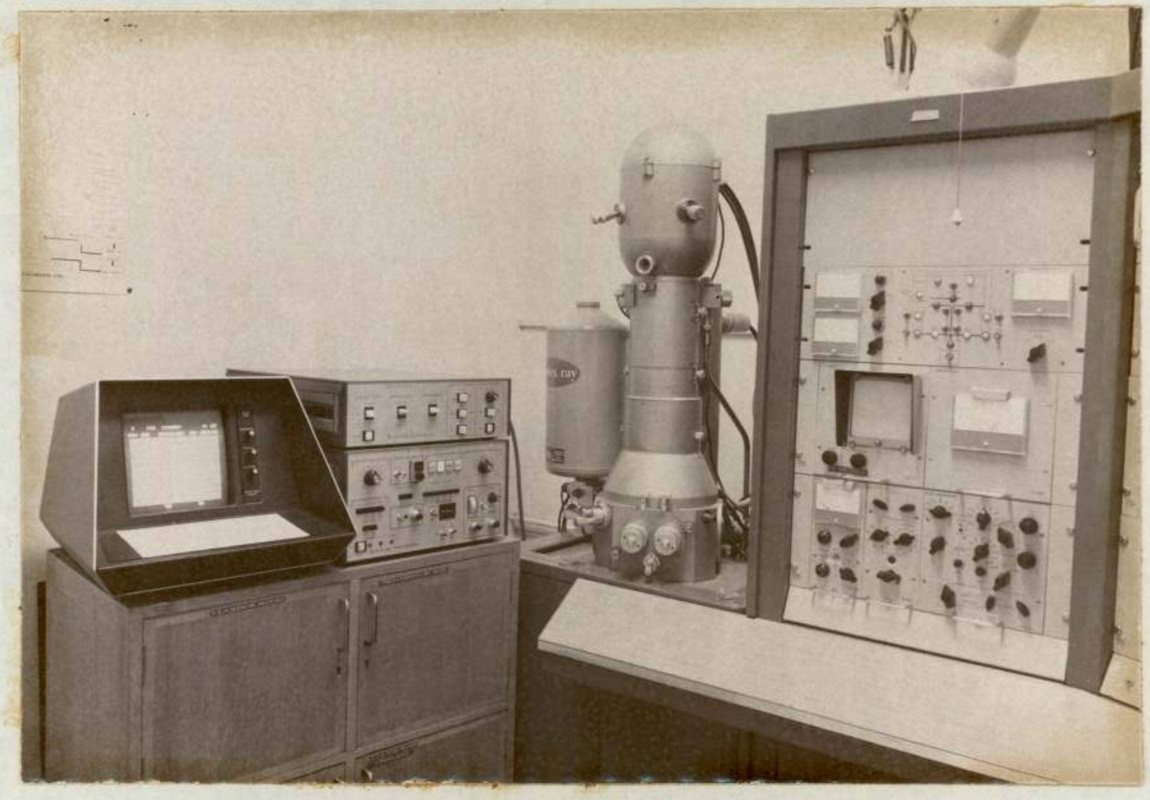


PLATE 10 - View of the Stereoscan Mark 2A scanning electron microscope (right), showing (left) its Kevex-ray energy dispersive X-ray analyser accessory.

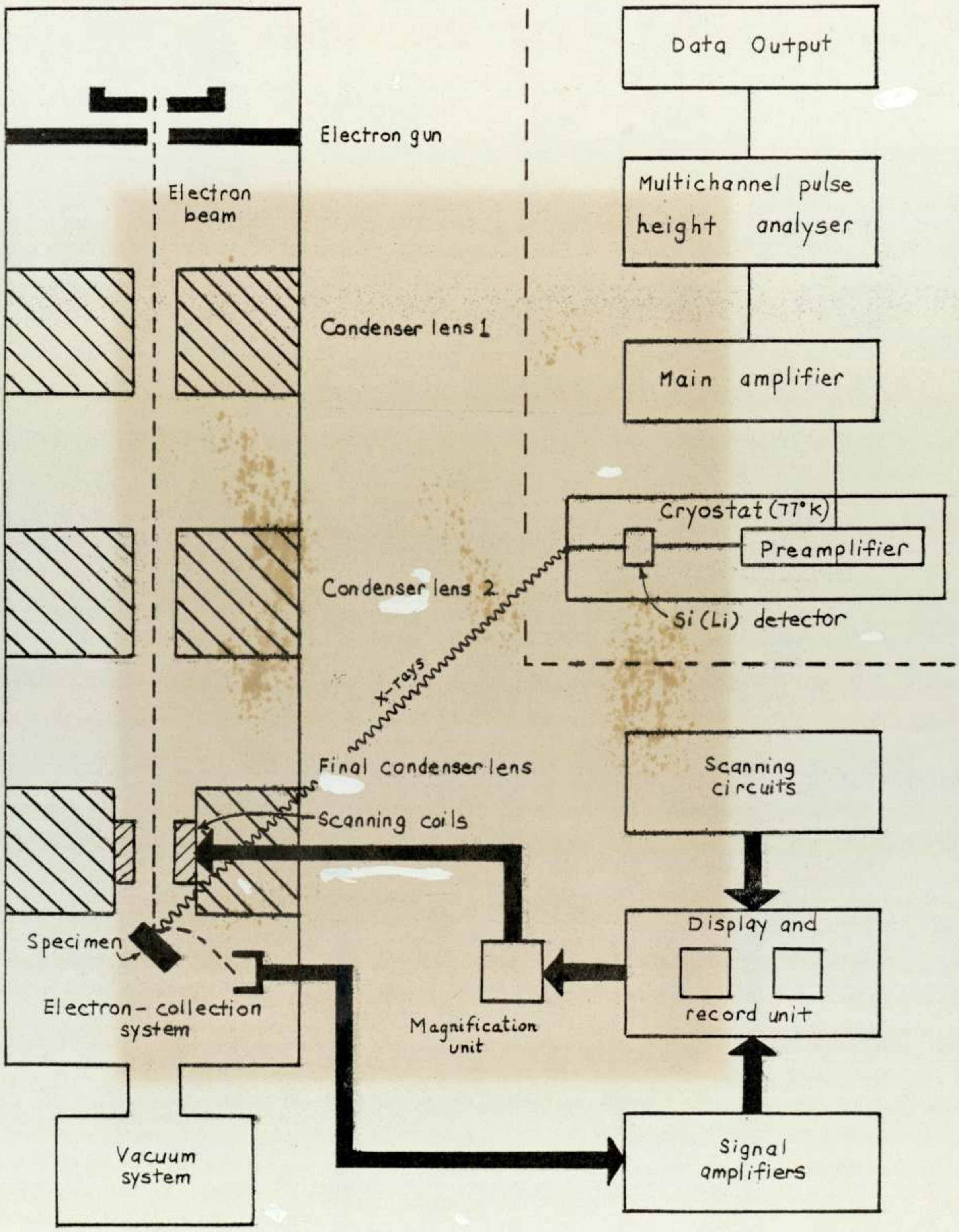


FIGURE 9 - Schematic representation of the basic principles of operation of tl STEREOSCAN Mark 2A scanning electron microscope, in conjunction with its KEVEX energy dispersive X-ray analyser accessory (top right).

Finally, samples for SEM analysis were mounted on to small, circular aluminium stubs (1 cm. diam.), with up to as many as eight samples per stub in recognisable shapes. The mounted specimens were then coated with a thinly deposited layer (up to 500 Å thick) of either gold-palladium or carbon in order to make their surfaces electrically conductive as required for SEM analysis.

II.4.2 Energy Dispersive X-ray Analysis (EDXA)

Energy dispersive X-ray analysis (EDXA) provided a valuable means of determining the elemental composition of paint film surfaces, particularly in its conjunctive use with SEM which effectively provided the viewing facility necessary for selective EDXA to be carried out on sample areas of chosen interest. The particular instrument used for this purpose was the Kevex-Ray System 5000A X-ray Energy Fluorescence Spectrometer fitted with a Model 6000 XES Data Processor. This system is shown in Plate 10 (left) linked with the Stereoscan Mark 2A scanning electron microscope.

The basic principle of the Kevex's mode of operation is included schematically into Figure 9 (top right) in which it can be seen how conveniently it is integrated with that of the Stereoscan. In brief, the Stereoscan's electron beam, when focussed on the sample, causes the emission of X-rays which are characteristic of each element present in the area of sample surface analysed. With the aid of a solid-state detector(206) (semi-conductor crystal), these X-rays are transformed into electrical pulses whose heights are proportional to the energy of the incident X-ray quanta. These pulses are then amplified, sorted and stored in a multi-channel pulse-height analyser. Finally, after counting for either a pre-set time or to a pre-set count, the energy-dispersive (EDXA) spectrum of the characteristic X-rays is obtained, typically in the form of a counts/sec. or, simply, counts versus energy (eV) plot and, with the present instrument, down as far as atomic number 9 (fluorine). In this way, SEM/EDXA studies can be performed on either a specific spot, a line or, indeed, the entire surface area of a paint sample, along with the imaging and photographing of the distribution of any selected element, provided, of course, that it is within the resolving power of the instrument.

II.4.3 Surface Roughness Studies

Surface profile characterisation, involving the quantitative size measurement and peak count of roughness irregularities, offers a valuable means of, not only following the ageing deterioration in paint films per se, but also of studying, on a quantitative basis, the detrimental effects which surface defects are known to have on the observed level of gloss. In this respect, direct visualisation by scanning electron microscopy of the types of defects formed can be considered to complement these surface roughness measurements, thus presenting a more complete "picture" from which the gloss relationship can be developed.

During the course of this study, two separate instruments were used for surface profile measurement, although differing only in model type. Firstly, the Talysurf 100 instrument (Rank Precision Industries Ltd., Leicester, England) was used during the early part of the work, prior to the slightly more sophisticated Talysurf 4 gaining preference. The basic mode of operation is the same for the two instruments, each of which consist essentially of an amplimeter unit connected to a tracer point probe. The probe, which has a tracer point radius of 0.00014 - 0.0002 in. and a tracer point weight of approximately 0.4 g., moves slowly over the sample surface, tracing out, in the process, the contours of the surface irregularities which it traverses (Figure 10). Its movement up and down, in following the rugosity of the surface, is simultaneously transmitted to a coil, inside the tracer body, which moves in the field of a permanent magnet, thus producing a small fluctuating voltage relating to the height of the surface irregularities. This voltage is then fed from the coil into the amplimeter where it is amplified and integrated so as to actuate the direct-reading meter which, ultimately, shows the average height of the roughness irregularities (AHRI) as the tracer moves over the surface. However, this final step is, in fact, achieved via the instrument's centre-line averaging (CLA) of the roughness profile of the surface, followed by its inversion of that portion of the profile below the centre-line, review of the irregularities which it has measured, before finally computing their average height for meter display.

Each of the two Talysurf instruments used in this work has a range of path lengths, 0.15, 0.5, 1.5, 5.0 mm., the latter two of which employ a 0.75 mm. (0.03 in.) cut off with respect to the horizontal width of the irregularities, above which they are not recorded. However, the Talysurf 4 instrument, as compared with the 100 model, incorporates an added facility for simultaneous measurement of the AHRI, peak count per inch and also the bearing area. For each complete sample analysis, twenty measurements were made in different directions, with their mean values for AHRI and peak count being taken for the purposes of data presentation.

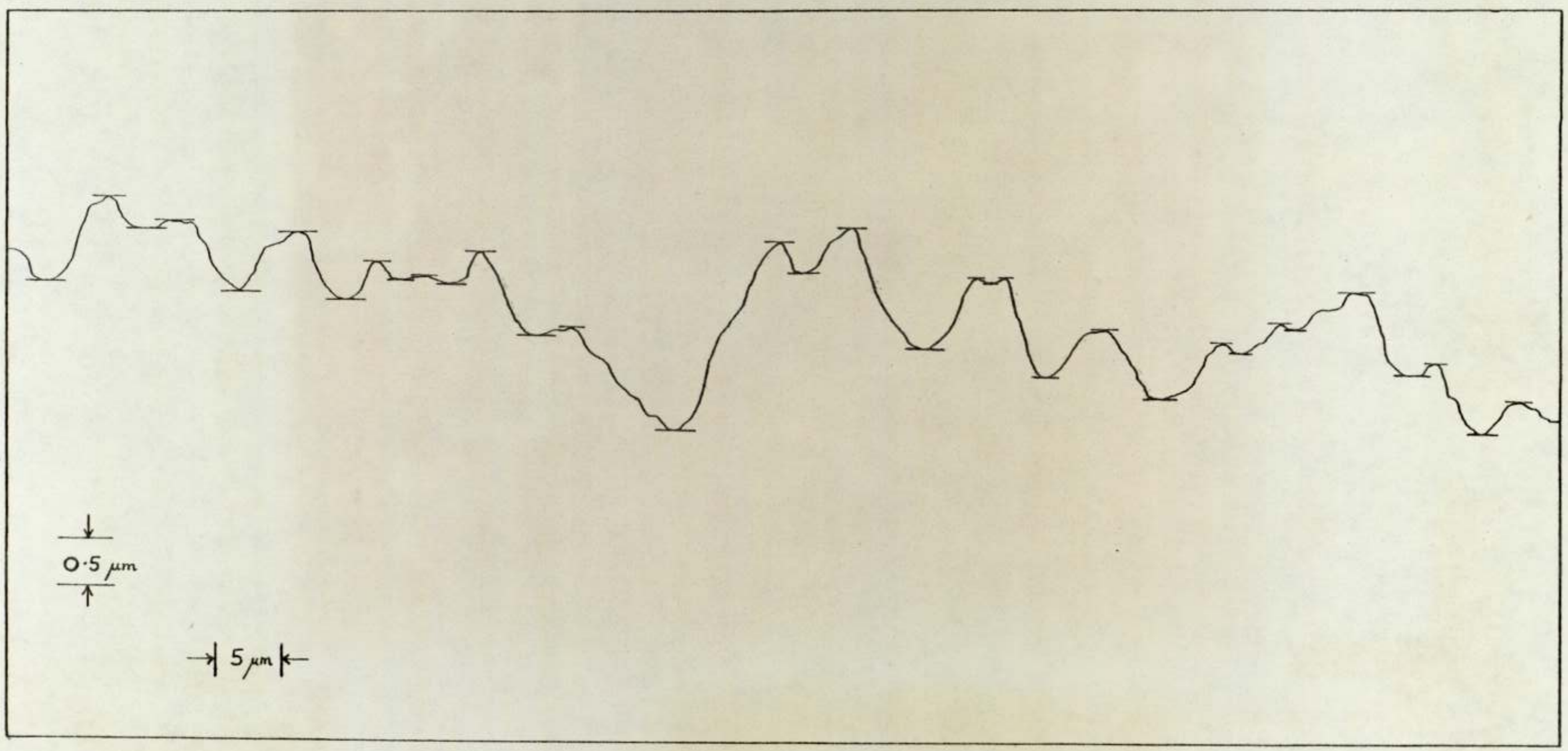


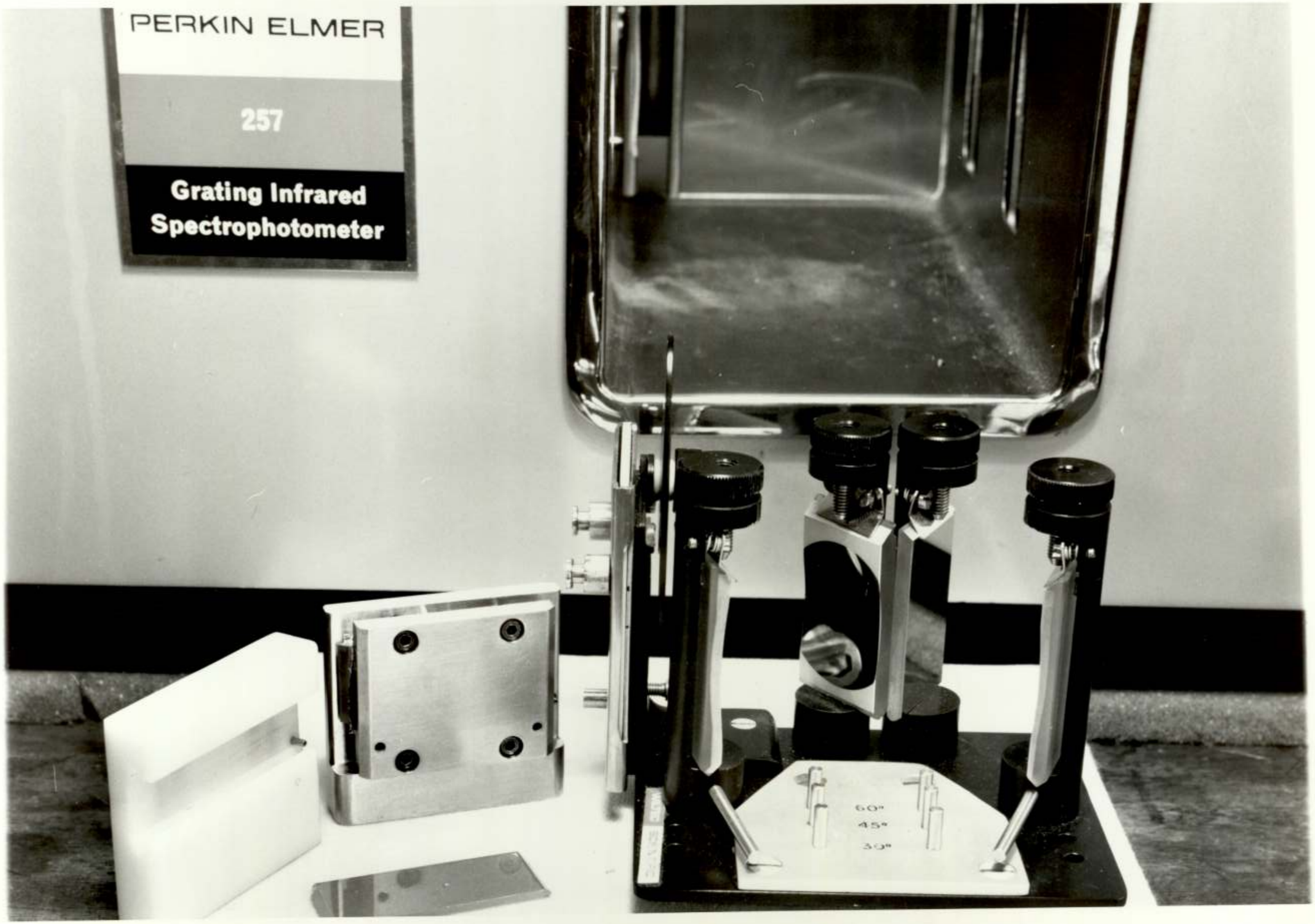
FIGURE 10 - Example of a Talysurf (100) trace of a surface coating profile (showing peaks/troughs marked off for counting).

Finally, this type of surface roughness measuring technique is relatively quick and simple to use, requiring little or no sample preparation, and has been found to be highly informative in ageing studies of paint films, especially in the case of those materials which develop relatively large irregularities during weathering. Nevertheless, it does have one or two disadvantages in that its reliability is impaired by substrate unevenness and it may also cause slight damage to the sample surface in certain cases. These particular drawbacks, however, are largely overcome in those instruments in which it is possible to have a reversal of the normal mode of operation, in which the sample supports the probe, to have one in which the probe, point uppermost, is merely brought into contact with the inverted sample supported above it.

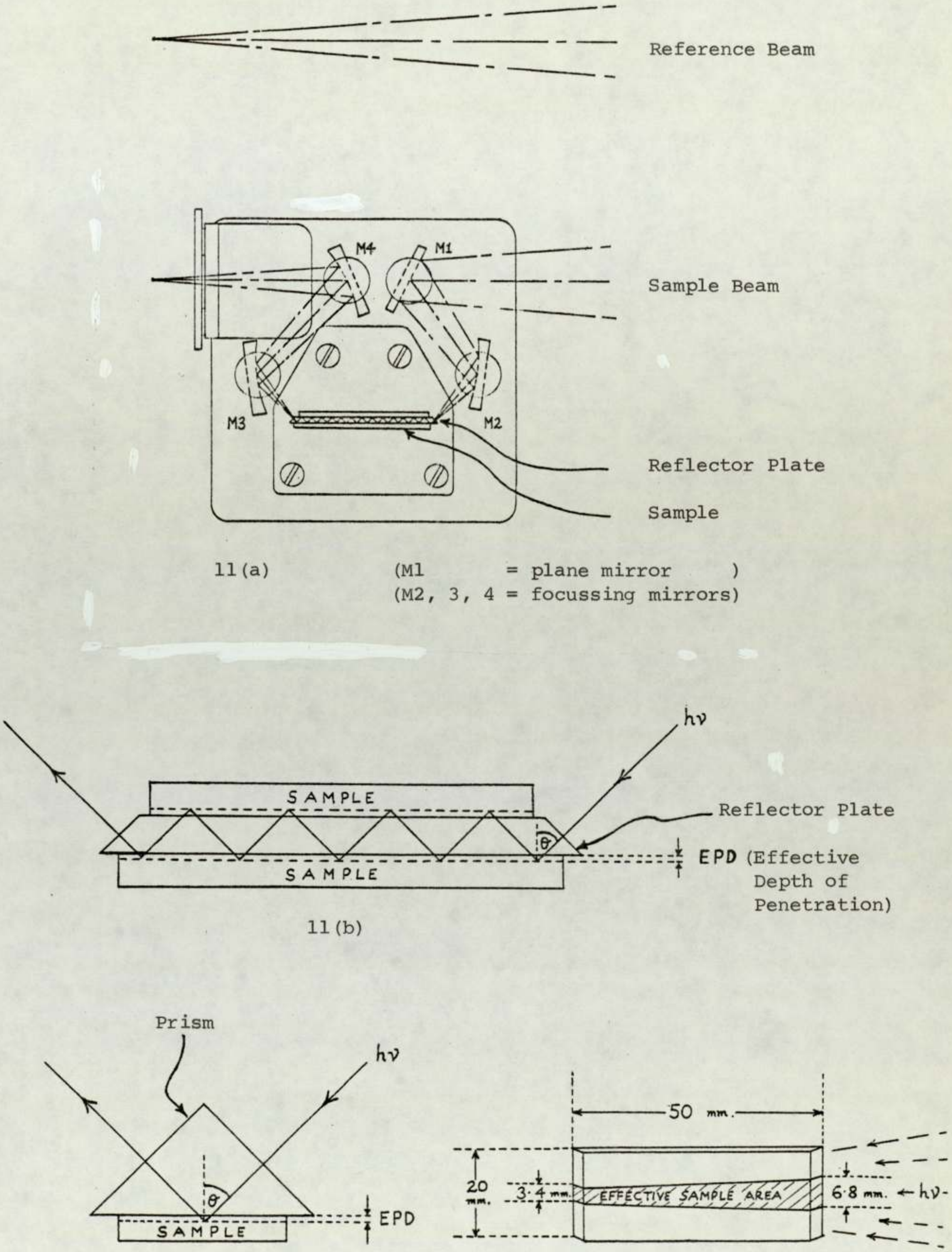
II.4.4 Multiple Internal Reflection Spectroscopy (MIRS)

Multiple internal reflection spectroscopy (MIRS) represented this project's major source of information relating to the nature of the chemical changes taking place at the surface of the paint films studied on ageing. The instrumentation associated with this technique is illustrated in Plate 11 and is seen to consist of a Perkin-Elmer Model 257 Grating Infrared Spectrophotometer, providing a continuous record of infrared transmittance as a function of frequency (expressed in wavenumber units), fitted with a Model 9T Single Beam Multiple Internal Reflection Attachment(204) (Wiltec Scientific Instruments Ltd., London NW9). The MIR attachment, which fits into the sample beam of the spectrophotometer, is shown removed and with its sample holder dismantled in Plate 12. Additionally, its mode of operation is represented schematically in Figure 11(a), showing how it effectively

PLATE 11 - Multiple internal reflection spectroscopy (MIRS) apparatus.



<u>PLATE 12</u> - Multiple internal reflection attachment.



11(a) (M1 = plane mirror) (M2, 3, 4 = focussing mirrors)

11(b)

11(c)

11(d)

FIGURE 11 - Schematic Arrangement employed in MIRS showing:-
(a) the operating layout of the Model 9T MIR attachment used;
(b) the MIR effect which it brings about (compared with
(c) the single internal reflection effect); and
(d) the dimensions and effective sample area of the KRS-5 MIR plate.

diverts the infrared sample beam through its multiple internal reflection element, thus bringing about the MIR effect from the sample as shown in Figure 11(b) (and compared, for interest, with its single internal reflection counterpart in Figure 11(c)).

The internal reflection element used in this attachment is a 45° KRS-5 2 mm. reflector plate, composed of a thallium bromide/thallium iodide eutectic mixture ($TlBr_2/TlI_2$ = 42/58 mole %), and is quoted as having a 30 - 40% transmittance with the particular Perkin-Elmer spectrophotometer used. Its dimensions are given in Figure 11(d) in which its effective sample area, as determined(173) by careful screening of the ends of its entrance and exit faces, is also indicated.

The actual mechanism by which MIR spectra are obtained in this way is given in Figure 11(b) which depicts how the infrared beam, at successive points of internal reflection throughout the KRS-5 plate, appears to penetrate slightly beyond the physical limits of the plate and into the sample before returning to the plate - a phenomenon which has been attributed to the wave-form nature of the radiation. However, during the course of this process, the amplitude of the beam decreases exponentially with depth of penetration into the sample, consequently becoming known as the "evanescent wave". Prior to its return to the reflector plate (or other type of element), this evanescent wave then undergoes selective attenuation characteristic of the infrared activity of the sample which, when measured in terms of transmittance and plotted as a function of wavelength by the spectrophotometer, gives rise to the internal reflection spectrum for the sample.

Thus, the effective depth of penetration (EPD) of the infrared radiation into the sample surface can be expected to be a particularly influential factor in determining the quality of spectra obtained by this method. Indeed, this aspect of IRS theory has received considerable attention(170, 171, 173, 174), resulting in the derivation of mathematical relationships which show the EPD to be a function of (1) the wavelength of radiation, (2) the angle of incidence of the radiation (θ in Figure 11(b)), and (3) the respective refractive indices of the internal reflection element and the sample. Hence, for the particular arrangement used throughout this work (i.e., KRS-5 2 mm. plate, angle of beam incidence = 45°, giving rise to approximately 25 internal reflections in practice(173)), it has been calculated(171) that, for a sample of refractive index 1.5, the approximate depths of beam penetration at 2.5 μm (4000 cm.$^{-1}$) and 20 μm (500 cm.$^{-1}$), i.e., covering the infrared scanning range, are approximately 0.7 μm and 5.8 μm respectively. This EPD range, coinciding, as it does, with typical depths of degraded surface layers reported(205) for PVC films on ageing, was therefore considered to provide a valid basis for deciding upon a working angle of incidence of 45° for the recording of all MIR spectra. The other two available angles of incidence of 30° and 60° could then be most usefully regarded as providing a valuable means of determining, wherever possible, the apparent depth of specific ageing effects, as indicated in specific regions of the spectrum.

The actual experimental procedure involved in the recording of all MIR spectra in this study can be summarised as follows. Firstly, the KRS-5 plate was carefully and thoroughly cleaned with a suitable solvent (e.g., methanol) and dried and polished on a soft felt cloth stretched over a plane glass plate. This process was then repeated, if necessary, until the MIR spectrum of the plate alone (Figure 12) showed that it was free from contamination. The coating sample to be analysed was cut to shape to fit either just the rear side of the plate or both sides, depending upon how strongly absorbing the sample was in contact with the plate, before being mounted in the sample holder. This holder was then located in the 45° angle of incidence position of the MIR attachment, ready for insertion into the sample beam of the spectrophotometer. Finally, having carried out the necessary initial spectrophotometer calibration, followed by the optical alignment of the attachment's mirror reflectors, and reference beam attenuation in order to balance the spectrophotometer for its energy loss in the sample beam, the MIR spectrum of the sample was recorded in either the "medium" or, as was more usual, the "slow" scan mode.

Further to its obvious qualitative value, MIR spectral data obtained in this way proved to be amenable to semi-quantitative analysis using the "absorbance ratio" method (175) of peak analysis. This treatment effectively involved ratioing the absorbance of those peaks in the sample spectrum which were affected by ageing with the absorbance of a suitably stable internal reference peak which was not. The absorbance (A) of a sample at a given wavelength is related to its transmittance (T) and concentration of the absorbing species (c) by the Beer-Lambert Law, eq. (1) below:-

$$A = \log_{10}(I_o/I) = \log_{10}(1/T) = abc \qquad \ldots\ldots (1)$$

where: I_o = intensity of radiation incident on the sample,

I = intensity of radiation transmitted by the sample,

a = absorptivity, and is specific for a particular material at a particular wavelength ($l.g.^{-1} cm.^{-1}$),

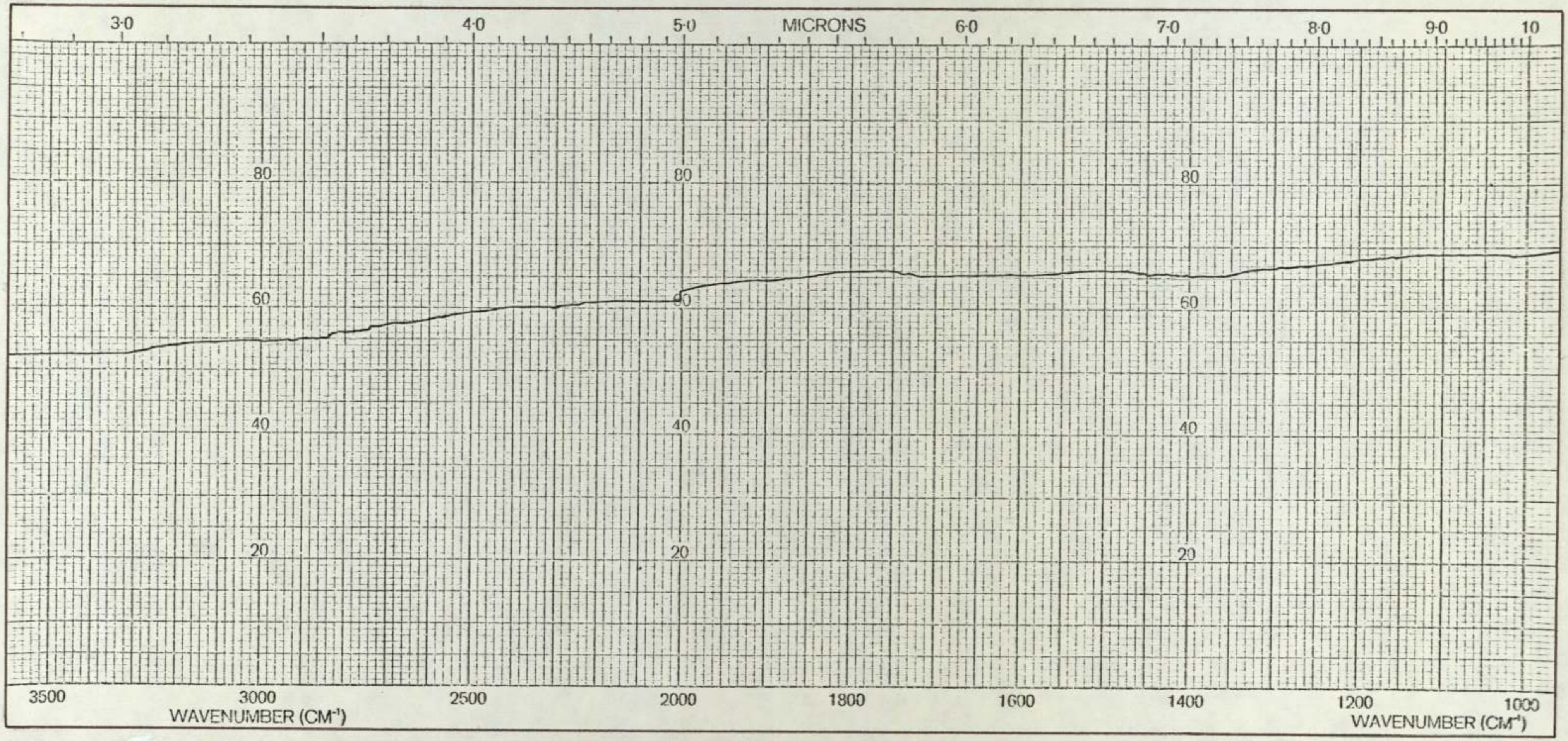


FIGURE 12 - MIR spectrum of the KRS-5 plate after cleaning.

and, b = path length through the sample (cm.).

This "absorbance ratio" method, in turn, was found to be most easily and reliably applied via the "tangent-line" technique$^{(175)}$, whereby a common tangent is constructed between the two transmission maxima on either side of the infrared peak of which the absorbance is to be determined (as shown in Figure 13). The true absorbance (A) of the peak is then obtained by simply subtracting the background absorbance (A_o), at the frequency of the absorption maximum, from the total absorbance (A_T), as given in eq. (2) below:

$$A = A_T - A_o \qquad \text{...... (2)}$$

This technique, whilst not yielding a "true" background absorbance, nevertheless yields a highly reproducible one with errors usually cancelling out, especially when absorbances are being related to that of an internal reference peak.

II.4.5 Weight Loss Measurements

Weight loss measurements on the PVC plastisol coatings previously described (section II.2.2) were conducted on both natural and artificial weathering samples coated on to weather-resistant stainless steel substrates. The actual weighings were made on an analytical balance which gave readings in grammes accurate to the fourth decimal place and allowed an estimate to be made of the fifth. Weight changes, when calculated, were then expressed in terms of either an overall percentage weight change or, as was more usual, a specific weight loss or gain per unit area (g./cm.^{2}).

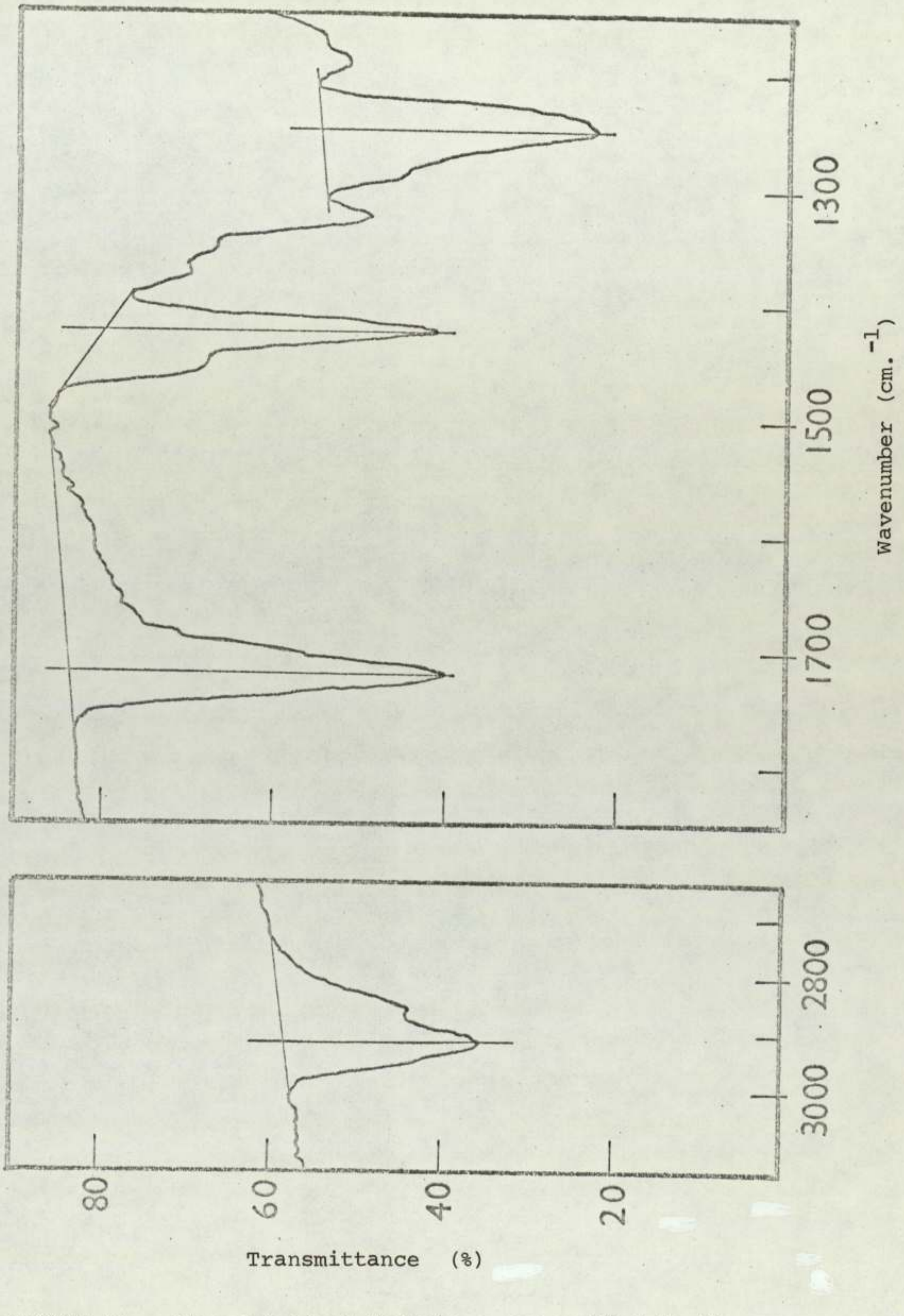


FIGURE 13 - "Tangent-line" Technique, as applied to the determination of absorbances of MIR spectral peaks.

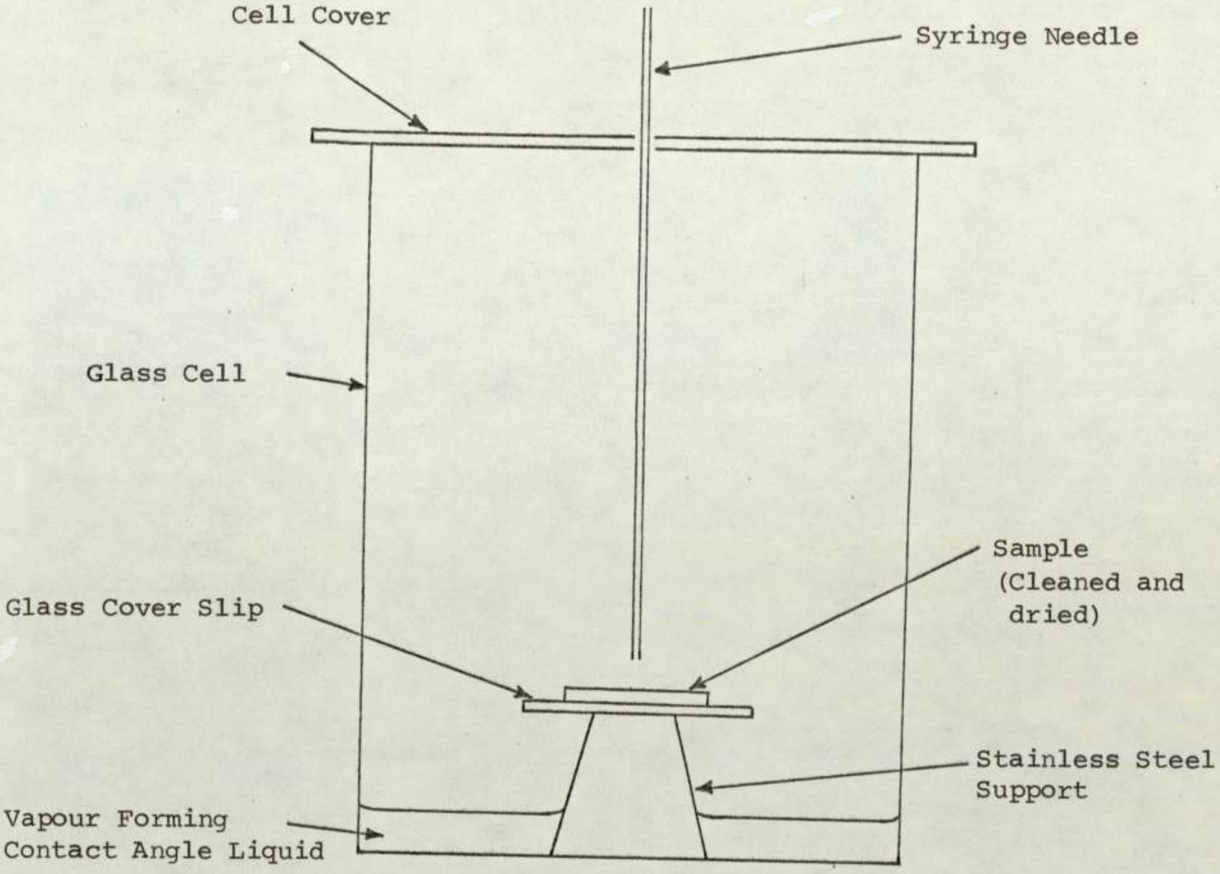
Prior to weighings being taken, each sample was very carefully and gently cleaned under running water (as will be described later in section III.5.2), so as to remove all traces of loose, unattached debris (e.g., "chalk", dirt particles, etc.) from the sample surface, before being left to dry thoroughly in a desiccator. This was particularly necessary, of course, in the case of outdoor weathering samples and was made even more so as a result of the relatively soft plastisol coatings tending to harbour dirt and other particulate matter on their surfaces. Additionally, by weighing outdoor exposure samples both before and after cleaning, some qualitative indication could be gained as to the dirt retention characteristics ("chalking" being at a minumum in plastisol formulations) of a given coating in a particular environment. Whilst weight loss measurements are usually most usefully applied to the study of erosion rates (see section I.5.1.2(d) previously), they are of further value to the study of plastisol coatings in particular insofar as they enable a close check to be maintained on the loss of plasticiser by, for example, volatilisation and leaching from the surface. These processes affect a variety of film properties and can often explain initial changes observed in plastisol coatings on weathering.

Finally, weight loss analysis of the range of commercial coatings studied (see section II.2.1), having been provided by the Building Research Station, had already been carried out by BRS workers and included in a recent publication(10).

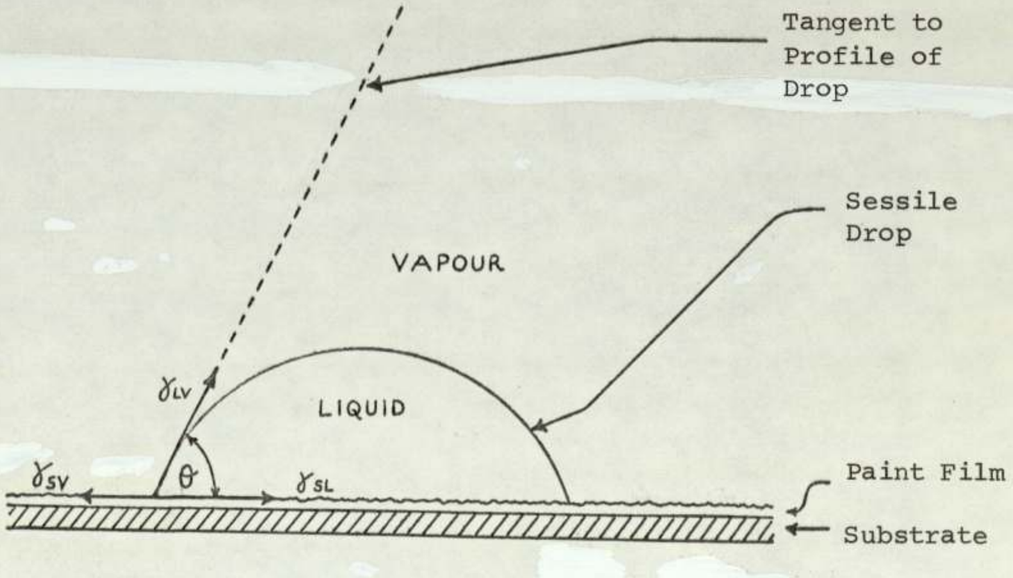
II.4.6 Surface Energetics

Studies under the general heading of "surface energetics" were most easily and conveniently carried out by means of measuring the respective contact angles which certain liquids made with coatings surfaces. Two liquids were chosen for this purpose - (a) water, and (b) diiodomethane (CH_2I_2) - water wettability, of course, being of particular relevance to a study, such as this, of the effects of weathering on paint films. However, water and diiodomethane are normally chosen on account of their ease of purification and quite different polar and dispersive contributions to their respective surface tensions.

The contact angles which each of these two liquids made with the coatings samples studied were, in fact, measured by a sessile drop method$^{(147, 218)}$ using the cell arrangement$^{(218)}$ shown in Figure 14(a). All contact angles observed in this way were taken to be equilibrium advancing contact angles (see Figure 14(b)) as distinct from dynamic advancing and receding angles. The further information which could subsequently be derived from this type of data is two-fold - firstly, it enables the critical surface tension (γ_c)$^{(142, 218 - 226)}$ of the coating surface to be calculated (where γ_c is defined as the surface tension of that liquid which just completely wets the solid surface), and, secondly, it affords a means of determining the coating's surface free energy$^{(142, 218, 219, 227)}$ together with its polar and dispersive components. Additionally, it is also found, in practice, that a reasonable correlation exists between the critical surface tension of a solid surface and the dispersive component of its surface free energy. It is in order to obtain values relating to the surface free energy of the solid phase that contact angles made by different liquids with the surface are measured. The liquids which are usually chosen for this purpose, on the basis of their widely differing polar and dispersive



14(a)



14(b)

FIGURE 14 - Diagrams showing (a) the glass cell in which contact angle measurements were made, and (b) the profile of a sessile drop resting on a paint surface, exhibiting the equilibrium advancing contact angle (θ).

components of surface tension, are water and diiodomethane (as in the case of this study) and, to a lesser extent, formamide. Final values for the surface free energy components are then obtained through the Owens and Wendt equation(227). In principle, changes in these components, as calculated in this way, can often yield a great deal of information concerning changes in the polarity of the surface, as brought about by weathering for example.

Nonetheless, there are certain difficulties associated with the contact angle technique, which, for most purposes, can be regarded as being two-fold. Firstly, the technique is extremely sensitive to surface contamination, monitoring, as it does, the uppermost monomolecular layer. Consequently, all coatings' surfaces examined needed to have been scrupulously cleaned (careful washing) and dried (vacuum desiccation) before contact angle measurements could be undertaken. Secondly, contact angles are also affected by surface roughness, which generally makes their accurate measurement more difficult; however, this effect has, in fact, been quantified by Wenzel(228) who developed a mathematical relationship, eq. (3) below, between the macroscopic surface roughness factor (r) and the measured contact angles for rough (θ') and ideally smooth (θ) surfaces.

$$r = \frac{\cos\ \theta'}{\cos\ \theta} \qquad \text{......} \ (3)$$

Hence, on the basis of these theoretical considerations, it would appear, in principle, that this method of analysis represents a sensitive means of following changes in both surface polarity and rugosity. This, of course, makes it particularly applicable to the study of paint films on ageing, thus providing, in the process, a useful supplementary technique to internal reflection spectroscopy (IRS) and surface roughness studies.

II.4.7 Thermal Analysis

Thermal analysis of PVC plastisol coatings materials was carried out primarily as a means of following any shifts in glass transition temperature (T_g) which might occur on outdoor weathering. The instrumentation used for this purpose comprised a Perkin-Elmer DSC-2 Differential Scanning Calorimeter fitted with a liquid nitrogen sub-ambient accessory, as shown in Plate 13.

Test samples were heated under a helium atmosphere over the termperature range 160 - 350°K. (-113 - 77°C) at a rate of 20°/min., and the thermograms recorded on a Smith's Industries Servoscribe 1S RE 542.20 potentiometric recorder equipped with temperature event marker. A sample's glass transition was observed as a step-wise change in the recorded base-line, the temperature (T_g) at which this occurred being conventionally taken as that temperature at which the change in heat capacity of the sample was at its mid-point.

II.4.8 Microindentation - Recovery/Time Analysis

Mechanical testing of PVC plastisol coatings was carried out by means of a microindentation - recovery/time technique; the range of commercial coatings studied having already been characterised in this way by workers at the Building Research Station(10). The instrument used was an I.C.I. Pneumatic Micropenetrometer which provided an automatic record of, initially, the indentation (μm), followed, on

PLATE 13 - Thermal analysis: the Perkin-Elmer DSC-2 Differential Scanning Calorimeter with sub-ambient accessory.

removal of the indentor load, by the sample recovery profile over preset time intervals (typically 1 or 2 mins.).

Because of the extremely soft nature of the plastisol coatings, it was considered likely that, in order for this technique to be sensitive to the expectedly small changes in hardness brought about by ageing, relatively small indentations (i.e., from larger-radius indentors with smaller sized loads) would need to be employed.

II.4.9 Goniophotometry

Goniophotometry represents the main analytical technique used throughout this project for characterising the surfaces of paint films and for studying their ageing deterioration. As described in the previous introductory chapter (see section I.5.1.1(a)(ii)), goniophotometry provides a valuable means of quantitatively characterising the manner in which a given surface spatially reflects light which is incident upon it. Whereas the basic goniophotometric technique, itself, is by no means new in the field of gloss measurement, particularly with regard to the correlation of its data with subjective visual gloss assessments, its application to the more specific study of ageing effects on the reflectance properties of paint films does appear to have been, as yet, almost totally neglected. This is, indeed, rather surprising when one considers the technique's undisguised potential in this respect, coupled with the obvious importance of gloss retention as the surface property by which a coating's weathering performance is most readily judged.

However, before going on to describe the goniophotometer and its mode of operation, it is appropriate at this stage in the text to consider the relevant background theory of light reflection from solid surfaces, and also to take account of some of the more phenomenological aspects which are peculiar to paint films in their role as light reflecting media.

II.4.9.1 Theory of Light Reflection from Paint Film Media

When light is incident upon the surface of a paint film, it is subsequently reflected by a combination of two entirely different processes. Firstly, a certain proportion of the incident light undergoes surface reflection in the normal way at the surface-air interfacial boundary in accordance with the laws which govern this type of process. Reflection in this way occurs mostly at an angle equal to or very close to the angle of incidence, deviations from this being ascribable to the irregularity of the paint surface. Secondly, however, the greater part of the incident light actually penetrates the surface by refraction into the bulk, where, depending upon whether the paint film is pigmented or not, it either undergoes scattering by pigment particles, or is internally reflected at the lower surface-substrate boundary, prior to its eventual re-emergence from the top surface. The mechanism by which light passes through the interior of films in this way, particularly via the scattering route through pigmented systems, still requires further elucidation, although it is true to say that in recent years a much deeper understanding of this phenomenon has been gained, as will be discussed later.

To start with, however, let us consider in more detail the underlying theory of surface reflection from paint films.

II.4.9.1(a) Surface Reflection

Paint surfaces, in common with all other "real" surfaces, can be most usefully regarded as being intermediate between perfect "mirror" and perfect matt surfaces when it comes to considering their reflection characteristics; each is now described:

II.4.9.1(a)(i) Perfect "Mirror" Surfaces

A perfect "mirror" surface is defined as "a plane surface which reflects all incident light unidirectionally at an angle equal to the angle of incidence", thus rendering the surface, in the process, effectively invisible to an observer. This type of reflection, as depicted in Figure 15(a), is termed "specular" reflection and is well known to be completely governed by Fresnel's Law(216), developed in the early nineteenth century. From the Fresnel equation, it is clear that the amount of light reflected increases with increasing angle of incidence, this being the reason why specular gloss-meters employ larger angles of incidence for the measurement of matt surfaces than they do for glossy surfaces (i.e., 85° as opposed to 20° respectively; as recommended in ASTM D523-53T).

Examples of 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.

II.4.9.1(a)(ii) Perfect Matt Surfaces

A perfectly matt surface is often defined, to greatest effect, as a surface which reflects incident light equally in all directions,

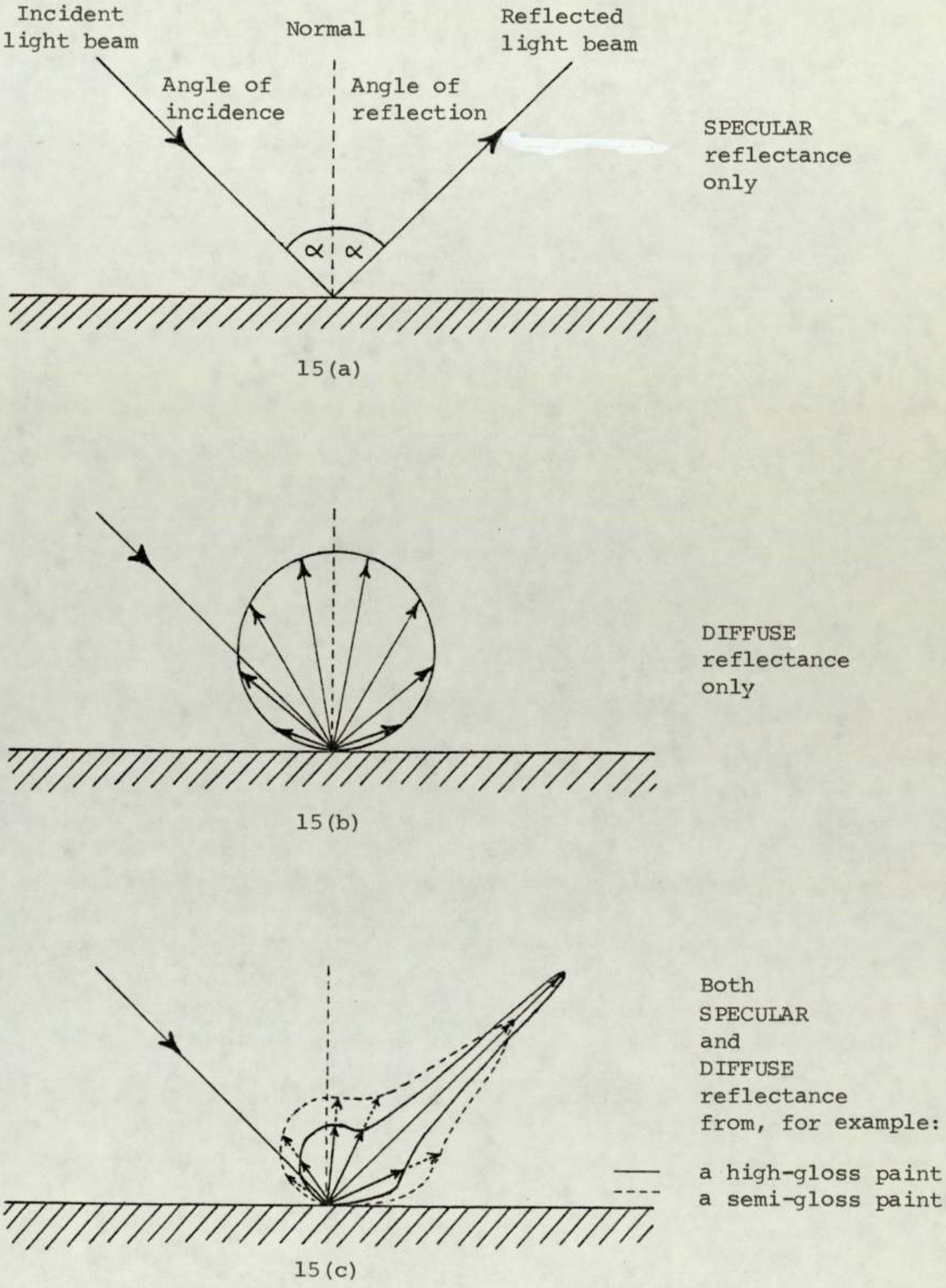


FIGURE 15 - Ray diagrams of the surface reflection characteristics of
(a) a perfect "mirror" surface (inc. definition of terms),
(b) a perfectly matt surface, and
(c) typical paint (i.e., "real") surfaces.

i.e., it appears equally bright from whatever angle it is viewed and is, itself, clearly visible to the naked eye. However, although this statement is certainly "apparently" true in practice as far as an observer of the surface would be concerned, it is not strictly true in theory.

The origin of the basic theory, which still remains valid today, for matt reflection can be attributed to Lambert(217) as long ago as the eighteenth century. On observing that a white wall illuminated by sunlight appeared equally bright at all angles of observation, Lambert assumed that such a surface behaved as though it were reflecting independently of the angle of incidence of the light radiation. This initial observation subsequently lead to the derivation of the Lambert Cosine Law(217) (eq. (4) below) in which the intensity of reflected light, B, in any direction is given by:

$$B = (I_o/\pi)\cos\alpha\cos\theta \qquad \ldots\ldots (4)$$

where: I_o = the intensity of incident light along the normal,

α = the angle of incidence, and

θ = the angle of reflection (observation).

The equation states, therefore, that a perfect matt reflector spatially distributes incident light in intensity proportional to the cosine of the angle of reflection. This, in turn, determines that the shape of the envelope of reflected light is, therefore, a sphere, as shown in Figure 15(b), and not a hemisphere as the initial definition of a matt reflector would seem to suggest. As regards the visual perception of a perfect matt surface as being apparently equally reflective over all angles of observation, this can be accounted for in terms of a combined viewing/reflection effect. When a large area of illuminated surface is viewed, the projected area of surface scan in a cone of fixed angle is inversely proportional to the cosine of the angle with the normal. Consequently, this effect tends to counterbalance the Cosine Law-dependent surface reflection, thus giving rise to an equally bright appearance from whatever angle the surface is viewed.

This type of matt reflection, as depicted in Figure 15(b), is termed "diffuse" reflection. Unlike specular reflection from perfect mirror surfaces which, as mentioned previously, is completely governed by Fresnel's Law, no such general law exists for diffuse reflection, although all formulae incorporate the Lambert Cosine Law.

Finally, it has often been suggested that a matt surface may be looked upon as a collection of an infinite number of microscopic or submicroscopic plane elements, randomly distributed within the macroscopic plane of the surface. However, in practice, perfectly matt surfaces, or perfect Lambertian diffusers as they are sometimes referred to, are extremely rare, barium sulphate and smoked magnesium oxide surfaces currently providing the closest approximations.

II.4.9.1(a)(iii) Paint Surfaces

Paint surfaces, in common with all other "real" surfaces, are obviously intermediate in nature between the two extremes of reflection previously described. Whereas perfectly smooth mirror surfaces and perfect matt surfaces exhibit only specular and diffuse reflectance respectively, the surface reflection from paint films is made up of both specular and diffuse components. As illustrated in Figure 15(c), the ratio of these two components largely determines the overall gloss of the surface, as characterised by the angular distribution of the reflected light. Thus, all reflection other than at the specular angle can be regarded as diffuse reflection resulting from the presence of irregularities in the paint surface. (A more important additive source of diffuse reflection, however, and one which will be discussed in the following section under "Bulk Reflection" (see II.4.9.1(b)(ii)), arises from the scattering of absorbed light by pigment particles below the surface).

Nowadays, the specular and diffuse components of a paint's reflectivity are commonly referred to as "specular gloss" and "haze", and, as such, can be related to the visual brightness and sharpness, respectively, of the image of an object viewed on reflection at the surface. Consequently, it can be appreciated from this how the total visual impression of gloss is characterised by the angular distribution of reflected light rather than just its specular component; hence the positive requirement for a goniophotometer rather than just a simple specular gloss-meter.

II.4.9.1(b) Bulk Reflection

Under the heading of "bulk reflection", we now consider the mechanisms by which the greater part of the incident light on a paint film penetrates the surface and is subsequently re-emitted as the (still) greater part of the paint's total reflectivity. The main process by which this occurs, however, depends upon whether the coating material is pigmented or not; consequently, these two cases are now given separate attention.

II.4.9.1(b)(i) Unpigmented Coatings

When a ray of light is incident, at an angle (θ), in air of refractive index (n), upon the surface of an optically homogeneous unpigmented coating of refractive index (n'), provided that, compared with the wavelength of the incident light, the air/coating interface is regular and the coating thickness is large, that portion of the light which is not surface reflected will be transmitted by refraction at an angle (θ') in accordance with Snell's Law, eq. (5) below:

$$\frac{\sin \theta}{\sin \theta'} = \frac{n'}{n} \qquad \text{......} \ (5)$$

This situation is depicted in Figure 16(a) in which the refracted light pathway through the coating medium can be plotted exactly, according to the laws of refraction and reflection at the air/coating and coating/substrate interfaces respectively, prior to its eventual re-emergence from the coating surface.

However, as we have seen previously, "real" surfaces contain intrinsic profile irregularities which, when of a size-order comparable to the wavelength of light, give rise to the scattering effects illustrated in Figure 16(b). In this situation, the simple ray treatment breaks down, although the behaviour of light can generally still be predicted using the wave theory. Furthermore, although this type of light scattering might be expected to detract from the transparency of an unpigmented coating, in practice, this effect is almost negligible compared with what the effect of scattering by inhomogeneities en route through the coating would be. Consequently, as homogeneous unpigmented media are non-scattering in this respect, the only light energy which is

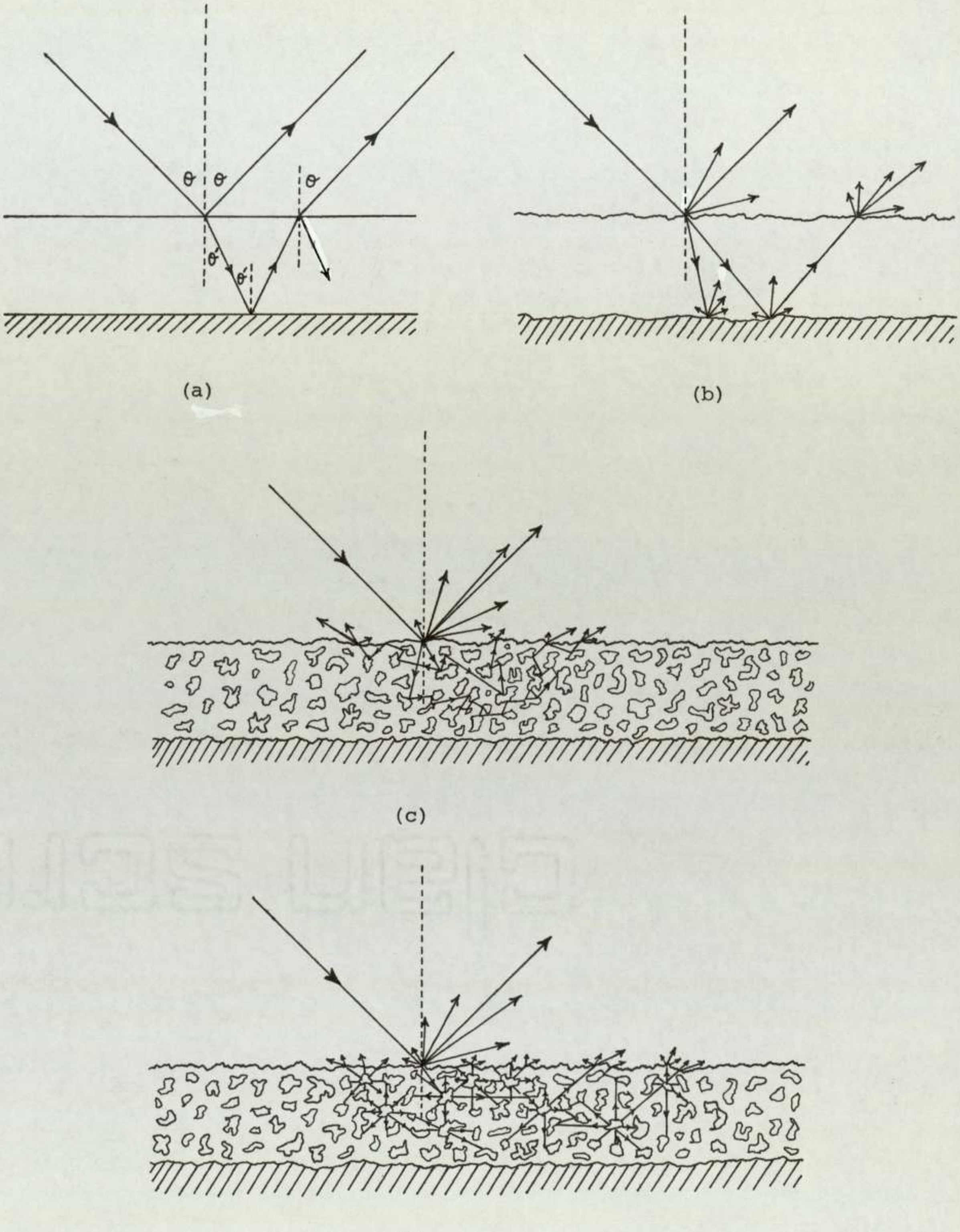


FIGURE 16 - Ray diagrams of the total (i.e., surface and bulk) reflection characteristics of (a) ideally smooth, and (b) typical (i.e., "real") unpigmented coatings; and (c) conventional, and (d) more recently proposed(235) schematic representations of pigmented coating reflection.

lost on passage through the film is due to absorption in accordance with Bouguer's Law, eq. (6) below:

$$I/I_o = e^{-\alpha d} \qquad \ldots\ldots (6)$$

where: I = the intensity of light after travelling a distance (d) through the medium,

I_o = the initial intensity, and

α = the coefficient of absorption.

However, at the film thicknesses normally encountered in unpigmented coatings, even this absorption effect is extremely small, which is why transparent films may be said to be totally lacking in hiding power. This, therefore, now leads us to consider the practical situation which exists in pigmented coatings and the way in which the pigment particles maximise the scattering and absorption of light within the film.

II.4.9.1(b)(ii) Pigmented Coatings

Not surprisingly, pigmented coatings, representing, as they do, the vast majority of practical coating systems, have attracted by far the greater interest in respect of their light reflection characteristics. The manner in which pigmentation confers opacity and hiding power to the coating is almost entirely bound up with the combined effects on the incident light of scattering and absorption by the individual pigment particles. In the case of a white pigment of good hiding power, scattering is the dominant effect, whereas, for black and strongly coloured pigments, absorption also plays an important part in the hiding of the substrate.

This scattering process is depicted, somewhat simplistically, in Figure 16(c) as arising from a succession of irregular reflections at the surfaces of individual pigment particles. However, owing to the random nature of the system, the path of an arbitrary ray of light cannot be predicted, and so the theories of light behaviour in such optically inhomogeneous systems must assume a statistical bias. Nevertheless, despite the inherent complexity of light scattering phenomena in disperse systems, many general treatments of the problem have been proposed, the ones most usually applied to pigmented coatings being those due to Kubelka and Munk(64 - 67, 92, 229, 230) and to Mie(231 - 234), or, as has been suggested(235), to a combination of the two. However, rather than enter into detail here concerning the exposition of these theories, the reader is referred to the literature references cited.

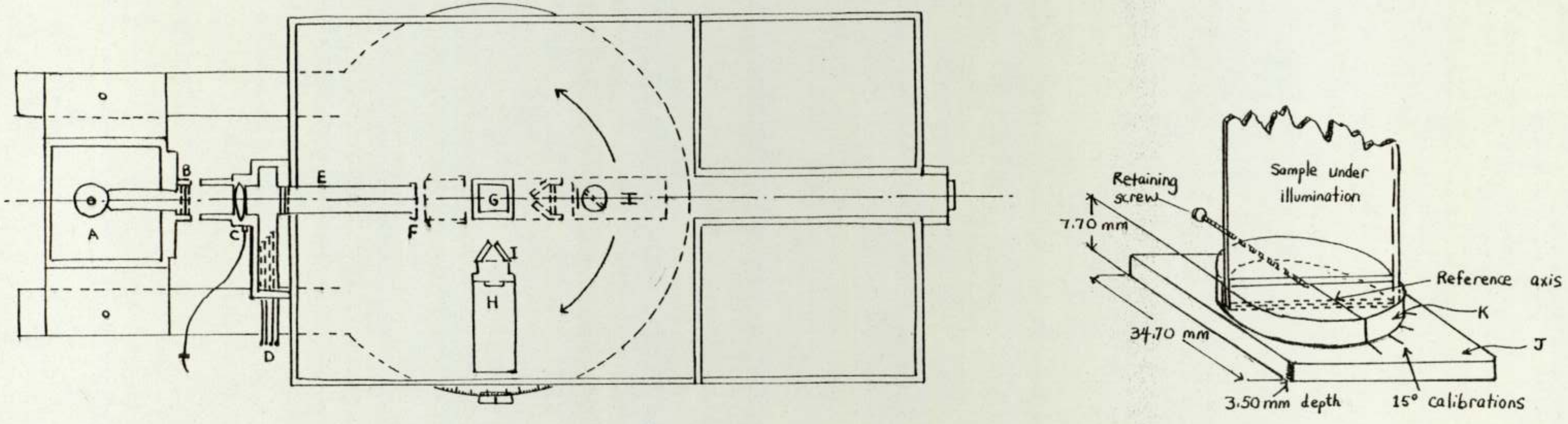
Instead, let us now look more closely at the light scattering representation given in Figure 16(c). Although this is the customary way of depicting the passage of light through a pigmented paint film, strictly speaking, this type of mechanism, whereby the light undergoes a succession of surface reflections at the irregular interfaces of individual pigment particles, would only be expected to prevail if the particles were consistently very much larger in size than the wavelength of the light. However, in order for pigment particles to be effective in practice, they must be of dimension fairly close to the wavelength of light, in which case their interaction with the light is more correctly represented as shown in Figure 16(d), with the light being radiated from pigment particles in all directions(235). In support of this latter model is the fact that, whilst it may appear to present a more complicated scattering "picture", it does go a long way towards explaining why neither Kubelka-Munk nor Mie theory can ever be singly predictive of the opacity and reflectance of pigmented films, and also why a combination of the two theories would be more appropriate.

In conclusion, it is interesting, as well as highly relevant, to note that when incident light is scattered back diffusely from the interior of a pigmented coating, it invariably appears to have emanated from the topmost surface layer. Indeed, the fact that the radiation has penetrated the coating surface and has subsequently undergone multiple scattering prior to reflection is by no means apparent. This phenomenon can be illustrated more clearly by considering the example of snow. Now, snow, itself, consists of a variety of complex hexagonal crystals of between 0.25 and 10 mm. in diameter. When light falls on a layer of snow, approximately 3 - 4% is reflected back by the uppermost surfaces of the top layer of crystals, but the random arrangement of the crystal faces causes these reflected beams to be returned in many different directions. Most of the light, however, is refracted into the surface crystals and travels through them until it strikes their lower faces. Here again, the greater part will be refracted more deeply into the snow, but in some crystals the light undergoes total internal reflection. For these latter beams, all the energy is redirected back towards its ultimate escape through the top layer of snow again. The majority of the light beams, however, travel into the lower crystal layers, giving up, at each face, more of their energy by random reflections, and changing direction at each refraction. Finally, the light in each original beam becomes so attenuated by repeated reflections that it becomes insignificant. All its reflected elements, however, still remain subject to additional reflections and refractions until the majority of the original light re-emerges into the air. These beams are so numerous and random in direction at their points of emergence that each point in the surface acts as if it were radiating light in all directions. This is why one is not conscious of looking into the interior of the surface, even though the light has actually come from within.

Hence, it can be visualised as being via an analogous type of bulk light scattering process that pigment particles give rise to a background of diffuse reflection in much the same way that snow crystals do. Finally, now that we have seen how and why pigmented and unpigmented coatings reflect incident light characteristically over a 180° angular range, the reflectance data obtained from goniophotometry can be more readily understood.

II.4.9.2 The Goniophotometer

At the outset of this project, the goniophotometer was of the form described by Quinney and Tighe(74) in an earlier paper. The instrument, itself, is a Brice-Phoenix (Series 2000) Light Scattering Photometer(63), the optical layout of which (Figure 17(a)) can be briefly summarised as follows. The light beam from the high-pressure (Type AH-3) mercury vapour lamp (A) passes through a pre-selected wavelength filter (B) and shutter unit (C) into a collimating tube (E) incorporating a removable polariser and variable slit aperture (F). The light intensity is accurately controlled by means of a series of neutral filters (D) which enable precise variations in transmittance to be employed over a wide range. The light beam then impinges on the specimen mounted at (G) and the intensity distribution of its reflection measured over the angular range 0 - 90° (starting from the normal to the



17(a)

17(b)

FIGURE 17 - Diagrams showing (a) the optical layout of the goniophotometer, and (b) the specimen mount.

sample surface) by the photocell (H). The rotating photocell, which, on its turntable, actually has an angular travel of up to 270°, also has a removable analyser and variable slit aperture (I). Finally, the signal from the photocell is then amplified and registered on a "spot" galvanometer.

The specimen mount which was specially designed for use in this type of reflectance work is shown in Figure 17(b). The mount has a calibrated brass base (J) 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 (K), which can be rotated through 360°, fits into the base and will take any optically flat specimen up to a maximum thickness (film plus substrate) of 2 mm. The optical precision of the specimen mount was confirmed by the absence of dissymetry in readings taken with the baseplate located in each of its four possible orientations and the mount/photocell set (at 10° intervals) in all the possible "mirror image" positions. Finally, the mount was coated with matt black paint so as to prevent stray light reflections from it reaching the photocell.

However, the goniophotometer, in this form, still required manual operation for sample analyses to be carried out. Complete goniophotometric curves obtained in this way involved rotating the photocell manually over the 0 - 90° angle of reflection range, taking reflectance readings at, initially, 5° intervals, narrowing progressively down to 0.1° intervals in the region of the specular angle. Thus, it can be appreciated that the large number of readings needing to be taken in order to be able to plot each goniophotometric curve accurately meant that the procedure was somewhat slow and rather tedious for the operator.

It was for these reasons, therefore, that the possibility of automating the goniophotometer's mode of operation was investigated, and this, along with one or two other instrumental refinements, will now be described in the following chapter.

CHAPTER III

MODIFICATIONS TO THE GONIOPHOTOMETER

CHAPTER III

MODIFICATIONS TO THE GONIOPHOTOMETER

III.1 Introduction

In this chapter, the modifications which were carried out to the goniophotometer(236) as part of the present work in order to make it quicker and easier to use are now described. Such requirements of the technique are, after all, essential if goniophotometry is ever to be regarded as a feasible routine analytical technique for use in industrial research laboratories. Whilst these modifications are primarily concerned with the automation of the recording of goniophotometric curves, other refinements such as a beam narrowing device and an improved specimen mount design are also detailed.

In addition to describing the automation of the goniophotometer and its analytical use in this mode, the subsequent interpretation and manipulation of goniophotometric data so obtained, with reference to a particular case study, is also demonstrated; the case in point being a combined study of (a) the natural and artificial weathering of commercial poly (vinylidene fluoride) (trade name: "Kynar") surface coatings, coupled with (b) the variable effects which the severity of the sample cleaning method may have on test results.

III.2 Modifications to the Goniophotometer

III.2.1 Automation of the Instrument

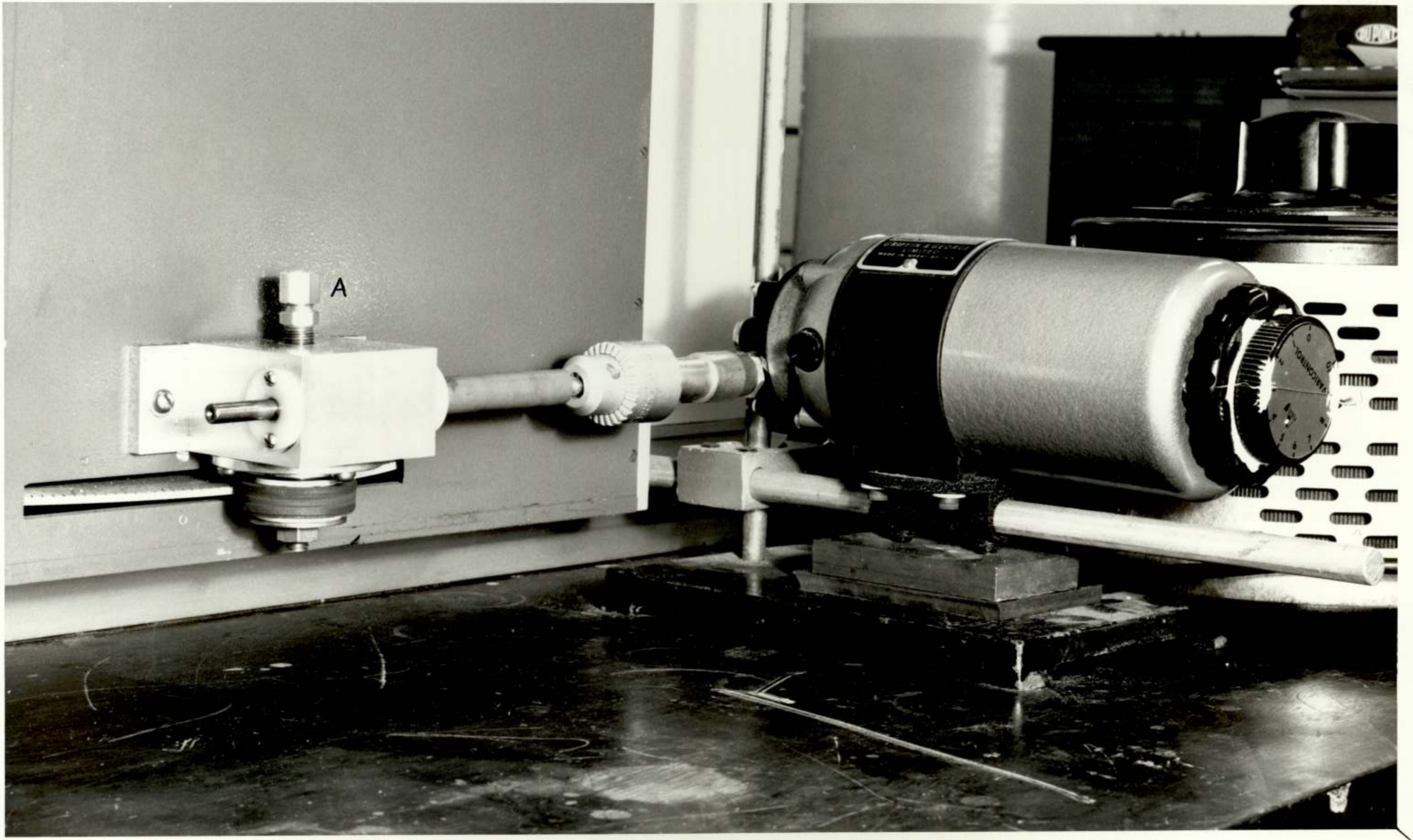
The automation of the goniophotometer effectively involved the replacement of manual adjustment, as the means of rotating the photocell through the scanning angle, by an automatic drive mechanism. The automatic drive was provided by a high-torque Citenco precision electric motor (Griffin and George Ltd.) which was connected, at the rear of the photometer, to the protruding serated edge of the turntable upon which the photocell is mounted. This drive mechanism, complete with its turntable connection/disconnection device, is illustrated in Plate 14. Additionally, the motor was also connected to a Variac control which permitted fine adjustments of the motor's speed, and hence the photocell's rate of rotation, to be made. The practical range of uniform rotational speeds at which the photocell could be driven through its angular movement in this way was approximately 0.5 - 5 secs./degree, with a rate of around 2 secs./degree being found, in most cases, to combine speed and accuracy of measurement most effectively.

Finally, the galvanometer, which was formerly used to register amplified signals from the manually operated photocell, was replaced by a multi-range potentiometric flatbed recorder (Smith's Industries; Servoscribe 1S, Type RE 544.20) for automatic plotting of the goniophotometric curve. The recorder additionally incorporated facilities for integration and also for logarithmic, as well as linear, data plotting, both of which provided extremely useful extensions of the basic data presentation as will be seen later.

The automated goniophotometer, together with its recording system, as described, is shown in Plate 15.

III.2.2 Specimen Mount Re-design

The specimen mount was re-designed from that shown previously



<u>PLATE 14</u> - The goniophotometer's automatic drive mechanism with connection/disconnection device (A).

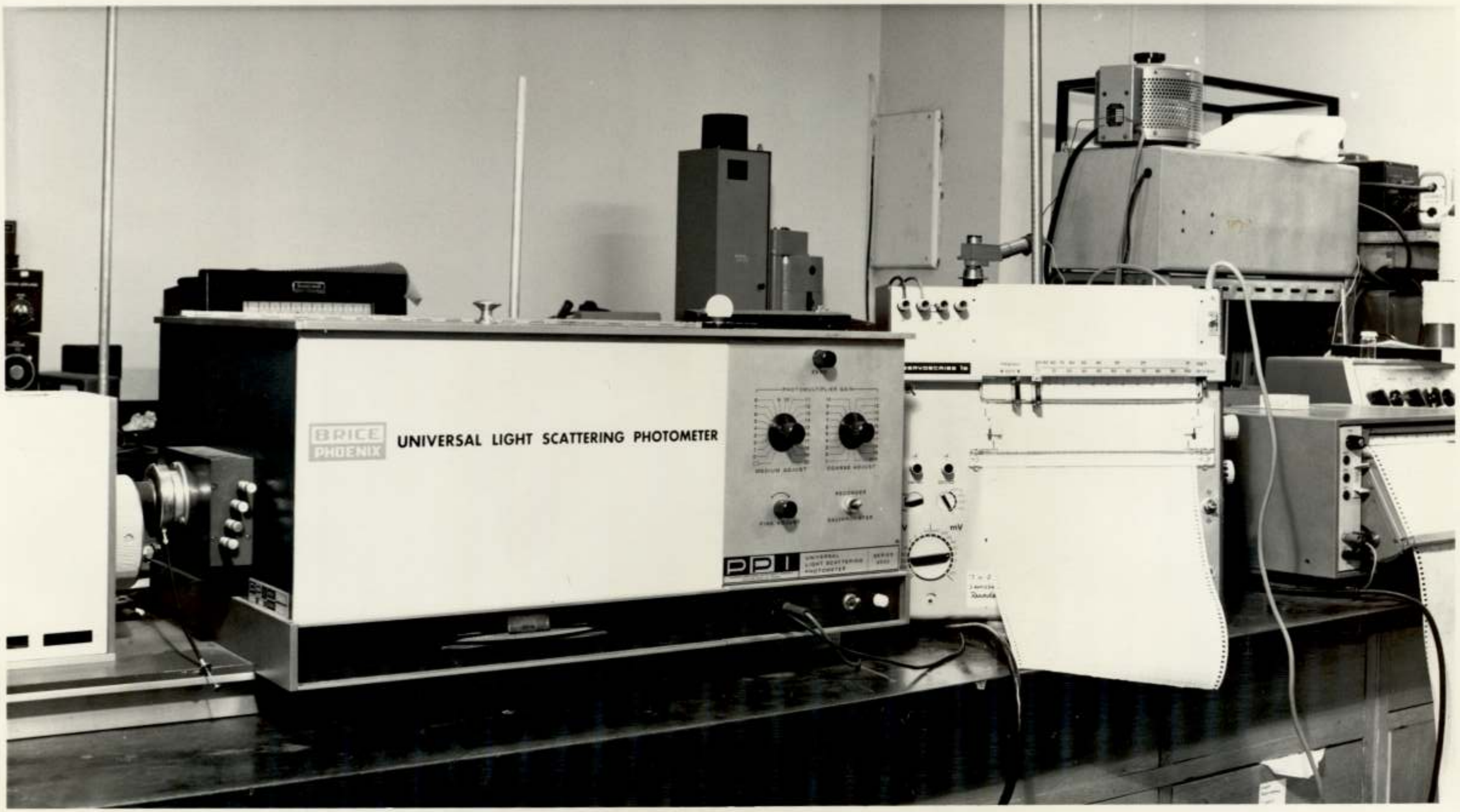
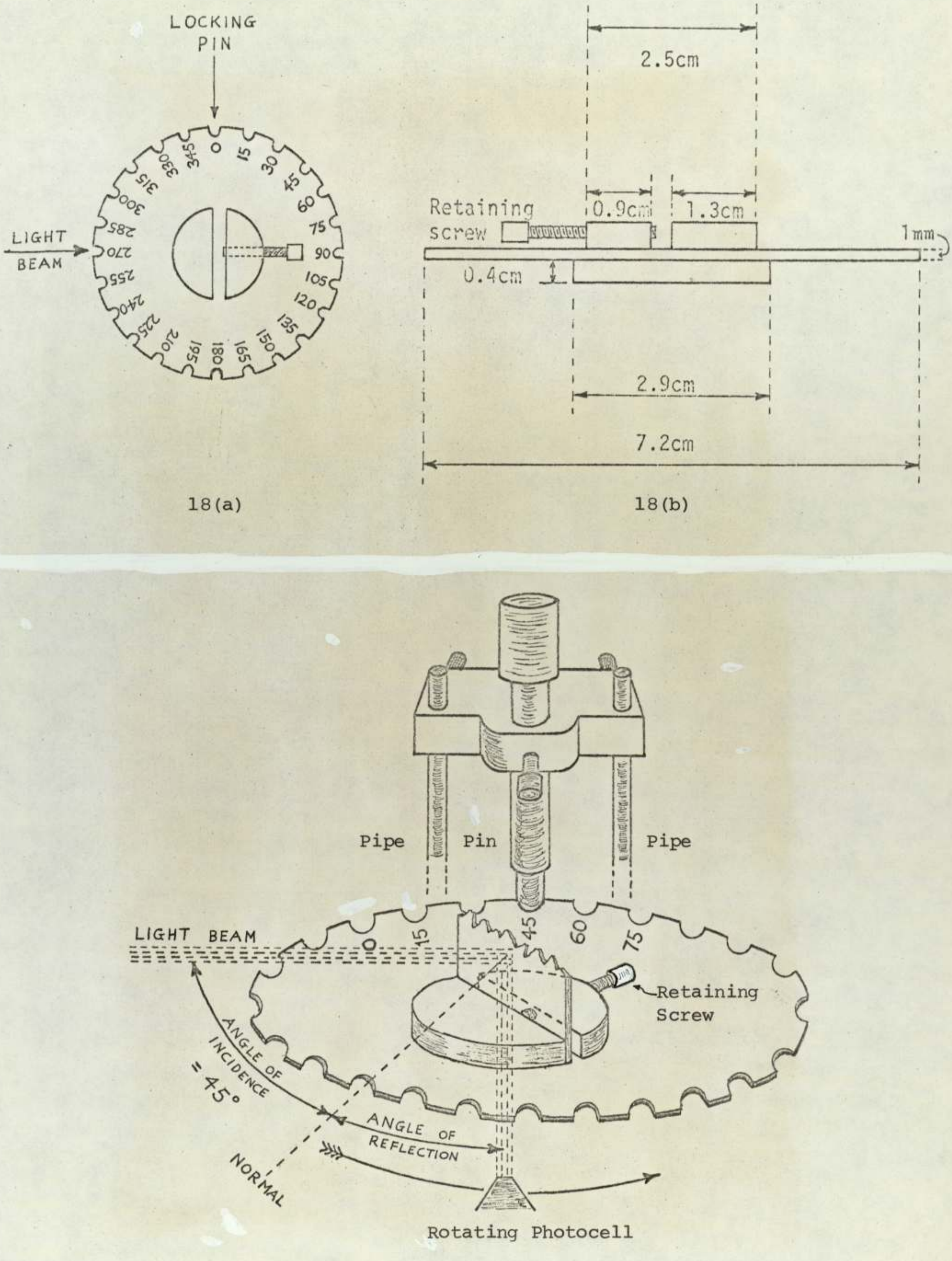


PLATE 15 - The automated goniophotometer.

in Figure 17(b) in order that certain inadequacies in its former design might be overcome. The main disadvantage associated with its original design was that the mount could not be easily and reproducibly located in a given fixed position. This meant that at the outset of each sample analysis, the chosen angle of incidence, at which the mounted sample was to be set in relation to the light beam, had to be found via a somewhat laborious trial and error process involving the use of a glass microscope slide as an assumed mirror-reflector.

However, the improved specimen mount (Figure 18) eliminates the need for this initial procedure by incorporating into its design a means by which it can be fixed into a range of angular positions. This is achieved, as shown in Figure 18(c), by taking advantage of the adjacency to the specimen table of two pipe fittings which are conveniently deployed as a means of supporting a locking pin. The pin can then be used, as shown, to fix the specimen mount securely in any of its 15^{o}-spaced, notched positions. The angle of incidence to which each of these positions corresponds in practice is indicated on the mount itself (Figure 18(a)), although these obviously each require accurate optical determination via measurement of the angle at which a calibration glass slide specularly mirror-reflects.

Finally, the specimen mount, which was made from brass according to the dimensions given in Figure 18(b), was sprayed with matt black paint so as to prevent stray light reflections emanating from it during sample analysis.



18(a) 18(b)

18(c)

FIGURE 18 - Re-designed specimen mount for goniophotometry:-
(a) plan view,
(b) side elevation, and
(c) fixed-angle location.

III.2.3 Beam Narrower

The beam narrowing device, depicted in Figure 19, was developed as a means of reducing the sample area illuminated and analysed in goniophotometry. The extent of this reduction was from an oblong illuminated area of approximately 1.2 cm.^{2}, as provided by the so-called "wide" beam, to a "narrow" beam area of approximately 0.2 cm.^{2} Whilst the wide beam remained in general purpose use throughout the course of this work, the narrow beam had various advantages associated with it in certain instances. For example, it aided the selectivity with which sampling areas could be chosen, and was particularly useful in avoiding scratch marks or other types of visible surface defects not attributable to ageing. Of further benefit in this respect was the fact that reflectance measurements taken from smaller areas of sample tended to minimise the error-introducing effects which substrate non-planarity had on the results; punched discs from aluminium coated panels, for example, being particularly susceptible to slight substrate curvature. Finally, of course, beam narrowing in this way allowed for a greater number of different areas of the same sample surface to be analysed and checked for reflectance uniformity, this being facilitated by the fact that the re-designed specimen mount could be removed for the sample to be re-positioned and then be straightway re-located exactly in its former fixed-angle position.

III.3 Goniophotometric Analysis - Automated Procedure

The procedural format of a complete goniophotometric sample analysis using the automated instrument (Plate 15) is now described in some detail, with reference made wherever appropriate to the following Figures 20 and 21.

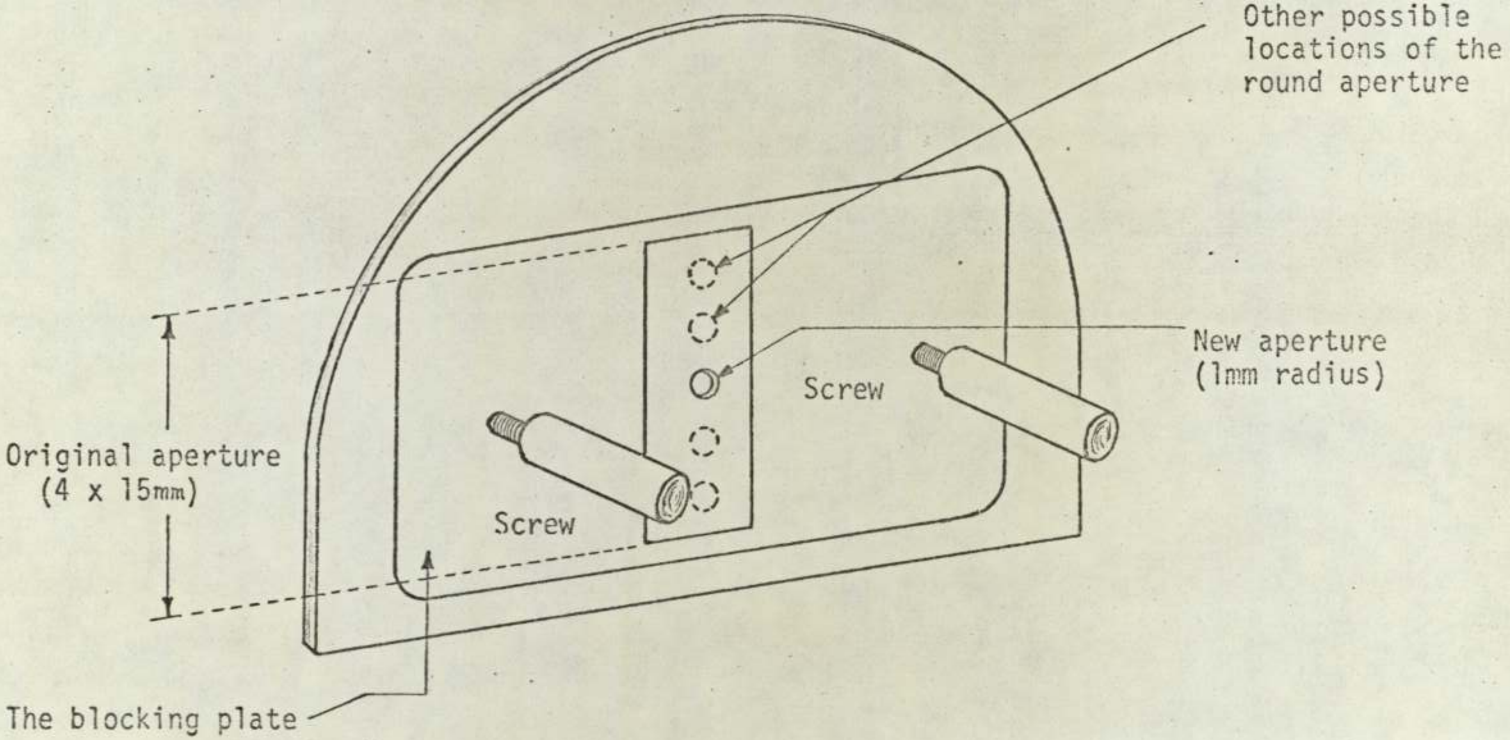


FIGURE 19 - Beam Narrower used in Goniophotometry .

Prior to measurements being taken, the recommended "warm-up" procedure, as laid down in the photometer's instrument manual, is followed and the apparatus as a whole allowed to stabilise for a minimum period of one hour after switching on. Having decided upon whether the wide or the narrow beam is to be used, the first step in the actual analysis is to calibrate the intensity of the light beam. As shown in Figure 20, this is done by manually rotating the photocell into the so-called "straight through position" (i.e., in direct line with the light beam) and, by means of the photometer's photomultiplier gain controls, adjusting the reading on the recorder (set to a 5 mV sensitivity) to an arbitrary (calibration) value of 54 units of deflection on the chart paper (see Figure 21 at start). The mounted sample which is to be analysed is then positively located on the specimen table to give the desired angle of incidence with the light beam, this angle having previously been accurately determined (to 0.1°) by noting what is assumed to be an equal angle of perfect mirror reflectance at which an optically flat glass slide specularly reflects.

Thus, having completed these preliminaries, the sample measurements can be taken. For the sake of optimum accuracy, however, the two specific angular reflectance quantities which, together, are the most relevant as far as subsequent calculations arising from the goniophotometric curves are concerned, are statically recorded, i.e., as in the manual mode. These two measurements are those of (i) the specular reflectance, at the angle of maximum reflection, and (ii) the diffuse reflectance at an angle of reflection of 0° (i.e., along the normal to the sample surface), this latter quantity being recorded both (a) at its maximum chart value, by use of the appropriate filter(s), and (b) at its "base-line" value for the subsequent gonio-

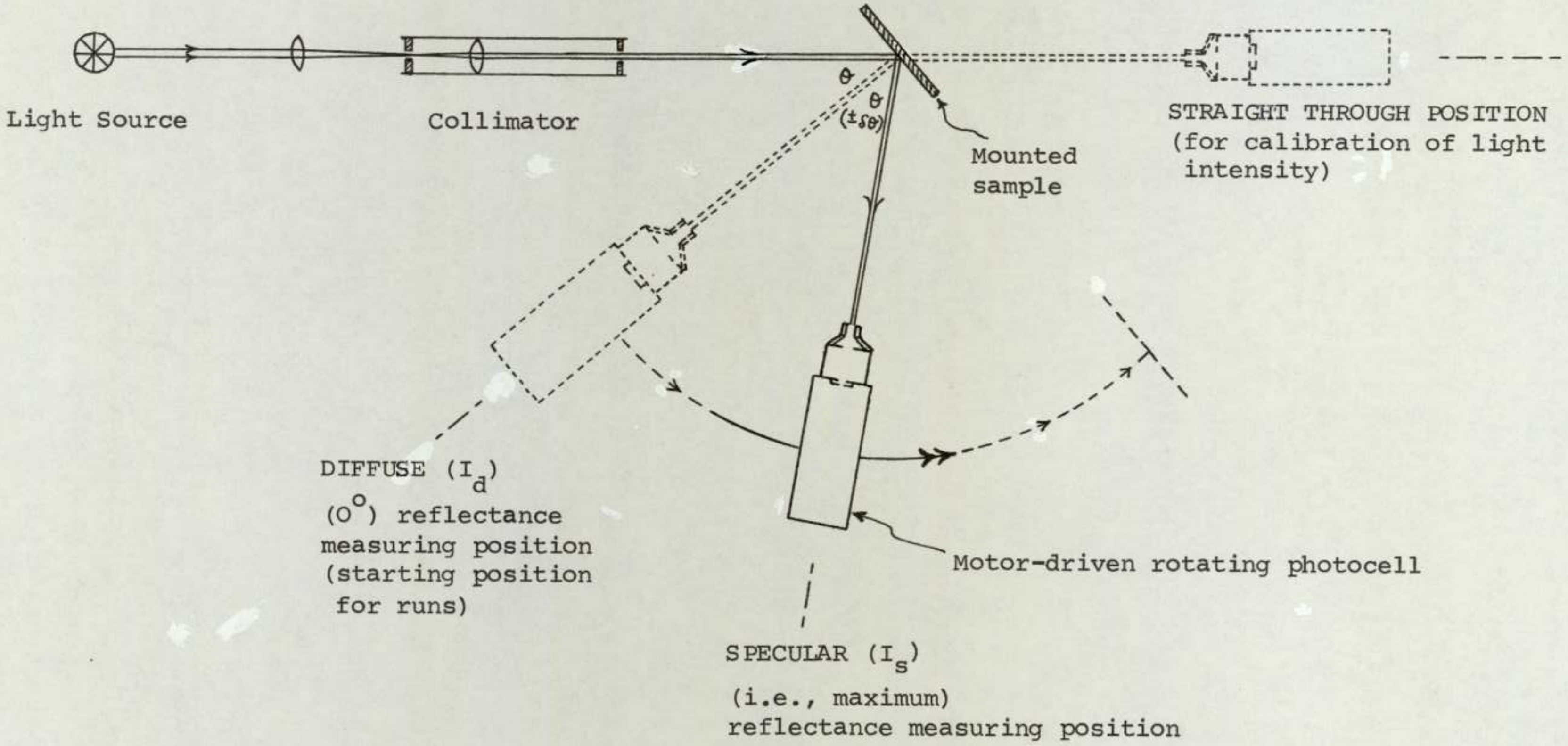
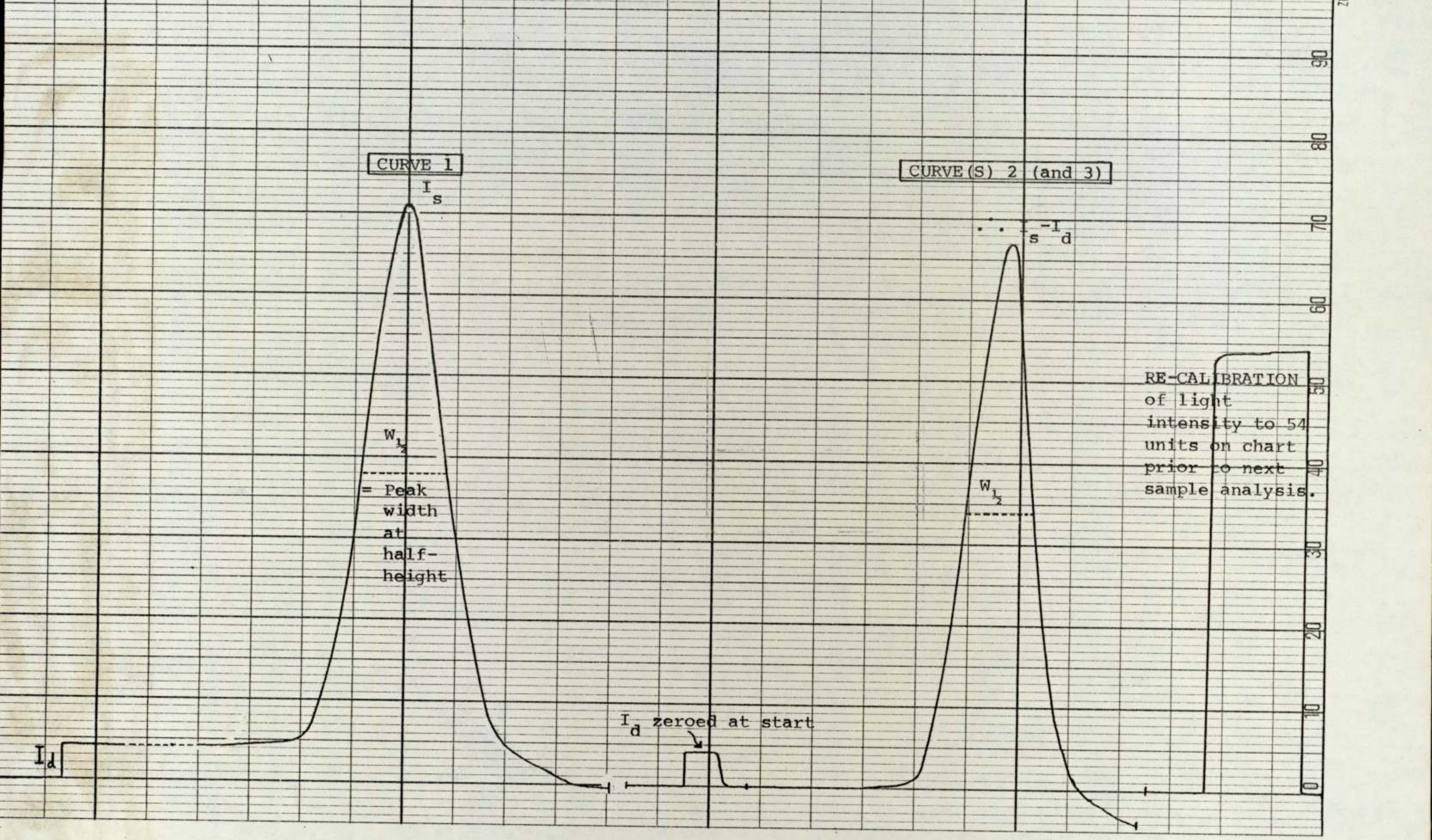
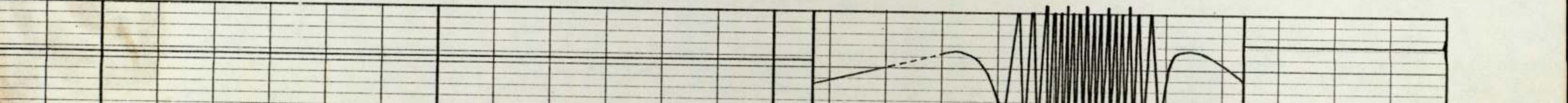


FIGURE 20 - Goniophotometric analysis : schematic arrangement employed in the automated instrument.



$\therefore$ GLOSS FACTOR = GF = $I_s - I_d/W_{\frac{1}{2}}$

PEAK (ONLY) AREA INTEGRATION



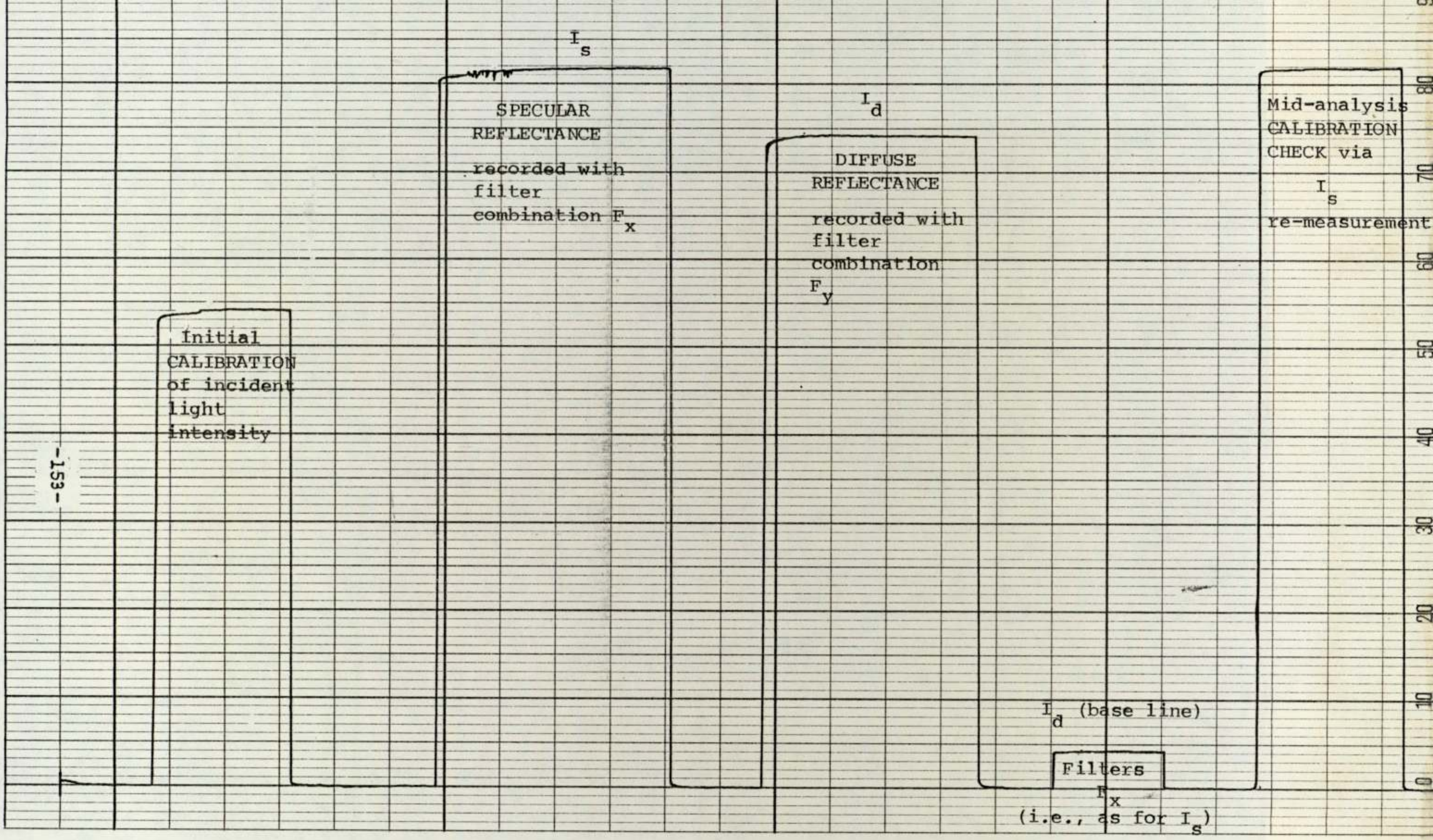
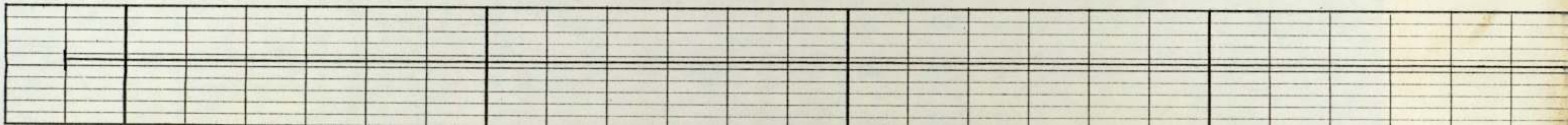


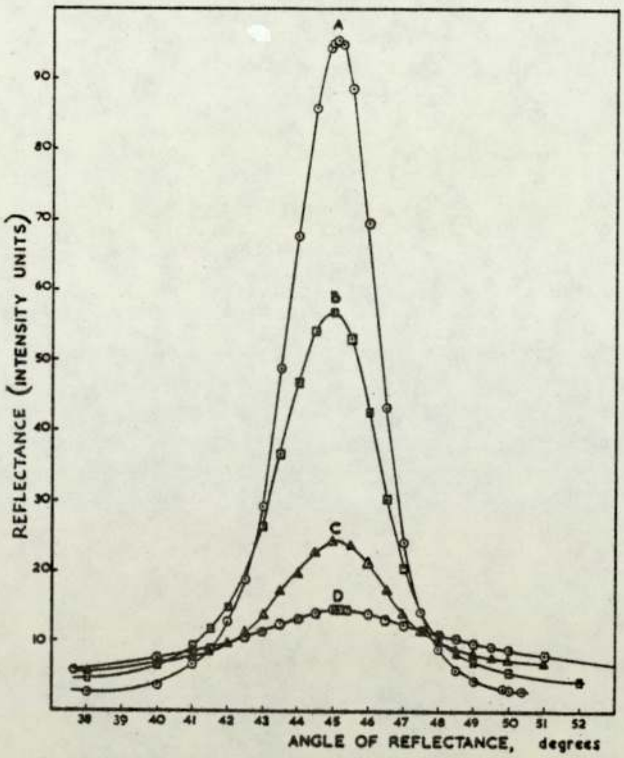
FIGURE 21 - Goniophotometric data as obtained from a complete sample analysis via the automated procedure.

photometric curves, employing the filter combination used in recording the specular reflectance in (i) above. Then, following a precautionary, mid-analysis check and, if necessary, re-calibration of the light beam intensity (found to be most conveniently carried out, without the need for sample removal, by simply re-measuring the sample's specular reflectance), the complete goniophotometric curves are automatically recorded as follows. With the light beam incident upon the sample, and with the photocell in its starting position normal to the sample surface, as shown in Figure 20, the connecting stop (A in Plate 14) is screwed down fully in order to engage the photocell turntable's automatic drive mechanism. Then, as the photocell starts its angular movement, the recorder chart drive is actuated and, as the goniophotometric curve is being plotted out (as in curve 1 in Figure 21), the rate of rotation of the photocell is measured with a stop-watch over an angular range covering the reflectance peak so that the peak-width may later be transposed from units of length (mm.) to degrees of angle. As soon as the curve is completed, the photocell and recorder chart drives are disconnected and the light shutter closed. The photocell is then returned to its former starting position for the procedure to be repeated for the subsequent curves 2 and 3. However, for the recording of these latter two curves, an addition to the previous procedure is made at the start of each "run". As shown in Figure 21, this entails the initial diffuse (0°) reflectance reading, obtained with the photocell in its normal starting position, being zeroed to the chart baseline, by means of the recorder's zero-adjustment, so as then to enable the area under the goniophotometric peak alone to be determined via the recorder's integrating facility. Finally, after the three curves have been recorded in this way, the sample is removed and its exact position in the mount marked for future reference. The light beam intensity, which, incidentally, generally varies by no more than ±2% during the course of a single sample analysis, is then re-calibrated with the photocell in its "straight through" position (Figure 20) prior to the next sample being examined. This is not intended to imply, however, that a variation of this magnitude will be found in the results.

Typically, the length of time it would take for a single sample analysis to be carried out using this automated procedure is approximately 20 - 30 minutes, with the goniophotometric curve being recorded in triplicate as described. This can now be compared with the upwards of one hour required for the 20 or so readings to be taken and plotted in order to obtain just one complete goniophotometric curve via the manual procedure. Furthermore, close comparison of corresponding data obtained by both methods (Figure 22) indicates that the accuracy, sensitivity and reproducibility of the measurements has not suffered significantly in the automation step. Indeed, the two sets of curves shown in Figure 22 are similar enough to suggest that the goniophotometer, in its automated mode, is already very close, in terms of its performance, to being quite capable of accurately characterising the gloss of a surface in just a single 2-minute curve recording, thus proving itself as a potentially valuable routine means of rapid, accurate gloss assessment.

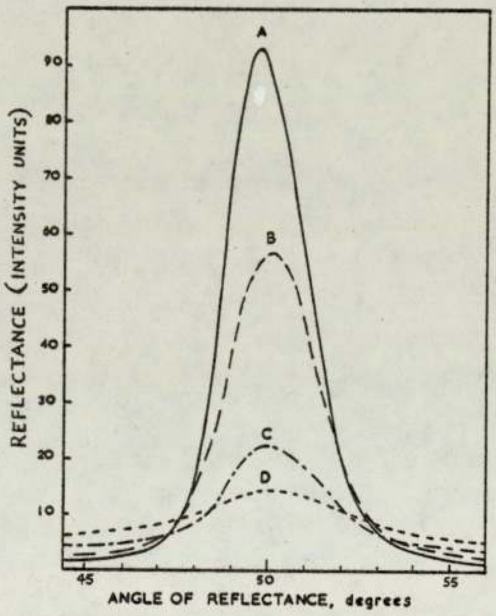
III.4 Goniophotometric Parameters

III.4.1 Definition of Terms

The various goniophotometric parameters which can be derived from the sample data, as obtained in the form shown in Figure 21, are now listed, together with their respective symbols and units, and



22(a)



22(b)

FIGURE 22 - Comparison of goniophotometric curves, relating to the natural weathering of a vinyl toluene-modified alkyd gloss finish paint, obtained via:-
(a) the manual, and
(b) the automated procedures;

angle of incidence: (a) 45°, and (b) 50°;
exposure time : (A) 0, (B) 3, (C) 12, and (D) 25½ months.

defined as follows:-

(i) the specular reflectance (I_S, intensity units) - this is defined as the maximum angular reflectance from the sample and, according to the laws of reflection, occurs at or near an angle equal to the angle of incidence of the illuminating light. Hence, the specular reflectance, or specular intensity as it is sometimes known, obviously corresponds to the intensity of reflection at the top of the goniophotometric peak, and it is also this specular component of a surface's overall gloss that specular gloss-meters set out to measure. Finally, the objective determination of the I_S in this way can be considered to correspond, on a purely subjective basis, to the visually perceived brightness of an image observed on reflection at the sample surface;

(ii) the specular angle (degrees) - as its name suggests, this is the angle at which the specular reflectance (I_S) occurs, i.e., the specular angle is the angle of maximum reflectance. Whereas for perfectly smooth "mirror" surfaces, and also for most high-gloss paints, the specular angle equals the angle of light incidence (see Figure 15(a) and (c)), for imperfect irregular surfaces there is invariably a slight discrepancy between the two, this variance usually being termed the "angular displacement" (see (iii) following);

(iii) the angular displacement (degrees) - as mentioned above, this parameter is defined simply as the difference between the angle of incidence of the illuminating light and the specular angle at which maximum reflection occurs from the sample surface. However, although, in theory, the angular displacement might be expected to provide useful supplementary information concerning the extent to which the surface deviates from perfect mirror planarity, in practice, the smallness of its value, usually only a fraction of one degree, often determines that interest in it remains largely theoretical rather than practical;

(iv) the diffuse reflectance (I_d, intensity units) - whereas, in theory, the diffuse reflectance refers to all reflectance other than at the specular angle, in this present context and throughout the following text, the diffuse reflectance (or intensity), as denoted by I_d, specifically refers to the reflectance at an angle of reflection of 0^o, i.e., along the normal to the sample surface. As such, the I_d is taken to represent the "background" reflectance from the sample surface as a whole which, over its wider angular range, manifests itself, to a visual observer of the surface, in the perception of "haze" which tends to impair the sharpness of image definition;

(v) peak height (I_s - I_d, intensity units) - rather than just being taken as the specular reflectance (I_s) value alone, the goniophotometric peak height is defined as the difference between the I_s and I_d values previously described. In this way, the peak is therefore regarded as representing that component of a sample's reflectivity, in the specular region, which, despite being superimposed upon a continuous background of diffuse reflection, lends itself to the surface's mirror-imaging capability;

(vi) the peak width at half-height ($W_{\frac{1}{2}}$, degrees) - this parameter provides an important measure of the extent to which a reflecting surface spatially distributes, around the specular angle, light which is incident upon it. As mentioned previously in the introductory chapter, it is this facility which the goniophotometer has for taking account of the angular distribution of the reflected light which represents the essential difference between it and the specular gloss-meter. However, as has already been stressed, it is this angular distribution, rather than just its specular component, upon which the total visual impression of gloss is based. In visual terms, whereas the specular reflectance and, hence, the peak height are related to the brightness of an image viewed at the surface, the peak width is related to image sharpness which, incidentally, tends to be a more popular criterion by which observers subjectively make their assessment of surface gloss;

(vii) the gloss factor (GF, intensity units/degree) - whereas the previous parameters described can be considered as being, primarily, data directly derivable from the goniophotometric curve, the gloss factor is a computed term obtained by dividing the peak height ($I_s - I_d$) by the peak width at half-height ($W_{\frac{1}{2}}$) (i.e., $GF = I_s - I_d/W_{\frac{1}{2}}$). Consequently, the gloss factor, encompassing in one term both the elements of specular reflection and its angular distribution, is undoubtedly the most meaningful single goniophotometric parameter in terms of its potential correlation with visual gloss ratings. Furthermore, the gloss factor, quite simply, provides a convenient vehicle for incorporating into a single term its three component parameters (I_s, I_d and $W_{\frac{1}{2}}$), thus enabling changes in each to be more closely related to resultant changes in gloss; and finally,

(viii) the peak area (A, integration units) - the area under the goniophotometric peak, as obtained by integration of the "peak only" curves (2 and 3) in Figure 21 previously, is rather more difficult to interpret in terms of gloss changes than were the previous parameters. For example, whereas a reduction in peak height and in increase in peak width (both symptomatic of loss in gloss) reinforce each other in the gloss factor term, they have opposite effects on the peak area. However, in this particular case, the peak area would be able, instead, to give some idea as to the relative contribution which these two effects each make to the overall gloss factor change. Consequently, although the peak area's individual significance might appear less obvious, when considered in conjunction with changes in other parameters, it can often prove additionally informative. However, it is probably still true to say that the peak area is more of a manipulative term that those previously mentioned.

III.4.2 Effects of Surface Defects

Before discussing, within the context of an ageing study, the changes which are brought about in the reflectance characteristics of a given surface, as sensed by goniophotometry, it is useful to outline briefly at this stage the effects which surface defects have on the various goniophotometric parameters previously defined. In order to gain some idea as to the size-range of surface defect which we are dealing with in an ageing study, we can conveniently compare defect size with, towards the lower end of the scale, the wavelength of light used in the goniophotometer (436 nm. - monochromatic blue light), and, towards the higher end, the minimum size resolvable with the naked eye (approximately 50 - 100 μm).

Let us consider, therefore, the case of a high-gloss paint on weathering. Invariably, the initial change observed in its goniophotometric response is a gradual reduction in specular reflectance (I_s) and, hence, a lowering of the peak height ($I_s - I_d$). Visually, this change is perceived as a slight dulling of the surface which tends to impair the brightness of an image viewed at the surface. This initial effect is attributable to the formation of microscopically small surface irregularities whose size (i.e., height and lateral extent) are still smaller than the wavelength of the incident light used in the goniophotometric analysis. These so-called MICRO-defects reduce the I_s by removing energy from the incident light beam by means of diffraction and/or Mie-type scattering processes; they do not, however, cause any widening of the reflected beam's angular distribution and, therefore, the surface continues to behave as a good plane reflector. Hence, the surface's specular reflectance and goniophotometric peak height progressively decrease in this way as the density of micro-defects in the surface increases with ageing. This situation continues to prevail until such time as some of the defects attain a size-order in excess of the wavelength of the light, whereupon, as so-called MACRO-defects, they now become capable of causing an angular divergence of the reflected beam by simple geometric optical means. This latter effect manifests itself, to a visual observer of the surface, as a loss in image sharpness (i.e., definition), although it is unlikely, even at this relatively advanced stage in their "growth", that there will be any defects visibly discernable in the surface. Consequently, this "transition", as it were, from energy dissipating micro- to beam diverging macro-defects, as determined by the goniophotometer, is reflected in the data as a partial transposition from the predominant trend of peak height ($I_s - I_d$) reductions without accompanying peak width ($W_{\frac{1}{2}}$) increases to the reverse situation. This gives rise to the overall shape of the goniophotometric peak changing from its former sharp triangular form to a broader curved profile. Finally, the paint's ageing deterioration process continues with its surface macro-imperfections increasing further in size and number until the surface is visibly degraded, by which stage the paint film has generally "outlived" its usefulness.

On the other hand, however, gross macro-defects (e.g., nibs, brushmarks, "orange peel" defects, etc.) which are principally a function of the shortcomings of particular application techniques, and which are sometimes clearly visible even in freshly applied gloss finish coatings, generally give rise to characteristic distortions in what would otherwise still be triangular-shaped goniophotometric peaks.

In summary, therefore, it is clear from what has been stated here that the convenient MICRO/MACRO distinction which the goniophotometer is able to make concerning the size of surface defects in relation to the wavelength of its illuminating light (rather than, say, to what is or is not resolvable with the naked eye), provides us with an important criterion by which to interpret goniophotometric data. These two defect sizes can, therefore, now be formally defined as follows; firstly, MICRO-defects of the surface are those whose size are less than or of the order of the wavelength of the incident light, as used in their goniophotometric analysis. Micro-defects act as centres of energy removal from the beam, thus lowering the recorded I_s, $I_s - I_d$, gloss factor and peak area values although having relatively little or no effect on the I_d, $W_{\frac{1}{2}}$ or angular displacement of the specular beam; whilst, secondly, MACRO-defects of the surface are those whose size are sufficiently greater than the wavelength of the incident light to cause an angular divergence and displacement of the specular beam by geometric optical effects; hence, goniophotometrically, the "graduation" in defect size to macro-scale is manifested as an increase in $W_{\frac{1}{2}}$, peak area and, to a lesser extent, I_d, accompanied by a consequent drop in gloss factor and change from triangular peak shape to broader curves, although with relatively little or no further decrease in I_s or peak height.

III.4.3 Effect of Sample Cleaning Technique

Paint films which are exposed outdoors as part of a natural weathering programme inevitably attract a certain amount of surface contamination. This capacity for dirt retention, which obviously depends on the nature of the particular coating material as well as of the outdoor site, invariably poses problems for the analyst in tests such as gloss measurement in which the results are likely to be influenced by the soiling. The main problem centres around how to apply an efficient cleaning treatment to the paint surface without, in any way, affecting the fragile microscopic surface irregularities which represent the effects of weathering in which, of course, interest principally lies. However, a complete solution to this problem becomes extremely difficult, if not impossible, when a proportion of the dirt is positively embedded in the paint surface. Whereas careful washing under running water is adequate to remove all loose (i.e., unattached) forms of particulate matter, it is insufficient to remove the more engrained dirt which has, as it were, become part of the surface.

Consequently, a decision needs to be made as to whether (a) the cleaning process is allowed to be as severe as is necessary in order to remove all traces of visible dirt from the surface, whilst accepting, at the same time, that subsequent goniophotometric data may be representative of not only the effects of weathering but of the effects of cleaning as well, or (b) a compromise is reached in which the cleaning process is just sufficient to remove all of the loose, unattached surface debris (i.e., dirt, "chalk" particles, etc.), whilst preserving at all costs the micro-structure of the weathered surface layer; this approach, of course, standing to suffer from any error which might be introduced into the results by the remaining dirt firmly engrained in the surface, or finally (c) that, in the case of severely "chalking" paints, their surfaces should, indeed, be cleaned at all (238), as, by removing the "chalk", the washing will preclude the effects on gloss of this genuine paint film property from being measured.

However, in view of the fact that none of the coatings to be studied here are what could be classed as severely chalking paints, alternative (c) above is discounted from this study, thus leaving treatments (a) and (b), as so-called severe and gentle cleaning methods respectively, to be now compared in the following section III.5.2 within the context of a natural weathering experiment.

III.5 Natural and Artificial Weathering of Poly (vinylidene fluoride) Surface Coatings

III.5.1 Introduction

The natural and artificial weathering of poly (vinylidene fluoride) (PVF_2) surface coatings were conducted at the Building Research Station exposure site and in the UV exposure cabinet respectively. These commercial (trade name: "Kynar") semi-matt PVF_2 coatings, described previously in section II.2.1 and Table 1, are well known for their exceptionally high durability in all common ageing environments; as such, they provide a particularly stern test of the ability of the analytical techniques used to sense the subtle changes which occur in them on ageing, as well as, of course, setting something of a performance standard with which the range of other types of coatings studied can be subsequently compared. The techniques which were used in this part of the work were goniophotometry and scanning electron microscopy (SEM)/energy dispersive X-ray analysis (EDXA), their results being most conveniently discussed in combination rather than separately.

Altogether, a total of ten PVF_2 coatings, differing only in colour (i.e., pigmentation) were studied, although, for the sake of brevity in the text which follows, only the results for three of them are presented here.

III.5.2 Natural Weathering (including "Effect of Cleaning" Study)

Naturally weathered, as well as corresponding "control" (i.e., unaged) PVF_2 coated aluminium panels (6 in. x 4 in.) were supplied for this study by the Building Research Station. The weathered coatings, which had been exposed for approximately 2 years, had picked up a certain amount of dirt during this time and, thus, required some form of cleaning prior to their analysis. For the purpose of this study, two cleaning methods were adopted which differed in their severity (as described in section III.4.3 previously).

Firstly, half of each weathered panel was cleaned using a cotton wool pad and a 2% Lissapol N detergent solution with the object being to remove all visible signs of surface contamination. This approach effectively returned what were originally semi-matt coatings anyway to being visually "as good as new" in appearance, although the accompanying danger was, of course, that the severity of the cleaning process required to remove the really embedded dirt might abrade and consequently damage the weathered surface.

The second cleaning method, however, as applied to half of the remaining uncleaned panel area, employed a much gentler approach aimed at removing all loose (i.e., unattached) surface debris (e.g., "chalk", dirt particles, etc.) whilst preserving at all costs the underlying fragile micro-texture of the coherent, weathered, surface layer. However, with this now the prime objective, this much less severe cleaning treatment is not sufficient to remove the engrained dirt which has become part of the paint surface as distinct from merely resting upon it.

Consequently, it can be seen that this study essentially entails comparisons being drawn between the reflectance properties and surface topographies of equally aged, yet differently cleaned, sample areas. The "gently cleaned" and "severely cleaned" areas (hereafter referred to in the text as the GC and SC areas respectively) are now compared within the context of the natural weathering performance of these PVF_2 surface coatings.

Goniophotometric data relating to the three PVF_2 coatings reported is compiled in Table 6, analyses having been carried out using the so-called "wide" beam at an angle of incidence of 45° to the sample surface and monochromatic blue light of wavelength 436 nm. From Table 6, it can be seen that, in all cases, the specular reflectance (I_S), as measured from the GC areas, has decreased on weathering. Indeed, this was true for the complete range of ten coatings measured, with the variable extents of these decreases appearing to be mainly a function of the initial (i.e., unaged) states of the respective surfaces. This general decrease in I_s is indicative of an increase in the number of MICRO-defects in the paint surfaces (as discussed previously in section III.4.2), a unique visual insight into which can be valuably gained from scanning electron microscopy (SEM) using the Stereoscan. For example, the <u>WHITE</u> coloured coating (GC areas), whose I_s value has decreased by 12.7% on ageing (from Table 6), is illustrated both before and after exposure in Plates 16 - 19. Bearing in mind that, by definition, micro-defects are of the order of or less than the wavelength of light (436 nm.) used in the goniophotometric analysis, and that in the micrographs a distance of 1 cm. at 1000x magnification corresponds to an actual distance of approximately 10 μm., this means that the micro- designation is applicable to those defects in Plates 17 and 19 at 5000x magnification which are of 2.5 mm. or less in lateral extent. Hence, it is therefore now apparent from a comparison of these two Plates that it is the large number of small, finely dispersed surface irregularities shown in Plate 19 (as opposed to, say,

PVF_2 coating colour	WHITE			TERRA COTTA			MIST GREY				
Length of Exposure	0	≈ 2 years		0	≈ 2 years		0	≈ 2 years			
Cleaning Method	GC	GC	SC	GC	GC	SC	GC	GC	GC (x2)	GC (x3)	SC
I_s (intensity units)	98.22	85.75	92.34	60.35	57.43	69.20	92.87	72.12	82.12	86.46	92.87
I_s , % change in	0	−12.70	−5.99	0	−4.84	+14.66	0	−22.34	−11.58	−6.90	0
I_d (intensity units)	29.10	19.96	26.24	1.49	1.51	1.54	22.00	14.39	16.10	16.70	20.24
$\therefore I_s - I_d$ (intensity units)	69.12	65.79	66.10	58.86	55.92	67.66	70.87	57.73	66.02	69.76	72.63
$W_{\frac{1}{2}}$ (degrees)	12.01	10.34	11.68	13.39	11.91	12.23	12.14	11.73	11.57	11.50	11.02
$\therefore GF = (I_s - I_d)/W_{\frac{1}{2}}$	5.76	6.36	5.66	4.40	4.70	5.53	5.84	4.92	5.71	6.07	6.59
GF , % change in	0	+10.42	−1.74	0	+6.82	+25.68	0	−15.75	−2.23	+3.94	+12.84

TABLE 6

GONIOPHOTOMETRIC DATA RELATING TO THE NATURAL WEATHERING OF PVF_2 SURFACE COATINGS

MAGNIFICATION

x 1000

PLATE 16

x 5000

PLATE 17

PVF$_2$ semi-matt surface coating;
Colour : WHITE (TiO$_2$ - pigmented);
Gently cleaned (GC) surface area;
CONTROL (i.e., UNaged) sample.

MAGNIFICATION

x 1000

PLATE 18

x 5000

PLATE 19

PVF_2 semi-matt surface coating;
Colour : WHITE (TiO_2 - pigmented);
Gently cleaned (GC) surface area;
After approximately 2 years natural weathering.

the large hollow (top left) which is obviously MACRO-scale) which are evidently responsible for the fall in I_s on weathering.

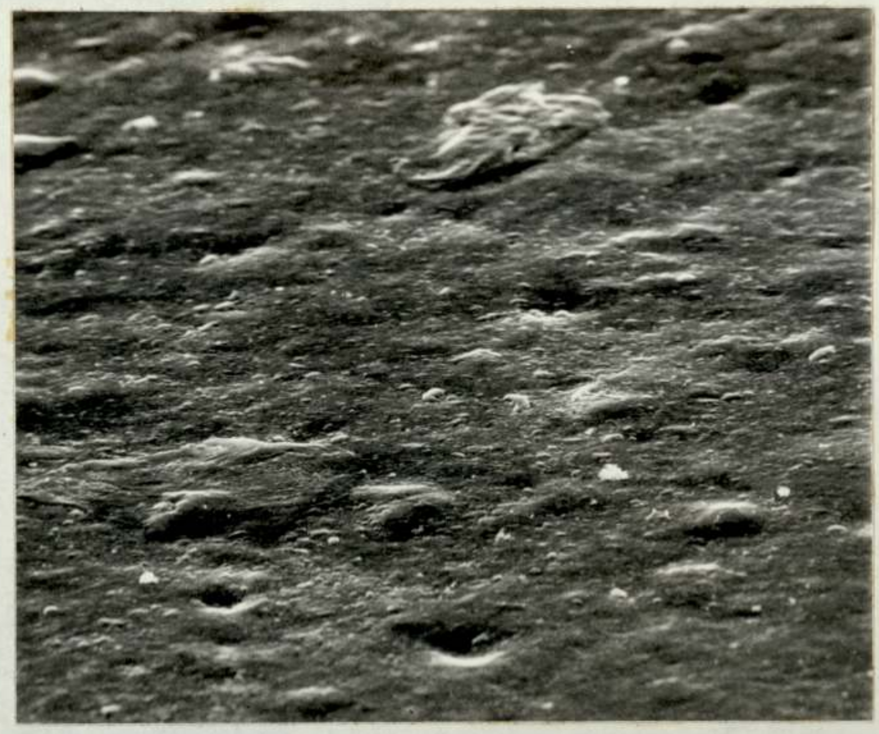
However, perhaps the most striking difference between these unaged and aged (GC) white panel areas is more evident in the lower, 1000x magnification micrographs (cf. Plates 16 and 18 respectively) in which there appears to be, if anything, an apparent smoothening of the coating surface on ageing as far as a reduction in the number and steepness of the larger (i.e., MACRO) defects is concerned. This observation is, indeed, sensed by the goniophotometric technique as a decrease in peak-width at half-height ($W_{\frac{1}{2}}$) from 12.01° to 10.34° (see Table 6), symptomatic of the aged surface's diminished geometric capacity for angular divergence of the specular beam. This effect is observed for all three PVF_2 coatings in Table 6 and, for the white and terra cotta panels, is large enough to offset the respective decreases in peak height ($I_s - I_d$), thus giving rise to slight increases in the gloss factor term ($GF = I_s - I_d/W_{\frac{1}{2}}$) on ageing. This can be considered to be an indication of just how resilient, towards developing and sustaining anything more serious than micro-irregularities, the PVF_2 coatings, collectively, have shown themselves to be over a 2 year period.

However, although the simpler, measured goniophotometric parameters (i.e., I_s, $I_s - I_d$, $W_{\frac{1}{2}}$) of the gently cleaned (GC) surface areas all show consistent upward or downward trends from panel to panel on ageing, the corresponding results for the severely cleaned (SC) areas are at variance in some cases. For example, from Table 6 again, it can be seen that the specular reflectance (I_s) for the three differently coloured coatings varies almost as if at random. Whereas in the case of the WHITE SC coating area, the I_s decreased (as for all the GC areas previously), in contrast to this, the I_s value for the MIST GREY coating remained constant and, for the TERRA COTTA coating, actually increased by almost 15%. Indeed, although results for these three panels only are presented here, the I_s values of the SC coating areas were consistently higher than those of the GC areas for all ten of the aged PVF_2 panels measured, and were, as seen above, even higher in some cases than those of the corresponding control panels.

Changes in diffuse reflectance (I_d) and peak height ($I_s - I_d$) for SC surfaces tended, in all cases, to follow the I_s trends, whereas the peak width ($W_{\frac{1}{2}}$) values consistently decreased on ageing. Meanwhile, the gloss factors (GF) varied, as before, according to the relative changes in peak height and peak width values which make up the GF term.

Thus, compared with the relatively consistent trends described previously for the GC coating areas, the somewhat more erratic data obtained from the corresponding SC areas leads one to suspect that these latter results are not singly representative of the weathering process alone, but are a function of the cleaning treatment as well. The main consequence of this appears to be the effective erasure of some of the fragile micro-defects formed on ageing by the severity of cleaning necessary to remove embedded dirt particles from the surface. This view is supported by the Stereoscan evidence in which the micro-textural imperfections discernable, at high magnification, in the aged surface of the gently cleaned white PVF_2 coating (Plate 19) feature less prominently in the severely cleaned coating area (Plate 21). Indeed, this SC area compares more closely in micro-structure with the original unaged surface (cf. Plates 17 and 21), although, on the macro-scale, it does appear to be significantly smoother (i.e., fewer

MAGNIFICATIO



x 1000

PLATE 20

x 5000

PLATE 21

PVF_2 semi-matt surface coating;
Colour : WHITE (TiO_2 - pigmented);
Severely cleaned (SC) surface area;
After approximately 2 years natural weathering.

protuberances) in common with its GC counterpart (cf. Plates 16, 18 and 20). The respective specular reflectance (I_s) and peak width ($W_{\frac{1}{2}}$) values are also seen in Table 6 to be encouragingly further supportive of this expressed view on the effect of cleaning severity.

Another notable feature arising from the Stereoscan work is that the gentle cleaning process does, in fact, appear to succeed, as intended, in washing away the sessile particulate matter which can be seen to "litter" the corresponding uncleaned surface area (cf. Plates 18 and 19 with 22 and 23). This, at least, justifies the reflectance data, pertaining to the GC surfaces, being taken as representative of a continuous, as opposed to a composite, surface profile. Additionally, it is also significant that repeated gentle cleanings of the same aged area of the MIST GREY coloured coating gives rise to slight increases in specular reflectance (I_s) (see Table 6). These successive increases tend to converge to a limiting I_s value, although this is still less than the SC surface reflectance. However, they do not seem to be attributable to further dirt removal which, thus, appears to remain beyond the capability of the gentle cleaning treatment.

Finally, the energy dispersive X-ray analysis (EDXA) traces relating to these PVF_2 coatings failed to reveal any significant changes in the elemental composition of any of the surfaces on ageing. Nevertheless, EDXA, when used in conjunction with the Stereoscan, still provides a useful means of "fingerprinting" viewed surfaces with respect to their elemental make-up, as shown in Figures 23 and 24 for the unaged white and terra cotta PVF_2 coatings respectively.

MAGNIFICATION

x 1000

PLATE 22

x 5000

PLATE 23

PVF$_2$ semi-matt surface coating;
Colour : WHITE (TiO$_2$ - pigmented);
UNcleaned surface area;
After approximately 2 years natural weathering.

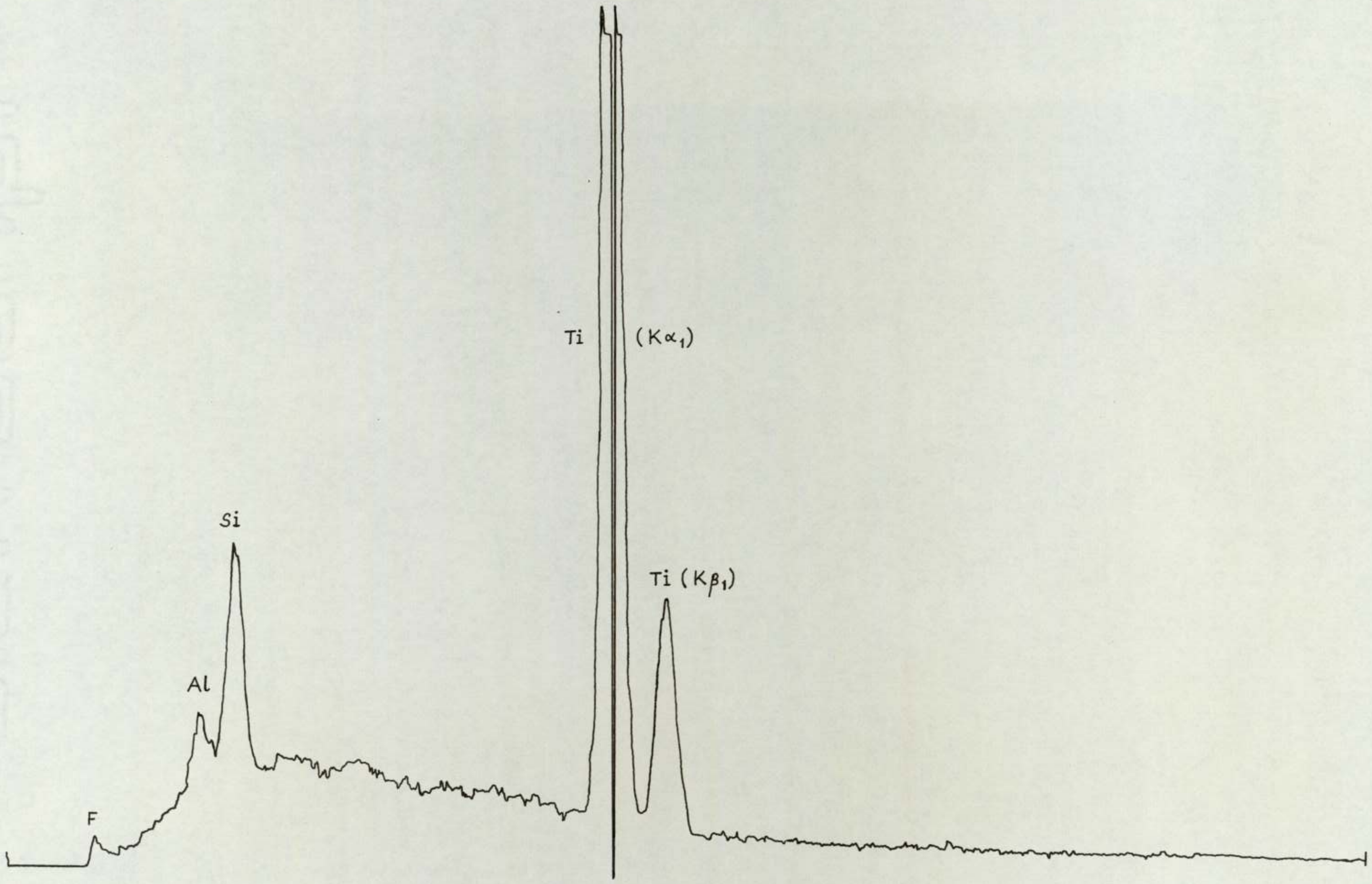
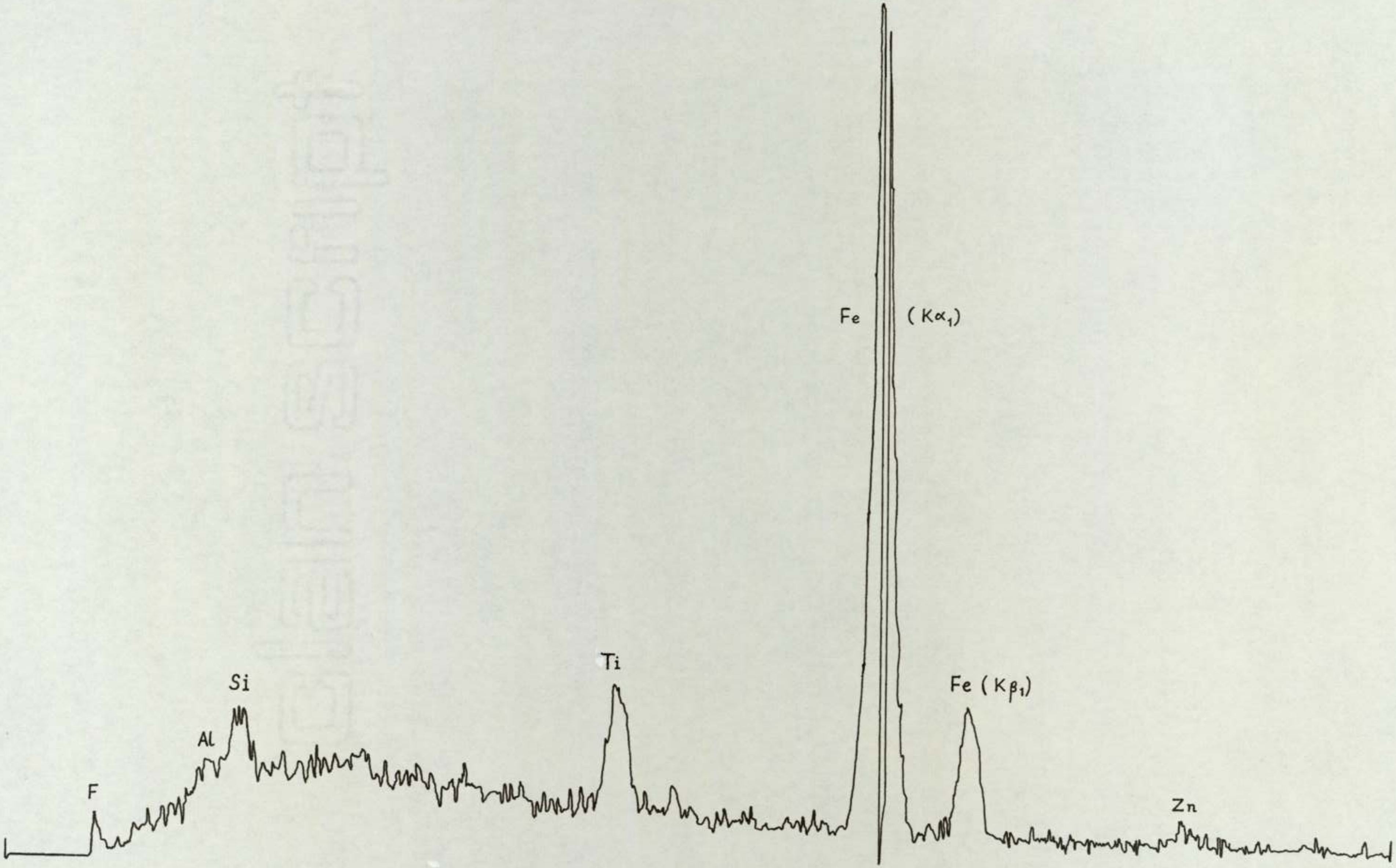


FIGURE 23 - Energy dispersive X-ray analysis (EDXA) spectrum relating to an unaged, white (titanium dioxide - pigmented) PVF_2 surface coating.



<u>FIGURE 24</u> - Energy dispersive X-ray analysis (EDXA) spectrum relating to an unaged, terra cotta (iron oxide - pigmented) PVF_2 surface coating.

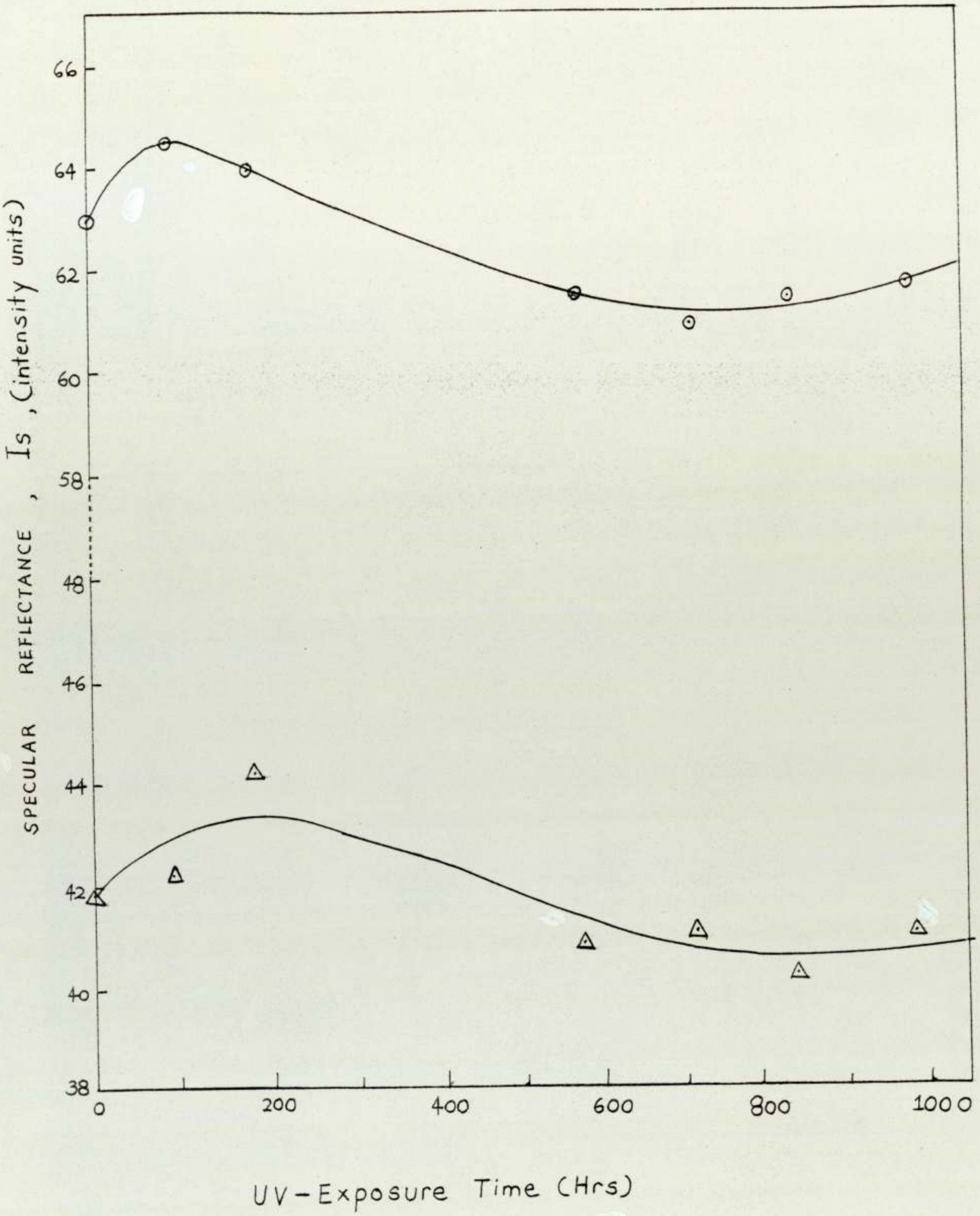
III.5.3 Artificial (UV) Ageing

Artificial ageing of PVF_2 ("Kynar") surface coatings was conducted in the uv exposure cabinet previously described in section II.3.2.2 and shown in Plate 6. The study samples comprised two, 1 inch diameter, punched discs from the white and terra cotta coloured PVF_2 panels already reported on in respect of their natural weathering performances.

This particular uv ageing study was extended up as far as 1000 hours with sample analyses being carried out, initially, every 100 hours and then, later on, at slightly longer time intervals after it had become obvious from the early results that initial changes were only relatively small. As with the natural weathering experiment, sample analysis again took the form of goniophotometry, although, this time, using the instrument's so-called "narrow" version of the previously used "wide" beam, again at a 45° angle of incidence and in conjunction with monochromatic blue light of 436 nm. wavelength.

During the course of this uv exposure, successive goniophotometric analyses, in the case of each of the two coatings studied, were conducted on the same area of sample throughout, thus avoiding any non-ageing variations which might be introduced into the results due to disparities in different areas of the sample surface. Additionally, sample cleaning prior to each analysis, simply to remove any adventitious dust particles or loose particles of "chalk" formed at the surface, was greatly facilitated in the absence of complicating dirt pick-up as encountered in natural weathering. Thus, for these uv exposure samples, only a token "gentle" cleaning (as defined previously) was considered to be necessary, i.e., a light brushing of the sample surface with a soft bristle (artists') paint brush under running water and using a 2% Lissapol N detergent solution.

Let us now consider the goniophotometric data presented for these two PVF_2 samples in Figures 25 - 28. Firstly, Figure 25 illustrates the relatively small extent to which changes in the specular reflectance (I_s) have occurred during 1000 hours of uv-irradiation. After slight initial increases, both samples exhibit similarly slight decreases which then appear to level out after about 600 hours. In each case, the minimum I_s value recorded only amounts to an approximate 4% reduction in the initial reflectance value, a figure which can be compared with the previous 4.8% and 12.7% decreases for the 2 year, naturally weathered terra cotta and white PVF_2 coatings respectively (Table 6). However, in the case of these latter outdoor samples, of course, there was the added complication of dirt pick-up to contend with, which could conceivably have had a lowering effect on recorded I_s values. Consequently, in the absence of such surface contamination, the I_s changes brought about by uv-ageing, as shown in Figure 25, can be attributed with more certainty to inverse changes in the number and/or size of what the goniophotometer regards as MICRO-defects of the surface. This is then followed in Figure 26 by similarly small changes in the respective peak width at half-height ($W_{\frac{1}{2}}$) values which, like the I_s values previously, appear to level out after slight initial increases. This is symptomatic of the aged surfaces retaining their MACRO-profile, such that the light divergent properties of the surfaces remain relatively constant.



<u>FIGURE 25</u> - UV ageing : PVF_2 semi-matt surface coatings; variation in specular reflectance (I_s) on exposure;

⊙ : white (TiO_2 - pigmented) sample,

△ : terra cotta (iron oxide - pigmented) sample.

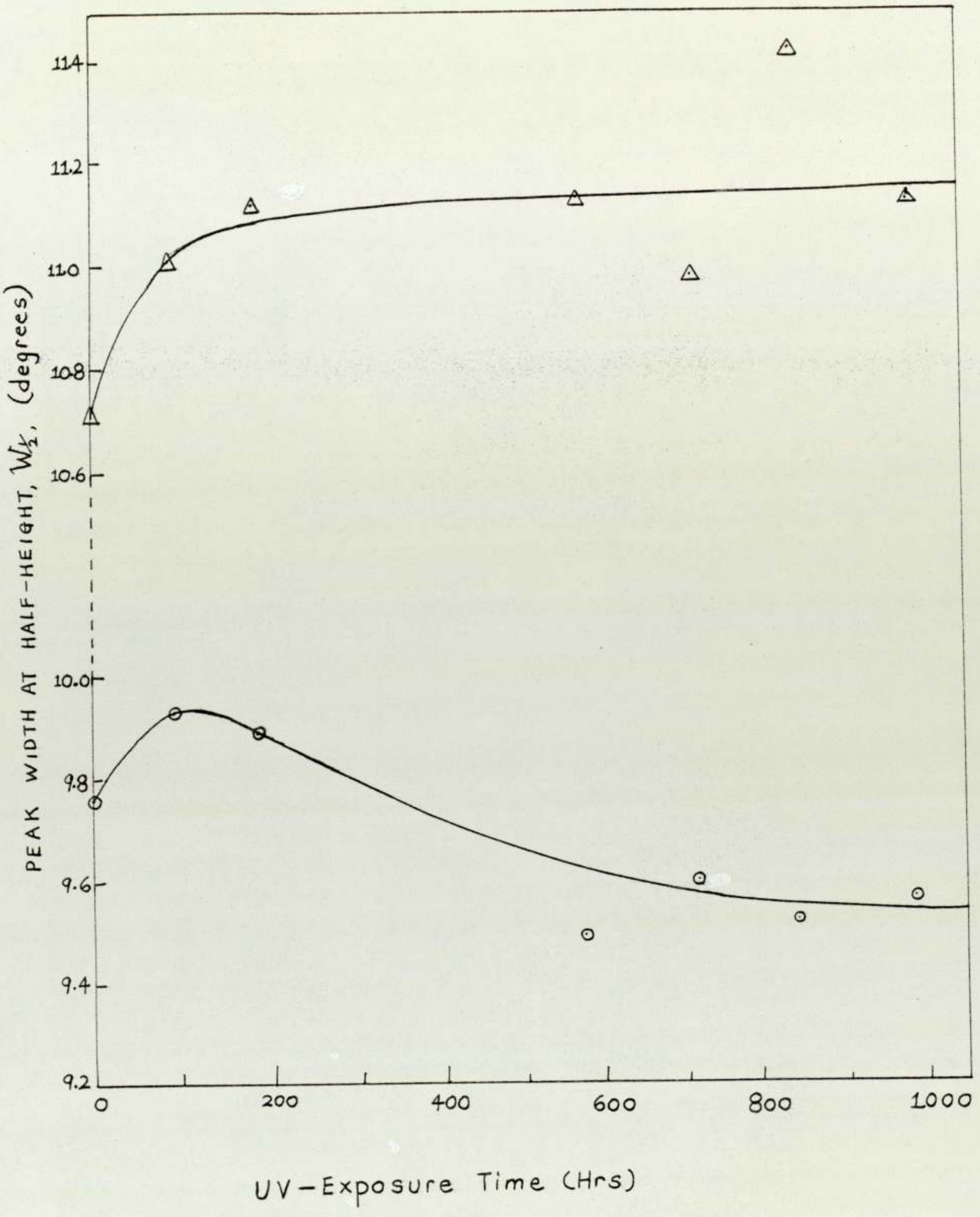


FIGURE 26 - UV ageing : PVF_2 semi-matt surface coatings; variation in peak width at half-height ($W_{\frac{1}{2}}$) on exposure;

⊙ : white (TiO_2 - pigmented) sample,

△ : terra cotta (iron oxide - pigmented) sample.

Thus, in the case of their uv-ageing, it appears that the only significant change in the two coatings surfaces is the development of MICRO-irregularities superimposed upon a relatively unchanging MACRO-profile. This can be compared with their previously discussed natural weathering responses which exhibited similar trends, although with the additional element of erosion outdoors lending itself to an apparent MACRO-smoothening of the surface.

However, when it comes to interpreting such subtle reflectance changes as those observed here for these extremely stable PVF_2 coatings, the possibility must also be considered that the changes are, indeed, becoming so small as to approach the limiting sensitivity of the goniophotometer, whereupon recorded differences become merely attributable, to some extent at least, to an artefact of the instrumentation. Therefore, it is significant in this respect that the peak width at half-height ($W_{\frac{1}{2}}$) changes for the two samples (Figure 26) should, at least, show different trends from each other which, in relation to the I_S changes (Figure 25), give rise to the contrasting gloss factor (GF) variations shown in Figure 27. These GF changes, which are plotted on a percentage basis in Figure 28 (in which their respective "2 year" points are also included for comparison) serve to illustrate that their component I_S and $W_{\frac{1}{2}}$ changes are, at least to some extent, disproportionate and, as such, are indicative of slight changes in the actual shape of the goniophotometric curves on uv exposure. This, of course, can only be a consequence of genuine surface reflectance changes in the samples on ageing, as opposed to factors which are more to do with the instrumentation.

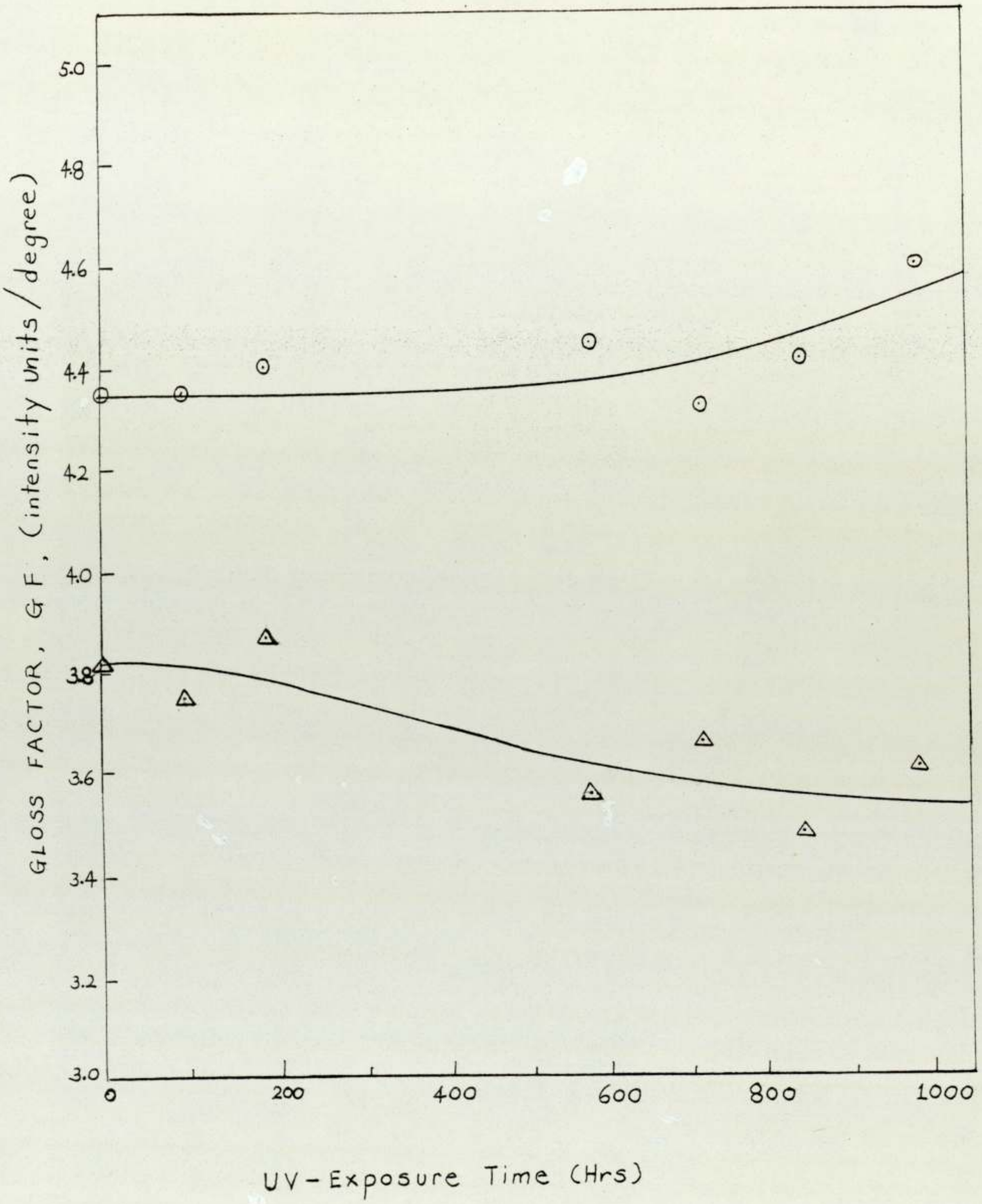


FIGURE 27 - UV ageing : PVF_2 semi-matt surface coatings; variation in gloss factor (GF) on exposure;

⊙ : white (TiO_2 - pigmented) sample,

△ : terra cotta (iron oxide - pigmented) sample.

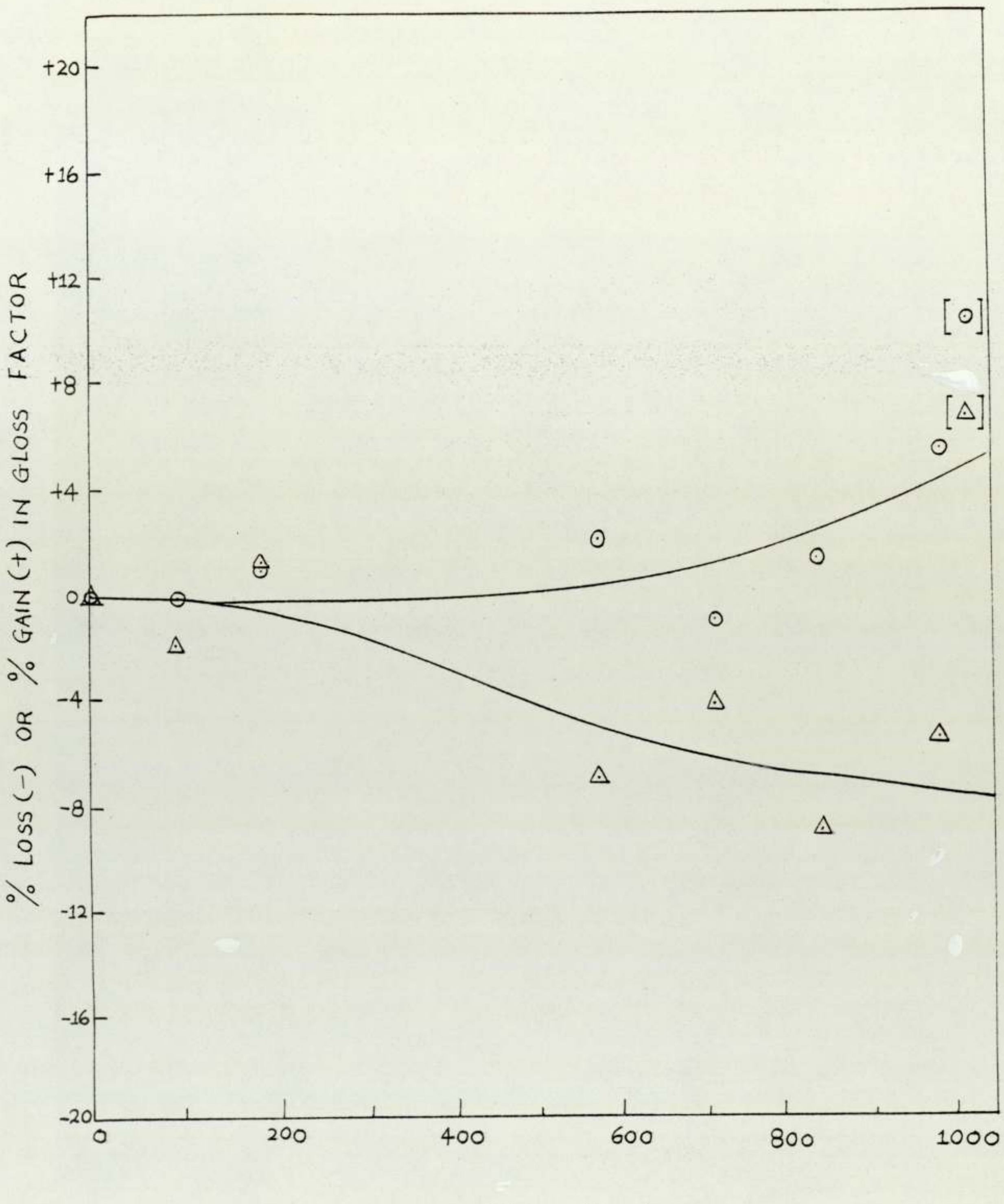


FIGURE 28 - UV ageing : PVF_2 semi-matt surface coatings; percentage change in gloss factor (GF) on exposure;

⊙ : white (TiO_2 - pigmented) sample,

△ : terra cotta (iron oxide - pigmented) sample,

cf. [ ] : after 2 years natural weathering.

Hence, this particular study can be seen to have not only shown these PVF_2 coatings to be extremely durable towards uv-ageing, as indeed they were towards natural weathering previously, but has also usefully served to demonstrate that the goniophotometer is quite capable of monitoring even the most subtle of those surface changes which are likely to affect the reflectance properties of paint films on ageing.

III.5.4 Summary

In brief summary of the previous findings, it is clear that the semi-matt PVF_2 surface coatings studied here have shown themselves to be extremely durable materials with respect to both natural and artificial (in this case, ultraviolet) ageing. In each environment, their pattern of ageing was essentially similar with the predominant surface change appearing to comprise a slow, gradual build-up in the number and/or size of so-called micro-irregularities. This effect tended, in the case of uv-ageing, to be superimposed upon a relatively unchanging macro-profile such that, while the specular reflectance may have changed slightly, the total angular reflectance distribution remained fairly constant throughout the exposure. However, in the natural weathering environment, in which erosion by wind and rain, etc., came into effect, the coatings were all found to have undergone, during the course of their 2 year exposure period, an actual surface smoothening on the macro-scale. Indeed, this latter effect tended to offset the lowering effect which the micro-deterioration had on the surfaces' measured gloss factors. Thus, with mild physical erosion appearing to compete kinetically with micro-defect formation as regards influencing surface reflectance, it can be appreciated just how slowly these PVF_2 coatings degrade in temperate climates such as in the U.K.

Understandably, therefore, they have come to be regarded as high durability coatings which, in most of their exterior applications, might reasonably be expected to last for up to 10 - 15 years. However, in commercial practice, this high performance aspect tends to be offset somewhat by their relative expense and difficult processing and application.

In addition to the ageing characteristics of the PVF_2 paint films, this study also included an investigation into the effect which varying the severity of the pre-analysis cleaning treatment had on the results. From the combined goniophotometric/micrographic evidence obtained, it is clear that the severity of cleaning required in order to remove the surface-embedded portion of a sample's visible dirt pick-up exceeded that which was still preservative of the surface's fragile micro-structure. Consequently, in an ageing study such as this in which attention is focussed on the development of so-called micro-defects during the early stages of weathering, a subjectively "complete" cleaning of the surface is not possible if the analytical results are to be solely representative of the effects of weathering, as of course they should be, rather than reflecting the effects of the cleaning process as well. Hence, in all of the ageing experiments which are to be subsequently reported, the previously described "gentle cleaning" technique will have been used to prepare test samples for analysis.

Finally, the extreme subtlety of surface profile and, hence, reflectance changes brought about during uv exposure provided a particularly stern test of the sensitivity of the goniophotometer towards monitoring such changes. However, the instrument was able to detect variations in reflectance which, from a collective consideration of the derivable reflectance parameters, could be simply shown to be genuinely descriptive of ageing effects as opposed to instrumental factors. In this way, the goniophotometer is demonstrated as being a powerful analytical tool, eminently suited to the quantitative study of surface coatings deterioration as will be seen in the following chapters.

CHAPTER IV

NATURAL AND ARTIFICIAL WEATHERING OF SELECTED COMMERCIAL SURFACE COATINGS

CHAPTER IV

NATURAL AND ARTIFICIAL WEATHERING OF SELECTED COMMERCIAL SURFACE COATINGS

IV.1 Introduction

The natural(239) and artificial(240) weathering of the following commercial surface coatings, viz.:-

(i) phthalic alkyd)
)
(ii) epoxy/polyamine)
) GLOSS finish
(iii) polyurethane alkyd)
)
(iv) vinyl toluene - modified alkyd)
(v) thixotropic chlorinated rubber) SEMI-GLOSS finish

was conducted at the Building Research Station (BRS) exposure site and in the BS 3900 Part F3 apparatus respectively. These coatings, which have been detailed in Table 1 (section II.2.1) previously, have already been characterised with respect to certain of their mechanical properties by BRS workers(10). However, rather than being an in-depth study of each of the above coatings systems in turn, this section of the work is intended as more of an "across-the-board" study of a fairly representative cross-section of the current range of commercial paint systems using the following combination of analytical techniques:-

(i) goniophotometry;
(ii) multiple internal reflection spectroscopy (MIRS); and
(iii) surface roughness measurements, i.e., average height of roughness irregularities (AHRI) and associated peak count (PC) studies.

Thus, it is now under these separate technique headings that, firstly, the natural and, secondly, the artificial weathering performances of these selected coatings materials will be compared and, for each individual coating, correlated wherever possible. Additionally, the range of applicability of each technique to these five paints can be assessed in terms of the usefulness of the data which they each provide and the respective ease with which it is obtained.

IV.2 Natural Weathering

The natural weathering results presented here relate to a twelve month exposure period which commenced on 1st July, 1966, at the Building Research Station's semi-rural site. As mentioned previously, the weathered coatings were originally the subject of an earlier study concerning changes in their mechanical properties(10), after which they had been carefully stored prior to forming part of this present work as now described.

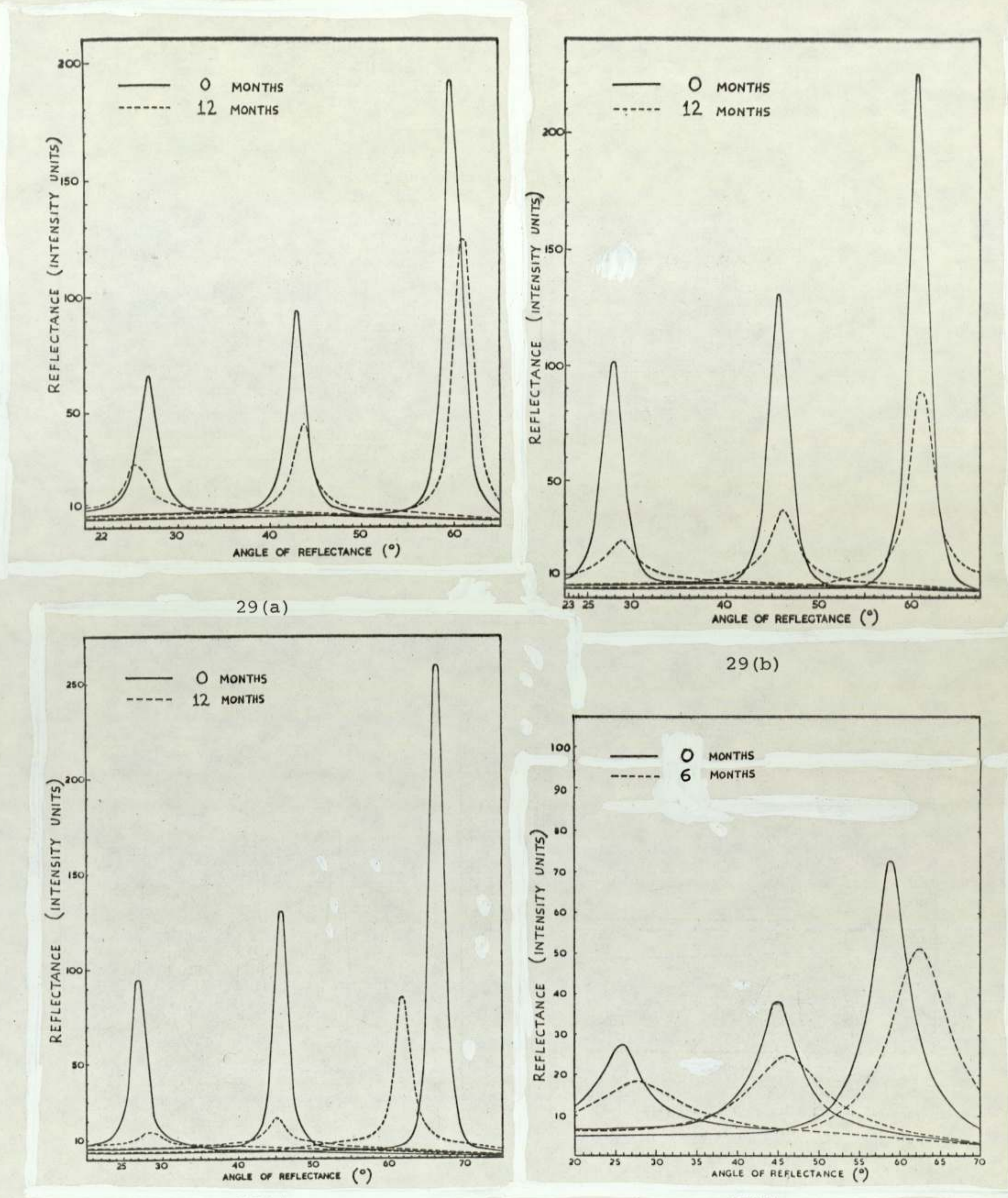
IV.2.1 Goniophotometry

Goniophotometric studies during this part of the work were conducted using the, then, still manually operated instrument; "wide beam" monochromatic blue light (436 nm.) illumination being employed over a range of angles of incidence (30°, 45°, 60°, 75°) to the sample surface.

On natural weathering, the reflectance characteristics of the five coatings studied all exhibited significant changes. This was evident from their respective goniophotometric curves which are shown in Figure 29(a), (b) and (c) for the initial and final exposure samples of three of the four gloss finish paints studied. In each case, the main change in the shape of the curve is a decrease in peak height which can be clearly seen over all examined angles of incidence. In relation to this effect, however, the increase in peak width on weathering is proportionately small such that the triangularity of each of the peaks is still apparent, even after twelve months' exposure, in the case of these gloss finish coatings. This observation is more clearly illustrated for just the epoxy/polyamine paint alone in Figure 30 from which it may be deduced that visually perceived gloss reductions, over the first six months at least, can be almost entirely associated with progressive decreases in merely the specular component of reflectance rather than in its angular distribution as a whole. This manifests itself visually as a loss in image brightness rather than image sharpness on subjective gloss assessment of the paint surface.

In contrast to the initially sharp triangular goniophotometric peaks and their changes on weathering as described for the three gloss finish paints in Figure 29(a), (b) and (c), the unaged semi-gloss chlorinated rubber coating (Figure 29(d)) is characterised by a relatively broader reflectance curve which, after six months' weathering, is not only smaller in peak height but is significantly wider at the half-height as well. This useful comparison can be considered to be related to the differing orders of defect size initially present in what are regarded as gloss and semi-gloss paints.

However, one, rather more general, aspect of reflectance which is not particularly obvious from the goniophotometric curves in Figure 29 is the asymmetry of their relatively small "background" (i.e., diffuse) reflectances over the 0 - 90° angular range as a whole. A



29(a)

29(b)

29(c)

29(d)

FIGURE 29 - Goniophotometric curves relating to the natural weathering of:-

(a) phthalic alkyd - gloss finish,
(b) epoxy/polyamine - gloss finish,
(c) polyurethane alkyd - gloss finish,
(d) chlorinated rubber, thixotropic - semi-gloss finish.

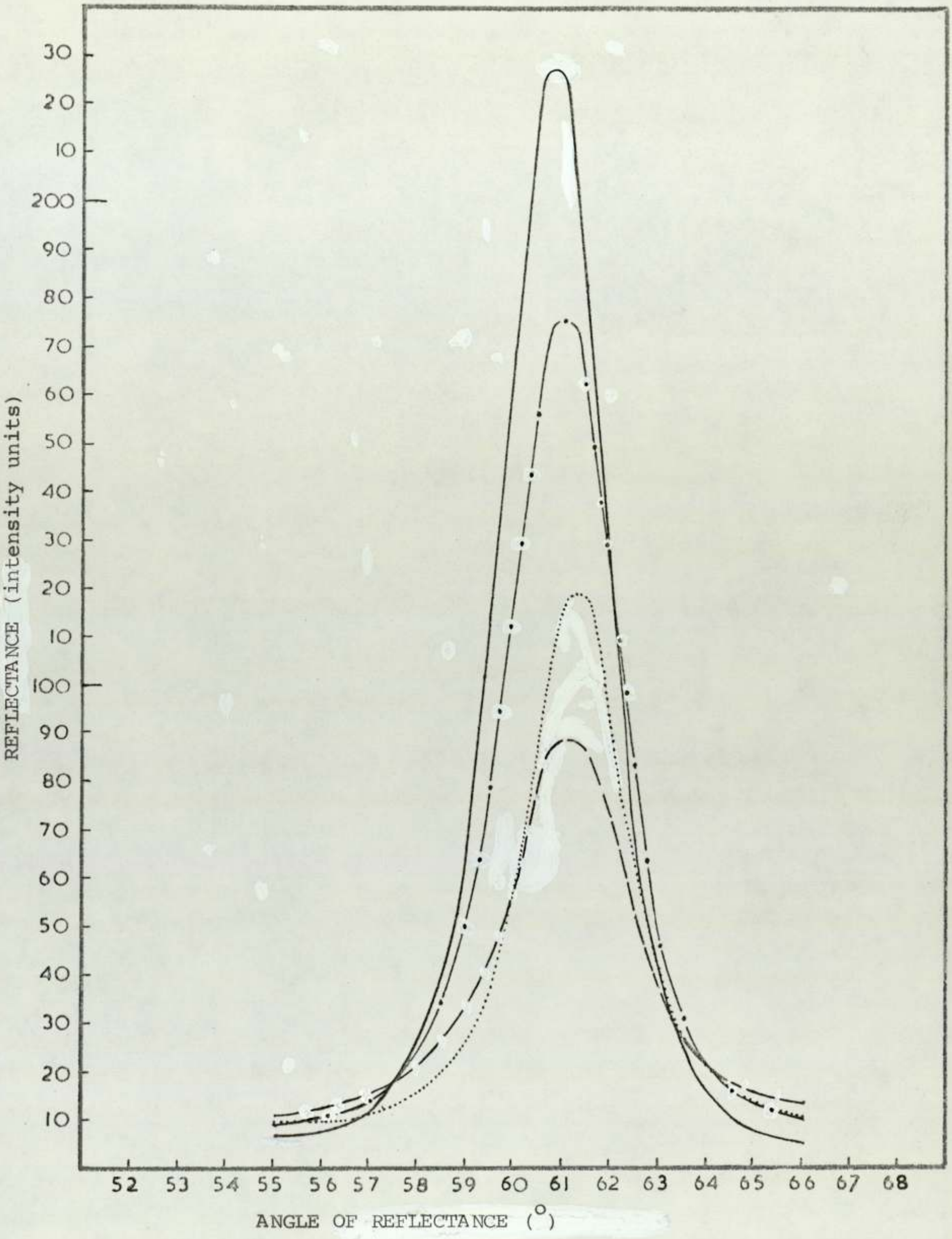


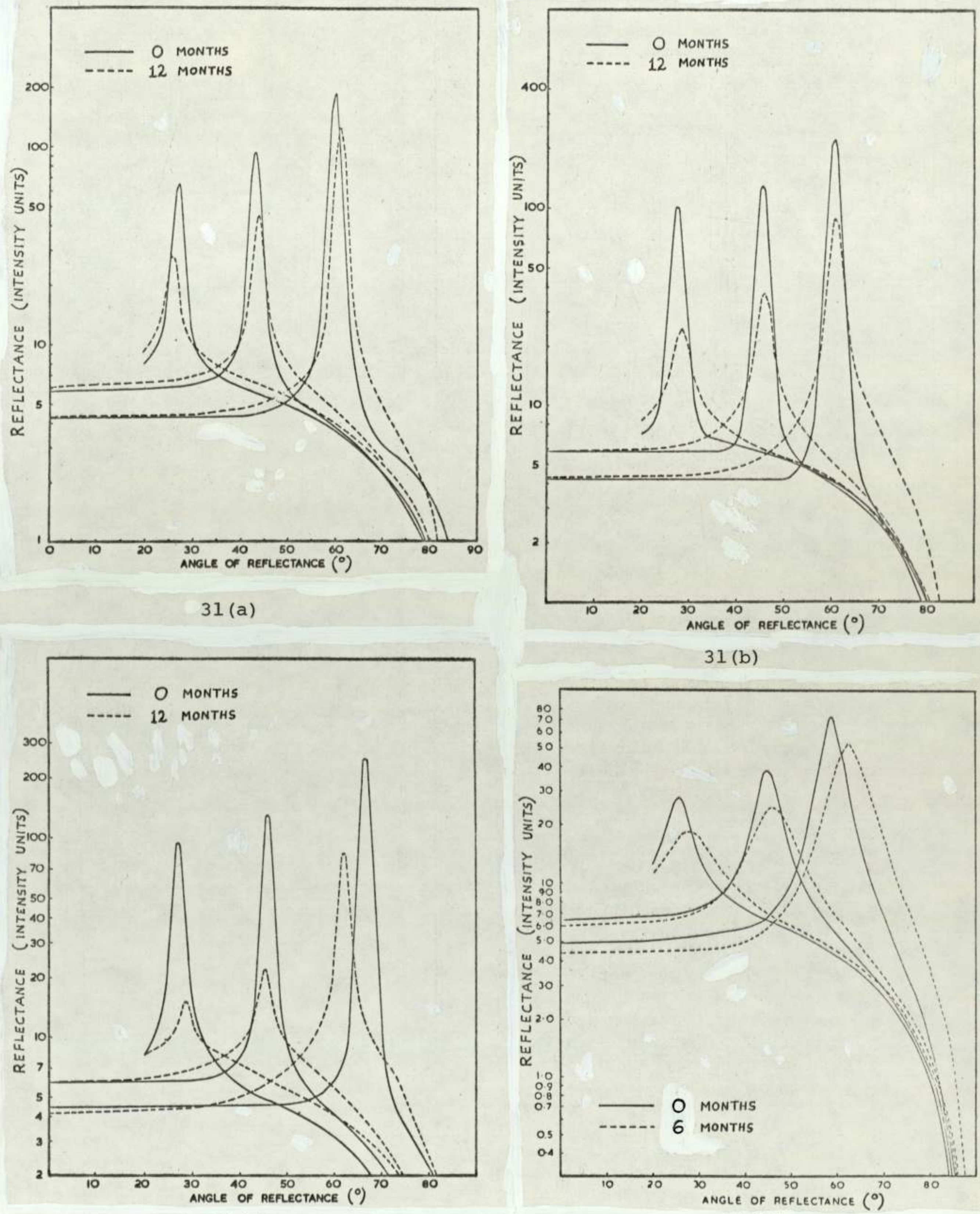
FIGURE 30 - Goniophotometric curves: Natural Weathering of epoxy/polyamine gloss finish coating;

————	:	0 months	(date: 1/7/66)
·—·—·	:	3 months exposure	(date: 30/9/66)
…………	:	6 months exposure	(date: 23/12/66)
— — — —	:	12 months exposure	(date: 8/7/67)

much clearer impression of this is, in fact, gained from a logarithmic presentation (Figure 31) of the curves in which peak asymmetry can also now be seen to be affected by weathering.

NOTE: When viewing goniophotometric data logarithmically in this way, it is extremely interesting to note that it is considered to be a physiological fact that linear variations in light intensity, as received by the eye, tend then to be transduced into approximately logarithmic responses at the brain. This visual "experience" is described by the Weber-Fechner Law(34), the validity of which, with regard to quantities describing gloss phenomena, has additionally been proved by Kosbahn(82). This means, therefore, that subjective visual assessments of the gloss changes brought about by weathering in the coatings studied here are more likely to be correlative with goniophotometric data in logarithmic (Figure 31) rather than linear (Figures 29 and 30) form.

Let us now consider in more detail the comparative natural weathering performances of the coatings listed at the outset of this chapter, firstly through the various goniophotometric parameters derivable from their respective reflectance curves (Figures 29 and 30). In Figure 32, for example, it can be seen how the specular reflectance (I_s) varies on exposure for the four gloss finish paints studied, the graphs, incidentally, being plotted on a linear energy rather than time of exposure basis. In the case of the epoxy/polyamine, polyurethane alkyd and vinyl toluene (VT) alkyd coatings (Figures 32(b), (c) and (d) respectively), their I_s values decreased, as expected, from the beginning of exposure with, if anything, the epoxy/polyamine showing a slightly



31(a)

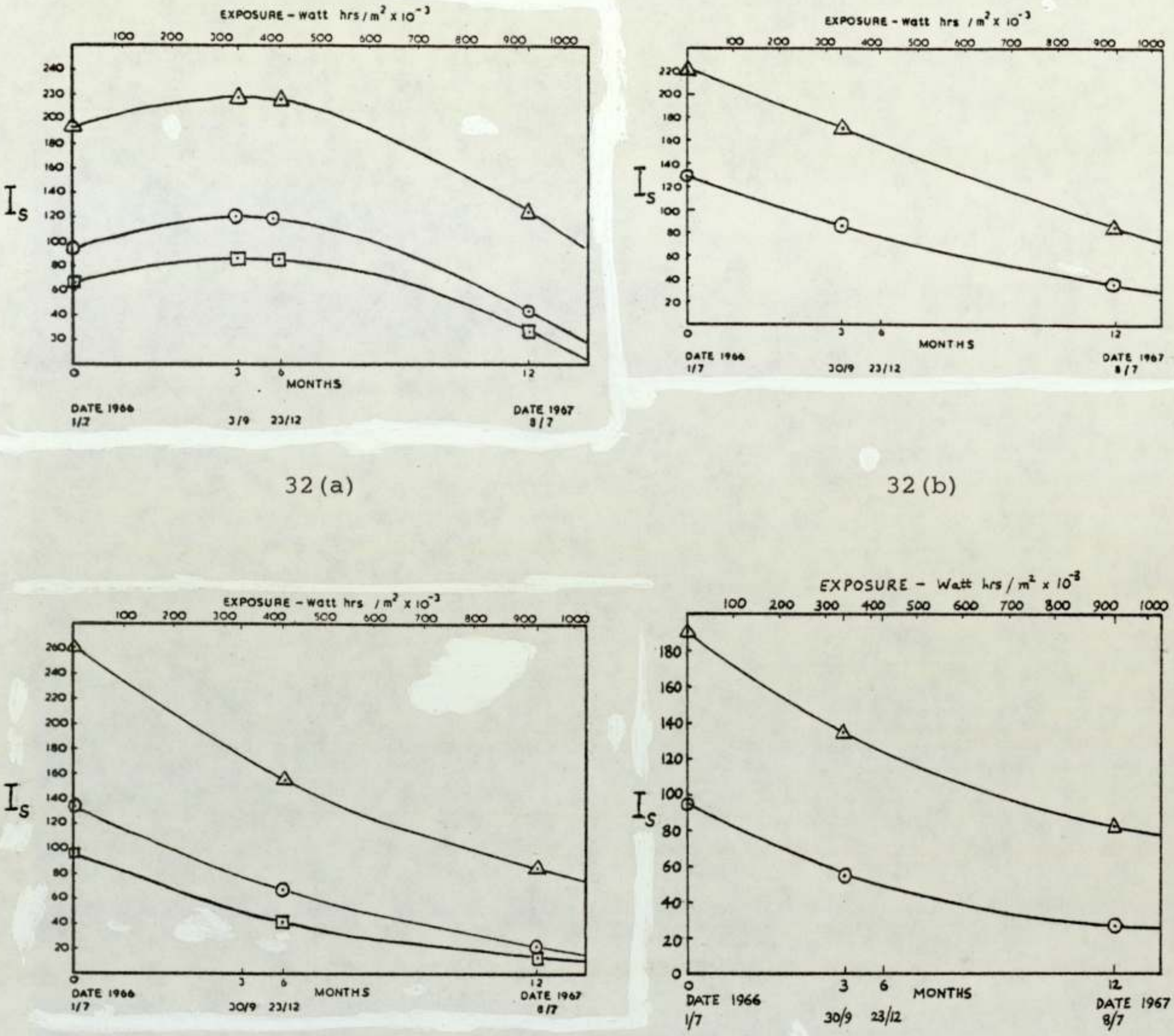
31(b)

31(c)

31(d)

FIGURE 31 - Goniophotometric curves (logarithmic presentation) relating to the natural weathering of:-

(a) phthalic alkyd - gloss finish,
(b) epoxy/polyamine - gloss finish,
(c) polyurethane alkyd - gloss finish,
(d) chlorinated rubber, thixotropic - semi-gloss finish.



32(a)

32(b)

32(c)

32(d)

FIGURE 32 - Variation in specular reflectance (I_s, intensity units) at angles of incidence of:-

⊡ = 30°

⊙ = 45°

△ = 60°

on natural weathering exposure of:-

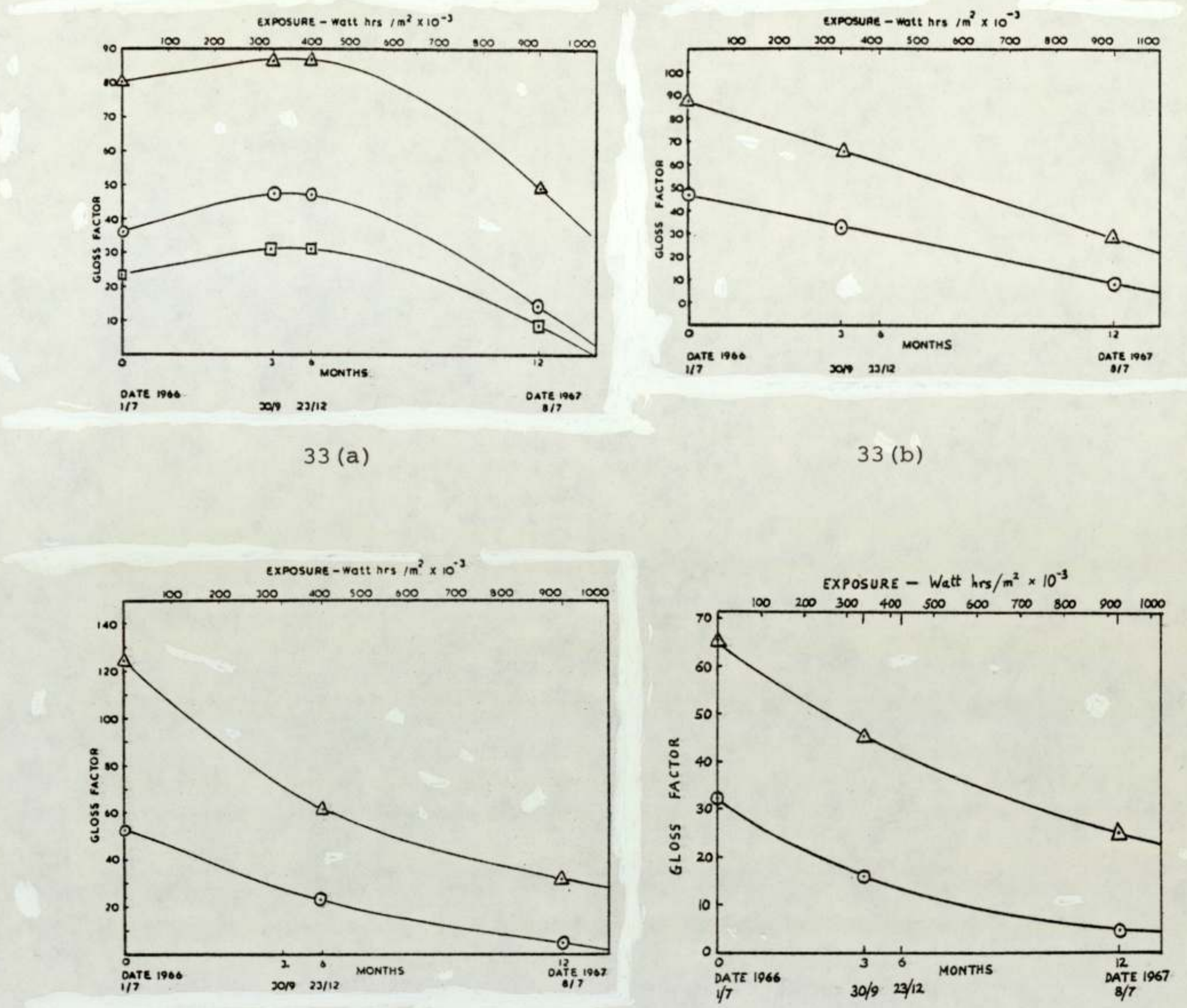
(a) phthalic alkyd
(b) epoxy/polyamine
(c) polyurethane alkyd
(d) vinyl toluene - modified alkyd

gloss finish paints.

slower rate of change than the other two. However, the overall trend of maximum rate of I_s decrease during the summer months followed by a subsequent levelling out during the winter and spring is seen to be essentially the same for all three. In view of this, therefore, it is somewhat surprising to find that the fourth of these gloss finish paints, the phthalic alkyd, exhibits an initial increase in I_s up to the end of the summer (Figure 32(a)) before decreasing in common with the other three. Whilst the reason for this obviously still requires elucidation, an initial consideration must be that, possibly, incomplete drying of this latter sample prior to exposure may be at least partly responsible.

Considering next the variations in the gloss factor (GF) term on ageing for these four gloss finishes (Figure 33), their most striking feature is the extent to which they "mirror", in each case, their component I_s changes described previously - a preview of which was afforded by what were seen to be predominantly peak height changes in the reflectance curves (Figure 29) on weathering. Consequently, it can be said that the measured specular reflectance (I_s) changes (as might have also been determined by a conventional gloss-meter) are still very largely descriptive of the overall gloss changes to date in the coatings studied. Where these changes are in fact decreases, they are perceived, subjectively, as a visible "dulling" of the surface lustre which leads to an impairment of image brightness.

However, as noted previously, subjective gloss assessments correspond more closely to logarithmic rather than linear variations in surface reflectivity. Hence, objectively, the plots of log "gloss-factor" (in this case, at 45°) against exposure (Figure 34) provide us with a truer picture than, say, the linear graphs in Figure 33, of the



33 (a)

33 (b)

33 (c)

33 (d)

FIGURE 33 - Variation in gloss factor (GF, intensity units/degree) at angles of incidence of:-

⊡ = 30°

⊙ = 45°

△ = 60°

on natural weathering exposure of:-

(a) phthalic alkyd
(b) epoxy/polyamine
(c) polyurethane alkyd
(d) vinyl toluene - modified alkyd

gloss finish paints.

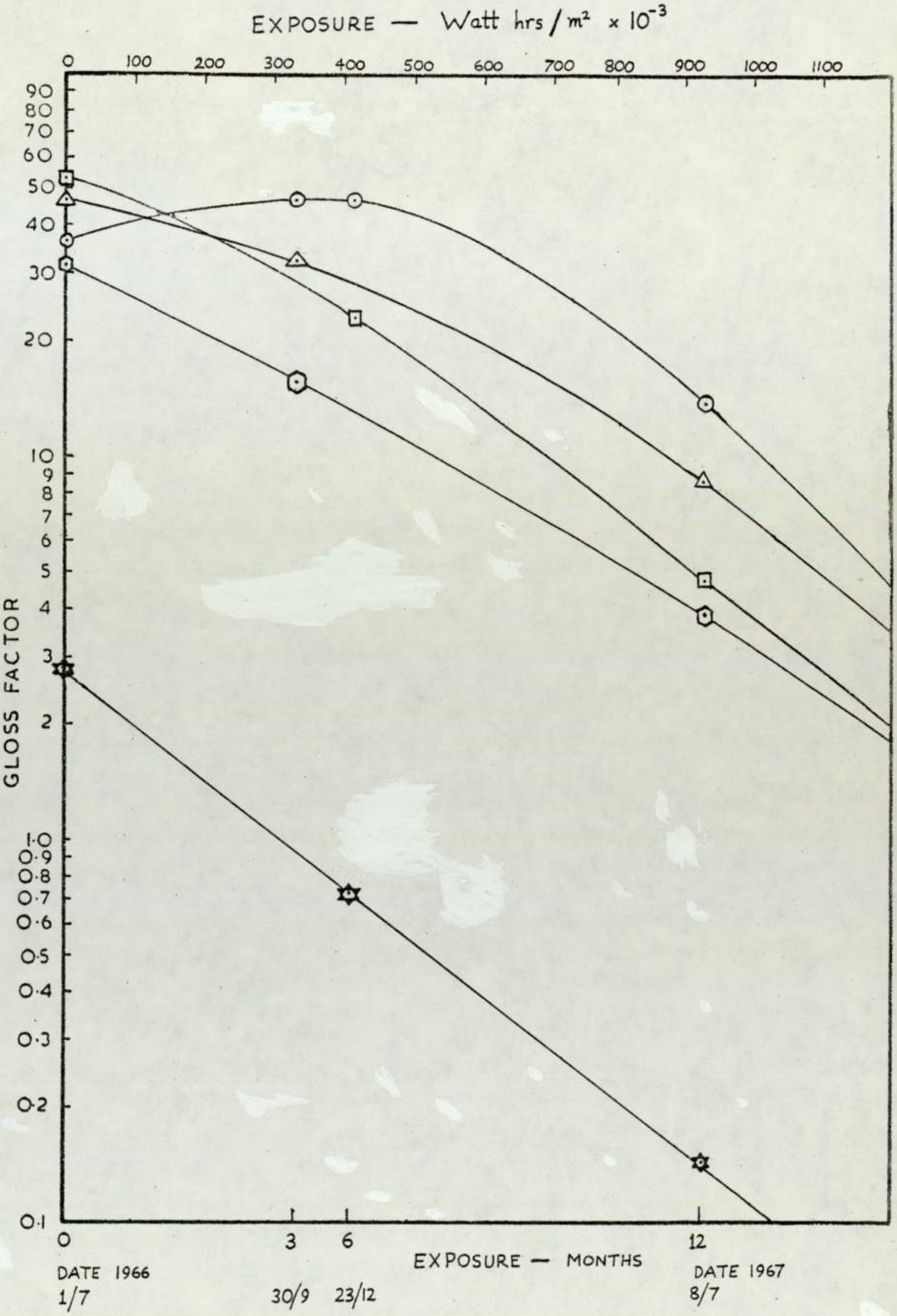


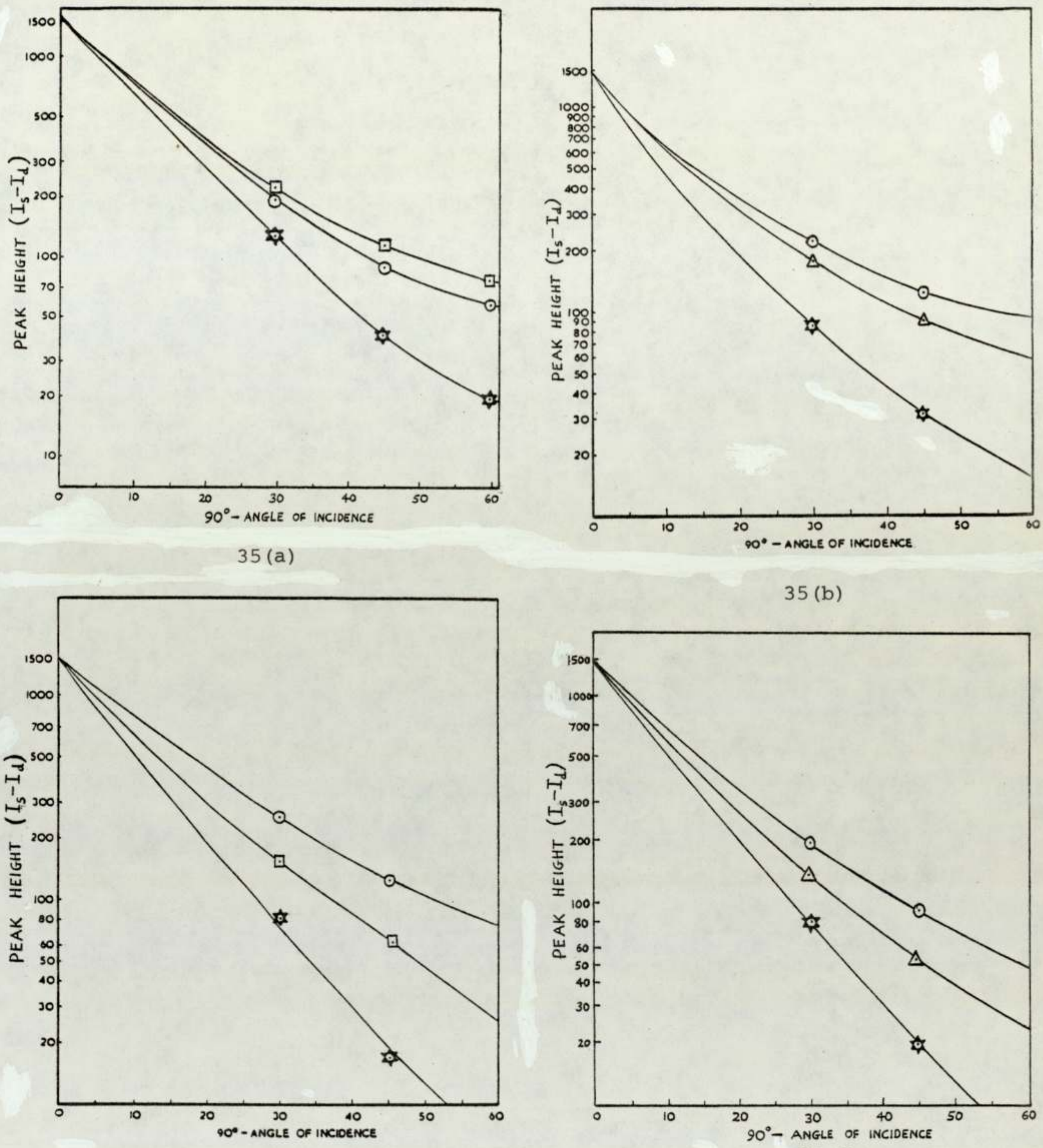
FIGURE 34 - Variation in log "45°-gloss factor" on exposure; natural weathering of:-

⊙ : phthalic alkyd - gloss finish,
△ : epoxy/polyamine - gloss finish,
⊡ : polyurethane alkyd - gloss finish,
⬡ : vinyl toluene - modified alkyd - gloss finish,
✡ : thixotropic chlorinated rubber - semi-gloss finish.

visual gloss changes which an observer of the surfaces would perceive at the same 45° angle of viewing. From the shapes of the graphs in Figure 34, it can be seen that the five coatings included in this study are now shown to be not all that dissimilar in terms of their relative "rates of weathering", as taken from the slopes of the graphs under consideration, once surface deterioration has set in. This suggestion accords well with subjective visual gloss ratings made of the weathered gloss surfaces.

Finally, an alternative way of presenting goniophotometric data is depicted in Figure 35 whereby the particular reflectance parameter, in this case log "peak height (I_s - I_d)", is plotted as a function of (90° - the angle of incidence) for each exposure sample in a given series. This produces a fan of lines or curves which can be extrapolated back to a common point on the peak height axis which, at an angle of incidence of 90°, obviously corresponds to the intensity of the incident blue light beam itself (approximately 1500 intensity units). Thus, each of the four graphs shown in Figure 35 reflect, through the relative spacings of their constituent curves, the weathering changes brought about in their respective paints. In this way, goniophotometric weathering data covering the entire 0 - 90° reflection range can be easily and conveniently set out in a single graph as a useful supplement to the more conventional exposure-based representation (Figures 33 and 34).

Having, therefore, looked at the information which goniophotometry can provide, let us now consider the results obtained from surface roughness measurements and multiple internal reflection spectroscopy.



35(a)

35(b)

35(c)

35(d)

<u>FIGURE 35</u> - Plots of log "peak height $(I_s - I_d)$" versus (90° - angle of incidence) after:-

⊙ : 0 months
△ : 3 months
⊡ : 6 months
and ✡ : 12 months natural weathering exposure of:-

(a) phthalic alkyd
(b) epoxy/polyamine
(c) polyurethane alkyd
and (d) vinyl toluene - modified alkyd

gloss finish paints.

IV.2.2 Surface Roughness Measurements

Surface roughness measurements, using the Talysurf 100 instrument, were unfortunately found to be unreliable for the gloss finish paints studied here due to the smallness of their recorded average heights of roughness irregularities (AHRI) even after weathering. For example, the AHRI values determined for the vinyl toluene - modified alkyd coating after 0, 12 and, more recently, 25½ months natural weathering were 52, 72 and 111 mμ respectively. This relatively small order of defect size (cf. 300 mμ upwards for the semi-gloss chlorinated rubber coating) not only begins to approach the limiting sensitivity of the Talysurf but is also in the range where substrate aplanarity is likely to influence adversely the accuracy and, hence, reliability of the results.

Finally, although the chlorinated rubber semi-gloss coating proved to be sufficiently more rugous for meaningful data to be obtained, results are currently only available for artificial weathering as will be described later in section IV.3.2.

IV.2.3 Multiple Internal Reflection Spectroscopy (MIRS)

In general, the quality of the infrared spectra obtainable by the MIRS technique for the coatings under examination was largely dependent upon the surface condition of the samples and, hence, the intimacy of their contact with the MIR reflector plate. However, whilst adequate spectra, of reasonable peak definition and absorbance, were recorded for the unexposed glossy paints (see upper spectra in Figures 36, 40 and 43), this spectral quality suffered progressively as surface deterioration increased on weathering (cf. lower spectra in Figures

36, 40 and 43). Consequently, as the spectra became generally more diffuse, not only were individual peak absorbancies less trustworthy, but also it became more difficult to locate reliably stable peaks in each of the spectra to act as internal reference standards.

However, this effect of surface deterioration in detracting from efficient sample-to-reflector plate contact, is often offset to some extent during sample analysis by heat transfer to the sample from the infrared beam. Depending upon the coating's softening point, this latter effect can cause the sample to flow under the pressure with which it is clamped to the reflector plate, thus promoting improved contact with the plate and helping to redress the loss in spectral quality. However, as this heat transfer process is obviously time-dependent, it was found necessary, for each sample analysis, to re-record the spectrum, usually up to between 7 - 10 times at the slow scan speed, until a satisfactorily stable spectrum was obtained. Hence, in this way, MIR spectra were eventually obtained which were suitable for semi-quantitative analyses to be made in respect of the natural weathering of the phthalic alkyd, polyurethane alkyd and epoxy/polyamine gloss finish coatings, as now described in turn.

Firstly, the <u>phthalic alkyd</u> exhibits in its MIR spectrum (Figure 36) the infrared peaks listed in Table 7 overleaf, amongst which are featured the characteristic ortho-phthalate bands.

On ratioing the absorbances of these various peaks to that of the carbonyl band at 1720 cm.$^{-1}$ as a reference, it was found that their respective indices all increased on weathering (Figure 37). However, as it is unreasonable for this to suggest that, for example, because the

Frequency ($cm.^{-1}$)	Corresponding bond vibration
3450	O - H stretching of (initially) unreacted hydroxyl
2920	C - H stretching (aliphatic)
1720	C = O stretching (esteric)
1650	C = C stretching (oil modification)
1600 1580	C = C stretching (aromatic) doublet
1460	$-CH_2-$ bending (methylenic)
1380	$-CH_3$ bending (methyl)
1255	C - O stretching in $-\underset{\overset{\Vert}{O}}{C}-O-$
1118	C - O stretching in $-O-CH_2-$
1070	C - O stretching (alcoholic) in - C - OH

TABLE 7

INFRARED SPECTRAL DATA RELATING TO THE PHTHALIC ALKYD COATING

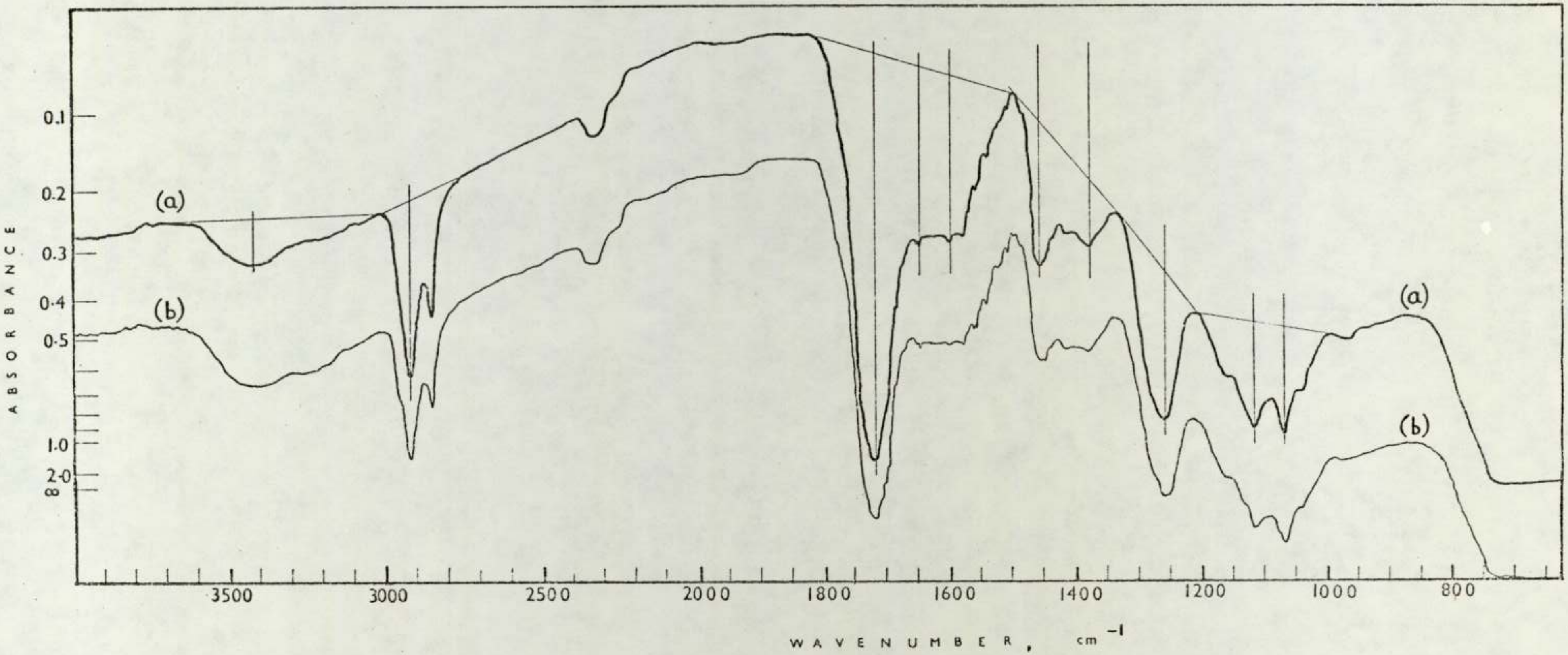


FIGURE 36 - MIR spectra of the PHTHALIC ALKYD gloss finish coating (a) before, and (b) after 12 months natural weathering.

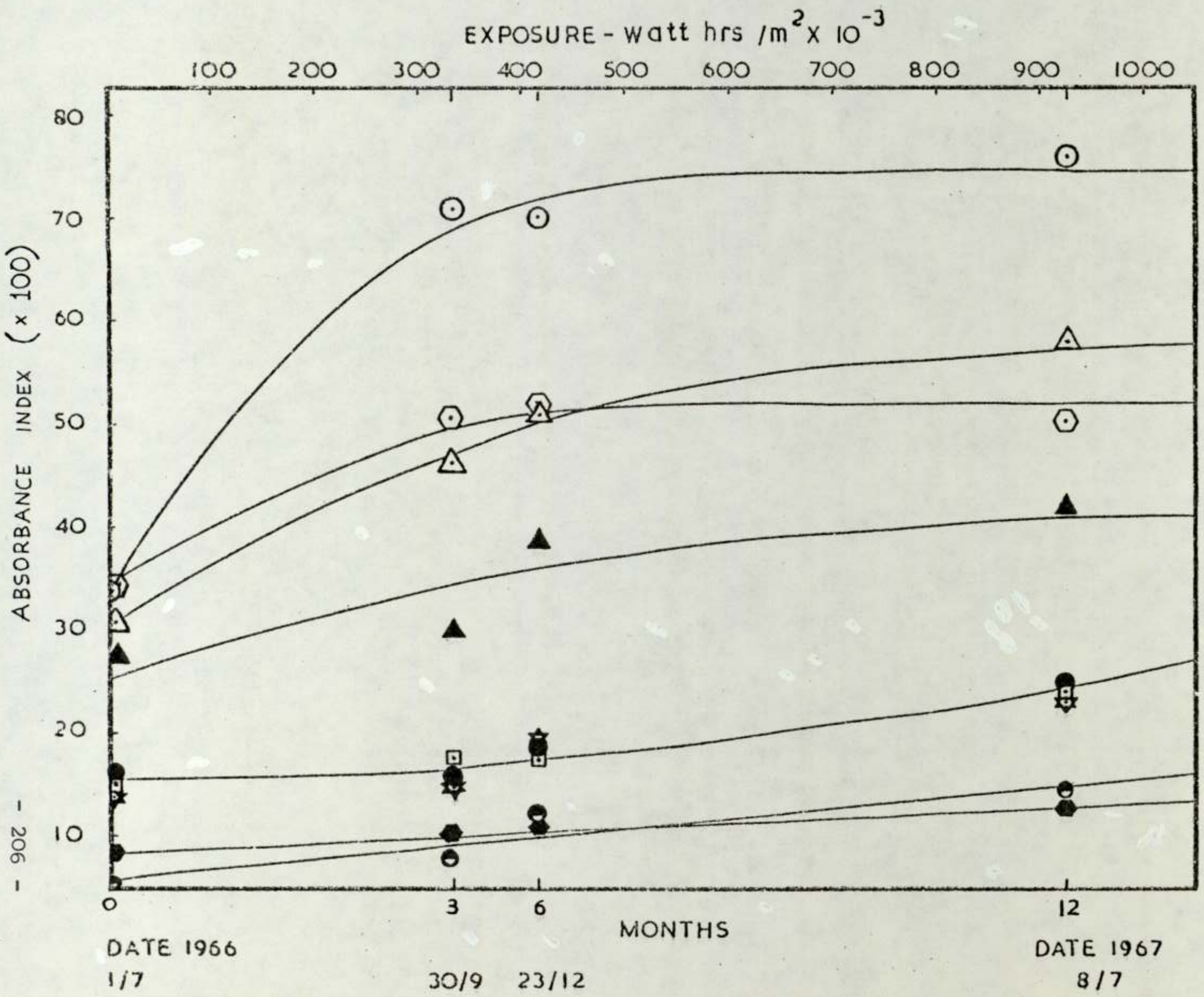


FIGURE 37 - Natural Weathering of the PHTHALIC ALKYD gloss finish; dependence of infrared peak absorbance indices on exposure:-

⊙ = index of C–O at 1070 cm^{-1}

△ = index of C–O at 1118 cm^{-1}

⬡ = index of C–O at 1255 cm^{-1}

▲ = index of C–H at2920 cm^{-1}

⊡ = index of the peak at 1600 cm^{-1}

● = index of the peak at 1650 cm^{-1}

✡ = index of C–H at 1460 cm^{-1}

⬢ = index of C–H at 1380 cm^{-1}

◓ = index of O–H at 3450 cm^{-1}

relative to the carbonyl (C = O) stretching peak at 1720 $cm.^{-1}$

aromatic ring (C = C) stretching peak (1600 cm.$^{-1}$) index increases with exposure, the aromaticity of the coating's surface structure must also be doing so accordingly, the common upward trends shown in Figure 37 are taken as being rather more indicative of the fact that the reference carbonyl (1720 cm.$^{-1}$) absorbance itself must conversely be decreasing on ageing. This view is subsequently supported by the combined results of Figures 38 and 39 which arise from relating the various peak absorbances to that of the C - H stretching peak at 2920 cm.$^{-1}$. The fact that those spectral peaks whose absorbances would not be expected to change significantly on weathering (e.g., those at 1600 and 1380 cm.$^{-1}$ (see Table 7)) are now seen to remain constant throughout exposure (Figure 38), suggests that the 2920 cm.$^{-1}$ peak is, indeed, a more reliable reference peak. Hence, it now appears from Figures 38 and 39 that the most diagnostic peaks, as far as weathering is concerned, are those associated with the various C - O, C = O, and O - H stretching vibrations at 1070, 1118, (1255), 1720 and 3450 cm.$^{-1}$, each of which displays significant changes on exposure. Certainly among the most interesting of these changes are the parallel increases which occur, particularly during the summer months, in the O - H (3450 cm.$^{-1}$) and C - OH (1070 cm.$^{-1}$) stretching peaks in Figures 38 and 39 respectively. This would seem to suggest that oxidation and/or hydrolysis of the binder is taking place during the time of the year when radiation is at its most intense and, very likely, its most potent in combination with air and/or moisture. Meanwhile, the less interpretive initial increase in the 1118 cm.$^{-1}$ peak index (C - O stretching of - O - CH_2 -), together with its subsequent slow terminal decay towards the end of the exposure (Figure 38), can tentatively be ascribed to a further uptake of oxygen by the coating on initial exposure by reaction with its linseed oil modification, only to be followed later on by the relatively slow

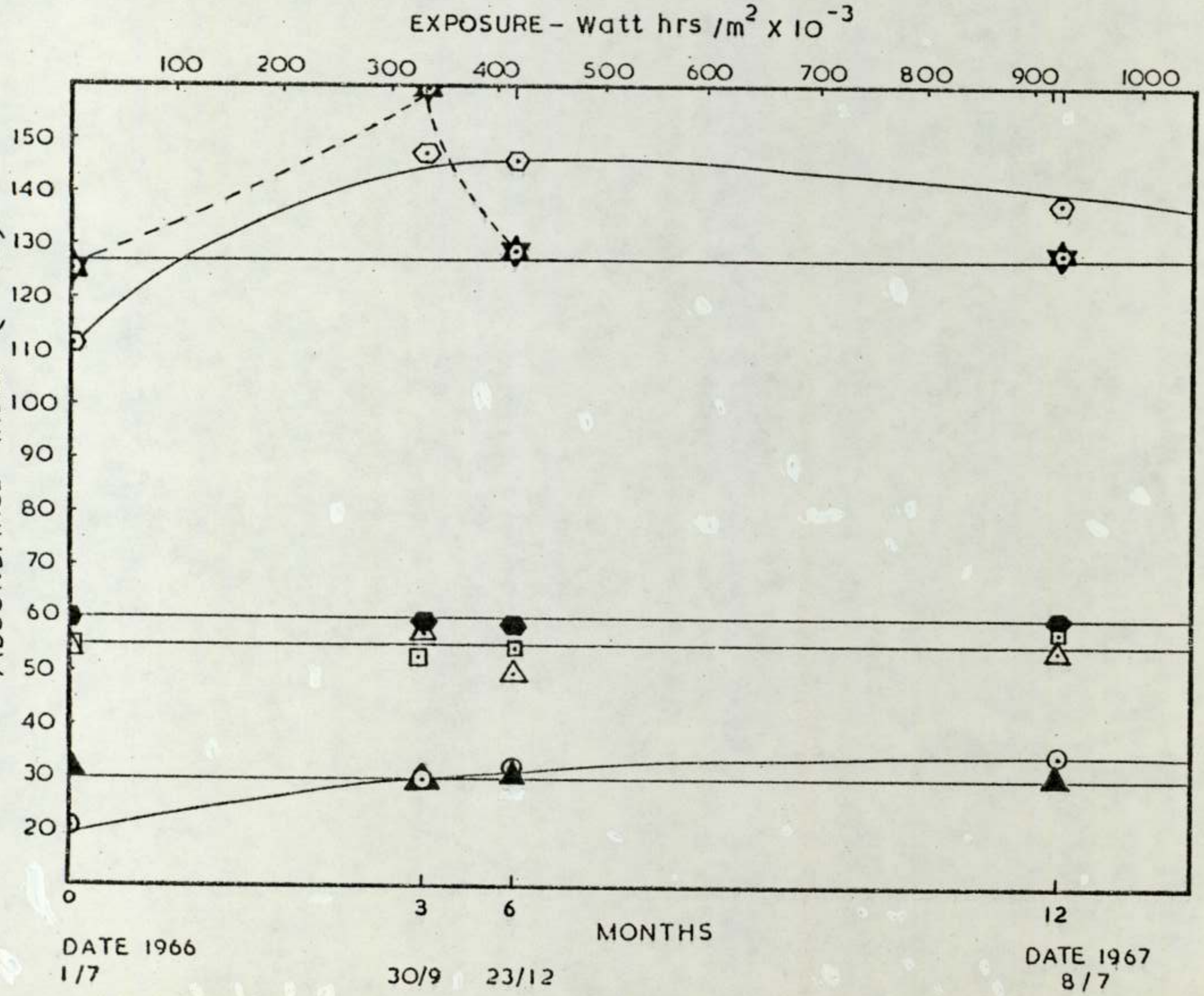


FIGURE 38 -
Natural weathering of the PHTHALIC ALKYD gloss finish; dependence of infrared peak absorbance indices on exposure:-

⬡ = index of C–O at 1118 cm^{-1}
✡ = index of C–O at 1255 cm^{-1}
⬢ = index of the peak at 1650 cm^{-1}
⊡ = index of the peak at 1600 cm^{-1}
△ = index of the C–H at 1460 cm^{-1}
⊙ = index of O–H at 3450 cm^{-1}
▲ = index of C–H at 1380 cm^{-1}

relative to the methylenic (C - H) stretching peak at 2920 cm.$^{-1}$

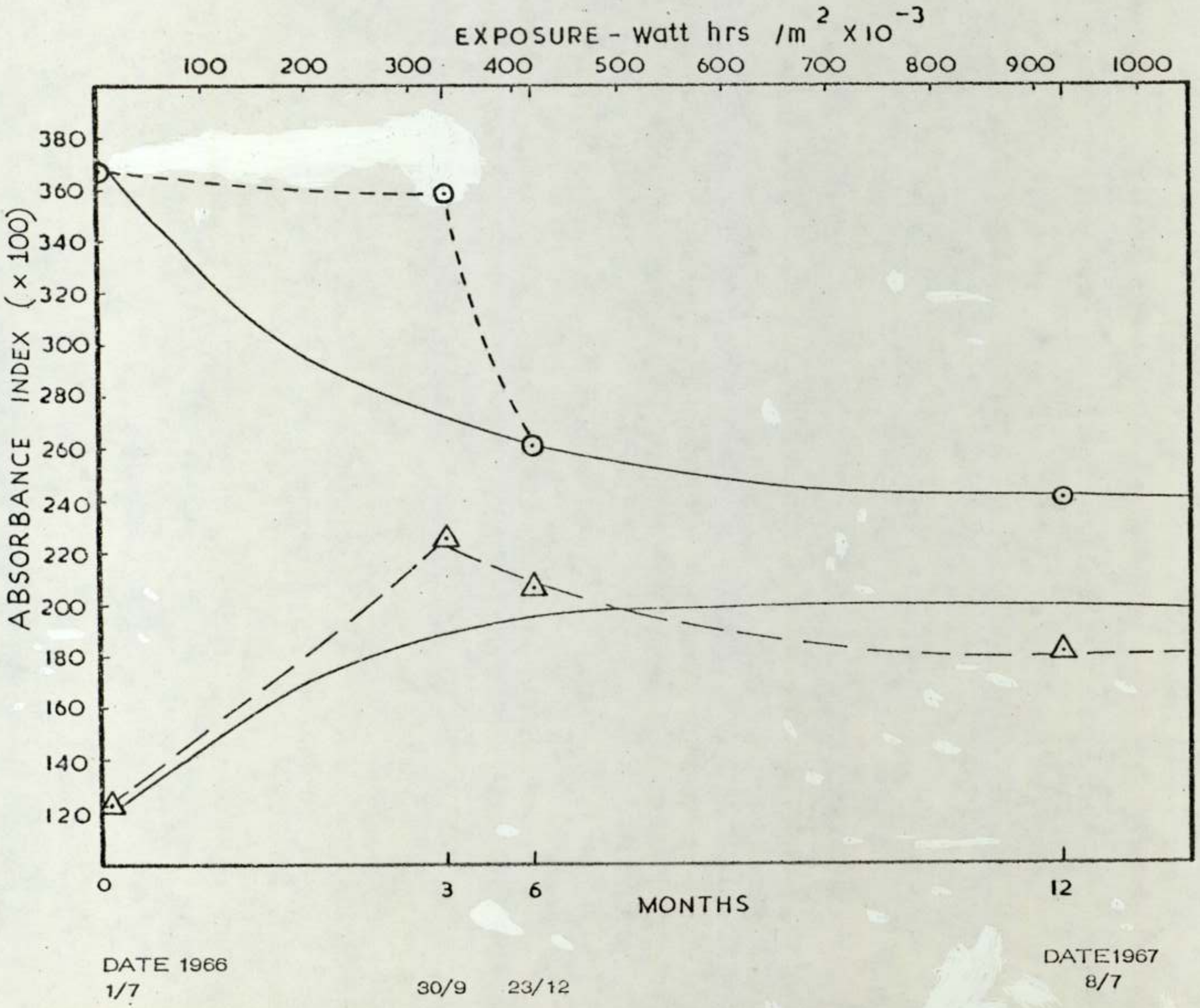


FIGURE 39 -
Natural weathering of the
PHTHALIC ALKYD gloss finish;

⊙ = index of the carbonyl C=O at 1720 cm^{-1}

△ = index of C–O at 1070 cm^{-1}

dependence of infrared peak absorbance indices on exposure, relative to the methylenic (C - H) stretching peak at 2920 cm.$^{-1}$

breakdown in part of this oxygenated network into volatile products. Indeed, it is this type of volatilisation/leaching of low molecular weight pre-exposure air-drying products, as well as any initially formed post-exposure hydrolysis products that could, conjecturably, account for the initial carbonyl (1720 cm.^{-1}) index decrease on weathering (Figure 39). Whilst these latter submissions are by no means conclusive, they must be considered on the basis of the limited evidence available.

Finally, even allowing for some degree of completive air-drying taking place in this alkyd coating during the initial stages of its weathering (i.e., after its 72 hour pre-exposure drying period), its likely effect on the paint's reflectance properties could not reasonably be expected to account for the unexpected increase in specular reflectance (Figure 32(a)) and, hence, gloss factor (Figure 33(a)) previously observed goniophotometrically after the first three months' exposure. Indeed, in view of the apparent spuriousness of some of the three months' MIR results (see dotted lines in Figures 38 and 39), the possibility must be considered here that certain anomalies may exist amongst the early weathering data. However, although these anomalies defy explanation from the limited evidence presented here, the corresponding artificial weathering results in the following section may hopefully go some way towards clarifying this situation somewhat.

Moving on now to the second of the three gloss finish coatings studied by the MIR technique, the polyurethane alkyd exhibits in its infrared spectrum (Figure 40) the various peaks detailed in Table 8 overleaf.

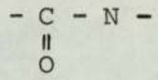
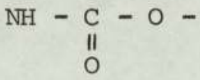
Frequency (cm.$^{-1}$)	Corresponding bond vibration
3470 (broad)	O - H (alcoholic) stretching, with adjacent N - H stretching
3200	O - H (carboxylic) stretching
2920	C - H stretching (aliphatic)
1718	C = O stretching (esteric)
1687	C = O stretching in  $- \underset{\overset{\Vert}{O}}{C} - N -$ (Amide I band)
1600	C = C stretching (aromatic)
1528	N - H bending, in combination with C - N stretching (Amide II band)
1457	$-CH_2-$ bending (methylenic)
1220 (broad)	C - O stretching in  $- NH - \underset{\overset{\Vert}{O}}{C} - O -$
1073	C - O stretching (alcoholic) in - C - OH

TABLE 8

INFRARED SPECTRAL DATA RELATING TO THE POLYURETHANE ALKYD COATING

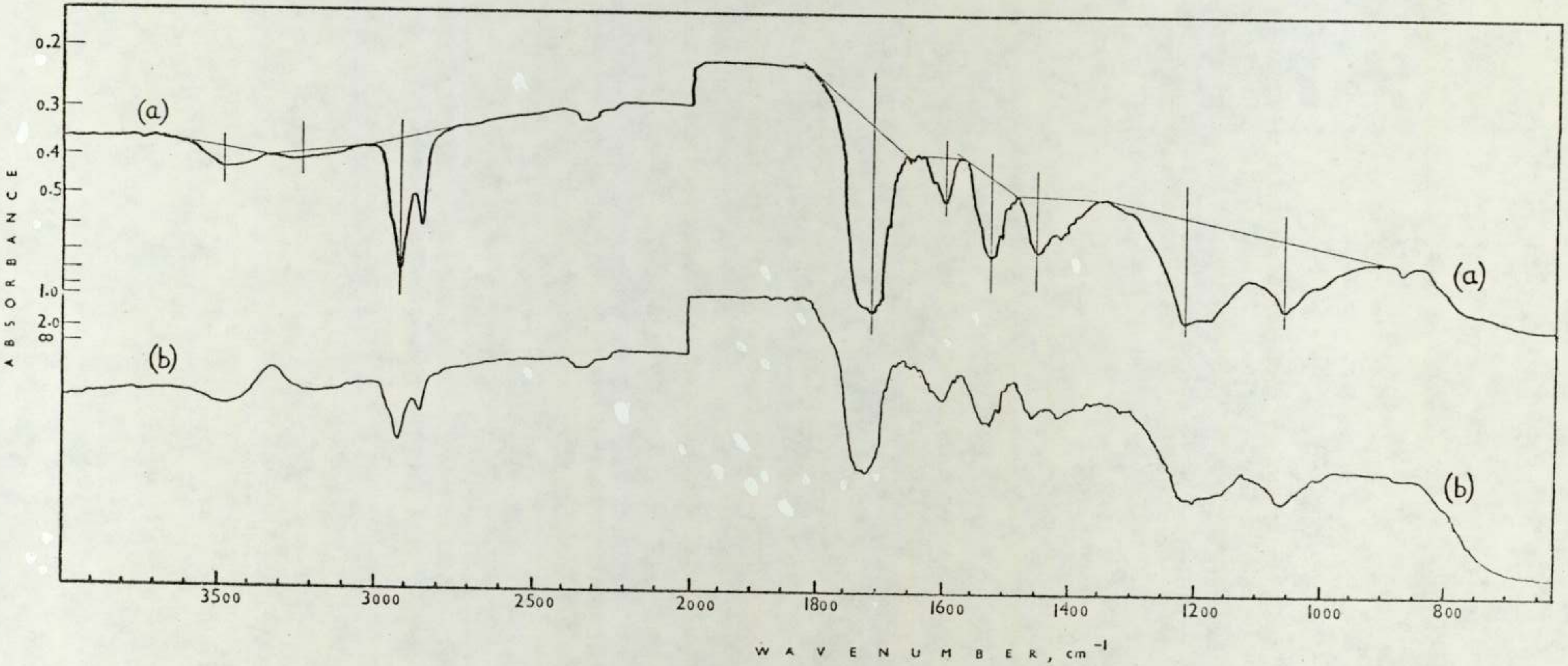


FIGURE 40 - MIR spectra of the POLYURETHANE ALKYD gloss finish coating
(a) before, and (b) after 12 months natural weathering.

On relating the absorbances of the above peaks to, firstly, the 2920 cm.$^{-1}$ methylene peak (Figure 41) and, secondly, the 1718 cm.$^{-1}$ carbonyl peak (Figure 42), similar weathering trends were observed in each case with, again, certain of the related peaks exhibiting significant changes during exposure. Additionally, and in contrast to the previous phthalic alkyd study, the two reference peaks (2920 and 1718 cm.$^{-1}$) were found to remain fairly constant relative to each other and were thus considered to be equally suitable for referencing purposes.

As regards the various weathering changes indicated by the results in Figures 41 and 42, undoubtedly the most notable one is that associated with the urethane C - O stretching peak at 1220 cm.$^{-1}$. The relatively rapid decrease in the absorbance of this peak during the summer and autumn months is seen to be followed by a partial recovery throughout the winter and spring. This seemingly cyclic trend is reflective, in the first part, of the progressive dismission of urethane C - O linkages, either by direct hydrolytic attack, together with concomitant decarboxylation, at these points in the polymer chain, or by the possible cleavage of adjacent bonds by alternative (e.g., photooxidative) means. This suggestion of hydrolysis, in particular, receives valuable support from the observed increases in the absorbance indices of the alcoholic O - H and/or N - H (3470 cm.$^{-1}$) and, to a slightly lesser degree, the carboxylic O - H (3200 cm.$^{-1}$) and alcoholic C - O (1073 cm.$^{-1}$) stretching vibrations (Figure 41) during this initial period of apparent degradation. However, whilst the appearance/disappearance of hydrolysed/hydrolysable groups can be readily accounted for, the reason for the incremental rise in the aromatic peak (1600 cm.$^{-1}$) index is less obvious at this stage.

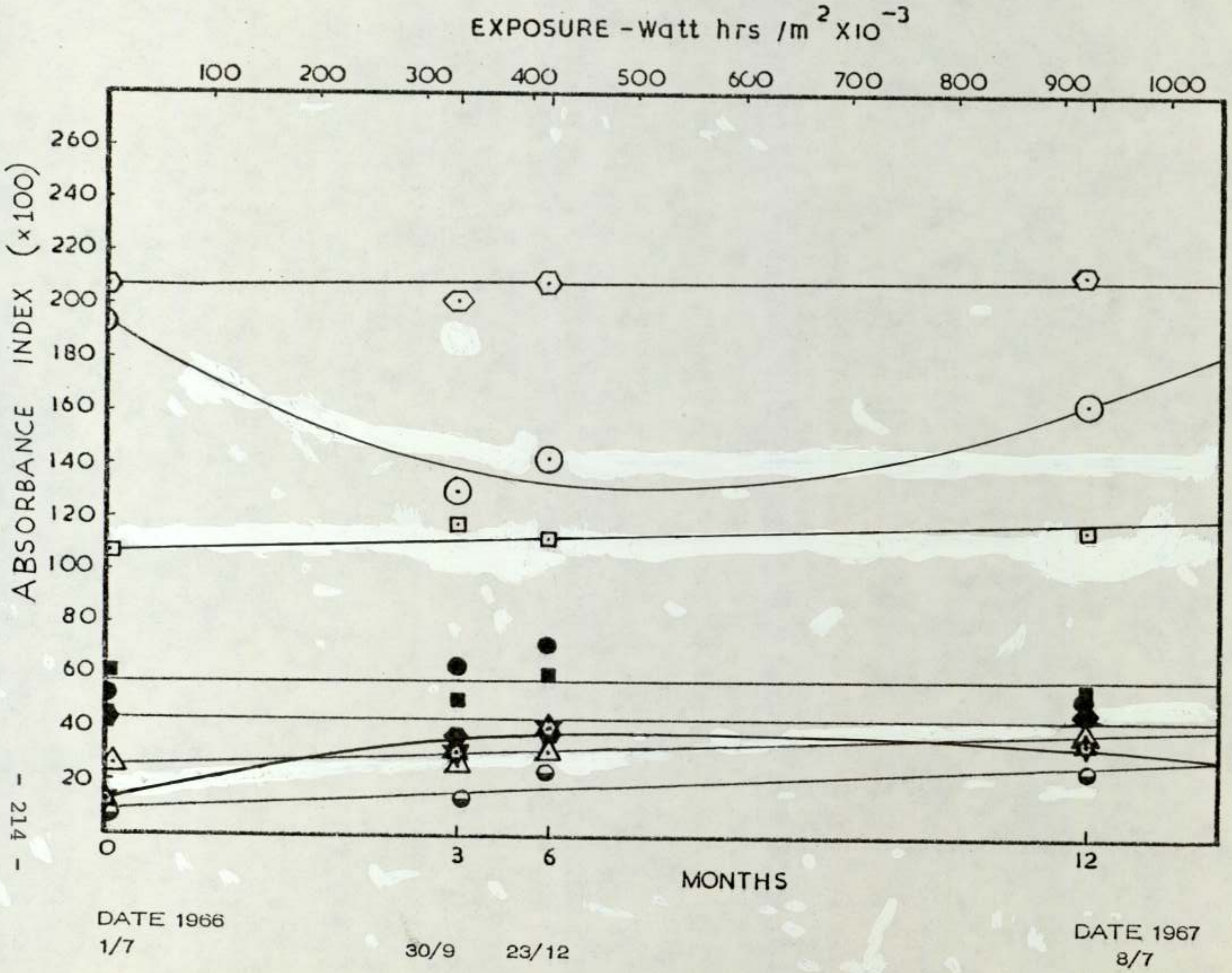


FIGURE 41 - Natural weathering of the POLYURETHANE ALKYD gloss finish; dependence of infrared peak absorbance indices on exposure, relative to the methylenic (C - H) stretching peak at 2920 cm.$^{-1}$

⬡ = index of the carbonyl C=O group at 1718 cm^{-1}

⊙ = index of C–O at 1220 cm^{-1}

⊡ = index of C–O at 1073 cm^{-1}

● = index of amide I at 1687 cm^{-1}

■ = index of amide II at 1528 cm^{-1}

⬢ = index of C–H at 1457 cm^{-1}

△ = index of the peak at 1600 cm^{-1}

✡ = index of O–H or N–H at 3470 cm^{-1}

◒ = index of the carboxylic OH at 3200 cm^{-1}

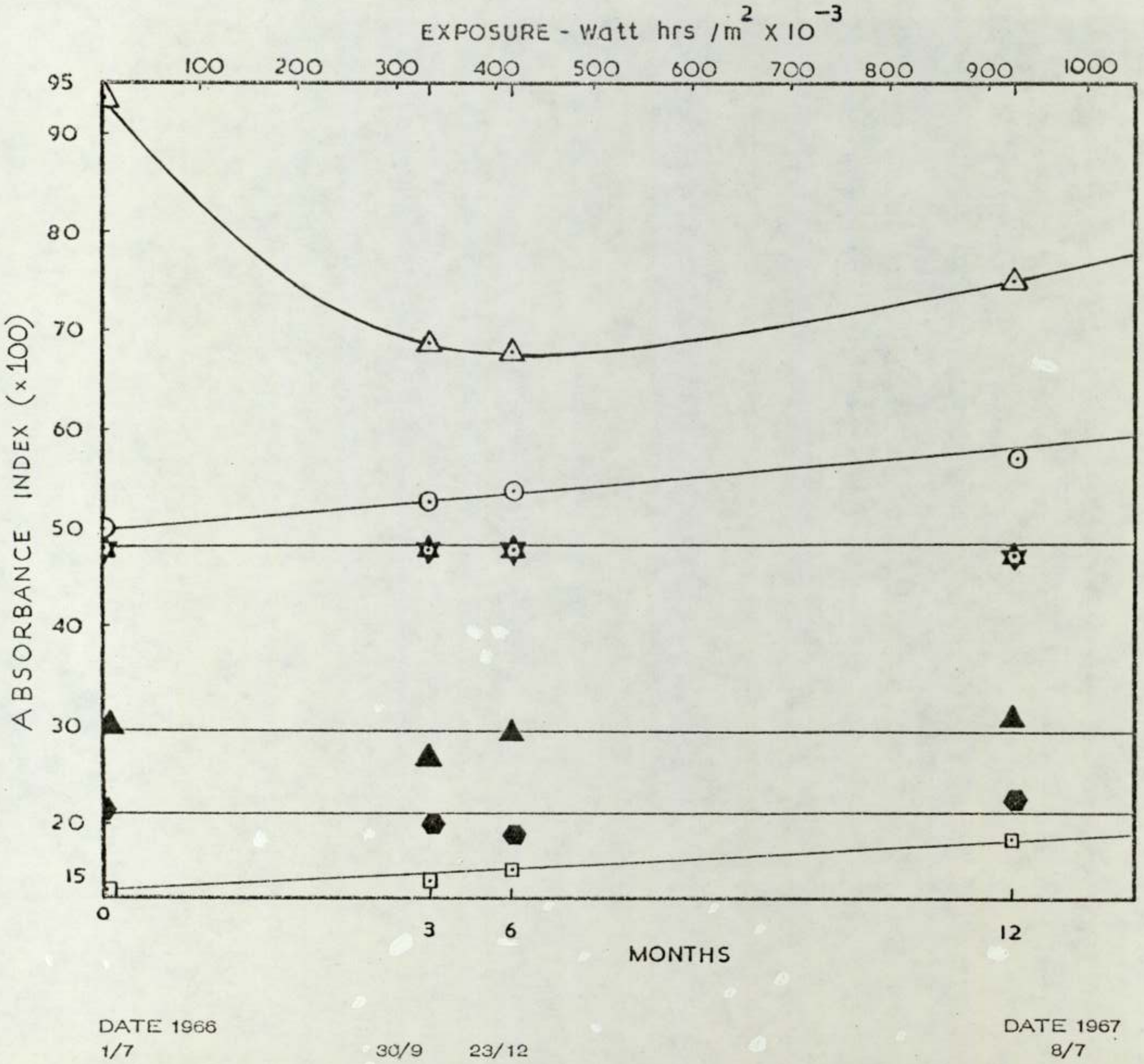


FIGURE 42 -

Natural weathering of the POLYURETHANE ALKYD gloss finish; dependence of infrared peak absorbance indices on exposure:-

△ = index of C-O at 1220 cm^{-1}

⊙ = index of C-O at 1073 cm^{-1}

✡ = index of C-H at 2920 cm^{-1}

▲ = index of amide I at 1687 cm^{-1} and of amide II at 1528 cm^{-1}

⬢ = index of C-H at 1457 cm^{-1}

⊡ = index of the peak at 1600 cm^{-1}

relative to the carbonyl (C = O) stretching peak at 1718 $cm.^{-1}$

Finally, the apparent reversal, during the latter half of the exposure, of the most notable of the changes described here can be attributed to the exposure/removal of fresh/degraded areas of the coating surface as a result of the increasing effects of physical erosion during the winter and spring competing with, and eventually outweighing, the decreased rate of chemical breakdown.

In conclusion of this section on infrared analysis, we now come to the last of the three gloss finish coatings studied by the MIRS technique, namely the epoxy/polyamine. The MIR spectra obtained for this coating (Figure 43), both before and after ageing, were generally found to be of somewhat poorer quality than those of the two previous paints (Figures 36 and 40). Nevertheless, it was still possible to calculate absorbance indices for the various peaks in the spectrum (as detailed in Table 9), although, as spectral definition deteriorated on weathering (Figure 43(b)), it became increasingly doubtful in one or two cases as to whether the accuracy of the measured changes was sufficient to justify them being discussed on a semi-quantitative basis.

On relating weathering changes to the methylenic C - H stretching vibration (2920 cm.$^{-1}$) as reference peak, almost all of the peak indices increased on exposure (Figure 44). The improbability that this could be genuinely representative of a surface improvement, bearing in mind, of course, the surface's steadily decreasing reflectivity (Figures 32(b) and 33(b)) during this period, suggests, therefore, that the 2920 cm.$^{-1}$ reference peak is itself decreasing, possibly due to some degree of volatilisation and/or leaching of low molecular weight methylenic residues from the paint system during exposure.

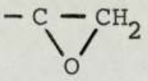
Frequency (cm.$^{-1}$)	Corresponding bond vibration
2920	C - H stretching (aliphatic)
1648	N - H bending (polyamine)
1606 1507	C = C stretching (aromatic ring)
1458	$-CH_2-$ bending (methylenic)
1380 1360	$-CH_3$ bending (gem - dimethyl group of the bisphenol—A)
1238	C - O stretching (aromatic, i.e., phenyl-oxygen)
1180	C - H in-plane bending (aromatic)
1105	C - O stretching in $-CH_2-O-CH_2-$
1037	C - O stretching (aliphatic) in $-CH_2-O-$phenyl
945	C - O stretching in the terminal  (unreacted) epoxy group
828	C - H out-of-plane bending of the two adjacent hydrogens on the para-disubstituted aromatic ring

TABLE 9

INFRARED SPECTRAL DATA RELATING TO THE EPOXY/POLYAMINE COATING

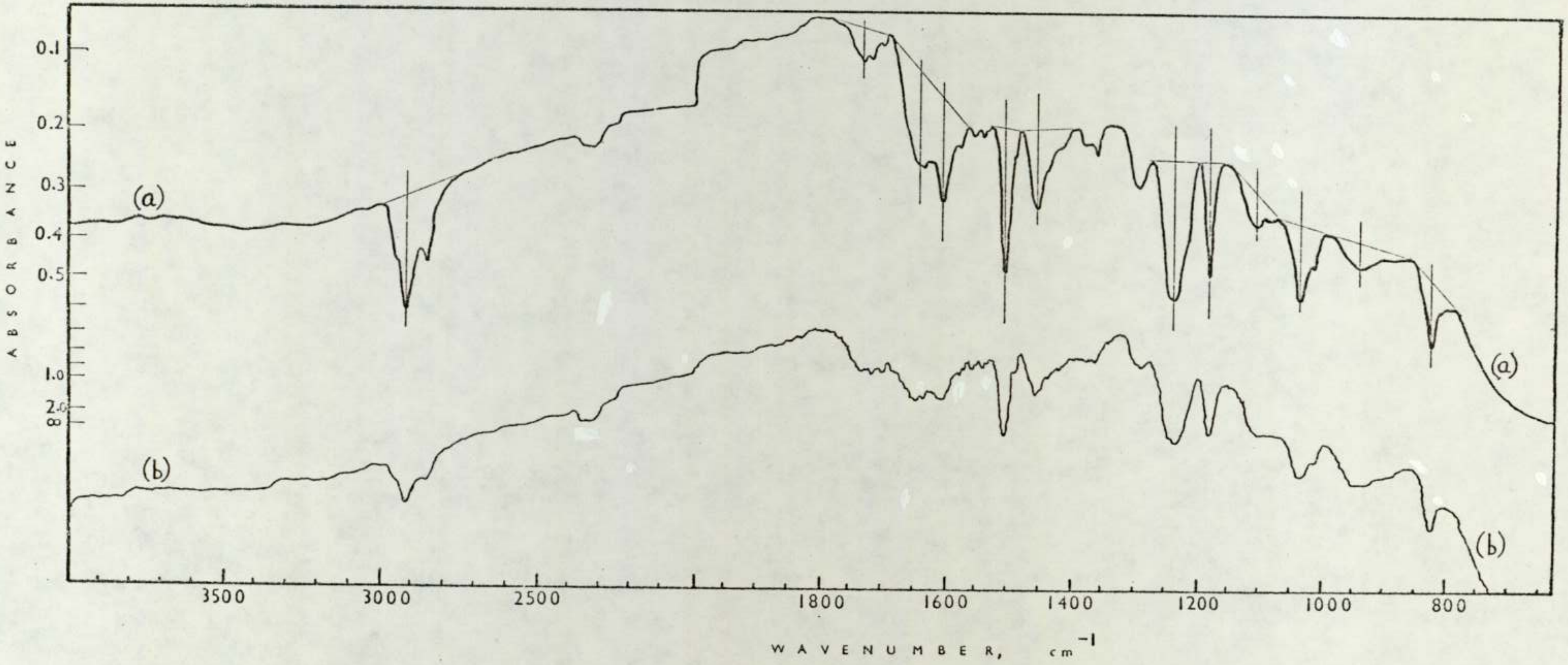


FIGURE 43 - MIR spectra of the EPOXY/POLYAMINE gloss finish coating
(a) before, and (b) after 12 months natural weathering.

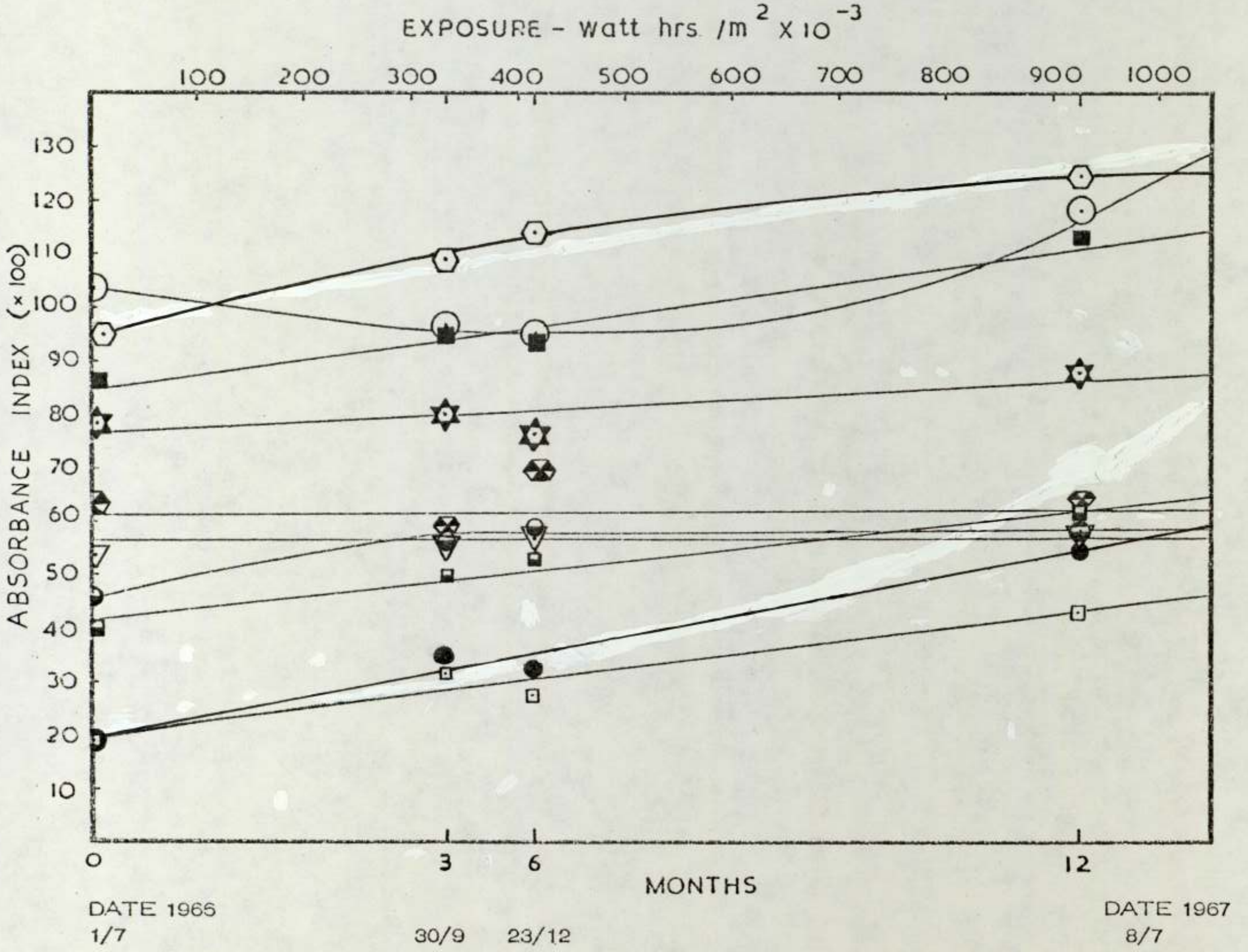


FIGURE 44 - Natural weathering of the EPOXY/POLYAMINE gloss finish; dependence of infrared peak absorbance indices on exposure, relative to the methylenic (C - H) stretching peak at 2920 cm.$^{-1}$

⬡ = index of the aromatic peak at 1507 cm^{-1}

⊙ = index of the C–O of the aromatic ether at 1238 cm^{-1}

■ = index of the para-substituted benzene ring at 828 cm^{-1}

✡ = index of the peak at 1180 cm^{-1}

⬢ = index of the C–O of the aliphatic ether at 1037 cm^{-1}

▽ = index of the aromatic peak at 1606 cm^{-1}

◒ = index of the peak at 1648 cm^{-1}

⬓ = index of the peak at 1458 cm^{-1}

● = index of the peak at 945 cm^{-1}

⊡ = index of the peak at 1105 cm^{-1}

Hence, it was considered that a more reliably stable reference peak for this particular coating would be more likely to come from one of the aromatic vibrations. This was, in fact, found to be the case on indexing the peaks relative to that at 1507 $cm.^{-1}$ (Figure 45), the sharpest and most intense of the aromatic bands. However, of the changes which appear in Figure 45, it is only really those associated with the more intense 1238 and 2920 $cm.^{-1}$ bands that can be relied upon with any degree of assurance as being genuinely more descriptive of the deteriorating coating surface than of the consequential deterioration in spectral quality. The apparent periodicity of the change in the 1238 $cm.^{-1}$ peak index, which can be likened to that seen previously in the 1220 $cm.^{-1}$ peak of the polyurethane alkyd (Figures 41 and 42), indicates that the phenyl-oxygen bond is the main point of attack in the epoxy/polyamine coating's polymer structure during its chemically deteriorative summer and autumn exposure. Then, as the balance of weathering factors tilts in greater favour of its more physically erosive elements during the winter and spring, it can be envisaged how the coating surface's uppermost degraded layer may become, to some extent, eroded away, thus revealing, as it were, "fresh" areas of surface. This is then sensed by this type of infrared spectroscopic analysis as an increase in what was a previously decreasing peak absorbance index on exposure as seen here.

Thus, having looked at the natural weathering of these various commercial surface coatings, in turn through the particular information which each of the analytical methods used provides, let us now turn our attention to the corresponding artificial weathering study of these materials, again using the same combination of techniques, and also to

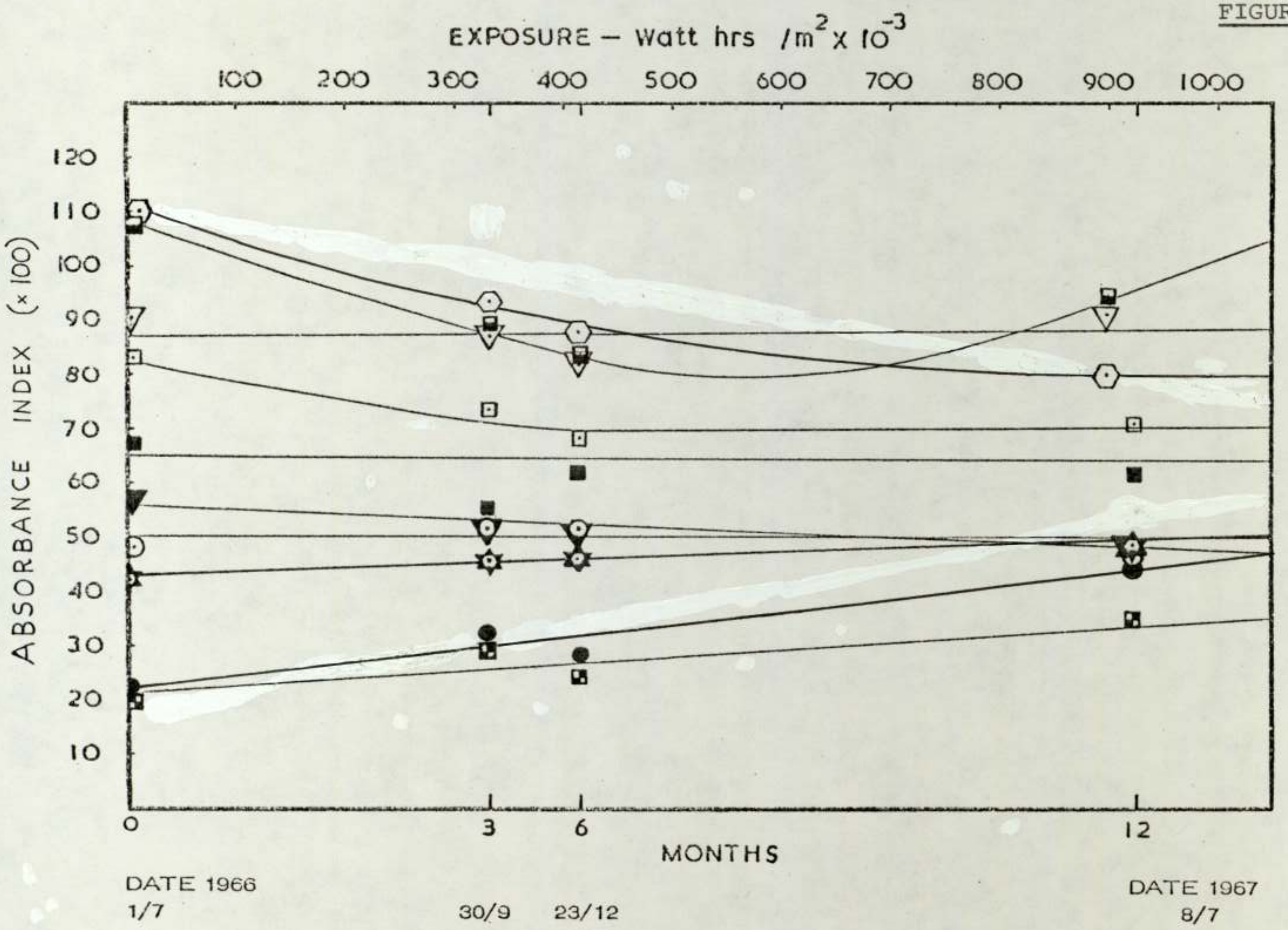


FIGURE 45 - Natural weathering of the EPOXY/POLYAMINE gloss finish; dependence of infrared peak absorbance indices on exposure, relative to the aromatic ring (C = C) stretching peak at 1507 cm.$^{-1}$

the correlativity of the two sets of ageing results.

IV.3 Artificial Weathering

The artificial weathering of the coatings previously described was conducted in a BS 3900 Part F3 artificial weathering apparatus (see section II.3.2.1) for upwards of 4000 hours. Purely and simply on an energy of exposure basis, 4000 hours artificial weathering by this method subjects test samples to a total amount of energy of radiation roughly equivalent to that received on average over a period of two years natural weathering in the U.K., as measured at the Building Research Station site.

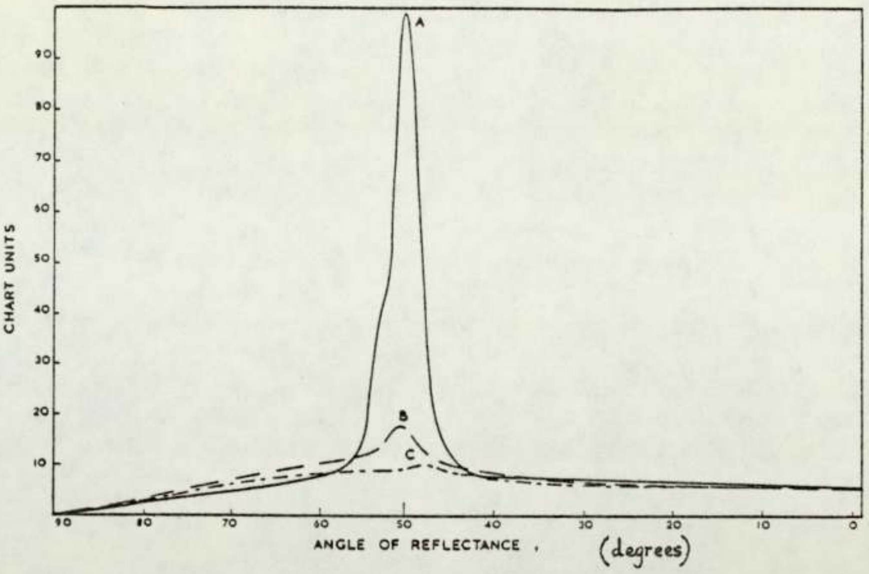
Finally, the results presented in this section also appear in a supporting publication(240) to this thesis (see inside back cover).

IV.3.1 Goniophotometry

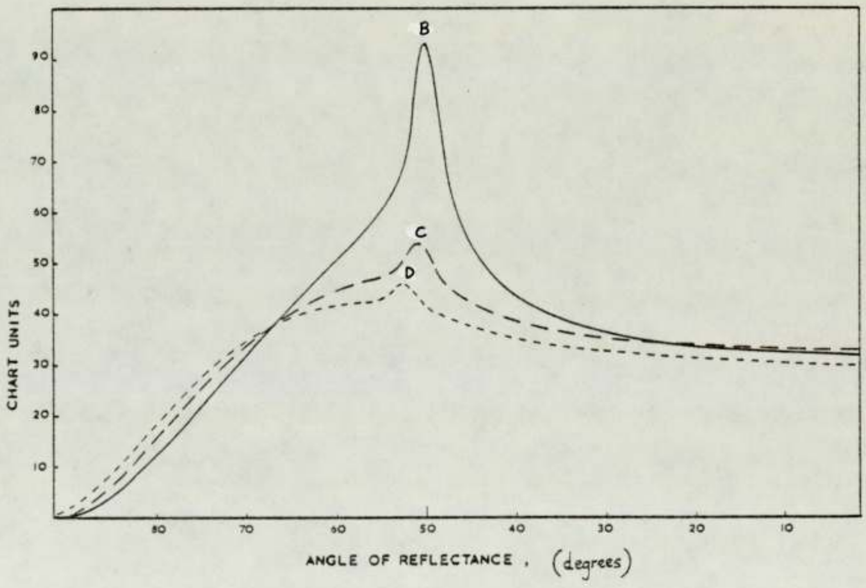
Goniophotometric studies during this part of the work were conducted using the automated instrument and employing "wide beam" monochromatic blue light (436 nm.) illumination at angles of incidence which were intended as being 45^o and 60^o, so as to correspond with the previous natural weathering results. However, when these angles were determined accurately for the 45^o and 60^o positions as marked on the re-designed specimen mount (see Figure 18 previously), they were actually found to be 49.3^o and 64.3^o respectively. Hence, for the sake of simplicity, they will subsequently be referred to in the following text as 50^o and 65^o angles of incidence.

In common with the previous natural weathering results, artificial weathering also induced significant changes in the reflectance properties of each of the five commercial coatings systems studied. Of these coatings, undoubtedly the most drastic change was observed in the case of the epoxy/polyamine gloss finish, as can be gauged from its goniophotometric curves shown in Figure 46. The magnitude of the reflectance change taking place between 600 and 900 watt hours/m.^{2} exposure is strikingly depicted in Figure 46(a), whilst Figure 46(b) serves to illustrate the wide ranging versatility of the goniophotometer, by virture of its variable incident light transmittance facility, in being able to re-record curves such as B and C in Figure 46(a), to maximum effect as in Figure 46(b). Similarly, reflectance curves for the semi-gloss chlorinated rubber coating are given in Figure 47 which also depict marked changes brought about by this type of artificial weathering, even in a case such as this where the paint surface is, to some extent, roughened to start with.

When we come to consider the individual goniophotometric parameters, it is clear that the main reasons for the various gloss factor (= peak height ÷ peak width at half-height) changes, shown in Figure 48 on a logarithmic scale for collective comparison, are corresponding changes in the respective goniophotometric peak heights (Figure 49) rather than in the peak widths (Figure 50). This is certainly true throughout the entire exposure period for the phthalic and polyurethane alkyd gloss finish coatings (A and B in Figures 48 - 50) and is indicative of the fact that the micro-irregularities formed in the surfaces of these two paints have not yet attained a macro-size order, in excess of the 436 nm. incident light wavelength, whereby they become capable of effecting an angular divergence of the specular beam.



46(a)



46(b)

FIGURE 46 - Goniophotometric curves: artificial weathering of EPOXY/POLYAMINE gloss finish coating;

Exposure: A = 600 x 10^3 watt hrs./m^2,
B = 900 x 10^3 watt hrs./m^2,
C = 1250 x 10^3 watt hrs./m^2,
D = 2050 x 10^3 watt hrs./m^2;

Curves recorded at an incident light transmittance of (a) 2.88%, and (b) 25.5%.

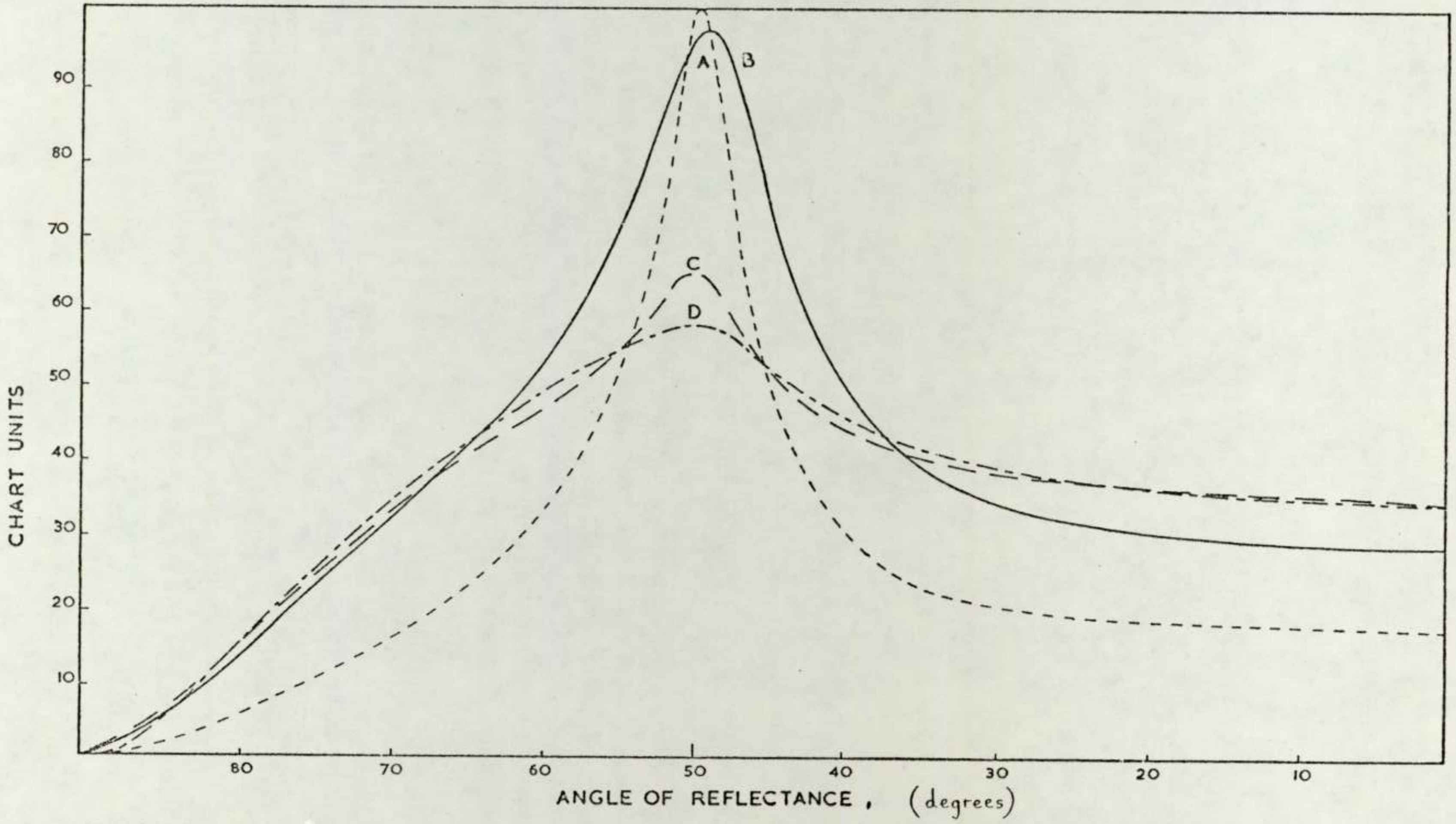


FIGURE 47 - Goniophotometric curves; angle of incidence = 50°;

Artificial weathering of THIXOTROPIC CHLORINATED RUBBER semi-gloss coating;

Exposure: (A) = 0, (B) = 230, (C) = 600, and (D) = 1250, x 10^3 watt hrs./m^2;

Transmittance: for (A) = 12.7%, and for (B), (C) and (D) = 25.5%.

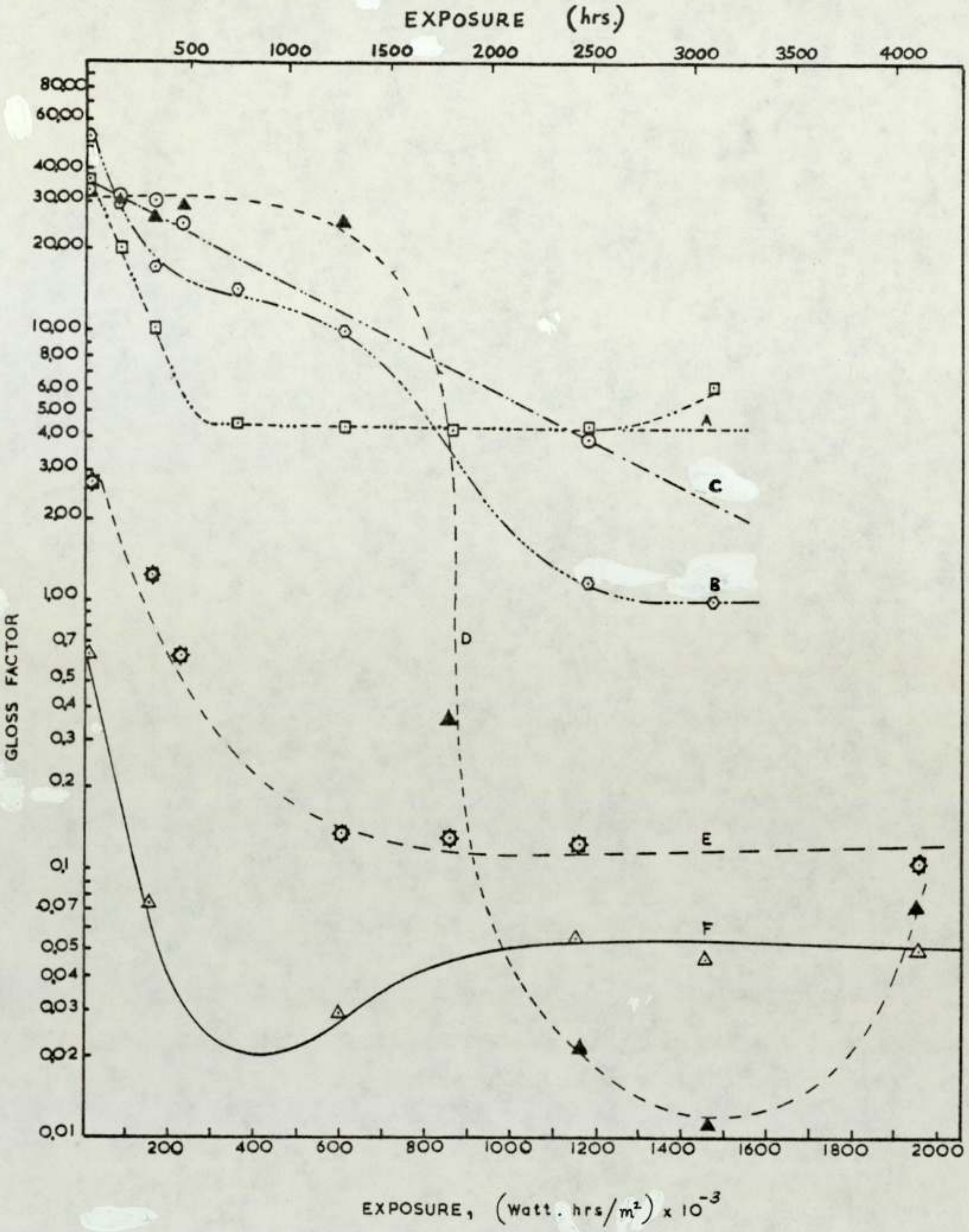


FIGURE 48 - Variation in log "50°-gloss factor" on exposure; artificial weathering of:-

A : phthalic alkyd - gloss finish,
B : polyurethane alkyd - gloss finish,
C : vinyl toluene alkyd - gloss finish,
D : epoxy/polyamine - gloss finish,
E : chlorinated rubber - semi-gloss finish,
cf. (F : PVC organosol - matt finish).

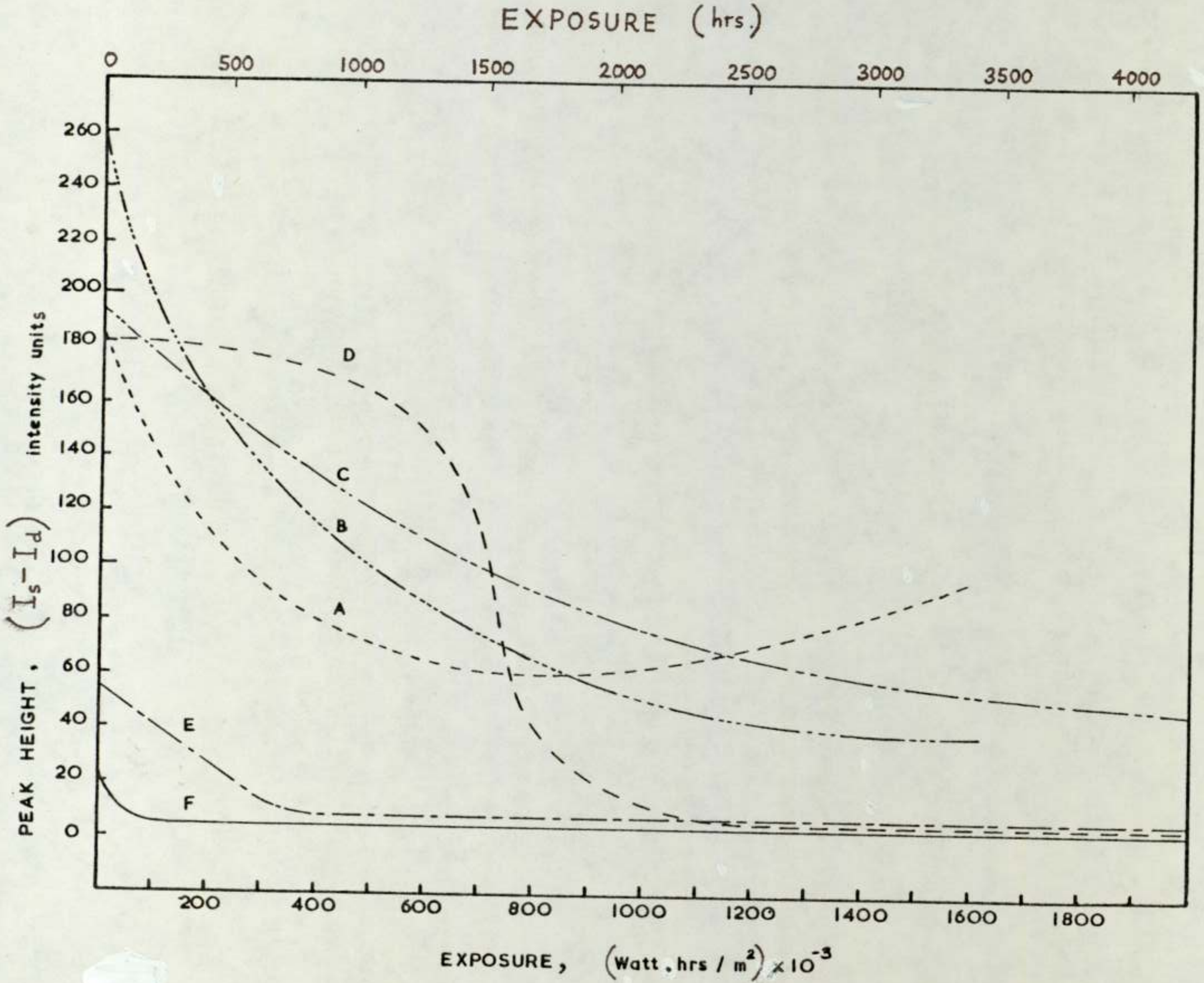


FIGURE 49 -

Variation in peak height $(I_s - I_d)$ on exposure; angle of incidence = 65°; artificial weathering of:-

A : phthalic alkyd

B : polyurethane alkyd

C : vinyl toluene alkyd

D : epoxy/polyamine

E : chlorinated rubber

(F : PVC organosol)

surface coatings.

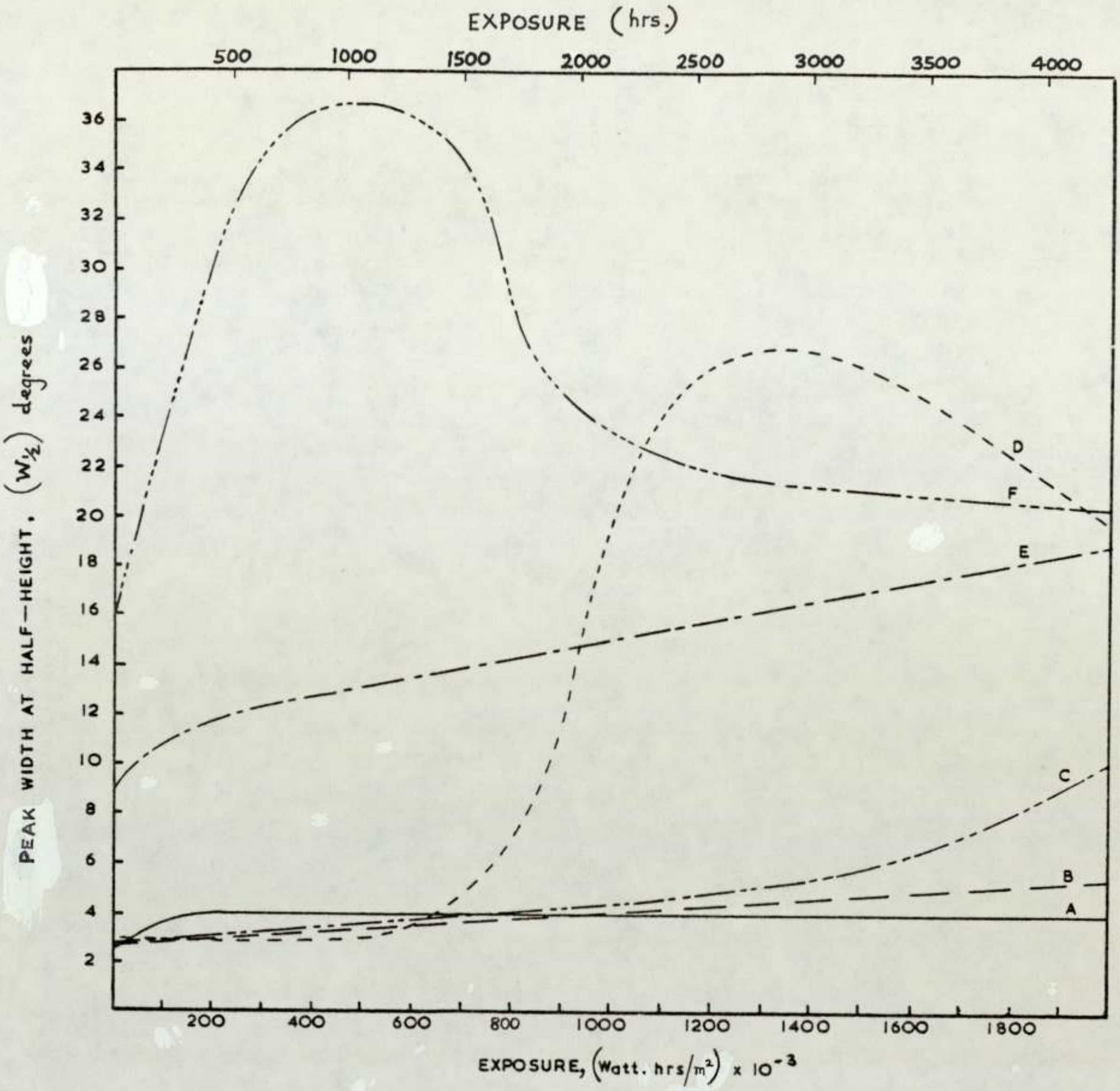


FIGURE 50 - Variation in peak width at half-height ($W_{\frac{1}{2}}$) on exposure; angle of incidence = 65°; artificial weathering of:-

A : phthalic alkyd

B : polyurethane alkyd

C : vinyl toluene alkyd

D : epoxy/polyamine

E : chlorinated rubber

cf. (F : PVC organosol)

However, this latter size "graduation", as it were, is, in fact, just on the verge of being observed for the vinyl toluene alkyd during the terminal stages of its exposure (Figure 50), but the most striking example of this transition is obviously seen with the epoxy/polyamine half way through the exposure period. Indeed, the exceptional magnitude and suddenness of this latter change will clearly need to be considered in more detail in the following "Discussion" section. It is also interesting to note and understand from Figure 50 the contrasting trends between the gloss, semi-gloss and, additionally included for comparison, a matt finish PVC coating. Whereas the glossy paints are able to show fairly clearly the onset of the macro-size transition as $W_{\frac{1}{2}}$ starts to increase, the semi-gloss chlorinated rubber coating exhibits a gradual increase from the very beginning of exposure due, of course, to the fact that its surface contains a certain amount of macro- and near-macro irregularities initially. The matt finish PVC organosol, meanwhile, displays an even more pronounced $W_{\frac{1}{2}}$ increase from the outset of exposure and, furthermore, is able to show how, after a maximum $W_{\frac{1}{2}}$ value is reached, $W_{\frac{1}{2}}$ can subsequently decline as erosion of the macro-profile appears to take place.

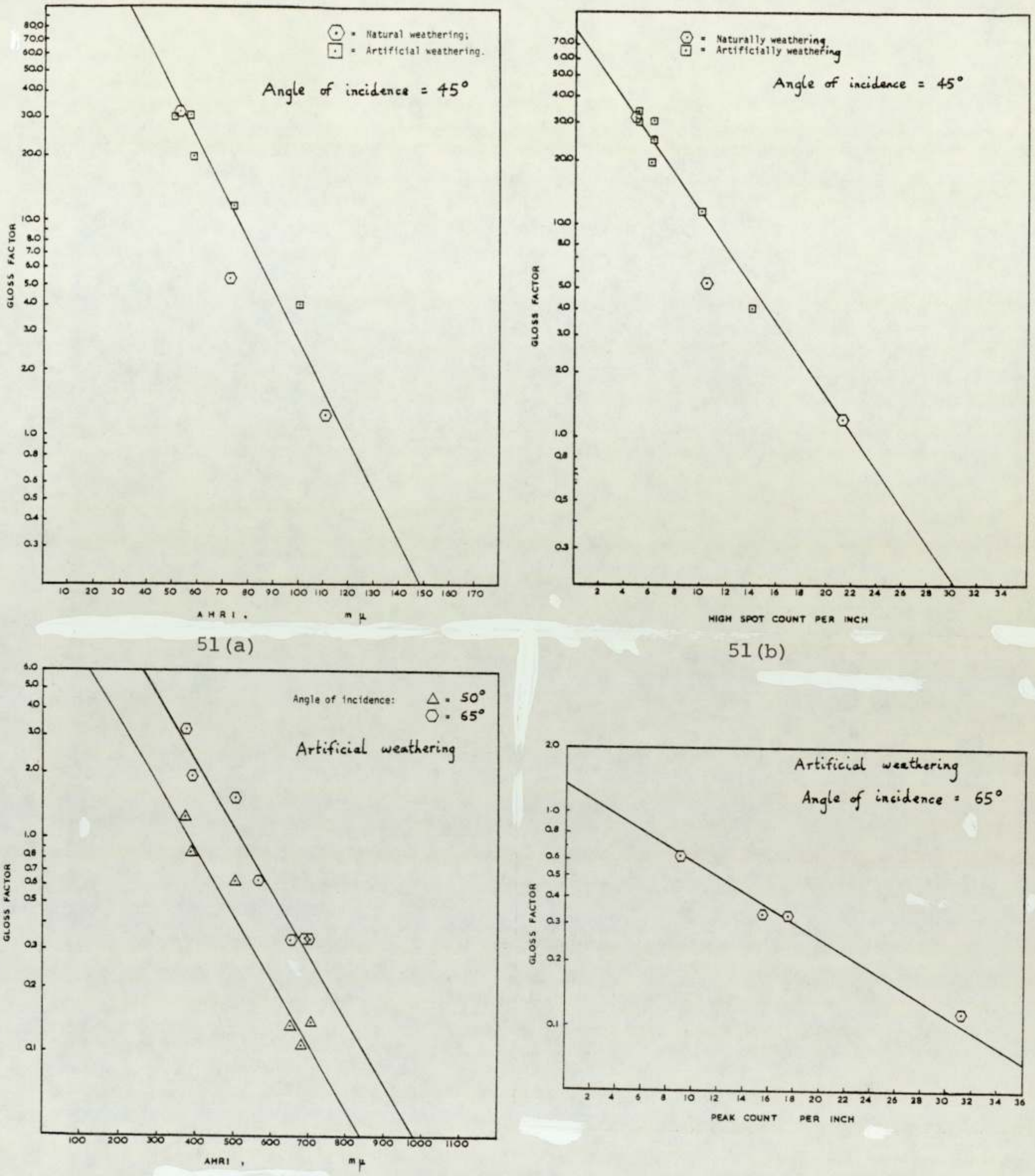
Finally, weathering changes in the diffuse reflectance (I_d), as measured at a 0° angle of reflection, were found in all cases to be relatively small compared with the dominant specular reflectance (I_s) changes. Hence, they were considered to be of comparatively little value as weathering parameters.

IV.3.2 Surface Roughness Measurements

Surface roughness measurements, which for the naturally weathered gloss finish coatings were previously found to be relatively uninformative due to the smallness of their defect size, were repeated for these artificially weathered samples using the Talysurf 4 instrument (as opposed to the Talysurf 100 before). The slightly greater sensitivity of the Talysurf 4 meant that its measurements of micro-irregularities in the 50 - 100 mμ size range in the case of the glossy paints were less unreliable than those previously obtained, although some doubt must still be held concerning their accuracy on a semi-quantitative basis.

However, reliable data could be obtained for the semi-gloss chlorinated rubber coating on account of its intrinsically rougher surface. The average heights of its roughness irregularities (AHRI), as computed by the Talysurf, were in the region of 300 - 800 mμ for the artificial weathering series of samples. Additionally, the obvious interdependence of the AHRI values on the gloss factor was investigated and it was found that close straight line relationships existed between "log (gloss factor)" and AHRI (Figure 51(c)). This logarithmic gloss dependence also appeared to hold for the peak count per inch (PC) (Figure 51(d)), as also measured by the Talysurf. Indeed, even when these plots were applied to the allegedly unreliable vinyl toluene alkyd gloss finish data, for both natural and artificial weathering, reasonable linearity was obtained (Figures 51(a) and (b)) which was only seriously deviated from at low AHRI values (around 50 mμ) in which region the Talysurf probe is not considered to be particularly sensitive.

The implications of this interesting logarithmic relationship between these objectively determined gloss and surface roughness parameters will be considered further in the "Discussion" section at the end of this chapter.



51(a)

51(b)

51(c)

51(d)

FIGURE 51 - Artificial weathering of:-

(a) and (b) : vinyl toluene - modified alkyd gloss finish;
(c) and (d) : thixotropic chlorinated rubber semi-gloss finish;

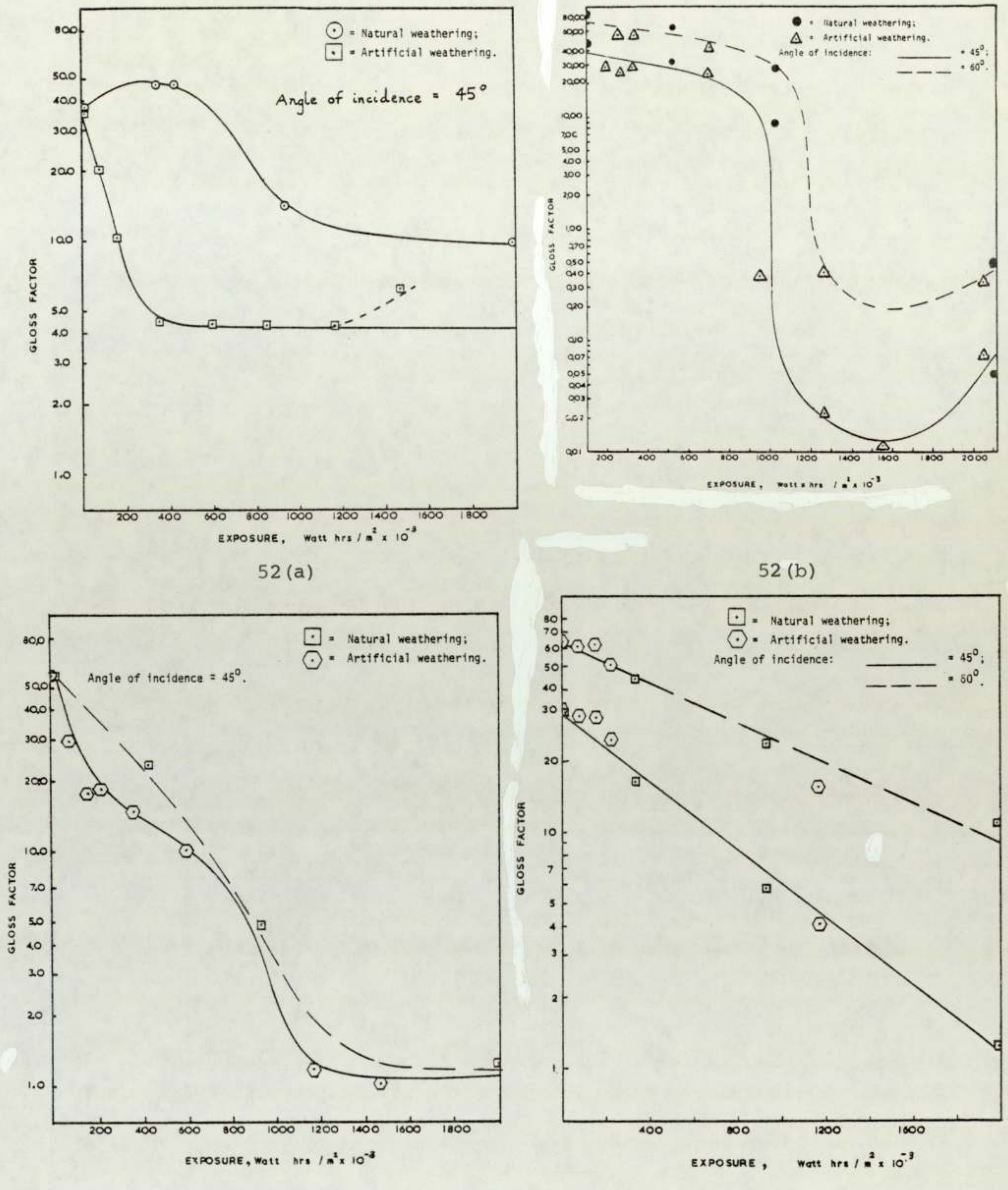
dependence of log (gloss factor) on:-

(a) and (c) : average height of roughness irregularities (AHRI),
(b) and (d) : peak count (PC) per inch.

IV.4 Comparison between Natural and Artificial Weathering

On comparing the natural (Building Research Station) and artificial (BS 3900 Part F3) weathering performances to date, on an energy of exposure basis, of the four gloss finish coatings studied, it was found that the respective variations in the log (gloss factor) term, considered to be the most meaningful weathering parameter, showed an encouraging degree of correlation between the two sets of data in all cases bar one (Figure 52). The one exception was that of the phthalic alkyd (Figure 52(a)) in which the previously suspected anomolous initial increase in gloss on natural weathering was not, in fact, observed on artificial weathering, even though the initial gloss factors prior to exposure were almost identical. However, following their differing initial gloss changes, both weathering series did exhibit subsequent decreases to a "plateau" value (Figure 52(a)).

In contrast to the phthalic alkyd, however, the epoxy/polyamine, polyurethane alkyd and vinyl toluene alkyd coatings (Figures 52(b), (c) and (d) respectively) each showed good correlation between the two types of weathering; this being despite the fact that each of these three coatings appeared to have its own characteristic weathering pattern which would undoubtedly be a function of not only the material but also of the ageing environment's particular "balance" of weathering factors. Indeed, the epoxy/polyamine's initial stability prior to its drastic mid-exposure deterioration (Figure 52(b)) contrasts vividly with the relatively consistent decreasing trends for the polyurethane alkyd (Figure 52(c)) and vinyl toluene alkyd (Figure 52(d)) of which the former displays slightly the greater rate of gloss reduction prior to a minimum value being reached.



52(a)

52(b)

52(c)

52(d)

FIGURE 52 - Variation in log (gloss factor) on exposure;
comparison of natural and artificial weathering of:-

(a) phthalic alkyd,
(b) epoxy/polyamine,
(c) polyurethane alkyd,
(d) vinyl toluene alkyd,

gloss finish coatings.

This data correlation has obviously been strengthened by the late inclusion in the Figure 52 results of additional 25½ months natural weathering points which were not available at the time of the previous 12 months natural weathering study. Finally, it also requires noting that the so-labelled 45° and 60° gloss factors in Figure 52 are, in fact, nearer 50° and 65° for the artificial weathering results which, as mentioned earlier, were obtained using the automated goniophotometer's re-designed specimen mount.

IV.5 Discussion

This section of the work, describing the natural and artificial weathering of a range of commercial surface coatings, has provided a great deal of useful information relating to the likely in-service performances and patterns of behaviour of these materials. However, rather than being intended as an in-depth study of any one of these paint systems, this study has concerned itself more with investigating the extent to which a selected combination of analytical techniques can collectively describe the process by which a paint degrades, both physically and chemically, on weathering. It was, therefore, with this latter object in mind that goniophotometry was chosen as the main analytical technique for following the effects of weathering, and rightly so in view of the fact that, subjectively, paint performance is judged most readily on the basis of visual gloss assessment. However, whilst goniophotometry may therefore be regarded, with some justification, as being, in a sense, the most "meaningful" technique so far as its relevance to what an observer of the paint surface perceives is concerned, it obviously cannot explain the phenomena which actually give rise to reflectance changes. Consequently, in order for the background history of these changes to be unveiled, goniophotometry needs to be supplemented by appropriate additional methods of analysis.

Generally, when a gloss paint such as those studied here is exposed in an ageing environment, its initial surface lustre is seen to diminish during the early stages of weathering. This initial "dulling" of the surface can in most cases be largely, if not wholly, attributed to the progressive development of micro-defects which, by definition, are still smaller both in height and lateral extent than the wavelength of the light under which the surface is viewed. Goniophotometrically, these so-called micro-defects are only capable of reducing the peak height, by energy removal from the incident beam, an effect which is perceived visually as an impairment of image brightness rather than as a loss in definition. This process then continues as the number and size of the micro-defects increases on exposure until a sufficient number of these irregularities attain a size-order in excess of the wavelength of the illuminating light. When this stage is reached, the now-termed macro-defects render the coating surface capable of actually effecting an angular divergence of the specular beam by geometric means, as sensed objectively as an increase in the goniophotometric peak width and, subjectively, as the blurring of an image viewed on reflection at the surface. It is this effect which is responsible, in the case of gloss finish paints, for transforming their characteristically sharp, triangularly shaped goniophotometric peaks into broader curves during the later stages of weathering.

Hence, it can now be appreciated how goniophotometric data can be interpreted in terms of the progressive development of what the goniophotometer, itself, regards as micro- and macro-defects. Furthermore, this convenient size-distinction made, as it is, in relation to the known wavelength of the incident light, enables useful comparisons to be drawn between different glossy paints on the basis of the time taken for surface deterioration to reach this size "transition". However, although individual goniophotometric parameters, such as specular reflectance (I_s) and peak width at half-height ($W_{\frac{1}{2}}$), are each highly informative in their own right, particularly during their respective periods of change, it can be seen now how they are each only partially descriptive of the ageing process as a whole, not to mention, of course, the fact that the optical property to which they both relate, i.e., gloss, is a function of them both. Consequently, the computed "gloss factor" term ($GF = I_s - I_d/W_{\frac{1}{2}}$), encompassing, as it does, both the specular and angular components of reflectance, is obviously not only the singly most descriptive gloss parameter but, in its wider context, the most meaningful weathering parameter as well.

Certainly one of the most interesting features to emergy from this section of the work has been the way in which the goniophotometric data has combined with surface roughness measurements in characterising the weathering process, from the visual gloss changes which we see, back as far as the initial appearance of micro-defects in the paint surface. Furthermore, the conjecture that variations in both the number and size of the surface irregularities could, in some way, be mathematically related to the gloss factor changes, to which they obviously give rise, has been examined and logarithmic relationships shown to exist. From the relevant plots (see Figure 51 previously), these relationships can be expressed as follows:-

$$\log \frac{GF}{k} = - a.AHRI \qquad \text{......} \ (7)$$

and,

$$\log \frac{GF}{k'} = - a'.PC \qquad \ldots\ldots (8)$$

where:- GF = gloss factor

AHRI = average height of roughness irregularities

PC = peak count per unit length

k) = constants, characteristic of the angle of incidence
k')

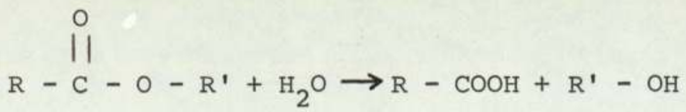
a) = constants, characteristic of the paint system.
a')

An interesting application of eqs. (7) and (8) thus arises out of the fact that goniophotometric data is more correlative with subjective visual gloss ratings when in logarithmic rather than linear form (see NOTE on page 194, section IV.2.1 previously). This suggests, therefore, that progressive visual gloss assessments of a given paint film during weathering exposure are more in line with surface roughness measurements than instrumental gloss readings.

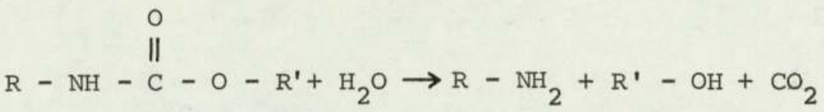
However, when we discuss paint film degradation as a whole, ultimately we have to consider the complex chemistry of the various reactions taking place at the paint surface and, to a certain extent, within the bulk as well. Although other types of degradation, such as by physical, mechanical, biological and/or electrical means, generally occur, it can be said that chemical degradation is invariably at the root of the majority of weathering effects such as those which have been previously observed.

Unfortunately, however, it is still true to say that convenient analytical methods for obtaining unequivocal quantitative information relating to the chemical changes occurring (predominantly) at paint surfaces are sadly lacking in the field of coatings' analysis. Nonetheless, techniques such as multiple internal reflectance spectroscopy (MIRS), as used in this study, can often provide a wealth of semi-quantitative information. Indeed, despite its procedural difficulties, MIRS has proved here to be at least capable of signifying what the dominant chemical change is in a given paint system on weathering.

For example, in the case of the phthalic alkyd gloss finish coating, it appeared that oxidation and/or hydrolysis of the ester linkages of the binder were the main deteriorative mechanisms which gave rise to defect formation with concomitant loss in gloss. This view subsequently received some support from the similar findings obtained with the polyurethane alkyd which, in addition to its hydrolysable ester groups, also contains, of course, similarly susceptible urethane groups. However, although it has been suggested by previous workers(241) that, of the polyurethane family, it is only really its polyester-based members that are particularly sensitive to hydrolysis (on account of the ester groups being considered the principal points of attack), the related MIRS evidence presented here (see Figures 41 and 42 previously) indicates that the apparently likewise susceptibility of the urethane moiety is also a determinative factor in weatherability. These hydrolysis proposals, furthermore, are able to account for the MIRS-observed increases in the $-NH_2$, alcoholic -OH and carboxylic -OH end group concentrations at the paint surface on exposure, as shown below:-

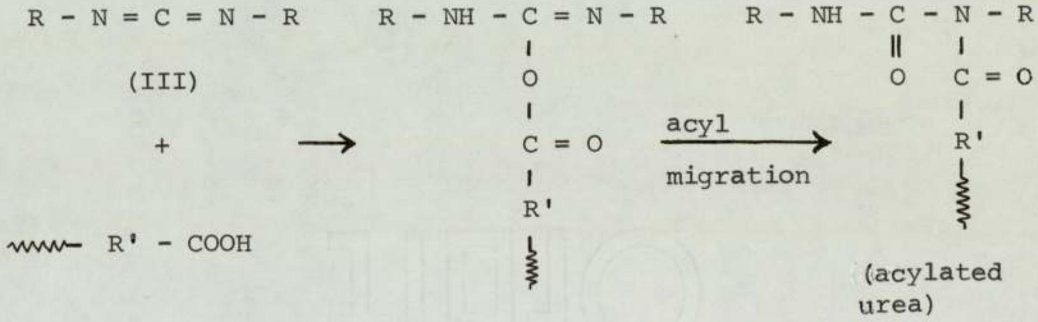


$$R - \overset{\overset{O}{||}}{C} - O - R' + H_2O \rightarrow R - COOH + R' - OH$$



$$R - NH - \overset{O}{\overset{\|}{C}} - O - R' + H_2O \rightarrow R - NH_2 + R' - OH + CO_2$$

Additionally, hydrolytic reactions of this nature may be catalysed by residual polymerisation catalysts in the binder and also, in the case of polyurethane alkyds, by the carboxylic acid (-COOH) groups liberated by hydrolysis. In this latter respect, therefore, the degradation tends to become autocatalytic(242), which is why commercial polyester-based urethane coatings systems usually incorporate a stabiliser, typically, a carbodiimide(241, 243) (see (III) below), to reduce the rate of hydrolysis by reaction with the free -COOH groups, probably as follows(244):-



Thus, it is along the lines discussed here that MIRS data can, in most cases, qualitatively describe the more important chemical reactions taking place during the weathering of a given surface coating. In addition to this, however, it has also been shown in the preceding text that MIRS peak absorbance indexing, relative to suitably stable reference peaks, can yield useful semi-quantitative information regarding, for example, any periodicity or seasonal dependence which the changes taking place may appear to have. This latter effect was, in fact, observed with the polyurethane alkyd (Figures 41 and 42) and epoxy/polyamine (Figure 45) gloss finish coatings which each exhibited seemingly cyclic main change trends denoting initial summer/autumn deterioration followed by a partial recovery during the winter/spring months; this weathering pattern, incidentally, receiving encouraging support from their corresponding gloss factor changes (Figures 33(b) and (c)).

Let us now consider the various paint systems studied in this section of the work collectively, with a view to commenting, wherever possible, on their relative durabilities. Firstly, however, let it be said that such comparisons are invariably hampered by the difficulty in knowing by which criterion, and over what period of time, weatherability should be judged. For example, if, for the gloss finish coatings studied here, the rate of fall in log "gloss factor" (see Figure 34 previously) were to be taken as a measure of weatherability, since log GF is both proportional to defect size and correlative with subjective gloss assessment, then, over the first 12 months natural weathering, the order of weatherability would appear to be:-

phthalic alkyd $>$ epoxy/polyamine $\simeq$ VT-alkyd $>$ polyurethane alkyd

although the outright superiority of the phthalic alkyd is questionable on account of the previously mentioned dubiety concerning the accuracy of some of its early gloss readings. Indeed, its eventual rate of log GF decrease (Figure 34) towards the end of the exposure period would put it more on a par with the epoxy/polyamine and vinyl toluene alkyd coatings. However, although the above order of performance, as it were, is somewhat tentative, interestingly enough, it does happen to compare favourably with the results of mechanical testing carried out earlier on the same samples by workers at the Building Research Station (10). In this latter work, the phthalic alkyd was regarded as an example of a good durability air-drying paint which, in average outdoor conditions, could reasonably be expected to last for 4 - 6 years.

However, the element of uncertainty which often surrounds this type of comparative performance rating is subsequently instanced by the epoxy/polyamine coating during its second year of exposure (Figure 52(b)). After appearing at the end of 12 months weathering to be certainly one of the more durable paints studied, on the basis of its gloss retention properties, it then undergoes a sudden and drastic deterioration in appearance in marked contrast to the uniform/tending to levelling out trends shown by the three alkyd-based coatings (Figure 52). This unheralded change, resulting in a complete loss of gloss, is confirmed by artifical weathering (Figure 52(b)) and prompts a revision of the epoxy/polyamine's previous performance rating. This exemplifies the difficulties which exist when weathering data pertaining to a range of different coatings is compared with a view to predicting their likely in-service performances in a given application over a given period of time. However, although such comparisons are often all that are possible, they do stand to be strengthened considerably wherever previous weathering experience with related coatings systems is available.

In conclusion of this section of the work, let us consider finally the correlativity of the natural and artificial weathering results. As already pointed out in section IV.4 previously, the log "gloss factor" term (Figure 52) appears to be an encouragingly correlative parameter for the range of coatings studied in the environments in which they were exposed. The greatest disparity in response was surprisingly observed in the case of the phthalic alkyd (Figure 52(a)) which, considering that the BS 3900 Part F3 artificial weathering apparatus was originally designed around alkyd performance, only serves to support earlier suspicions that this coating's initial natural weathering gloss data is somewhat anomalous. However, the high degree of correlation shown by each of the other three gloss finish paints (Figure 52(b), (c) and (d)), which, for the epoxy/polyamine, is despite its markedly different pattern of behaviour, propounds that the BS 3900 Part F3 weathering cycle is capable of inducing, in a range of commercial coating materials, similar gloss changes to those brought about by natural weathering here in the U.K. This view reinforces similar findings arising from an earlier comparison of the results of mechanical testing(10) at the Building Research Station.

CHAPTER V

NATURAL AND ARTIFICIAL WEATHERING OF A COMMERCIAL POLY (VINYL CHLORIDE) ORGANOSOL SURFACE COATING

CHAPTER V

NATURAL AND ARTIFICIAL WEATHERING OF A COMMERCIAL POLY (VINYL CHLORIDE) ORGANOSOL SURFACE COATING

V.1 Introduction

The natural (245) and artificial (240) weathering of a commercial, white-pigmented, matt finish, poly (vinyl chloride) organosol surface coating was conducted at the Building Research Station (BRS) exposure site and in the BS 3900 Part F3 apparatus respectively. Although this coating was originally a member of the same series of commercial coatings described in the previous chapter, it was singled out for special attention in view of the accent which was to be subsequently placed, during the latter half of this project, on poly (vinyl chloride) (abbr., PVC) based surface coatings. In addition, a more in-depth ageing study of this particular coating was facilitated by the fact that (a) its initially matt finish meant that its surface roughness was such that it could be accurately and reliably characterised by Talysurf measurements from the start, and (b) the relative softness of the coating, coupled with the relatively lower durability of PVC as a material, were likely to lead to more pronounced changes on weathering.

In common with the previous paints studied, this PVC organosol coating had also already been characterised with respect to changes in certain of its mechanical properties (10) on both natural and artificial weathering. However, with regard to its formulation, all that is known is that it is a plasticised, white-pigmented organosol coating material.

Thus, having established in the preceding chapter how a selected combination of analytical techniques can be used collectively to characterise and compare the weathering performances of a variety of paints, let us now take a more detailed look at a particular coating type, viz., that based on PVC, with a view to describing more fully its ageing process.

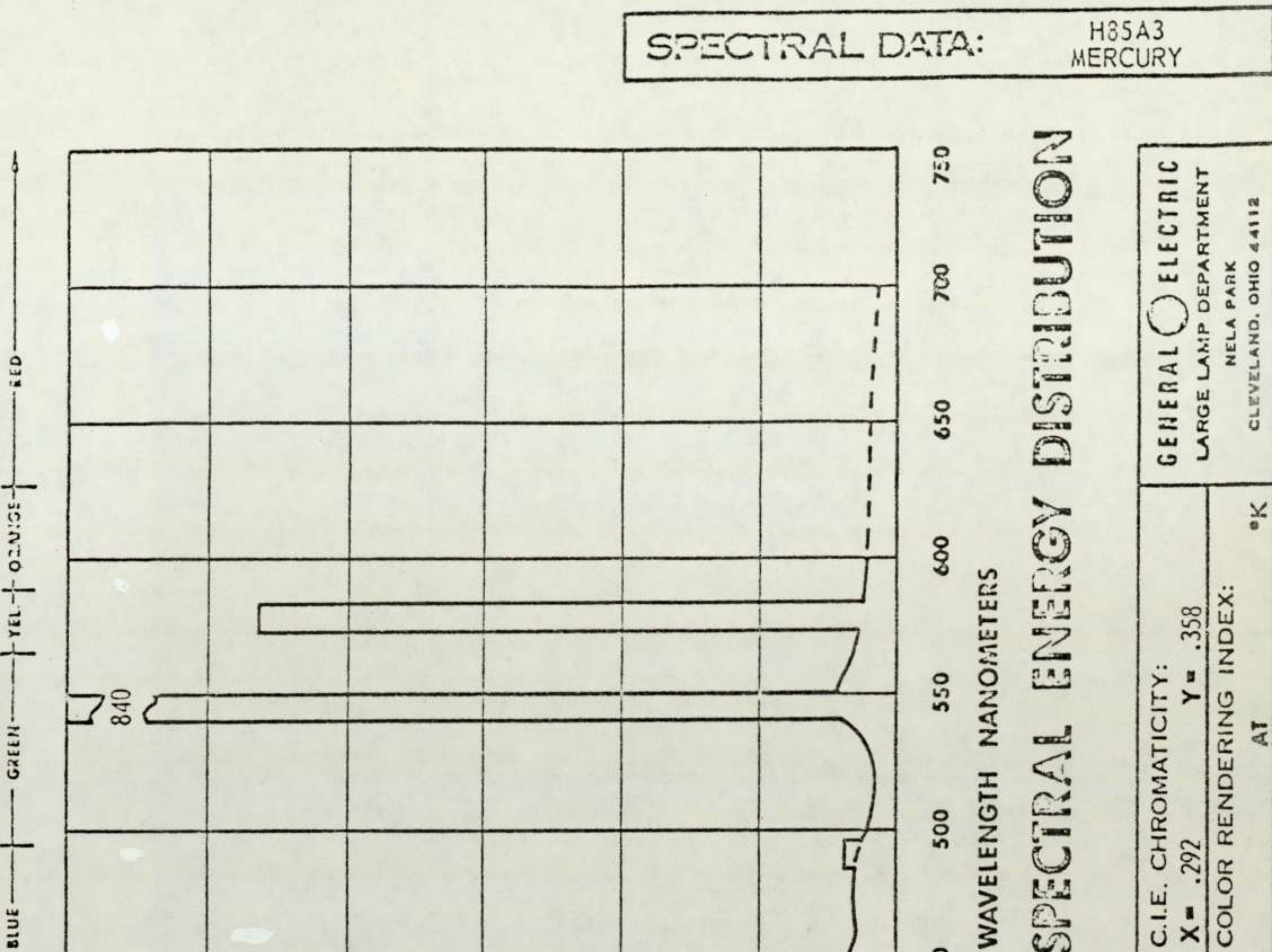
Finally, the results reported in this section of the work have recently been the subject of a short paper (246) presented at a conference on "Polymer Surfaces". A reprint of the transcript is submitted as a supporting paper to this thesis (see inside back cover).

V.2 Natural Weathering

The natural weathering data reported here relates to the same twelve month exposure period, commencing on 1st July, 1966, at the BRS exposure site, as for the range of coatings featured in the preceding chapter. However, in addition to the three techniques previously used (i.e., goniophotometry, MIRS and surface roughness studies), scanning electron microscopy (SEM) is now introduced as a means of directly observing the surface changes which give rise to the measured reflectance and surface roughness measurements.

V.2.1 Goniophotometry

Goniophotometry was carried out using the, then, still manually operated instrument and employing "wide" beam illumination over a range of angles of incidence (30°, 45°, 60° and 75°) to the sample surface. However, in contrast to the previous paint films studied, it was decided that, in the case of this matt finish PVC organosol coating, instead of using monochromatic blue incident light of 436 nm. wavelength, the goniophotometer lamp's unfiltered (i.e., multichromatic) mercury light would be employed for illuminating the sample. The reasons for this were two-fold; firstly, it enabled the obviously greater light intensity of the unfiltered mercury light (approx. 7000 intensity units compared to 1500 intensity units for just its monochromatised blue component) to be taken advantage of in view of the low and largely diffuse reflectivity of this matt finish PVC coating, whilst secondly, and perhaps more importantly, the spectral output of the mercury lamp (Figure 53) was such that it presented a well-defined lower (365 nm.) wavelength threshold limit followed by a discrete series of four longer wavelength bands extending as far as 578 nm. and superimposed upon a low background emission. Thus, it was hoped that this effectively "five-wavelength" composition of the mercury light would consequently introduce five quasi-size graduations into the progressive goniophotometric (peak width, $W_{\frac{1}{2}}$) response to increasing defect size, i.e., instead of having just one (436 nm.) micro/macro size transition, above which $W_{\frac{1}{2}}$ starts to increase, we now have five such transitions (at around 365, 406, 436, 546 and 578 nm.) which conveniently fall within the defect size range for this PVC coating. In this way, the goniophotometric data which follows can be regarded as being in closer touch still with the developing surface deterioration which is, in turn, giving rise to the measured reflectance changes.



LAMP DESCRIPTION: H85A3
CLEAR
MERCURY

DATE: JUNE 18, 1965

C.I.E. CHROMATICITY:
X = .292 Y = .358

COLOR RENDERING INDEX:
AT °K

FIGURE 53 - Spectral output of the goniophotometer's mercury light source.

Turning our attention, therefore, to the data itself, significant changes in the reflectance characteristics of this PVC organosol paint were observed on natural weathering. This is clearly illustrated in Figure 54 in which its goniophotometric curves before and after 12 months' exposure are compared at various angles of incidence. However, as discussed in the previous chapter, the extent of these changes bear more resemblance to would be visual effects when presented logarithmically (Figure 55), although, of course, in this case, the coating's matt finish precludes subjective gloss assessments from being made. Nevertheless, these logarithmic curves are still useful in emphasising the gross asymmetry of the spatial distribution of surface reflectance and the relatively enhanced contribution which diffuse (i.e., non-specular) reflectance now makes to this coating's overall matt finish. A more gradual look at the progressive changes in reflectance taking place during exposure is afforded by Figure 56, again at various angles of incidence. Here it can be seen how, except at high angles of incidence (e.g., 75°, Figure 56(d)), the initial goniophotometric curves rapidly lose their semblance of triangularity on ageing. Furthermore, it appears that, at angles of incidence as low as 30° (Figure 56(a)) or as high as 75° (Figure 56(d)), some of the parameters derivable from the curves tend to become less determinable. This is certainly true of changes in the angle of maximum reflectance (i.e., angular (specular) displacement) at both 30° and 75°, with the 30° peak width at half-height (and, hence, gloss factor) also becoming instrumentally immeasurable (Figure 56(a)). Thus, it would appear that the intermediate 45° and 60° angles of incidence are more generally workable angles for gloss factor characterisation although, if specular reflectance alone will suffice, then, in common with specular gloss-meters, higher angles

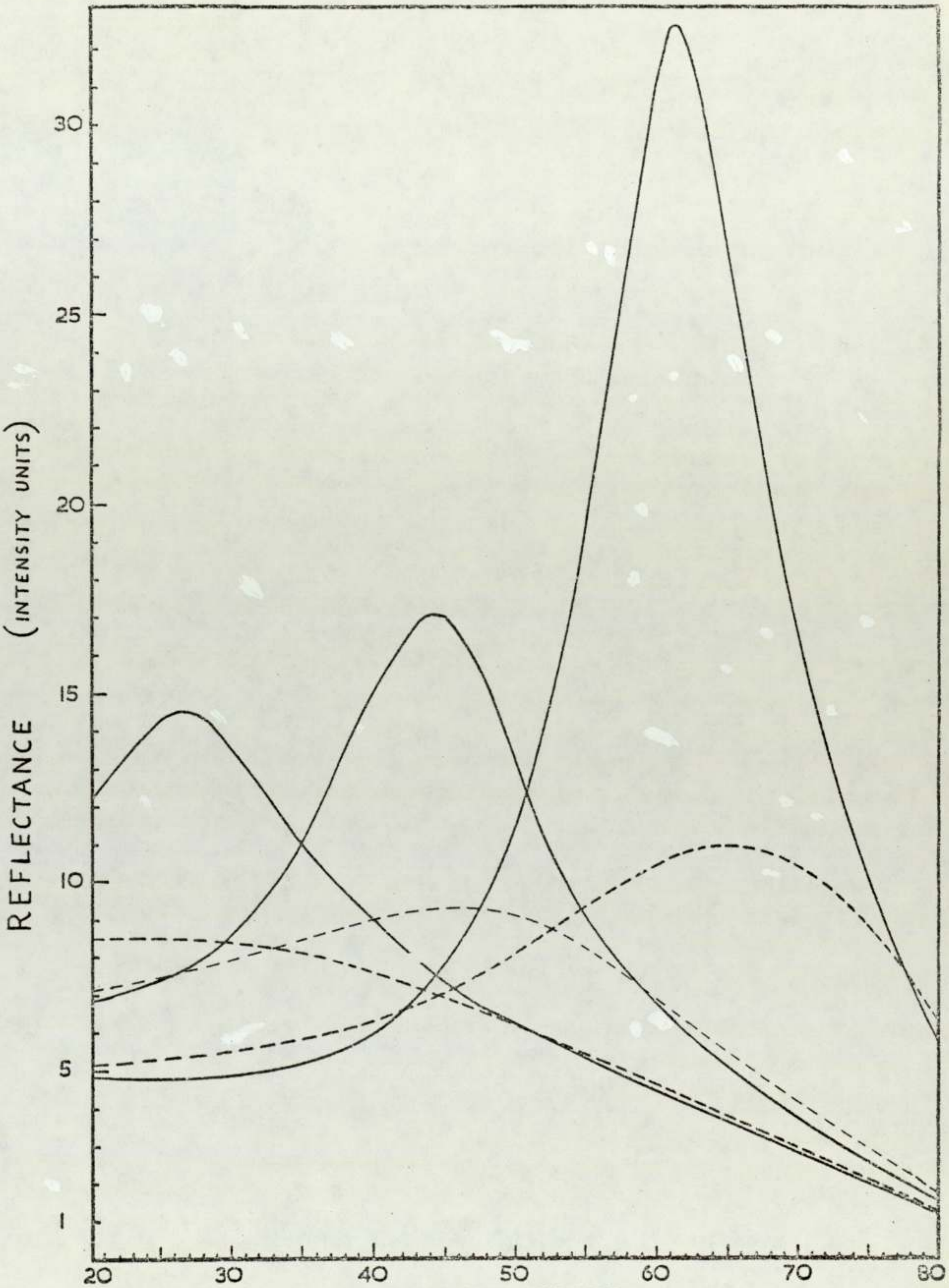


FIGURE 54 - Goniophotometric curves relating to the natural weathering of PVC organosol matt finish coating;

after ——— 0 months,

and ----- 12 months exposure.

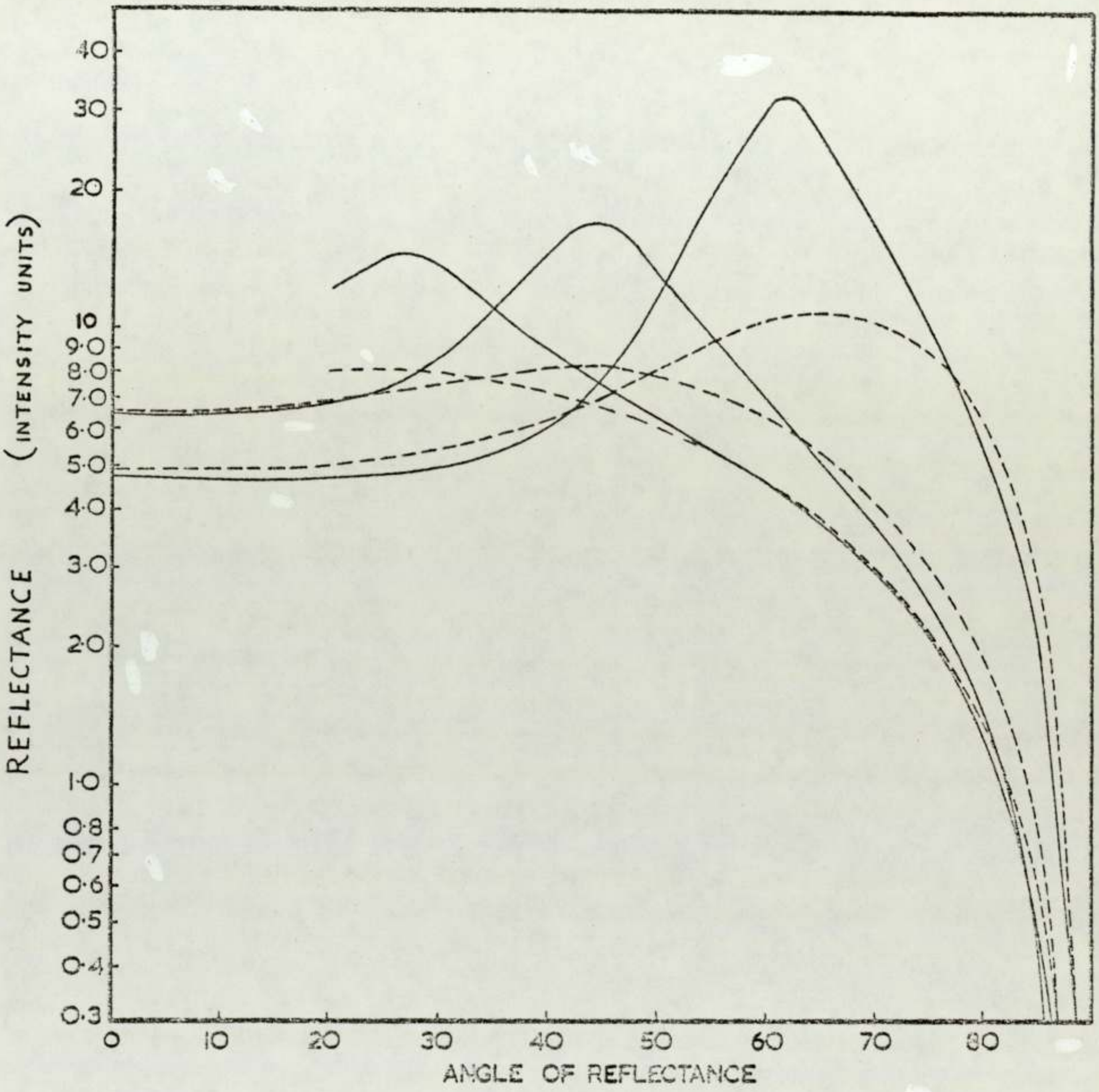
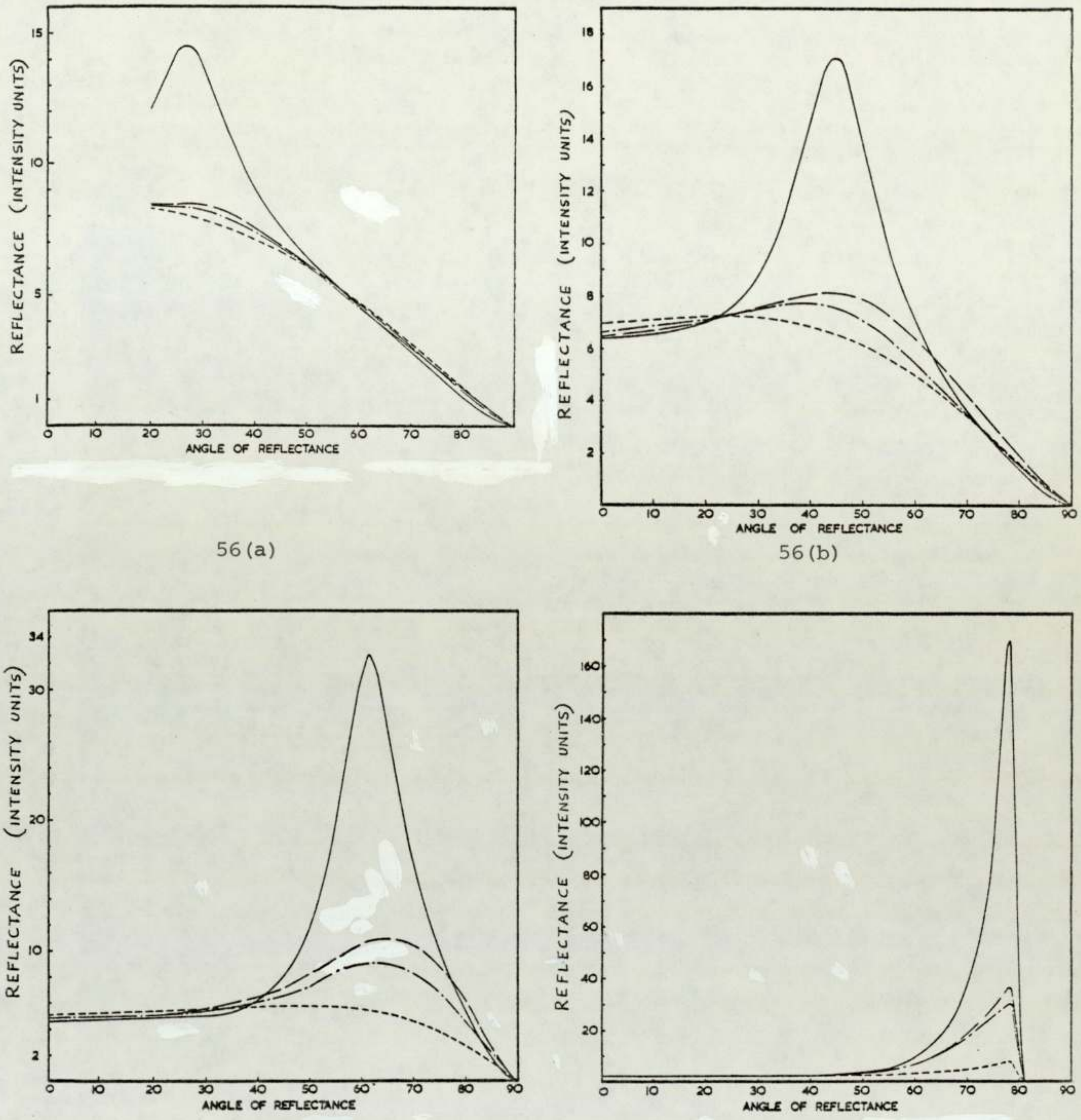


FIGURE 55 - Goniophotometric curves (logarithmic presentation); natural weathering of PVC organosol matt finish coating, exposure: ——— 0 months, ----- 12 months.



56(a)

56(b)

56(c)

56(d)

FIGURE 56 - Goniophotometric curves at angles of incidence of (a) 30°, (b) 45°, (c) 60°, and (d) 75°;

effect of natural weathering on PVC organosol matt finish coating after:-

——— : 0 months (date: 1/7/66)
·—·—· : 3 months exposure (date: 30/9/66)
------- : 6 months exposure (date: 23/12/66)
— — — : 12 months exposure (date: 8/7/67)

such as 75° are more sensitive and applicable to matt finish coatings such as this.

However, from the point of view of ageing, the most striking feature of the curves in Figure 56 is the apparent reversal, during the latter 6 months (winter and spring) exposure, of the deteriorative trend established during the preceding summer and autumn. This seemingly cyclic pattern of behaviour was also previously observed in the case of one or two of the gloss finish coatings, although not to the extent that a positive improvement was brought about in surface reflectance as seen here. These goniophotometric changes are depicted graphically for this PVC organosol coating in Figures 57 and 58 in which their apparent seasonal dependence is clearly shown. As with the glossy paints discussed previously, although not quite so completely, the specular reflectance (I_s) changes (Figure 57) are still largely descriptive of the overall gloss factor changes (Figure 58). If anything, this seems to be more especially true during the later stages of weathering after the accompanying initial peak width ($W_{\frac{1}{2}}$) increases have subsided. As regards the other derivable goniophotometric parameters, changes in the diffuse reflectance (I_d) at 0° angle of reflection were relatively small (compared to those in I_s), as were the shifts in the specular angle which, as deterioration progressed, tended to decrease slightly.

Thus, it appears that the rapid fall in gloss factor (GF) during the initial July-September (summer) exposure represents the combined effects of the I_s decreasing whilst the $W_{\frac{1}{2}}$ concurrently increases. This trend continues, albeit much more slowly, throughout the autumn, prior to winter and spring exposure bringing about a slight

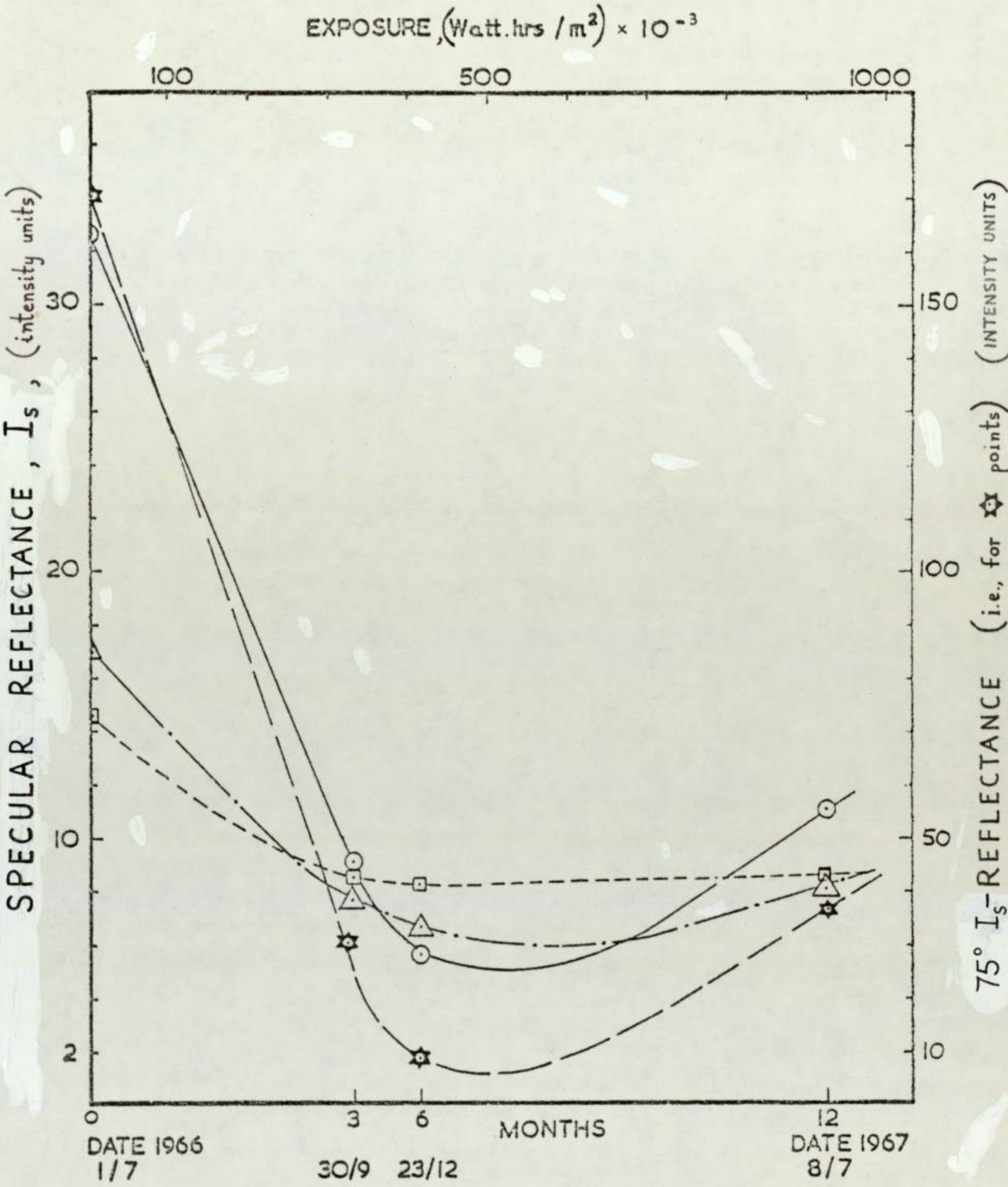


FIGURE 57 - Variation in specular reflectance (I_s) on natural weathering exposure;

PVC organosol matt finish coating;

angle of incidence:-

- - - ⊡ - - - : 30°
·—·△·—· : 45°
——⊙—— : 60°
— —✡— — : 75° (see right-hand I_s axis)

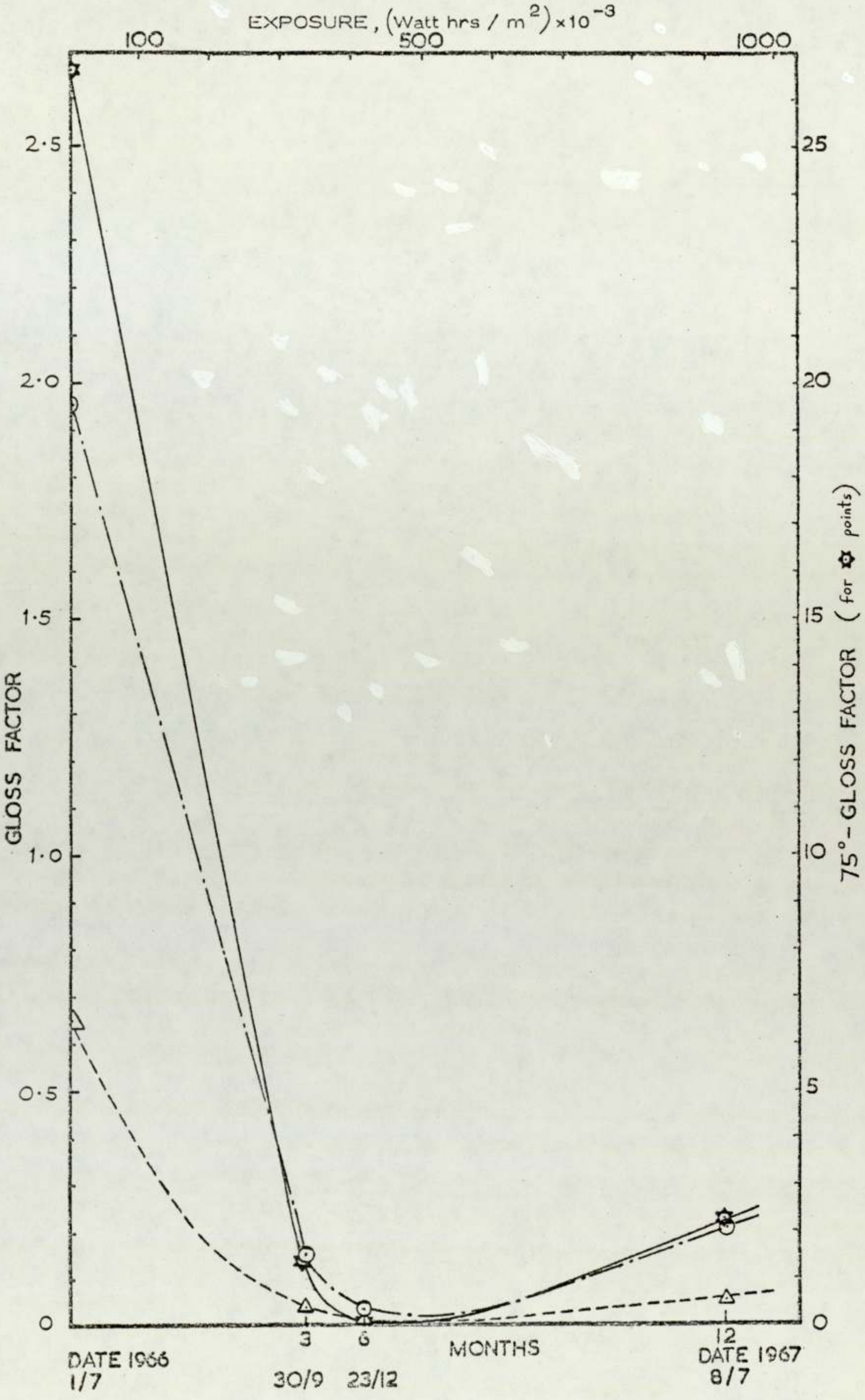


FIGURE 58 - Variation in gloss factor (GF) on natural weathering of PVC organosol matt finish coating;

angle of incidence:-

△ = 45° ⊙ = 60° ✡ = 75° (right-hand axis) recovery in GF, predominantly due to a related improvement in I_S. These results can now be considered in the light of those which follow from alternative sources, along with which they will then be discussed at the conclusion of this chapter.

V.2.2 Surface Roughness Measurements

Surface roughness measurements, carried out using the Talysurf 100 instrument, were able to provide reliable and reproducible results in contrast to those obtained for the gloss finish paints earlier. This was made possible by the fact that this PVC coating's matt finish gave rise to a surface profile which was composed of inherently larger sized irregularities and which was, therefore, more amenable to this type of analysis.

On weathering, it was found that the average height of the roughness irregularities (AHRI), contained in the surface of this PVC coating, increased steeply from an initial value of 310 $m\mu$ to 700 $m\mu$ after three months of summer exposure (Figure 59). This change then continued throughout the autumn, with the AHRI increasing further to 943 $m\mu$, before slowing down and ultimately reversing its trend during the winter and spring (final AHRI = 660 $m\mu$). Thus, this sequence of changes in surface asperity appears to be consistent with the corresponding variations in reflectance to which they indubitably give rise. This can be easily seen on comparing the exposure dependence of reciprocal surface roughness (surface smoothness) (Figure 59) with the previous similarly shaped graphs of specular reflectance (Figure 57) and gloss factor (Figure 58). As regards the interdependence of the AHRI and gloss factor (GF) values for this PVC

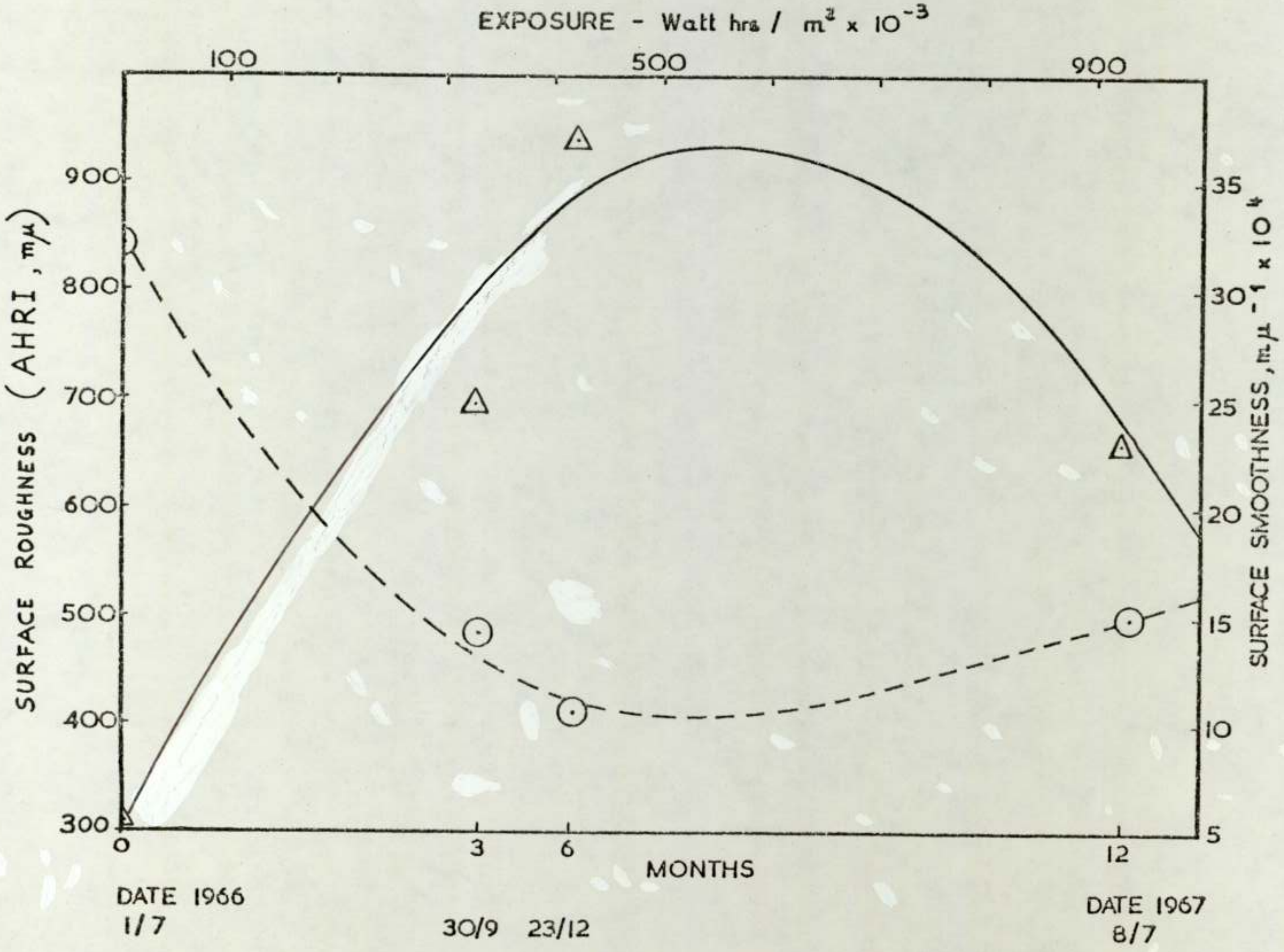


FIGURE 59 -

Variation in:-

△ surface roughness (AHRI) and its reciprocal

⊙ surface smoothness

on natural weathering of PVC organosol matt finish coating.

coating, it was found that they, too, conformed closely (Figure 60) to the logarithmic relationship (eq. 7 below) formulated (see section IV.5) for the previous coatings studied:-

$$\log \frac{GF}{k} = -a.\mathrm{AHRI} \qquad \ldots\ldots (7)$$

where (a) and (k) are constants characteristic of the paint system and the angle of incidence respectively. The validity of this equation thus receives considerable support from the linearity of these more reliable log GF versus AHRI plots (Figure 60) for this PVC coating.

Of further interest is the effect which the increasing AHRI eventually has on the angle of maximum reflectance (i.e., the specular angle). As shown in Figure 61, it is not until the AHRI attains a value in the region of 700 mμ that the coating surface becomes capable of effecting a measurable angular displacement of the specular beam. This interesting phenomenon is known to be related to the wavelength or, in this case, the wavelength distribution (Figure 53) of the goniophotometer's incident light which, from Figure 53, is seen to have a maximum wavelength emission at 568 mμ . Thus, it appears from this that it is not until the average height of the surface defects sufficiently exceeds the uppermost wavelength limit of the incident light that any specular displacement is recorded goniophotometrically. However, this may well be at least partly due to the fact that the mercury light's two longest wavelength bands at 546 and 568 mμ account for such a significant portion (est. 30%) of the total light intensity. If, say, they were not so intense, maybe the trio of lower wavelength bands at 365, 408 and 436 mμ would, collectively, be more determinant of the "critical" AHRI value at which an angular displacement of the

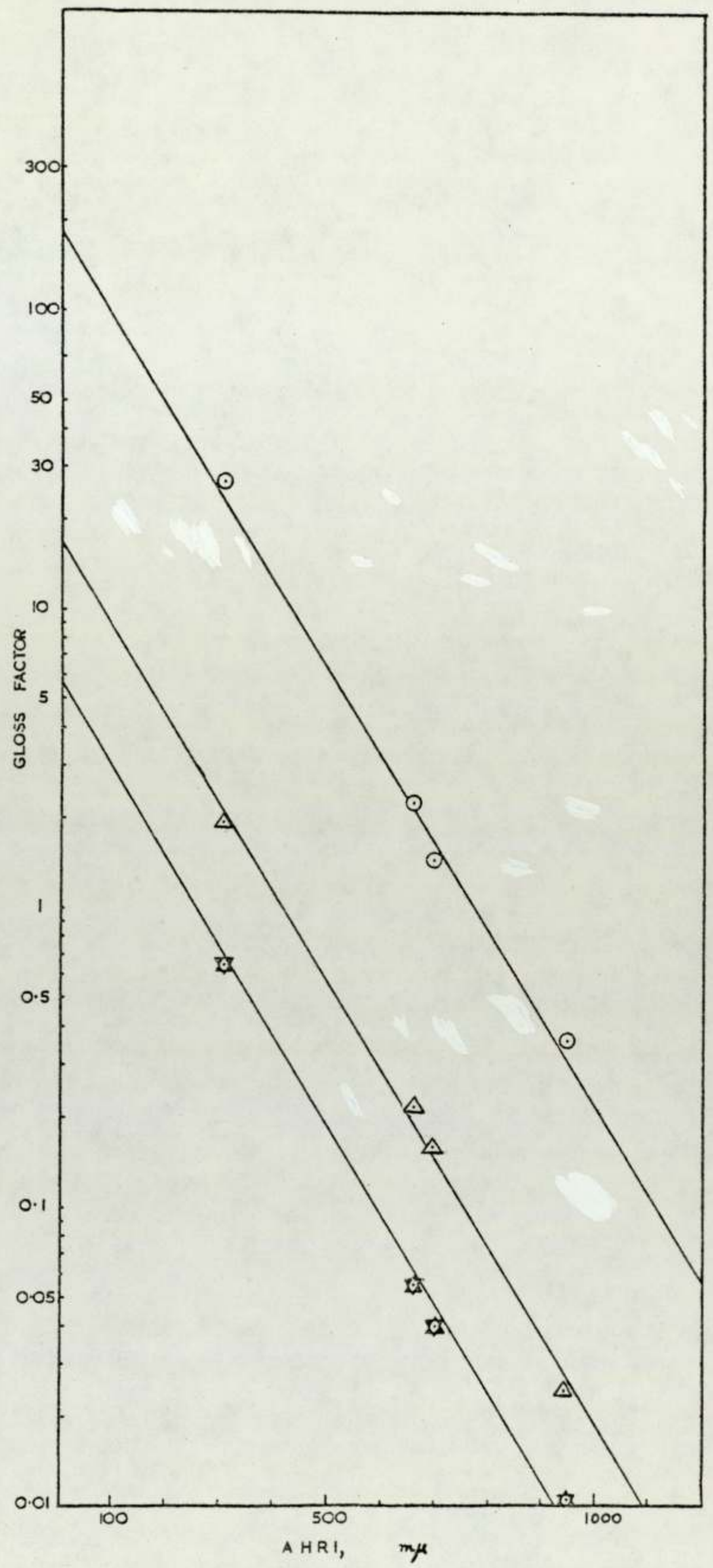


FIGURE 60 - Natural weathering of PVC organosol matt finish; dependence of log (gloss factor) on the average height of roughness irregularities (AHRI);

angle of incidence:-

✡ = 45°, △ = 60°, and ⊙ = 75°.

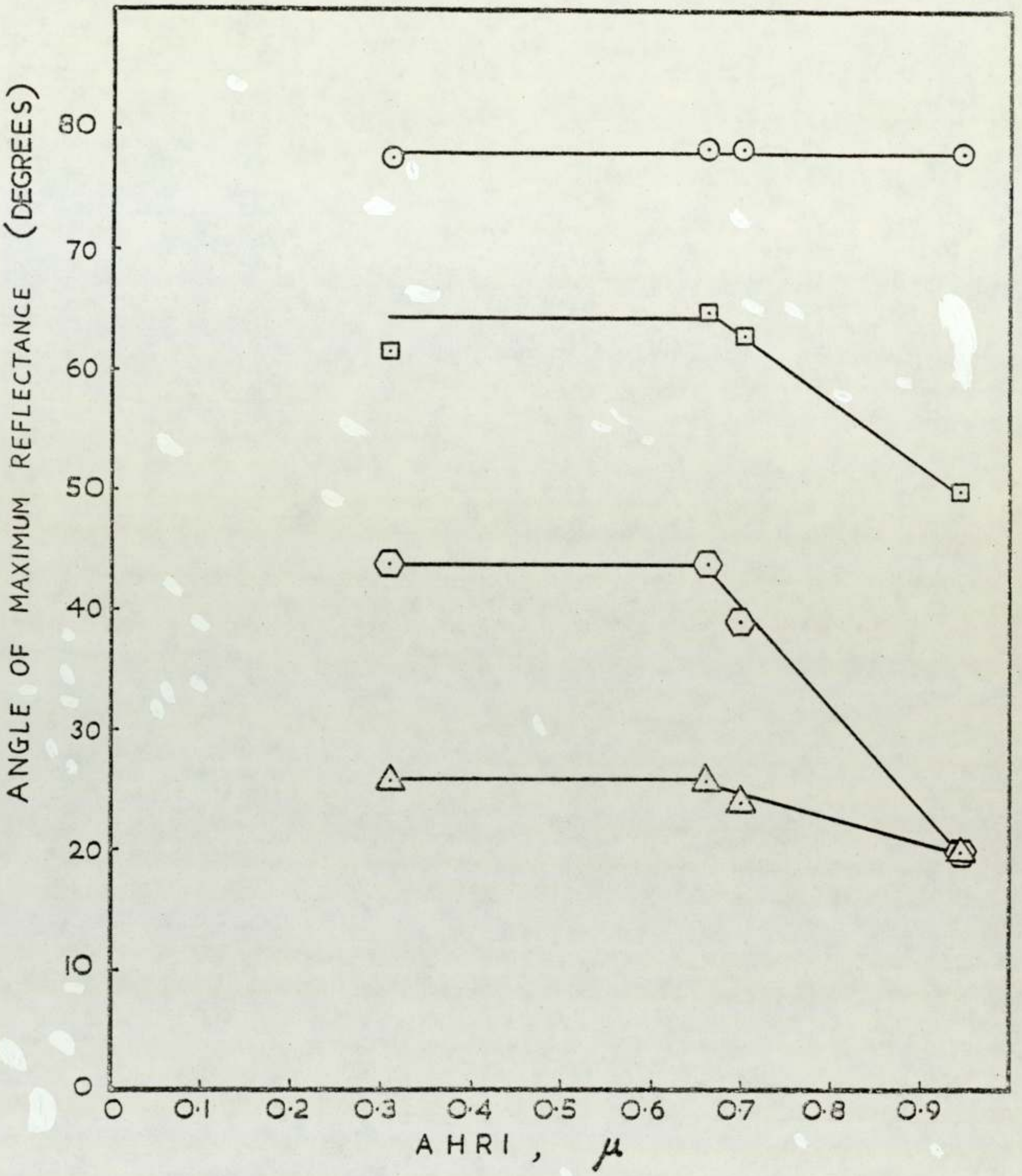


FIGURE 61 - Natural weathering of PVC organosol matt finish; dependence of angle of maximum reflectance (i.e., specular angle) on AHRI;

angle of incidence:-

△ = 30°, ⬡ = 45°, ⊡ = 60°, and ⊙ = 75°.

specular beam is sensed goniophotometrically.

Thus, having seen here how the surface roughness data can go a long way towards explaining the observed reflectance changes, let us now consider if the available chemical data can shed some light on the nature of the underlying mechanisms of degradation.

V.2.3 Multiple Internal Reflectance Spectroscopy (MIRS)

Whilst good quality MIR spectra proved difficult to obtain for this matt finish PVC coating, the spectra which were recorded (Figure 62) nevertheless proved adequate for semi-quantitative purposes. The most prominent peaks in the spectrum (Figure 62) were those detailed in Table 10 overleaf.

For each sample analysis, the MIR spectrum was re-recorded until a stable spectrum was obtained. In this way, it was possible to demonstrate that, during the course of the analysis, two "procedural" effects were taking place simultaneously. Firstly, there was the, by now familiar, improvement in the intimacy of contact between the sample surface and the internal reflector plate, as a result of them being held together under pressure in the infrared beam. This tended to bring about a general improvement in spectral quality over a period of the first 3 hours or so, as reflected in the proportionate increases in absorbance (Figure 63) of all the peaks in the spectrum - with one exception, that of the carbonyl (C = O) stretching peak at 1720 cm.^{-1}. As shown in Figure 63, the carbonyl peak absorbance continues to increase for a further two hours/runs after the other peak absorbances have all simultaneously reached constant levels. This appears to be a

Frequency ($cm.^{-1}$)	Corresponding bond vibration
2920	C - H stretching (aliphatic)
1720	C = O stretching (esteric - plasticiser)
1423	$-CH_2-$ bending (methylenic)
1331 1257	C - H bending in ClC-H (chloromethylenic)

TABLE 10

INFRARED SPECTRAL DATA RELATING TO THE PVC COATING

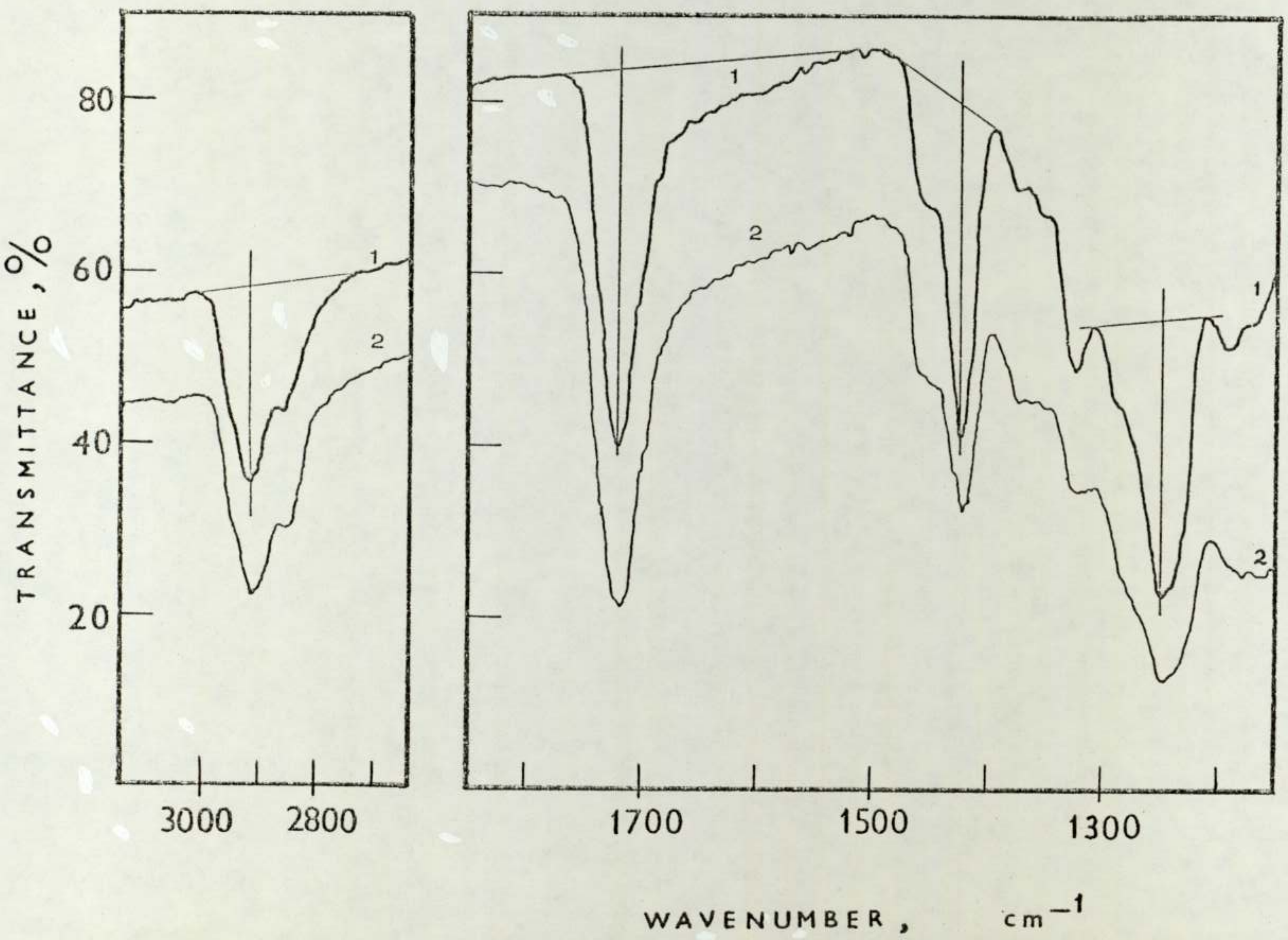


FIGURE 62 -
MIR spectra of the PVC ORGANOSOL matt finish coating after:-
(1) 0 months, and
(2) 12 months natural weathering.

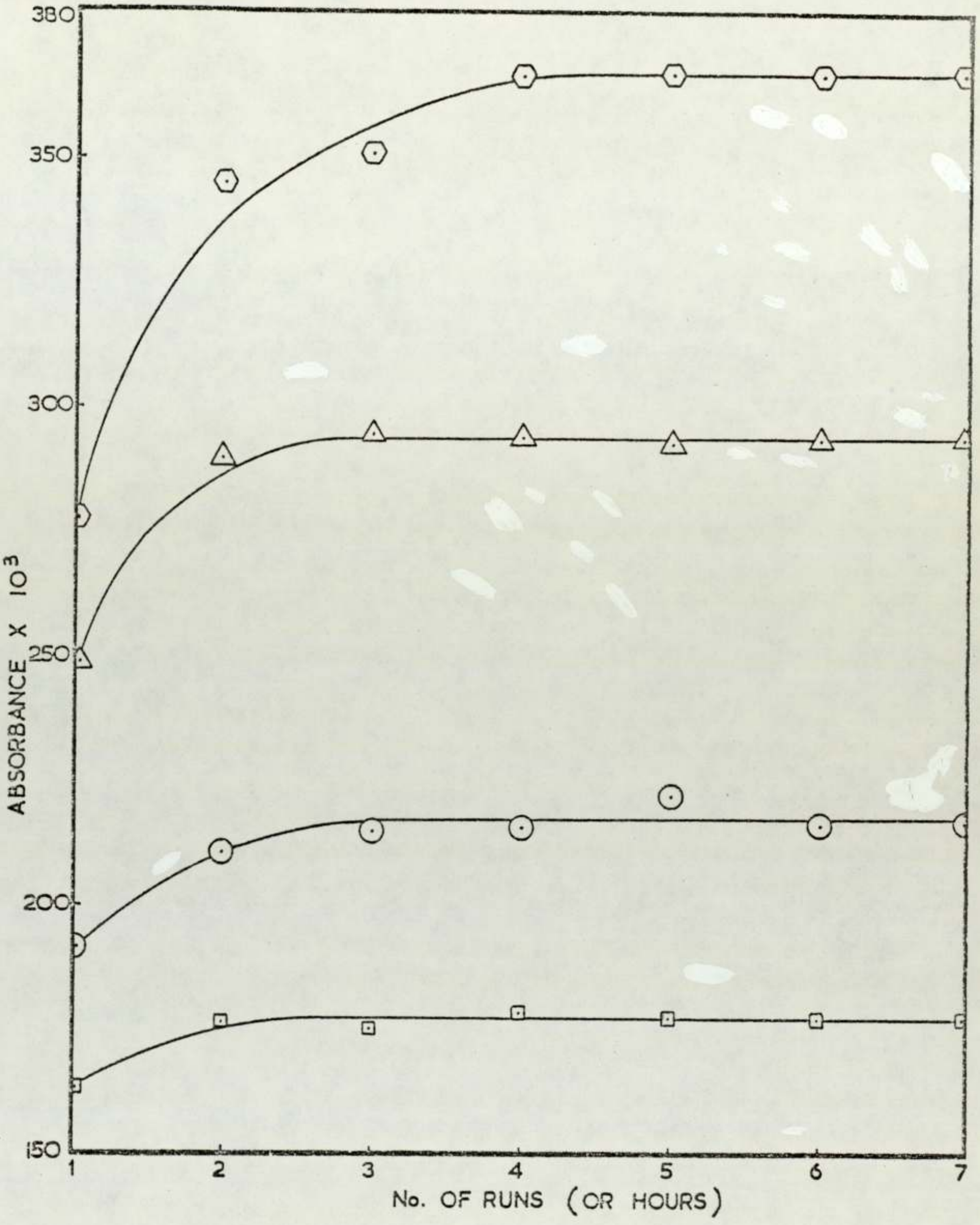


FIGURE 63 - MIRS analysis of PVC organosol coating (after 6 months natural weathering);

⬡ = $-\overset{O}{\overset{\|}{C}}-$ peak at 1720 cm^{-1}
△ = $-CH_2-$ peak at 2920 cm^{-1}
⊙ = ClC-H peak at 1257 cm^{-1}
⊡ = $-CH_2-$ peak at 1423 cm^{-1}

Variation in peak absorbance with time/number of analysis/runs consequence of the second procedural effect which is associated with the migration of plasticiser from the coating's interior to its surface during analysis, ultimately forming, presumably, an "equilibrium" surface layer at the sample-reflector plate interface. This view is substantiated by the fact that residual carbonyl absorption is detectable in the spectrum of the reflector plate alone after sample removal.

Thus, it can now be appreciated why, owing to these two processes, up to as many as seven hour-long (i.e., slow scan) runs were usually needed before reliably stable spectra were obtained for subsequent semi-quantitative study.

As with the previous coatings studied, it was once again found that, on comparing the stable MIR spectra on weathering, the spectral quality varied between samples according to their surface condition and, hence, their achievable degree of contact with the reflector plate. Hence, for semi-quantitative treatment of the data, it became necessary to find a suitable reference peak(s) in the spectrum which was unaffected by weathering and to which changes in other variable peaks could be related. This selection was made, as before, via peak absorbance indexing from which it was determined that the $-CH_2-$ and $C = O$ stretching peaks at 2920 and 1720 $cm.^{-1}$ respectively were each suitable for use in this role as internal reference peaks. The constancy of their ratio (index) to one another throughout the exposure period is shown in Figure 64. However, on relating to these two reference peaks the absorbances of the other two main peaks in the spectrum (Figure 62) - namely, those due to methylenic C - H (1423 $cm.^{-1}$) and chloromethylenic C - H (1257 $cm.^{-1}$)

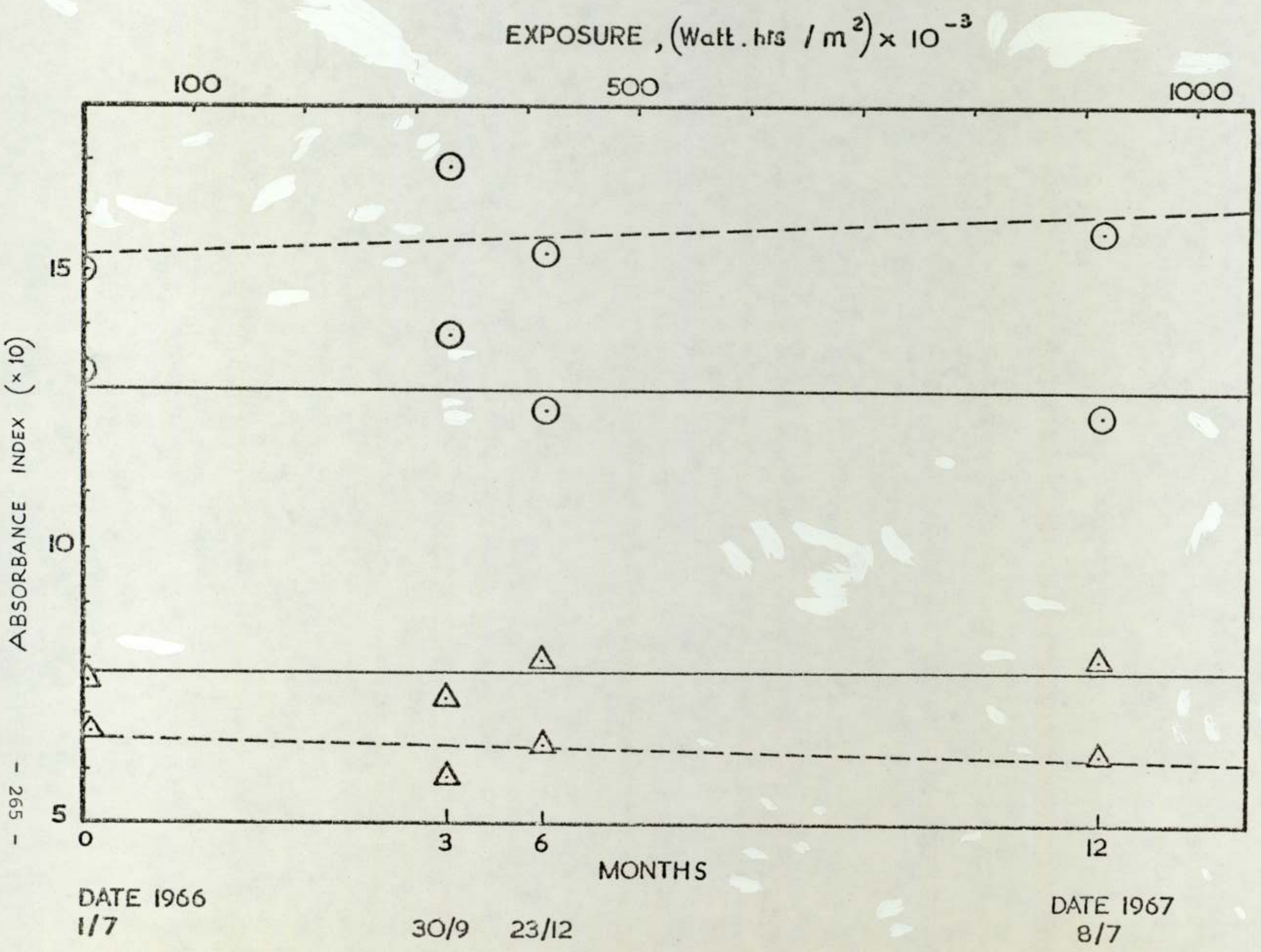


FIGURE 64 - Natural weathering of PVC organosol coating; dependence of infrared peak absorbance indices on exposure:-

⊙ = The index of the carbonyl (1720cm^{-1}) relative to $-CH_2-$ (2920 cm^{-1})

△ = The index of $-CH_2-$ (2920 cm^{-1}) relative to the carbonyl (1720 cm^{-1})

---- = Medium chart speed

—— = Slow chart speed

bending (see Figures 65 and 66 respectively) - significant changes were observed on weathering. In each case, the absorbance index decreased fairly rapidly during the initial summer exposure, less so throughout the autumn, before levelling out during the winter and spring. Furthermore, the extents of their respective index changes were similar throughout such that, when these 1257 and 1423 cm.$^{-1}$ peaks were related to each other (Figure 66), an essentially constant index was obtained.

Hence, it appears from this that the MIRS results presented here are, indeed, descriptive of the chemical changes which are mainly responsible for the parallel changes in surface smoothness and reflectance. This encouraging degree of correlation between data of differing type (Figure 67), thus represents powerful evidence upon which to base a characterisation of the overall weathering process, as will be discussed at the end of this chapter.

V.2.4 Scanning Electron Microscopy

Finally, in the light of the foregoing evidence, scanning electron microscopy (SEM) of this natural weathering series of PVC coating surfaces afforded a valuable means of obtaining qualitative observational support for the weathering proposals. Photomicrographic SEM analysis was carried out using the Stereoscan Mark 2A scanning electron microscope (Cambridge Instruments) at working magnifications of x240 and x6000.

The micrographs obtained show how the initial (i.e., unexposed) paint surface (Plate 24) becomes relatively roughened after

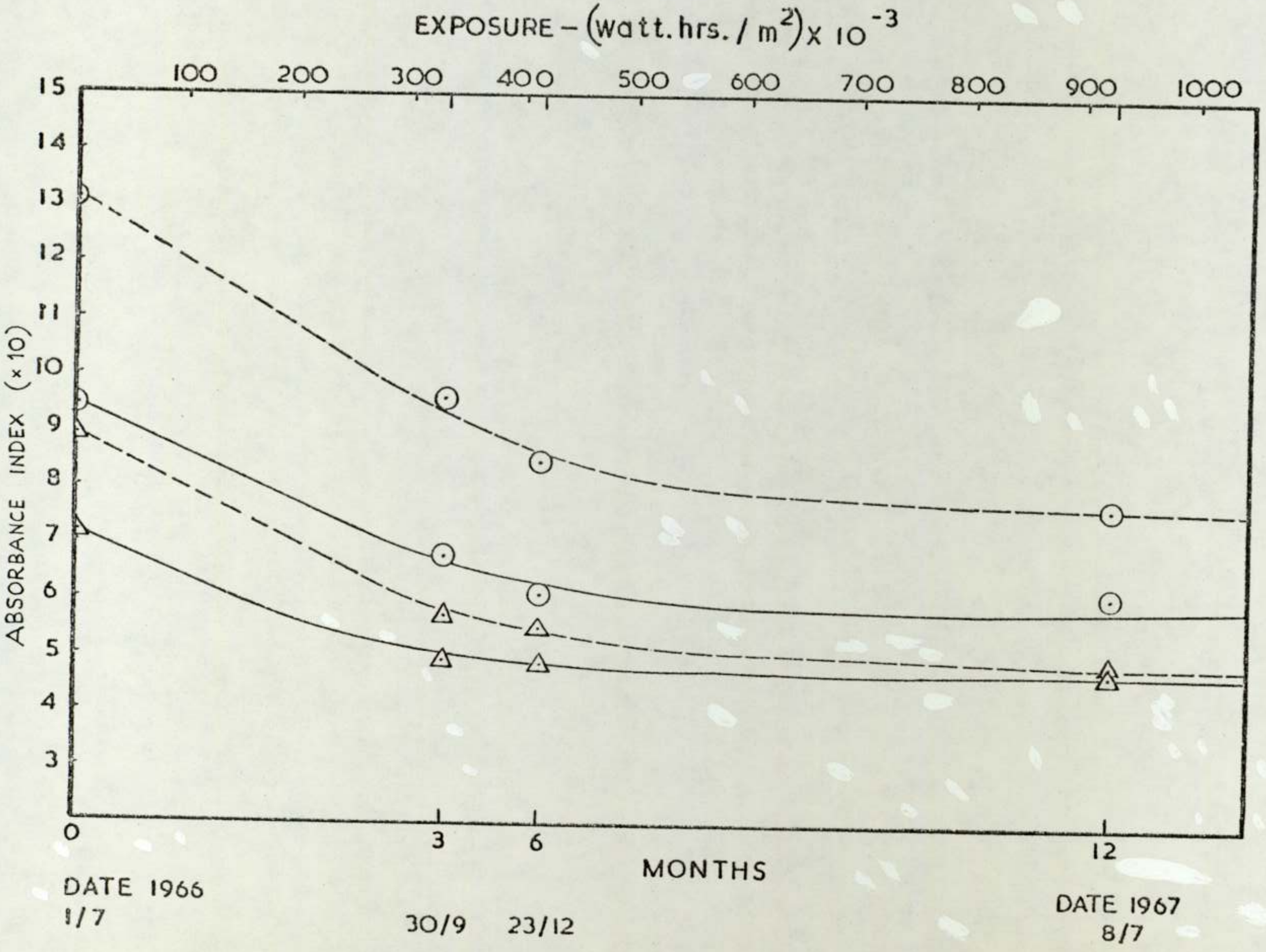


FIGURE 65 - Dependence of the $-CH_2-$ bending (1423 cm.$^{-1}$) peak absorbance index on exposure:-

⊙ = Relative to $-CH_2-$ (2920 cm^{-1})

△ = Relative to $-\overset{O}{\overset{\|}{C}}-$ (1720 cm^{-1})

---- = Medium chart speed

—— = Slow chart speed

natural weathering of PVC ORGANOSOL matt finish coating.

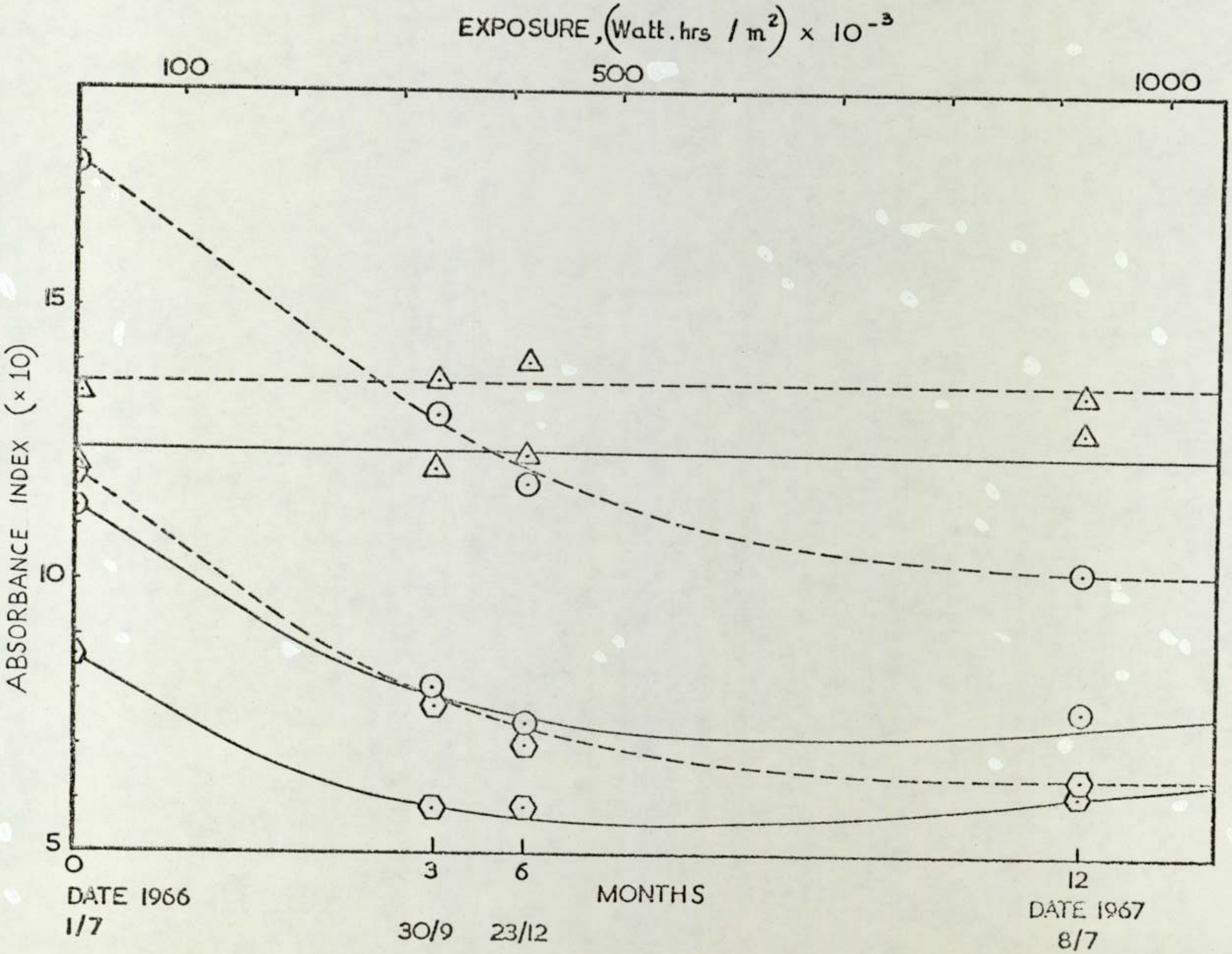


FIGURE 66 - Dependence of the ClC - H bending ($1257\ cm.^{-1}$) peak absorbance index on exposure:-

⊙ = Relative to $-CH_2-$ ($2920\ cm^{-1}$)

⬡ = Relative to $-\overset{O}{\overset{\|}{C}}-$ ($1720\ cm^{-1}$)

△ = Relative to $-CH_2-$ ($1423\ cm^{-1}$)

---- = Medium chart speed

—— = Slow chart speed

Natural weathering of PVC ORGANOSOL matt finish coating.

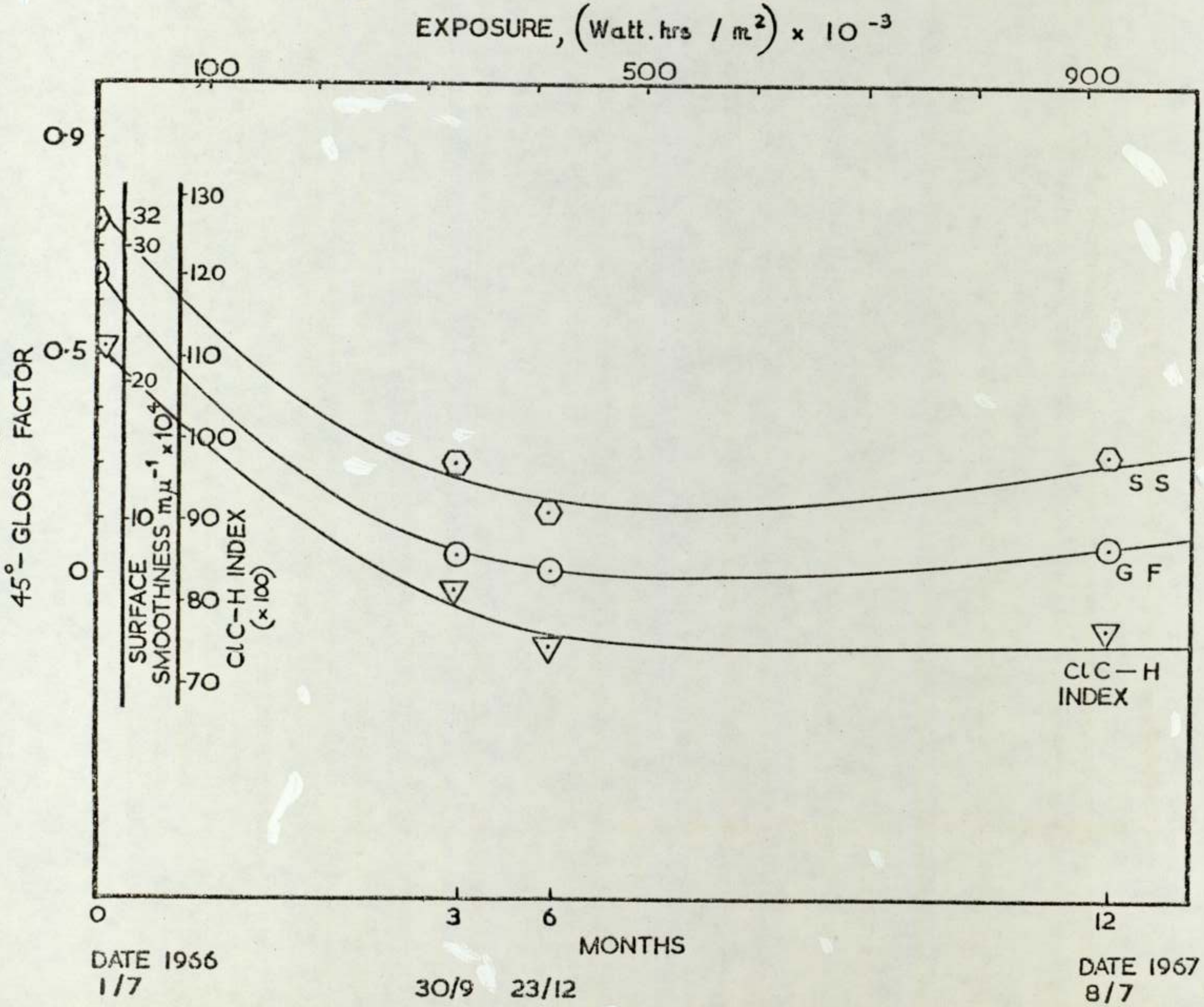


FIGURE 67 -

Exposure dependence of:-

⬡ : surface smoothness (i.e., reciprocal AHRI)

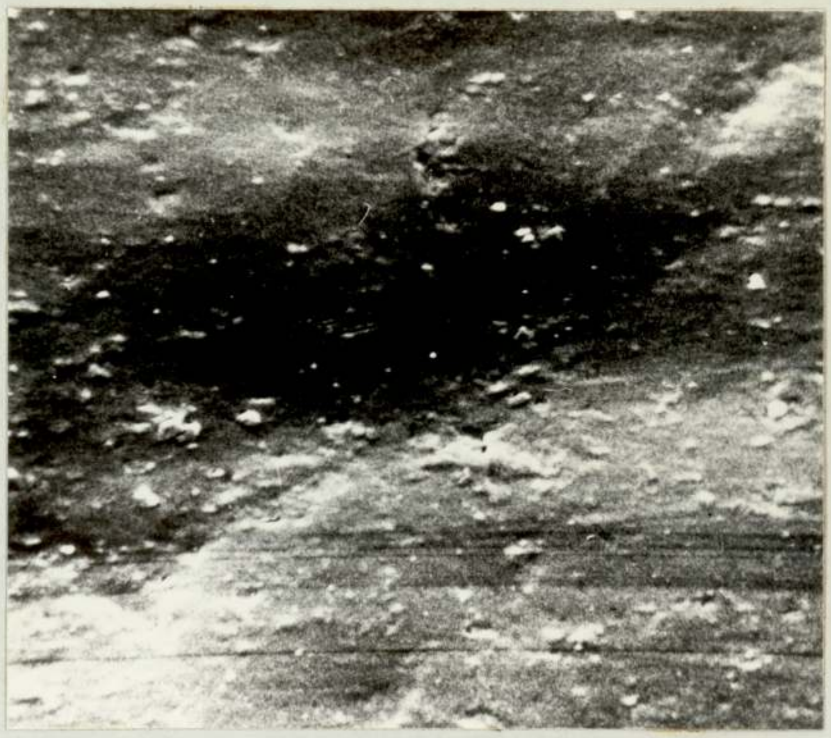
⊙ : (45°) gloss factor

▽ : ClC - H (1257 $cm.^{-1}$) absorbance index (relative to $-CH_2-$ reference peak at 2920 $cm.^{-1}$).

Natural weathering of PVC ORGANOSOL matt finish coating.

3 months of summer exposure (Plates 25 and 26) with the formation of microscopically small cracks in the surface, as observed at the higher (x6000) magnification (Plate 26). This surface deterioration is then seen in Plates 27 and 28, after a further 3 months (autumn) exposure, to be even more pronounced, in accordance with all previous data. Finally, and to particularly striking effect, Plates 29 and 30 confirm how the damaged surface becomes eroded after the winter and spring, relinquishing, in the process, its uppermost degraded layer and exposing fresh areas of surface, as if in readiness for the weathering cycle to repeat itself.

In connection with the surface defects illustrated in the micrographs, there are two further points of interest which need mentioning. Firstly, the multitudinous protuberant irregularities featured in Plates 25 and 27 are unquestionably what the goniophotometer would regard as MACRO-defects, i.e., defects whose size are sufficiently in excess of the wavelength of the instrument's incident light (in this case, considered to be in the region of 700 mμ) to cause angular divergence of the specular beam (cf., 1 cm. in the micrographs at x240 magnification corresponds to an actual lateral distance of approximately 40μ). Hence, it can now be more clearly appreciated that it is this type of relief feature, and its variations on exposure, which are responsible for the coating's initial matt finish and its subsequent weathering changes. The second point of note concerns the micro-cracks evident in the 3 and 6 months weathered surfaces (see Plates 26 and 28 respectively). The likelihood is that, in contrast to protuberant defects, cracks or holes or, for that matter, any openings in the surface tend to act as centres of light dissipation rather than light deflection. Hence, the contribution which these micro-cracks



MAGNIFICATION

x 6000

PLATE 24

PVC ORGANOSOL matt finish coating;

Natural weathering at the BRS exposure site;

Exposure : 0 months (i.e., UNaged sample).

MAGNIFICATION

x 240

PLATE 25

x 6000

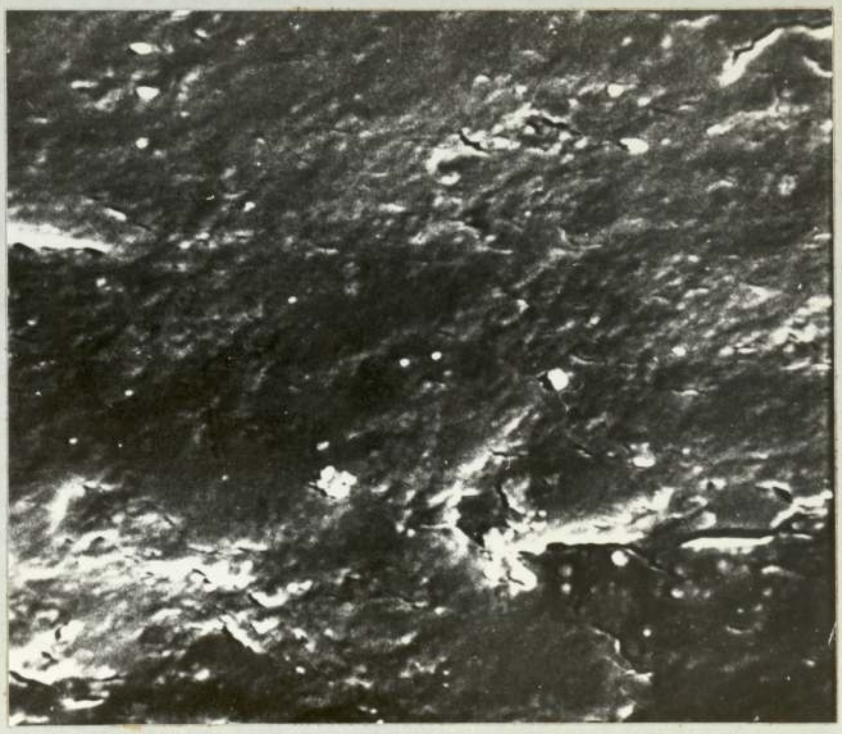
PLATE 26

PVC ORGANOSOL matt finish coating;
Natural weathering at the BRS exposure site;
Exposure : 3 months (summer).

MAGNIFICATION

x 240

PLATE 27



x 6000

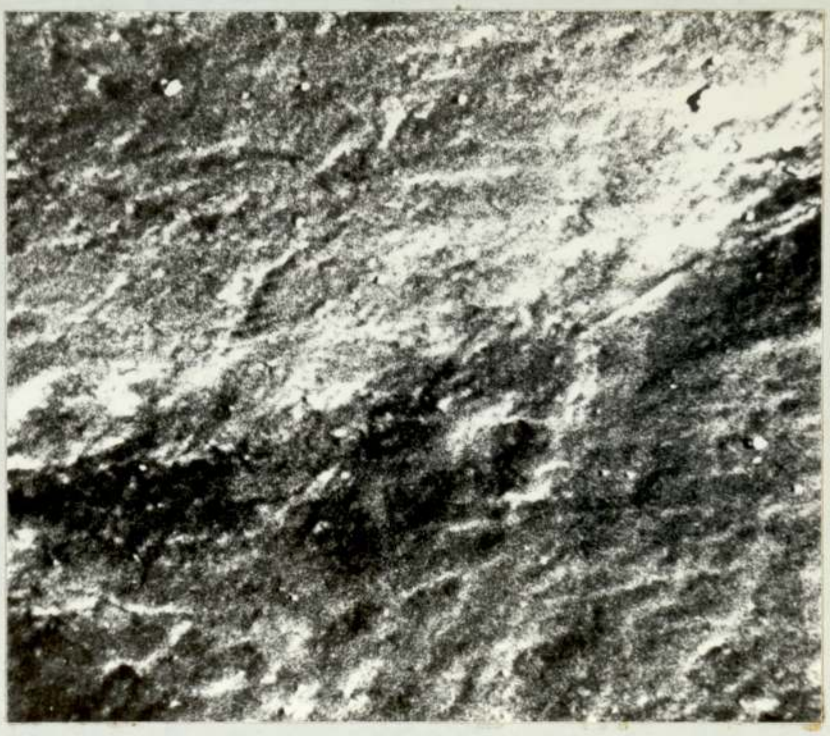
PLATE 28

PVC ORGANOSOL matt finish coating;
Natural weathering at the BRS exposure site;
Exposure : 6 months (summer and autumn).

MAGNIFICATION

x 240

PLATE 29



x 6000

PLATE 30

PVC ORGANOSOL matt finish coating;
Natural weathering at the BRS exposure site;
Exposure : 12 months.

are likely to make to the weathered surface's goniophotometric response will be associated more with a reduction in specular reflectance and, therefore, peak height rather than with any significant increase in peak width (i.e., beam divergence).

(FOOTNOTE: (247) according to the ASTM Designation: D660 - 57, this type of micro-crack formation, as it has been referred to here, is, in fact, more correctly described as micro-CHECKING (in this case, of the so-called "irregular-pattern type"); the distinction being that a break in the surface of a paint film is only termed a crack when it extends through the thickness of the coating to the underlying substrate).

V.3 Artificial Weathering

Artificial weathering of this PVC organosol coating was conducted in the BS 3900 Part F3 apparatus alongside the range of coatings described in the previous chapter. Exposure was extended as far as 4000 hours (approx. 2000 x 10^3 watt hrs./m^2) which roughly corresponds, on an energy of radiation basis, to around two years natural weathering at the Building Research Station exposure site. Sample analysis was by means of goniophotometry and peak count (surface roughness) measurements.

V.3.1 Goniophotometry

Goniophotometry was carried out using the automated instrument and employing wide beam unfiltered mercury light illumination at angles of incidence of 50° and 65°.

On artificial weathering, similar goniophotometric changes to those observed on natural weathering were observed. After fairly rapid early reductions in gloss factor (Figure 68), a period of improvement followed before a terminally stable value was reached. The individual parameter changes in peak height ($I_s - I_d$) and peak width ($W_{\frac{1}{2}}$), as included in Figures 49 and 50 previously, denote the almost exclusive extent to which $W_{\frac{1}{2}}$ changes account for those in the gloss factor. The transitional period which occurs around 600 x 10^3 watt hrs./m^2 (Figure 68) is described further by the goniophotometric curves shown in Figure 69 which serve, once again, to illustrate how visually indiscernable reflectance changes are captured just as vividly by the goniophotometer as those which can be seen in gloss finish paints. Additionally, and highly significantly, of course, Figure 68 also displays extremely close agreement between the results of natural and artificial weathering. This correlation will be discussed at greater length at the close of this chapter.

V.3.2 Surface Roughness Measurements

Surface roughness measurements, in this case, in the form of peak count (PC) analyses, were conducted using the Talysurf 4 instrument. As was suggested by earlier results (Figure 51 in section IV.3.2) relating to the previous coatings studied, the peak count per unit length of the surface again appears to be linearly related to the log (gloss factor) term (Figure 70). Thus, the reinforcement of this earlier view lends further weight to the argument that the number, as well as the size (AHRI), of the surface irregularities can be taken as being directly correlative, rather than merely contributive, to observed reflectance changes.

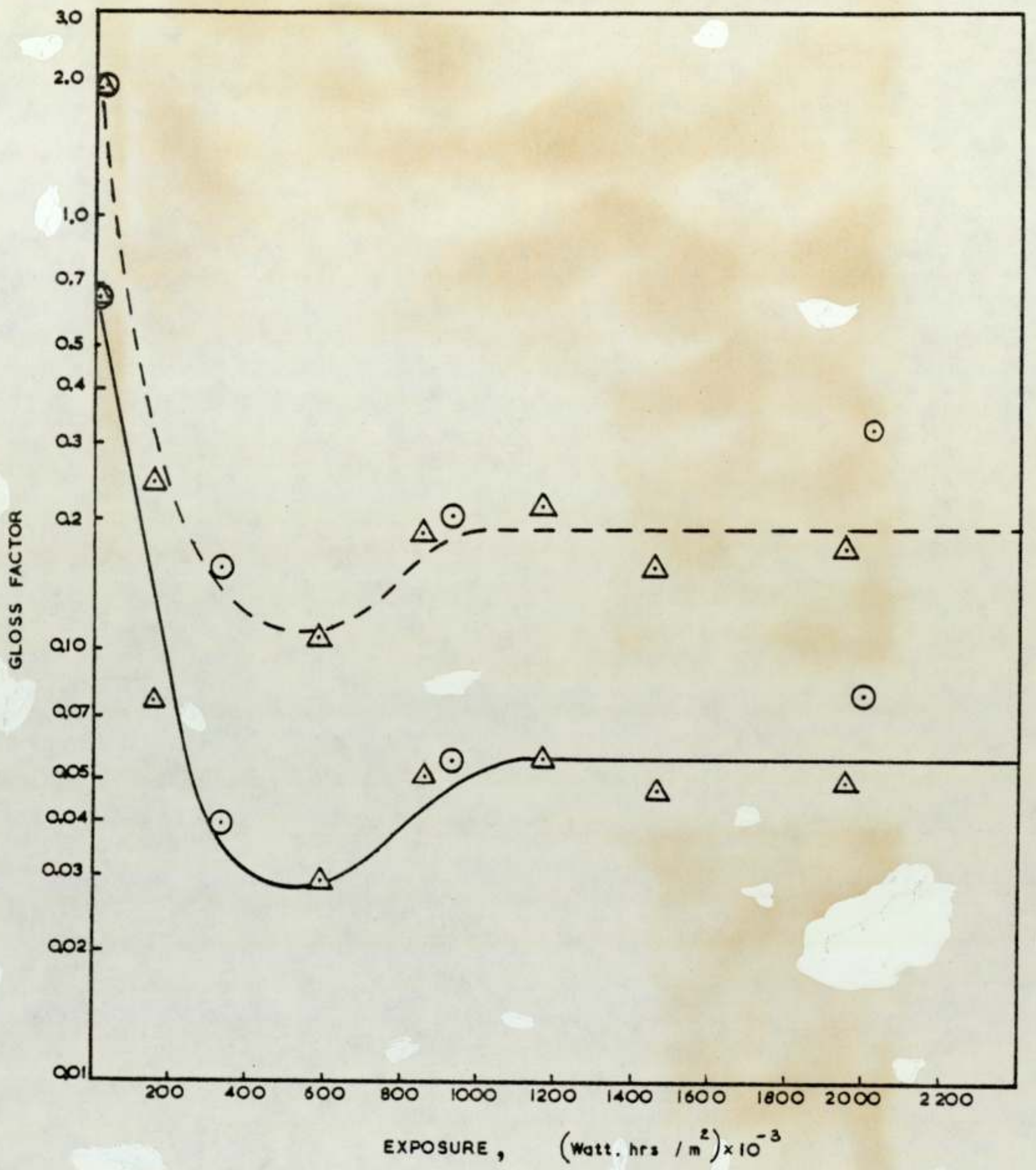


FIGURE 68 - Variation in log (gloss factor) on

⊙ : natural weathering

△ : artificial weathering

of PVC organosol matt finish coating;
angle of incidence:-
——— = 50°, and ----- = 65°.

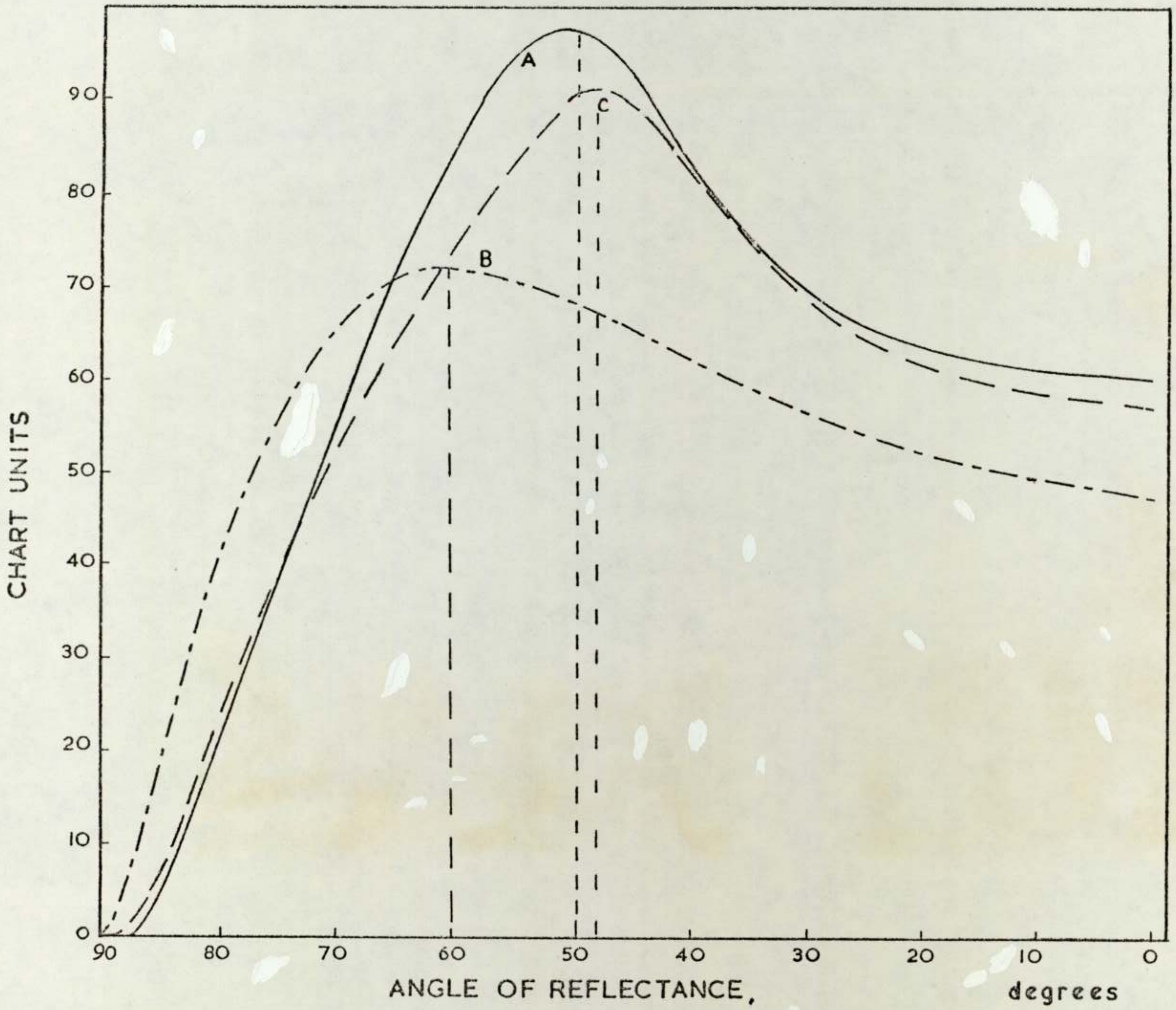


FIGURE 69 -
Goniophotometric curves
relating to PVC organosol
matt finish coating after:

A = 150,

B = 600,

C = 1250

watt hrs./m^2
artificial weathering;

angle of incidence
= 50^o.

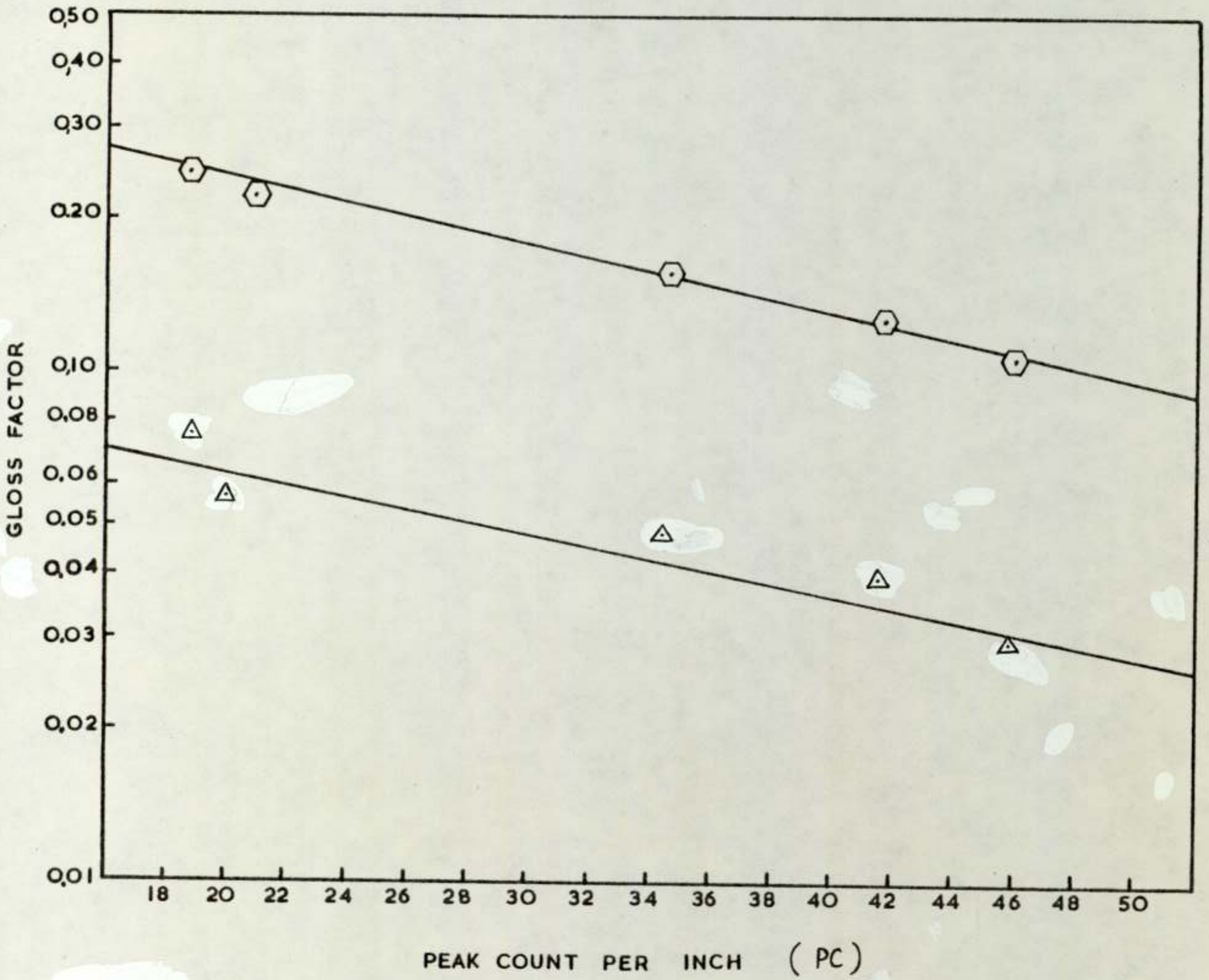


FIGURE 70 -

Dependence of log (gloss factor) on peak count per inch;

angle of incidence:-

△ = 50°,

⊙ = 65°;

artificial weathering of PVC organosol matt finish coating.

V.4 Discussion

Whereas the main theme of the previous chapter was essentially concerned with the application of a selected combination of analytical techniques to the ageing study of a variety of commercial paint systems, this chapter has followed on from this by taking a more in-depth look at a particular coating material. The coating chosen for this study, a PVC organosol matt finish paint, has been found here to be eminently suited to the methods of analysis utilised previously.

Hence, on the basis of all of the foregoing evidence relating to this PVC coating, it is considered useful here to try to compile a chronological "calendar" of events by which to describe the weathering process over the first 12 months. In any such discussion of paint film deterioration, we must firstly consider the chemical processes which invariably form the roots of the major degradative mechanisms. From the MIRS data presented earlier in this chapter, it appears that, in accordance with generally accepted theories, the dominant chemical changes induced during the PVC coating's initial summer exposure are triggered off by both methylenic and chloromethylenic hydrogen abstraction from within the polymer. This is evident from the related decreases in their associated 1423 and 1257 $cm.^{-1}$ peak absorbance indices (Figures 65 and 66) which, furthermore, indicate that these two alternative initiation steps are highly competitive with respect to one another. However, these changes were not accompanied by any significant increase in absorption in the (C = C) double bond region (around 1650 $cm.^{-1}$) of the spectrum. This suggests that reaction subsequently proceeds via chain radical combination with, for example, oxygen or a stabilising additive in the system rather than by dehydrochlorination leading to structural unsaturation. This is not to say, however, that dehydrochlorination does not occur, but merely that, in this instance, and at this stage, it is of apparently minor importance.

Thus, whatever the exact nature of the ensuing degradation process is, it is undoubtedly this which is predominantly causative of the measured surface roughness changes during the summer. These latter rugosity changes appear, from combined Talysurf/goniophotometric data, to consist of a certain amount of MICRO-defect formation superimposed upon a concurrent augmentation of the existing (matt finish) MACRO-profile. These separate developments account for the respective specular reflectance (I_s) and, hence, peak height ($I_s - I_d$), decreases and the peak width at half-height ($W_{\frac{1}{2}}$) increases observed goniophotometrically (Figure 56). Normally, these reflectance changes would now forge the last remaining link with subjective visual gloss assessments of the surface, although, of course, this coating's matt finish precludes this final interrelation from being made.

Having, thus, characterised the effects of summer exposure, the subsequent weathering changes can also be interpreted in a similar way. Hence, during the following three months autumn ageing, it is clear that a general slowing down of all of the aforementioned (summer) processes takes place, almost certainly as a direct result of the lower autumnal solar radiation intensity and, therefore, reduced rate of photolytic initiation. However, this, as yet, almost exclusively photochemical weathering deterioration, gradually becomes offset during the winter and spring by the countervailing, physically erosive effects of wind and rain, etc., which start to exert proportionately more influence on the proceedings. This change in weather conditions manifests itself in the coating's ageing response as a slight improvement in surface condition, presumably brought about by means of physical erosion; this view being confirmed by a decrease in the average height of the roughness irregularities (Figure 59) leading to a slight improvement in reflectivity. Additionally, the combined specular reflectance (Figure 57) and Talysurf (Figure 59) data indicate, respectively, that erosion is of both the fragile micro-imperfections formed during the earlier exposure and the underlying macro-profile. The net result, therefore, is that fresh areas of surface become exposed during the spring, as substantiated by the infrared spectral data of Figures 65 and 66.

Hence, the previously claimed suitability of this particular PVC organosol coating for this type of study can now be more readily appreciated. Not only does the inherent susceptibility of PVC to photodegradation allow for more pronounced changes to be monitored during the summer and autumn, but the relative softness of this coating is subsequently able to reflect the changing pattern of weathering behaviour during the winter and spring, as the physico-chemical balance of weathering factors shifts in greater favour of its physically erosive elements.

Of further significance in this study has been the way in which scanning electron microscopy (SEM) of these PVC coating surfaces has been able to lend valuable qualitative support to these weathering proposals. As seen previously in Plates 24 - 30, the micrographs are largely confirmative of the proposed summer/autumn deterioration - winter/spring erosion cycle, a pattern of behaviour, incidentally, which

is not all that uncommon in the weathering of paints and plastics (139).
However, although SEM is, indeed, an extremely powerful research tool in any surface study, it is also probably true to say that, when applied to the study of paint film deterioration, its micrographic data tends to be more interpretive when viewed in conjunction with other more quantitative information than if merely considered on its own.

As regards the three main techniques used, however, - goniophotometry, MIRS and surface roughness studies - they have each been re-affirmed here as valuable methods of analysis which are particularly suitable for monitoring the types of changes encountered in most paint films on weathering. Goniophotometry, especially, has been shown to be extremely versatile as regards its applicability to a wide variety of surfaces ranging from the smooth, gloss finishes of the coatings examined in the previous chapter, to the relatively rough, matt finish of the PVC organosol coating studied here. Surface roughness (Talysurf) and MIRS analyses, however, each have their own procedural disadvantages which tend to impose limitations on their applicability in certain instances. On the one hand, Talysurf characterisation of smooth (glossy) surfaces is often instrumentally unreliable, whereas, in the case of MIRS analysis, it is as the surface gets rougher that spectral quality suffers. Nonetheless, the combination of analytical techniques used here have proved, in the particular case of this PVC coating, to be extremely informative in respect of its weathering performance, certainly more so than the mechanical testing methods employed in earlier studies carried out by Building Research Station workers (10).

A further interesting feature to emerge from this study concerns the utilisation of unfiltered (i.e., multichromatic) mercury light as the incident light employed in the goniophotometric analysis of this PVC paint. As was hoped, this measure appears to have succeeded in integrating a "graduated" light wavelength-defect size dependence into the measured reflectance changes. Theoretically, this allows for closer interrelation to be progressively maintained between the reflectance and surface roughness changes, as, indeed, appears to be borne out by the results presented here. One possible example of this is illustrated by the fact that the logarithmic dependence of the gloss factor on both the average height (AHRI) and number (i.e., peak count) of the roughness irregularities, as first proposed in the previous chapter, is even more closely confirmed (Figures 60 and 70) in this latter study. With further regard to the interrelation between goniophotometric and surface roughness data, it was also interesting to note, in the case of this PVC coating, that for the deteriorating surface to become measurably efficacious of an angular displacement of the specular beam, the AHRI appeared to need to attain a value in sufficient excess of the (maximum) wavelength of the incident light (Figure 61).

Finally, and in common with the previous coatings studied, close agreement was found to exist between the gloss factor changes brought about by natural and artificial weathering (Figure 68). Whilst this is highly encouraging from the point of view of being able to predict, from BS 3900 Part F3 tests, the likely outdoor performance of this type of coating, the high degree of correlation is, to some extent, surprising, bearing in mind the believed importance of the more physical aspects of natural weather in giving rise to an apparently seasonally dependent ageing response. However, despite the fact that (a) the BS 3900 Part F3 weathering cycle cannot even hope to duplicate the allegedly erosive physical elements of winter/spring exposure, coupled with (b) the 24 hour periodicity of its repeating cycle as opposed to the yearly cycle of natural weather, it is still seen to induce a highly comparable, energy-based sequence of gloss changes (Figure 68) to that of natural weathering. One possible explanation of this which must be considered here is that the gloss changes in this PVC coating on outdoor exposure are not as singularly descriptive of seasonal weather variations as was thought. This consequently raises the question as to whether this particular paint system has an in-built capacity of its own for surface "renewal" when deterioration reaches a certain stage. Hopefully, the more detailed look at PVC-based coatings which now follows may go at least some way towards clarifying this point.

CHAPTER VI

NATURAL WEATHERING OF POLY (VINYL CHLORIDE) PLASTISOL SURFACE COATINGS

CHAPTER VI

NATURAL WEATHERING OF POLY (VINYL CHLORIDE) PLASTISOL SURFACE COATINGS

VI.1 Introduction

In this and the following chapter, the weathering characteristics of poly (vinyl chloride) (PVC) as a paint vehicle are examined more fundamentally within the simplified framework of purpose-formulated plastisol coatings, as detailed in Tables 2 and 3 previously (see section II.2.2, page 69). As can be seen from these Tables, the most "complete" formulation, containing pigment and two stabilisers, is broken down as far as, simply, plasticised PVC (i.e., with no additives) so as to form a series of eight coatings. Consequently, this also allows for appropriate weathering combinations to be selected across the series in order to "isolate", hopefully, the effects of individual additives within the coating system on exposure. In addition, and partly as a result of natural weathering experience gained here with the first plastisol series (i.e., Series I in Table 3), a second, parallel, but lower-plasticised series of coatings (Series II in Table 3) was studied in order to elucidate upon suspected plasticiser effects. However, this latter series comparison is only made for artificial weathering in the following chapter, the natural weathering results presented here relating exclusively to the more highly plasticised (Series I) coatings.

Natural weathering exposure was conducted at three vastly different outdoor locations (each of which have previously been described in section II.3.1), viz.:-

(i) at the Building Research Station (BRS), Garston, exposure site,

(ii) at the Gravelly Hill motorway link, and,

(iii) on the Aston University roof.

This study, therefore, also affords an insight into the influence which the individualistic nature of each outdoor site has on weathering behaviour, whilst the length of exposure for which results are reported here ranges from 12 months at Gravelly Hill and Aston to up to 27 months at the BRS site.

Finally, the three main analytical techniques employed in this study were goniophotometry, multiple internal reflectance spectroscopy (MIRS) and scanning electron microscopy (SEM), in support of which some preliminary contact angle hysteresis, thermal (glass transition temperature, T_g), mechanical (microindentation) and energy dispersive X-ray (EDXA) analyses were also carried out.

VI.2 Garston Exposure

Natural weathering of the Series I (see Table 3) PVC plastisol coatings at the BRS exposure site at Garston consisted of two separate exposures, firstly involving three and then, later, four of the eight possible formulations. By far the major of these two studies was the earlier one involving the coatings trio:-

(i) plasticised PVC (clear),

(ii) plasticised PVC + pigment,

(iii) plasticised PVC + pigment + UV and thermal stabilisers.

Exposure of these three coatings was commenced on 29th June, 1973, at the beginning of the summer season, with the main study period covering the following 17 months up to 29th November, 1974; however, at the time of writing, it has also been usefully possible to include here some terminal 27 month (2nd October, 1975) data.

The second exposure series, on the other hand, comprised the following four unpigmented coatings:-

(i) plasticised PVC alone,

(ii) plasticised PVC + UV stabiliser,

(iii) plasticised PVC + thermal stabiliser,

(iv) plasticised PVC + UV and thermal stabilisers,

which, apart from being supplementary to the earlier exposure series, primarily formed, in conjunction with parallel-running exposures at Aston and Gravelly Hill, part of a wider, although less detailed, study encompassing a comparison of weatherability in differing outdoor environments. This latter experiment was of 12 months duration and, so as to provide a further comparison with the previous experiment, was initiated during the early autumn (2nd October, 1973) as opposed to at the beginning of summer. The report of this second exposure, which is restricted to goniophotometric and SEM(/EDXA) data, is presented at the end of this section VI.2.

VI.2.1 Goniophotometry

Throughout this entire section of the project dealing with

PVC plastisol coatings, goniophotometric analyses were carried out using the automated instrument and employing, exclusively, multichromatic (i.e., unfiltered) mercury light illumination at an angle of incidence to the sample surface of 50°. Also, unless otherwise stated, the so-called "wide" beam was used in common with most of the previous work.

On natural weathering of the:-

(i) plasticised PVC,

(ii) plasticised PVC + pigment,

(iii) plasticised PVC + pigment + UV and thermal stabilisers,

gloss finish coatings' series, significant reflectance changes occurred in each case. As seen in Figure 71, after varied early changes during the first two months exposure which, in the case of such soft coatings as these, are somewhat suggestive of sample equilibration effects dependent on the initial state of the coating surface, relatively marked decreases in specular reflectance (I_s) then followed. However, these decreasing I_s trends, representative of progressive micro-defect formation, are subsequently and abruptly reversed for each of the three coatings, the respective improvements in reflectance appearing after 6 months weathering in the case of the two pigmented formulations and after 9 months for the clear (i.e., unpigmented) sample. These intervals of recovery in surface condition, however, are seen in Figure 71 to be relatively short-lived before they are just as quickly followed by further periods of deterioration exhibiting substantially similar rates of I_s decrease to those which were in evidence immediately prior to the improvements taking place. The progressive reductions in I_s, in the case of the two pigmented coatings,

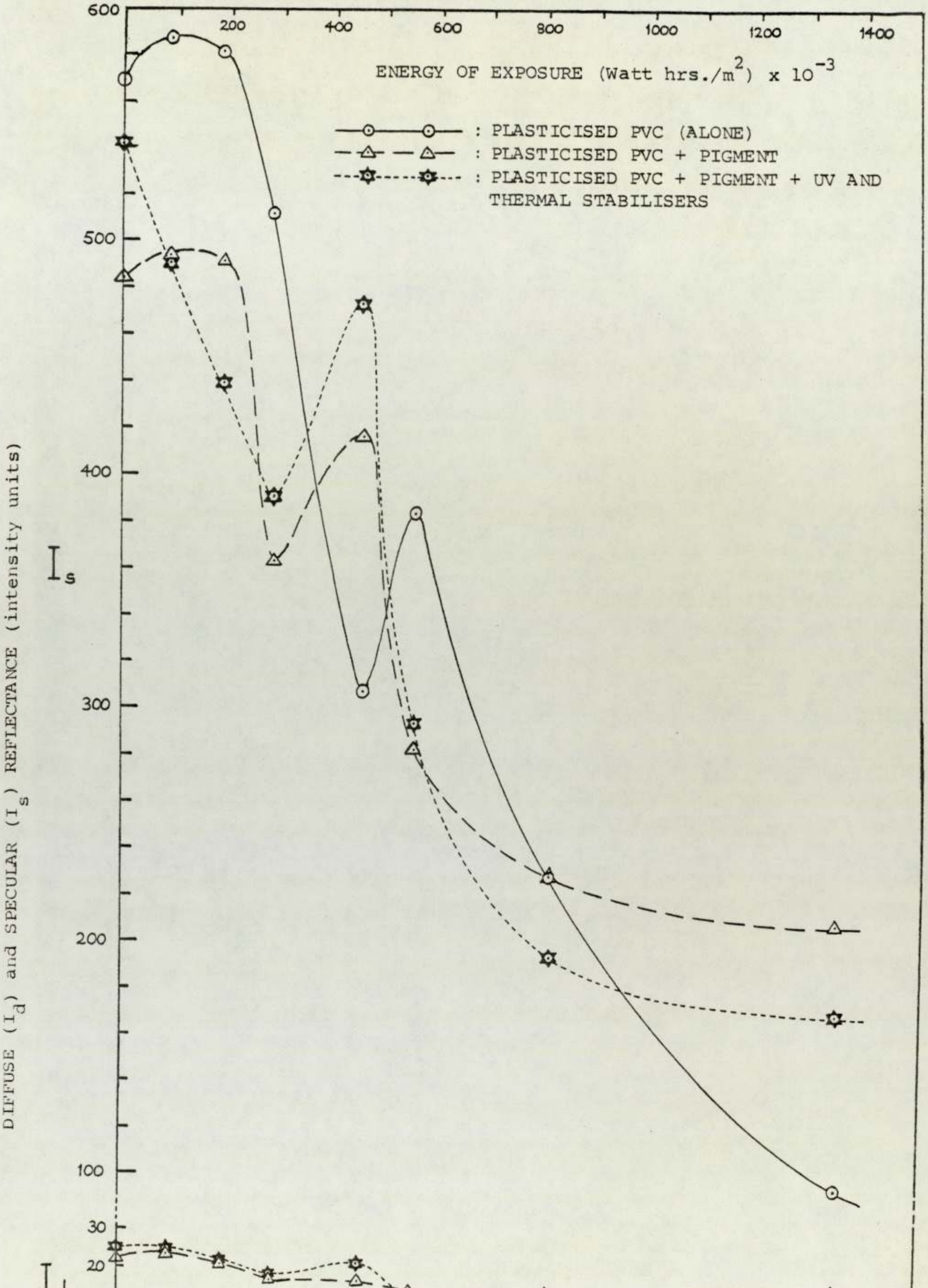


FIGURE 71 - Natural weathering of PVC plastisol coatings at the BRS site (Garston); variation in specular (I_s) and diffuse (I_d) reflectance on exposure.

then tail off towards the end of the reported exposure period, in contrast to that of the clear coating which continues its rapid decline. Indeed, this latter unpigmented sample, by the end of 17 months ageing, appeared extensively degraded with small, dark brown spots liberally covering its entire surface area. On the other hand, the two pigmented films were still very much intact and, apart from being appreciably dirtied by the end of the exposure, were not noticeably discoloured.

In comparison to the specular reflectance (I_s) changes, the variations in diffuse reflectance (I_d) are seen, also in Figure 71, to be relatively insignificant. Hence, the I_s changes can be regarded as being predominantly determinative of the overall peak height ($I_s - I_d$) changes. Similarly, on comparing the I_s and gloss factor graphs (Figures 71 and 73 respectively), the extent to which changes in the former are clearly descriptive of those in the latter, indicate that the magnitude of the peak width ($W_{\frac{1}{2}}$) changes, shown in Figure 72, contribute relatively little towards the overall gloss factor changes, except in the terminal stages of the unpigmented coating's exposure and after 6 months in the case of the pigmented, unstabilised sample.

Thus, it appears that the observed reflectance changes can still be largely accounted for in terms of the progressive formation/dismission of what the goniophotometer still regards as micro-imperfections of the surface. However, before any firm conclusions can be drawn, this suggestion obviously requires some support, which, hopefully, surface microscopy can now provide.

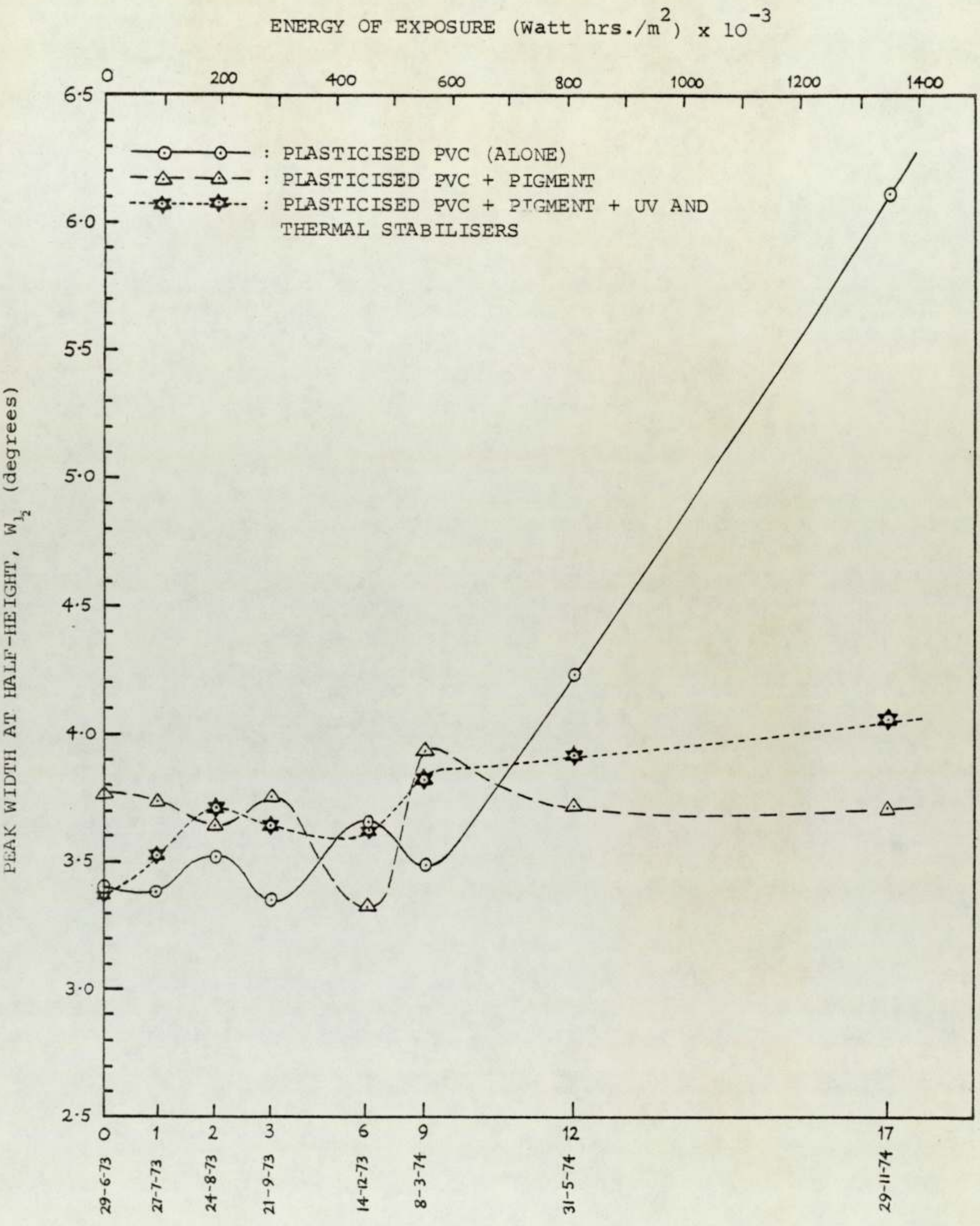


FIGURE 72 - Natural weathering of PVC plastisol coatings at the BRS site (Garston); variation in peak width at half-height ($W_{\frac{1}{2}}$) on exposure.

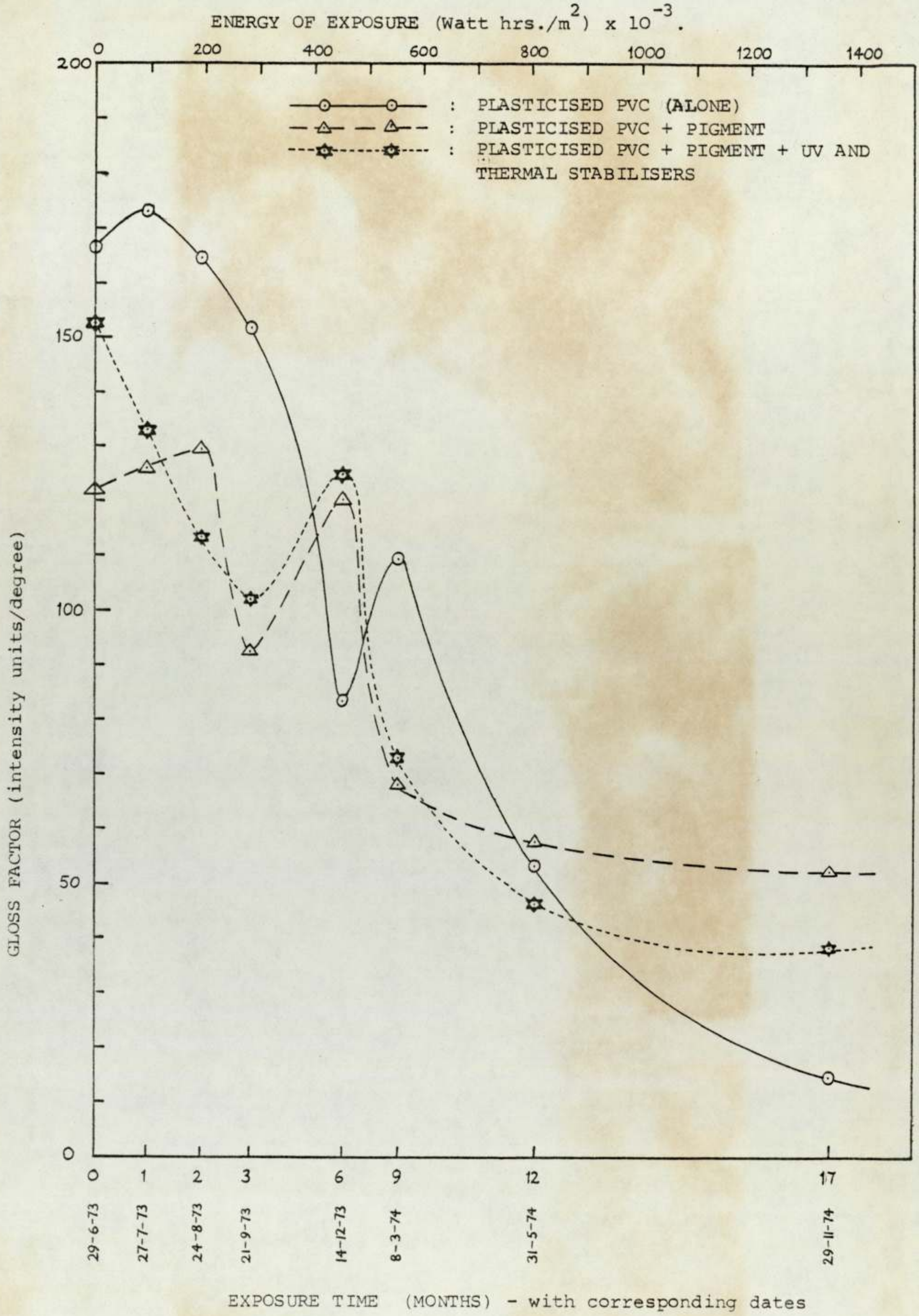


FIGURE 73 - Natural weathering of PVC plastisol coatings at the BRS site (Garston); variation in gloss factor on exposure.

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VI.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) of weathered coating samples, taken specifically from goniophotometric areas of analysis, was carried out using the Stereoscan Mark 2A instrument previously described. Attention in this particular SEM study was focussed on the significant changes apparently taking place in the two pigmented coatings between 3 and 9 months weathering exposure, during which period their respective gloss factors displayed transitionary trends (Figure 73). The Stereoscan micrographs obtained of the pigmented, but unstabilised, plasticised PVC coating after 3, 6 and 9 months weathering, and at approximate magnifications of x200, x1000 and x5000, are presented as Plates 31 - 39 alongside each other for ease of comparison.

On comparing the micrographs of the 3 and 6 months weathered surfaces, differences in surface appearance are only really noticeable at the highest (ca. x5000) magnification (cf. Plates 33 and 36). This is consistent with the goniophotometric view that the improvement in reflectance brought about during the second three months of exposure is mainly, although, in this particular case, not entirely, due to a micro-textural surface improvement. Thus, bearing in mind that the goniophotometric micro-macro size "transition" occurs at around an average defect height/lateral extent of 700 $m\mu$ (when unfiltered mercury incident light is used), which corresponds in Plates 33 and 36 to a lateral distance of approximately 4 mm., it can therefore now be seen that the dismission of the obvious mixture of both micro- and macro-irregularities in the 3 months weathered surface (Plate 33) is in powerful agreement with the related goniophotometric (I_S, $W_{\frac{1}{2}}$ and, hence, gloss factor) changes previously described. This apparent surface

PLATE 31

3 months

x 235

PLATE 32

3 months

x 1170

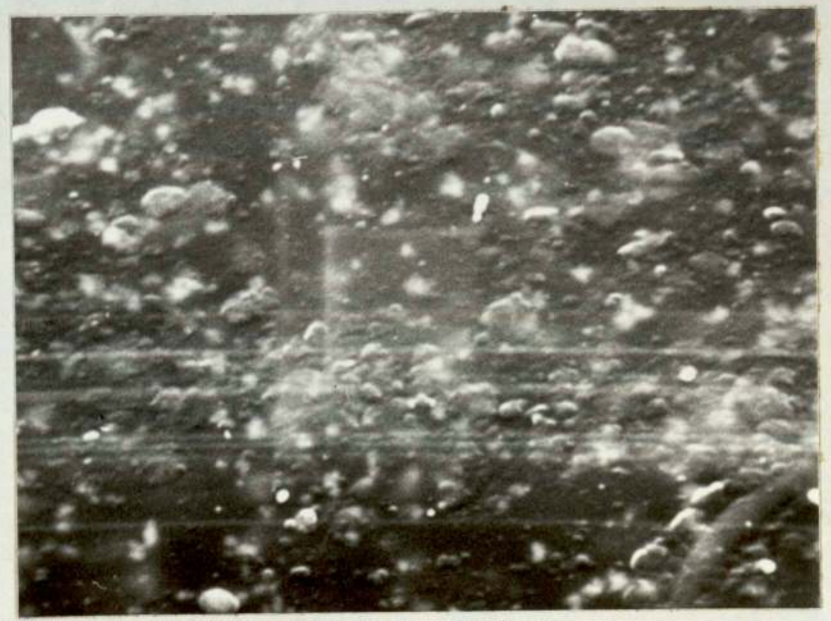


PLATE 33

3 months

x 5800

PLASTICISED PVC + PIGMENT plastisol coating;
Natural weathering at the BRS exposure site.

PLATE 34

6 months

x 225

PLATE 35

6 months

x 1100

PLATE 36

6 months

x 5500

PLATE 37

9 months

x 225

PLATE 38

9 months

x 1110

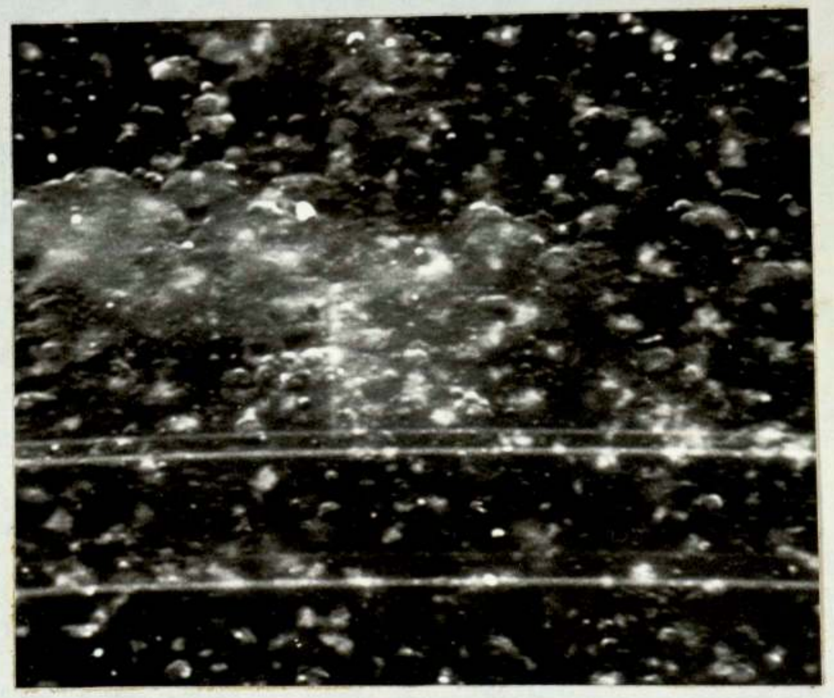


PLATE 39

9 months

x 5550

improvement after 6 months, however, is subsequently followed by a period of second-stage deterioration which, after 9 months, has reached the stage shown in Plates 37 - 39. Whereas the general re-roughening of the surface (cf. Plates 36 and 39) was previously indicated by goniophotometry, one aspect of deterioration which it was not able to sense, and which the SEM micrographs here show quite clearly, is the onset of "flaking" in the coating surface (Plate 38). Although this development obviously constitutes macro-deterioration, it is evident from goniophotometry that it is not sufficiently far advanced to effect a commensurate enhancement of the surface's light divergent (i.e., peak width, $W_{\frac{1}{2}}$, increasing) properties. Indeed, it can be seen from Plate 38 that most of the flakes are not yet completely detached in a way which would allow for their residual surface impressions to be effectively light divergent. The various stages of this flaking process are strikingly captured in the micrographs from the earliest outline of a potential flake (Plate 39) through to its actual detachment from the surface (see additional Plates 40 and 41 overleaf). Finally, essentially matching micrographic data to that described here was also obtained for the "complete" (i.e., pigmented + UV and thermally stabilised) coating and is, therefore, open to similar interpretation.

Hence, this SEM study has provided a classic example of the way in which SEM can combine most effectively with goniophotometry in characterising surface deterioration and its effect on gloss. These two techniques have shown themselves here to be manifestly complementary in the manner in which they not only aid but also add to the interpretation of each other's data.

MAGNIFICATION

x 2200

PLATE 40

x 5500

PLATE 41

PLASTICISED PVC + PIGMENT plastisol coating;
Natural weathering at the BRS exposure site.
Exposure : 9 MONTHS (June - March).

VI.2.3 Multiple Internal Reflectance Spectroscopy

Due to the soft, pliable nature of these plastisol coatings, promoting intimate surface-to-reflector plate contact, good quality MIR spectra were generally obtained. However, this advantage was largely offset by the high plasticiser content of the coatings giving rise to spectral absorbancies which tended to mask the most diagnostic peaks due to the polymer. On comparing the MIRS spectra obtained (Figures 74 and 75) with reference infrared spectra of PVC and the diisooctylphthalate (DIOP) plasticiser (Figures 76(a) and (b) respectively), the sample polymer peaks which appeared to be the least affected by plasticiser interference and whose possible weather dependency could, therefore, be monitored by absorbance indexing were those at around:-

3450 cm.$^{-1}$		due to alcoholic O - H stretching,
1423 cm.$^{-1}$		due to C - H bending in $-CH_2-$, and,
1334 cm.$^{-1}$	(shoulder)	due to C - H bending in ClC - H;

Of these peaks, by far the most reliable, in terms of combined binder (i.e., PVC) ageing diagnosis/ease of measurement, was the one at 1423 cm.$^{-1}$. In comparison, the 1334 cm.$^{-1}$ (shoulder) absorbance was relatively indistinct to start with (due to the adjacency of plasticiser absorbance) and became progressively more so on weathering, whereas the 3450 cm.$^{-1}$ O - H peak, although easily measurable throughout, could not unequivocally be attributed to oxidation of the polymer alone in view of the plasticiser's own known oxidisability on ageing.

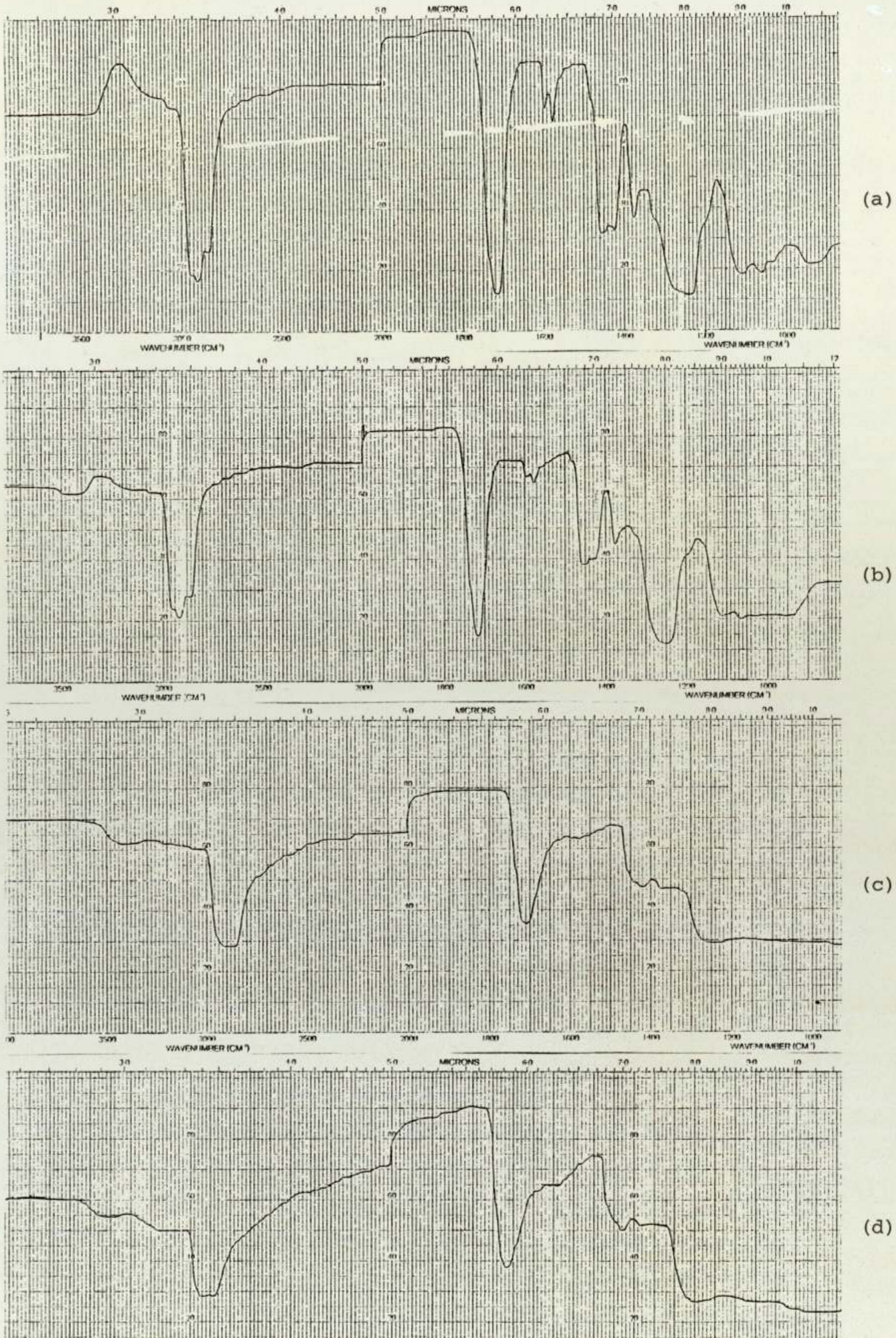
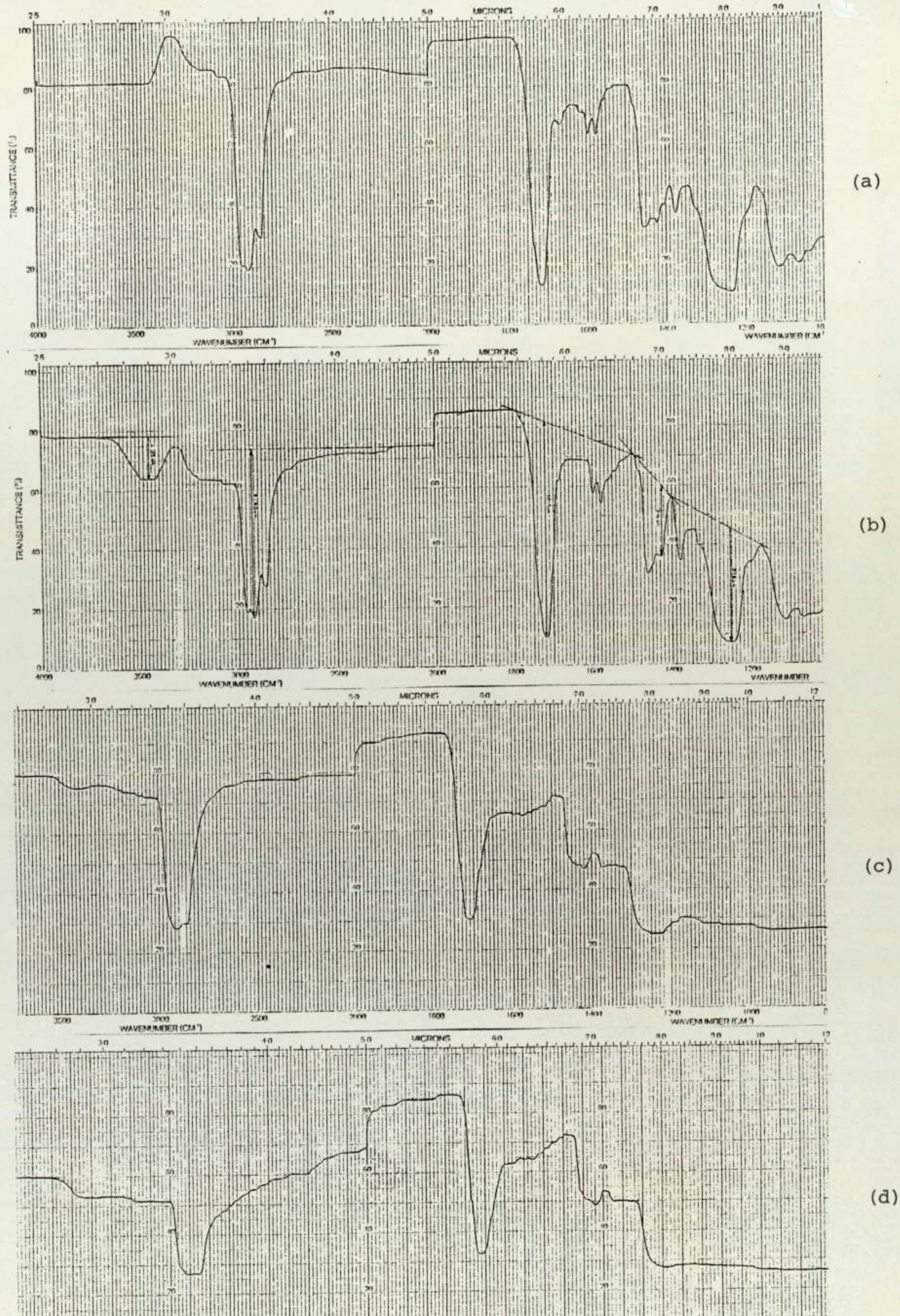


FIGURE 74 - MIRS spectra relating to the natural weathering (Garston) of the PLASTICISED PVC + PIGMENT coating after (a) 0, (b) 3, (c) 6, and, terminally, (d) 27 months exposure.



<u>FIGURE 75</u> - MIRS spectra relating to the natural weathering (Garston) of the PLASTICISED PVC + PIGMENT + UV + THERMAL STABILISERS coating after (a) 0, (b) 3, (c) 6, and, terminally, (d) 27 months exposure.

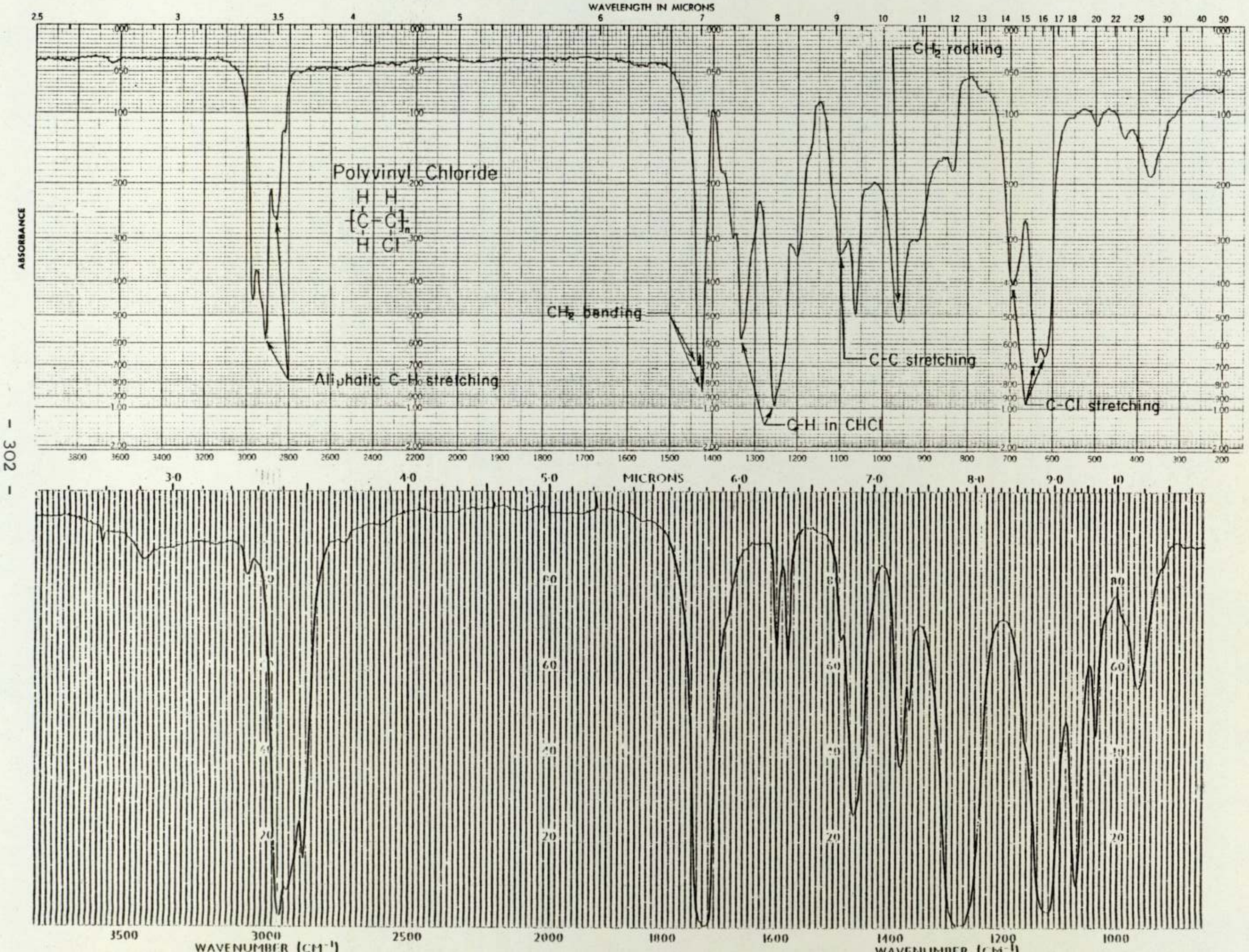


FIGURE 76 -

Reference infrared spectra of

← (a) poly (vinyl chloride) (PVC)

and

← (b) the diisooctylphthalate (DIOP) plasticiser used in the plastisol coatings studied.

As regards the actual recording of the spectra, it was again found that reliably stable spectra were only obtained on completion of the plasticiser migration effect (see section V.2.3, page 260) previously believed to occur during sample analysis. Confirmation of this could obviously be more easily obtained in this plastisol study by recording the spectrum of the reflector plate after sample removal and observing the residual plasticiser peaks (Figure 77).

Considering now the weathering implications of the data, it was found that, on relating the absorbances of the 1423 and 3450 $cm.^{-1}$ peaks to that of the stable 2920 $cm.^{-1}$ (C - H stretching) reference peak, significant changes occurred in each of the three plastisol coatings examined here (Figures 78 - 80). Whilst these changes are difficult to interpret point by point in the graphs, they are able to provide some interesting general impressions of the chemistry which lies behind the surface effects observed microscopically. For instance, it appears from the most diagnostic of the changes, i.e., in the respective 1423 $cm.^{-1}$ peak indices, that after the initial summer and autumn fluctuations, relative stability prevails except in the case of the clear coating (Figure 78) which continues to decline. Furthermore, it is also interesting to note that, whereas the terminal 1423 $cm.^{-1}$ indices for the clear and (solely) pigmented coatings are approximately 75% and 60% down on their respective initial values (Figures 78 and 79), that of the stabilised pigmented sample (Figure 80) is only around 5% lower. However, if this is a genuine reflection of this latter sample's UV-stabilisation, it is certainly not further reflected, to any noticeable degree, as a commensurate improvement in this sample's weathering performance compared to that of its unstabilised counterpart, these two pigmented coatings having already been seen to be essentially

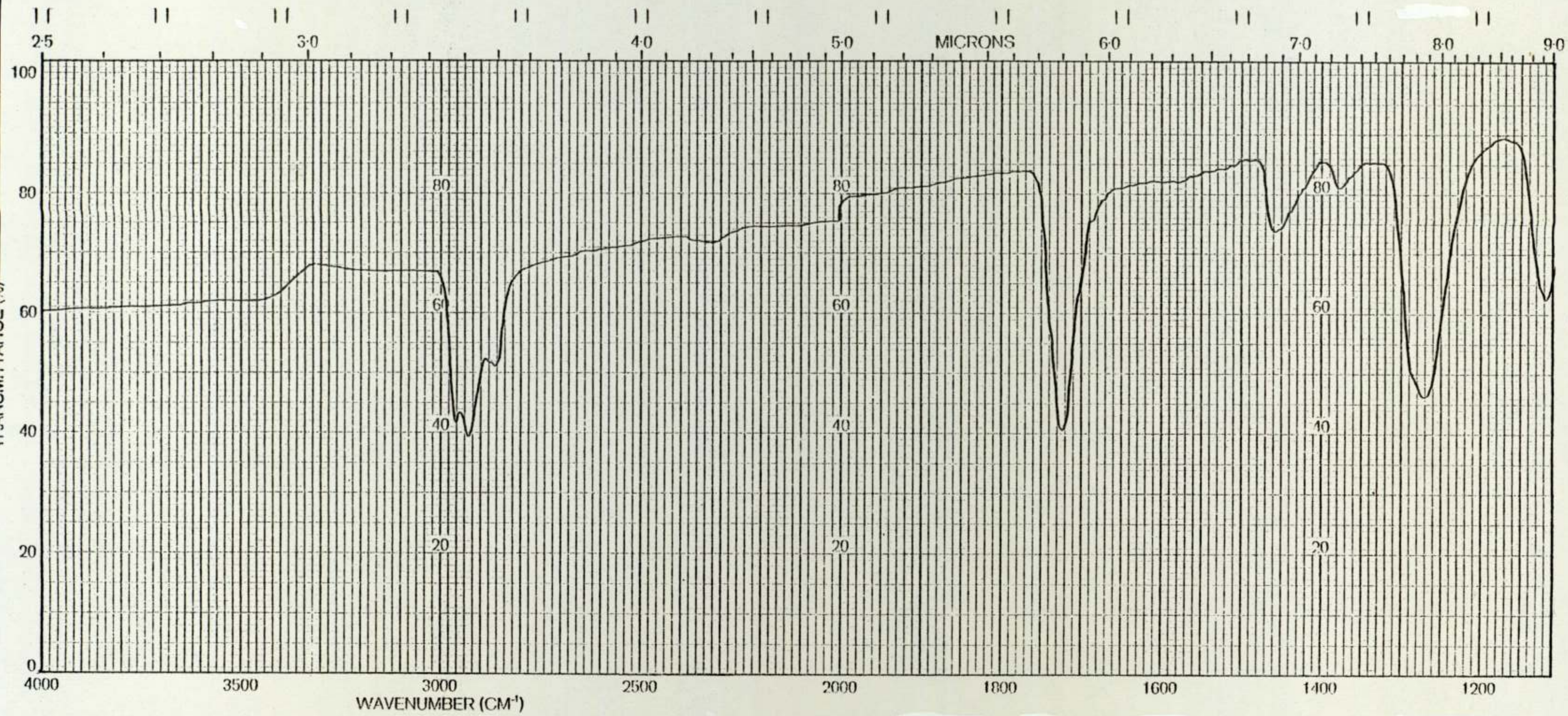


FIGURE 77 - MIRS spectrum of the KRS-5 internal reflector plate after removal of a PVC plastisol coating sample - showing the residual (DIOP) plasticiser peaks.

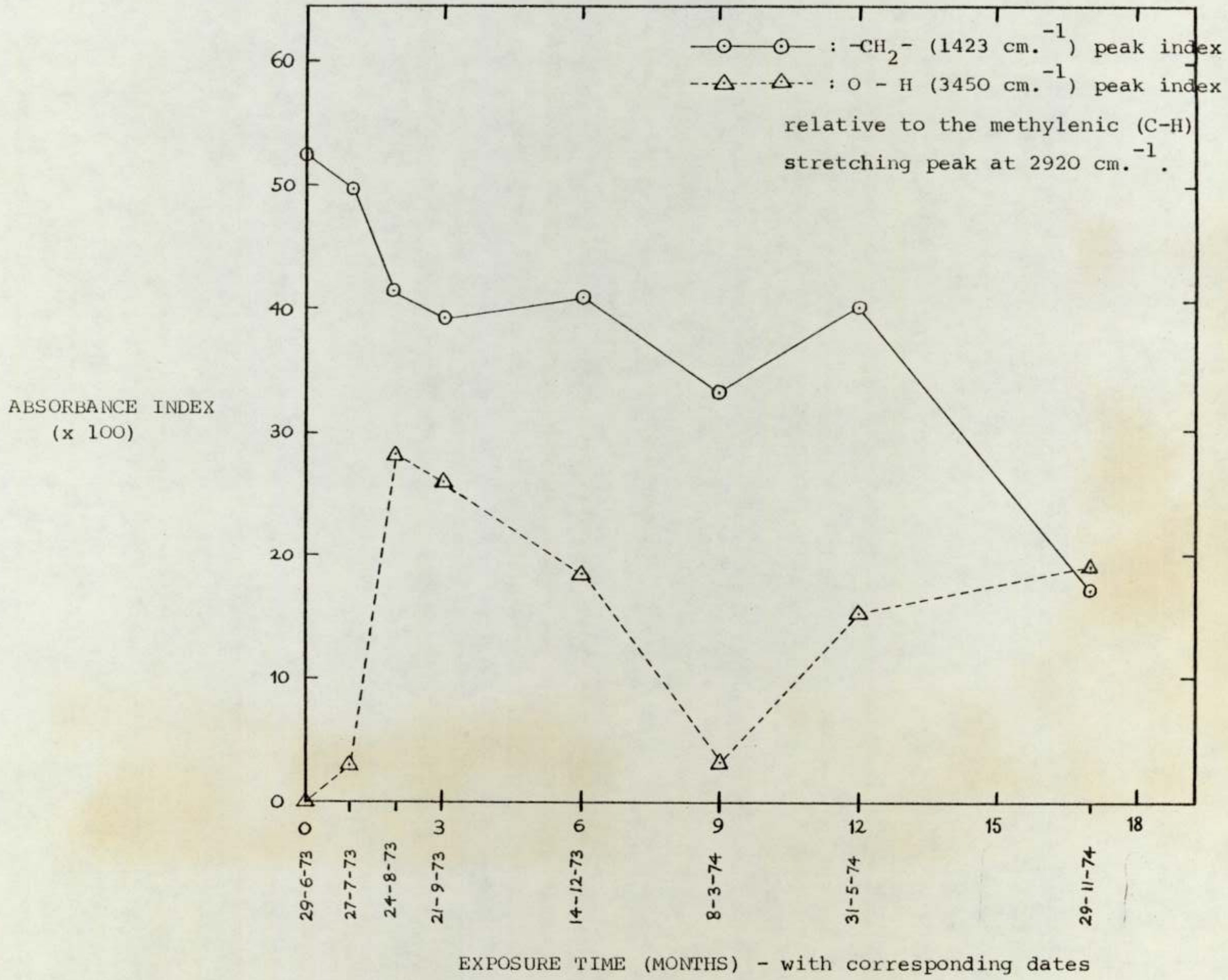


FIGURE 78 - Natural weathering of PLASTICISED PVC (clear) coating; dependence of infrared peak absorbance indices on exposure.

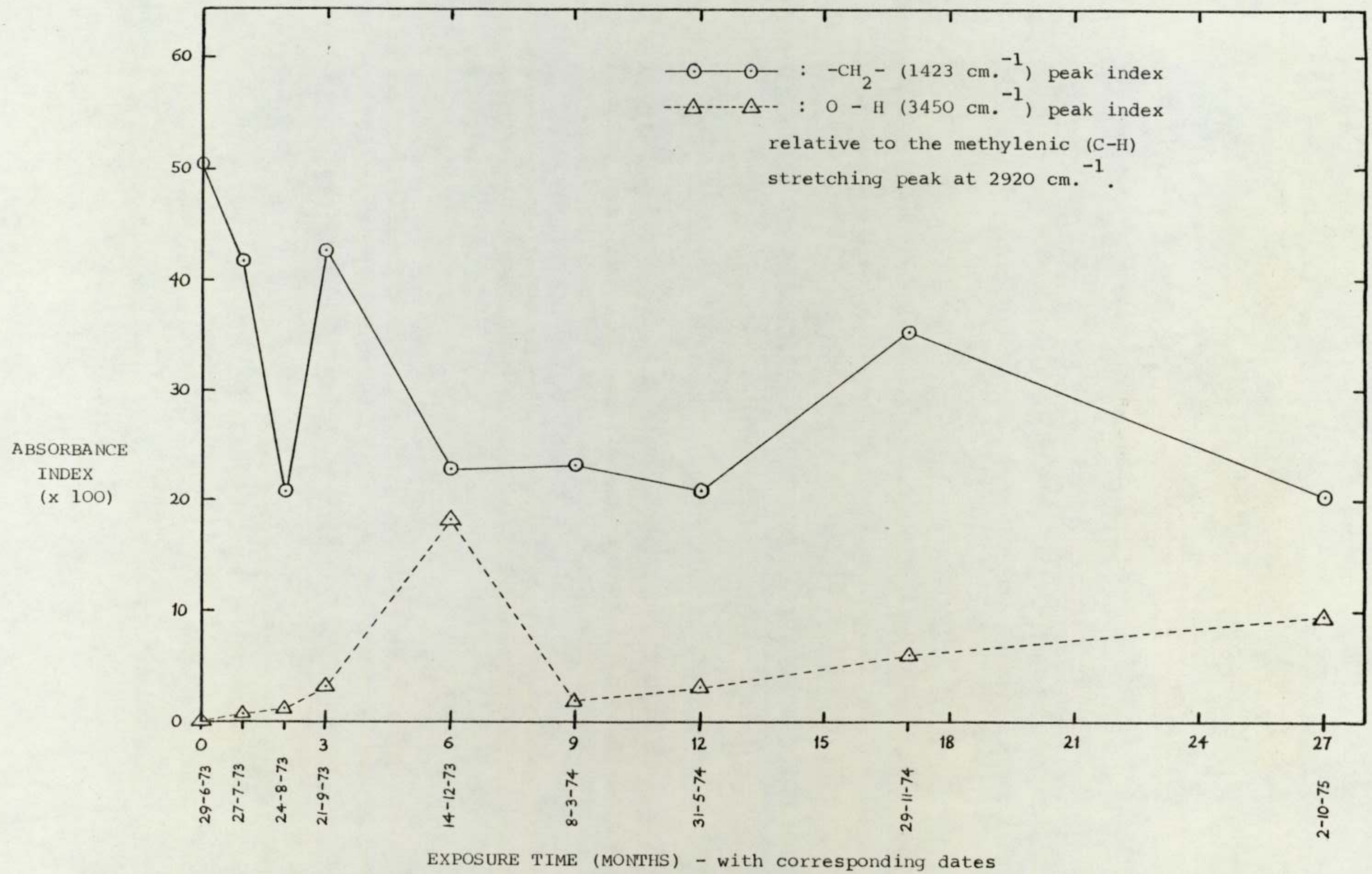
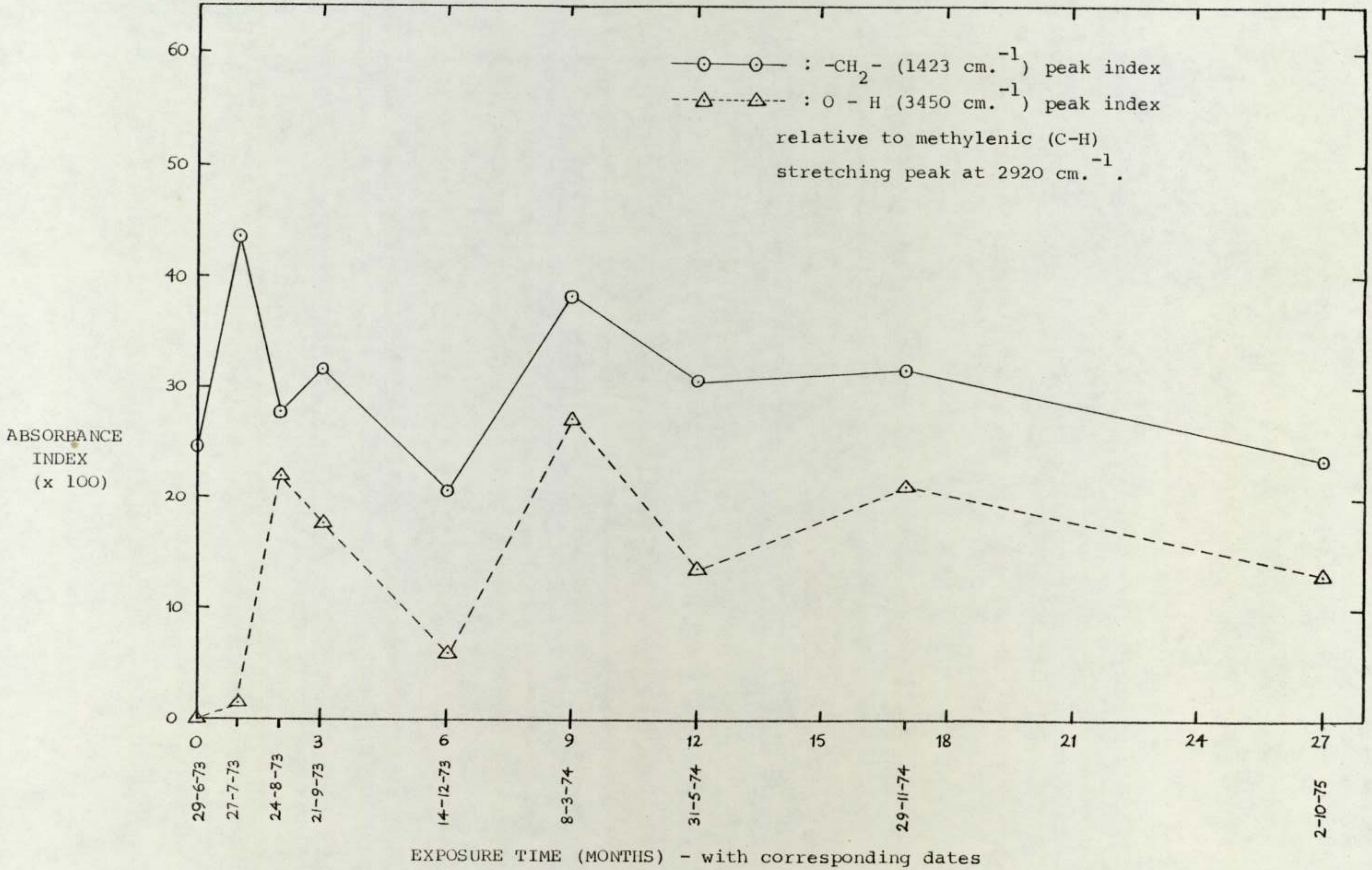


FIGURE 79 - Natural weathering of PLASTICISED PVC + PIGMENT coating; dependence of infrared peak absorbance indices on exposure.



<u>FIGURE 80</u> - Natural weathering of PLASTICISED PVC + PIGMENT + UV and THERMAL STABILISERS coating; dependence of infrared peak absorbance indices on exposure.

similar in this respect.

Indeed, the less obvious correlativity here between the MIRS results and the previous goniophotometric/micrographic data, compared to that observed earlier in the PVC organosol study, suggests that the peak absorbance indices of Figures 78 - 80 may be a function of more than just the extent to which structural changes have occurred in the polymer at given points in time. For example, whereas in the organosol coating a uniformly degraded layer appeared to be progressively formed over the surface as a whole before being subsequently eroded, in the case of these soft plastisol coatings, SEM analysis indicates that surface deterioration proceeds in more localised fashion leading to a greater openness of surface structure and, hence, a possible increase in polymer exposure at or near the surface. This suggestion receives some support from the fact that the major changes in 1423 $cm.^{-1}$ peak index, especially for the two pigmented coatings (Figures 79 and 80), roughly correspond to inverse reflectance changes (Figures 71 and 73), i.e., in direct contrast to the previous organosol results (see Figure 67, page 269).

A further weathering possibility which warrants some consideration, although, unfortunately, not one which the MIRS data here can elucidate upon due to the procedural plasticiser effects, is that sequential plasticiser migration to/volatilisation from the coatings' surfaces may be at least partly responsible for changes in the surface concentration and, hence, MIRS absorbance of polymer related groups. Such an effect, superimposed upon the chemical breakdown of the polymer, would undoubtedly detract from the interpretability of the MIRS data with respect to weathering.

It is also evident from the MIR spectra (Figures 74 and 75) that a certain amount of oxidation takes place in the coating on ageing. However, whether this is mainly of the PVC or of the plasticiser is still uncertain at this stage, although the noticeable similarity shown by the O - H (3450 cm.$^{-1}$) and polymer C - H (1423 cm.$^{-1}$) absorbance indices (Figures 78 - 80) during the later stages of weathering, especially after such contrasting early changes, tentatively suggests that, initially, oxidation is predominantly of the plasticiser before, latterly, becoming more associated with the polymer. Finally, it is worth noting that, although appreciably dirtied, neither of the two white-pigmented coatings showed any significant signs of discoloration even after 27 months exposure; this being despite the suggestion in the 6 micron region of their MIRS spectra (Figures 74(d) and 75(d)) of some C = C unsaturation.

VI.2.4 Contact Angle Studies

Measurements of the equilibrium advancing water contact angle on the simplest of the three plastisol coatings' systems studied here, i.e., plasticised PVC (clear), were carried out by means of a sessile drop technique using the cell previously described (see pages 121 and 122). The water contact angle values quoted in Table 11 represent the mean of several successive determinations and are paired with the estimable upper and lower limits of 12° and 15° for the observed diiodomethane (CH_2I_2) contact angles in order to compute the dispersive (γ_D) and polar (γ_P) components of surface free energy. This two-system analysis is more valuable than a simple water contact angle study which only indicates surface wettability by hydrogen-bondable liquids.

As seen from Table 11, the γ_D and γ_P values obtained via this technique remain substantially constant throughout the weathering series up until the last two samples which show fairly slight but, nevertheless, definite increases - predominantly in their polar components (γ_P) of surface free energy. However, these results ought really to be considered in the light of the corresponding literature$^{(227)}$ data relating to rigid (i.e., unplasticised) PVC:-

H_2O - contact angle = 87°

CH_2I_2 - contact angle = 36°

γ_D = 40.0 dynes. $cm.^{-2}$,

γ_P = 1.5 dynes. $cm.^{-2}$,

from which it can be seen that it is essentially in the CH_2I_2 figures that the plastisol results differ. Indeed, it was noted with particular interest at the time they were measured that the CH_2I_2 contact angles for the plastisol coatings were very low ($12^\circ - 15^\circ$); furthermore, they were virtually identical, certainly within the limits of experimental error, for the entire weathering series, in contrast to the water contact angles which showed significant decreases in the case of the last two samples.

Although it is not within the scope of this work to examine in detail the nature of the surface free energy of plasticised PVC systems, it does seem fairly apparent that the differences noted here between them and 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. However, this initial suggestion, together with the possible interpretations of the terminal changes which take place in the coating surface, will be

EXPOSURE (months)	CONTACT ANGLE (^{o})		SURFACE FREE ENERGY (dynes. cm.$^{-2}$)		
	H_2O	CH_2I_2	γ D	γ P	∴ Total
0	84	12	48.54	1.15	49.69
1	87	12	49.22	0.60	49.82
2	84	12	48.54	1.15	49.69
3	83	12	48.32	1.37	49.69
6	85	12	48.77	0.94	49.71
9	84	12	48.54	1.15	49.69
12	78	12	47.22	2.76	49.98
17	69	12	45.33	6.35	51.68
0	84	15	47.86	1.22	49.08
1	87	15	48.53	0.65	49.18
2	84	15	47.86	1.22	49.08
3	83	15	47.63	1.45	49.09
6	85	15	48.08	1.01	49.09
9	84	15	47.86	1.22	49.08
12	78	15	46.54	2.87	49.42
17	69	15	44.67	6.51	51.18

TABLE 11

CONTACT ANGLE/SURFACE FREE ENERGY DATA RELATING TO

THE NATURAL WEATHERING OF THE PLASTICISED PVC (CLEAR) COATING discussed later in Chapter 8 in the light of other (e.g., infrared spectroscopic) relational data.

VI.2.5 Thermal Analysis

Thermal analysis of the weathering series of plasticised PVC (alone) coatings, whose surface energetics have just been reported, comprised the differential scanning calorimetric determination of their glass transition temperatures (T_g), as previously described (see section II.4.7, page 124). The results which are presented in Table 12 represent the mean T_g values of several determinations and are supplemented by some preliminary data obtained for the comparable pigmented coating.

As seen from Table 12, the T_g of the clear coating shows no significant change on natural weathering until after 17 months exposure, by which time the coating had extensively degraded. The results, therefore, are suggestive of having a certain amount in common with the previous contact angle/surface free energy data. However, the possibility that these two sets of data may be descriptive of related changes in the surface and bulk interior of the coating will be discussed later in Chapter 8. Finally, it is also interesting to note from Table 12 that the low level of pigmentation used in these plastisols (approx. 7½% by weight) apparently has no discernable effect on the initial T_g. In addition, the constancy of the pigmented coating's T_g, even after 27 months exposure, endorses the visual impression it gives of still being relatively intact (certainly compared with the clear coating which, by now, no longer even provides a coherent coverage of the substrate).

Garston exposure (months)	0	1	2	3	6
	9	12	17	27	
Plasticised PVC (alone) : T_g (°C.)	-41	-39	-39	-43	-37
	-34	-34	- 8	+23	
Plasticised PVC + pigment : T_g (°C.)	-43	-	-	-	-
	-	-45	-	-40	

TABLE 12

VARIATION IN GLASS TRANSITION TEMPERATURE (T_g °C.)

ON NATURAL WEATHERING OF PVC CLEAR AND PIGMENTED

PLASTISOL COATINGS

VI.2.6 Microindentation-Recovery/Time Analysis

Microindentation-recovery/time analysis was carried out with interest centred once again on the plasticised PVC (alone) weathering series which appeared most likely to exhibit measurable changes. Not surprisingly, however, in view of the preceding thermal analysis results, a significant deviation from the indentation-recovery/time profile shown in Figure 81 for the unaged clear coating was not observed until after 17 months exposure, despite the much earlier onset of visible sample deterioration. Thus, the coating's resistance to discernable changes in microhardness on weathering correlates closely, as might be expected in plastisol systems, with the similar stability in glass transition temperature (T_g). Furthermore, the identical indentation/recovery profiles obtained for both clear and pigmented unaged coatings (Figure 81) confirms the previous T_g-based indication that the low level of pigmentation used in these materials has little or no rigidifying effect on the coating.

However, although the results would seem to suggest that, in the case of such highly plasticised systems as these, this technique is relatively uninformative until the terminal stages of weathering deterioration, preliminary results obtained using larger (e.g., 1/16 inch) radii indentors with smaller loads have suggested that more subtle earlier changes might also be occurring which can be measured.

VI.2.7 Weight Loss Measurements

Weight loss measurements, which, it was hoped, would prove valuable in view of the expected plasticiser loss from the coatings on outdoor exposure, were, as feared, invalidated by the tendency of the

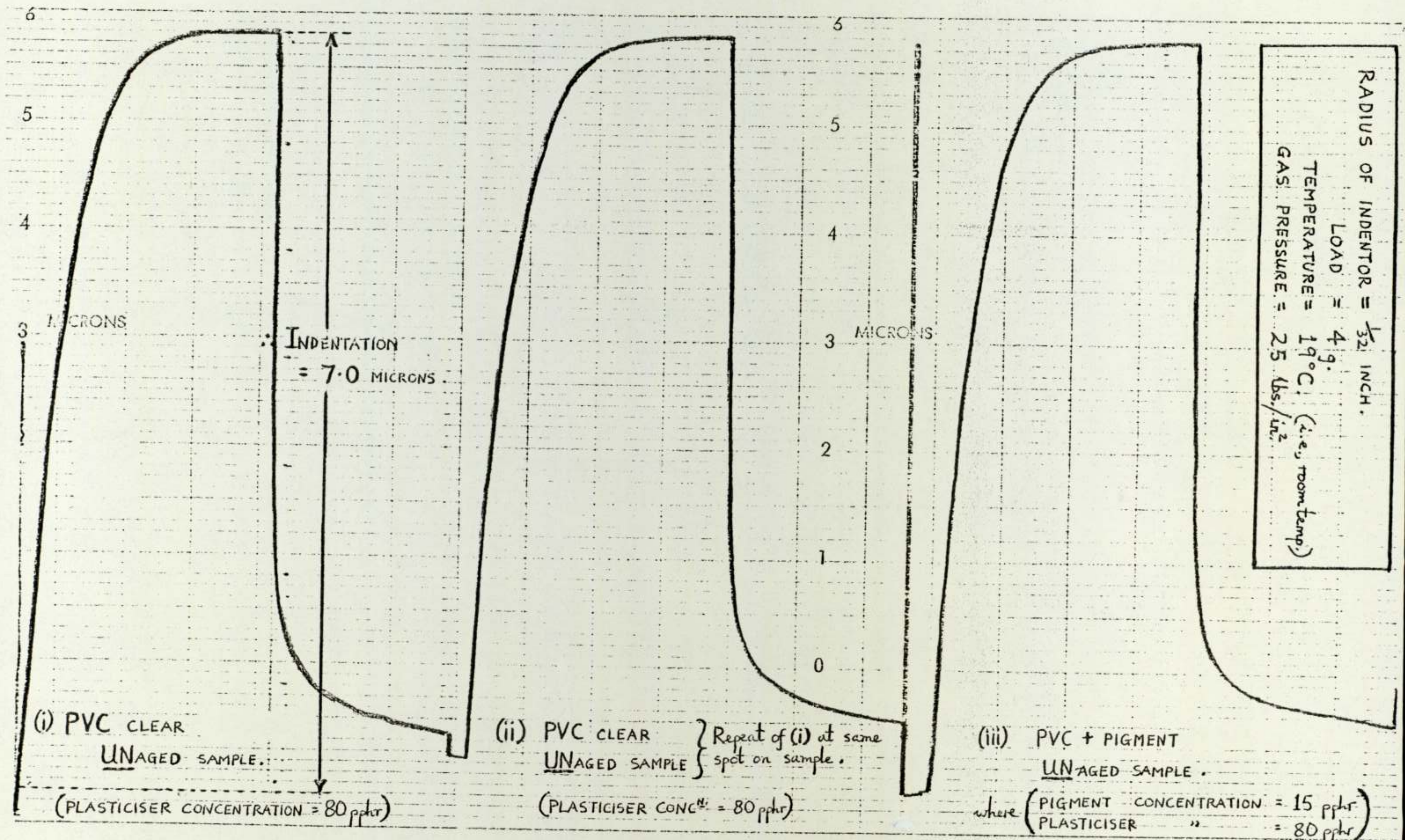


FIGURE 81 - Microindentation - recovery/time profiles relating to PVC plastisol coatings.

samples to retain trace amounts of dirt not just on but <u>in</u> their surfaces. Despite this, however, the fact that the coatings all appeared to have similar affinities for dirt, etc., meant that it was still possible, from their net weight losses, to detect what appeared to be fairly definite lower weight losses from the pigmented coatings. Hopefully, this point will receive clarification from the corresponding artificial weathering weight loss data to be reported in the following chapter.

Finally, the second series of PVC plastisol coatings to be exposed at the Building Research Station site at Garston comprised the following four formulations:-

(i) plasticised PVC alone,

(ii) plasticised PVC + UV stabiliser,

(iii) plasticised PVC + thermal stabiliser,

and (iv) plasticised PVC + UV and thermal stabilisers.

Weathering of this coatings series, which was for a 12 months period, was commenced during the early autumn and thus provided an interesting comparison with the previous trio of coatings whose exposure was initiated at the beginning of summer. However, as stated at the outset of this chapter, rather than being programmed as an extension of the previous work, this second Garston exposure series, in combination with parallel exposures at Gravelly Hill and Aston University, formed part of a wider-based study encompassing a comparison of site weatherability.

As regards sample testing, however, this was restricted to goniophotometric analysis, employing the same conditions as for the previous series. On weathering, almost identical changes in reflectance were observed throughout exposure in each of these four, unpigmented, but differently stabilised, coatings. This is strikingly illustrated by the gloss factor graphs in Figure 82 which, incidentally, are plotted to a linear time (rather than energy) of exposure scale so as to facilitate comparison with the other site data which follows. From Figure 82, a number of interesting points emerge. Firstly, and in common with the previous coatings trio, the first-stage deteriorative trends are followed in each case by positive recoveries in gloss factor. Even more significantly, these general improvements in gloss appear to occur after around 9 months exposure and are thus seen to be in further agreement still with the corresponding plasticised PVC (alone) results (Figure 73) in the preceding summer-initiated study. However, whilst first impressions centre most readily around these similarities, the less obvious differences in behaviour (cf. Figures 73 and 82), such as the immediately decreasing gloss factor trends coupled with terminally higher gloss values, in the case of the four coatings studied here, will also undoubtedly warrant serious consideration when it comes to discussing these various points later on in Chapter 8.

Thus, having observed the apparently stabiliser-independent behaviour of this Garston-exposed quartet of plastisol coatings, let us now compare this with their parallel performances at the Gravelly Hill and Aston University roof sites.

VI.3 Gravelly Hill Exposure

On natural weathering of the four unpigmented plastisol

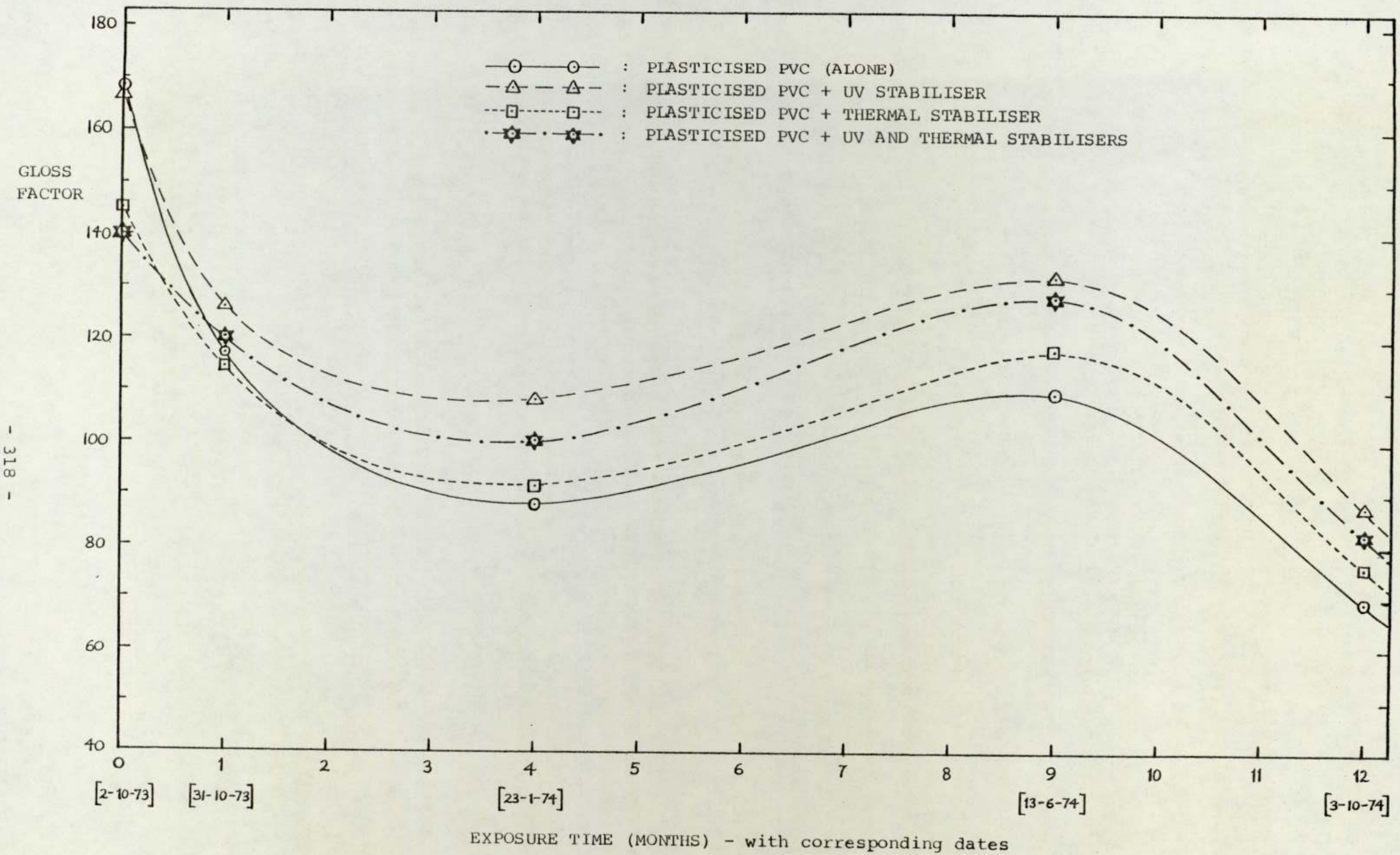


FIGURE 82 - Natural weathering of PVC plastisol coatings at the BRS (GARSTON) exposure site; variation in gloss factor on exposure.

coatings at the Gravelly Hill site, it was found that, by the time the second sampling date came round, i.e., after four months exposure, the coatings' surfaces had all become liberally covered with an adherent layer of particulate contamination. This unfortunate occurrence was clearly not just a function of this site's high air pollution, coupled with its sheltered nature from the potential washing effects of rain, but had been further accentuated by the softness and, hence, high dirt retention characteristics of the materials themselves. Consequently, this exposure was effectively invalidated as regards being a genuine test of weatherability. Instead, it seemed rather ironic that, in such a potentially deteriorative environment as this, the coatings should remain ostensibly unscathed beneath their protective layers of surface contamination.

However, despite the failure of this particular case study experiment to provide what could have been extremely interesting data for comparison with the concurrent Garston and Aston exposures, this Gravelly Hill site undoubtedly still provides a unique weathering opportunity if the problem of sample "poisoning" can be overcome.

VI.4 Aston University (Roof) Exposure

On natural weathering at the Aston University roof site, it was found that the prevailing conditions provided for an effective combination of site hostility in an industrialised environment with site cleanliness. Consequently, the goniophotometric and Stereoscan data presented here are able to reflect some interesting features of advanced deterioration without the encumbrance of sample contamination.

Unlike the corresponding set of Garston-exposed panels detailed previously, it was possible to distinguish in this case, both subjectively and objectively, between the relative performances of the four unpigmented plastisol coatings studied, as now described.

VI.4.1 Goniophotometry

Goniophotometric analysis of the weathered plastisols revealed, initially, similar gloss factor changes (Figure 83) to those induced in the Garston samples (cf. Figure 82). However, whereas the latter all exhibited intermediate recoveries in gloss (Figure 82), these Aston samples, with the exception of the dually stabilised coating, displayed consistently deteriorative trends which, by the end of the 12 months exposure period, had reached near-minimum gloss factor values (Figure 83). In fact, in the case of the plasticised PVC (alone) coating, deterioration was visibly complete, with this originally clear film having been degraded to what could only be described as a dark brown "layer" of material. The build-up to this state of total breakdown had earlier been observed through the appearance of isolated dark brown spots after about 6 months exposure, which then gradually developed in size and number until, after 9 months, they had formed themselves into patches of localised deterioration. However, although this unstabilised coating continued to total destruction, the two singly stabilised samples, after 12 months exposure, still only showed patchy coverage of these degraded areas. Furthermore, there was a distinct suggestion from their comparative visual appearances that the uv stabiliser had imparted a greater measure of weathering protection to its coating than the thermal stabiliser had. Meanwhile, the twin-stabilised formulation had withstood these more drastic ageing advancements and was still terminally free from

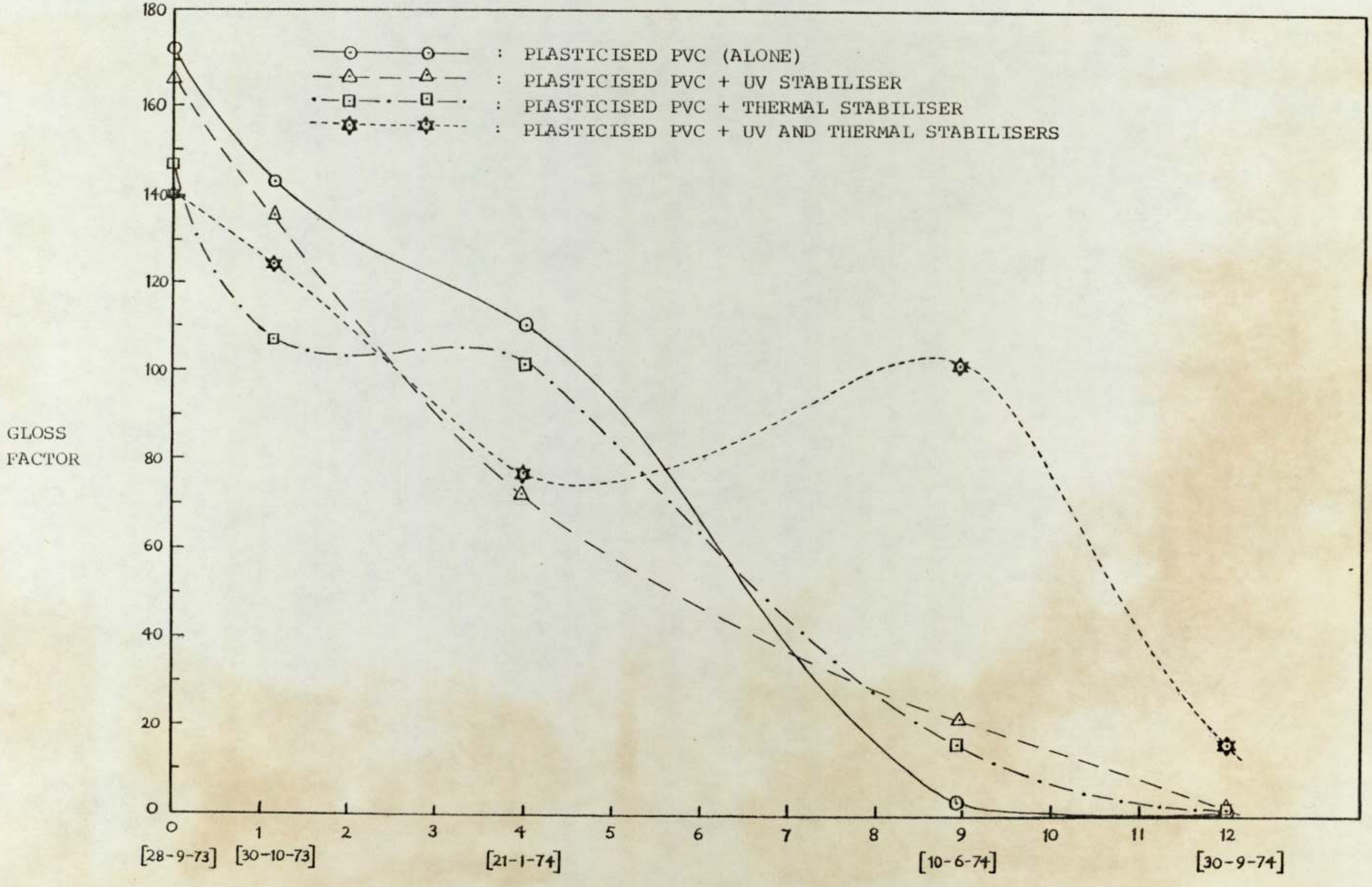


FIGURE 83 - Natural weathering of PVC plastisol coatings at the Aston University (roof) site; variation in gloss factor on exposure.

even the initial "spotting" effect. Indeed, this latter sample's ageing response appeared to be an essentially similar, if more exaggerated, version of its Garston performance.

Hence, quite apart from the unprecedented extent to which deteriorative changes have occurred, this Aston exposure test has also been able to provide the first clear indication of the conferment of improved weathering resistance on the plastisol coatings by their respective stabilising additives. Furthermore, these relative improvements have not only been to an objectively measurable degree but, due to the visible extent of the degradation, have been subjectively discernable as well.

VI.4.2 Scanning Electron Microscopy

A more detailed insight into the actual nature of the weathering process in the case of the unstabilised coating (i.e., the most degraded of the four studied) was provided by scanning electron microscopy (SEM) of its surface at the same reflectance testing times of 0, 1, 4, 9 and 12 months. The resultant micrographs (Plates 42 - 51) show to great effect the progression of surface deterioration leading to the utter devastation of the coating after 12 months weathering. Firstly, the initially smooth coating surface (Plate 42) appears to become slightly roughened after the first month's autumn exposure as illustrated in Plate 43 which, in addition to the adventitious sessile debris, also depicts the odd spot of localised surface damage (see top right of Plate 43). These signs of deterioration subsequently become even more prevalent after 4 months exposure (Plate 44) with flaking now having emerged as the prime manifestation (Plate 45). However, even these obviously precursory degradative features could hardly have forewarned of the way in which the surface would start to break up during the late winter and spring to the extent shown in Plates 46 - 48 after 9 months exposure. By this stage, patches of brown deterioration were clearly visible in the coating surface even though the intervening areas appeared relatively unaffected. This was then rapidly followed, after the final three months of summer exposure, by a complete breakdown of the sample as a coating material (Plates 49 - 51) to yield what, perhaps, can best be described as an alligatored(247) surface (Plate 49) made up of discrete "islands" of cross-linked matrix surrounded by dried up (stress-cracked) "rivers" of plasticised lower molecular weight material (Plates 49 and 50). Indeed, at their similar magnifications, Plates 42 and 50 could hardly form a more striking comparison between the initial and final sample surfaces in a 12 months weathering exposure.

Additionally, and at the same time that the SEM analyses were being conducted, it was also possible to carry out energy dispersive X-ray analyses (EDXA) of the viewed surfaces. However, whilst quantitative "chlorine-mapping" by this means was still in the process of evaluation at the time of writing, a significant preliminary qualitative indication was that open structure (e.g., cracks, hollows, etc.,) in the weathered surfaces tended to be relatively chlorine-rich compared with the surrounding areas. This suggestion, interestingly enough, is thus in agreement with previous infrared (MIRS) spectroscopic results (see section VI.2.3).

Finally, having already seen in earlier sections how effectively SEM can combine with goniophotometry, it has been further

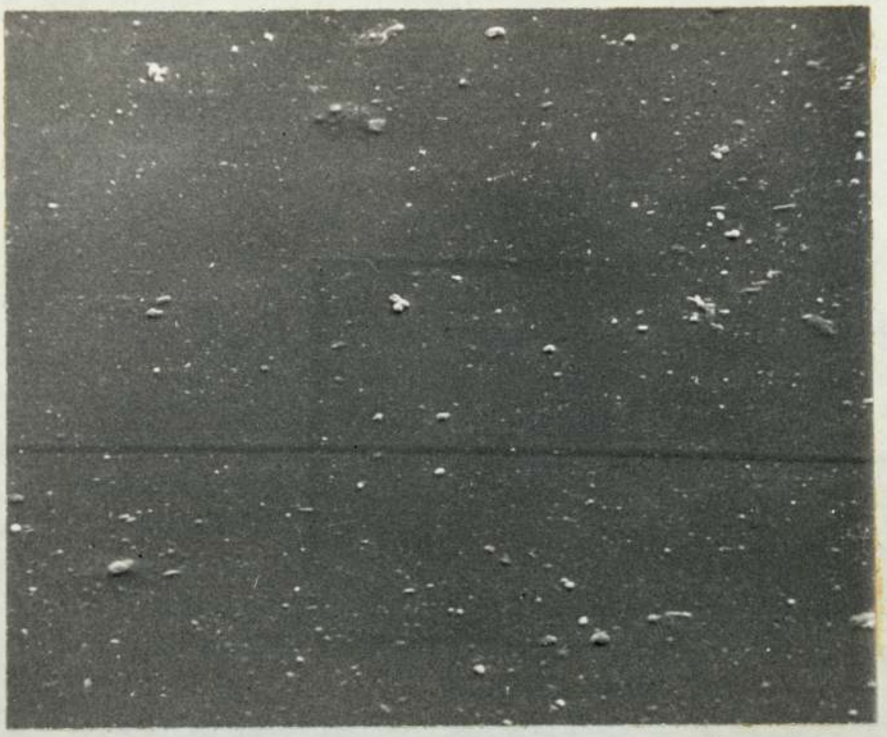


PLATE 42

0 months

x 210

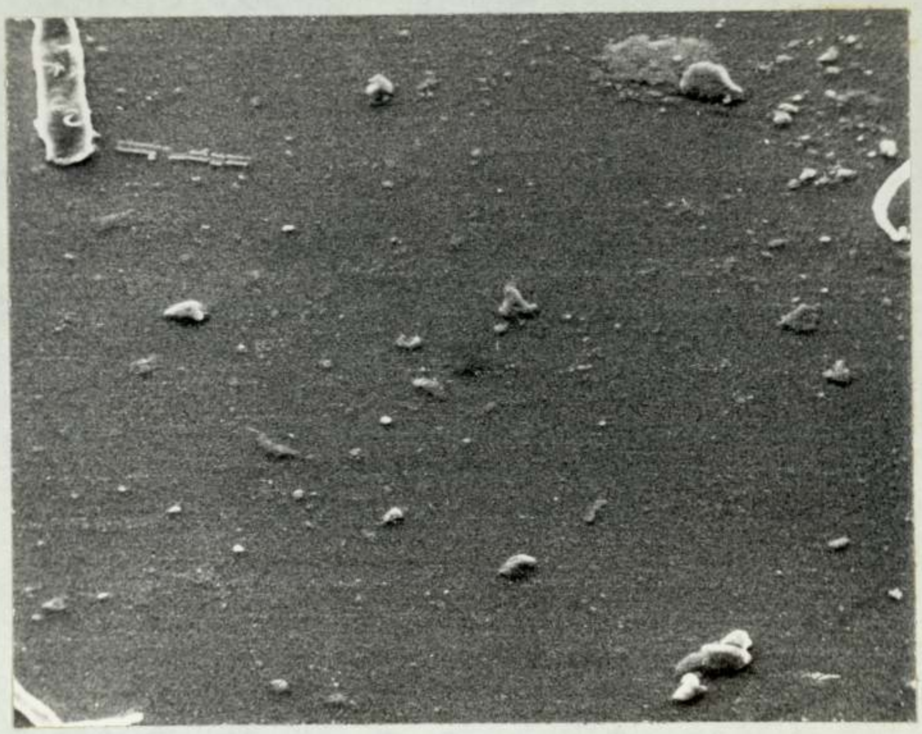


PLATE 43

1 month

x 230

PLASTICISED PVC (alone) plastisol coating;

Natural weathering at the Aston University roof site.

PLATE 44

4 months

x 260

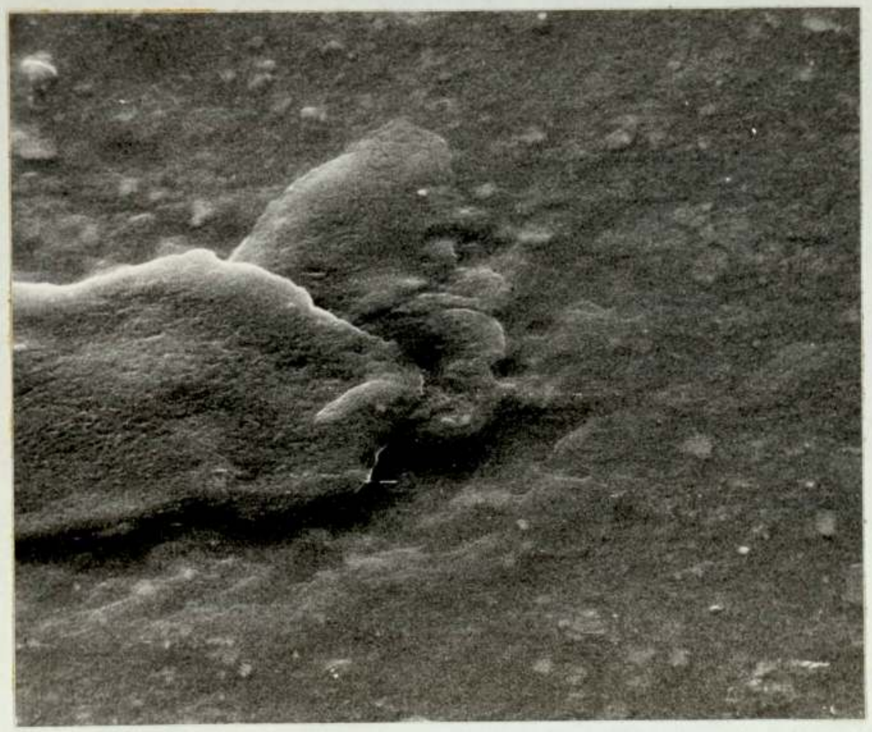


PLATE 45

4 months

x 1300

PLATE 46

9 months

x 100

PLATE 47

9 months

x 200

PLATE 48

9 months

x 500

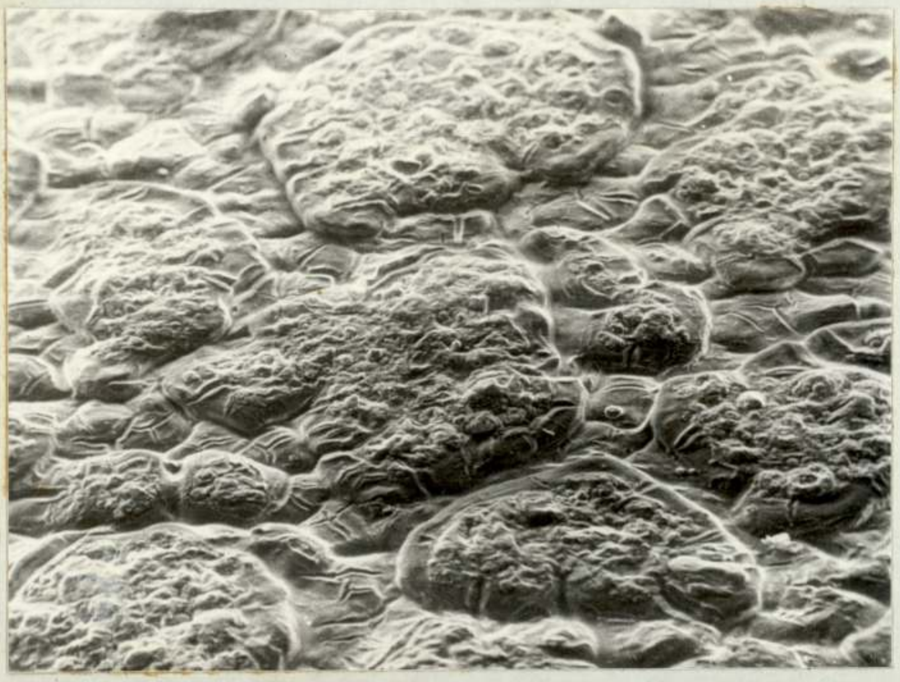


PLATE 49

12 months

x 65

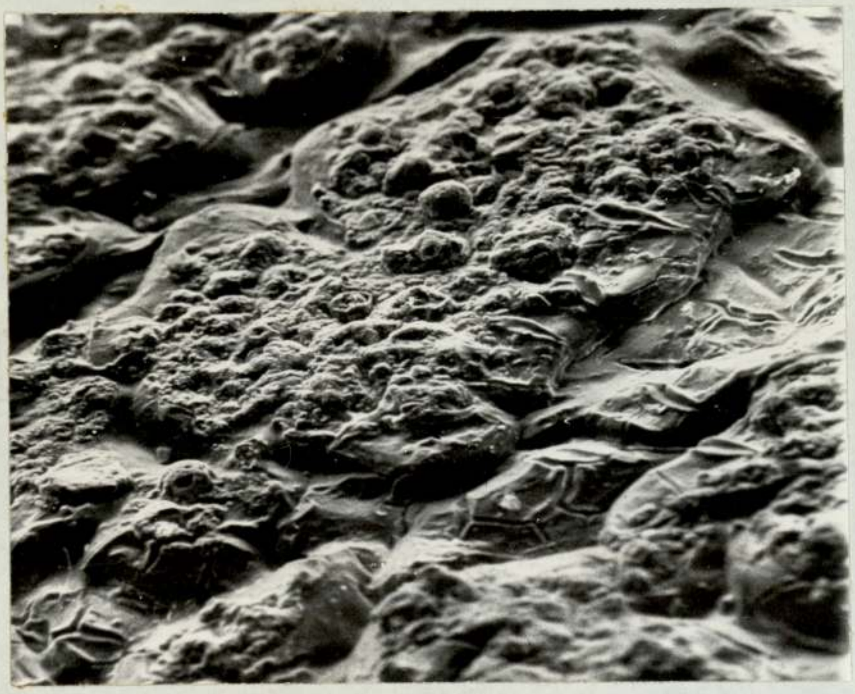


PLATE 50

12 months

x 140

PLATE 51

12 months

x 720

shown in this latter study that, in certain cases, SEM can assume the leading role as the more predictive analytical technique, especially when deterioration is of a localised rather than disperse nature which might not detract commensurably from the surface's reflectivity. Thus, having considered the natural weathering of these PVC plastisol coatings, the following chapter now deals with their artificial weathering (along with that of their lower plasticised (Series II) counterparts), after which the combined results of these two chapters will be discussed.

CHAPTER VII

ARTIFICIAL WEATHERING OF POLY (VINYL CHLORIDE) PLASTISOL SURFACE COATINGS

CHAPTER VII

ARTIFICIAL WEATHERING OF POLY (VINYL CHLORIDE) PLASTISOL SURFACE COATINGS

VII.1 Introduction

Having looked at the natural weathering of the Series I (see Table 3, page 69) PVC plastisol coatings in the previous chapter, this chapter now deals with their artificial weathering and also includes corresponding data for their Series II (i.e., lower plasticised) counterparts. The results presented here relate solely to exposure in the BS 3900 Part F3 artificial weathering apparatus for periods of up to 3000 hours, which corresponds, on energy terms, to approximately 18 months outdoor exposure at the Building Research Station site at Garston. Finally, the sample combination studied comprised the trio of coatings which formed the major study in the previous chapter, i.e.,

i) plasticised PVC (clear),
ii) plasticised PVC + pigment,
and iii) plasticised PVC + pigment + UV and thermal stabilisers;

their analysis being by means of goniophotometry, scanning electron microscopy and, as a supplement, weight loss measurements.

VII.2 Goniophotometry/Scanning Electron Microscopy

Considering firstly the Series I, i.e., higher (80 pphr) plasticised, coatings trio, it is clear from Figure 84 that exposure to the BS 3900 weathering cycle has brought about significant gloss changes in each of the three samples. The overall trends shown in Figure 84 are seen to be not all that dissimilar from the previous natural weathering (Garston) responses (Figure 73) in as much that, after what appear to be initial sample equilibration effects, they depict common decreases in gloss followed by an intermediate period of stabilisation in each case. This intermediate stage, which obviously compares, in less exaggerated form, with the actual mid-term improvements in gloss observed on natural weathering (Figure 73), is subsequently followed by a further period of general gloss reduction during which the "complete" (i.e., pigmented and stabilised) coating distinguishes itself from the other two by virtue of its slower rate of "second stage" deterioration (Figure 84). Indeed, the contrast which this latter observation makes with the previous natural weathering results (Figure 73), in which it was the unpigmented coating which was different from the other two, undoubtedly represents, along with the generally lesser severity of the artificial weathering changes, the most noticeable differences between the two sets of weathering data (Figures 73 and 84), the implications of which will be discussed in the following chapter. However, these dissimilarities are ostensibly variations upon what appear to be basically similar trends. It is also significant to note that the gloss factor changes shown in Figure 84 are predominantly a function of specular reflectance (I_s) (Figure 85), and, hence, peak height (I_s - I_d) changes rather than those in the peak width ($W_{\frac{1}{2}}$) (Figure 86); this, again, being in common with natural weathering findings.

Finally, it is worth adding that there were still no visible signs in the clear coating, at the end of the 3000 hours exposure period, of the brown "spotting" effect first observed in the Garston samples after 9 months weathering; neither was there any discernable discoloration in the pigmented coatings.

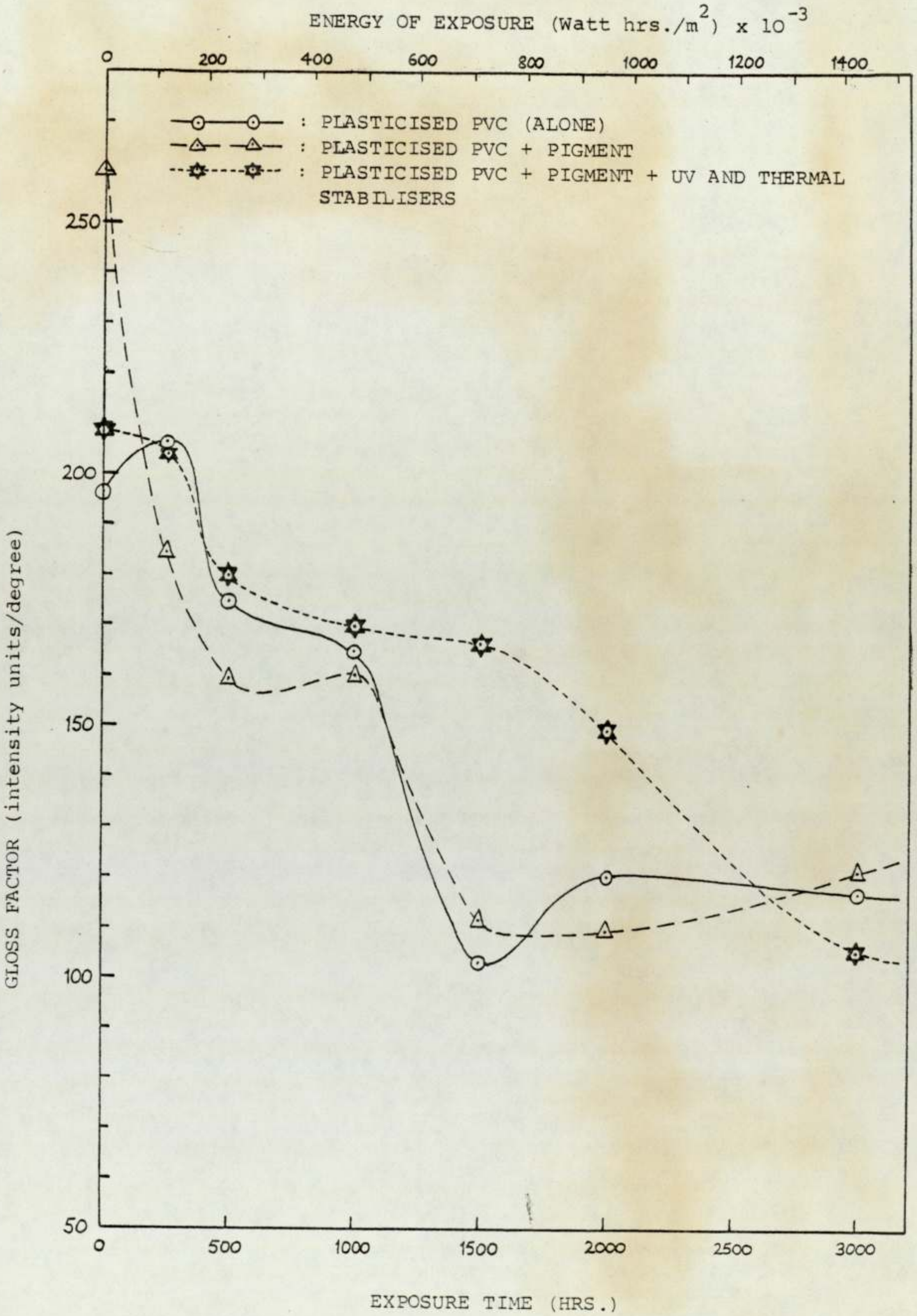


FIGURE 84 - Artificial (BS 3900 Part F3) weathering of PVC plastisol coatings (Series I : 80 p.p.h.r. plasticiser); variation in gloss factor on exposure.

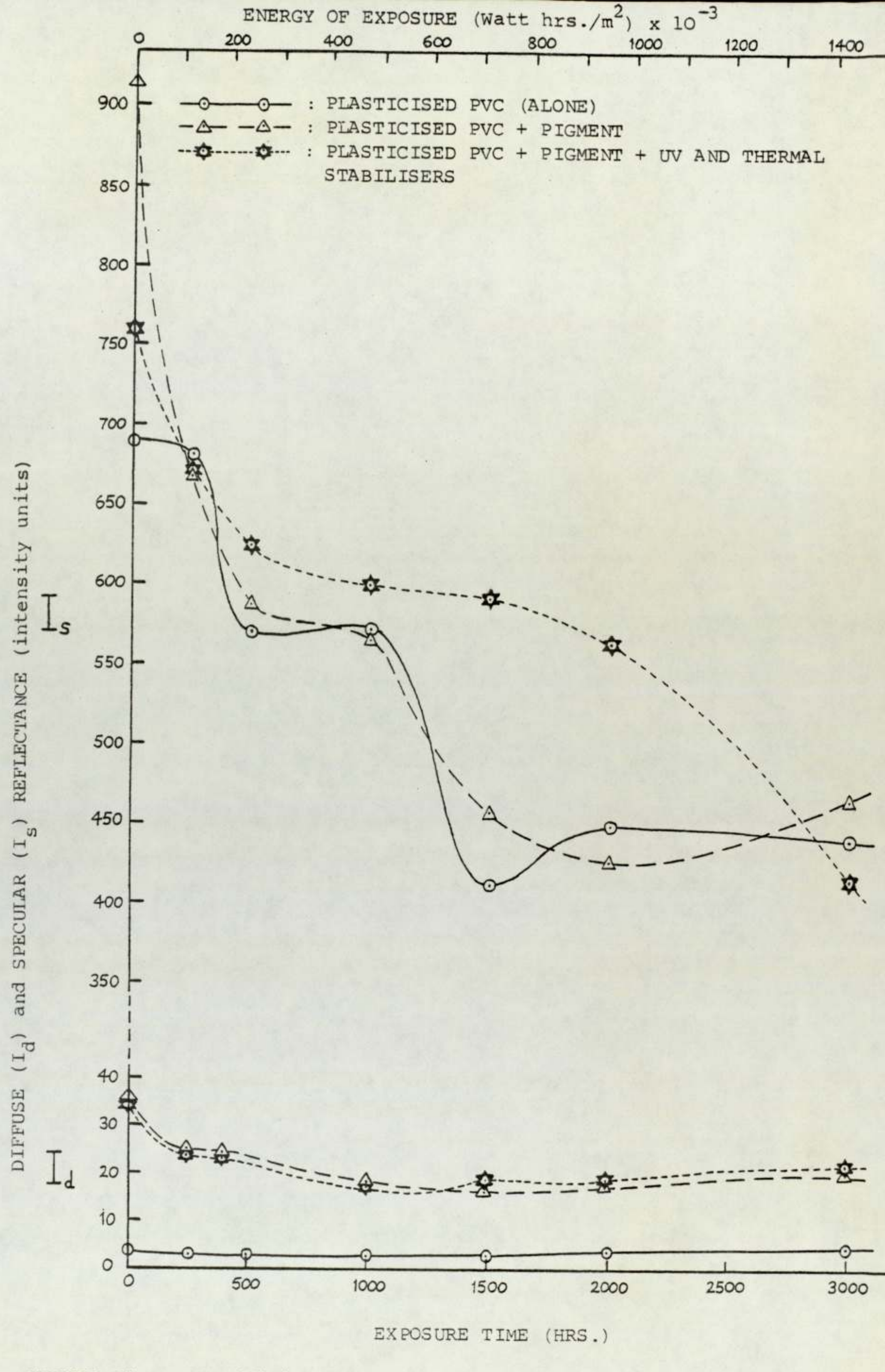


FIGURE 85 - Artificial (BS 3900 Part F3) weathering of PVC plastisol coatings (Series I : 80 p.p.h.r. plasticiser); variation in specular (I_s) and diffuse (I_d) reflectance on exposure.

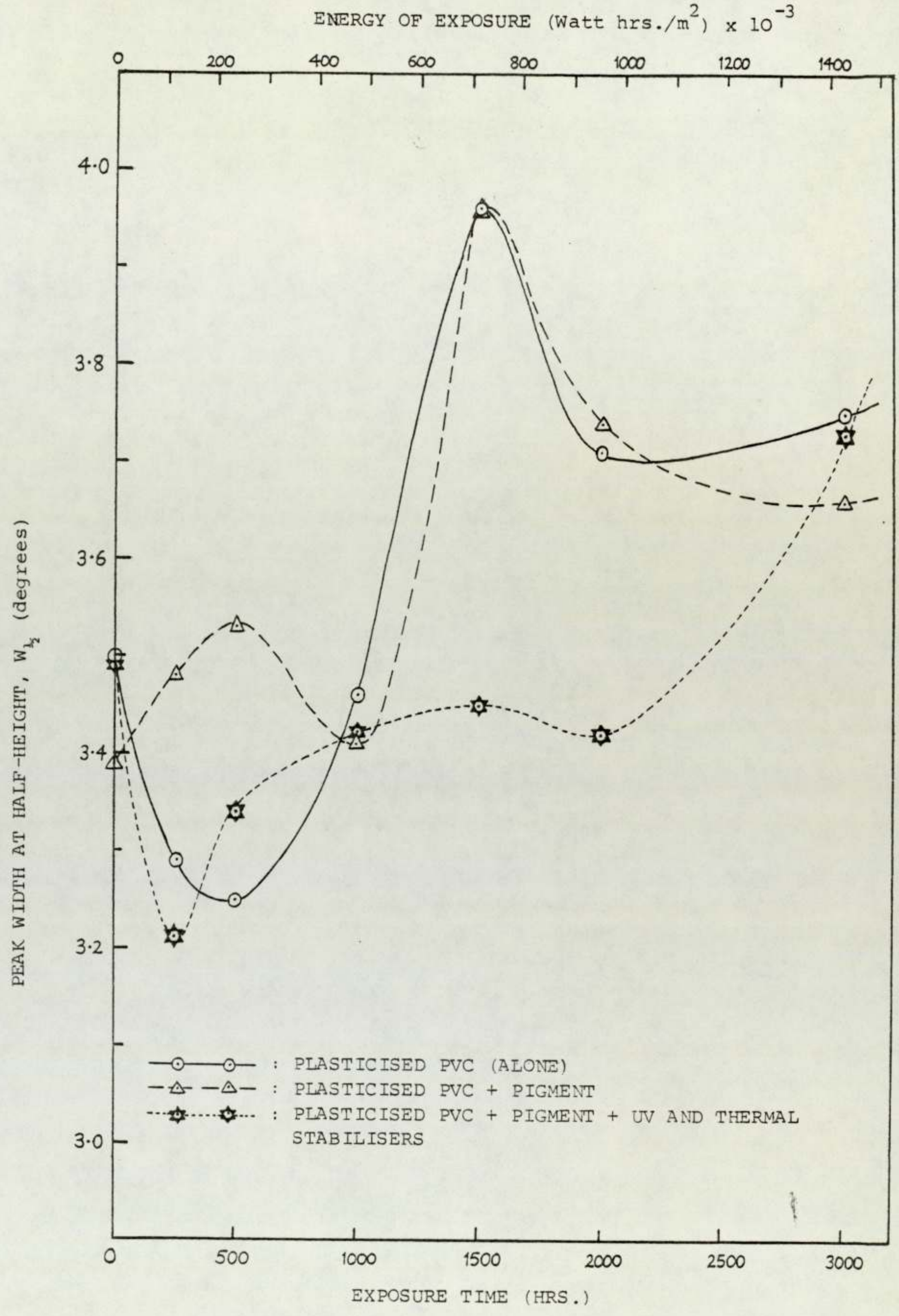


FIGURE 86 - Artificial (BS 3900 Part F3) weathering of PVC plastisol coatings (Series I : 80 p.p.h.r. plasticiser); variation in peak width at half-height ($W_{½}$) on exposure.

This BS 3900 weathering experiment was then repeated, up as far as 2000 hours exposure, for the corresponding trio of Series II, i.e., lower (50 pphr) plasticised, coatings. Apart from providing an indication of the degree to which the plasticiser influences weathering performance, these Series II coatings are also more closely representative, in terms of their hardness, of the actual commercial plastisol product on which these study materials are modelled.

On artificial weathering, this second series of coatings, whilst, not surprisingly, showing a certain amount in common with their Series I counterparts, nevertheless also exhibit some interesting and significant differences in gloss factor change (Figure 87) (as determined, incidentally, by narrow, as opposed to wide-beam goniophotometry). Whereas their short-duration initial decreases in gloss, followed by periods of relative gloss stabilisation, are in agreement with the previous Series I trends (cf. Figures 87 and 84), this intermediate "recovery" stage, in the case of the two pigmented coatings, is then followed by quite definite increases (Figure 87) in gloss which are reminiscent of earlier natural weathering observations (Figure 73). Finally, the reported 2000 hours exposure period then ends with each of the three samples in their apparent second stage decline.

As seems to be the general rule with these plastisol coatings, the gloss factor changes (Figure 87) are again mainly descriptive of variations in specular reflectance (I_s) (Figure 88) rather than beam divergence (i.e., peak width, $W_{\frac{1}{2}}$; Figure 89). This, by now, familiar

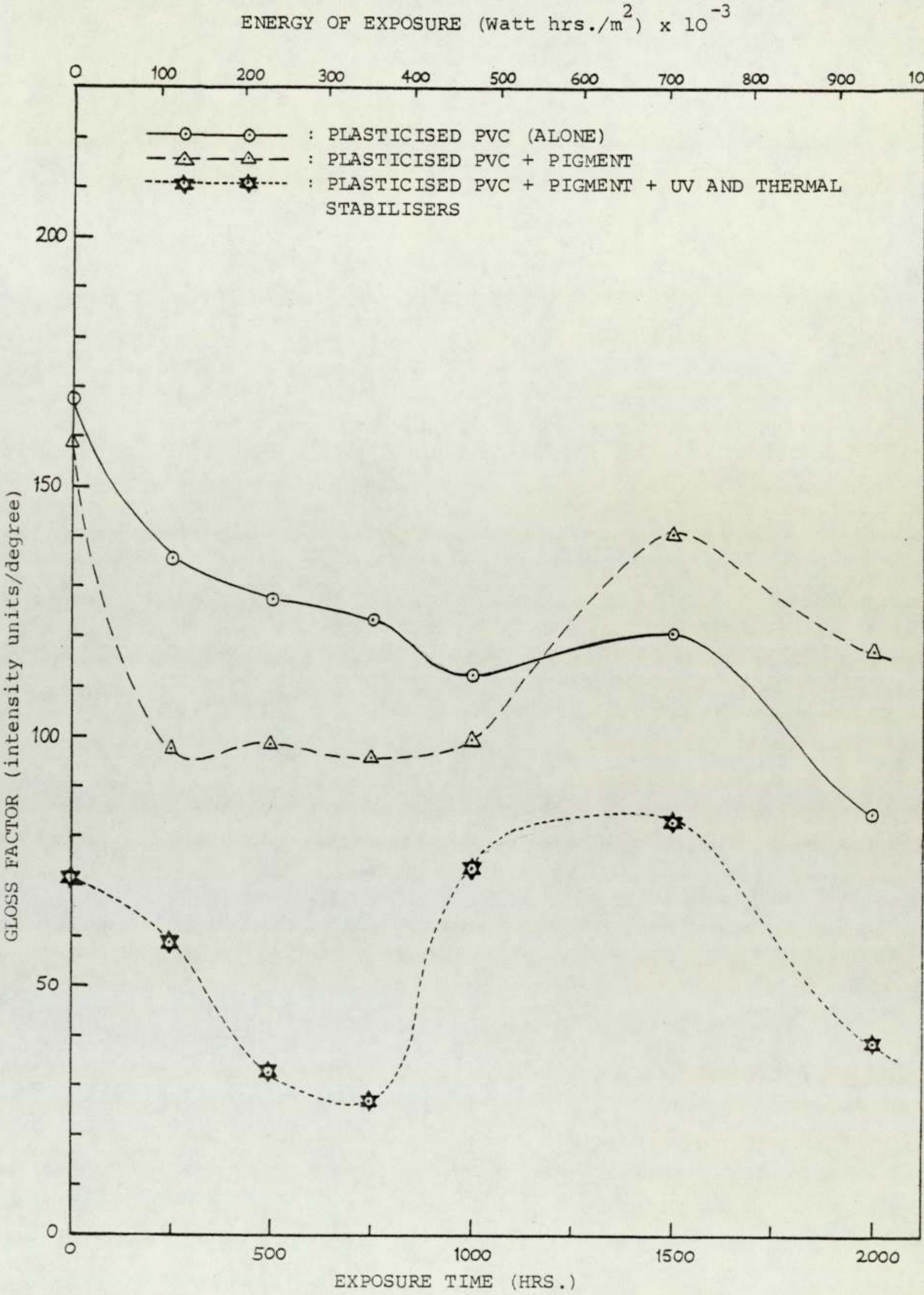


FIGURE 87 - Artificial (BS 3900 Part F3) weathering of PVC plastisol coatings (Series II : 50 p.p.h.r. plasticiser); variation in gloss factor on exposure.

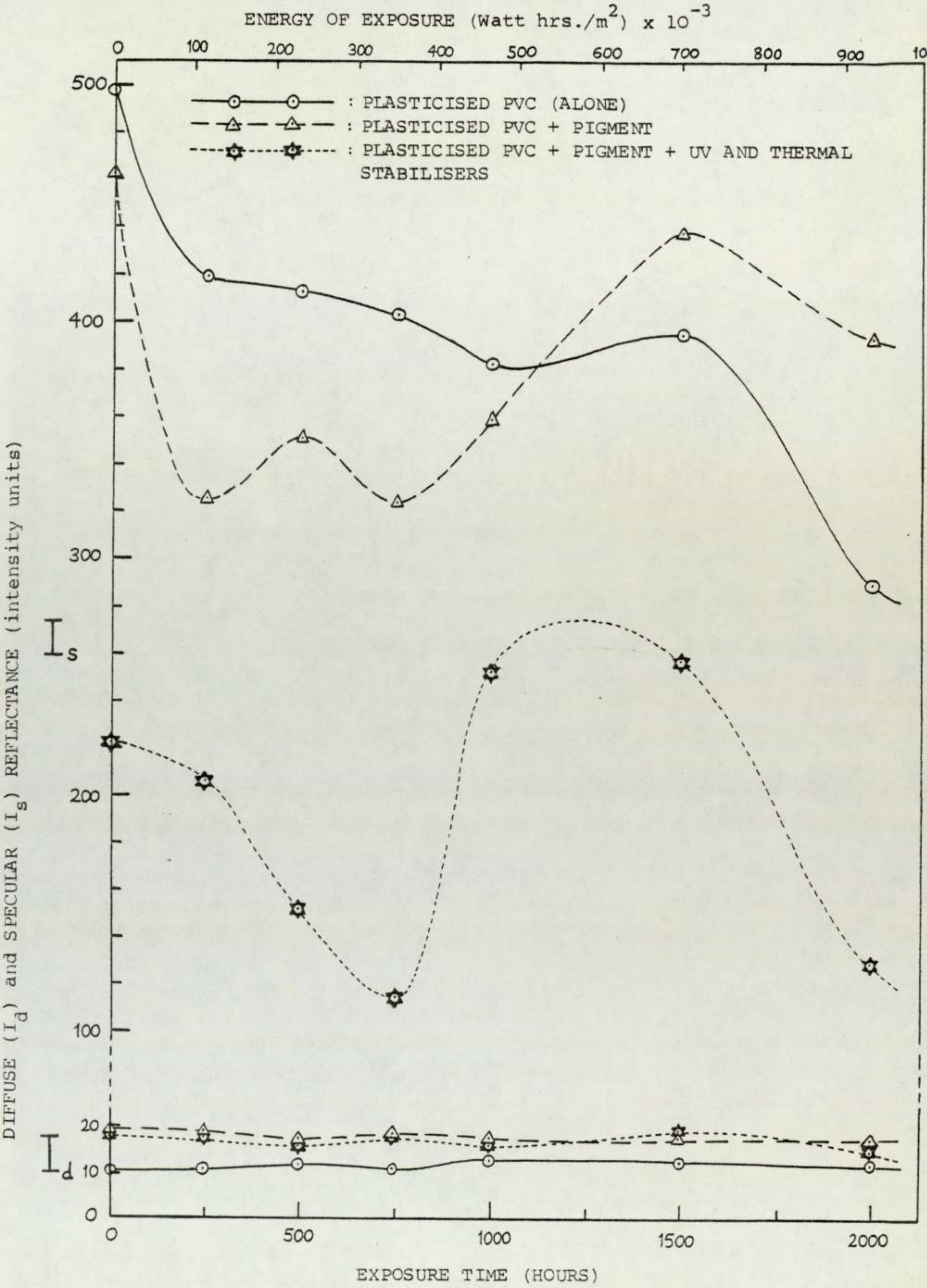


FIGURE 88 - Artificial (BS 3900 Part F3) weathering of PVC plastisol coatings (Series II : 50 p.p.h.r. plasticiser); variation in specular (I_s) and diffuse (I_d) reflectance on exposure.

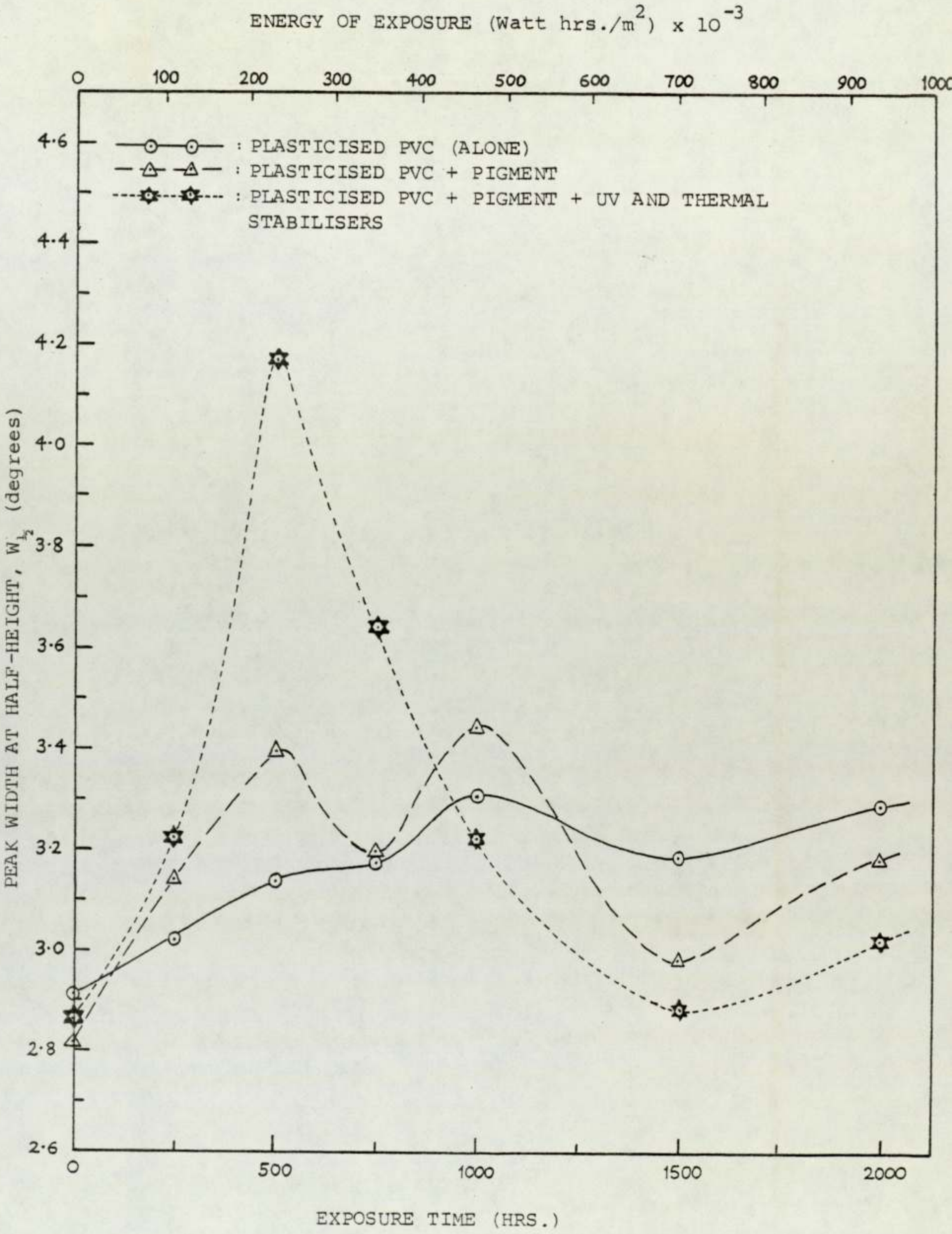


FIGURE 89 - Artificial (BS 3900 Part F3) weathering of PVC plastisol coatings (Series II : 50 p.p.h.r. plasticiser); variation in peak width at half-height ($W_{\frac{1}{2}}$) on exposure.

goniophotometric pattern has already been seen in earlier natural weathering studies to be a reflection of the way in which the major deteriorative ageing changes in plastisol surfaces tend to manifest themselves as isolated localised effects, the net result being that the vast majority of the surface area merely experiences the progressive formation/dismission of micro-defects, as sensed goniophotometrically.

This important finding is substantiated further by micrographic data relating to the Series II samples under current consideration. For example, the surface of the pigmented (unstabilised) coating after 1500 hours BS 3900 artificial weathering is seen at relatively low magnification (Plate 52) to embody patchy deterioration amongst what otherwise appear to be largely unaffected areas which still compare favourably with the unaged surface. The particular patch of deterioration appearing in the centre of Plate 52 is magnified in Plates 53 and 54 from which it can be characterised as consisting partly of "micro-checking" of the "irregular-pattern type". However, referring back to the centre of Plate 52, it can be seen that this small area of micro-checking, focussed on in Plates 53 and 54, adjoins a larger patch of deterioration of somewhat different appearance. This latter area, which barely gains inclusion into Plate 53 (right hand edge), appears in Plate 52 to represent the most common type of surface damage. This is confirmed to some extent by its greater prominence in Plate 55 which thus shows the added extent to which the coating has degraded during its final 500 hours weathering. The detailed nature of these degraded areas can now be seen in Plates 56 and 57 to embody mainly a somewhat "scalier" form of micro-checking which seems most likely to be precursory to actual flake detachment at a later stage. It is also relevant to note in Plates 53 and 56 how

PLATE 52

x 110

PLATE 53

x 1100

PLATE 54

x 5500

PLASTICISED PVC + PIGMENT plastisol coating;

Artificial weathering : BS 3900 Part F3; Exposure : 1500 hours.

PLATE 55

x 105

PLATE 56

x 1050

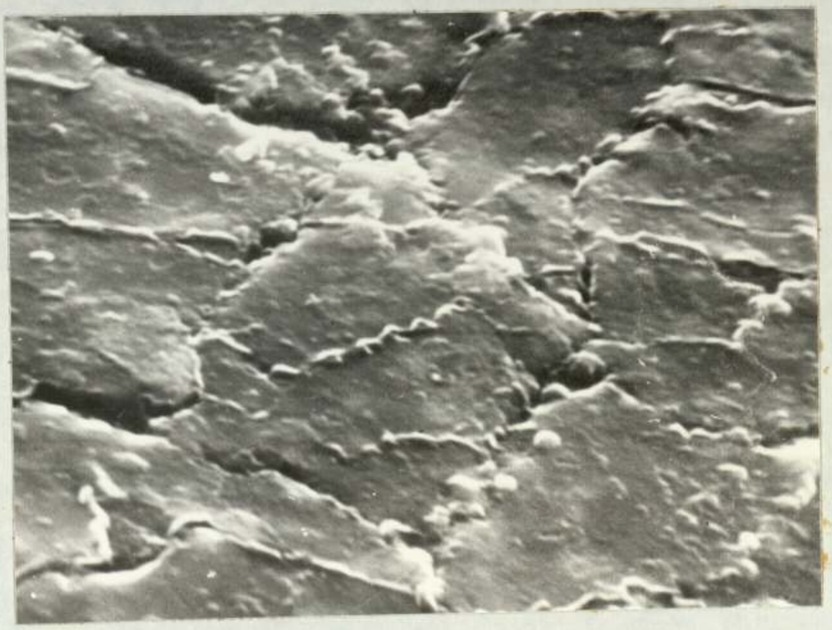


PLATE 57

x 5250

PLASTICISED PVC + PIGMENT plastisol coating;

Artificial weathering : BS 3900 Part F3; Exposure : 2000 hours.

strikingly the degraded areas contrast with their comparatively micro-deteriorated adjoining regions which, being considerably more expansive, tend, therefore, to remain more determinative of the ensuing goniophotometric changes.

Finally, the initially low gloss of the "complete" (i.e., pigmented + stabilised) coating (Figure 87) is seen in Plate 58 to be caused by what are believed to be microscopically small "blow-holes" resulting from incomplete de-aeration of the viscous plastisol paste prior to its relatively thick, single coat application (247). This diagnosis seems more likely than, say, overcuring in the fusion process in view of the lack of obvious discoloration in the cured film.

However, although this pre-exposure effect impairs the coating's subsequent ageing comparability with the other two samples, it nevertheless visualises, somewhat fortuitously, one or two other interesting impressions. Firstly, from a purely goniophotometric viewpoint, it is interesting to note that, despite their undoubted MACRO-size (estimated average diameter = 1 - 2 μm), the blow-holes (Plate 58) make no apparent contribution to the surface's light divergent ($W_{\frac{1}{2}}$ increasing) properties (cf. initial $W_{\frac{1}{2}}$ values for the three coatings in Figure 89); indeed, their goniophotometric effect is exclusively one of reflectivity reduction (Figure 88) by energy removal from the beam. The mechanism behind this is not difficult to visualise when one considers that cavities in an otherwise smooth surface are not as geometrically capable of incident light deflection as protuberant defects of the same size would be. Hence, light entering a surface cavity which is only slightly greater in diameter than the wavelength of the light invariably suffers energy attenuation rather than re-emergent angular divergence. This instrumental characterisation was additionally supported by visual examination of the surface which, despite its duller appearance, still displayed a capacity for image definition comparable to the other two coatings.

The second interesting feature is the way in which the outline and depth of the holes in the unaged surface (Plate 58) provide convenient, if undesigned, reference markers against which to gauge the extent of surface erosion which, against a smooth background, is often difficult to discern. In this way, the micrographs of this pitted surface on artificial weathering (Plates 58 - 61) are able to account for the observed goniophotometric changes (Figures 87 - 89). The apparent widening of the holes as their edges become rounded on exposure (750 hours, Plate 59) followed by their becoming shallower on further erosion of the surface (1500 hours, Plate 60) accords well with the corresponding reflectance data (Figure 88). Terminally, after 2000 hours weathering, the holes can be seen to have been almost "planed" away (Plate 61) by the time the surface has started to show signs of the type of patchy scaling/flaking deterioration observed previously in the case of the pigmented (unstabilised) sample.

Hence, this latter pitted sample has, admittedly, by accident rather than design, afforded a clearer view of the general background erosion which is taking place in these soft plastisol coatings' surfaces, superimposed upon which there are the more recognisable and, at the same time, more serious localised forms of film breakdown occurring.

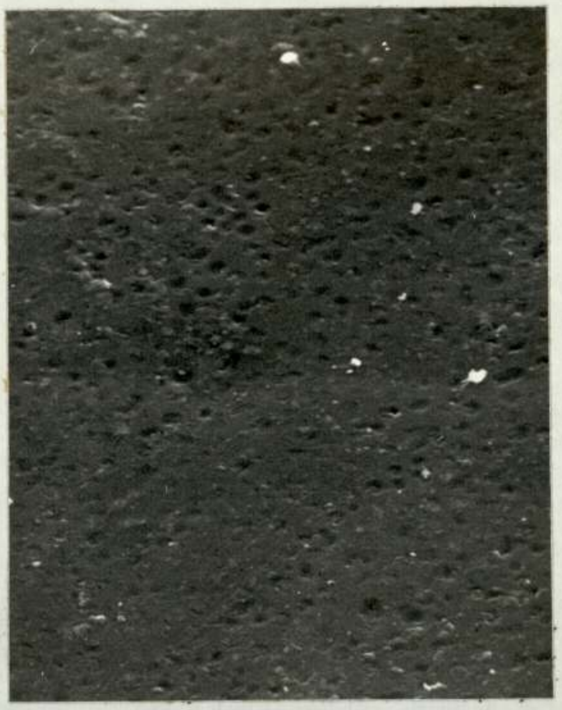


PLATE 58

0 hours

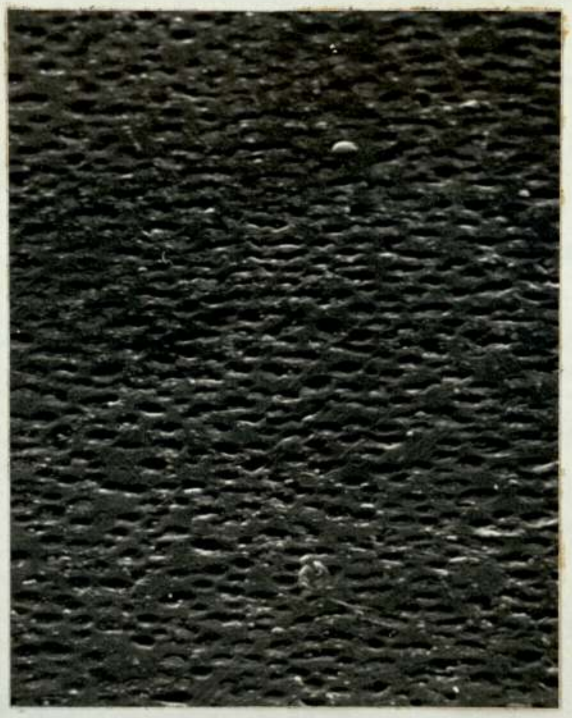


PLATE 59

750 hours

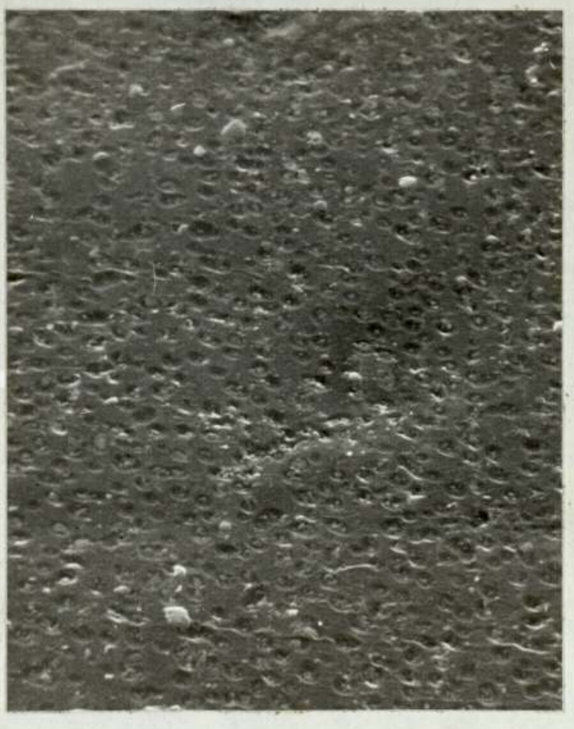


PLATE 60

1500 hours

PLATE 61

2000 hours

PLASTICISED PVC + PIGMENT + UV and THERMAL STABILISERS

Artificial Weathering : BS 3900 Part F3;

Magnification : x 1000

VII.3 Weight Loss Measurements

Weight loss measurements relating to the three (Series II) coatings under latter consideration plus a fourth - the twin-stabilised unpigmented coating - were taken over a period of 1500 hours BS 3900 Part F3 artificial weathering. In the absence of sample contamination, which had earlier invalidated similar natural weathering measurements, reliable weight loss data was obtained (Figure 90) which could be viewed within the context of the corresponding reflectance changes. However, as seen from Figure 90, the weight losses of what are considered most likely to be plasticiser from the samples are difficult to relate to changes in specific film properties due to the uncertainty which invariably surrounds their exact nature and cause. Nonetheless, the results in Figure 90 are at least able to show that, after similar initial weight changes in each of the four samples, the two pigmented coatings subsequently differentiate themselves from their clear counterparts by virtue of their reduced rates of further weight loss. Whether this is simply due to an inhibiting effect of the pigment on the ease of plasticiser migration to and, hence, volatilisation/leaching from the coating surface or is more to do with genuine ageing effects is impossible to say with any certainty. However, of these two suggestions, the former "non-ageing" pigment effect does seem the more plausible of the two in view of the still relatively early stage of weathering at which this weight loss disparity occurs.

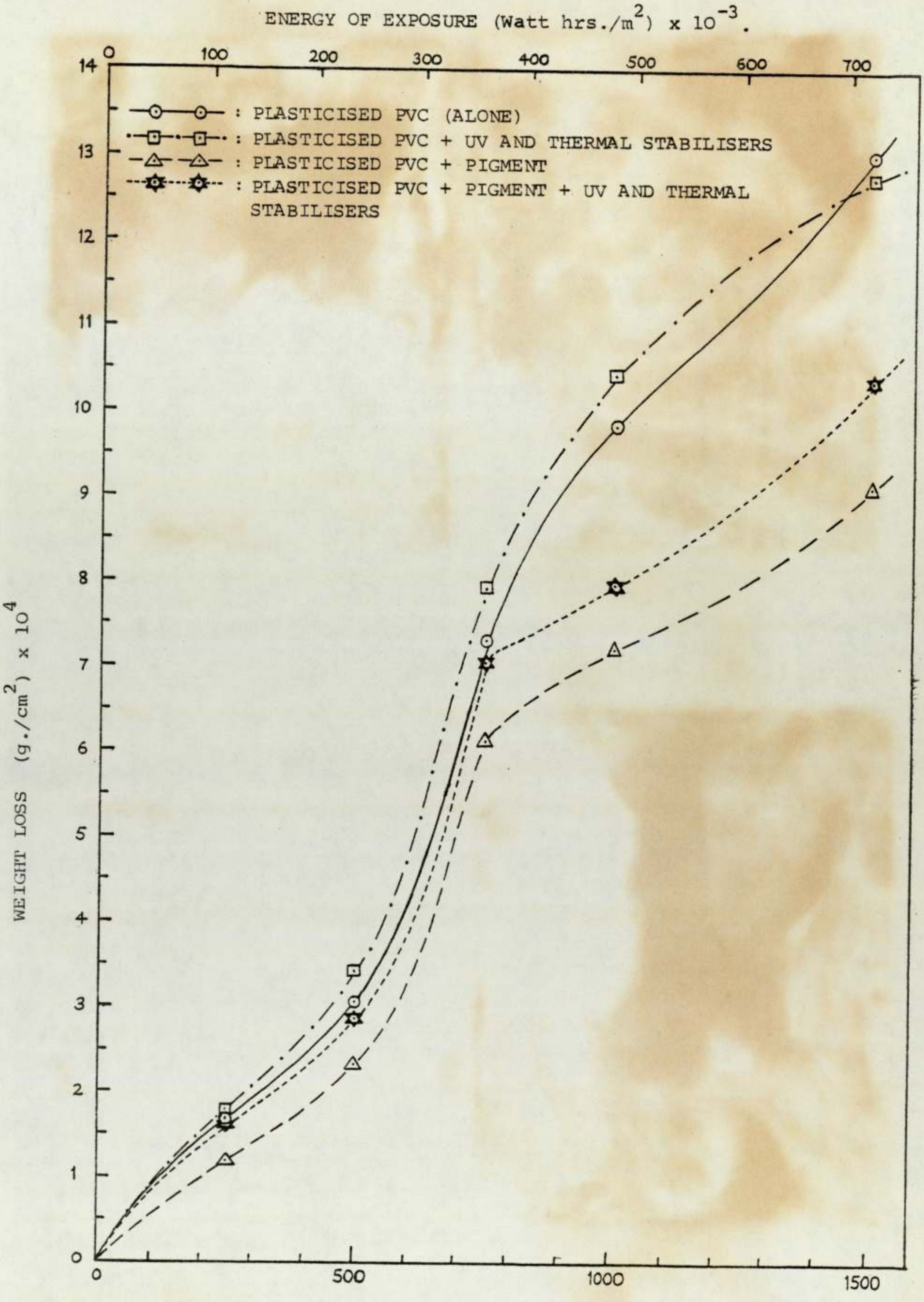


FIGURE 90 - Artificial (BS 3900 Part F3) weathering of PVC plastisol coatings weight loss variation on exposure.

CHAPTER VIII

DISCUSSION

CHAPTER VIII

DISCUSSION

In this chapter, the PVC plastisol results presented in the two previous chapters are discussed with reference, wherever appropriate, to earlier sections of the work. The main objective of this final discussion is to bring together now the various aspects of weathering behaviour which the results have spotlighted in the hope that, through their collective consideration, they can be crystallised into a physico-chemical characterisation of the obviously complex mechanism of coating deterioration. This, thus, sees the fulfilment of the five main objectives which were envisaged at the outset of this project (see section I.2 on page 6) with this, as seen at the time, being the ultimate aim.

The many and varied aspects of this in-depth study of PVC plastisol weatherability can be discussed most easily and intelligibly on the basis of 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 natural weathering features, including seasonal variations and the nature of the outdoor site;

(c) comparison of artificial and natural weathering performance;

(d) apparent effects of the various additives incorporated into these purpose-formulated plastisol coatings;

(e) mechanistic proposals relating to the complex chemistry of the ageing process, and,

(f) any final thoughts on the theories put forward.

Thus, these main topics for discussion can be regarded as forming "imaginary" sub-headings within the following "Discussion" text.

The general impression which has been gained throughout this latter study is that plastisol weathering consists essentially of a relatively uniform erosion of the soft coating surface superimposed upon which there are more serious forms of localised film breakdown taking place. The "background" erosion appears to involve the progressive formation/dismission, from the beginning of exposure, of what the goniophotometer consistently regards as MICRO-irregularities of the surface (i.e., $\leqslant$ approximately 700 mμ in height/lateral extent). In company with this, although not usually apparent until some time after initial exposure, the further advancement of the film's chemical deterioration then becomes seemingly concentrated into isolated spots, as if autosensitized in this direction. This subsequently leads to the more serious forms, goniophotometrically speaking, of MACRO-defect formation, the prime manifestation of which, certainly in natural weathering, is the onset of <u>FLAKING</u>. Indeed, the emergence of flaking as the apparently intrinsic plastisol surface defect formed on outdoor exposure is arguably the most striking feature of the previous test results. In comparison, artificial (BS 3900 Part F3) weathering has been seen to induce a slight variation on this type of surface defect which can perhaps be more accurately described as SCALING. The signs are, however, that these similarly isolated scaling patches, accompanied in certain instances by fringe areas of MICRO-CHECKING, could well prove to be precursory to the type of flake-detachment observed in natural weathering. Finally, it was observed in the case of naturally weathered clear (i.e., unpigmented) coatings that, during the later stages of exposure, the chemical degradation which had been responsible for the microscopic flaking had advanced to the stage whereby a dark brown SPOTTING effect was clearly visible to the naked eye and which, in some cases, was seen to develop further into patchy and, ultimately, total surface coverage.

These isolated, yet, at the same time, concentrated forms of plastisol surface deterioration can be compared with the way in which the more rigid PVC organosol coating previously supported the development of a more coherent coverage of growing MICRO ⟶ MACRO-defects whose number/size progression of formation/dismission could be closely characterised by means of goniophotometry as well as surface microscopy. However, in contrast to this, plastisol deterioration is such that the initially isolated outbreaks of flaking/scaling tend to be comparatively uninfluential as regards affecting surface reflectance relative to their much more expansive intervening areas which are merely experiencing "background" MICRO-textural changes. Consequently, the fact that the extent to which ageing degradation may have progressed does not necessarily lead to a commensurate decrease in gloss determines that goniophotometry alone is not so closely descriptive of plastisol weatherability as it was for the organosol system previously. Thus, this plastisol study has provided an ideal opportunity for scanning electron microscopy (SEM) to assume the leading role as the more diagnostic technique as far as predicting the likely life expectancy of the coating is concerned. Additionally, of course, SEM, apart from recognising that the major film deterioration is of a localised rather than disperse nature, is also able to identify the type of characteristic defect(s) formed.

Considering now the various seasonal changes taking place during the course of natural weathering, one or two significant differences from earlier studies were apparent in the plastisol trends. Although summer exposure again proved to be the most generally deteriorative period, plastisol deterioration taken over the year as a whole did not appear to revolve quite so markedly around the solar radiation element alone as in the case of the commercial coating systems previously studied. This is not meant to imply, however, that photodegradation is no longer the main degradative route but merely that the softness of the plastisols, if nothing else, renders them that much more responsive to the more physical elements of natural weather. This is borne out by the fact that the decreasing gloss trends exhibited by the pigmented plastisols during their initial summer exposure are reversed as early as the autumn before being just as promptly re-established during the winter and spring. This pattern of behaviour can be compared with the more predictably radiation-orientated organosol cycle discussed earlier in section V.4 (page 280). It was also interesting to note in this respect that, although twelve months weathering of plasticised PVC (unpigmented and unstabilised) initiated during the early autumn proved, as expected, to be somewhat less severe than a corresponding summer-initiated exposure, as measured in terms of gloss reduction, the by now characteristic mid-term recovery period was similarly evolved after around nine months exposure in each case, this being despite the different starting times. This lends further weight to the argument that, compared with the previous coating types studied, plastisol materials, by virtue of being more responsive to a wider range of natural weathering factors, therefore tend to be not so predominantly a function, in their weathering pattern, of seasonal radiation variations in particular but rather more of weathering conditions as a whole.

Not surprisingly, therefore, the nature of the outdoor site has been seen to have an important influence on plastisol performance. Particular site effects observed in this work, in relation to Building Research Station (Garston) semi-urban exposure, have ranged from the paradoxical coating protection afforded by the high dirt pick-up in polluted environments, such as at the Gravelly Hill site, to the genuinely hostile site-induced breakdown at the industrialised Aston University roof site; twelve months weathering at this latter location appearing to be equivalent to nearer two years exposure at Garston.

On comparing with these natural weathering findings those of artificial (BS 3900 Part F3) weathering, for the higher plasticised (Series I) coatings, it was found that artificial weathering was able to induce a similar sequence of gloss changes of similar energy-based periodicity. However, these latter changes tended to be less exaggerated than those of natural weathering with rates of gloss reduction being generally lower and mid-exposure trend transitions depicting not so much positive improvements as merely periods of gloss stability (i.e., non-change). Whether these relatively milder artificial weathering changes are due to the fact that (a) the more physically erosive aspects of natural weather are not simulated in the

BS 3900 F3 apparatus and/or (b) that the slightly above ambient temperature inside the BS apparatus promotes plasticiser migration and, hence, the in-built "surface-mending" facility which the plastisol coatings appear to possess, can be at least partly answered by the corresponding lower plasticised (Series II) sample results. The fact that these latter samples depict intermediate gloss increases during BS 3900 exposure which approach those of natural weathering indicates that plasticiser effects are, indeed, being enhanced in the Series I/ BS 3900 samples, thus lessening the severity, although not the basic pattern, of the observed changes. It is also significant that despite the fact that the artificial weathering cycle cannot hope to match the inherent complexity and diversity of seasonal natural weather variations, it has nevertheless been shown micrographically that the Series II coatings undergo a natural weathering type surface roughening/ erosion cycle even in the BS 3900 apparatus. Furthermore, the BS cycle is also seen to induce the type of localised surface deterioration which previously characterised outdoor exposure. That BS 3900 exposure can still correlate this closely with natural weathering, even in the case of experimental plastisol coatings such as these which are believed to be particularly responsive to the more physical elements of natural weather, raises again an interesting possibility first considered on the basis of similar findings to these with the PVC organosol previously - i.e., that PVC-based systems tend to reflect, through their ageing response, their own compulsive, self-directing pattern of deterioration which, once initiated, is then, to a certain extent, relatively unconcerned with the particular intricacies of the ageing environment. This possibility seems all the more reasonable in view of the way in which degrading PVC is known to autosensitize its own further decomposition, a fact which has already been used to account for the plastisol coating tendency to concentrate surface deterioration into localised areas.

This seemingly in-built predisposal for determining its own weathering fate reflects the general concensus of opinion that PVC alone is not an inherently weather resistant material, deriving most of its properties in this respect mainly through skilful formulation(327). Furthermore, this degree of instability tends to be aggravated by the presence of plasticisers and other additives which are themselves prone to degradation(328). Not surprisingly, therefore, plasticised PVC alone is also found(328) not to be a weather resistant combination, with a year's outdoor exposure, or, in some cases, even less, being sufficient to cause degradation (darkening/embrittlement) to occur to the point where the specimen is of no practical importance as a product; this finding having been strikingly confirmed in this current study. Some further interesting generalisations regarding plasticised PVC compositions have been made by Estevez(5) who claims that optimum weatherability is obtained when the plasticiser content is between 40 and 50%. However, Darby and Graham(329) have put this figure at roughly 35 p.p.h.r. for plasticised PVC film (cf. 50 and 80 p.p.h.r. used in this work), 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(205, 344, 345) have shown to be very much a surface reaction.

On the other hand, at higher than optimum plasticiser levels, the advantage gained from efficient stabiliser mobility starts being outweighed by the increasing photosensitization (i.e., radical forming UV absorptivity) of the film by its increasing carbonylic content.

As regards the plastisol coatings studied here, they would undoubtedly fall into the latter (i.e., above optimum) plasticisation category. Certainly, results from this study have shown that the migration of plasticiser within even the pigmented coatings is far from lacking as far as stabiliser mobilisation would be concerned. Indeed, in the case of the higher plasticised (Series I) coatings, plasticiser migration to the surface is operational to the extent that is masks certain of the observable polymer/surface changes which occur during weathering. This has lead to earlier speculations of the plasticiser in a "surface mending" role whereby the true extent of chemical changes, surface roughening and, hence, gloss reduction is not always appreciated analytically.

The preponderance of plasticiser at the surface of the plastisol coatings during exposure has been usefully demonstrated in this study by contact angle/surface free energy analysis. Differences in related data between a natural weathering series of plasticised PVC (alone) coatings and known values for rigid PVC (see section VI.2.4 previously) have been attributed to the effect at the coating surface of the aromatic and aliphatic hydrocarbon groups, as opposed to the ester groups, of the DIOP plasticiser. The surface excess of the former can, in turn, be ascribed to the effective shielding of the ester groups by the sterically hindering isooctyl moieties. However, of greater interest to this study have been the weathering changes or, as it turned out, the lack of them, at least until after twelve months exposure, in the water and methylene iodide contact angles and polar and dispersive components of surface free energy of the coating surface. This apparently stable state of affairs can be interpreted in different ways:

(a) that there is no backbone modification to the polymer during this period of non-change, or,

(b) that there is backbone change but that, in an above-T_g (i.e., chain rotational) situation, the plasticiser allows for surface formed polar groups to equilibrate with the more polar coating sub-surface.

This then allows for the eventual changes (i.e., lowering of the water contact angle and increase in the polar component of surface free energy) in the final two (12 and 17 months) exposure samples to be interpreted on the basis of:

(a) a marked increase in surface oxidation, and/or,

(b) loss of plasticiser resulting in a greater effective residual, surface, polymer concentration.

Additionally, however, it must also be recognised that a sufficient increase in surface roughness, usually to an average defect size of at least around 500 mμ, can cause a lowering of contact angle. Whilst this effect should, in theory, cause both the water and the methylene iodide values to fall, the surface tension difference between these two would make it more obvious in the water measurements as, indeed, observed. This rugosity effect, therefore, lends itself to a third possible interpretation of the observed weathering pattern:

(c) that there is no surface oxidation contributing to changes in polarity, nor any significant rugosity effect, up until the time of the terminal changes taking place when the surface does suddenly become more rugous.

However, this latter interpretation (c) seems the least likely of the three, especially in view of the corresponding micrographic/goniophotometric data relating to the sample areas analysed which, incidentally, comprised the more expansive micro-deteriorating areas, thus avoiding any localised brown "spots" present in the surface after 12 and 17 months exposure.

Of the previous alternative interpretations, the most likely one is evidenced by the results of thermal analysis (see section VI.2.5) which, after a similarly lengthy period of apparent non-change, show a marked increase in the coating's glass transition temperature (T_g) after 17 months weathering, symptomatic of a, by now, significant loss of plasticiser. This, therefore, indicates that the most likely effect giving rise to the significant increase in the water wettability of the coating surface during the terminal stages of weathering, even after the onset of visible "spotting", is loss of plasticiser to the extent that the "reservoir" of what is left can no longer maintain its previously "steady state" surface concentration in replenishment of its continued leaching/volatilisation from the surface. This results in greater exposure of the oxidised polymer at the surface and, hence, a lowering of the water contact angle.

Hence, this latter study has been able to demonstrate the value of specialist techniques, such as surface free energy studies, in providing useful supportive evidence for determining the nature of particular effects. Having been primarily concerned here with the effects of the plasticiser on coating weatherability, let us consider the various roles played by the other additives incorporated into the plastisol coatings studied - namely, the pigment and the two stabilisers.

Firstly, the pigment used (rutile titanium dioxide) has emerged from this experimental plastisol study as the singly most stabilising additive, in the proportion (15 p.p.h.r.) in which it was incorporated. Its stabilising action is well known as being that of a UV absorber, although this obviously only applies to degradation in depth as the degradation of the superficial layer of clear plastisol above the uppermost pigment particles continues. Hopefully, in practice, this top layer would be well protected by the presence of a specialist UV stabiliser. Titanium dioxide (TiO_2) pigments can also give rise to a variety of degradation processes in paint films(330), notably in their role as oxidation catalysts in the photolysis of the binder(331, 332) and also in their tendency to cause "chalking"(31, 247, 333, 334), this latter process often proving a concomitant of the former. However, at the relatively low levels of pigmentation used in plastisols (approx. 7½% and 9% by weight respectively in the Series I and II coatings studied here), these deteriorative pigment effects are minimised with the result that the pigment is more in evidence in its stabilising capacity. Indeed, in these current samples, the TiO_2 pigment, in the proportion in which it was incorporated (15 p.p.h.r.), appeared to afford a greater degree of weathering protection to the plastisol coatings than did the (0.5 p.p.h.r.) UV stabiliser, without, at the same time, giving rise to any discernable film rigescence. Even at its lower, 7½% weight concentration in the Series I coatings, the presence of pigment alone was able to transform plasticised PVC film from a material which, on its own, had completely degraded after 17 months weathering at the Building Research Station site, to one which was still ostensibly intact after 27 months exposure. Furthermore, over this 27 month period, this "plasticised PVC + pigment" natural weathering performance was not significantly improved upon by the added incorporation of UV and/or thermal stabilisers. However, in the case of artificial (BS 3900 F3) weathering, in which the radiation (UV/ir) element is both relatively intensified and proportionately magnified, the additional effect of the stabilisers in pigmented films has also been distinguished.

However, the effectiveness of the stabilisers, both in combination and individually, is most readily observed in the clear coatings relative to plasticised PVC alone. Natural weathering of the four clear films at the Aston University roof site was able to show that the UV stabiliser, on its own, was somewhat more protective than the thermal stabiliser and that the two in combination were better still. Whilst these findings are, in themselves, not exactly revelational, they serve to at least confirm that the stabilisers are effective at the coating surface despite the relative difficulty with which this is observed in pigmented media.

Thus, having now looked at the effects of the various additives in terms of their influence on surface properties, let us consider finally the complex chemistry which forms the basis of understanding of the observed weathering changes. The chemical information obtained from this study in the form of infrared spectroscopic data is, however, rather limited in what it can advise in this respect. Nevertheless, despite the various procedural and plasticiser interference effects described earlier in section VI.2. 3 , some interesting qualitative impressions have been gained concerning the chemical processes which are operational in the natural weathering of PVC-based surface coatings. These can be summarised briefly as involving:-

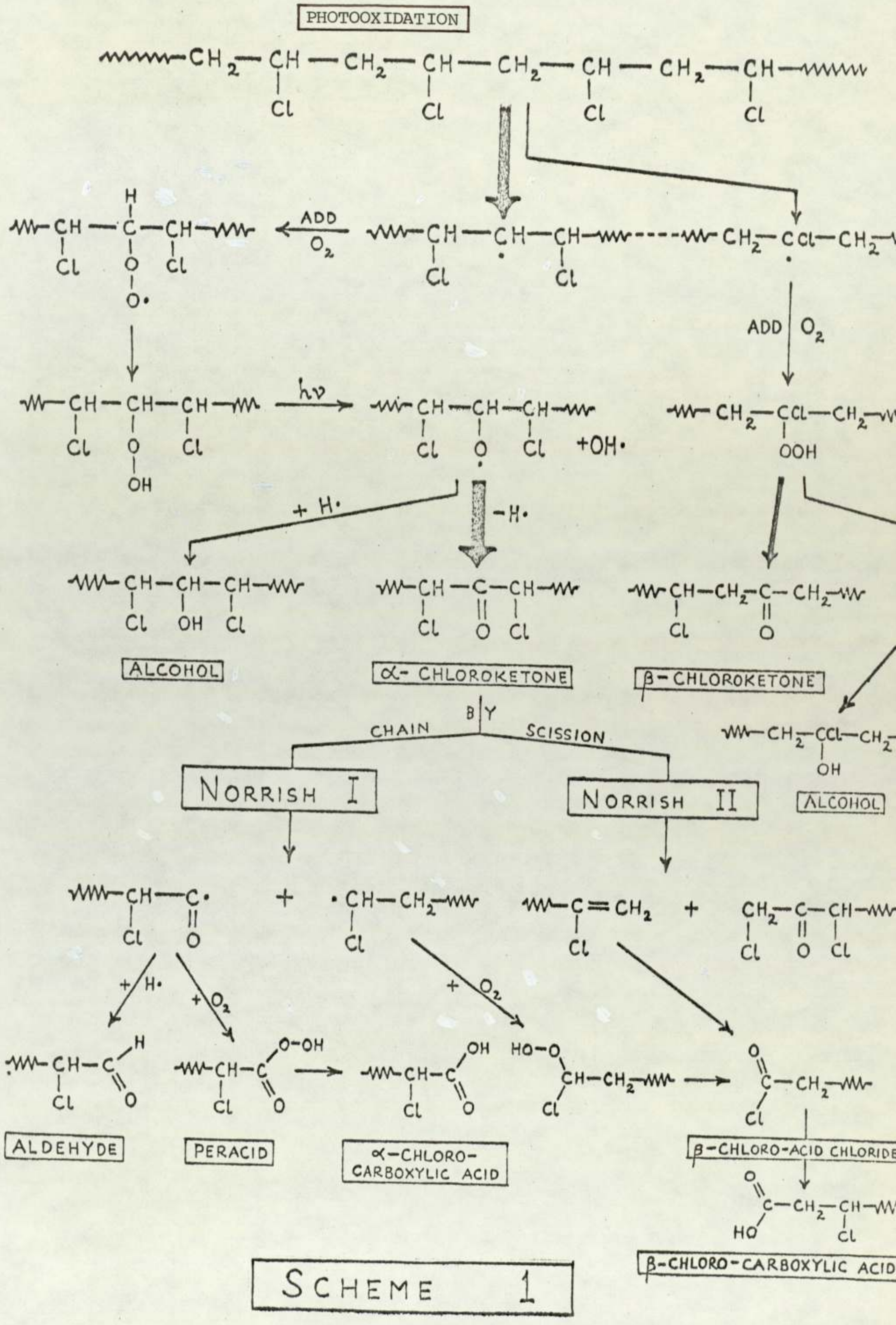
(a) photolytic hydrogen abstraction from the polymer chain - although it is not possible to say here to what extent methylenic or chloromethylenic hydrogen abstraction is favoured; the indication from the previous organosol study, however, was that these two initiation steps were extremely competitive;

(b) concomitant oxidation of the binder and, undoubtedly, the plasticiser as well - the combined nature of this effect serving to detract from the correlativity of this with the previous process in (a); and,

(c) in a negative sense, little or no C = C double bond formation until towards the terminal stages of weathering; sample discoloration, the requirement for which is a minimum of seven conjugated double bonds in a sequence(335), was not noticeable in the white-pigmented coatings even after 27 months Garston exposure, although isolated brown spots were evident in the plasticised PVC clear coating after just 9 months.

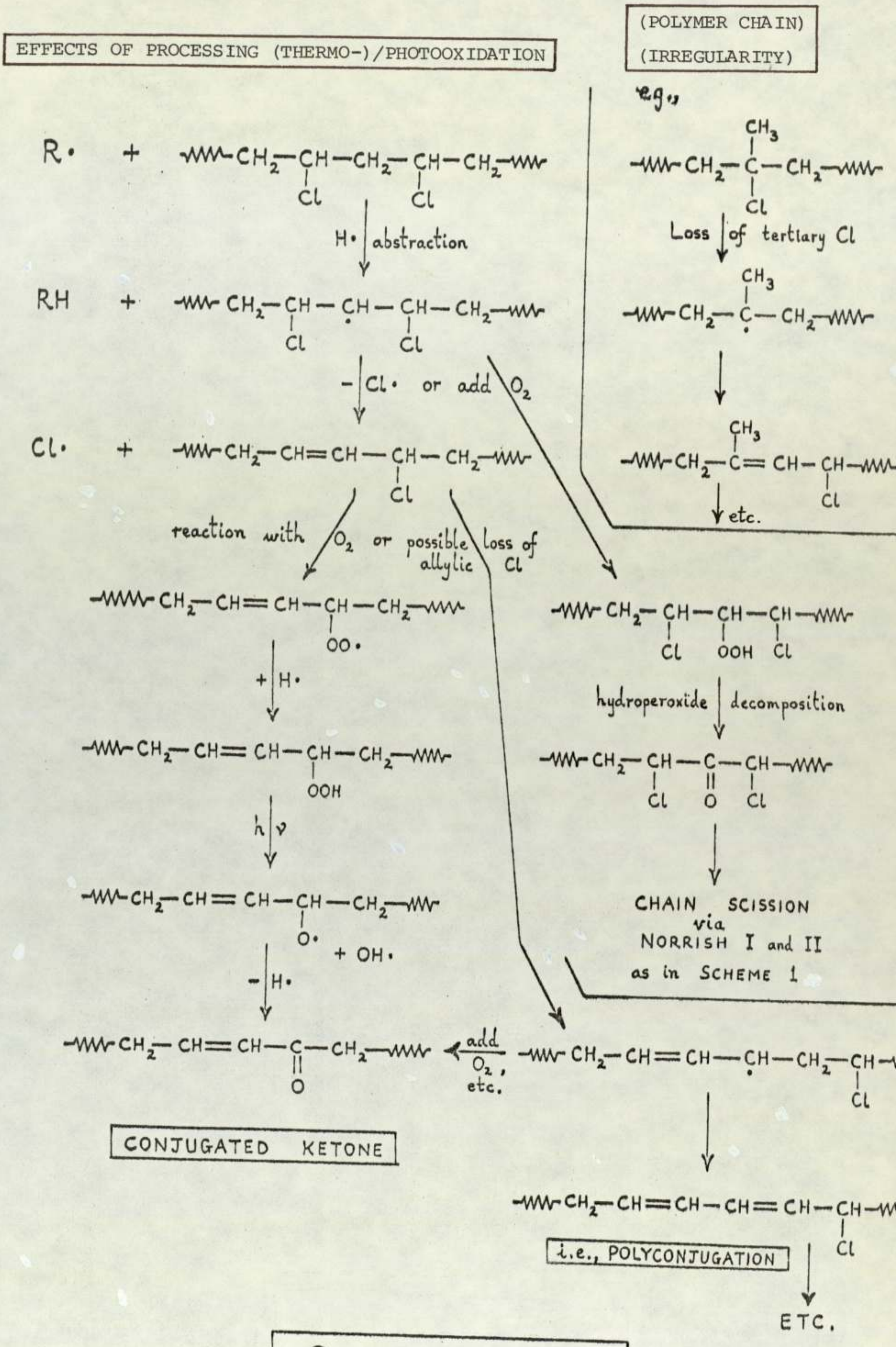
Whilst these findings may merely appear to comply with what is already known about the photooxidation of PVC, they are probably as much as could reasonably have been expected from a spectroscopic study such as this of materials as analytically complex as even these relatively simplistic plastisol coatings. However, a valuable extension to this discussion can be gained by considering these findings within the context of those of other research workers (336, 337) at this University involving related studies on pure PVC films either cast from solution (i.e., unprocessed) or processed under controlled conditions. The results of these latter studies are presented in Schemes 1 and 2 overleaf in company with other current ideas for the unprocessed (purely photooxidative) and processed (thermo/photooxidative) cases respectively. Scheme 1, first of all, depicts the photooxidation of unprocessed PVC as a predominantly chain scission process leading, ultimately, to the formation of carboxylic acid groups. Although the precise mechanism of this process is by no means certain, the fact that more than one carboxylic acid is formed suggests that there are two alternative modes of photolysis (Norrish I and II) of the intermediate α -chloroketone, whose apparent prevalence over the β -chloro adduct supports the now growing school of thought in favour of initial methylenic, as opposed to chloromethylenic, hydrogen abstraction. In addition, the chain scission process is also found to be auto-accelerating, presumably due to the photosensitizing effect of the initially formed carbonyl groups.

Processing of the polymer prior to ageing, on the other hand, introduces other highly photosensitized (e.g., allylic) structures into the polymer chain (Scheme 2) which 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.



SCHEME 1

Current theories on the photooxidation of PVC.



SCHEME 2

Current theories on the photooxidation of processed PVC.

Despite the enormous amount of research which has been conducted into the photooxidative degradation of PVC, in addition to that described here, it is still not fully understood, as reflected in the several different mechanisms which have been proposed(338 - 343). Indeed, it should be emphasized here that the overall photooxidation of unprocessed/processed PVC will inevitably comprise a complex, interdependent "balance" of the various types of reactions included in Schemes 1/2 and whose relative rates will determine their respective contributions to the overall reaction.

Hence, it is on the basis of these mechanistic considerations that the plastisol coating effects observed in this work can be more readily understood. For instance, because the presence of plasticiser tends to keep the polymer chains apart, chain scission reactions of the type shown in Scheme 1 are more likely to occur than, say, cross-linking. This consequently results in a reduction in molecular weight which, coupled with the effects of thermal expansion/contraction of the film, leads to micro-checking, as observed micrographically in this study. Furthermore, the apparently in-built tendency which degrading PVC has for not only auto-accelerating its own chain scission but also for concomitantly concentrating this degradation into localised areas of the coating surface, on account of its own preferential auto-sensitization, provides, in likely combination with mechanical stresses, ideal conditions for flaking to occur.

In conclusion, therefore, it really goes without saying that mechanistic insights such as these into the nature of the chemical changes which ultimately give rise to coating failure obviously must form an essential part of any study such as this which sets out to try to establish the complete weathering "picture" relating to a given type of coating system. Clearly, for PVC to prove really useful as a coating binder, it has to be suitably stabilised, and the characterisation of its fundamental mode of breakdown in this way represents the first logical step towards effecting an improvement in its stabilisation.

CHAPTER IX

THE INTERACTION OF NITRIC OXIDE WITH POLY (VINYL CHLORIDE) PLASTISOL SURFACES

- A CASE STUDY

CHAPTER IX

THE INTERACTION OF NITRIC OXIDE WITH POLY (VINYL CHLORIDE) PLASTISOL SURFACES - A CASE STUDY

IX.1 Introduction

This final section of the work now takes an adjunctive look at the way in which the poly (vinyl chloride) (PVC) plastisol coatings studied previously interact with a known reactive gaseous constituent of the atmosphere other than oxygen - namely, nitric oxide (NO). Although this is very much a case study rather than an ageing study in as much as the experimental nature of both the test materials and their testing environment are far removed from a "real" weathering situation, the fact that nitric oxide, together with other oxides of nitrogen and sulphur as well as ozone(248, 249), has long been considered to have deleterious effects on paint films, even at its intrinsically low atmospheric concentrations, serves to illustrate the relevance of this type of mechanistic experiment to the wider concept of an ageing study.

Nitric oxide (NO) is initially formed in the atmosphere by the solar-initiated photodissociation of nitrogen dioxide (NO_2) (see eq. (9) below) which is the principal light-absorbing species present in smog(250, 251, 261).

$$NO_2 + h\nu \quad (295 - 430\ \text{nm}) \longrightarrow NO + O \qquad \text{......} \quad (9)$$

However, although efficiently photodissociated in this, the primary photochemical act, nitrogen dioxide is then, somewhat paradoxically, ultimately reformed in highly complex photooxidation processes at a much faster rate than it was initially destroyed(252), the net effect being a very rapid conversion of NO back to NO_2 which, in smog, occurs by three major paths, eqs. (10 - 12):-

(i) reaction with ozone : $NO + O_3 \longrightarrow NO_2 + O_2$ ...... (10)

(ii) thermal oxidation by molecular oxygen : $2NO + O_2 \longrightarrow 2NO_2$ ...... (11)

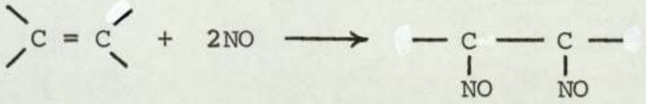
(iii) reaction with radicals :

$$NO + \begin{cases} HO_2 \\ RO_2 \\ RCO_3 \end{cases} \longrightarrow NO_2 + \begin{cases} HO \\ RO \\ RCO_2 \end{cases} \qquad \text{......} \; (12)$$

The net result of all this is that nitric oxide (NO) exists quite stably in the atmosphere in intrinsically small concentrations dependent 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(250) and dense traffic areas(192).

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 deal mechanistically with this particular aspect. Indeed, this can even be said to be true of this type of study in general which, in many ways, is somewhat surprising considering the amount of "bad publicity" which gaseous atmospheric pollutants have long received in respect of their observed deteriorative effects on paint films. However, these latter studies have invariably only been 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 (253 - 257), concerning the reaction of nitrogen dioxide (NO_2) with hydrocarbon polymers, and to Ogihara et al. (258, 259) 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, although one or two of the more recent contributions (200, 201), conveniently for this present study, happen to have been within the context of poly (vinyl chloride) (PVC) thermal decomposition.

Indeed, 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 (201) 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:-



$$>C=C< + 2NO \longrightarrow -\underset{NO}{\underset{|}{C}}-\underset{NO}{\underset{|}{C}}-$$

This latter proposal was later supported by Mladenov and Slavov(200) 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.

In summary, therefore, it has been found that, in stark contrast to its common classification together with the other gaseous atmospheric pollutants as being harmful towards organic coatings materials, nitric oxide acts as more of a stabiliser in its reaction with PVC. This is achieved in two possible ways, (a) via its well-known inhibition of free radical reactions, and (b) through its addition to double bonds formed in the polymer as a result of dehydrochlorination. Indeed, nitric oxide has actually been used as a stabiliser in PVC(260) and, on this basis, would appear to be an ideal material for a study of inhibition in PVC degradation. However, this current study will now concern itself primarily with the chemistry of the PVC/NO interaction, and its possible ageing implications, rather than with the reflectance and topographical changes in the coatings' surfaces as in previous studies.

IX.2 Experimental Aspects

For the purpose of this study, the following four PVC plastisol (Series II, i.e., lower plasticised) coatings were selected for testing:-

(i) plasticised PVC alone,
(ii) plasticised PVC + UV and thermal stabilisers,
(iii) plasticised PVC + pigment,
and (iv) plasticised PVC + pigment + UV and thermal stabilisers.

Samples of these four coatings were then exposed to each of the following three sets of conditions:-

(a) thermal ageing at 100°C. in nitrogen ("blank" exposure),
(b) thermal ageing at 100°C. in nitric oxide/nitrogen,

for up to 60 hours in the apparatus shown in Plates 7 and 8 on pages 95 and 97, and:-

(c) UV ageing at room temperature in nitric oxide/nitrogen,

for up to 250 hours in the quartz glass vessel shown in Plate 9 on page 101. The concentration of nitric oxide in nitrogen used throughout was 3140 p.p.m. (see Table 5, page 100). Finally, as can be seen in Plates 8 and 9, the test-pieces of each coating exposed comprised three different types:-

(i) punched discs on aluminium substrates for goniophotometric analysis,

(ii) square-cut samples on stainless steel substrates for weight change measurements, and,

(iii) in the case of the two unpigmented coatings studied, pressed films as window-inserts in cards designed for transmission infrared spectroscopy — these films, which were required to be of 0.001 - 0.002 in. thickness in order for satisfactory spectra to be obtained, were prepared by pressing the 0.008 in. thick films (as supplied) for 30 seconds at 200°C. at a pressure of 30 p.s.i.

IX.3 Results

The results relating to each of the three exposure tests carried out here can be most easily and conveniently assimilated by the collective consideration of the various analytical data. Additionally, the reflectance and weight changes were, in the main, found to be such that they can be quite adequately described in the following text without the need for graphical representation.

IX.3.1 Thermal Ageing in Nitrogen

The thermal ageing in nitrogen of the four plastisol coatings listed previously was carried out at 100°C. with sample analyses being conducted after 0, 5, 10, 20, 35, 50 and 60 hours. Changes in reflectance over this 60 hour exposure period were found in all cases to be only relatively small, the common trend being slight initial changes (usually increases) in specular reflectance (I_s) during the first 10 hours exposure after which a "plateau" value was then maintained up to the end of the reported 60 hour period. These I_S changes, which, considering the softness of the coatings and, hence, their likely flow tendencies, could be initially attributed to thermal equilibration effects, again appeared to be the governing influence on the calculated gloss factor changes. However, during the latter half of the experiment, some slight, yet significant, accompanying peak width at half-height ($W_{\frac{1}{2}}$) increases were also sensed goniophotometrically which, on Stereoscan (SEM) analysis, were found to be due to a microscopic "wrinkling" of the surface. This effect is illustrated in Plates 62 - 64 for the "plasticised PVC + pigment" sample after 35 hours thermal exposure.

Weight changes in the samples were also found to be small and tended on the whole to be slight increases, although this was not a general rule. However, whilst the individual sample weight changes were somewhat difficult to define, it was significant to note that, whereas in the previous artificial weathering (BS 3900 Part F3) test, the presence of pigment appeared to be the differentiating factor in respect of weight change (see section VII.3 on page 342), in this thermal environment it was the incorporation of the stabilisers which had this similarly definite influence - suggestive, in this latter case, as being related to a suppression of thermal dehydrochlorination.

However, it was really the nature of the chemical changes taking place which was of primary interest as, indeed, it had to be in

PLATE 62

x 190

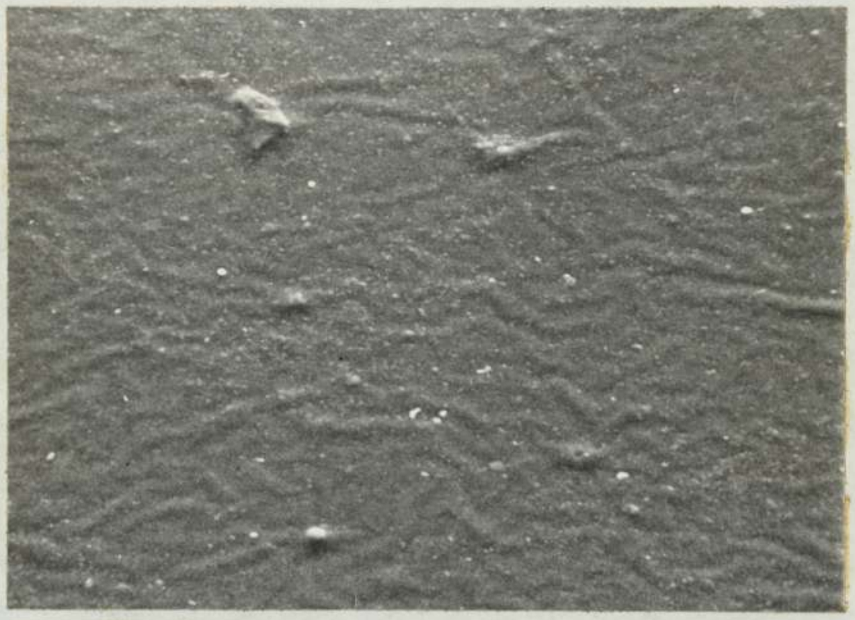


PLATE 63

x 470

PLATE 64

x 960

PLASTICISED PVC + PIGMENT plastisol coating;
Thermal ageing at 100°C. in nitrogen; Exposure : 35 hours.

as specific a study as this. Yet, as in the case of previous multiple internal reflectance infrared spectra obtained for these plastisol coatings, the transmission spectra of the pressed clear films were also dominated by the peaks due to the plasticiser which threatened to mask the otherwise observable polymer changes. However, in the transmission infrared mode, this problem could be more easily alleviated, if not overcome, by means of a "compensation" technique involving the placement of an unaged film sample, of as similar thickness as possible to the test-piece, in the reference beam of the spectrophotometer, so as then to record the differential infrared spectrum of the changes brought about in the test sample on exposure. Differential infrared spectra obtained in this way for the two clear plastisol films studied here are shown in Figures 91 and 92, from which it can be seen that the plasticiser peaks immediately re-appear on thermal ageing, increasing in absorbance for the first 20 hours exposure before subsequently retracting. However, rather than these spectral changes being interpreted solely in terms of a plasticiser migration effect, the fact that the 1423 $cm.^{-1}$ PVC peak also varies along similar lines suggests that we are observing here the added effect of film thickness variations, conceivably by downward flow on suspension of the sample in the heating medium. These physical processes, of course, serve to detract from the quantifiability of whatever genuine chemical changes may be spectrally measurable. However, even from a purely qualitative angle, the spectra in Figures 91 and 92 fail to show any significant change in the C = C double bond region of the spectrum (around 1650 $cm.^{-1}$) despite slight discolorations in the samples. Nonetheless, these findings now form a basis upon which to compare the following nitric oxide in nitrogen test results.

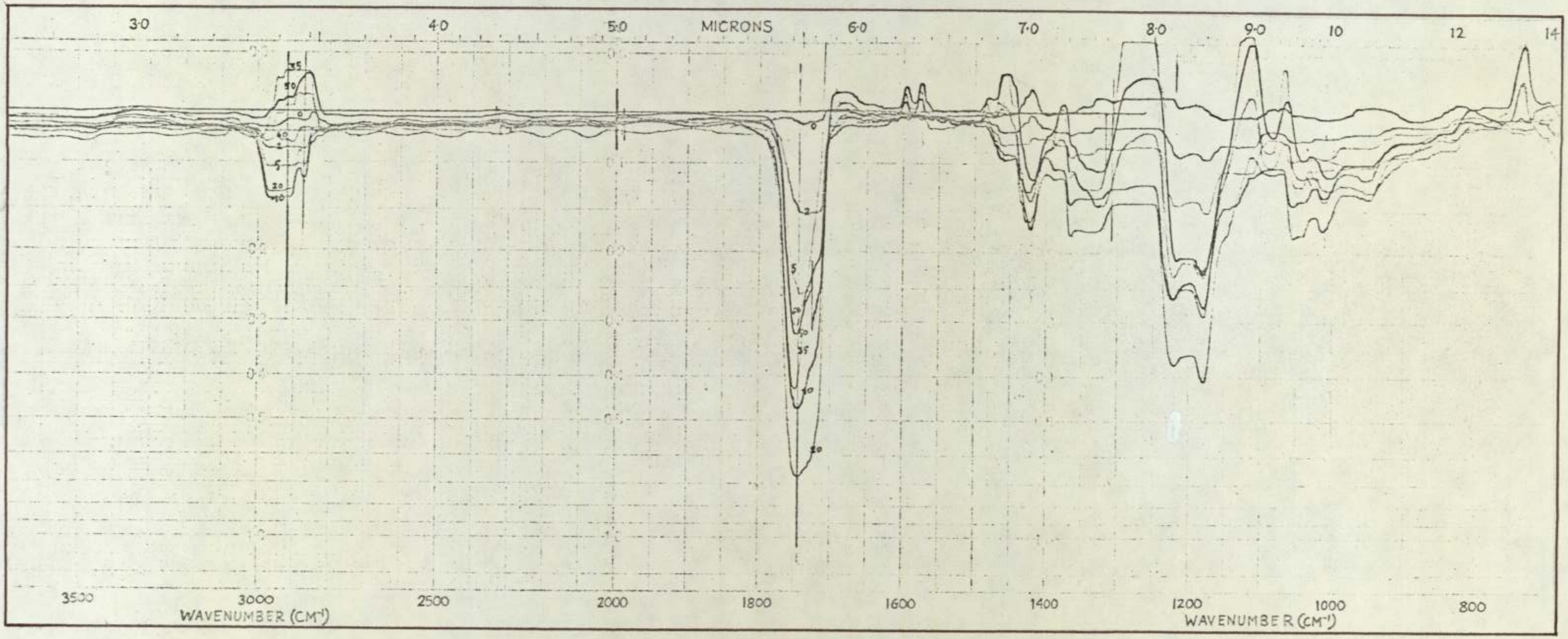
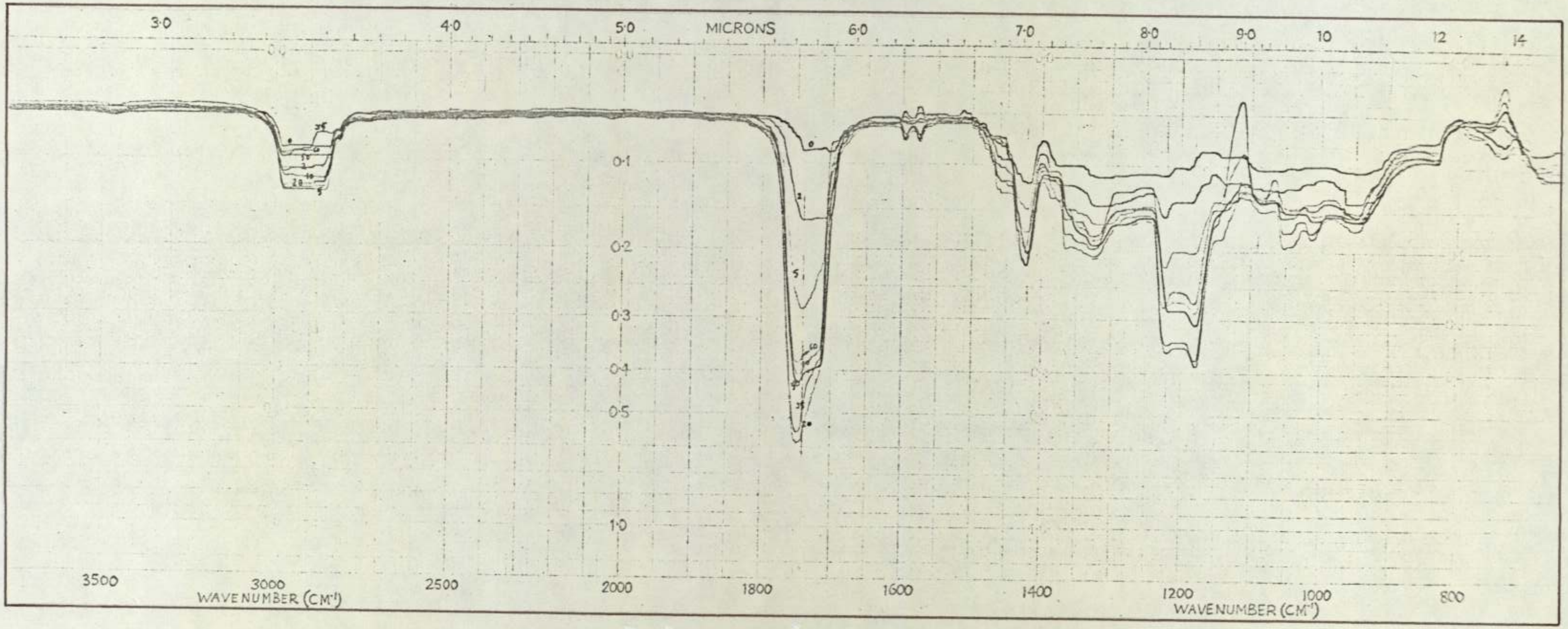


FIGURE 91 - Differential transmission infrared spectra relating to:-

PLASTICISED PVC (alone) clear film; thermal ageing at 100°C. in nitrogen.



<u>FIGURE 92</u> - Differential transmission infrared spectra relating to:-

PLASTICISED PVC + UV + THERMALLY STABILISED clear film;

thermal ageing at 100^{o}C. in nitrogen.

IX.3.2 Thermal Ageing in Nitric Oxide/Nitrogen

Thermal ageing in a flowing nitric oxide (3140 p.p.m.)/ nitrogen (NO/N_2) atmosphere at 100°C. for 60 hours induced strikingly similar reflectance changes in the four samples studied to those observed in the previous "blank" (nitrogen only) exposure. The same could almost also be said of the recorded weight changes, although these were at slightly greater variance insofar as the NO/N_2 exposed samples showed slightly greater weight gains which, furthermore, appeared to attain rather more of a "plateau" value after 20 hours.

However, a significant difference was clearly evident from the transmission infrared spectra of the NO/N_2 exposed films, which are shown in both their "normal" and "compensated" forms for comparison in Figures 93 amd 94. On ageing, a new growing multi-peak absorbance appeared in the spectrum of each of the clear films in the 1500 - 1550 cm.$^{-1}$ region which could clearly be assigned(262, 263) to the formation of nitroso (-N=O) groups in the polymer. However, in the light of this positive evidence of interaction between PVC and nitric oxide, it was of equal significance, in a negative sense, to note from the lack of absorbance in the O - H stretching regions of the spectra, the apparent non-formation of oxime (=N-OH) groups via the tautomerism of α-hydrogenated nitroso groups. The significance of this latter observation will be discussed later.

Finally, it could just about be discerned visually that there was less discoloration in the NO/N_2 exposed samples than in those from the previous "blank" exposure in the absence of NO. However, this decolourising effect of NO was not as obvious here as that apparently observed by previous workers(200, 201).

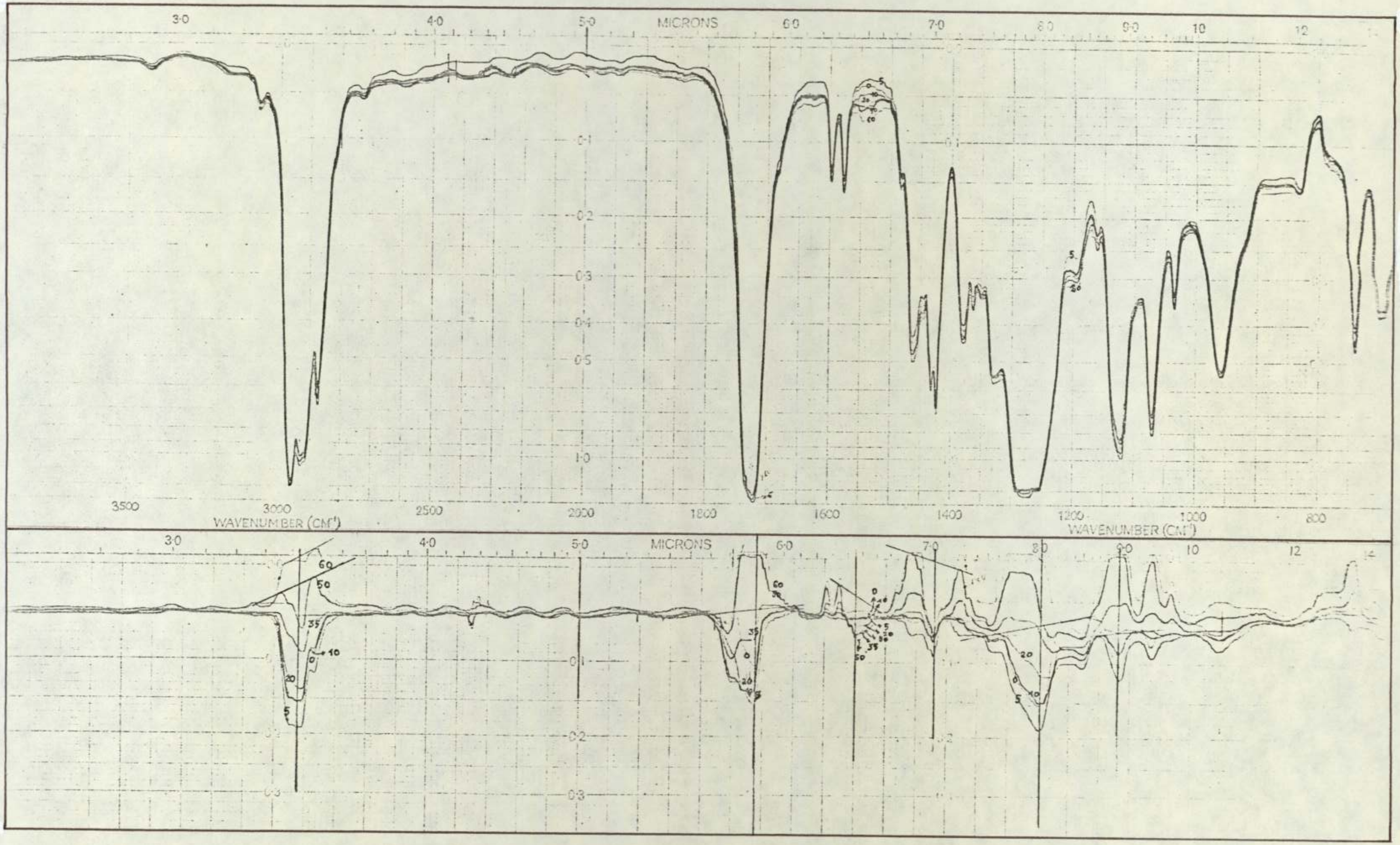


FIGURE 93 - Normal (upper) and differential (lower) transmission infrared spectra relating to:-
PLASTICISED PVC (alone) clear film; thermal ageing at 100°C. in nitric oxide/nitrogen.

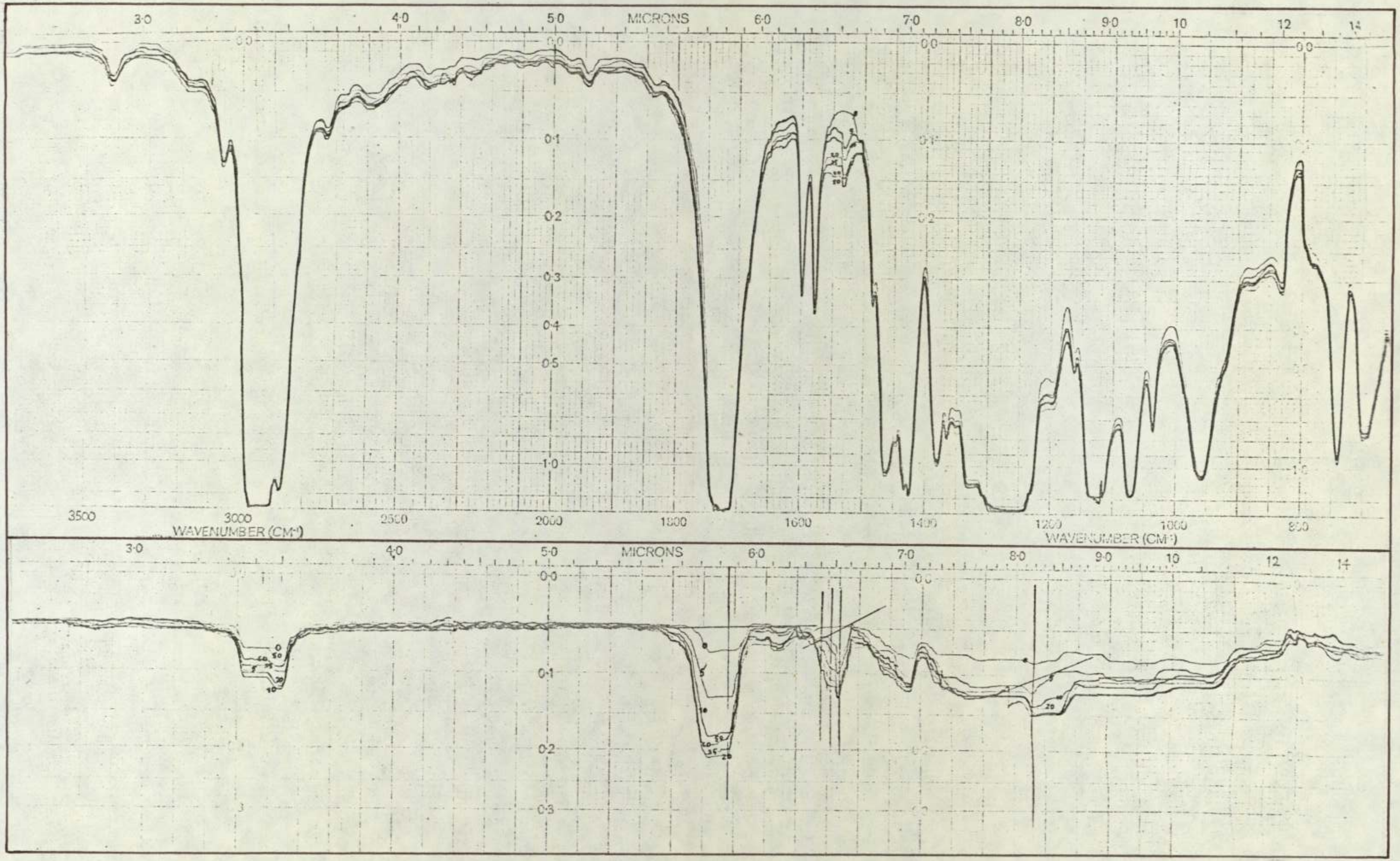


FIGURE 94 - Normal (upper) and differential (lower) transmission infrared spectra relating to:-
PLASTICISED PVC + UV + THERMALLY STABILISED clear film: thermal ageing at 100°C, in nitric oxide/nitrogen.

IX.3.3 UV-Ageing in Nitric Oxide/Nitrogen

The UV-ageing in nitric oxide/nitrogen of the four test coatings was conducted in a closed (i.e., non-flowing) system at what was probably slightly above ambient temperature (say, 30°C.) due to the heat generated in the UV cabinet. Exposure was extended up as far as 250 hours, with sample analyses being carried out at 50 hour intervals.

On exposure, only relatively slight reflectance changes were brought about in each of the samples, in common with the previous thermal ageing results. Again, those changes which did occur were mainly during the initial stages and could be attributed almost exclusively to specular reflectance (I_S) and, hence, MICRO-defect variations. Weight change measurements, on the other hand, did exhibit significant differences from the previous thermal data in that the presence of pigment seemed to be rather more determinant than the stabilisers of the ensuing weight gain. In addition, the weight gains, common to all four samples, each attained a fairly well-defined "plateau" value after approximately 100 hours, this value being higher in the case of the pigmented pair.

However, it was again the infrared data which provided the most significant ageing information. From the normal/compensated transmission infrared spectra of both the unstabilised and stabilised clear films, shown for the former in Figure 95, it appeared that exposure to nitric oxide in a photochemical environment promoted the formation of oxime (=N-OH) groups in the polymer in preference to the seemingly stable nitroso (-N=O) groups formed under the influence of heat. This

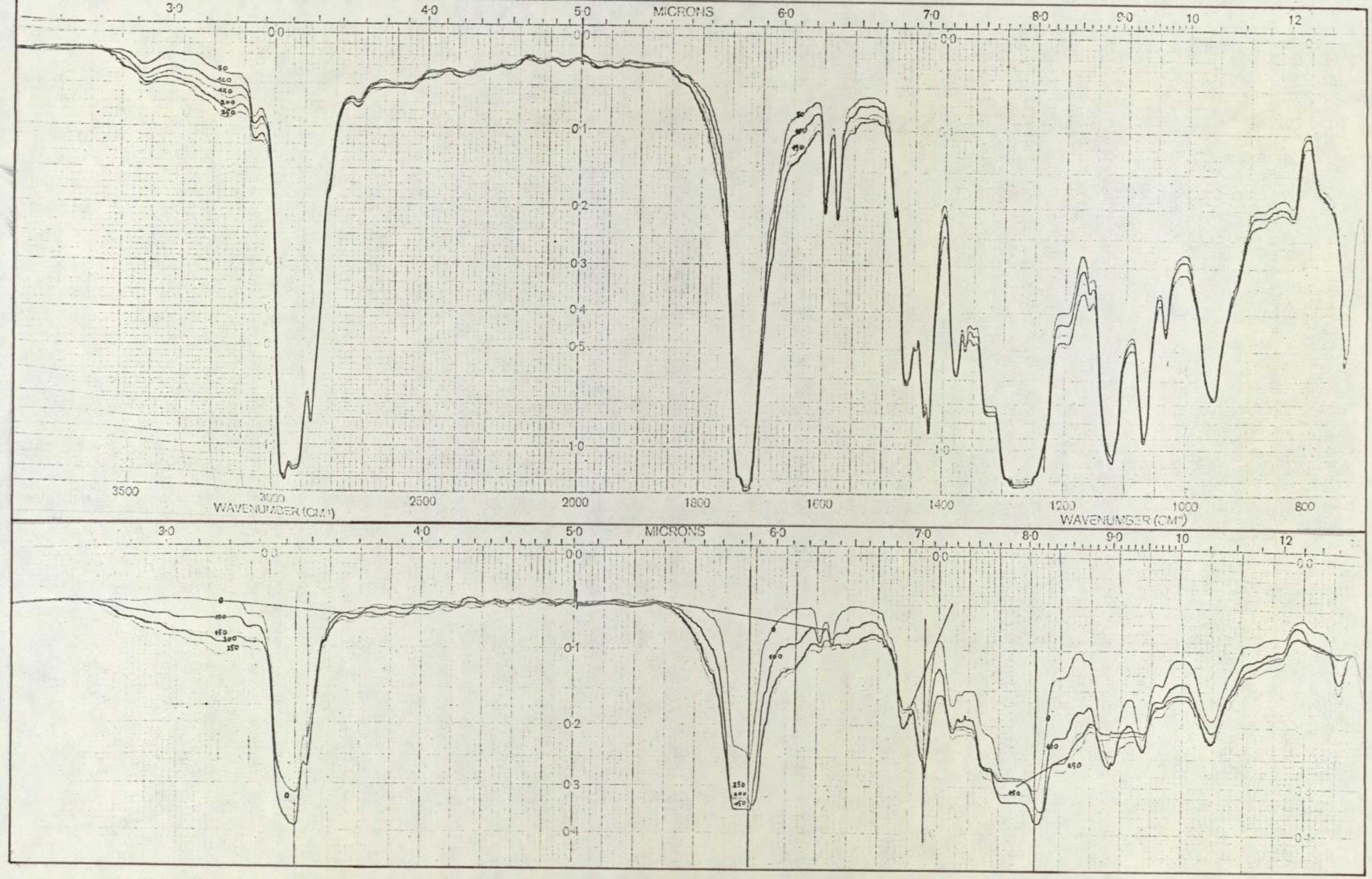


FIGURE 95 - Normal (upper) and differential (lower) transmission infrared spectra relating to:- PLASTICISED PVC (alone) clear film; UV-ageing in nitric oxide/nitrogen.

is readily seen in Figure 95 from the progressive and parallel developments, on UV/nitric oxide exposure, of the low frequency O - H stretching peak centred at 3160 $cm.^{-1}$ and the C = N stretching band in the 1620 - 1650 $cm.^{-1}$ region of the spectrum. Whilst there is also a suggestion of accompanying N = O stretching absorbance in the 1500 - 1550 $cm.^{-1}$ region, it is visibly less definite than in the spectra of the previous thermally aged samples (Figures 93 and 94) and is therefore indicative of the fact that stable (i.e., in the sense of being non-tautomerisable) nitroso groups are much less readily formed.

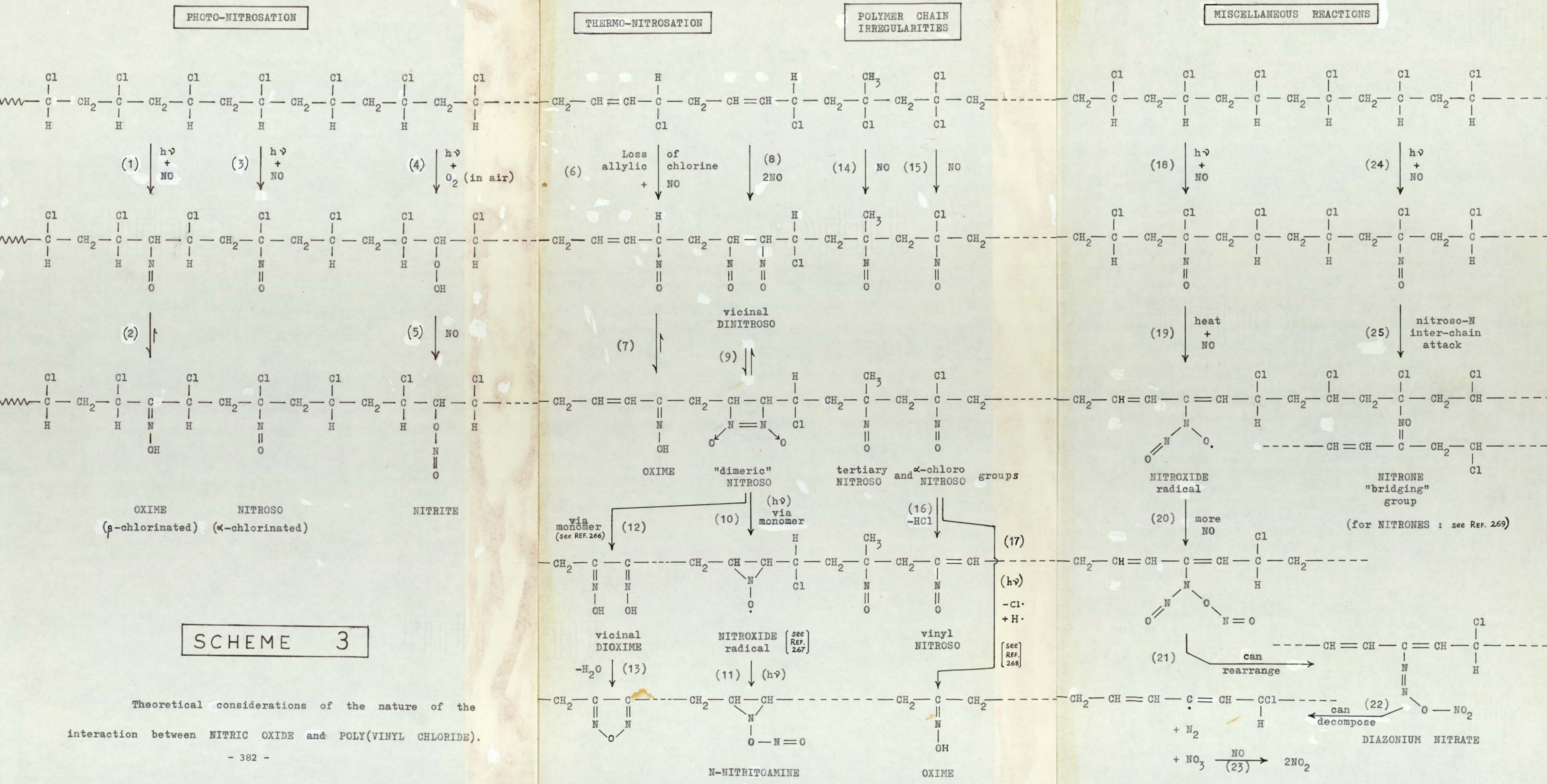
Thus, on the basis of this spectral evidence, the apparent differences which exist between the thermally and photolytically induced nitric oxide interactions with degrading PVC can now be discussed in the light of the relevant group theory.

IX.4 Discussion

The results described in this chapter are seen to be in agreement with the finding of previous workers(200, 201) that nitric oxide does chemically interact with poly (vinyl chloride) in a degradative (radical-producing) environment. However, perhaps this, in itself, is not all that surprising in view of the fact that nitric oxide is a well-known inhibitor of radical reactions and, like oxygen, is not so restricted in PVC as, say, solid or liquid inhibitors with bulky molecules would be.

The most interesting feature of the PVC-nitric oxide interaction to emerge from this brief study has been the seemingly different mechanistic pathways which the reaction prefers to follow depending upon whether the polymer is undergoing photolytic or thermal degradation. This presumably must relate to the fact that whereas UV irradiation of the polymer is primarily concerned with the initial production of chain radicals, which are then rapidly consumed by nitric oxide, the action of heat additionally gives rise to dehydrochlorination by a "zipper" type reaction (which, incidentally, nitric oxide has been reported (200) to accelerate) leading to the formation of polyene structures to which nitric oxide has been shown (201) to add. Consequently, it is more judicious here to start off by considering the less complex UV-initiated interaction. However, before doing so, it is worth emphasising at this point that, as in the case of photo- and thermo-oxidation previously (Schemes 1 and 2 in the preceding chapter), the corresponding nitric oxide interactions with PVC are just as likely to be similarly complex "balances" of a number of different, yet inter-dependent, processes of varying importance in the overall scheme. Indeed, one only has to combine what little is known about the reaction of nitric oxide with PVC with the basic chemistry of the initially formed nitroso group (263) to be able to compile a whole range of possible reactions, as shown in Scheme 3 overleaf - this scheme merely being intended to suggest rather than propose the actual operational existence of the possibilities shown.

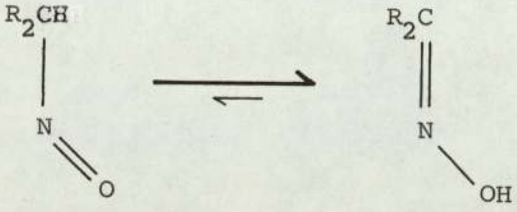
Thus, considering now the UV/nitric oxide results obtained in this study, the major outcome appeared to be the formation of oxime groups in the polymer. This finding coincides with what would be predicted from the known theory, i.e., preferential photolysis of methylenic hydrogen from the polymer chain, followed by rapid uptake of nitric oxide by radical combination and, finally, tautomeric re-arrangement of the ensuing α-hydrogenated nitroso group to the more



SCHEME 3

Theoretical considerations of the nature of the interaction between NITRIC OXIDE and POLY(VINYL CHLORIDE).

stable oxime. This process is represented in Scheme 3 as the reaction sequence (1) → (2). The nitroso-oxime tautomerism, as shown below in eq. (13):-



(NITROSO) (OXIME) ...... (13)

is, in theory, an equilibrium rearrangement, although it is so heavily weighted in favour of the oxime that it is apparently irreversible. In addition, it is interesting to note that tautomerism to oxime has been reported as being catalysed by nitric oxide (264), whilst, oppositely, as the molecular weights of the substituents (R) increase, the rate of conversion may decrease (265).

However, there is also evidence from this work to suggest that UV/nitric oxide exposure allows for some stable nitroso groups to be formed via competitive routes, one of which will almost certainly be chloromethylenic hydrogen abstraction leading to an α-chloronitroso group (see step (3) in Scheme 3). Other possible routes stem from, say, initial polymer chain irregularities such as tertiary chlorine or dichloro groups which, on chlorine abstraction and combination with nitric oxide, also give rise to α - hydrogen free and, hence, non-tautomerisable nitroso groups (see reactions (14) and (15) in Scheme 3). Indeed, in the case of pure, unprocessed PVC films cast from solution, interaction with nitric oxide would appear to provide a useful discriminatory means of determining the relative photolytic reactivities of the two types of abstractable hydrogen present in the polymer.

Having thus considered the photonitrosation of the PVC samples studied, let us now consider the thermonitrosative case in which oximes fail to feature spectroscopically to any appreciable extent, the predominant effect being that of nitroso group formation. These findings, which are less readily explained than the previous data, are more interpretative in terms of the addition of nitric oxide to $C = C$ double bonds in the polymer (arising from preferred dehydrochlorination) than to its radical combination. This type of addition reaction consequently gives rise to vicinal-dinitroso groups in the polymer (step (8) in Scheme 3) which, on the basis of previous statements, would each be expected to rearrange to their oxime tautomers. However, this tendency is effectively discouraged by the stabilising dimeric character of vicinal-dinitroso groups (see step (9), Scheme 3). Furthermore, it has been suggested(266) for the comparable case of secondary nitroso dimers, whose rearrangement in the presence of hydrogen chloride is dependent only on dimer concentration, that the rate-determining step is likely to be dissociation to monomer, whose intermediacy is clearly a requirement for conversion into corresponding oximes.

Thus, it can now be more clearly understood how the thermal ageing environment, through its characteristic inducement of dehydrochlorination, makes available to the nitric oxide an additive interaction, leading to stabilised nitroso groups, which is largely pre-empted in photonitrosation by radical combination leading through tautomerisable nitroso groups to oxime formation. Clearly, the subsequent fate of these oxime groups will be of paramount importance in determining the ultimate effect, whether stabilising or otherwise, which <u>photo</u>nitrosation has on PVC. It has been suggested(322) that, in the presence of nitric oxide, oximes pyrolytically decompose via a predominantly free radical mechanism, the exact nature of which is still not clear, although the reaction may also possibly proceed to some extent through a molecular mechanism. Additionally, the hydroxy group of oximes is also known to be capable of nucleophilic addition to C = C double bonds(323). However, one possible fate which would not be expected to befall oximes in the presence of flanking polymeric (i.e., non-migratory) substituents is their known Beckmann rearrangement to substituted amides(323). Although each of these conjecturable oximic conversions undoubtedly warrant serious consideration, one cannot overlook the fact that, just as stable nitroso groups are formed in the thermonitrosative case, so apparently stable oxime groups, supposedly of the types indicated in Scheme 3, are formed over the period (250 hrs.) for which photonitrosation has been studied here. Obviously, the elucidation, probably by more sophisticated spectroscopic techniques than those used here, of the initial stable formation/subsequent fate of oximes formed in this latter environment would be one of the prime objectives of any continuation of this work.

Finally, it is also interesting and relevant to note that O'Sullivan and Sadler(324) have found a linear correlation to exist between the N = O stretching frequencies (ν) in compounds of the general formula RNO and the Taft (σ^*) aliphatic polar substituent constants. The relations are expressed as:-

$$\nu = 1500 + 110\,\sigma^* \text{ (vapour phase)} \qquad \ldots\ldots \ (14)$$

$$\nu = 1458 + 124\,\sigma^* \text{ (condensed phase)} \qquad \ldots\ldots \ (15)$$

On plotting the reported literature values(263, 325, 326) for the monomeric N = O stretching frequencies ($\nu_{N=O}$) of carbon-nitroso compounds whose structures can be related to those which might conceivably be stably formed in nitrosated PVC, against their corresponding Taft σ^* polar substituent constants[(237)] (see Figure 96 overleaf), it was found that reasonable linearity was obtained in accordance with O'Sullivan and Sadler's[(324)] correlation. However, of more significance to this study is the fact that the graph in Figure 96 indicates that monomeric nitroso groups which absorb in the 1500 - 1550 cm.$^{-1}$ region of the infrared spectrum (i.e., the "active" region in this polymeric study) have substituents whose σ^* values are less than 0, i.e., which are more electron-releasing than the methyl (CH_3-) group. This interesting suggestion argues, therefore, that the relatively low frequency nitroso group absorbancies observed spectroscopically in this PVC study are more likely to be associated with, say, tertiary, allylic or, possibly, vinyl rather than the more polar α- or even β-chlorinated nitroso groups. However, whilst this accords well with what would be expected in a dehydrochlorinating, thermonitrosative environment, strictly speaking, the application of monomeric data to polymeric systems in this way should only be taken to provide useful indications of likely substituent group polarity rather than allow for unequivocal conclusions to be drawn.

In conclusion, it can be said that this case study has revealed some interesting features of the interaction between nitric oxide and PVC. Although the receptiveness of PVC towards nitric oxide attack is, in itself, by no means revelational, having already been recognised by previous workers, the exact nature of its chemical interaction does not appear to have been studied systematically and has thus remained largely unresolved. However, whilst this study can at least claim to have "scratched the surface" in this respect, obviously the

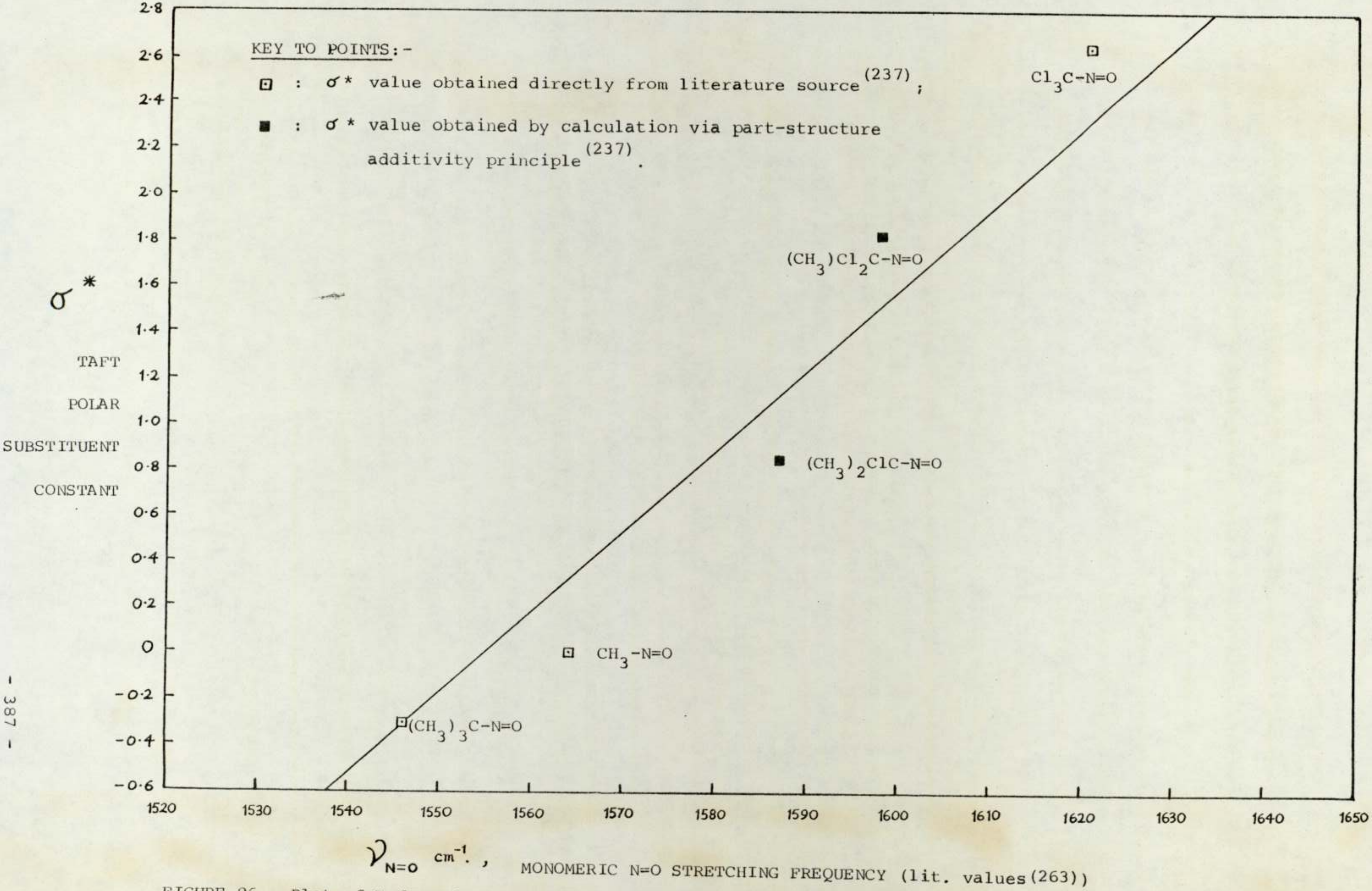


FIGURE 96 - Plot of Taft polar substituent constant (σ^*) versus monomeric N=O frequency ($\nu_{N=O}$ cm.$^{-1}$) for various PVC structure-related C-nitroso compounds

ideas and mechanistic proposals put forward here now need to be examined in greater depth, probably demanding more powerful spectroscopic techniques, before the intricate nature of the PVC/nitric oxide interaction can be characterised to the extent that, say, the corresponding oxygen interactions have.

CONCLUSIONS

CONCLUSIONS

The main concern during the early part of this work was whether or not goniophotometry could be successfully applied to the quantitative weathering study of surface coatings deterioration - an application of the technique which, curiously, had not been previously reported to any notable extent. As the results presented in this thesis have shown, the goniophotometric technique is eminently suited to this type of study and appears to be universally applicable to most, if not all, types of surfaces encountered in practice. In addition to its demonstrably high sensitivity towards even the most subtle of surface reflectance changes, even above and beyond visual perceptibility, goniophotometry has the added advantages of being completely non-destructive and also, in its automated form, quick and easy to use - this latter development having transformed what was formerly a rather laborious instrumental procedure into one which can be considered to be of potentially routine value.

In extension of the proven value of goniophotometry as a powerful analytical tool in its own right, goniophotometric data has also been found to be directly correlative with other types of analytical data - notably, surface roughness measurements. Indeed, an actual mathematical relationship expressing an apparently logarithmic dependence of gloss on both surface defect size and number has been established; this, when combined with the eye's approximate logarithmic response to linear variations in light intensity, propounds that subjective visual gloss ratings are more linearly relational to rugosity than objectively determined reflectivity changes. Furthermore, in coatings systems which experience a reasonably uniform (i.e., disperse) surface deterioration on weathering, not only is surface roughness correlative with the commensurate gloss changes but also spectroscopic chemical (e.g., functional group) changes can be as well. This, thus, provides an extremely powerful combination of analytical techniques for the characterisation of film deterioration processes from the time of initial chemical attack through to the visual gloss changes which may result.

However, forming what is, perhaps, an even more effective partnership with goniophotometry, scanning electron microscopy (SEM) has been shown during the course of this study to be of immense value in directly visualising and, hence, understanding more intimately the nature of the surface profile changes which are influencing the measured/observed gloss. Whilst not able to provide the kind of quantitative/semi-quantitative information which surface roughness/infrared spectroscopic analysis can, SEM is able to afford instead a unique insight into the exact nature of the surface deterioration caused by weathering. In this way, SEM bridges the information gap between the nature and extent of the chemical degradation which has taken place and the effect which this has on surface roughness and, hence, gloss. Indeed, had it not been for SEM's direct observational facility, the early recognition of the localised nature of PVC plastisol deterioration and the specific identification of flaking, scaling and micro-checking would not have been possible. Hence, SEM analysis allied to more quantitatively informational techniques such as goniophotometry forms a powerful analytical combination for all coating types and modes of breakdown.

In contrast to the previously mentioned localised nature of PVC plastisol film breakdown, in which flaking appears to be the intrinsic defect formed, weathering deterioration of the more rigid, commercial PVC organosol coating studied is characterised by a more coherent surface coverage of roughness irregularities whose size/density variations can, therefore, be more closely related to the reflectance changes to which they give rise. This uniform spread of surface attack, which, from the point of view of the coating's life expectancy, is to be preferred to a concentration of localised effects in "activated" areas, represents the most common type of weathering development encountered in commercial paint coatings. Furthermore, the overall weathering pattern appears to comprise, most typically, a surface roughening/erosion cycle governed mainly by seasonal shifts in the delicate physico-chemical balance of natural weathering factors. This cycle is seen to be of seemingly yearly periodicity in the temperate U.K. climate compared to nearer two years in sunnier (e.g., tropical) climates in the U.S.A.(139). However, although this basic trend is fairly widespread, individual ageing responses are still generally characteristic for a particular paint system in a given environment. This has been amply demonstrated in this work via the goniophotometric study of both the natural and artificial weathering of a selected cross-section of commercially available paints. Their differing ageing patterns, however, have tended to complicate relative assessments of their likely in-service performances in a given application. Despite this, the alkyd-based coatings which were studied have been able to confirm their long-standing acceptance as examples of good durability paints which should last for up to six years in temperate climates such as in the U.K. However, not even this can compare with the outstanding weatherability shown by the poly (vinylidene fluoride) coatings which, in average outdoor conditions, may last for 15 - 20 years.

Of further importance to this work has been the extent to which artificial (BS 3900 F3) weathering has proved to be correlative with natural weathering (Garston) for the various coatings studied; this being despite the fact that, in some cases, certain test materials were particularly responsive to natural weathering elements (e.g., wind, frost and sudden appreciable temperature changes) not catered for in the BS cycle.

Finally, just as PVC, as a material, tends to be receptive towards photo/thermo-initiated oxygen attack, a related case study has shown that it is similarly, if not more, interactive with nitric oxide in a radical producing environment. However, whereas simple oxidation, in the absence of overriding dehydrochlorination, leads to an autocatalytic chain scission process via precursory ketone formation, nitrosation tends, if anything, to have a stabilising effect, particularly if stable nitroso groups are formed. Alternative oxime formation, however, is somewhat less translational in terms of its net effect, whether stabilising or otherwise, and will remain so until the subsequent fate of oximes in PVC has been more firmly established.

SUGGESTIONS FOR FURTHER WORK

SUGGESTIONS FOR FURTHER WORK

In conclusion now of this thesis, the following suggestions for further work are made, both from within and slightly beyond the scope of this present study:-

1) a continuation of the current PVC plastisol analyses to completion, plus the initiation of any further useful weathering exposures;
2) as regards the goniophotometer, a further useful instrumental refinement would be to mount a transducer on to the drive shaft of the motor and to link the photocell to an X-Y recorder. In this way, a direct plot of reflectance versus angle of reflectance could be obtained, thus reducing data processing time by eliminating the need for converting the peak width at half-height from its measured units of length to degrees of angle. Additionally, of course, this modification would also allow for the rate of photocell rotation to be slowed right down for maximum sensitivity and, hence, accuracy of measurement in the region of the peak (i.e., specular angle). Finally, complete automation of data processing is then made possible by feeding the goniophotometric data output directly into an in-line computer for calculation of all derivable parameters;
3) it would also be useful if goniophotometric data obtained via the present set-up were in future to be "normalised" by percentaging it against corresponding values relating to a standard black tile of the type used for calibrating specular gloss-meters. By doing this, reflectance values, up until now expressed in arbitrary

intensity units only, could then be co-ordinated with existing industrial (gloss-meter) gloss terminology;

4) having used in this work just one monochromatic incident light wavelength (blue : 436 nm.) for goniophotometry, additional single wavelengths could be used in order to investigate further, in conjunction with surface roughness measurements, the goniophotometrically defined micro → macro-defect size transition and its relevance to visual effects. In this latter respect, green light (546 nm.) would appear to be of likeliest value with the eye's maximum sensitivity suggested as being in the green region of the visible spectrum. A further advantage to be gained from having a range of monochromatic wavelengths to choose from is that if the approximate defect size range for a particular paint on weathering happens to be known (this often being an intrinsic property of a given paint system), then a wavelength of light can be chosen which falls conveniently within this range for maximum goniophotometric change to be sensed;

5) another especially worthwhile goniophotometric study would be to investigate systematically the particular effects which specific types of surface defect have on the shape of the goniophotometric curve. Whilst the effects of microscopic irregularities have been characterised in this work, a "fingerprint" dossier of curve distortion effects relating to those gross defects which are more a function of application than weathering might usefully be compiled along the lines of previous workers(59, 73). These larger, visible imperfections (e.g., nibs, brush marks, orange peel defects, etc.), which tend to give rise to characteristic gloss deficiencies, are easily identifiable via scanning electron microscopy;

6) a final goniophotometric proposal worth considering is the examination of clear, unsupported films by a combined reflectance/transmittance technique using the goniophotometer simultaneously in its proper use as a light scattering photometer. In this way, a greater understanding can be gained concerning what happens to light which is incident upon a coating surface, reflectance studies alone tending to obscure the fact that most of the light does actually penetrate the surface. Thus, apart from providing an objective measurement of film clarity, the relative extents to which gloss reduction by surface roughening is due to an increase in surface scatter and/or an increase in light admission followed by re-emergent scatter can also be determined; at the same time, the results would re-examine the derived logarithmic dependence of gloss on surface roughness;

7) as regards surface roughness studies, it would be interesting to see if Talysurf values of the average height/number of roughness irregularities could be correlated with the surface roughness factor obtainable from the Wenzel equation (see page 123) via contact angle measurements. Additionally, in view of the Talysurf's unreliability for gloss finish paints, an alternative method such as ray deflection mapping/Schlieren optics(140) might also be tried;

8) however, it is really in respect of the chemical methods that analytical advancements need to be made. Multiple internal reflection spectroscopy, whilst having proved extremely useful in this study, nevertheless has its procedural disadvantages as well as only being indicative of the major functional group changes. Even transmission infrared spectroscopy of thin films finds great difficulty in distinguishing between, say, the different types of

carbonyl groups formed during the oxidative degradation of PVC. Obviously, for this type of work, essential as it is to any mechanistic study, more powerful analytical techniques are sorely needed. At present, two of the more likely possibilities for fulfilling this need would appear to be Raman spectroscopy and electron spectroscopy for chemical analysis (ESCA : see page 51). Also, in the case of PVC degradation, "chlorine mapping" by scanning electron microscopy/energy dispersive X-ray analysis (see page 106) has been seen, from preliminary work carried out here, to be potentially highly informative and worth pursuing further;

9) the PVC/nitric oxide interaction study, having been developed to the stage reported here, now requires the sort of powerful chemical technique as those mentioned in (8) above in order to be able to distinguish between related groups. The fate of oximes once formed appears to represent one of the most immediate aims of any further work in this field. In the wider context of the relevance of this type of interaction to natural weathering, evidence of its occurrence at outdoor locations such as the Gravelly Hill motorway link site will only be detectable if a way can be found of protecting exposed samples from contamination by the airborne particulate pollution;

10) finally, having observed during the course of this work how correlative BS 3900 Part F3 artificial weathering has been on an energy of exposure basis with natural weathering in an average (semi-urban) environment, the BS apparatus can now be usefully employed in assessing the likely in-service effectiveness of various new stabiliser systems in PVC-based coatings now that the weathering mechanism of PVC is more clearly understood.

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REFLECTANCE AND RELATED STUDIES OF POLY(VINYL CHLORIDE) SURFACE COATINGS

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INTRODUCTION

The deterioration of various types of poly(vinyl chloride) (PVC) surface coatings has been studied in both natural and accelerated weathering environments. Because of the large surface area to bulk ratio in this type of application, changes in the surface characteristics of the polymer provide a great deal of information concerning degradation processes.

Particular emphasis in this paper is placed on the results of work carried out on a commercial, white-pigmented PVC organosol coating(1,2) but within this context, studies involving rather more simplistic, experimental PVC plastisol coatings are also discussed.

ANALYTICAL TECHNIQUES

The ageing characteristics of these materials mentioned above were followed by means of a selected combination of both novel and well-established techniques which, it was hoped, would prove to be complementary to one another.

Of particular interest, however, has been the development of an automated goniophotometer(1,3) which has since been used with considerable success as a quantitative means of monitoring the surface reflectance properties of a wide variety of surface coatings(1-4).

Examples of the additional techniques used are:
multiple internal reflectance spectroscopy (MIRS),
average height of roughness irregularities (AHRI) studies,
and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

PVC Organosol Studies

The natural(1) and accelerated(2) weathering performances of a commercial, white-pigmented PVC organosol surface coating (supplied by the

Building Research Station*) have been studied by means of the techniques previously mentioned and their results compared(2).

(a) Natural Weathering

Natural weathering of the PVC organosol coating was carried out at the Building Research Station's semi-rural exposure site, commencing a the beginning of the summer season and for which solar radiation data was supplied by the BRS uv sensor(5).

On weathering, the goniophotometric curves recorded at various angles of incidence revealed significant changes in the reflectance properties of the PVC film in being transformed from sharp "triangular" peaks to relatively broad curves. This is illustrated in Fig.1 for the initial and final samples in the series. However, the effects of weathering on the inherent assymetry of the spatial distribution of surface reflectance can be more easily appreciated from a logarithmic presentation of the goniophotometric data (Fig.2). A more gradual look at the progressive changes in reflectance taking place during weathering is afforded by Fig. at a particular angle of incidence, in this case 45°. For each of the curves in Fig.3, the so-called "gloss factor" term can be computed from the respective (peak height)/(peak width at half-height) ratios. Variations in the gloss factor on exposure are seen in Fig.4 to imply that an apparent cycle of change takes place during the course of the year.

Significantly, this cyclic pattern of ageing is similarly depicted by changes in the average height of roughness irregularities (AHRI) i the paint surface (Fig.5) which, in addition, is found to be linearly related to the logarithm of the gloss factor (Fig.6).

Some degree of chemical insight into the nature of the ageing process is provided by multiple internal reflectance spectroscopy (MIRS) of the paint surface. Notably, changes in the absorption indices of spectral peaks due to C-H bending in $-CH_2-$ (1420 cm.$^{-1}$), Fig.7, and in ClC-H (1250 cm.$^{-1}$), Fig.8, both followed the same sequence to that observed for the gloss factor and surface smoothness previously (Fig.9).

On the basis of all of the foregoing evidence, the seasonally dependent weathering effects observed in the case of this PVC organosol coating are interpreted in terms of an HCl evolution during the summer, continuing, to a lesser degree, throughout the autumn, and giving rise to subsequent surface defect formation with resultant loss in gloss. This <u>chemical</u> degradation then becomes "outweighed" during the winter and spring by the <u>physical</u> effects of wind and rain etc., which tend to bring about an apparent surface "improvement" (i.e., renewal) by means of erosi

Qualitative support for this view is provided by scanning

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* Building Research Station, Garston, Watford, Herts., WD2 7JR.

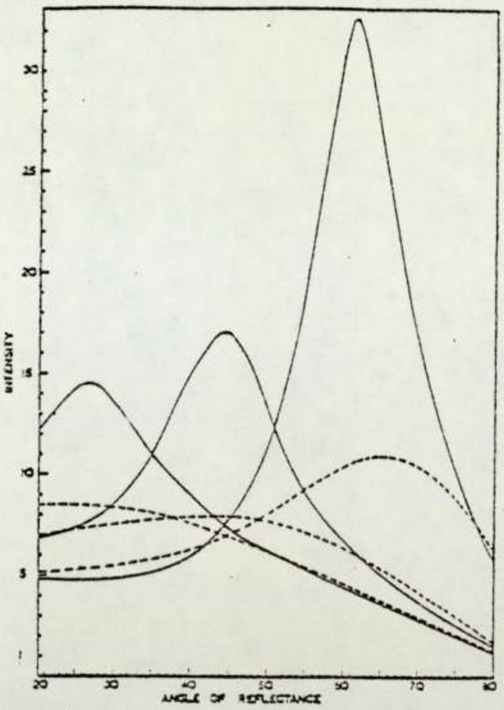

Figure 1—Goniophotometric curves: PVC organosol matt finish. Exposure time: solid line = 0; dotted line = 12 months

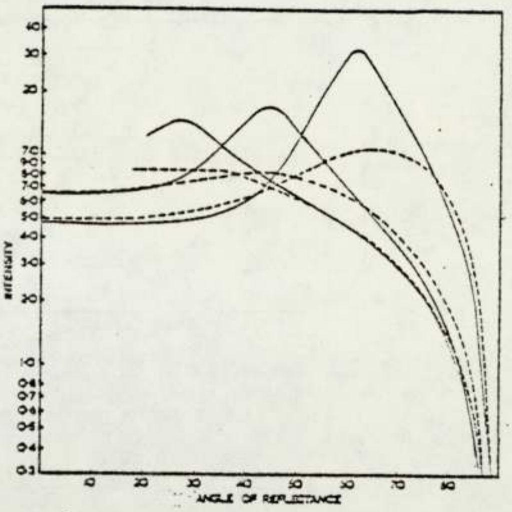

Figure 2—Goniophotometric curves (logarithmic presentation): PVC organosol matt finish. Exposure time: solid line = 0; dotted line = 12 months

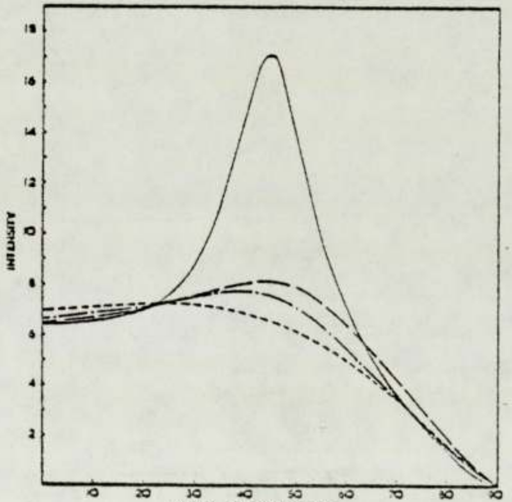

Figure 3—Goniophotometric curves: PVC organosol matt finish. Exposure time: solid line = 0; dash-dot = 3 months; dotted line = 6 months; broken line = 12 months

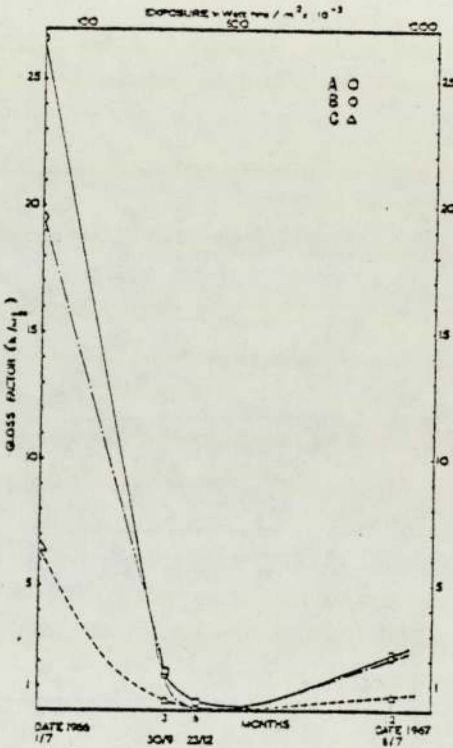

Figure 4—Dependence of gloss factor on exposure: PVC organosol matt finish. Angle of incidence: A = 75°; B = 60° (gloss × 10); C = 45° (gloss × 10)

electron microscopy (SEM).

(b) Accelerated Weathering

Accelerated weathering of the PVC organosol coating was conducted in a B.S.3900 Part F3 accelerated weathering machine. Comparison of the ageing response with that previously obtained from natural weathering (e.g., Fig.10), on an energy of exposure basis, showed there to be a reasonable correlation between the two and suggested that a basis exists for predicting the life expectancy of this type of paint system from this type of accelerated weathering test.

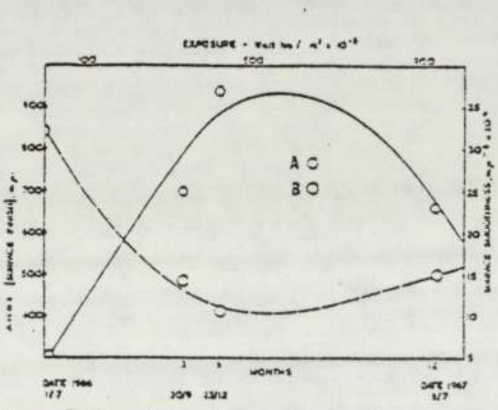

Figure 5 —Dependence of average height of roughness irregularity (AHRI) on exposure. A = Surface roughness; B = Surface smoothness

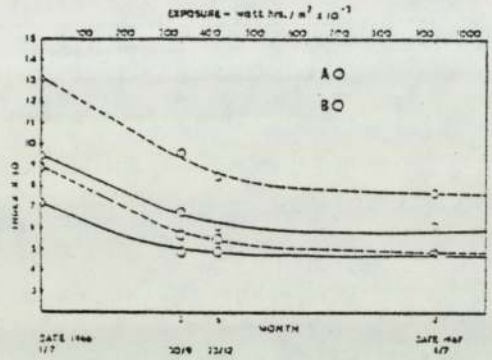

Figure 7 —Dependance of $-CH_2-$ 1420 cm⁻¹) index on exposure: PVC organosol matt finish. Broken line = medium chart speed; solid line = slow chart speed.

A = Relative to $-CH_2-$ (2920 cm⁻¹); B = relative to $\overset{O}{\overset{\|}{-C-}}$ (1720 cm⁻¹)

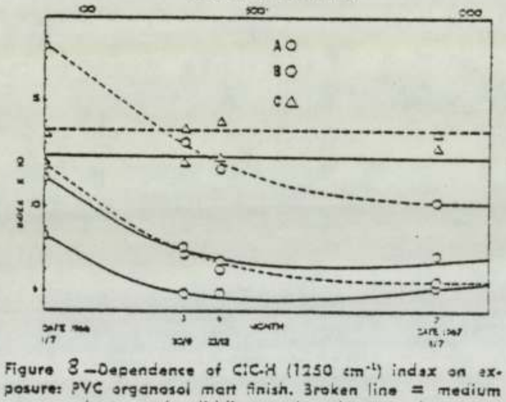

Figure 8 —Dependence of ClC-H (1250 cm⁻¹) index on exposure: PVC organosol matt finish. Broken line = medium chart speed; solid line = slow chart speed.

A = Relative to $-CH_2-$ (2920 cm⁻¹); B = Relative to $\overset{O}{\overset{\|}{-C-}}$ (1720 cm⁻¹); C = Relative to $-CH_2-$ (1420 cm⁻¹)

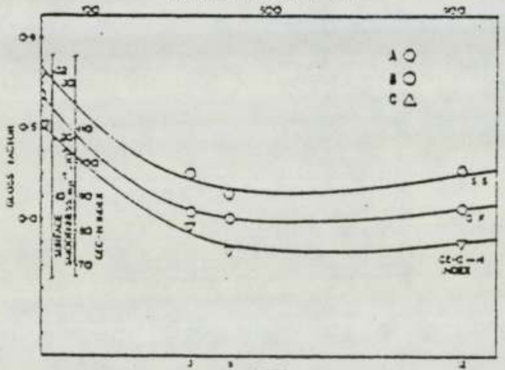

Figure 9 —Dependence of: A — Surface smoothness; B — Gloss factor; and C — ClC-H index on exposure

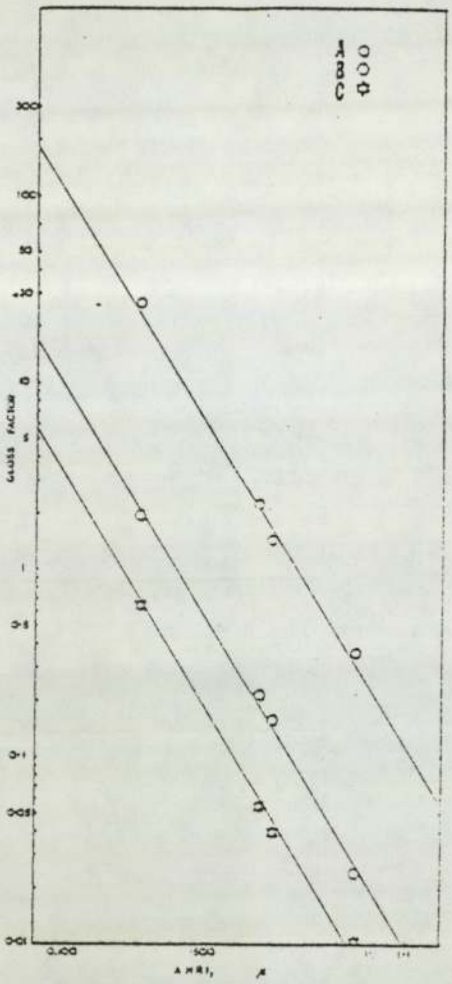

Figure 6 —Dependence of gloss factor on average height of surface roughness irregularities (AHRI): PVC organosol matt finish. Angle of incidence: A = 75°; B = 60°; C = 45°

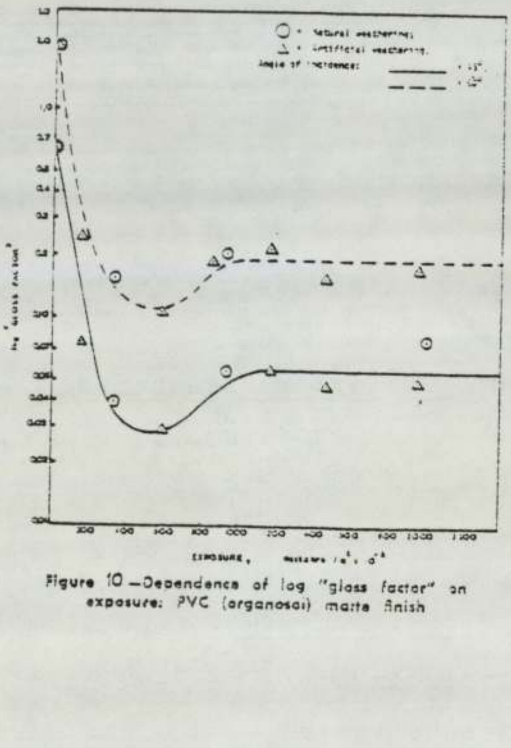

Figure 10 —Dependence of log "gloss factor" on exposure: PVC (organosol) matte finish

PVC Plastisol Studies

Natural and accelerated weathering of a set of three experimental PVC plastisol coatings were conducted as part of a more simplified, mechanistic study of the ageing processes involved in PVC-based paint systems.

The three coatings' formulations consisted of:

(i) plasticised PVC,

(ii) plasticised PVC + pigment,

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

(a) Natural Weathering

Natural weathering (also at the BRS exposure site) induced similar cyclic changes in gloss (Fig.11) to those observed previously with the PVC organosol coating (Fig.4). However, the sequence of these changes is apparently not influenced quite so markedly, in the plastisols' case, by the seasonally dependent intensity of solar radiation. Indeed, it would be reasonable to expect that other weathering factors, notably temperature, would have proportionately greater effect on relatively softer plastisol coatings such as these.

(b) Accelerated Weathering

Accelerated weathering (B.S.3900 Part F3) brought about less severe changes in gloss (Fig.12) when compared with natural weathering on an energy of exposure basis. This can be considered to be, to some extent, supportive of the above view that the natural ageing response of the plastisols is determined by a different "balance" of the prevailing weathering factors.

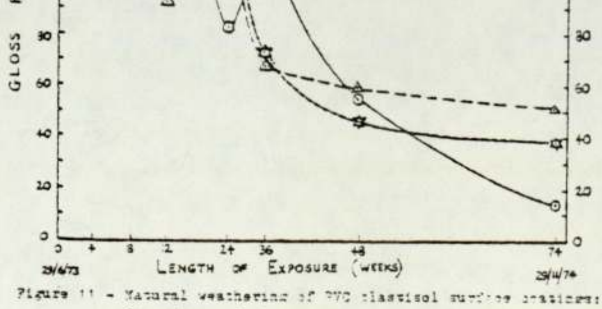

Figure 11 - Natural weathering of PVC plastisol surface coatings: dependence of gloss factor on exposure.

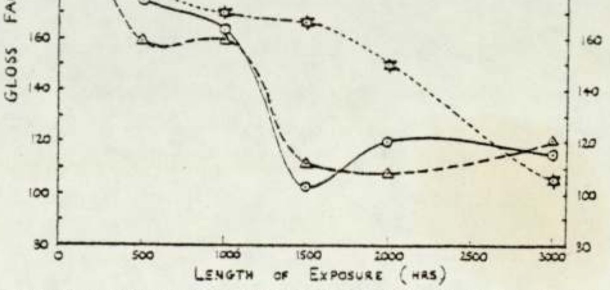

Figure 12 - Accelerated weathering of PVC plastisol surface coatings: dependence of gloss factor on exposure.

1) Tahan, M., J. Paint Technol., 46, 590, 35, (1974).
2) Tahan, M., Molloy, R., Tighe, B.J., J. Paint Tech., 47, 602, 52, (1975).
3) Tahan, M., J. Paint Technol., 46, 597, 52, (1974).
4) Tahan, M., Tighe, B.J., J. Paint Technol., 46, 590, 48, (1974).
5) Capron, E., Crowder, J.R., Smith, R.G., Polymer Age, 4, 3, 97, (1973).

Comparison of Reflectance And Related Methods For Studies of Film Surface Deterioration

IV. Artificial Weathering of Alkyd, Urethane, Epoxy/Polyamine, Chlorinated Rubber, And PVC Coatings

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Artificial weathering of pigmented surface coatings based on polyurethane, epoxy/polyamine, linseed oil modified alkyd resin, vinyl-toluene alkyd, chlorinated rubber and PVC organosol, was followed by goniophotometry and surface roughness measurements.

It was found that goniophotometry provided convenient parameters for following surface deterioration and for comparing the weatherability of different surface coatings. The height of the goniophotometric peak was sensitive to the early deterioration of glossy coatings, the width of the peak at half height was sensitive to the deterioration of semi and fully matte finishes, and the "gloss factor" suited all cases.

A linear relationship was found between the logarithm of the "gloss factor" and both the number and average height of the surface irregularities.

The results were compared with natural weathering and favorable agreement was obtained.

KEY WORDS: Goniophotometry; Gloss factor; Artificial weathering; Surface roughness; Alkyd; Polyurethane; Epoxy/polyamine; chlorinated rubber; PVC organosol.

INTRODUCTION

Correlation between natural and artificial weathering is especially important in predicting the life expectancy of surface coatings and plastic materials. However, there was no property or testing method which did not raise some problem in correlations of this kind.

In previous work,[1,2] natural weathering of a variety of surface coatings was followed by goniophotometry, attenuated total reflectance (ATR) spectroscopy, stereoscan-electron microscopic studies, and roughness measurements.

Goniophotometry was found especially suitable for a quantitative study of the film deterioration process even in its early stages.[1,2] It was also found adequate for comparing the extent and the rate of degradation of different coatings. In addition, the goniophotometric test has been recently[3] accelerated by modification of the goniophotometer. It was, therefore, of special interest to examine the efficiency of goniophotometry in correlating natural and accelerated weathering. For this reason, the artificial weathering of a variety of surface coatings was followed by goniophotometry using the modified machine,[3] and the results compared with those of naturally weathered samples.

EXPERIMENTAL

Materials

The coatings[4] were prepared and provided by the Building Research Establishment, Garston, England. With the exception of vinyl-toluene alkyd gloss finish, which was brown pigmented, all samples were pigmented with rutile titanium dioxide and applied to an aluminum substrate. The base resins were a poly-

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urethane, an epoxy/polyamine, a long oil linseed/pentaerythritol alkyd, a vinyl-toluene alkyd, a chlorinated rubber, and a PVC organosol.

The coatings were artificially aged in a weatherometer (British Standard 3900 F3). They have been previously described[4] and changes in certain mechanical properties (hardness, extensibility and weight) during weathering have been measured and reported by the Building Research Establishment.[4]

Instrumentation

Goniophotometric studies were carried out in the automated goniophotometer using experimental procedure previously described.[3] Angles of incidence of 45° and 60° were used.

Surface roughness (surface finish) studies were carried out using a Telysurf 4 instrument. The advantage of this model, compared to that previously described[1] (Telysurf 100), was the facility for simultaneous measurement of the bearing area, the average height of the surface irregularities (AHRI), and the number of peaks per inch.

RESULTS

Diffuse Reflection

As was found with natural weathering,[1,2] the goniophotometric curves from artificially weathered samples showed significant changes throughout the examined angles of incidence (45° and 60°). The main change was observed in the specular intensity of the peak (I_s) and in its width at half height ($W_{1/2}$). The diffuse reflectance (I_d) showed only small fluctuations and remained essentially constant on weathering (*Figures* 1-2). The value of I_d was small for glossy paints, but was higher for semigloss and matte finish coatings (e.g., *Figures* 1-2).

On the other hand, the value of I_d, in the case of unpigmented PVC (organosol), was negligible. This suggested that the diffuse intensity arose from the presence of the pigment. It may, therefore, be a characteristic of the pigment or the total paint system rather than the polymer alone.

Width at Half Height

The change in the width at half height with weathering was found to be fairly small in the case of the glossy paints (*Figure* 3). The epoxy/polyamine was exceptional in this respect. After an initial period of stability, $W_{1/2}$ increased steeply, then decreased slightly (*Figure* 3).

In general, the semigloss finish (chlorinated rubber) paint showed great change in $W_{1/2}$ with weathering compared to the glossy paints (*Figure* 3). The PVC organosol matte finish showed even greater change. In the latter case, $W_{1/2}$ increased steeply at the beginning of the exposure, then decreased later (*Figure* 3).

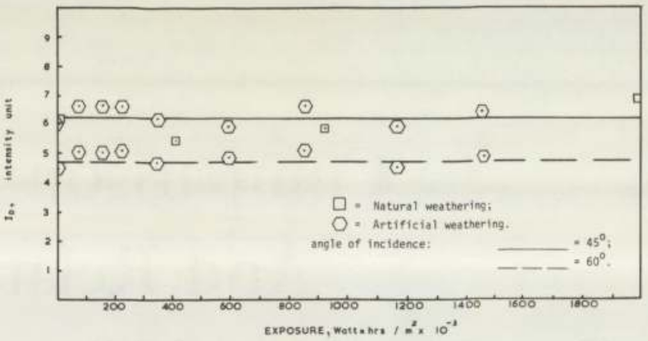


Figure 1—Dependence of diffuse reflectance (I_d) on exposure: Rutile/polyurethane gloss finish

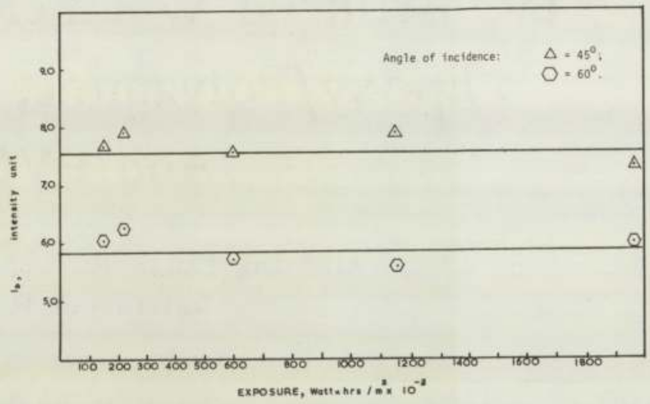


Figure 2—Dependence of diffuse reflectance (I_d) on exposure: Thixotropic chlorinated rubber

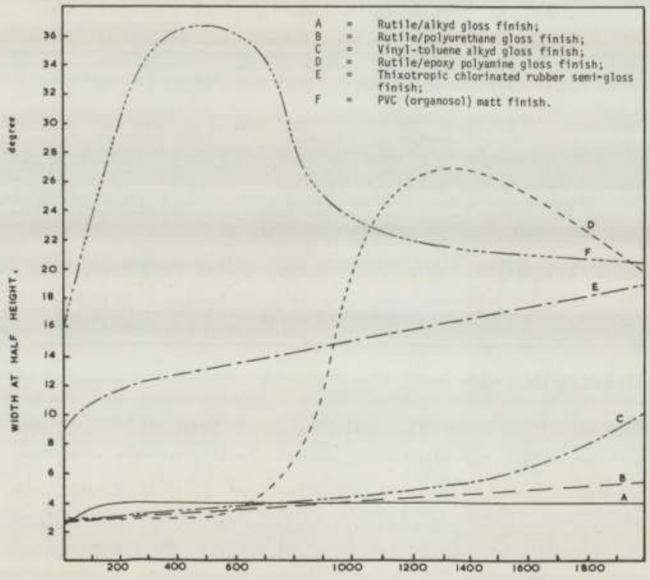


Figure 3—Dependence of width at half height ($W_{1/2}$) on exposure

Specular Intensity

The specular intensity (I_s) and the peak height (I_s-I_d) decreased gradually with weathering (*Figures* 4-8). In most cases they reached a certain level (plateau), though sometimes they reached a minimum and then increased again (*Figure* 4).

In contrast to $W_{1/2}$, the peak height showed a large decrease on aging in the case of the glossy paints, whereas for the semigloss and matte finish paints, it decreased only slightly (*Figure* 8).

The rate of decrease in the intensity seemed to differ from one paint system to another. The epoxy/polyamine gloss finish was unique in this respect. The peak height changed suddenly, after a period of slow change in rate, to reach a plateau having a value similar to the one of the matte paint (*Figure* 7).

Gloss Factor

As expected, the gloss factor (GF) decreased with aging (*Figures* 9-14). In most of the cases, it reached a plateau (as shown for the phthalic alkyd, polyurethane, chlorinated rubber, and PVC; *Figures* 9, 10, 12, and 13). During the same period of exposure, no plateau was observed for the vinyl-toluene alkyd. During that period, a linear relationship between log GF and exposure was observed (*Figure* 14).

The GF of epoxy/polyamine decreased steeply after a certain period of induction, and increased slightly after passing through a minimum (*Figure* 11). In fact, the GF of epoxy/polyamine decreased after $1000 \text{ watt} \times \text{hr/m}^2 \times 10^{-3}$ of exposure, reaching a lower level than that of the matte finish paint (PVC organosol). In the case of the latter, the GF reached a plateau again, after passing through a minimum (*Figure* 13).

Generally, the rate of change of GF with aging differs from one paint to another. The rate decreased in the following order: PVC > chlorinated rubber > epoxy/polyamine > polyurethane > vinyl-toluene alkyd.

Comparison With Natural Weathering

The comparison was based upon the total exposure in watt hr, and favorable agreement was obtained between natural and artificial weathering (*Figures* 11, 13, 14, and 15). Considerable difference was found only in the case of the phthalic alkyd (*Figure* 16).

Studies of Surface Irregularities

On weathering, both the number and height of the surface irregularities increased. Linear relationships were found between log GF and both the average height of surface irregularities (AHRI) and the

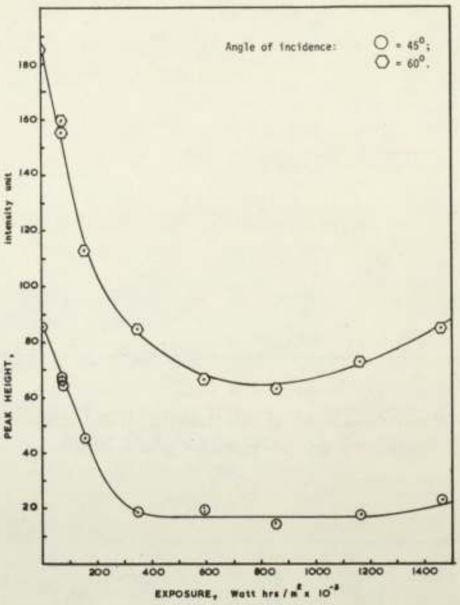


Figure 4—Dependence of peak height (I_s-I_d) on exposures: Rutile/alkyd gloss finish

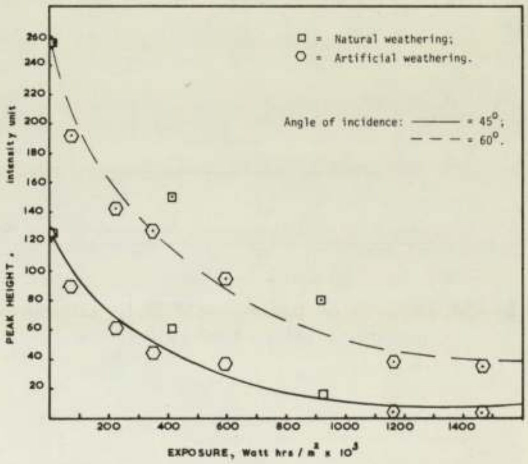


Figure 5—Dependence of peak height (I_s-I_d) on exposure: Rutile/polyurethane gloss finish

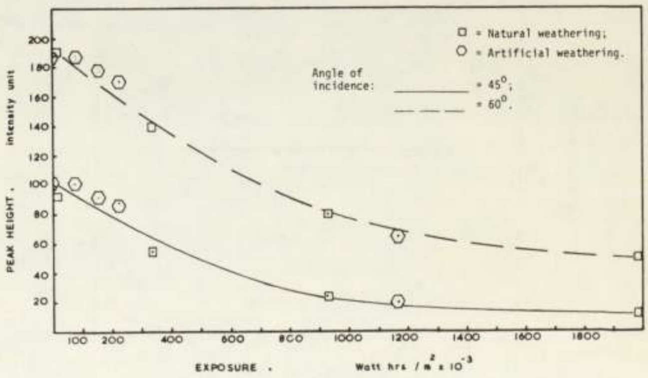


Figure 6—Dependence of peak height (I_s-I_d) on exposure: Vinyl-toluene alkyd gloss finish

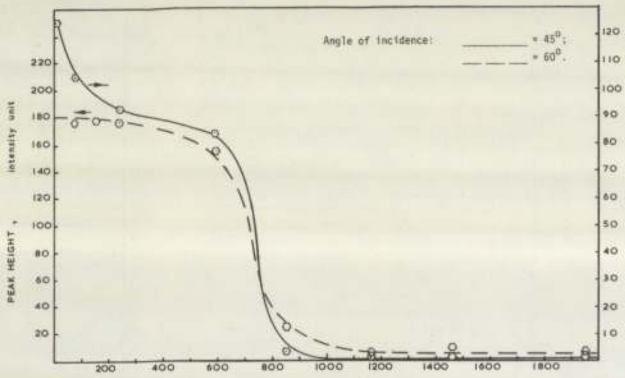


Figure 7—Dependence of peak height $(I_s\text{-}I_d)$ on exposure: Rutile/epoxy polyamine gloss finish

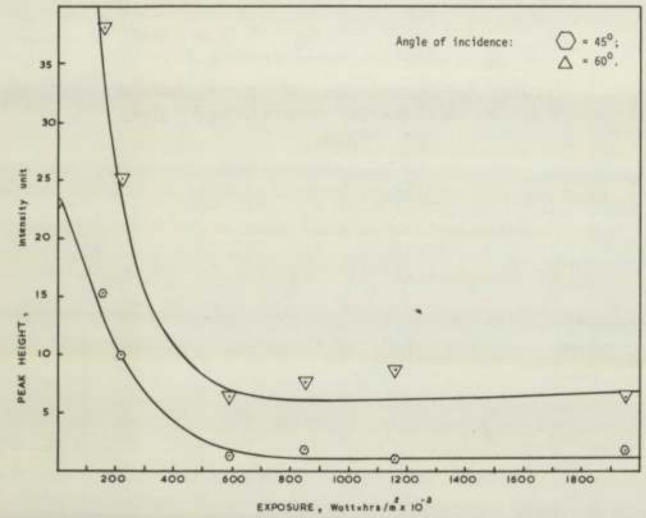


Figure 8—Dependence of peak height $(I_s\text{-}I_d)$ on exposure: Thixotropic chlorinated rubber

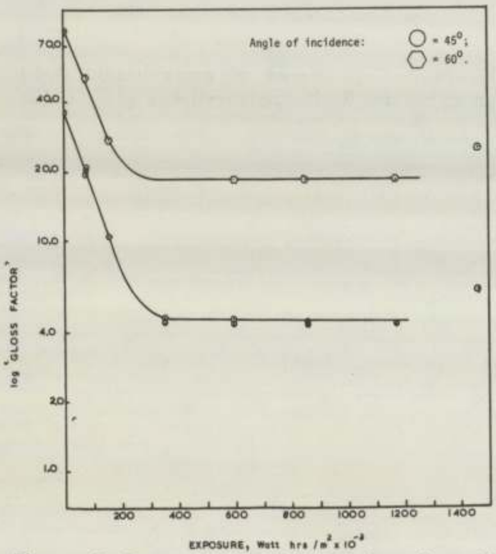


Figure 9—Dependence of log "gloss factor" on exposure: Rutile/alkyd gloss finish

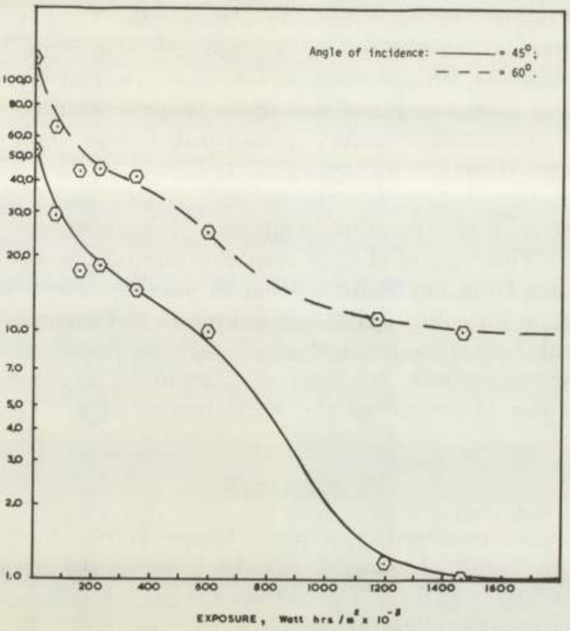


Figure 10—Dependence of log "gloss factor" on exposure: Rutile/polyurethane gloss finish

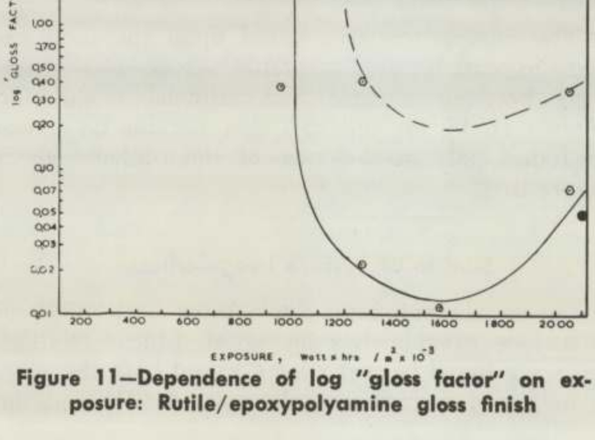


Figure 11—Dependence of log "gloss factor" on exposure: Rutile/epoxypolyamine gloss finish

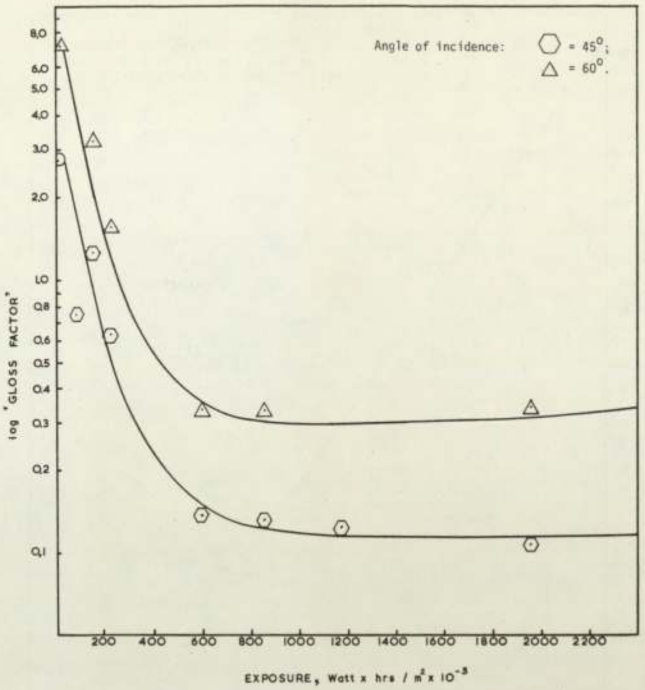


Figure 12—Dependence of log "gloss factor" on exposure: Thixotropic chlorinated rubber semigloss finish

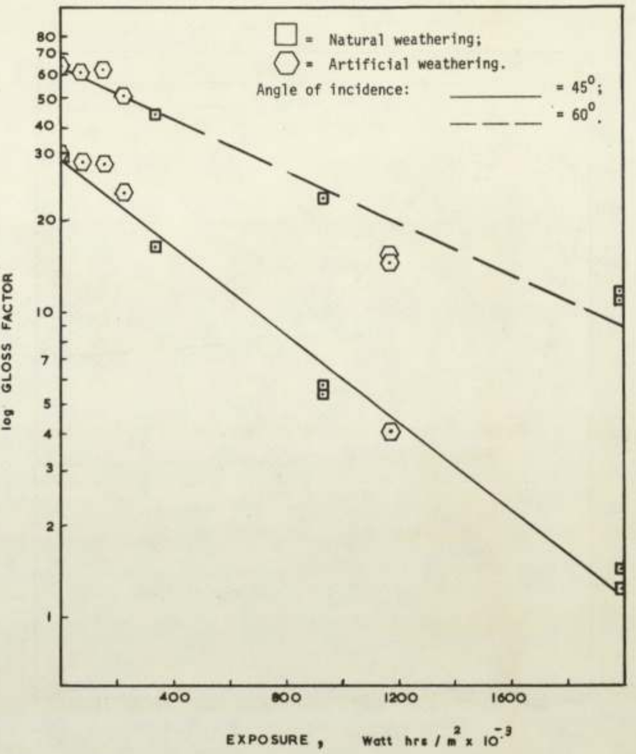


Figure 14—Dependence of log "gloss factor" on exposure: Vinyl-toluene alkyd gloss finish

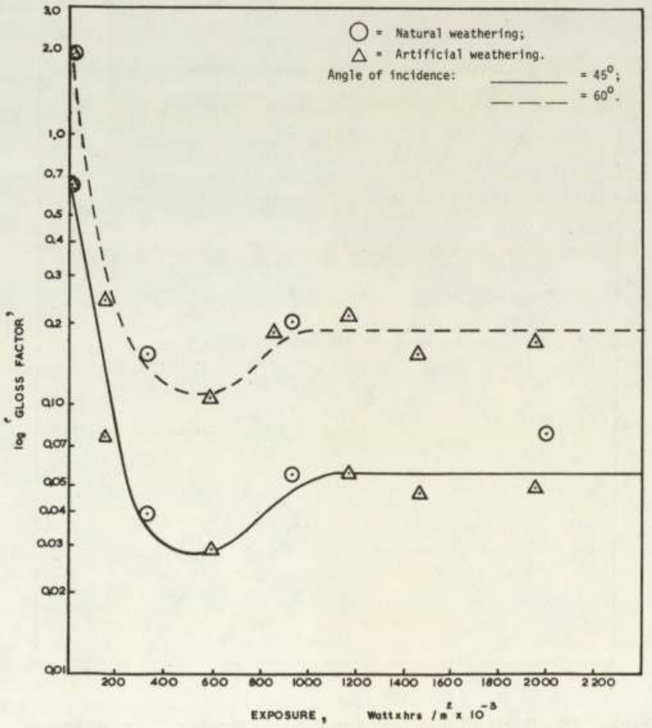


Figure 13—Dependence of log "gloss factor" on exposure: PVC (organosol) matte finish

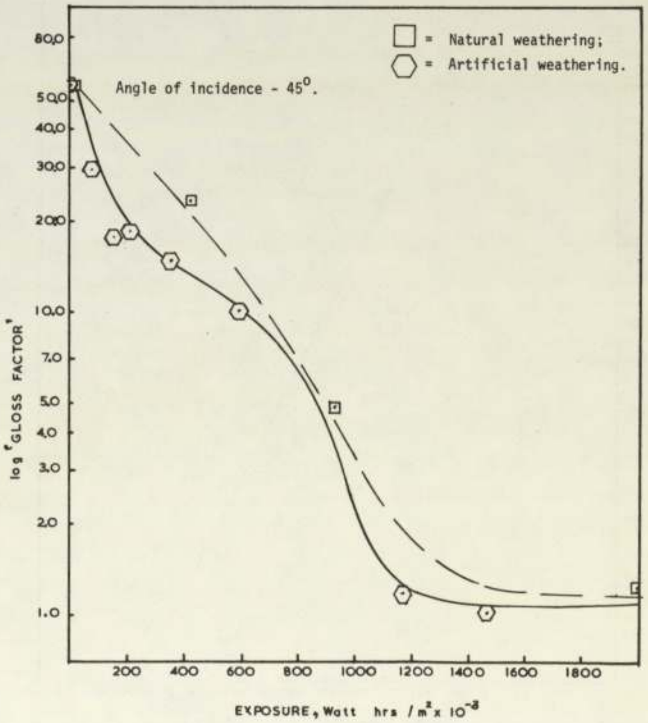
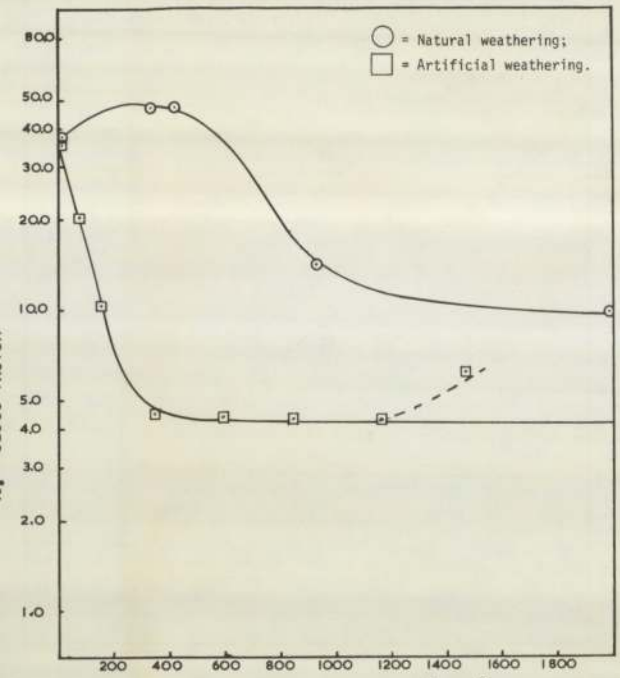
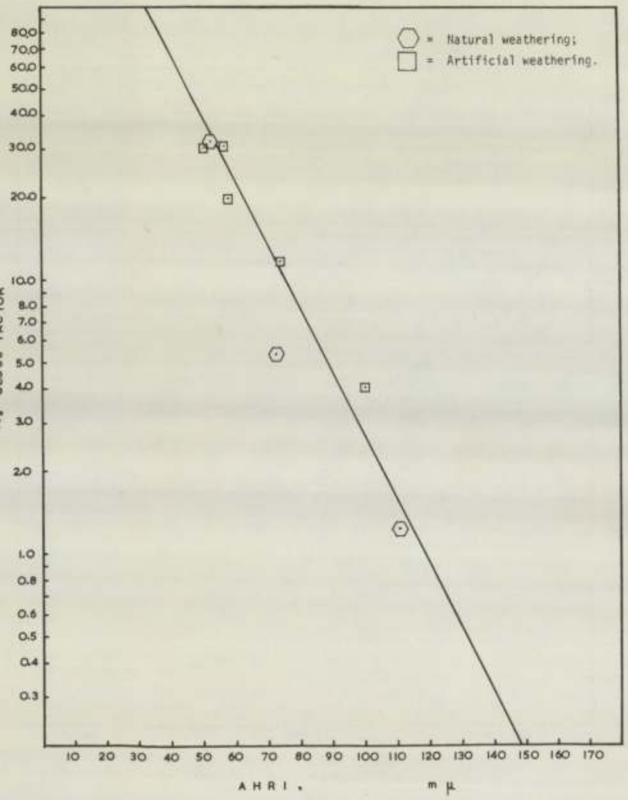


Figure 15—Dependence of log "gloss factor" on exposure: Rutile/polyurethane gloss finish



igure 16—Dependence of log "gloss factor" on exposure: Rutile/alkyd gloss finish



igure 17—Dependence of log "45° gloss factor" on peak count

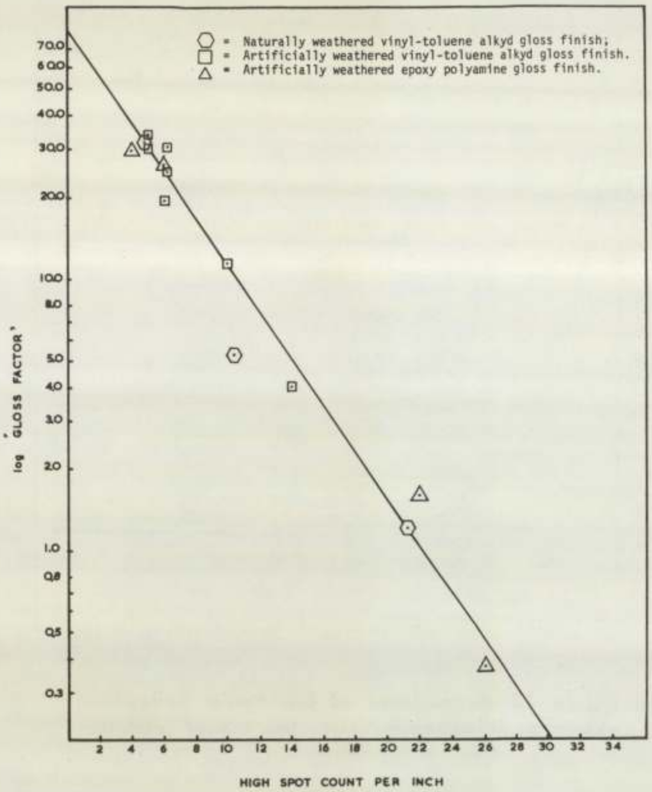


Figure 18—Dependence of log "45° gloss factor" on average height of surface irregularity (AHRI): Vinyl-toluene alkyd gloss finish

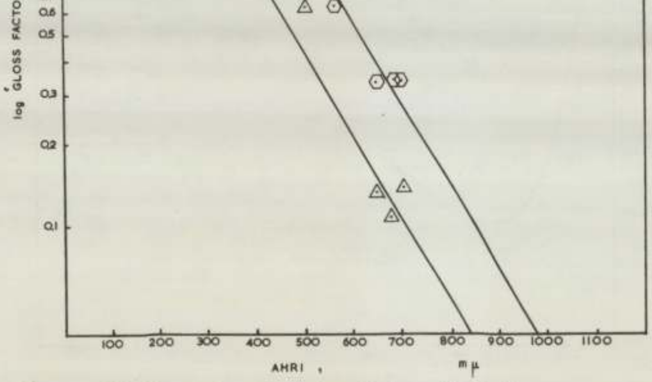


Figure 19—Dependence of log "gloss factor" on average height of surface irregularities (AHRI): Thixotropic chlorinated rubber

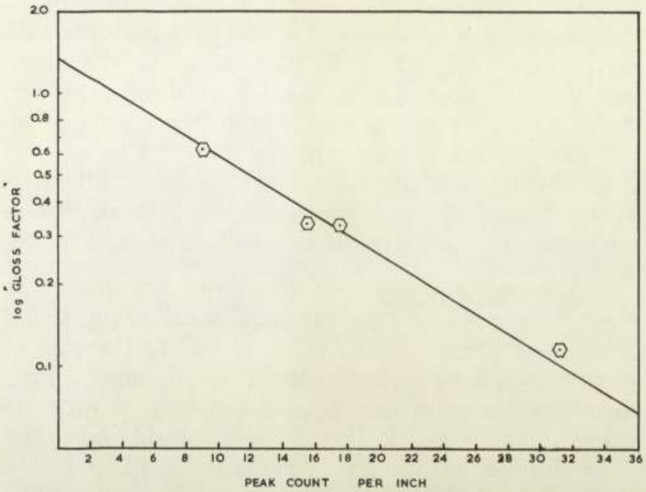


Figure 20—Dependence of log "60° gloss factor" on peak count: Thixotropic chlorinated rubber semigloss finish

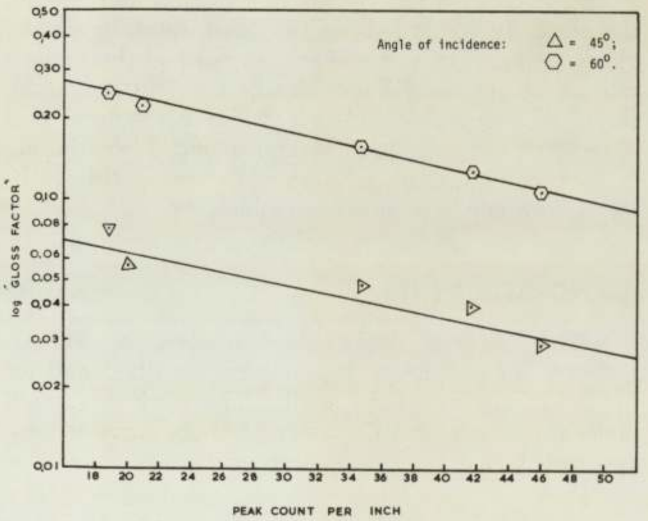


Figure 21—Dependence of log "gloss factor" on peak count: PVC (organosol) matte finish

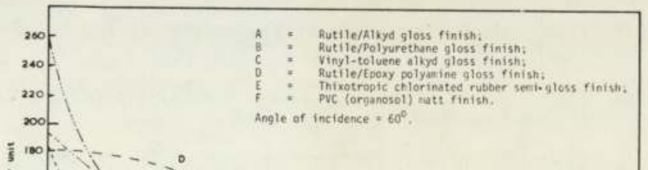


Figure 22—Dependence of peak height on exposure

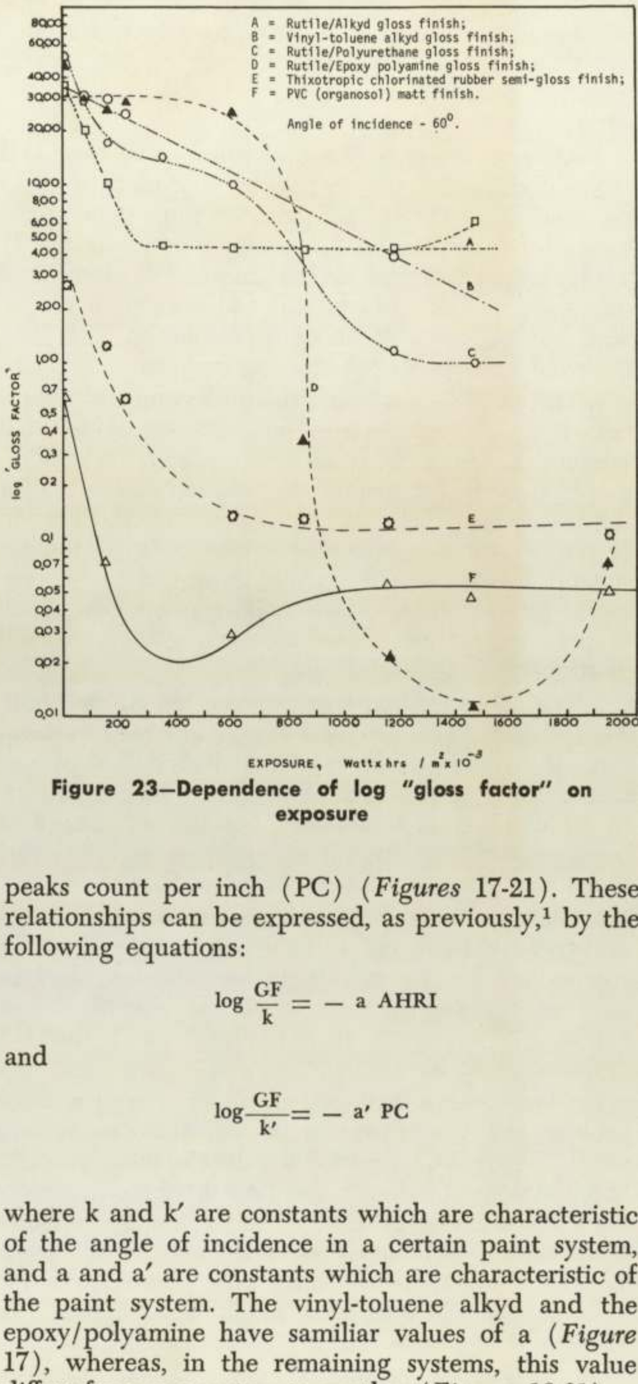


Figure 23—Dependence of log "gloss factor" on exposure

peaks count per inch (PC) (*Figures* 17-21). These relationships can be expressed, as previously,[1] by the following equations:

$$\log \frac{GF}{k} = - a \ AHRI$$

and

$$\log \frac{GF}{k'} = - a' \ PC$$

where k and k′ are constants which are characteristic of the angle of incidence in a certain paint system, and a and a′ are constants which are characteristic of the paint system. The vinyl-toluene alkyd and the epoxy/polyamine have samiliar values of a (*Figure* 17), whereas, in the remaining systems, this value differs from one system to another (*Figures* 18-21).

DISCUSSION AND CONCLUSIONS

The results obtained from artificial weathering agree with those of natural weathering. Linear relationships exist between log GF and AHRI, as well as between log GF and the peaks count.

On weathering, the surface imperfections increase. Surface irregularities increase in both number and size. Clark, et al,[5] measured the change in texture of different plastic materials on weathering. They concluded that roughness measurements could provide useful parameters for quantitatively characterizing early changes in surface texture of weathered plastics.[5] The number of peaks per inch on the surface was found to be a more sensitive parameter for plastics than was the arithmetic average height (which included waviness, lay of the material, and surface flaws).

After studying the weatherability of 20 clear and pigmented plastics, they concluded that plots of peaks per inch vs. exposure time gave the same general behavior for most plastics: (1) an induction period; (2) a very rapid increase in roughness; (3) a gradual smoothing of the surface; and (4) maximum roughness was observed at about 6-12 months. This was observed for exposures beginning in April.

The authors[5] confirmed the peak counts of roughness by scanning electron micrographs of selected samples. Excellent agreement was found. The micrographs proved that surface degradation accounted for the increase in the peak count and that the erosion of the weathered surface was the cause of the resultant smoothing. The technique proved to be very useful for quantitatively describing phenomena such as polymer erosion, fibre-bloom on glass-reinforced plastics, cracking, and crazing.[5]

The linear relationships between log GF and both AHRI and PC again show that goniophotometry measures the weatherability and the degradation of surface coatings, as did surface roughness measurements. In addition, goniophotometry has the advantage of being a nondestructive test, whereas the Telysurf sometimes damages the weathered surface.

Goniophotometry provides many convenient parameters for following surface deterioration and for comparing the weatherability of different surface coatings. Some of these parameters are: width at half height ($W_{1/2}$), peak height (I_s-I_d), and the GF (*Figures* 3, 22, 23).

Glossy paints have a narrow $W_{1/2}$ and a large peak height. The change of $W_{1/2}$ in this case is very small (*Figure* 3), indicating the development of micro imperfections. As already mentioned,[6] these imperfections do not change the shape of the goniophotometric curve, but merely alter the area of the peak. This means that when dealing with glossy paints, the main change will take place in (I_s-I_d) rather than in $W_{1/2}$.

The rate of change of (I_s-I_d) can be used, in this case, as a parameter for the weatherability. On the other hand, the goniophotometric curves of the semigloss and matte paints are broad (*Figure* 22). In their case, $W_{1/2}$ increases considerably with weathering, whereas the change in peak height is less prominent (*Figures* 3 and 22). Hence, $W_{1/2}$ can be used as a parameter of paint weatherability (*Figure* 3). The gloss factor is suitable for all cases and thus is a more universal test for comparing deterioration of paint surfaces (*Figure* 23).

For early detection and comparison of surface deterioration, it is adequate to compare both the rate of fall of the GF up to the plateau or the minimum, and the ultimate value of the GF at these extremes. Accordingly, we can conclude from the results (*Figure* 23) that the order of the durability of tested surface coating systems should be: phthalic alkyd > vinyl-toluene alkyd > polyurethane > epoxy/polyamine > chlorinated rubber > PVC organosol.

Although the phthalic alkyd did not show the slowest rate of change in artificial weathering, it did show the highest ultimate value of GF. In the case of natural weathering,[1] the phthalic alkyd showed both the slowest rate of change and the highest ultimate value of GF. It should, therefore, be considered as the most durable of all. The vinyl-toluene alkyd had a slower rate of change of GF than polyurethane, while the epoxy/polyamine showed a sudden fall in GF after about 800 watt × $hr/m^2 \times 10^{-3}$ of exposure. After this period, this paint became extremely rough and brittle. It became susceptible to scratches and should, therefore, be regarded as the least durable of the glossy paints. The soft PVC organosol had the highest rate of change in GF on weathering and it should, therefore, be considered the least durable system. This agreement between natural and artificial weathering is another important advantage for using this technique as compared to other techniques.

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