AUTOMATED TECHNIQUES FOR SURFACE COATING DETERIORATION STUDIES

by

Richard Ellison Raistrick

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

March 1984

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SUMMARY

This thesis describes the development of automated techniques for use in accelerated ageing studies involving polymer based surface coatings. These techniques were required in order that the effects of low concentrations of pollutant gases, specifically nitric oxide, on surface coatings could be investigated with a reasonable degree of precision.

As part of this programme, an automated accelerated ageing cabinet was constructed, to provide facilities which are capable of simultaneously or independently exposing coatings to various ageing elements under accurately controlled conditions. A second and more widely useful aspect involved the development of an automated goniophotometer interfaced to a micro computer data handling system. The automation and interfacing of the goniophotometer has converted a previously cumbersome and tedious analytical technique into a rapid, highly sensitive, non-destructive method for assessing the reflective characteristics of a surface. The computer programme provides a quick and accurate means of analysing the goniophotometric data, and combines this with rapid storage and retrieval for future analysis and comparison. By recording this data on a disk or cassette, a record is retained which encapsulates the essential reflective properties of a surface which are subjectively considered by an individual in assessing gloss and texture.

The automated goniophotometer and the accelerated ageing cabinet have been used, in conjunction with colorimetry and infrared spectroscopy, to investigate the reaction between nitric oxide and various polymer based surface coatings. These were, a series of poly (vinyl chloride) coatings and a selection of commercial powder coatings. The nature and roles of specific chemical intermediates, formed between these coatings and nitric oxide, has been considered. In particular, the results indicated that in weathering environments nitric oxide stabilises degradation caused by ultra-violet light. The computer was used extensively to superimpose goniophotometric curves to isolate individual deteriorative influences on the degradation of the coatings.

INDEX TERMS: Goniophotometry
Micro-computer interfacing
Accelerated ageing
Nitric oxide
Poly (Vinyl Chloride) deterioration

TO MY PARENTS

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LIST OF ABBREVIATIONS

NOx	Oxides of Nitrogen
Is	Specular Intensity
Id	Diffuse Intensity
$W\frac{1}{2}$	Peak Width at Half Peak Height
GF	Gloss Factor
CIE	Commission International de l'Eclairage
PVC	Poly (Vinyl Chloride)
THF	Tetrahydrofuran
A.C.	Alternating Current
D.C.	Direct Current
A/D	Analog to Digital
D/A	Digital to Analog
MSB	Most Significant Bit
LSB	Least Significant Bit
VDU	Visual Display Unit
F.E.T.	Field Effect Transistor
H	Henry
i.r.	Infrared
uv	Ultra-violet
p.s.i.	Pounds per square inch
p.p.h.	Parts per Hundred

CHAPTER 1

INTRODUCTION

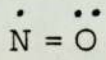
1.1 General Introduction

This thesis is concerned with the study of the effects of various gaseous pollutants, present in low concentrations in the atmosphere, on the deterioration of surface coatings. This is an area in which a considerable amount of work has been carried out on the nature and sources of the pollutants, but little has been done on the actual effects of the pollutants on the surface coatings. Although there is a general feeling that such effects would be deleterious there appears to be no available instrumentation for such studies, let alone results of experimentation. This is particularly the case with nitric oxide (nitrogen monoxide) which has been selected as being of particular interest.

Three main topics are therefore discussed within this introduction. Firstly, the nature of nitric oxide and the sources of this gas when present in the atmosphere as a result of industrial or other pollution. Secondly, the question of accelerated weathering, achieved by the use of artificial ageing systems, together with the question of the ability of these systems to provide background effects or directly useable results. Thirdly, the possible evaluative techniques that can be used to detect the initiation and continuing deterioration of the surface coatings are discussed.

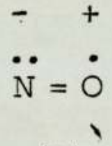
1.2 Nature and Sources of Nitric Oxide

Nitric oxide is a toxic, colourless, non-flammable gas. It is not very soluble in water and as a result it is only slightly irritating to the upper respiratory tract, allowing dangerous amounts of the gas to be inhaled before any discomfort is noticed. Nitric oxide (NO) has eleven valency electrons and is paramagnetic at ambient temperatures. In terms of the valence bond theory its structure may be considered as a resonance hybrid of structures (I) and (II) below with (I) predominating as shown by the very small dipole moment of 0.16 Debye.



$\dot{N} = \ddot{O}$

(I)



$\overset{-}{\ddot{N}} = \overset{+}{\dot{O}}$

(II)

Chemically nitric oxide behaves as a stable free radical since, as the unpaired electron is distributed over the whole molecule, the "sensitivity" and tendency for pairing of this electron is diminished$^{(1)}$. It does not readily combine with itself but is well known for its ability to combine with other free radicals. In all cases the NO associates initially with the radical at the nitrogen end.

$$R. + .NO = R\text{-}NO \quad .....(1)$$

There is no evidence for the initial association at the oxygen atom$^{(2)}$.

In the atmosphere nitric oxide (NO) is converted to nitrogen dioxide (NO_2) by a complex photooxidation process$^{(3)}$ which involves three major paths, eq (2, 3, 4)

(i) reaction with ozone : $NO + O_3 = NO_2 + O_2$ .....(2)

(ii) thermal oxidation by
molecular oxygen : $2NO + O_2 = NO_2 + O_2$ .....(3)

(iii) reaction with radicals:

$$NO + HO_2 = NO_2 + HO$$
$$NO + RO_2 = NO_2 + RO$$
$$NO + RCO_3 = NO_2 + RCO_2 \text{.....(4)}$$

* Note: In addition to these major paths a variety of subreactions occur. A generalised photochemical kinetic mechanism is given in Appendix 3.

The presence of NO and NO_2 as pollutants in town air is believed to be mainly due to the emission products of the internal combustion engine(4). The emission of nitric oxide is always accompanied by the presence of nitrogen dioxide. This is produced during combustion by a rapid reaction between hydroperoxyl radicals and nitric oxide. These combined emissions of oxides of nitrogen are referred to as NOx. The nitrogen dioxide content of NOx is generally not more than about 10%.

The concentration of NOx depends upon the exact nature of the particular location. However, this concentration, again depending on the nature of the site, can vary quite significantly on a diurnal basis, especially in the vicinity of dense traffic areas(5). Vehicle exhaust emissions may not apparently account for the total kerbside concentration of NO, since on occasions when elevated NOx concentrations have been detected, the carbon monoxide (CO) levels were no higher than normal. As both pollutants are present in vehicle exhaust emissions, and there is no reason to suppose that the CO/NOx ratio changes significantly, it has been suggested that low to medium level stationary sources such as power station boilers and industrial heating installations are responsible for up to 45% of the NO present at urban sites$^{(6)}$, while motor vehicles are responsible for 25%. Typically the kerbside concentration of NO in the presence of heavy traffic is in the region of one part per million$^{(4)}$. At this concentration the oxidation of NO to NO_2 takes place slowly so that the NOx present in polluted air is composed mainly of nitric oxide.

1.3 Weathering Techniques

The term weathering, when applied to surface coatings, refers to the deterioration of the coating as a result of exposure to outside elements. Various experimental procedures have been developed which aim to standardise the conditions under which a surface coating is exposed to the weathering elements$^{(7)}$. These procedures can be divided into two categories, natural and artificial.

1.3.1 Natural Weathering

Exposing a surface coating to a natural weathering environment, under controlled conditions, usually involves coating a specially prepared framework or test panel with the surface coating. The coated panel is allowed to dry or cure under specified conditions before being left for a number of months or years on an outside rack. Observations of the panel are made in a specified manner after specified intervals of ageing.

Outdoor weathering can be accelerated in order to produce the required degree of weathering in a shorter period of time. The acceleration can be achieved by various means. These usually include mounting the coatings at five degrees from the horizontal, using racks that rotate to follow the sun, or by having mirrors which concentrate the sun's rays onto the coating's surface. In addition, water sprays may be used to periodically wet the surface. Accelerated natural weathering can also be achieved by the selection of the site at which the coatings are exposed, such as in Florida in the U.S.A.(8). The deterioration of the coating is accelerated here, compared with other locations, due to the intense sunlight, high humidity and moderate rainfall combined with a minimal seasonal effect. Similar sites for accelerating particular aspects of weathering are found in Arizona in the U.S.A.(9) and Pretoria and Durban in South Africa(10).

1.3.2 Artificial Weathering

The main difference between natural and artificial weathering is that the coating is exposed inside a laboratory in an artificial weathering instrument. The elements of natural weathering (sunlight, temperature changes, humidity) are replaced by a combination of artificially produced elements. The light is usually supplied by a carbon arc, a xenon arc lamp, fluorescent lighting or some combination of them. Temperature changes, if required, are usually supplied by the cycles of the light source employed. Humidity is often supplied by a periodic water spray.

A number of commercial accelerated weathering instruments have been developed in recent years. The only significant way in which these differ from each other is in the manner of control and availability of the facilities for various operating cycles, and in the type of radiation source employed. Comparative assessments of the available instruments have appeared in the literature(11,12) in which varying degrees of correlation to natural weathering have been claimed for the different methods. One fundamental fault which all weathering instruments appear to have in common is their inability to reproduce satisfactorily the balance between all of the deteriorative factors which are present in a natural weathering environment. Artificial weathering may change the relative rate at which different deteriorative factors affect the coating, resulting in a type of coating failure which would not occur with natural weathering.

The particular feature of an artificial weathering instrument which has attracted most attention is the choice of uv radiation source that is employed. Ideally, the source should have a spectural wavelength distribution of emitted light which matches that of natural sunlight as close as possible. At present the xenon arc lamp is regarded as having the closest similarity to sunlight than any other source(13). The limitations of this source are the tendency for its spectural distribution to change during use and for the light intensity to diminish during ageing of the lamp(14). The favourable results obtained with the xenon arc lamp have led to the popularity of the Xenotest apparatus over recent years(15). In comparison the most popular instrument for its versatility in the cycling area of weathering is possible the Dew Cycle apparatus(16).

The original instruments were developed primarily for the study of oil modified alkyd decorative paints. For these paint systems 1000 hours in a Xenotest instrument roughly corresponds to two years exposure in the British climate. Despite this the general impression gained from the literature is that little correlation exists between artificial weathering and natural weathering. This situation is mainly due to the instruments' inherent deficiencies in obtaining a suitable balance between the different weathering elements. Because of this the role of an artificial weathering test is essentially limited to providing information on the relative effects of a formulation change in a coating.

1.3.3 Accelerated Ageing

The difference between artificial weathering and accelerated ageing is that ageing systems are not used in an attempt to simulate situations which occur naturally. They are used more as a means of elucidating the particular ageing effect of one or more deteriorative weathering factors.

Instruments designed for accelerated ageing that are commercially available usually provide facilities which operate one main ageing system, such as uv radiation or humidity, with a secondary facility such as temperature cycling. Examples of this type of instrument are the Atlas Fade-ometer, manufactured by the Atlas Electric Devices Co. Chicago, which is primarily used for studying the colour fastness of various coatings, textiles or inks. The Atlas UVCon exposes samples to uv light and condensation. Neither of these instruments make any attempt to simulate natural weathering conditions but are mainly intended for screening tests.

Ageing systems tend to use banks of fluorescent tubes as the uv radiation source, despite the fact that single lamp sources, such as the xenon arc lamp, can provide closer reproduction of solar radiation. The advantage of multiple source systems over a single source is that the tubes may be progressively renewed, one or more at a time, thus providing and maintaining a source of almost constant radiation intensity. It is important to note that none of the currently available accelerated weathering instruments provide the facility for NO deterioration studies. It is largely for this reason (i.e. the absence of suitable instrumentation), as stated at the beginning of the chapter, that no specific work on the effect of NO on surface coating deterioration has been recorded.

1.4 Analytical Techniques

There are many techniques available for use in the study of surface coatings. These techniques can be divided into two categories, those concerned primarily with monitoring surface changes and those concerned with bulk changes. Due to the large surface area to bulk ratio of surface coatings, the techniques which are likely to produce the most informative results are the surface techniques. These can be further sub-divided into predominantly optical, physical and chemical methods. The optical methods include such techniques as goniophotometry for measuring the surface gloss, colorimetry and microscopy of the surface. Physical methods include surface roughness measurements, surface energetics, ellipsometry and weight loss measurements. The chemical methods include infrared spectroscopy, electron probe micro-analysis and gas chromotography.

The disadvantage of many of the physical and chemical methods of analysis is that besides frequently being complicated, they are often destructive. Even in the case of surface energistics, which usually involves the wetting and spreading of a liquid in contact with the coating surface, some damage or contamination of the surface may occur. In contrast optical techniques, especially sophisticated methods such as goniophotometry, do not physically or chemically alter the surface of the coating. Additionally, they tend to be accurate and relatively quick to carry out. Because of these factors optical techniques are ideally suited for monitoring the ongoing deterioration of a coating. Two of these techniques, goniophotometry and colorimetry and the theories involved are discussed later in this section.

1.4.1 Goniophotometry - Theory of Light Reflection from Surface Coatings

A goniophotometer is an instrument which is capable of measuring the intensity of light reflected from a given surface as a function of viewing angle. The basic layout of a goniophotometer is shown in Figure 1.1. When light is incident upon the surface of a coating film it is subsequently reflected by a combination of two entirely different processes. Firstly, a certain proportion of the incident light undergoes surface reflection at the surface to air interface. 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 coating surface. Secondly, the greater part of the incident light actually penetrates the surface by refraction into the bulk,where, depending upon whether the coating is pigmented or not, it either undergoes scattering by pigment particles, or is internally reflected at the lower substrate boundary, prior to its eventual re-emergence from the top surface.

A coating can be considered as being intermediate between a perfect "mirror" and a perfect matt surface when considering its reflection characteristics. A perfect "mirror" surface is defined as "a plane surface which reflects all incident light unidirectionally at an angle

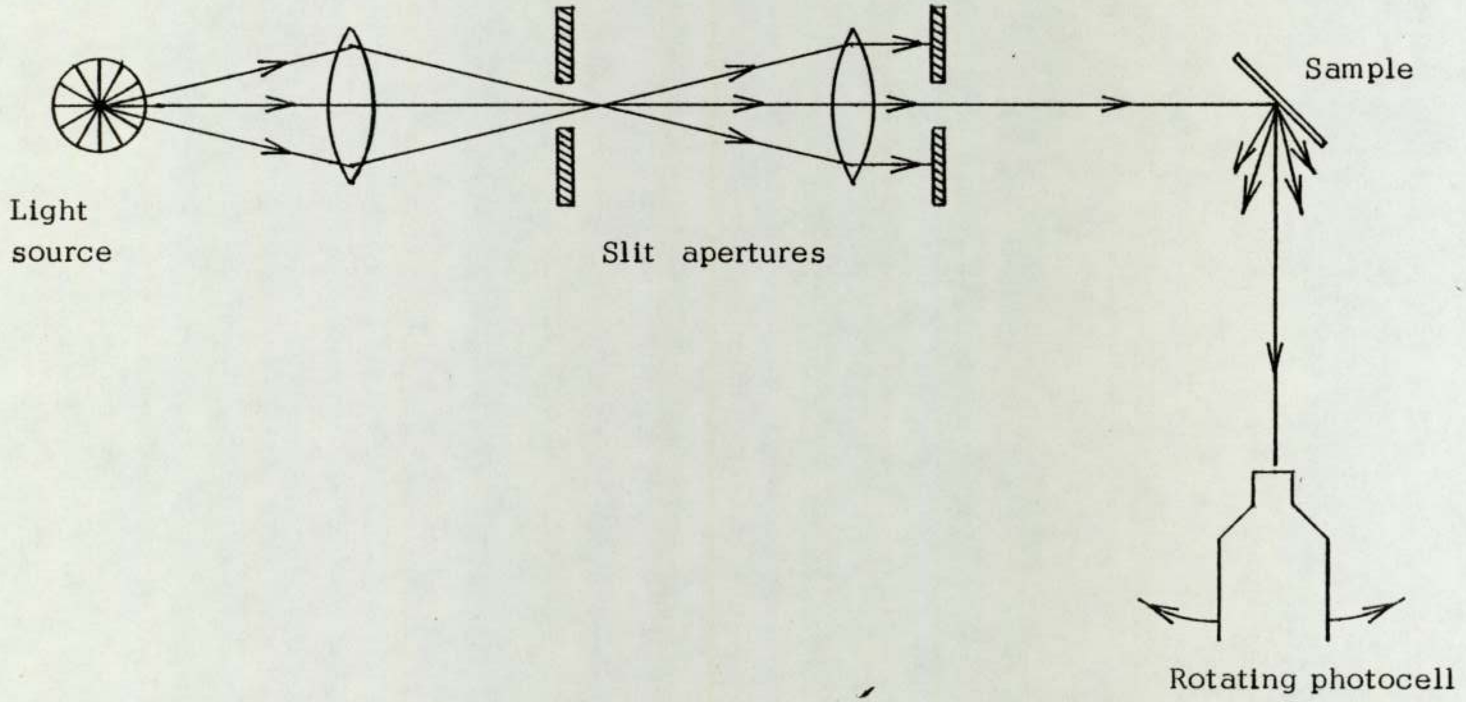
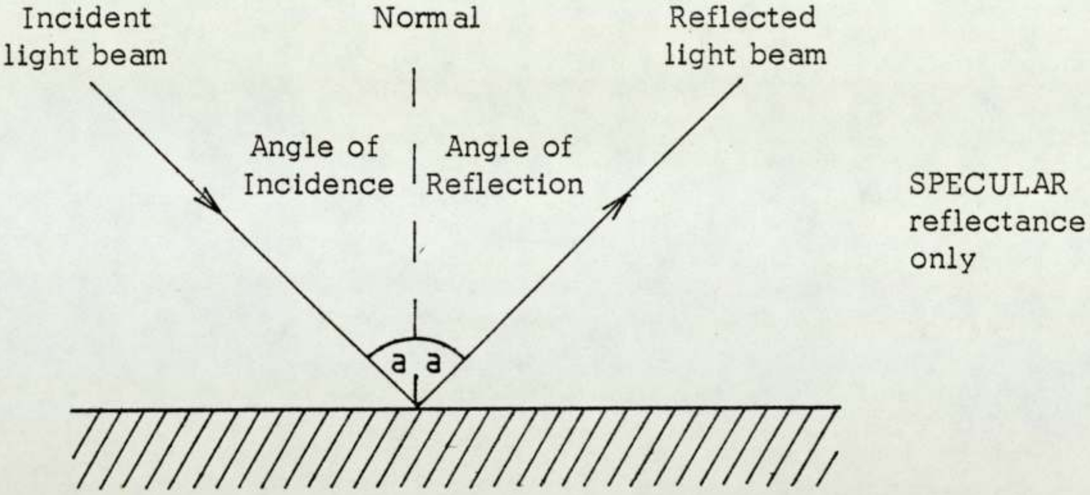


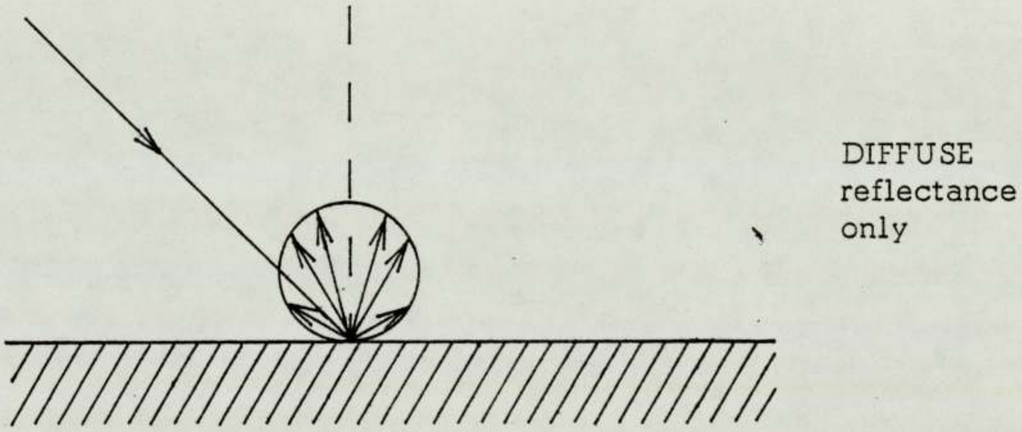
Figure 1.1: Basic layout of a goniophotometer

equal to the angle of incidence", thus rendering the surface effectively invisible to an observer. This type of reflection (Figure 1.2a) is termed "specular" reflection and is well known to be completely governed by Fresnel's Law(18). From the Fresnel equation it is clear that the amount of light reflected increases with increasing angle of incidence. A perfectly matt surface is often defined as a surface which reflects incident light equally in all directions. Although this statement is apparently true in practice, it is not strictly true in theory. The reflection of incident light by a matt surface closely follows Lambert's Cosine Law. This law states that a perfect matt reflector spatially distributes incident light in intensity proportional to the cosine of the angle of reflection. This determines that the shape of the envelope of reflected light is, therefore, a sphere and not a hemisphere as the original definition of a matt reflector suggests (see Figure 1.2b). This type of matt reflection is termed "diffuse" reflection. Unlike specular reflection from a perfect "mirror" surface, which is governed by Fresnel's Law, no such general law exists for diffuse reflection, although all formulae incorporate the Lambert Cosine Law.

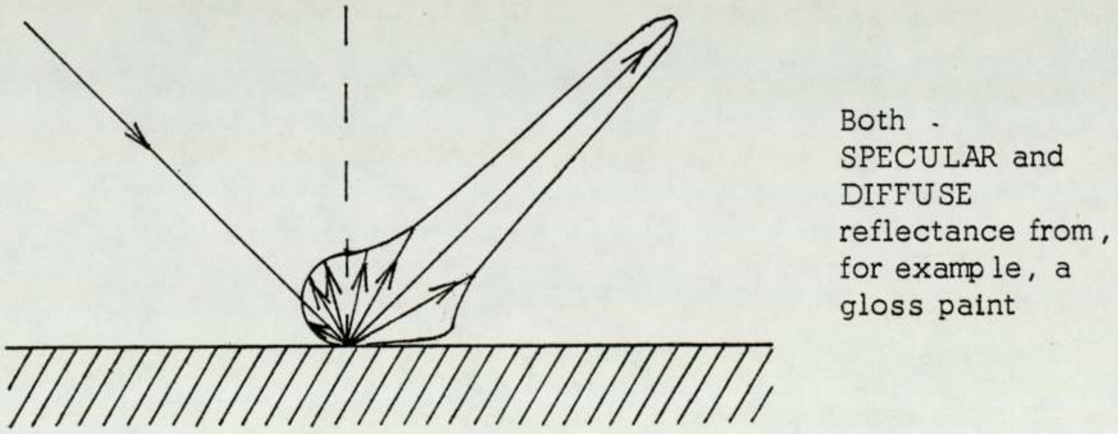
Whereas perfectly smooth mirror surfaces and perfect matt surfaces exhibit only specular and diffuse reflectance respectively, the surface reflection from surface coatings is made up of both specular and diffuse components. The ratio of these two components largely determines the overall gloss of the surface, as characterised by the



1.2(a)



1.2(b)



1.2(c)

Figure 1.2: Ray diagrams of the surface reflection characteristics of
(a) a perfect "mirror" surface,
(b) a perfectly matt surface, and
(c) a typical paint (i.e. "real") surface.

angular distribution of the reflected light. Thus all reflection other than that at the specular angle can be regarded as diffuse reflection resulting from the presence of irregularities in the coating surface (see Figure 1.2c). An additional source of diffuse reflection arises from the scattering of absorbed light by pigment particles below the surface.

The scattering of the incident light due to the bulk reflection of the coating occurs when light, which is incident on the surface of the coating, is partly reflected and partly transmitted. The transmitted light is refracted in accordance with Snell's Law$^{(18)}$, eq. (5) below:

$$\frac{\sin \theta}{\sin \theta'} = \frac{u'}{u} \quad \ldots\ldots\ldots (5)$$

where θ is the angle of incidence,

θ' is the angle between the refracted ray and the normal,

u is the refractive index of the medium on the side of incidence of the incident ray,

and u' is the refractive index of the medium on the side of the interface or the refracted ray.

This refracted light penetrates the surface and is subsequently re-emitted as the greater part of the coating's total reflectivity. The process by which the light is re-emitted depends upon whether the coating is pigmented or not.

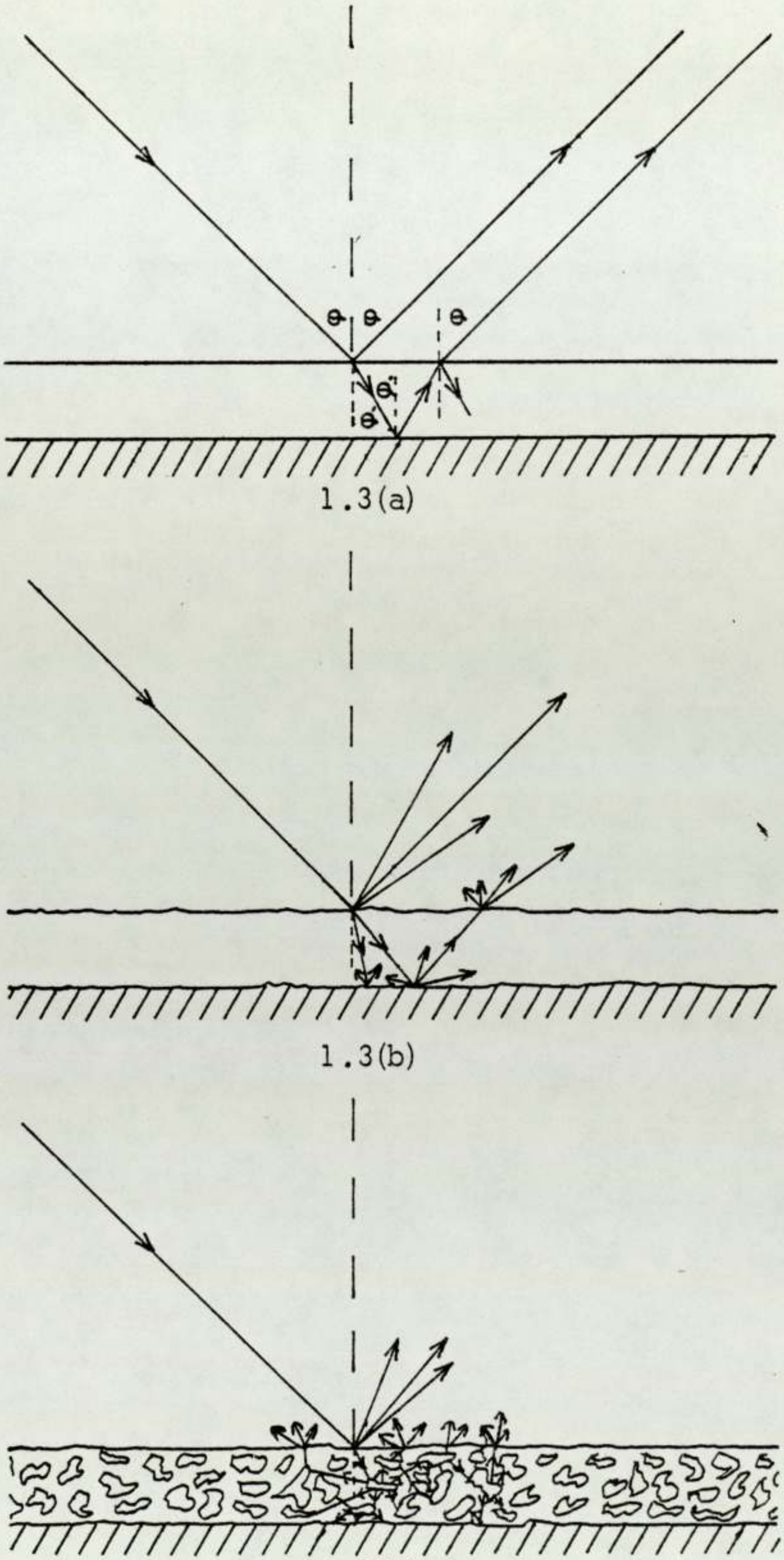
The situation with an unpigmented coating is depicted in Figure 1.3a, in which the refracted light pathway through the coating medium can be plotted exactly, according to the laws of refraction and reflection at the air/coating and the coating/substrate interfaces respectively, prior to its eventual re-emergence from the coating surface. However, as mentioned previously, coating surfaces contain irregularities which, when of a size order comparable to the wavelength of the incident light, give rise to the scattering effects illustrated in Figure 1.3b. In this situation, the simple ray treatment breaks down, although the behaviour of light can still be predicted using the wave theory.

Assuming that the pigment particles are of dimension fairly close to the wavelength of light, the scattering process that occurs in a pigmented film can be depicted as in Figure 1.3c. The light being successively and irregularly reflected in all directions by the pigment particles(19).

Using the above theories for pigmented and unpigmented coatings the reflectance data obtained from goniophotometry can be more easily understood.

1.4.2 Goniophotometry - Instrumentation and Data

The basic technique of goniophotometry can be dated as far back as 1762, when it was used in an attempt to corroborate Lambert's



1.3(a)

1.3(b)

1.3(c)

Figure 1.3: Ray diagrams of the total reflection characteristics of
(a) ideally smooth, and
(b) typical (i.e. "real") unpigmented coatings, and
(c) schematic representation of a pigmented coating reflection

Cosine Law for matt reflectors. Despite the fact that the first reference to a goniophotometer appears to have been made over fifty years ago(20), it is only in the last fifteen years that interest in the design and use of high performance goniophotometers has grown.

In 1966 a new commercial instrument, the Zeiss GP2 goniophotometer was described by Loof of the Carl Zeiss Company(21). Although only manual in operation the GP2 has found widespread use in practice because it combines sufficient accuracy of measurement for most purposes with an optical system that is limited to essential elements. Also, at this time Collings et al reported the modification of a Unicam SP500 spectrogoniophotometer(22) and Loof(23) the modification of the Zeiss DMC25 spectrophotometer, all for goniophotometric use. Both Billmeyer and Davidson(24) and Quinney and Tighe(25) have described the modification and use of the Brice Phoenix Light Scattering Photometer, which is in many ways ideally suited for this kind of work. The last three named instruments are, in strict terms, spectrogoniophotometers, since they are capable of measuring reflectance as a function of wavelength as well as angle. In addition to these instruments Edwards(26) has described the construction of a simple high resolution lasergonioreflectometer.

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 mainly Tahan et al[27-30] have used goniophotometry in conjunction with other surface techniques for the study of the deterioration of polymer surfaces in various natural and artificial environments. Goniophotometry is a particularly suitable method for following the deterioration of coatings as it is a sensitive technique capable of following even the most subtle ageing effects.

Finally, having obtained them, the question arises as to the best way to interpret goniophotometric curves, a typical example of which is shown in Figure 1.4. There are several ways of combining the experimentally determined values to yield a conveniently handled quantity which may be then compared with subjective gloss assessments. It has become commonplace to consider three quantities in particular, namely the intensities of the specular (Is) and diffuse (Id) reflections in conjunction with the peak width at half height (W1/2). These quantities correlate much more readily than simple photometer reflectance values with empirically judged image sharpness and contrast, and surface lustre. In addition, it has been shown[27,30], that the so called "gloss factor",

$$\frac{Is - Id}{W\,1/2} \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

being a useful single parameter that can be derived from a goniophotometric curve, does quantitively reflect the changing nature of a surface. It provides a very useful way of monitoring the change in reflectance properties of a coating during ageing or deterioration studies.

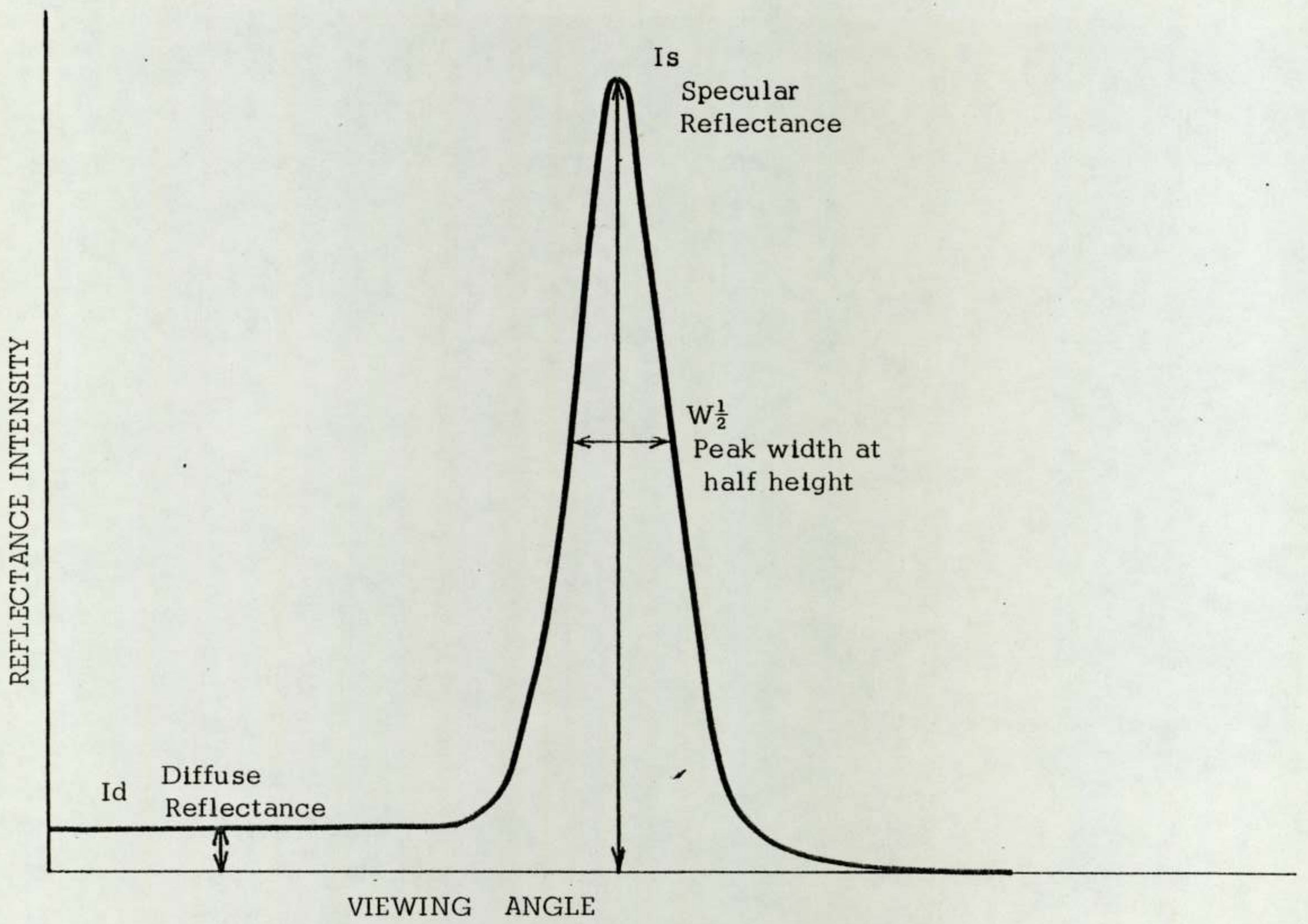


Figure 1.4: Example of a goniophotometric curve, indicating the main goniophotometric parameters

1.4.3 Colorimetry

Colorimetry is a method of specifying a colour by the amounts of specified primary colours that must be mixed to match the colour. Of the methods of mixing the colours, two, additive and subtractive, can be specified exactly by fairly simple mathematics. The first is typified by a colour mixture formed by shining coloured lights onto a screen. With no lights the screen is dark. Additional light sources are used to add light to the mixture. Placing a filter in the beam of a light source is an example of subtractive mixture. The filter absorbs or subtracts light from the beam, further filters subtracting more of the light. The colour resulting from an additive or subtractive mixture can be calculated exactly if the primary colours are specified accurately.

At the present time most colour measurements are made in terms of the internationally recognised CIE system (Commission International de l'Eclairage). This is based on visual colorimetry using additive colour mixtures and three primary colours. Three alternative standards are specified for the white light under which the sample is viewed. Illuminant 'A', defined as the radiation from a black body at 2848 degrees K, which corresponds to tungsten filament light, illuminant 'B' corresponding to sunlight and illuminant 'C' corresponding to North Sky light. The primaries chosen as standards are imaginary colours corresponding to a reddish purple, a green and a blue, all of greater saturation than any real colours of the same hues, but capable of producing mixtures matching all real colours. The tristimulus values in terms of the CIE primaries are usually denoted by X, Y and Z, and may be thought of as corresponding to the red content, green content and blue content of the colour. One of the features of the CIE system is that the 'Y' tristimulus value gives lightness directly. Strictly 'Y' is termed as the luminance factor, and is regarded as an objective measurement corresponding to and correlating closely with the subjective assessment of lightness.

Objective quantities corresponding to hue and saturation are obtained from the ratios of the tristimulus values, i.e. the trichromatic coefficients. These are written x, y and z and are given by eq. 7 - 9:-

$$x = \frac{X}{X + Y + Z} \qquad \ldots\ldots (7)$$

$$y = \frac{Y}{X + Y + Z} \qquad \ldots\ldots (8)$$

$$z = \frac{Z}{X + Y + Z} \qquad \ldots\ldots (9)$$

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

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. Most modern spectrophotometers are fully automated, including some with digital - computing accessories for the conversion of spectrogram data to CIE coordinates (which would otherwise be a tedious operation). Most spectrophotometers work on the principle of measuring the amount of reflected light from a coloured surface as a percentage of that reflected from a standard white surface.

With the CIE system in mind the more recent "generation" of photoelectric instrumentation, namely the tristimulus colorimeters, has been developed. These are instruments which evaluate directly the CIE system of tristimulus values of a given coloured specimen. The main difference between this type of colorimeter and the spectrophotometer is that in the latter monochromatic light is obtained by means of prisms or diffraction gratings, whereas in tristimulus colorimeters only three narrow bands of light are used corresponding to the three primary colour stimuli - red, blue and green light.

Tristimulus colorimeters are quick and easy to use, and tend to be robust and much cheaper than spectrophotometers. However, the disadvantage of tristimulus colorimeters is that the values which they give are more or less approximate, which may, in the case of certain instruments, show wide differences from the correct values in some regions. Due to this, they have tended, in the past, to be regarded as unsuitable for absolute measurements, but very useful in the measurement of colour difference.

1.5 Rationale for Nitric Oxide Studies

Of the various pollutant gases present in the atmosphere, NO presents a particularly interesting subject. This gas is well known for its radical interactions, due to its odd electron nature. Because of this, nitric oxide is likely to have a definite part to play in the degradation of polymers. For this reason the question of the effect of nitric oxide on the behaviour of surface coatings is potentially interesting, since the effect might be acceleration or stabilisation.

When it comes to the interaction of NO with polymers however, it is found that there are relatively few reports in the literature which deal with the topic. Such information as does exist is not concerned with surface coatings. Of the mechanistic studies involving oxides of nitrogen that have been undertaken with polymers, most are concerned with the reaction of nitrogen dioxide (NO_2)(31-35). As regards polymer interaction with nitric oxide (NO) the literature reports are confined to relatively less detailed investigations. Only two of these reports(36,37) deal mechanistically with the reactions of NO with polymers, but unfortunately, they are only involved with the thermal degradation of poly(vinyl chloride) in the presence of high concentrations of NO, and not with atmospheric concentrations of NO. However, these studies indicate that, in high concentrations and high temperatures, NO may act as a stabiliser by the possible inhibition of free radical interactions. NO is generally thought of as undesirable along with other atmospheric pollutants, due to the increasing concern about the adverse effect of pollution by industrial and car exhaust emissions. There is, however, little evidence for or against the claims about the destructive properties of NO with respect to surface coatings. It is with this topic that this thesis is concerned.

1.6 Aims of This Work

The overall aim of this work is to develop apparatus and instrumentation to:

(a) Carry out accelerated ageing of surface coatings in the presence of NO and other components of the spectrum of degradation agents, eg. uv radiation, heat and humidity. It is important that these should be individually controlled and programmable.

(b) Develop an analytical technique for use in conjunction with the above. It must be non-destructive and the data collection rapid with facilities for the comparison of data.

(c) Use those techniques developed in (a) and (b), to the limit that time permits, to study the degradation of selected surface coating systems used in situations where long term performance in industrial or urban environments is important. It is also important that the systems employed are representative of the different types of degradative environments, that may be present in addition to NO, in order to be able to judge the individual effect of this gas and the way that it may contribute in an overall degradative system.

Poly (vinyl chloride) was selected as being representative of polymers used in building and cladding applications. Epoxy and polyester powder coatings were selected as their structures are very different from that of poly (vinyl chloride). They show quite different properties and are widely used in industrial plant. It was hoped to include automobile coatings in the spectrum of those studied. However, the wide range of these used, and the fact that at the time of this project the proposed collaborator was about to change the types of material in their product range, led to the abandonment of this part of the project.

CHAPTER 2

METHODS AND MATERIALS

This chapter can be conveniently divided into three sections:-

1) Surface coatings systems studied
2) Ageing Techniques
3) Analytical Techniques

2.1 Surface coatings systems studied

In order to cover a spectrum of relevant types of organic coating in the course of this work, three types of thermosetting powder coatings were studied, along with part of a series of poly(vinyl chloride) (PVC) coatings. The description of these materials given here aims to explain the way in which they are used and, particularly, fabricated since this is often related to their subsequent ageing performance. The PVC series is comprised of eight formulations listed in Table 2.1 and detailed in Table 2.2. The "complete" formulation, i.e. no. 8, is intended to represent the basic framework of a commercial PVC plastisol coating manufactured by Vinatex Ltd, Havant, Hant. It can be seen from Table 2.1 how this "complete" formulation has been broken down in such a way as to enable appropriate formulation sequences to be conveniently selected from across the series.

Formulation Number	Formulation Description
1	Plasticised PVC clear
2	Plasticised PVC + uv stabiliser
3	Plasticised PVC + thermal stabiliser
4	Plasticised PVC + uv and thermal stabiliser
5.	Plasticised PVC + pigment
6	Plasticised PVC + pigment + uv stabiliser
7	Plasticised PVC + pigment + thermal stabiliser
8	Plasticised PVC + uv and thermal stabiliser

Table 2.1: LIST OF PVC PLASTISOL COATINGS

Formulation Number	Formulation Details (in p.p.h. of resin)				
	PVC resin	Plasticiser	Pigment	uv Stabiliser	uv Stabiliser
1	100	50	-	-	0.5
2	100	50	-	0.5	0.5
3	100	50	-	-	1.5
4	100	50	-	0.5	1.5
5	100	50	15	-	0.5
6	100	50	15	0.5	0.5
7	100	50	15	-	1.5
8	100	50	15	0.5	1.5

Table 2.2: DETAILS OF PVC PLASTISOL COATINGS

Only formulation numbers 6 and 7 were used, as it was believed that these particular formulations would be best suited to indicating the particular reactions, synergistic or not, of nitric oxide and ultra-violet light on the PVC films. In addition, a film of unstabilised, unplasticised and unpigmented PVC was produced. It was intended that this film would help to indicate which characteristics, if any, of the reaction between NO and/or ultra-violet light with the PVC were influenced by the additives or if they occurred as a direct result of the reactions involving the PVC.

Three types of powder coatings were studied, as follows:-

(i) Epoxy

(ii) Polyester

(iii) Epoxy/Polyester

These were manufactured by Croda Paints Ltd, Harefield, Middlesex.

2.1.1 PVC (Vynatex)

The films were prepared, by Vinatex Ltd, using an eight litre, high speed Popeneir Mixer, and then applied to each of the following substrates:-

i) Optical glass panels - primed by dip-coating with British Steel Corporation's coil coat primer and then cured at 225°C (for 30 secs.)

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 micro-indentation, recovery/time analysis).

*<u>NOTE</u>: A certain amount of thermal stabiliser was necessarily incorporated initially into all formulations for processing purposes. However, in the cases of nos. 1, 2, 5 and 6, which were to be regarded after processing as containing, effectively, <u>no</u> thermal stabiliser, only that amount (i.e. 0.5 p.p.h. of resin) of stabiliser was added which, it was estimated, would just about be consumed during processing.

The samples had been hand-coated to a film thickness of 0.007 - 0.009 inches using a bar applicator, before being first placed in an oven for 10 minutes, at 120°C, and then cured for 60 seconds at 225°C. The finished plastisol coatings were all glossy in appearance and relatively soft in surface texture, about 80 - 82° Shore A Hardness.

The coatings applied to the glass panels were detached from their substrates before any experimentation was carried out, in order to assess if the substrate had any influence on the diffusion and reactions of NO with the PVC coating. The coatings with aluminium substrates were left attached to the substrate whether primed or unprimed.

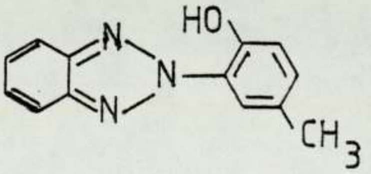
The formulation ingredients referred to in Tables 2.1 and 2.2 are identified more precisely below:-

(a) The poly(vinyl chloride) (PVC) resin used in the preparation of these plastisol coatings is a suspension polymer, manufactured by Bush, Beech and Segsser 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 and Wilson Ltd.

(c) The pigment is a white, rutile titanium dioxide grade (Tioxide R-CR3, British Titan Products Co Ltd). It is particularly suited for use in exterior plastisol coatings, combining extremely high capacity and gloss with durability at low pigment concentrations, along with outstanding chalk resistance.

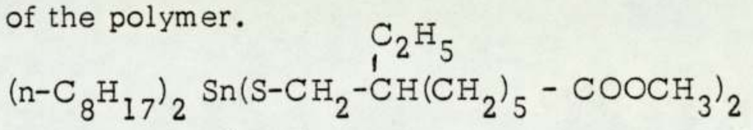
(d) The ultra-violet stabiliser is 2-(2 hydroxy-5-methylphenol) benzatriasole (I) which is marketed by Ciba-Geigy Ltd under the trade name of "Tinuvin P".



(I)

Its stabilising action is classed as being that of a "uv absorber" or "screening agent".

(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 and 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.



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

(II)

2.1.2 Preparation of unplasticised PVC

A weighed quantity of PVC (about 4g) was added to about 70ml of tetrahydrofuran (THF). The mixture was then refluxed until the polymer had dissolved (about 30 minutes) then cooled, made up to 100ml with THF and filtered through a No.1 filter paper.

The casting surface for the film was a 10.5 x 8cm glass plate which had been previously cleaned in chromic acid, washed with water and alcohol, and dried in an oven at 120°C. A 'frame' of aluminium foil was cut out and carefully glued to the underside of the glass. The sides of the foil were then bent up to form a tray about 2cm high and the glued assembly left to dry for several hours.

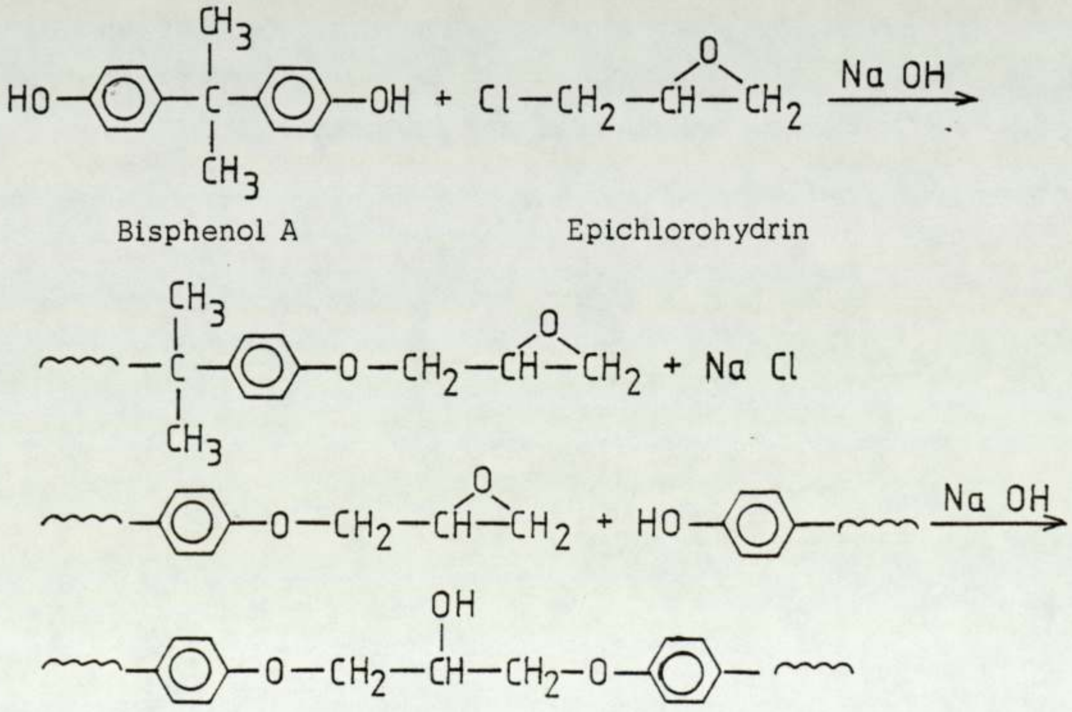
Thirty millilitres of the polymer solution was poured into the tray and left for several days. When only a slight trace of solvent remained the tray was placed in a vacuum oven at 50°C overnight. Afterwards the film was carefully separated from the glass surface and cut into smaller samples.

The tetrahydrofuran which was used was left standing over potassium hydroxide pellets for 48 hours in order to destroy the inhibitor present.

2.1.3 Epoxy Resin Powder Coatings

Epoxy based powder coatings are sold in greater volumes than any other class of powder coating. They possess excellent long term performance and corrosion resistance. Decorative epoxies are used for coating light fixtures, garden equipment, automobile items and in many other similar applications.

The raw materials used in the synthesis of epoxy resins are epichlorohydrin and bisphenol A (diphenylol propane). These materials are reacted together in the presence of excess caustic soda[38]. Synthesis of high molecular weight resins is a two stage reaction involving dehydrohalogenation of the epichlorohydrin followed by the addition of further bisphenol A to the epoxy group.



Bisphenol A

Epichlorohydrin

Most of the commercially available epoxy resins are today manufactured by the advancement process. This is a two stage operation involving the formation of a low viscosity resin of molecular weight between 750 and 900. The product is washed and purified so that it can be further combined with a calculated amount of bisphenol A and a polymerisation catalyst by an addition reaction between the terminal epoxide groups and the phenolic hydroxyl.

Epoxy based powder coatings are usually manufactured from resins with epoxy equivalents between 500 and 1000. This range is defined by the softening points of the resins; resins with epoxy equivalents lower than 500 have melting points in the region of 60-70°C and produce powder coatings with a pronounced tendency to cake. Resins with epoxy equivalents greater than 1000 have softening points above 100°C, producing powders with poor flow properties. The most suitable epoxy resins for powder coatings will be found in the range 850-950 epoxide equivalent.

The Crodalux PF20 series epoxy spraying powders, used in this work, consist of epoxy resin and an accelerated amine hardener. They were applied to mild steel substrates which had been degreased with Tri-chloroethylene vapour using electrostatic powder spraying equipment at voltages of between 30 - 80kV. The resulting coating, of approximately 60 microns thick, was finally cured at 180°C for 10 minutes.

2.1.4 Polyester Resin Powder Coatings

The advantages to be gained by the use of polyester resins in the place of epoxies are:-

- Improved heat and light stability.
- Better resistance to exterior weathering and freedom from chalking.
- Good gloss and improved levelling properties may be obtained.

Disadvantages compared with epoxies are:-

- A tendency to hydrolyse which results in coatings with lower chemical resistance.
- A wider molecular weight spread which lowers the gloss transition temperature and thereby causes blocking or lumping of the powder.

The major chemical reactions occurring during the formation of polyesters are condensation reactions of esterification between polybasic acids and polyhydric alcohols, etherification of the polyols and ester interchange[39]. A simple esterification reaction is an equilibrium system where the reaction is reversible. eq.(10)

$$R'.COOH + R.OH \rightleftharpoons R'.COOR + H_2O ...... (10)$$

When the reactants both possess more than one reactive group then polyesterification can result from a stepwise condensation process by the removal of the water formed during the reaction. An example is the formation of a linear polymer by reacting ethylene glycol and adipic acid. eq. (11).

$$n(HOCH_2CH_2OH + HOOC(CH_2)_4\ COOH) \rightleftharpoons$$
$$HO - [(CH_2)_2.OOC.(CH_2)_4] - COOH \quad + \ (n-1)\ H_2O\ ....(11)$$

With increasing molecular weight the product changes from a mobile liquid to a solid of high melting point.

Linear polymers will be formed if the acid and alcohol each have only two reactive or functional groups. If reactants are introduced with more than two functional groups then chain branching of the basic resin will occur with further crosslinking between resin molecules. In the design of polyester resins for powder coatings it is desirable to keep chain branching to a minimum so that the flow of the powder coating is not affected by the molecular complexity of the resin. However, a thermoset polyester powder coating must be cross linked during the stoving process to render the film infusible. To complete this process it is necessary to incorporate curing agents during the compounding process.

The polyester coatings used in this work were applied to the mild steel substrates in a similar manner to the epoxy coatings, but were cured at 190°C for 15 minutes.

2.1.5 Epoxy/Polyester Resin Powder Coatings

Epoxy/Polyester resins are relatively new in the powder coating field. They are hybrids produced from polyesters containing carboxyl groups, designed specifically for coreaction with epoxy resins[40]. A series of resins are available with equivalent weights of 600-1000. The properties are similar to those of a straightforward epoxy resin. They are more resistant than amine cured epoxies to colour change on overbake and exposure to uv light but only have a marginally superior resistance to chalking. Epoxy/polyesters require a longer cure time than fast cure epoxies and do not give as smooth a coating. Cured films are somewhat softer than a straight epoxy.

The epoxy/polyester coatings were applied to the substrates in a similar manner to the previous powder coatings, but were cured at 160°C for 10 minutes.

All three types of powder coatings contained white pigmentation.

2.1.5 Sample Preparation

The original specimen panels were each cut into four smaller samples measuring approximately 40mm by 30mm. This size was chosen for the specimens so that they could be conveniently accommodated in all the experimental apparatus and equipment to be used. The suffixes used to identify the different samples and the ageing techniques they were exposed to are given in Table 2.3.

After ageing all samples were gently cleaned with distilled water and dried before being subjected to goniophotometric or colorimetry analysis.

Sample Code	Specimen	Sample Description	Ageing Technique
6 & 7	1	PVC, Detached	None
	2	from glass	NO
	3	substrate	NO + uv
	4		uv
6 P & 7P	1	PVC, primed on	None
	2	aluminium	NO
	3	panels	NO + uv
	4		uv
6 NP & 7NP	1	PVC, unprimed	None
	2	on aluminium	NO
	3	panels	NO + uv
	4		uv
PVC UP	1	PVC, clear	None
	2	detached	NO
	3	unplasticised	NO + uv
	4	films	uv
EPC	1	Epoxy	None
	2	powder coating	NO
	3		NO + uv
	4		uv
PPC	1	Polyester	None
	2	powder	NO
	3	coating	NO + uv
	4		uv
EPPC	1	Epoxy/polyester	None
	2	powder coating	NO
	3		NO + uv
	4		uv

Code: 6 - Plasticised, pigmented PVC + uv stabiliser
7 - Plasticised, pigmented PVC + thermal stabiliser
PVC UP - Unplasticised, Unpigmented PVC
EPC - Epoxy coating, pigmented
PPC - Polyester coating, pigmented
EPPC - Epoxy/Polyester coating, pigmented

Table 2.3: IDENTIFICATION OF COATINGS

2.2 Ageing Techniques

The samples were exposed to nitric oxide of various concentrations and to ultra-violet light, separately and simultaneously, so that the combined and individual effects of NO and uv could be studied under identical conditions. This involved the use of a sealed system due to the toxic nature of the NO. The system consisted of three sets of glass vessels. Two of these sets were interconnected by a multiple input manifold to allow the free flow of gas between them. The use of a manifold allowed different concentrations of pollutant gas to be introduced as required. The second set of interconnected vessels was placed inside a Montford Environmental Chamber along with the third set of vessels. These last vessels were not connected to the gas system. An ultra-violet light source was placed in the top of the chamber. The chamber was used to maintain a constant temperature slightly above ambient and to restrict any stray uv radiation and is described in detail in Chapter 3. The glass vessels were manufactured from "Pyrex" glass. Each had a modified sealable lid to allow two tubes to be connected from the manifold. The base of each vessel was also modified in order to connect a tube for the outflow of gas. These vessels are described in greater detail in Chapter 3. As ultra-violet light of wavelenths of less than 340mμ would obviously be cut out by the glass, the ultra-violet source employed had to produce radiation with a wavelength higher than this.

Before any sample was subjected to ageing, goniophotometric curves and colour coordinates were obtained from the surface of the sample. Also, in the case of the PVC coatings, the bulk properties were characterised by use of a micro-indentor and with weight measurements. The specimens were clipped to a wire frame and placed inside the glass vessels. One specimen of each sample was placed in each set of containers. All the containers were then sealed and the two sets placed inside the chamber. With the chamber closed nitric oxide was flushed through the system until any traces of reddish brown gas disappeared. This gas is nitrogen dioxide formed by nitric oxide readily reacting with the oxygen present. The system was then sealed and the ultra-violet light switched on. The equipment was left in this state for two hours, in the case of neat nitric oxide, and for longer periods up to sixty hours for the dilute nitric oxide. During this period the nitric oxide continued to react with the small amount of oxygen present until by the end of the experiment both sets of vessels were again filled with a reddish brown gas.

After the required time had elapsed the system was thoroughly flushed through with nitrogen and then left overnight. This was done as a safety precaution to ensure that all traces of nitric oxide had been dissipated before the apparatus was dismantled. Finally, the samples were removed and weighed. The three main analytical techniques mentioned were then used to examine the treated specimens.

The neat nitric oxide was supplied by BDH Chemicals Ltd as being 99.6% pure. The lower concentrations of nitric oxide, of 3300 ppv and 2000 ppv in nitrogen were supplied by British Leyland Emission Department, Coventry.

2.3 Analytical Techniques

As mentioned previously, the three main analytical techniques used in the course of this work were:-

- 2.3.1 Colorimetry
- 2.3.2 Goniophotometry
- 2.3.3 Micro Indentation

2.3.1 Colorimetry

Colorimetry was one of the main methods used for the assessment of the change in properties which occurred on the surface of the films after treatment. A model V Colorimeter, manufactured by the Manufacturers' Engineering and Equipment Cooperation was the actual instrument employed. This instrument is a photoelectric tristimulus colorimeter. A simplified representation of the principle upon which this type of instrument works is shown schematically in Figure 2.1.

The colorimeter is first standardised by the use of two standards, calibrated with CIE values. One of these standards is continually employed throughout the operation of the instrument as a reference. The reflectance of the sample being examined is given as a percentage of the reflectance of the standard reference for each of the three primary colour stimuli - red, blue and green light. A conversion formula (12) is then used to convert these percentages into CIE -

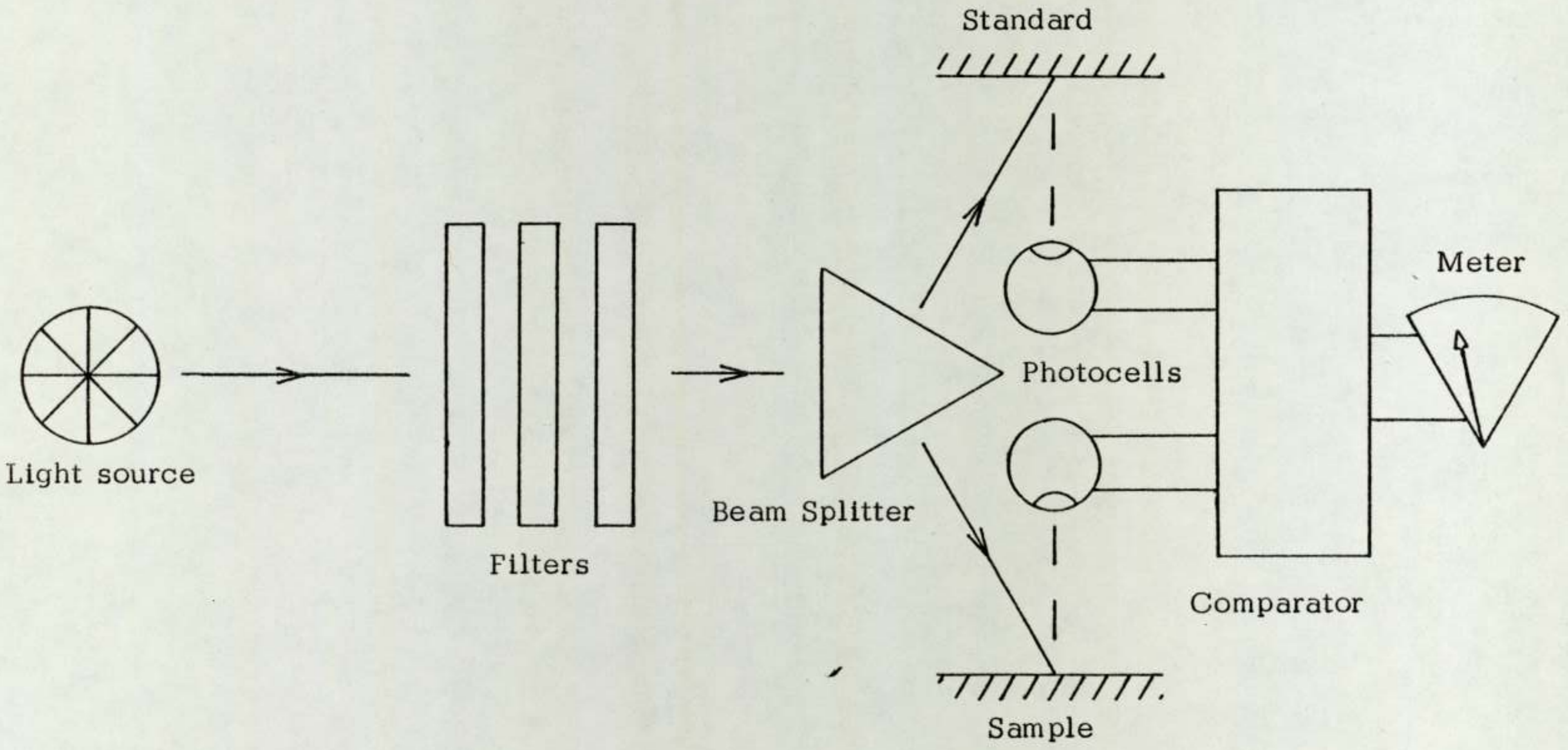


Figure 2.1: Schematic Representation of a Tristimulus Colorimeter

XYZ values

$$X = 0.7832R + 0.1972B$$

$$Y = G$$

$$Z = 1.181B \qquad \text{........ (III)}$$

Standardisation of the instrument requires the setting of a linear scale by the fixing of two points on that scale. For greatest accuracy these points should be in the vicinity of the ends of the scale. The model V Colorimeter is set at zero reflectance and at approximately 90% reflectance. Since there are three scales, one for red, blue and green filter positions, six settings are required to standardise the instrument. Three at the high end of each of the filter positions, and three at the zero indicating points of each of these.

When in use, the sample to be measured is placed over the sample part and the filter switch is set to a particular colour. The reflectance control is then adjusted until the meter indicates zero and the percentage reflectance is read from the dial. The process is repeated for each of the three filter positions.

2.3.2 Goniophotometry

Use was made of an automated goniophotometer, developed and modified in the Department of Chemistry, the University of Aston. The mechanical and electrical modifications are described in detail in Chapter 5. The optical layout (Figure 2.2) can be briefly summarised as follows. The light beam from the high pressure (Type AH-3) mercury vapour lamp (A) passes through a preselected wavelength filter (B) and shutter unit (C) into a collimating tube (E) incorporating a removable polariser and variable slit aperature (F). The intensity of the light beam is controlled by a series of neutral filters (D) which permit the intensity to be adjusted in order to give a suitable defection on the chart recorder. 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 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 removeable analyser and variable slit aperture (I). Finally the signal from the photocell is then amplified and recorded on a chart recorder or relayed to a computer.

The specimens are mounted vertically on a brass base located at (G). The specimen holder, 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 2mm. Throughout all the experiments the base was located so that the specimen subtended an angle of 45° to the light beam. Finally, the mount and the interior of the instrument is coated with matt black paint so as to prevent stray light reflections reaching the photocell.

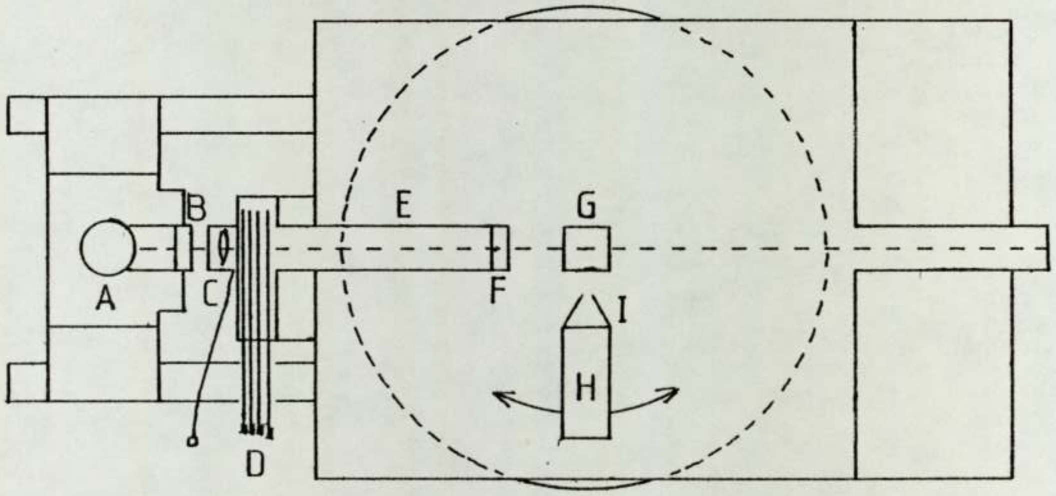


Figure 2.2: Optical Layout of the Goniophotometer

2.3.2.1 Calibration of Goniophotometer Turntable and Mount

Prior to measurements being taken the recommended "warm-up" procedure, as laid down in the instrument manual, is followed and the apparatus as a whole allowed to stabilise for a minimum period of two hours after switching on.

The turntable is calibrated so that the zero position of the turntable is accurately known. The zero position is when the photocell is directly in line with the light beam. The turntable is rotated, with all the neutral filters in position, until the maximum reading is obtained on the output meter. The angle is noted and subtracted from all subsequent angles read from the turntable.

The mount is calibrated by the use of an optically flat glass slide. It is assumed that the glass slide reflects at an equal angle of perfect mirror reflectance. By measuring the angle the exact angle subtended by the light beam on the surface of the specimen is known and hence the normal to the surface and the angle of maximum reflectance can be calculated.

Use of the goniophotometer for actual analysis is described in detail in Chapter 5.

2.3.2.2 Goniophotometric Terms

The various goniophotometric parameters which can be derived from the sample data are defined as follows:-

a) 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. 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.

b) The specular angle (degrees) - this is the angle at which the specular reflectance (I_s) occurs, i.e. the specular angle is the angle of maximum reflectance. For imperfect irregular surfaces there is invariable a slight discrepancy between this and the angle of light incidence, this variance usually being termed the "angular displacement".

c) The diffuse reflectance (I_d, intensity units) - this refers to the reflectance at an angle of reflection of 0°, 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. This appears to a visual observer of the surface as a "haze" which tends to impair the sharpness of image definition.

d) Peak height ($I_s - I_d$, intensity units) - the goniophotometric peak height is defined as the difference between the $I_s - I_d$ values previously described. In this way the peak is therefore regarded as representing that component of a sample's reflectivity which lends itself to the surface's mirror-imaging capability.

e) 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 incident upon it. In visual terms, the peak width is related to image sharpness which, incidently, tends to be the more popular criterion, by which observers subjectively make their assessment of surface gloss.

g) The gloss factor (GF, intensity units/degrees) - 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 width at half-height ($W_{\frac{1}{2}}$) (i.e. $GF = ((I_s - I_d)/W_{\frac{1}{2}})$. This 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 the changes in each to be more closely related to resultant changes in gloss.

2.3.3 Micro-Indentation

The basic instrument consists of a triangular chassis supported by three adjustable legs from the base plate. Two of these legs form the coarse and fine adjustment for zeroing the instrument, by raising and lowering the main chassis. This chassis supports the beam carrying the indentor stylus and the mechanisms used to apply and remove the load placed on the stylus. The sample is held down onto the specimen stage by a spring loaded lever. This specimen stage can be heated or cooled with respect to room temperature. All measurements involved with this work were carried out at room temperature.

The measuring and recording is carried out by a pneumatic system which is supplied with air at 20 pounds per square inch. The operation of a flapper valve by the stylus beam determines the air pressure developed by a single stage pneumatic amplifier. The amplifier incorporates a negative feedback design which improves the linearity and stability of the output. The final output is recorded on a 15 pounds per square inch strip chart air pressure recorder. The raising and lowering of the weight is controlled by an automatic timer, which also controls the chart drive on the recorder.

2.3.3.1 Calibration of the Micro-Indenter

In order to calibrate the micro-indenter and the chart recorder, the stylus is lowered onto a glass slide. It is assumed that no indentation of the surface of the slide occurs, hence the reading indicated by the chart recorder is taken as zero. The main chassis is now raised, by means of the fine adjustment leg, in order to simulate 6 microns movement of the needle. The value indicated on the chart recorder is now noted. Next intermediate readings are taken for simulated indentations of between 1 and 6 microns. These values are plotted as a graph. The calibration curve is shown in Figure 2.3.

2.3.3.2 Operation of the Micro-Indenter

The specimen is secured on the stage with the clip. The main chassis is now lowered until the stylus just makes

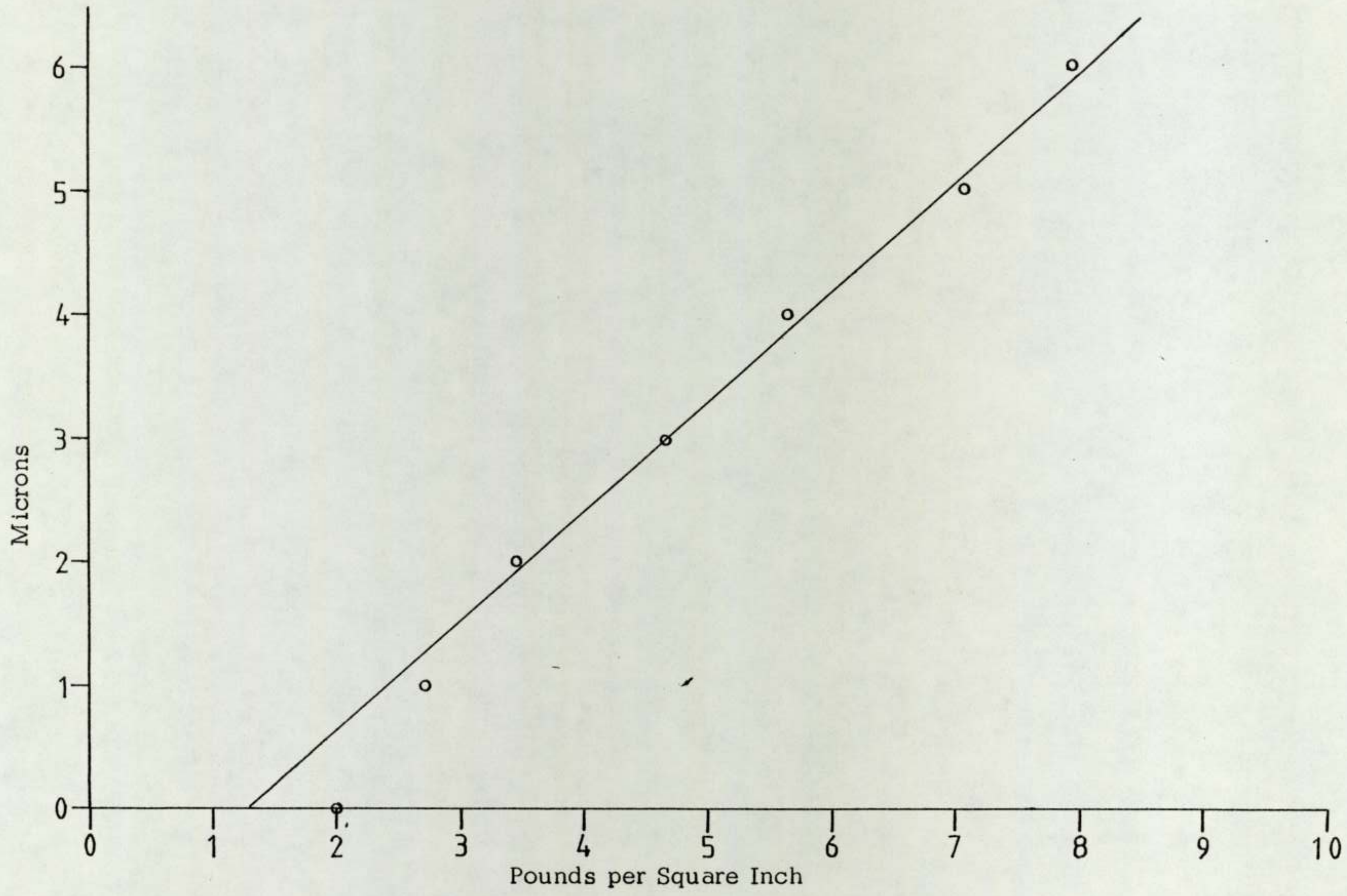


Figure 2.3: Micro-indentor Calibration Curve

contact with the surface of the specimen. The reading indicated on the chart recorder is taken as the minor load base line. The programmer is switched to "start" and the load automatically lowered onto the indenter stylus. During this work a load of 8 grams was used. After a preset length of time, about 60 seconds, the load is automatically removed so that indentation and recovery curves are recorded.

When the programmer completes the cycle, the main chassis is raised and the specimen removed. The whole cycle is now repeated on a different point on the surface of the sample.

CHAPTER 3

ENVIRONMENTAL TEST CHAMBER

3.1 Introduction

It was realised during the initial experimental work described in Chapter 6 that some form of automated ageing system was necessary. The main reason for automation was associated with the preferred use of lower concentrations of nitric oxide and the cyclic variation of nitric oxide concentrations at urban sites. Due to the high rate of reaction of nitric oxide with the oxygen present in the atmosphere, the dilute nitric oxide would require replacement at frequent intervals. As a period of accelerated ageing was likely to be in the region of five hundred hours, manual replacement of the dilute pollutant gas was not practical. The most convenient means of automating the ageing system would be by the purchase or construction of an artificial weathering machine possessing the appropriate facilities.

Bearing in mind the practical limitations, it was felt that the most important facilities that an artificial ageing machine should offer were:-

a) Control of ultra-violet radiation

b) Control of pollutant gases

c) Control of humidity

d) Wide operating temperature range, including subambient temperatures

e) Accurate and reproduceable control of heating and cooling rates

f) Long periods of unattended operation

g) Control of auxiliary equipment, eg. chart recorders.

Finally modifications to the machine should be relatively easy to carry out in order to adapt it to suit the requirements of future ageing systems as they arise.

In recent years a number of artificial weathering machines have been developed in order to simulate natural weathering conditions as a whole. These conditions mainly consist of ultra-violet radiation, humidity and temperature variations. Essentially the commercially available machines only differ in the types of radiation used and the degree of control available over the ageing elements and their respective operating cycles. The machines most commonly in use include the Atlas Weather-ometer [41], Dew Cycle(16), Xenotest, Climotest, and the A.U.V. Weathering Tester (42).

All of the equipment mentioned above provide weathering systems which are basically preset with few variables. Only the Atlas Ci65 Weather-ometer fulfills most of the mentioned requirements. The control and monitoring facilities on this particular cabinet are sophisticated and very accurate, but unfortunately they lack the versatility that was required of the proposed system. This, combined with the fact that the gas control apparatus which operates in conjunction with the cabinet is an optional attachment making the price prohibitive, ruled against the purchase of the commercial machine.

The decision was made to construct a more versatile, less sophisticated cabinet which could be more suitably applied to present studies. The design of this cabinet was aimed primarily at ageing samples under selected controlled situations. These were to be based on the individual conditions encountered in natural weathering, as opposed to attempting to simulate natural weathering systems as a whole at an accelerated rate.

At the start of this work consideration was given to the modification of a Montford Environmental Chamber, available from previous (non-environmental) studies, as this equipment already incorporated the necessary heating and cooling systems with their respective control units (see Figure 3.1).

3.2 Physical Description of the Montford Environmental Test Chamber

The environmental test chamber (see Plate 3.1) in its unmodified state comprised:

1) an insulated working chamber and heat exchanger
2) heating and cooling devices
3) control systems

3.2.1 The working chamber and heat exchanger

The main working chamber of the cabinet is manufactured from stainless steel with internal dimensions of 12" x 12" x 12". Heating and cooling of this chamber is achieved without any direct transfer of gas to or from the interior by means of a heat exchanger

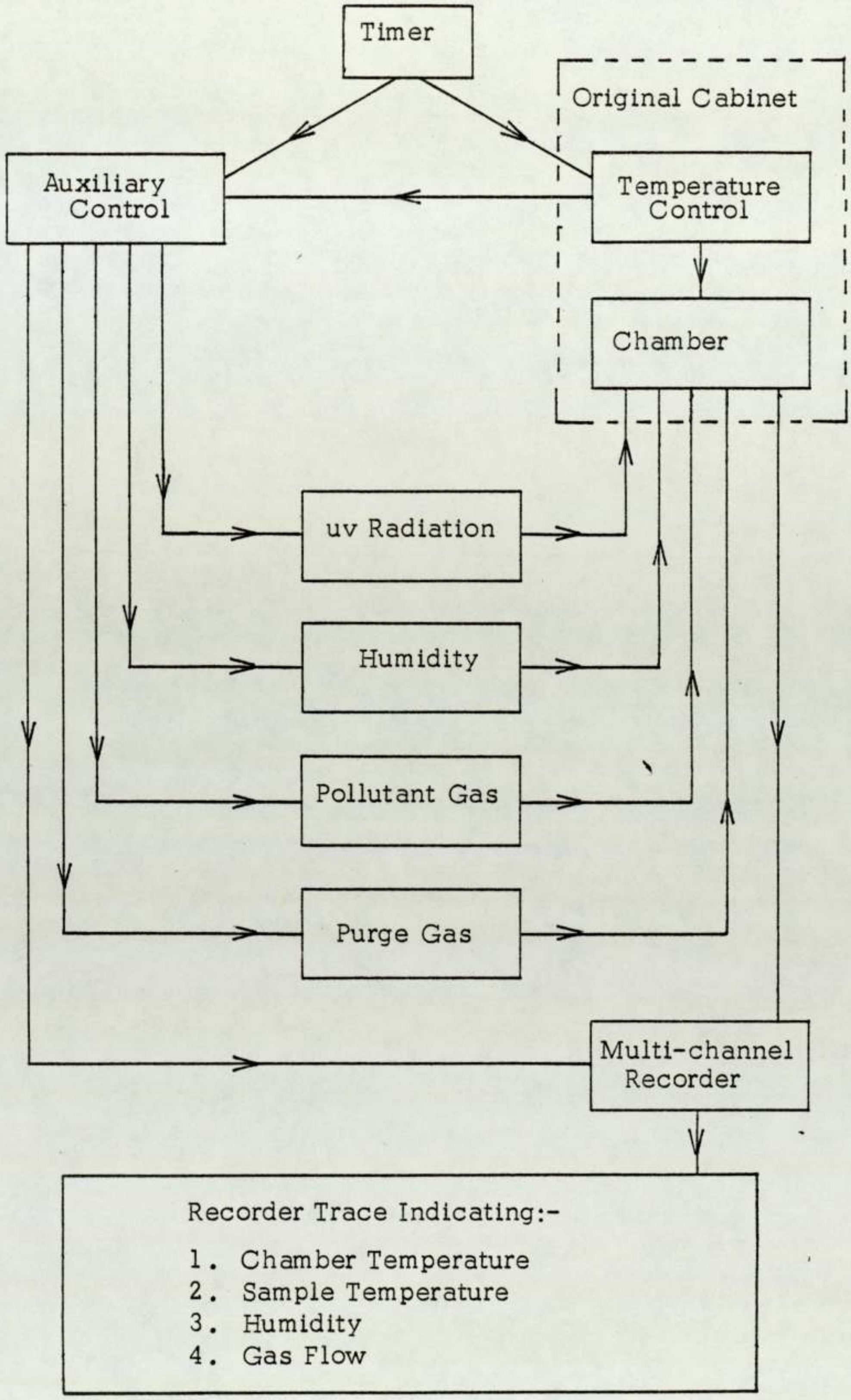


Figure 3.1: Schematic diagram of proposed cabinet

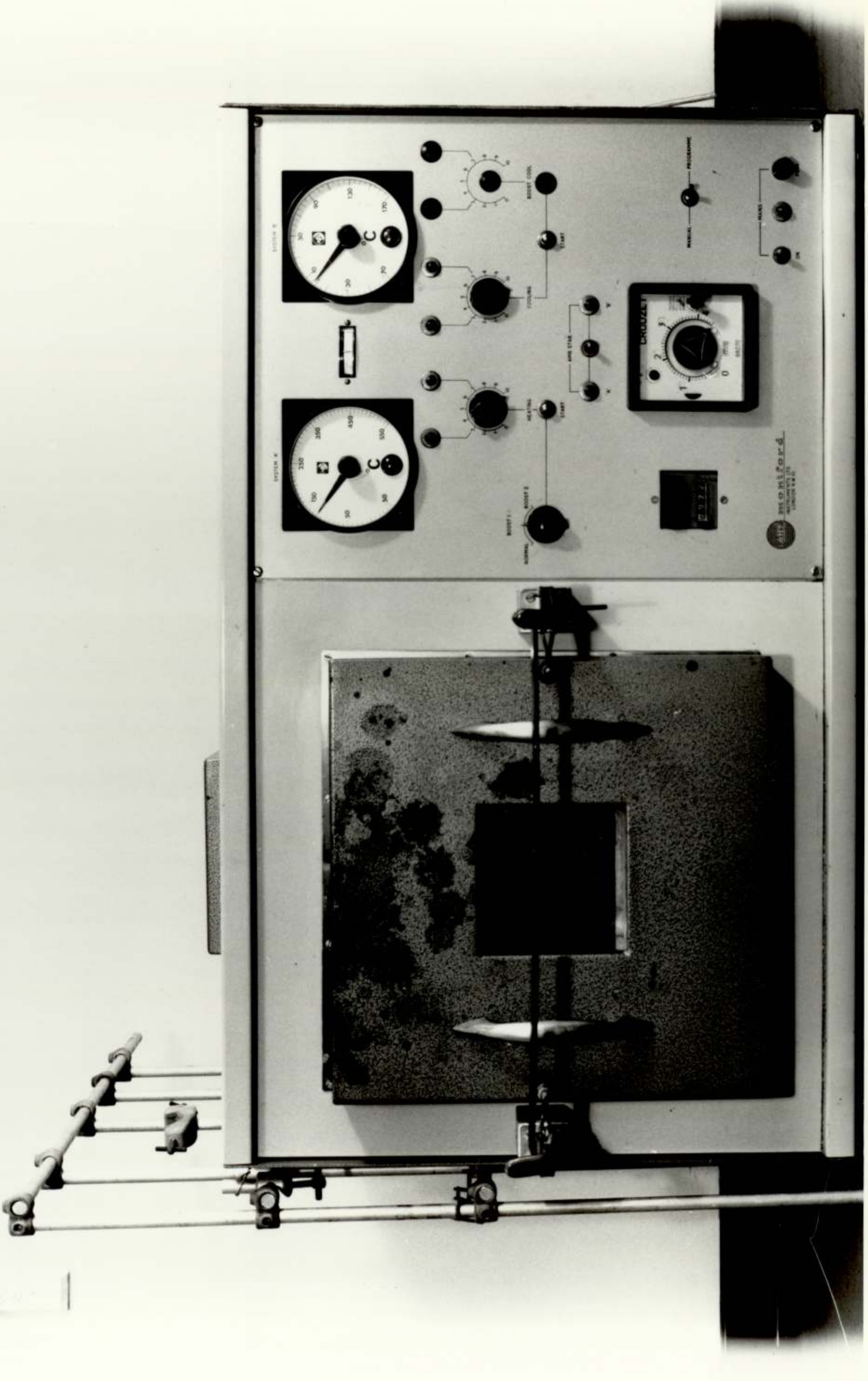


Plate 3.1: Montford Environmental Test Chamber

mounted at the rear of the cabinet. Forced air circulation is employed inside the chamber, drawing air from the rear and circulating it over the heat exchanger. The air is returned to the interior by two slots towards the front edge of the side walls. This system helps to minimise any temperature gradient within the working area of the chamber. Typically the gradient is within $\pm 0.5^{\circ}C$. Access is by means of a thermally insulated, totally removable door in the front of the cabinet. The door is fitted with a multipane viewing window. An aperture is fitted in the top of the chamber to take mounting brackets for auxiliary equipment. Additionally a 2" access point is provided in the left side wall for test leads and auxiliary gas inlets.

3.2.2 The heating and cooling devices

The exchanger is heated by four 850 watt electric heaters, which are fully enclosed in a stainless steel sheath. These heaters are operated by a three stage system:

1) Normal
2) Boost I
3) Boost II

Irrespective of which system is selected, the rate of heating is controlled by an energy regulator. This is a bi-metal unit which incorporates a heater. The regulator is set to open and close to produce a pulsed circuit, which enables the ratio of ON/OFF times to be varied. The higher the setting of the regulator the more rapid the increase in temperature of the exchanger.

The cooling of the heat exchanger is achieved through a two stage system. The first stage uses ambient air cooling. Air is drawn from the outside of the cabinet, by an axial fan, and blown through the heat exchanger, finally being expelled through a vent at the rear of the cabinet. This stage of the system operates in order to lower the temperature from the maximum of + 500°C down to +100°C. At this temperature the cabinet automatically switches to a liquid CO_2 cooling system. This also works through the heat exchanger so that no CO_2 is injected into the working chamber. The liquid CO_2 is released into the exchanger through a restrictive nozzle. At this point it expands in volume, thus absorbing heat during the transformation from liquid to gas. The spent CO_2 gas is expelled through the same vent as the air, in the rear of the cabinet. The CO_2 stage of the cooling system is designed to lower the temperature to a minimum of -30°C. Both cooling systems are controlled by an energy regulator in a similar manner to the heating system.

3.2.3 The control system

The electrical control system allows the cabinet to be operated in either manual or automatic modes. In the manual mode, any temperature within the range -30°C to + 500°C including at or near ambient may be selected and held with an accuracy of $\pm$ 0.5°C. The time taken to attain the selected temperature is controlled by the energy regulator. Once reached a stabilisation circuit accurately holds the chamber at the correct temperature by selecting different heating or cooling rates dependent upon the temperature drift.

In the automatic mode, the cabinet cycles between two set temperatures. The rate of heating and cooling is individually controlled by the respective energy regulators. When the chamber attains one of the set temperatures, it is held for a preselected period of between one second and forty hours. The system then continues to operate for a predetermined number of cycles. When the programme is completed the chamber returns to the ambient temperature and the cabinet is switched off.

A total of four temperature sensors are employed within the cabinet to monitor the state of the chamber and heat exchanger. Two of these, situated in the main working chamber, are platinum resistance probes connected to REC Type A2 temperature controllers. These independently control the upper and lower set temperatures of the chamber. The remaining temperature sensors are placed inside the heat exchanger. These sensors work in conjunction with the temperature controllers to select either ambient air or liquid CO_2 cooling. The automatic cycling and temperature holding is controlled by a timer which switches between the two temperature controllers.

3.3 Modifications to the original operating systems

In the original state a few faults existed within the cabinet. These needed to be rectified before any modifications could be carried out. A major handicap at this stage of the work was the lack of availability of circuit diagrams or any specifications for the particular version of the Montford Cabinet possessed by the Department of Chemistry. Due to this lack of information it was necessary to laboriously trace each wire through the wiring looms before it was possible to repair or modify the existing circuits. Fortunately in most cases the modifications only involved minor alterations to the control circuits. A typical fault was the cabinet's inability to hold a constant temperature for more than approximately five minutes. This fault was eventually traced to a faulty relay controlling the boost heating system.

The most substantial modification that was effected, involved the cooling system used in the heat exchanger. This system as previously described, using air and CO_2, was perfectly adequate assuming that a cooling rate of 5°C per hour was the maximum required below 100°C. As the main reason for modifying the existing cabinet, as opposed to purchasing a commercially produced system, was primarily because more versatility was required, it was desirable to have a system which was capable of much higher cooling rates.

In order to satisfy this requirement, it was decided to design and construct a boost system to be used in addition to the normal cooling system when a higher rate of cooling was necessary. For simplicity of control, the ideal way to achieve an increased rate was to construct a second CO_2 system identical in principle to the original, to be used in parallel with it, and controlled by the existing circuits.

In the original system the liquid CO_2 is delivered under pressure to the heat exchanger where it is allowed to expand. In doing so it removes heat from its surroundings and thus cools the chamber. It is essential that the expansion takes place within the heat exchanger for the system to be efficient. Therefore the first restriction to the gas flow must be located inside the main body of the exchanger.

When the access panels were moved from the rear of the cabinet it was discovered that the heat exchanger had been constructed as a very compact sealed unit. Unfortunately it would have been necessary to substantially modify the design of the main working chamber as well as the heat exchanger in order to install a second gas expansion nozzle. As this involved an excessive amount of complicated machining of the components, possible alternative methods of cooling were examined.

The original cooling system installed in the cabinet utilises the same principles as a conventional refrigerator, the main difference being that the cabinet vents the expanded gas directly into the room whereas a refrigerator recirculates the gas by means of a compressor within a sealed system. As the difficulties encountered with the proposed secondary cooling system were primarily concerned with construction and installation, not with the method of operation, the use of a commercially manufactured refrigerator unit was considered.

It was discovered that the only suitable position in which the cooling coil could be located was immediately in front of the heat exchanger. In this position air from the chamber was cooled as it passed over the coils before entering the heat exchanger. This method produced the required increase in the rate of cooling, but was unsuitable for permanent installation if the chamber was to be used in the automatic mode, due to the refrigerant vaporising during high temperature periods of the cycles.

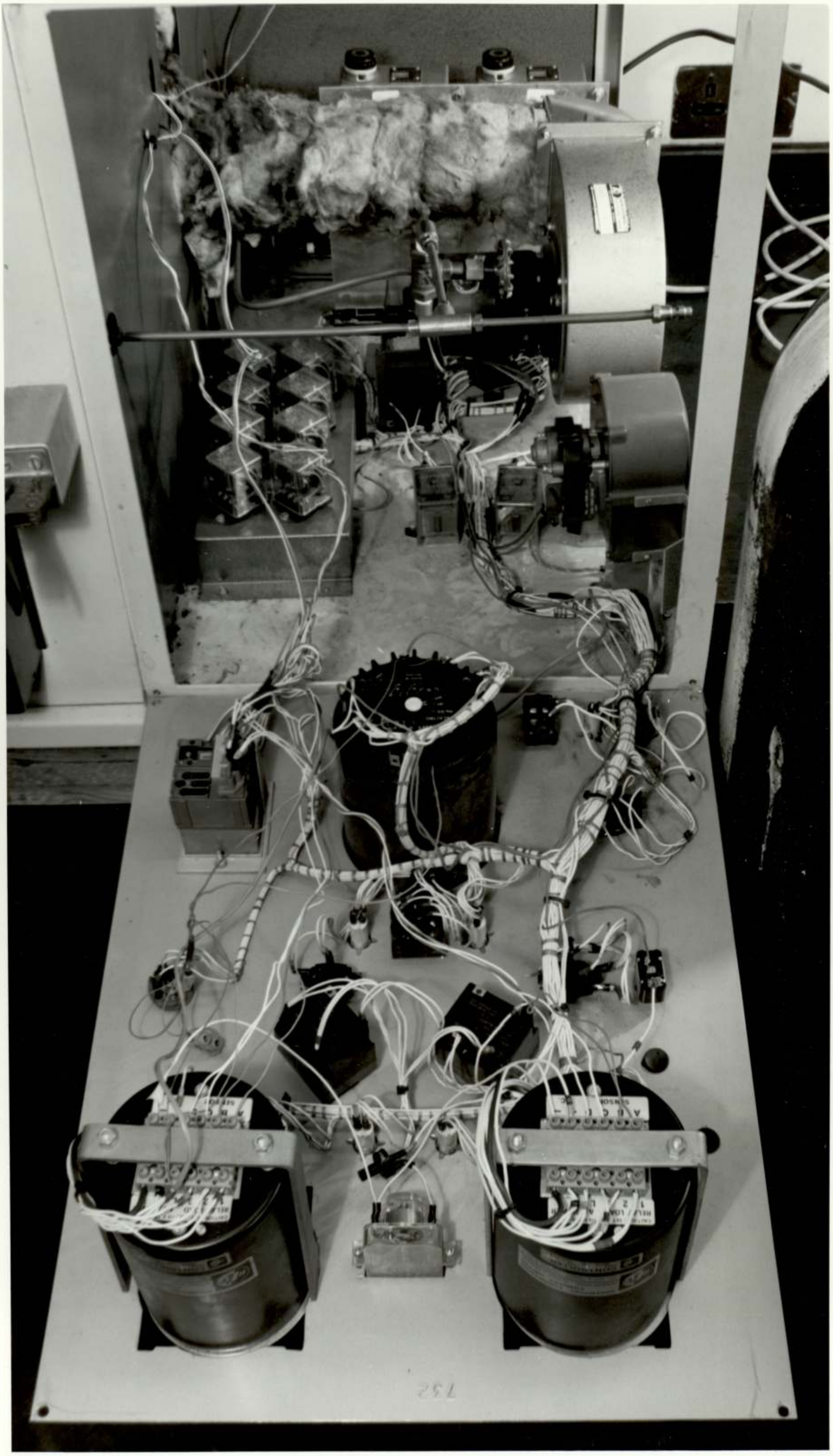
An alternative approach to the problem was to dispense with the heat exchanger and directly cool the interior of the chamber when a rapid rate of cooling was required. This facility was provided by installing a restrictive nozzle in the side wall of the chamber. This nozzle is connected to the liquid CO_2 supply by means of a solenoid valve. The valve is controlled by the original control circuits, the only addition to these being a switch which isolates the solenoid when the additional cooling is not required. The system allows the CO_2 to expand within the working chamber itself, thus eliminating the inefficiency of the heat exchanger.

Unfortunately when this facility is used the higher rate of cooling is achieved at the expense of the accuracy with which the temperature within the chamber is controlled. This loss in accuracy is mainly due to a whiplash effect produced as the chamber cools at a much faster rate than the heat exchanger. As a result, immediately after the chamber reaches the set temperature and the cooling system switches off, the interior temperature begins to rise due to the heating effect of the exchanger, which is often as much as 50°C hotter than the chamber. This increase in temperature triggers the cooling system again, causing the temperature within the chamber to fluctuate by as much as ± 15°C about the actual set temperature.

At this stage of the work it was realised that the only satisfactory solution to the problem would be to proceed with the modifications to the heat exchanger itself. As mentioned previously this involved the installation of a second expansion nozzle in the exchanger, positioned in a similar manner to the existing nozzle. The system which cools the chamber directly was left intact, thus providing facilities for extremely rapid cooling of the working chamber provided that accurate temperature control is not required.

After the nozzle had been installed in the chamber, the necessary 'plumbing' to carry the liquid CO_2 was constructed. The design and layout of the solenoid valves and pipes was critical as a substantial amount of the piping needed to be positioned above the main heating control relays (See Plate 3.2). Care had to be taken to ensure that there

Plate 3.2: Montford Cabinet Control Circuits



were no restrictions to the flow of liquid CO_2 before the heat exchanger. Any expansion of the CO_2 would cool the piping, allowing water to condense with possible disastrous results to the control circuits. Once a satisfactory pipe layout had been achieved it was tested up 2400 p.s.i. as a safety precaution. The normal operating pressure of the system is 800 p.s.i.

This final version of the modification has produced a boost cooling system which in operation has proved to be considerably more effective than the system originally installed within the cabinet. When selected, the boost system increased the rate of cooling from 5°C per hour to a maximum of 35°C per hour. This increase in rate was gained without any loss of accuracy in the temperature control, but the consumption of liquid CO_2 increased to such an extent that the supply of liquid had to be changed at least every twelve hours whilst the cabinet was in use. As the original design criterion was that the cabinet should be capable of running for approximately sixty hours without attention, it was necessary to alter the parameters within which the CO_2 cooling system was selected in preference to the forced air cooling. To achieve this the cooling control circuits were further modified in order to include an adjustable thermostat, which is controlled by one of the temperature sensors within the heat exchanger. This provides a facility which allows the temperature at which forced air cooling ceases and the liquid CO_2 takes over to be varied over the full temperature range that can be achieved by the cabinet. By careful setting of the thermostat, dependant upon the particular heating and cooling cycles being employed, the consumption of liquid CO_2 can be dramatically decreased while still enabling the same overall cooling rate of $35^{\circ}C$ per hour to be achieved. Typically one to two kilograms of liquid CO_2 are required to lower the temperature of the chamber by approximately $10^{\circ}C$.

3.4 Design and construction of auxiliary equipment

At this stage of the work the cabinet was still far from providing the facilities that an accelerated ageing system would require. In this basic state the cabinet was only capable of cycling between two selected temperatures, holding either temperature for a preselected time during each cycle. For an accelerated ageing system facilities are also required which provide:-

a) uv radiation

b) Controlled Humidity

c) Controlled Atmospheres of Pollutant Gases

As opposed to modifying the main cabinet in order to provide these facilities it was decided to construct individual units, each providing a separate facility. These units could be activiated by the cabinet as required. Further facilities can be added if required, by the construction of additional units in the future.

3.4.1 Auxiliary Control Unit

The main cabinet control circuits were only designed to monitor and control the temperature within the working chamber. Therefore before any additional facilities could be provided it was necessary to design and construct an auxiliary control unit. This unit (see Plate 3.3) is aware of the temperature and cycling conditions within the chamber at any given time. Dependant upon these conditions the unit selects the appropriate facility as required.

As the original cabinet control circuit only responded to four states within each cycle, it was decided that the auxiliary units would have to be selected according to the various permutations of these four states.

a) Start of heating cycle A
b) End of heating cycle A
c) Start of cooling cycle B
d) End of cooling cycle B

Throughout the design of the control unit care was taken to ensure that the unit is at least as reliable, if not more reliable, than the main cabinet, as it is required to operate for long periods unattended. This has been achieved by using as few components as possible, and by a preference for commercially available parts.

The final circuit only uses five, three pole, two way relays which

Plate 3.3: Auxiliary Control Unit

are controlled by the temperature cycling of the cabinet. These relays are completely compatible with each other and are mounted in plug in bases. Thus, if a failure does occur the faulty relay can be immediately replaced without the need to disconnect the unit from the rest of the equipment.

The circuit (see Figure 3.2) is capable of controlling any number of auxiliary units. Each unit can be individually selected by any permutation of the four previously mentioned states (see Table 3.1) without any interaction occurring between separate units on different permutations. Outputs are also provided to control chart recorder drives depending upon the section of the ageing cycle occurring within the chamber. The unit switches off all auxiliary units at the end of the cabinet's programme and indicates the completion of the programme.

3.4.2 Ultra-violet Radiation Unit

This unit (see Plate 3.4) consists of a base which locates in the aperture in the roof of the chamber, a uv source, and the lamp control gear.

The source is a mercury vapour discharge lamp in a quartz arc tube, loaded below 100 watts / cm. of arc length and operating at pressures of eight to ten atmospheres. The arc tube is enclosed in a pear shaped outer bulb of Black glass, which absorbs all

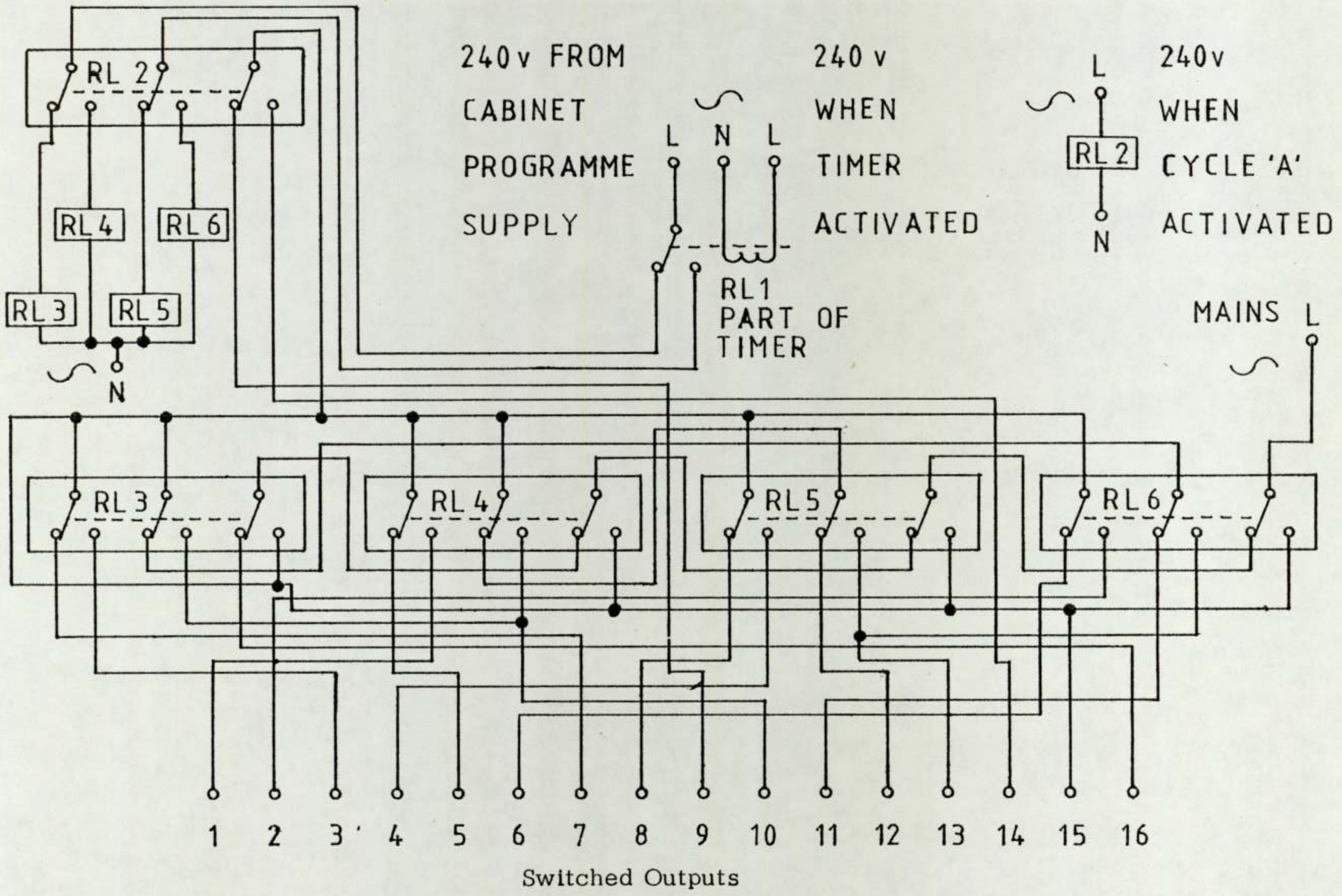


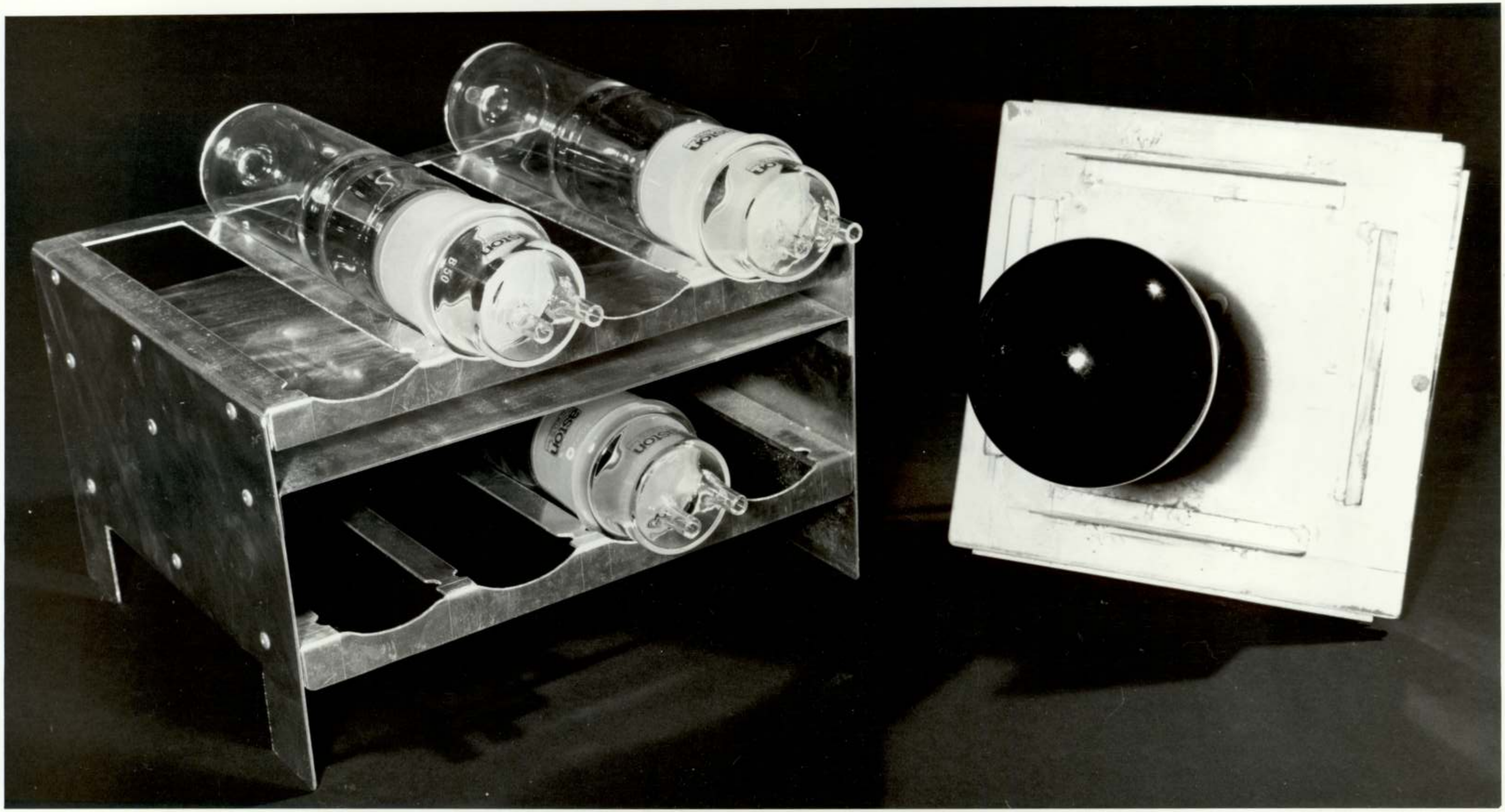
Figure 3.2: Auxiliary Control Circuit

<table>
<tr><th rowspan="2">Facility</th><th colspan="5">Circuit is on when:</th></tr>
<tr><th>Heating</th><th>Holding High Temp.</th><th>Cooling</th><th>Holding Low Temp.</th><th>End of cycle</th></tr>
<tr><td>1</td><td>✓</td><td></td><td></td><td></td><td></td></tr>
<tr><td>2</td><td></td><td>✓</td><td></td><td></td><td></td></tr>
<tr><td>3</td><td></td><td></td><td>✓</td><td></td><td></td></tr>
<tr><td>4</td><td></td><td></td><td></td><td>✓</td><td></td></tr>
<tr><td>5</td><td></td><td>✓</td><td>✓</td><td>✓</td><td></td></tr>
<tr><td>6</td><td>✓</td><td></td><td>✓</td><td>✓</td><td></td></tr>
<tr><td>7</td><td>✓</td><td>✓</td><td></td><td>✓</td><td></td></tr>
<tr><td>8</td><td>✓</td><td>✓</td><td>✓</td><td></td><td></td></tr>
<tr><td>9</td><td>✓</td><td>✓</td><td></td><td></td><td></td></tr>
<tr><td>10</td><td>✓</td><td></td><td>✓</td><td></td><td></td></tr>
<tr><td>11</td><td>✓</td><td></td><td></td><td>✓</td><td></td></tr>
<tr><td>12</td><td></td><td>✓</td><td>✓</td><td></td><td></td></tr>
<tr><td>13</td><td></td><td>✓</td><td></td><td>✓</td><td></td></tr>
<tr><td>14</td><td></td><td></td><td>✓</td><td>✓</td><td></td></tr>
<tr><td rowspan="2">15</td><td>✓</td><td>✓</td><td>✓</td><td>✓</td><td></td></tr>
<tr><td colspan="5">Only on when program operating. Can be used for recorder drive.</td></tr>
<tr><td>16</td><td colspan="4">Only on when cycle is completed</td><td>✓</td></tr>
</table>

CIRCUITS OFF AT ALL OTHER TIMES

Table 3.1 Auxiliary Control Unit Facilities

Plate 3.4: Sample Vessels and uv light unit



radiation other than that in the long wavelenth ultra violet band of predominantly 365 nanometres (see Figure 3.3). Very little visible light is emitted.

This particular source was chosen for the present studies as a convenient starting point since past research has shown that 365 nanometres is an active wavelength for photolytic degradation of poly (vinyl chloride) coatings. The present source is easily interchangeable with other uv sources if a different wavelength is preferred for future work.

The lamp control gear within the unit, consists of a series choke and a power factor correction capacitor. The supply for the lamp is obtained from the auxiliary control unit.

The design of the uv lamp unit is such that if a different source is employed in the future, very few modifications to the existing equipment should be necessary.

3.4.3 Pollutant Gas System

When the modifications to the cabinet were started, it was realised that one of the most difficult problems to solve would be that of the pollutant gas flow control systems. The problems faced can be divided into two main areas which will be discussed separately:-

1) the construction of the hardware required to control and regulate the flow of gas,

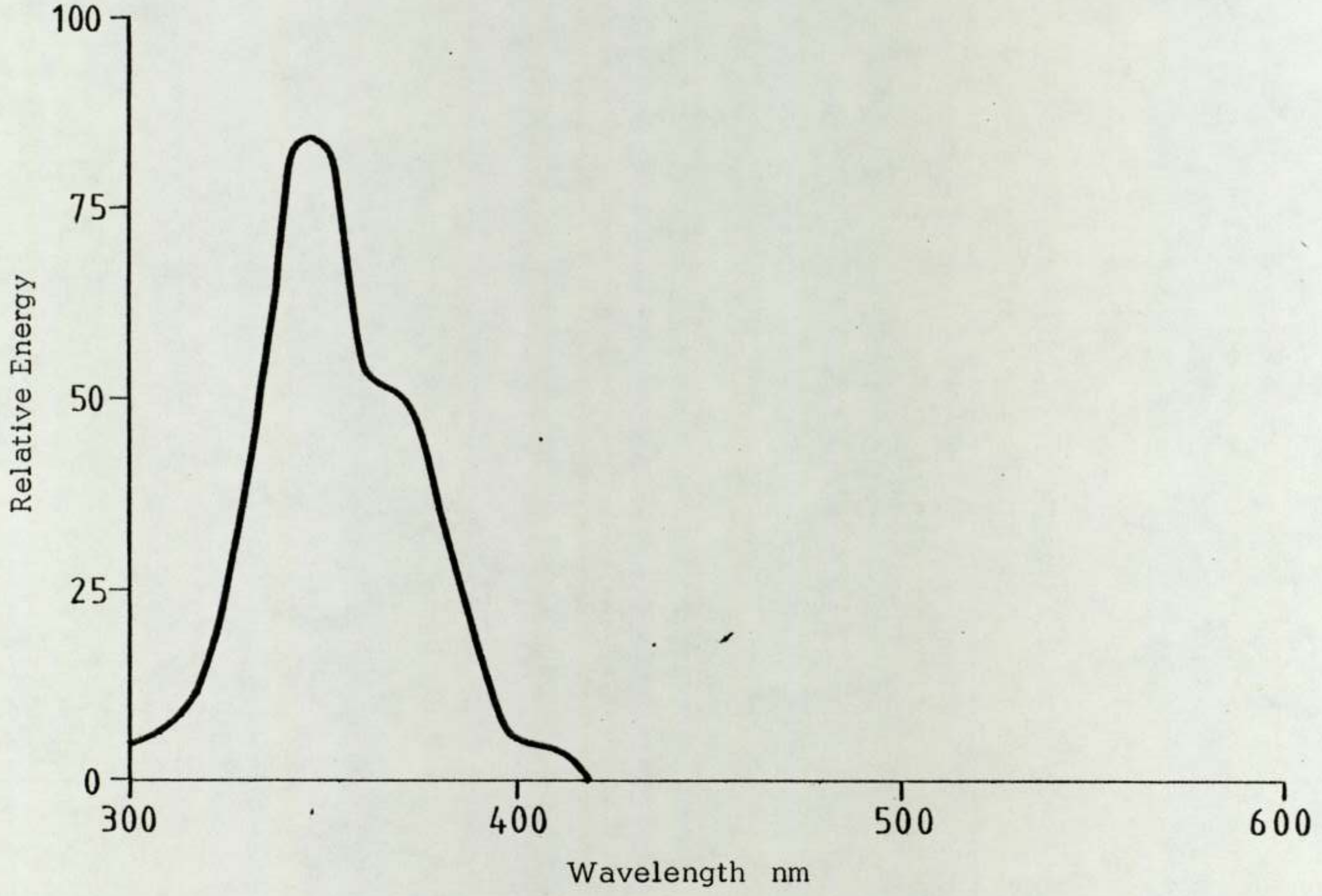


Figure 3.3: Spectral Energy Distribution of uv source

2) the construction of the control system required to operate the valves and meter the gas flow.

3.4.3.1 Gas Flow Hardware

The majority of pollutant gases are highly toxic and corrosive. This means that it is both impractical and dangerous to directly fill the interior of the main chamber with the gas. As one of the pollutant gases for examination was nitric oxide some thought as to its reactivity is relevant. This gas readily reacts with the oxygen in the air, so it would be necessary to completely purge the chamber of all oxygen before the nitric oxide could be introduced. This fact combined with the corrosive nature of nitric oxide led to the decision to use separate glass vessels within the chamber of the samples. The advantage of this approach to the problem was that a totally sealed system could be constructed which would use considerably lower volumes of gas. In addition, individual samples could be exposed to the pollutant gas while other samples remained in air.

The system which has been constructed along these lines, has two independently controlled gas inlets which are combined by a manifold mounted within the main chamber. This manifold has numerous outlets which may be connected to the individual glass sample vessels as required. The outflows from the sample vessels are connected to a second manifold, which is in turn connected to a non-return valve outside the chamber. The output from the valve is finally vented into a suitable fume cupboard duct.

The rate of gas flow is regulated by conventional gas cylinder heads and needle valves, to give a pressure which is slightly above atmospheric. The actual flow of gas is controlled by two solenoid valves operated by a separate control unit which is described in the next section.

All piping and connections which are likely to be subjected to the pollutant gas are made from stainless steel, as are the bodies and valve seals of the solenoid valves. The manifolds are made of glass.

3.4.3.2 Solenoid Valve Control Unit

The valves fitted to the pollutant gas system are operated by 240volt A.C. solenoids. These are totally compatible with the outputs from the auxiliary control unit, which are also 240 volts A.C. The need for a separate control unit for the valves arose because of the possibility of extended periods of constant temperature during an ageing cycle. For example, if the chamber was to be held at 40°C for fifty hours, the output from the auxiliary control unit, for this condition would also be energised for fifty hours. If the valve system was connected directly to this output a considerable amount of gas would be wasted. It was found in practice that a period of fifteen seconds was adequate to completely flush the system with fresh gas.

In addition facilities are necessary to allow manual operation of the gas system when access to the samples is required during a partially complete ageing cycle. This is essential in the case of nitric oxide studies as the toxic gas needs to be flushed from the system before the sample vessels can be safely opened.

In order to fulfil these requirements a control unit was designed which would independently operate the gas inlet solenoids when the respective outputs of the auxiliary control unit become live. The valves would then close after a preset time and continue to remain closed until the output from the auxiliary control unit was switched off. At this stage the gas control unit would then reset, ready to start the cycle again. The manual override was designed to bypass all of the timing circuits in order that the valves could be individually opened at any time without interrupting the operation of the cabinet.

The original circuit to be constructed (see Figure 3.4) consisted of two integrated circuits, a 74121 and a 555. These were powered by a stabilised supply derived from T1 and a 7805 voltage regulator.

A brief description of the circuit's operation is as follows. Pin 5 (B) of the 74121 is a level trigger and is enabled when its input is pulled high. This occurs when 240 volts A.C. from the auxiliary control unit is applied to T2. When B is pulled high $\overline{Q}$ which is normally high is driven low triggering the 555. The 555 is connected as a "one shot" mono-stable, so its output (Pin 3) goes high and energises the relay. The 555 is protected from solenoid switching transients by two high speed switching diodes (IN4148). The D.C. solenoid connected to the output of the 555 is compatible with TTL devices. The on time of the 555 is equal to 1.1 RaC, which for the values shown in Figure 3.4 is approximately 33 seconds. The 74121 automatically resets and will not be enabled until the mains supply from the auxiliary control unit has gone "off" and then "on".

When this prototype circuit was tested in use with the chamber it proved to be very unreliable, frequently operating the solenoids at the wrong moment in the ageing cycle. This, it is believed, was due to spurious voltage spikes from

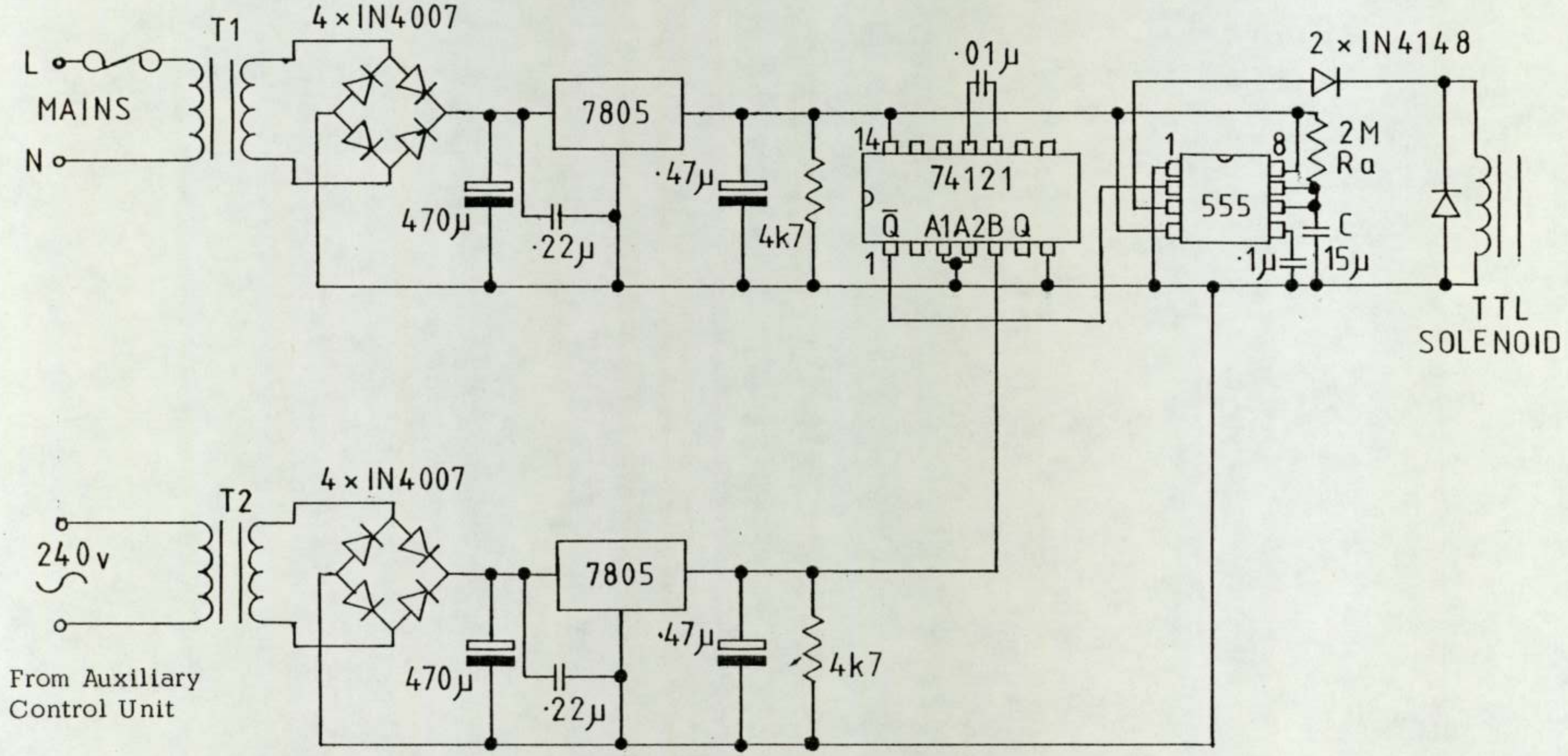


Figure 3.4: Solenoid Control Circuit: Design 1

nearby relays triggering the 74121. This problem was solved by heavily screening the circuit.

At this stage it was decided to try a different circuit layout as the prototype was proving to be very cumbersome in use, especially as a second complete unit would be required in order to operate the second gas inlet independently of the first. The second control circuit shown in Figure 3.5 uses a quad nand gate 4011B integrated circuit. A description of its operation is as follows.

The output from the auxiliary control unit is applied to the transformer TR1. This is rectified by the four diodes and then smoothed and stabilized at twelve volts by a network of capacitors and the regulator 7812. This voltage charges capacitor C4 via R3 pulling pins 1 and 2 of nand gate N1 low. As a result this pulls pin 3 high which in turn pulls pin 6 of gate N2 high. At the same time R5 pulls pin 5 of gate N2 high which forces pin 4 low, hence pulling pins 12 and 13 of gate N4 low. This puts pin 11 of gate N4 high allowing the transistors T1 and T2, which form a darlington pair, to conduct operating the relay RLA. Simultaneously, gate N3 pulls pin 10 high which locks pin 5 of gate N2 high.

After a preselected time governed by the equation 1.1R3.C4,

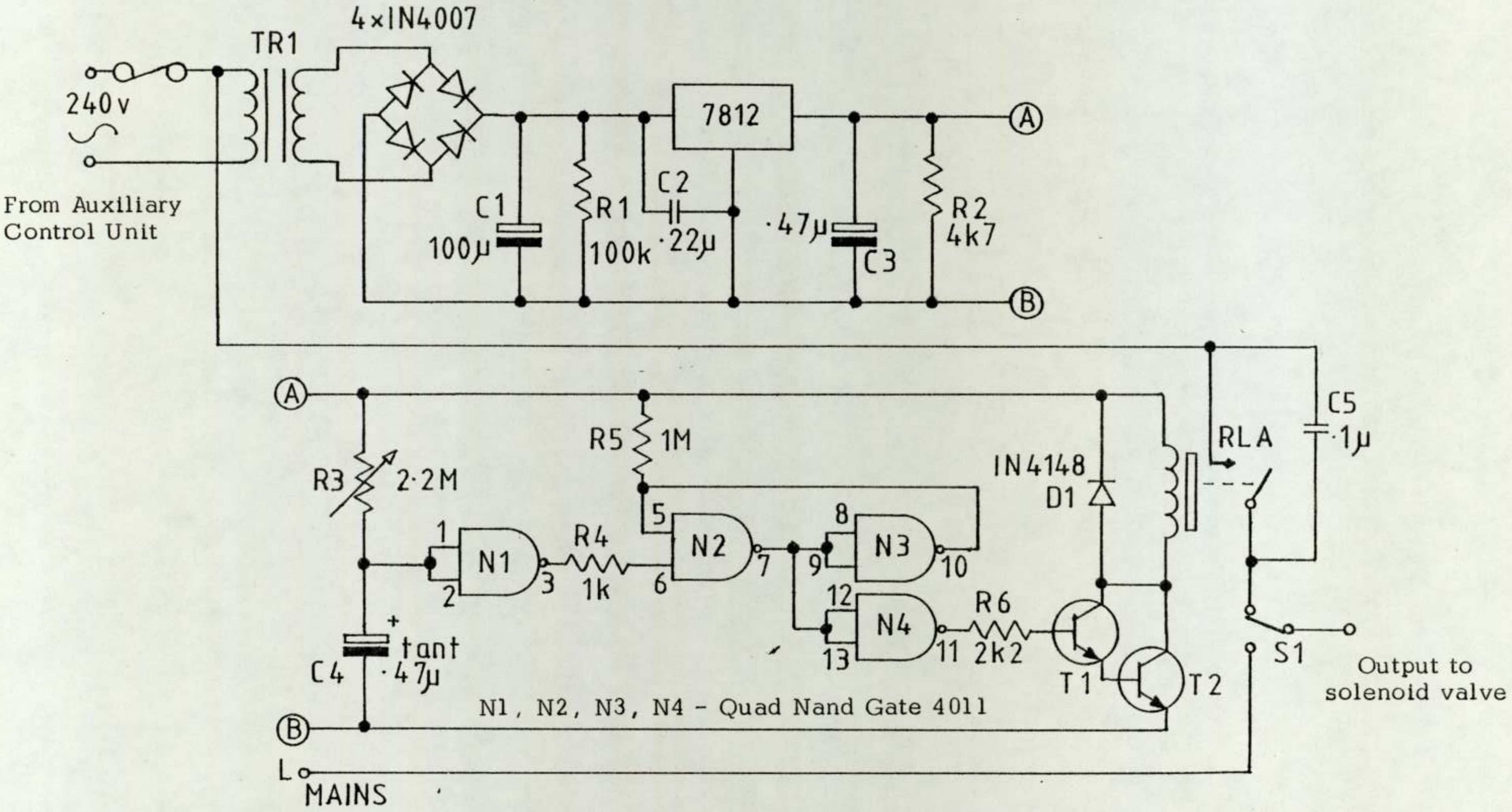


Figure 3.5: Solenoid Control Circuit: Design 2

pins 1 and 2 of gate N1 are pulled high. Pin 3 is pushed low as is pin 6 of gate N2. This puts pin 4 high with pins 12 and 13 of gate N4. Pin 11 is pulled low so T1 and T2 stop conducting and RLA is released. In the meantime gate N3 pulls pin 10 low which locks pin 5 of gate N2 permanently low. This state is then maintained until the supply voltage to the 4011B is removed, and the circuit allowed to reset. This occurs when the output from the auxiliary control unit is switched off.

As the 4011B is a member of the CMOS family of integrated circuits, it is not triggered by voltage fluctuations caused by spurious peaks. The preset resistor R3 is provided in order that the valve open time can be varied to suit different ageing systems. The bleed resistor R1 has been selected so as to keep the 4011B locked for at least five minutes after the input voltage has been removed. This is done to ensure that the circuit does not reset in the event of a short interruption to the mains supply. The diode D1 protects the transistor from solenoid switching transients. When the switch S1 is operated the control circuit is bypassed and the valves are opened independently of the cabinet.

A second identical circuit is used to control the other gas inlet valve.

3.4.4 Sample Holders

The glass vessels which are used to hold the ageing samples are 180mm long and 60mm in diameter. An 8mm diameter gas outlet is fitted at one end of the vessel and a removeable stopper at the other. The stopper has two inlets each 8mm in diameter. Each vessel can hold three sample plates of 50mm by 40mm. These plates are supported across the diameter of the vessel so as to allow water to be introduced above or below the sample face.

Eight of these vessels can be located horizontally in a rack which fits into the main working chamber of the cabinet (see Plate 3.5). The bottom row of four vessels are shielded from the uv source by an aluminium plate fitted across the full width of the chamber. This design allows the four following ageing systems to be conducted simultaneously:-

a) Temperature
b) Temperature + pollutant gas
c) Temperature + uv
d) Temperature + uv + pollutant gas

3.4.5 Humidity Control

A high relative humidity is produced by injecting distilled water into the required sample vessels through the second inlet in the stopper. Depending upon the orientation of the stopper the water will either collect on the sample surface or beneath the sample

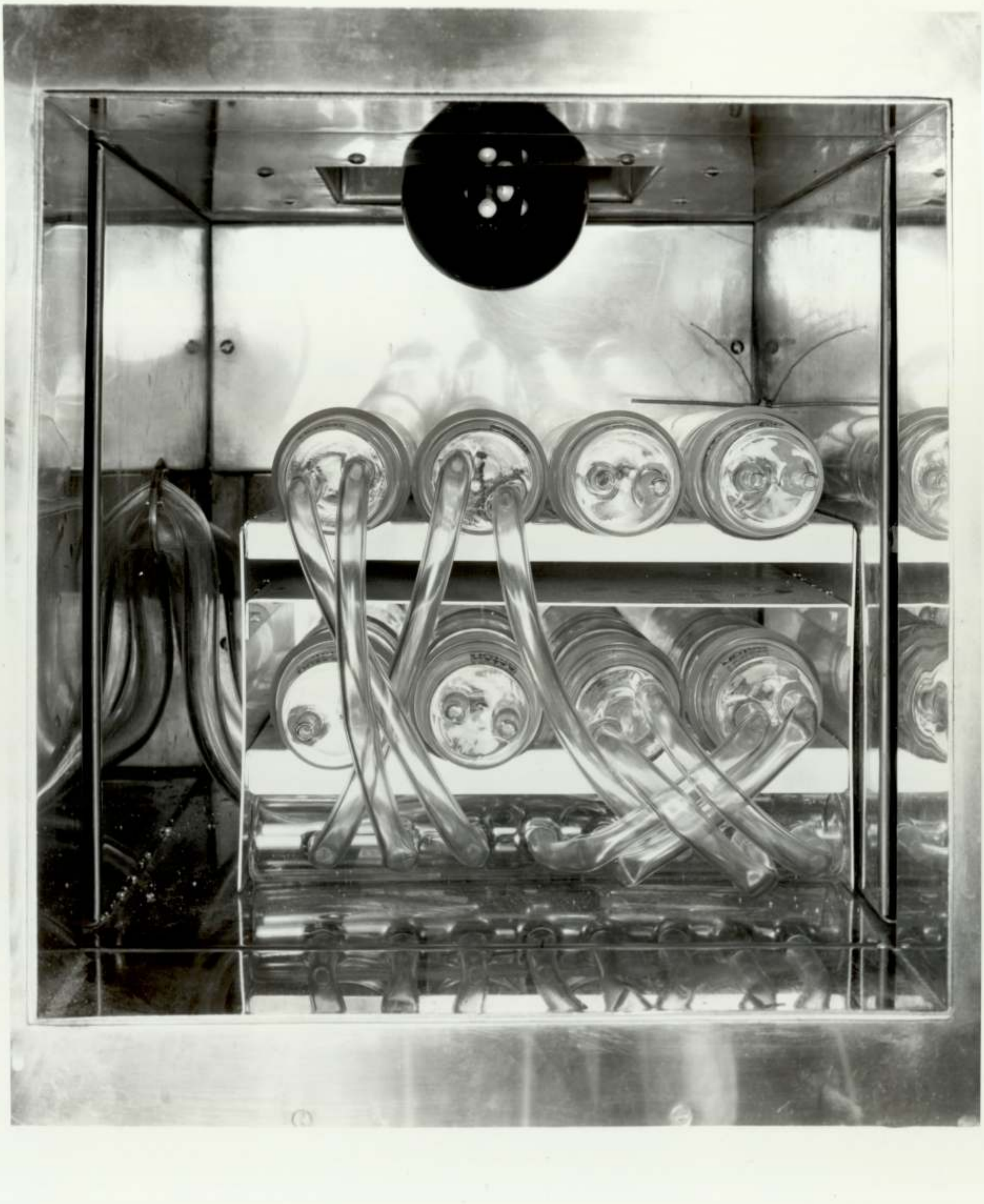


Plate 3.5: Sample Vessels Located in the Main Working Chamber

plate in the vessel.

The dispenser used is a type LFA/10 marketed by Fisons of Loughborough. The instrument consists of a twist valve, into which a syringe is fitted, operated by a synchronous motor. This same motor also drives a rack on which is mounted a bracket to hold the end of the syringe plunger. The syringe barrel is held firmly against the twist valve by an 'L' shaped clamp. As the rack moves backwards and forwards, so the plunger moves up and down the barrel sucking up and dispensing water, the inlet of the dispenser being connected to the water reservoir and the outlet to the sample vessels. Various flow rates can be achieved depending upon the size of the syringe used. Since the rack operates at a constant speed the larger the syringe used so the higher the flow rate.

The dispenser is connected to the auxiliary control unit via a "one-shot" control similar to that used by the gas control system.

The relative humidity is monitored by a hygrometer manufactured by Shaws of Bradford. Unfortunately, the sensor can only be located in a sample vessel which is not connected to the gas system or contamination of the sensitive element would occur. The sensing element will only give a linear response at a constant temperature, so it is necessary to calibrate the hygrometer for each different temperature range and cycle used. At present this is achieved by placing the sensor in a sealed container containing dry air. The container is then placed in the chamber and cycled between the two set temperatures to be used in the ageing programme. The output from the hygrometer is recorded on a chart recorder and the resulting curve used as a base line correction for future readings under similar temperature conditions.

3.4.6 Chart Recorder

One of the most important monitoring facilities attached to the cabinet is the multipoint chart recorder. This, by a system of thermocouples, monitors the temperature inside the actual chamber, and above all the samples' surfaces, independently of the cabinet's own temperature sensing circuitry. The recorder also indicates the relative humidity, the operation of the gas solenoid valves and of the uv source.

The chart recorder drive is controlled by the auxiliary control unit. This enables the drive to be halted if required, when a constant temperature is being maintained for a long period. The chart recorder is switched off automatically, as are all the other systems, when the cabinet completes the ageing programme.

3.5 Final Modifications to the Cabinet

During the operation of the modified cabinet a few further faults were discovered. The most serious fault occurred when a temperature sensor failed to operate correctly resulting in a temperature of $190^{\circ}C$ being attained within the chamber. To protect against a recurrence of this fault, an independent presettable thermostat has been installed in the heat exchanger, which switches the cabinet off if a predetermined temperature is exceeded.

A second modification has been carried out to protect the samples in the event of an interruption to the mains supply for the cabinet. Previously if the mains failed the cabinet would immediately proceed with the next section of the ageing cycle once power was restored. If the failure was only a brief interruption to the supply this could result in the pollutant gas being introduced at excessively high temperatures, or water being injected at subambient temperatures. The modification halts the programme after power has been restored until the chamber has returned to ambient conditions. The programme is then resumed from the point at which the interruption occurred.

3.6 Operating Procedure for the Modified Montford Cabinet

The operating procedure for the equipment can be summarized as follows (refer to Plate 3.1):-

1) Set the manual/programme switch to manual.

2) Set system controller 'A' to the lower required temperature and 'B' to the higher temperature.

3) Select boost heating and/or boost cooling if require.

4) Set the energy regulators to the heating and cooling rates required.

5) Check the liquid CO_2 cylinder and replace if necessary.

6) Switch the cabinet mains on.

7) Press system 'B' start button.

8) Wait for chamber to attain upper temperature, then switch on the chart recorder and press system 'A' start button.

9) Wait for the chamber to stabilize at the lower temperature then readjust the regulator to achieve the required cooling rate.

10) Press system 'B' start button.

11) Wait for the chamber to stabilize at the upper temperature then adjust the regulator to achieve the required heating rate.

12) Repeat 8 - 11, until the heating and cooling rates are satisfactory.

13) Calibrate the hygrometer.

14) Switch off the cabinet mains.

15) Set the time clock to the desired temperature hold period.

16) Set the cycle counter to the required number of temperature changes.
Note: Hot - Cold - Hot - Cold - OFF = 4 changes.

17) Connect the auxiliary units to the required outputs on the auxiliary control unit. (see Table 3.1)

18) Operate the manual control for the nitrogen gas system and adjust the cylinder regulator to give the required flow rate.

Note: An indication of the gas flow rate can be obtained by immersing the chamber outflow pipe in water.

19) Repeat for the pollutant gas cylinder.

20) Flush the system manually with nitrogen for 30 seconds.

21) Adjust the chart recorder drive to the required speed (usually $\frac{1}{2}$ inch per hour).

22) Remove the chamber door and load the sample vessels.

23) Carefully replace the vessels' stoppers, making sure that they are gas tight and that the water inlet nozzles are correctly orientated.

24) Flush manually with nitrogen and check for leaks.

25) Prime the water injection system.

26) Replace the chamber door.

27) If control of the temperature setting requires both heating and cooling, set the ambient stabilisation switch to its appropriate position.

28) Flush with nitrogen until it is certain that no air remains in the gas system.

29) Switch on the cabinet mains.

30) Press the appropriate systems start button.

31) Set the manual/programme switch to programme.

32) Readjust the heating and cooling rates and chart drive speed if necessary.

33) At the end of the programme, which is indicated when all the warning lights except the power light, are off, switch off the cabinet mains.

34) Purge with nitrogen.

35) Remove the chamber door and open the sample vessels.

36) Leave for a few minutes to allow any residual pollutant gas to disperse.

37) Remove samples and replace the chamber door.

38) For subsequent runs repeat operations 5, 16, 22 - 37.

39) Close all gas cylinders and switch off all auxiliary units.

3.7 Conclusion

In this modified form the cabinet is capable of accurately maintaining a constant temperature, above or below ambient, which is held with a maximum gradient, within the chamber, of $\pm \frac{1}{2}^{o}$C. This, combined with the additional functions which control the uv source, pollutant gases and monitor the humidity, provides a versatile and reliable machine for the accelerated ageing of surface coatings.

Supplementary Note

The work undertaken and described in subsequent chapters does not use the high humidity facilities. In simplifying the problem for the initial studies both oxygen and moisture were omitted. Oxygen obviously causes a reduction in the effective NO concentration and would complicate the reaction by introducing NO_2. High humidity conditions were avoided in the studies since the radical behaviour of NO and the radical degradation of polymers, which represent the most interesting part of the degradation process, occur simultaneously in clear sunny conditions rather than dull humid conditions.

CHAPTER 4

COMPUTER INTERFACING AND SOFTWARE DEVELOPMENT

4.1 Introduction

It was soon apparent that the major time consuming operation during this work was likely to be the processing of the analytical data produced by the goniophotometer. It was intended to monitor the state of the samples after every few hundred hours of ageing. As a result, the ageing of the samples would be delayed whilst goniophotometric analysis was completed on each sample. Ideally at least three curves were required from each sample to allow for experimental error. Since a goniophotometric scan took approximately 25 minutes to complete with a further hour to calculate the results from the data, various methods were studied that were likely to speed up the process of goniophotometric analysis. Some of these methods involved modifying the goniophotometer and are described in Chapter 5. The other modifications were primarily associated with the data handling.

During the actual goniophotometric scan the most difficult and time consuming operation was synchronising the chart recorder with the rate of rotation of the turntable. The synchronising of the two machines was also one of the major complications involved in the final calculation of the results, as inches per minute had to be converted to degrees per minute. Additionally, a calibration point was needed to indicate on the chart the instant at which the turntable started to rotate. Only when the scale of the 'x' axis had been calculated and calibrated could the specular angle, and the width at half peak, be calculated.

To aid in the calculations a high chart speed was usually used in order to expand the 'x' axis of the curve. Because of this a large volume of chart paper had to be stored if the results were to be kept for future reference.

After studying these problems it was decided that a practical solution would be to interface the goniophotometer to a micro-computer, which would be capable of collection, processing and storing the data produced by the machine. As a Sharp MZ80K micro-computer with a 48K byte memory was immediately available, the initial interfacing and software development was carried out using this machine.

4.2 Computer Interfacing

4.2.1 Analog to Digital Converter

The first obstacle in interfacing the majority of analytical machines to a computer is the different method that the two types of machine use for data handling. The output from an analytical machine such as an i.r. or uv spectrometer, or a goniophotometer, is in an analog form, while a computer can only deal with digital information. Hence, before there can be any communication between the machine and the computer, a device is required which converts an analog input to a digital output. There are many commercially available analog to digital converters on the market. These devices have varying facilities, such as the number of inputs or channels, different input voltage ranges and different methods by which the digital information is transferred to the computer.

The digital information is usually transferred to the computer by a serial or a parallel interface. A serial interface transfers the information a 'bit' at a time via a single connection. A parallel interface has a separate connection for each 'bit' of a word. Both methods have advantages and disadvantages over each other. If the A/D convertor is to be placed a considerable distance from the computer it is more practical to use a serial connection as fewer wires are involved. The disadvantages of a serial interface compared with a parallel one is the slower speed of information exchange and the software which is necessary to control and check the interchange of data via a single connection.

4.2.2 A/D Conversion Techniques

The majority of A/D units only contain one actual converter, even though there may be several independent inputs. Each separate input is usually connected to a multiplexer switch. When a particular input voltage is to be sampled, the multiplexer selects the appropriate channel and connects the input voltage to the converter.

There are three main methods of analog to digital conversion, successive approximation, counter ramp and parallel (simultaneous) conversion [43]. Of the three methods, parallel conversion is the fastest, but it requires the most equipment, especially for a digital output of more than four bits. This technique is ideally suited for specialist high speed applications such as video digitising or instrumention and signal analysis, but for general applications involving DC voltages, successive approximation and counter ramp conversion are more practical and easier to operate. Both these types of converter employ internal digital to analog decoders in the conversion process.

A block diagram of a simple D/A converter is shown in Figure 4.1. The basic parts of the converter are the storage register, the reference supply and the D/A decoder containing the analog switches and a resistor network. The input digital word to be converted is stored in a flip-flop register. Each flip-flop drives an analog switch which accurately connects the reference supply voltage or ground to the proper terminal of the resistor network. In the case of a ONE for a particular bit, the resistor network divides the reference voltage down so that a voltage is added to the D/A output whose magnitude is proportioned to the equivalent weight of that particular bit. A sign bit analog switch as shown in Figure 4.1 is only needed if a positive and a negative analog voltage output are required.

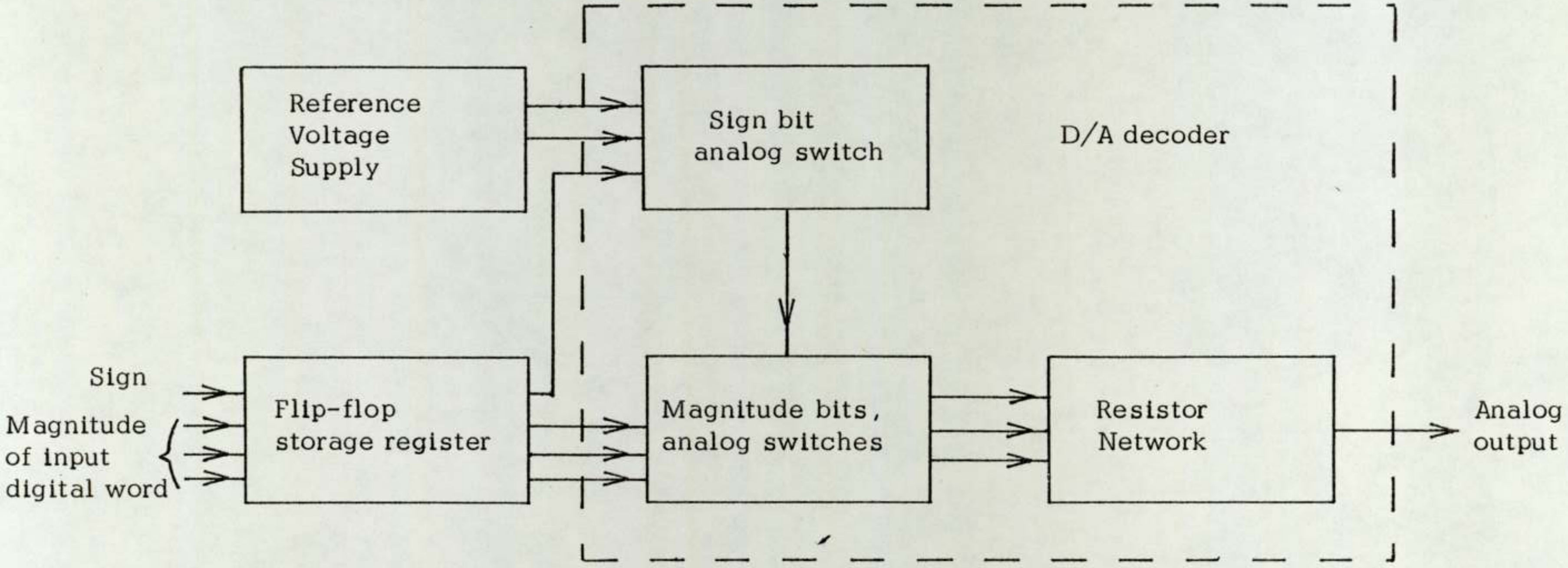


Figure 4.1: Three-bit plus-sign D/A converter

The analog to digital converters used in this work were of the successive approximation type. Figure 4.2 shows a typical A/D converter of this type. The conversion process is as follows. A multiplexer channel is selected by the programmer, and the transistor switches of this channel are closed. The analog voltage of the channel appears at the input to the comparator. At the same time, the flip-flop register is cleared and all ZEROs appear at the inputs of the D/A decoder. The comparator then compares this zero output voltage from the D/A decoder with the selected multiplexer analog output and determines the sign. The proper sign is next set in the flip-flop register by the programmer, which then sets a ONE in the MSB of the D/A decoder. The output of the decoder is compared against the analog input voltage, and the comparator determines which one is larger. The programmer then removes the ONE from the MSB if the comparator indicates that the D/A converter output was larger than the analog input or leaves it in if the comparator indicates that the reverse is true. This process continues until a ONE has been tried in turn in each succeeding less significant digital bit. The digital equivalent can then be read out of the storage register via the digital output lines shown in Figure 4.2.

Most A/D converters use an operational amplifier to buffer the multiplexer channel from the input. The gain of the operational amplifier decides the voltage range of the input that can be converted by the A/D.

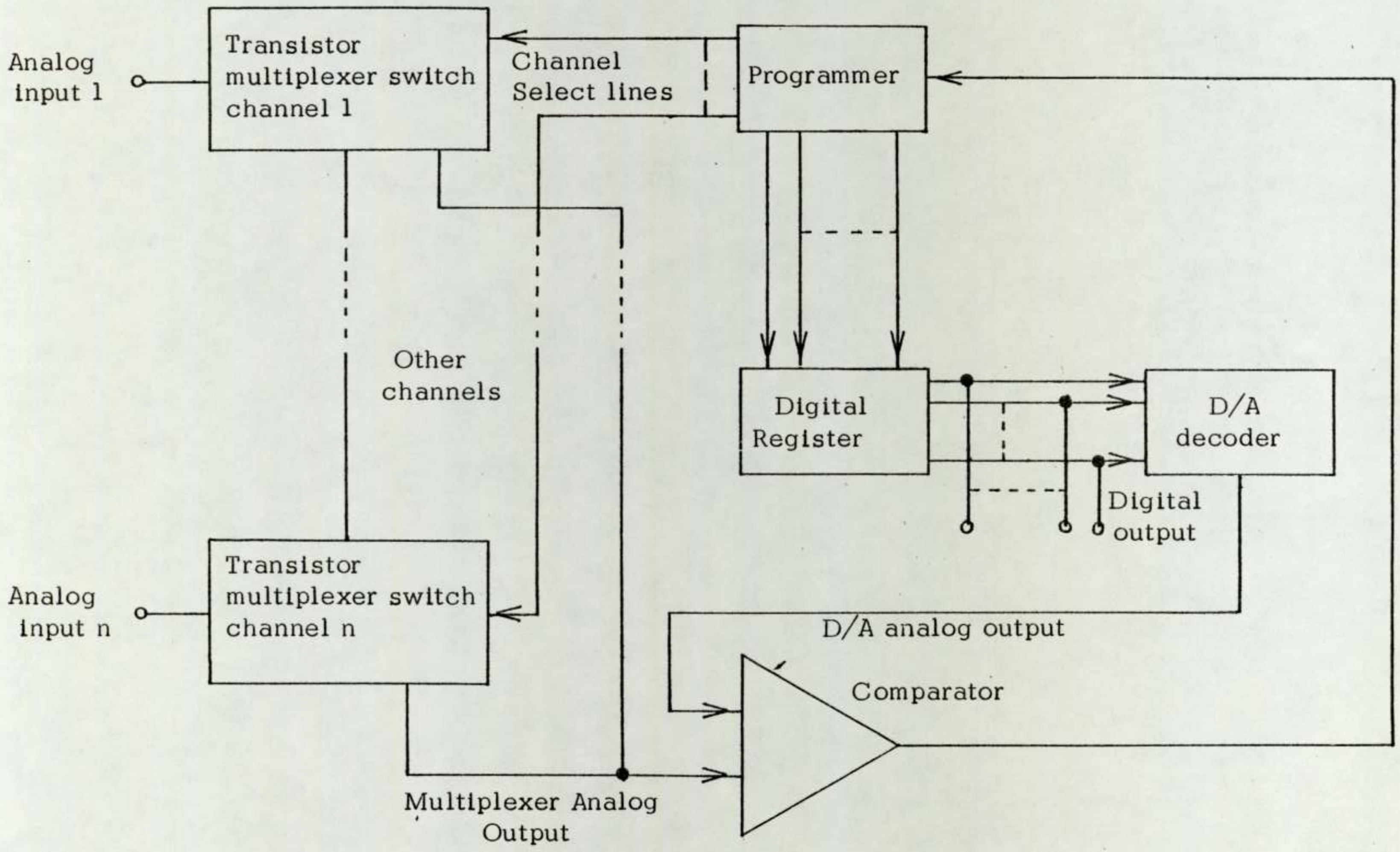


Figure 4.2: Successive approximation A/D conversion system

To control the operation of the A/D programmer it is necessary for the computer to talk to the converter. The nature of this 'handshaking' varies with different converters and computer systems. In general the handshaking is as follows. First the computer outputs to the port connected to the A/D, the multiplexer address and the channel number to be sampled. The A/D programmer resets and the multiplexer connects the respective input to the converter. Next the computer instructs the A/D to start the conversion. The A/D samples the voltage, converts it to a digital form and informs the computer when the end of conversion has occurred. The data is transmitted when the A/D receives the appropriate command from the computer, and it is kept on the line until the A/D programmer is reset by the multiplexer address.

4.2.3 Conversion Speeds and Resolution

Each step of the A/D conversion process requires a finite time for the completion of the transition from one state to another. Typically the voltage sampling time is in the region of 6μs and the conversion time about 10μs. The faster the A/D is required to operate the less accurate the conversion, due to switching transients, although this problem is unlikely to occur with micro-computers due to their relatively slow clock rate.

The optimum speed for sampling is achieved when as little analog information as possible is missed without the A/D converter losing the accuracy of conversion. Most A/D converters give the required accuracy when operated at conversion rates as fast as 25μs. This is adequate for simple data collection from most analytical machines, but can be a limiting factor if high frequency signals are to be converted.

In the case of interfacing the goniophotometer, the speed of conversion is critical in respect of the turntable rotation. If the A/D converter is run at slow sampling rate the computer will receive data from few positions during the scan. This problem could be solved by slowing the turntable, but this defeats the object of using a computer to speed up the data collection. As mentioned previously, in the case of micro-computers the handshaking is usually considerably slower than the maximum conversion rate of the A/D. One reason for this is the use of an interpreter which converts the user language into the machine code with which the computer works. The handshaking can therefore be considerably speeded up by compiling the finished programme to produce a machine code file which can be run without an interpreter.

The limiting factor as regards to the resolution of the converter is the number of bits used to represent the input voltage. The resolution of an eight bit converter is 256 parts. This is the maximum figure that can be represented by an eight digit binary number. A twelve bit machine has a resolution of 4096 parts. The greater the number of bits the slower the conversion, but the greater the resolution. A twelve bit machine also requires more complex handshaking routines, since the data usually has to be output as two separate eight bit words, the second of which has four data bits plus four trailing zeros.

Eight bit resolution was adequate for the intensity output from the goniophotometer, but was not ideal for the turntable output. If the turntable was set to scan through 130 degrees, the resolution of one part in 256 meant that the output could only be resolved down to ½ degree. This problem was solved when the software was written.

4.2.4 The Sharp A/D Converter

The A/D converter used for the initial work was marketed by Peterson Electronics Ltd of Aberdeen as a plug in unit for the Sharp MZ80K micro-computer. It is a 16 channel input, 8 bit converter with a parallel output. Unfortunately the operation of this unit was not as straightforward as the literature claimed. Before the converter could be connected to the computer it was necessary to purchase an interface box, which buffers the single port on the computer, and provides six separate individually addressable input/output ports. In addition, it provides an isolated power supply for each unit attached to the box.

The biggest problem encountered concerned the software which addresses the port and hence the A/D converter. Unfortunately the computer's BASIC interpreter does not provide any facilities for directly addressing the input/output ports. This had to be done in machine code, which initially, at the start of this work, was little understood. The addressing of the input/output port was further complicated as the manual supplied with the A/D converter was inaccurate and vague when describing the handshaking routines. A considerable amount of time was spent trying to master the machine code and operate the A/D converter before it was discovered that the A/D handshaking had actually been set incorrectly on the board by the manufacturers.

4.3 Computer Software

As mentioned in the previous section, the speed of operation of the computer is an important consideration to be taken into account when interfacing with an analog to digital converter. Bearing this fact in mind, it was decided to split the software into two main sections. The first section controls the data acquisition through the A/D and the second handles the data processing.

4.3.1 A/D and Data Collection Routines

The line number references in this section refer to the programme listing in appendix one.

In order to operate the A/D converter it is necessary to address the input/output port of the Sharp computer with a machine code routine. This routine is read into the memory by the subroutine starting at line 360 and finishing at line 520. When required the machine code is accessed by lines 80-150 and the digital data loaded into the two variables IN and PS. Due to the speed considerations, it is impossible to process the data in real time, so the data has to be stored in an array for future access. This is carried out by the routine starting at line 170. A two dimensional array is used as a solution to the turntable resolution problem mentioned earlier in this chapter. Since the A/D is operating at a relatively high speed, it is possible to take four or five readings for each indicated position. Assuming that the turntable rotates at a constant speed these successive readings can actually be taken to represent individual consecutive positions of the turntable. This effectively increases the resolution of the turntable output by a factor of four.

A further advantage of holding the raw data in an array as opposed to processing it as it is collected, is that it can be repeatedly accessed by the programme for different calculations. If it was converted for plotting immediately on loading any subsequent calculations using the modified data would include a certain degree of error. A major disadvantage with this technique is the amount of memory required to hold the data. Each element in the array requires two bytes of memory. As the array must be capable of holding all the data produced by the A/D converter, its size depends on the resolution of the A/D converter. An eight bit A/D converter can produce readings for up to 256 separate turntable positions, while a twelve bit would have 4096 separate positions. Because of this, the size of the available random access memory in the computer dictates the type of A/D converter that can be employed. With the present Sharp programme the arrays dimensional in line 50 account for 8K bytes of memory before any data processing is done.

The A/D subroutines are not only used for collecting the data from a goniophotometric scan, but also for calibration of the turntable output and the photomultiplier gain. The calibration routine starts at line 1050 and finishes at line 1500.

Besides loading data from the A/D converter the programme also has facilities which enable previously collected data to be loaded from a text file. This option is provided by the routine at line 1000 and carried out by lines 1660 to 1760.

4.3.2 Data Processing

The first stage of the data processing involves transferring the intensity values from a two dimensional array to a single dimensional array, lines 1800-1890. This second array is used in the calculations which find the peak height and the background intensity, as well as the peak width. The peak height is found by checking each subsequent value to discover whether it is greater or less than the previous value, lines 2050-2070. Multiple peaks can be found by checking for negative gradients, but this method was dispensed with, as it is very time consuming. In addition, double peaks are very rare in goniophotometric data, usually indicating faulty mounting of the specimen. Once found, the position and value of the peak height is flagged in a third array. This third array is required to allow for possible future editing of the curve without corrupting the original data. At the completion of the calculations it is used to overwrite the second array before the data is stored.

The background intensity is calculated by taking the average of the intensity value at about ten points either side of the calculated angle at which the photomultipler is normal to the specimen surface, lines 2100-2200. This result is also loaded into the third array. Once these preliminary calculations are completed, the data from the second array is rescaled, so as to fit the high resolution screen of the Sharp MZ80K and loaded into a plot array, lines 1900-1975. The curve is plotted on the screen by the subroutine located at line 2780.

At this point in the programme the operator is given the option of discarding the data and starting again. If the data is accepted the programme requests the filter combinations that were used during the scan, lines 2460-2740. The calculated filter value is used to convert the basic data into actual intensity units, (lines 5195-5220) for the final calculation of Is, Id and Gloss Factor (see Chapter 2). At no time is the displayed data used for the calculations. All work is carried out on the original inputed data.

The final sections of the programme display the values for the Is, Id, the angle of maximum reflectance, width at half peak height, and the Gloss Factor. At this stage in the programme options are provided to dump the results and/or the graph to a printer or to a tape file, lines 5330-5490. An edit facility is also provided in the programme, which allows the operator to indicate the positions and values of the peak height and background intensity. This facility is required for the occasional freak curve which confuses the programme. An additional feature of the edit facility is the rescale routine which allows the operator to expand or contract the 'x' axis of the displayed data. This rescaling is achieved when the data is transferred from the array used for the calculations, to the plot array. It is also possible to display individual sections of the curve for detailed examination and to overlay separate curves for comparison, for example before and after ageing.

The routines described above provided the basic units from which the final programme was built. The only disadvantage discovered in using the Sharp micro-computer was the method employed to display the high resolution graphics. It is not possible to retain the graphics page in the memory whilst displaying text on the VDU screen. As a result, every time the curve is shown it is necessary to reload the data into the plot array and replot the whole curve.

A large percentage of the completed programme is concerned with displaying various instructions or questions for the operator. The programme needs to be user friendly as it is likely to be used by operators with little experience of computer systems. The calibration instructions which the computer displays take the operator, step by step, through the necessary routines that are required to calibrate the goniophotometer output. Also, while the programme is running the display indicates which calibrations or routines are taking place.

The programme was slowly developed from the early data collection and display routines, up to the more complicated edit routines. Since, at the start of the programming, there were no facilities to list the routines on a printer, numerous bugs were present which were difficult to locate and rectify. To solve these problems it was decided to put the programme into general use and to note the faults as they occurred for future correction. Besides helping to locate the bugs in the programme, the initial trials showed that it was necessary to include various user traps into the routines. These traps stopped the programme from crashing when impossible commands or garbage were keyed in by the operator. These traps usually operate by halting the programme until one of two specific keys are pressed.

All other inputs are ignored. When inputs of codes or descriptions are requested, the programme will give the operator the chance to check and amend, if necessary, the last input.

4.4 Cifer Micro-computer Interfacing and Software

During this work a Cifer 2683 micro-computer became available (see Plate 4.1). This is a 64K byte machine with a separate graphics display processor. The system was supplied with twin five inch floppy disc drives, each with 256 K byte capacity. The disc operating system is Digital Research's CP/M version 2.2.

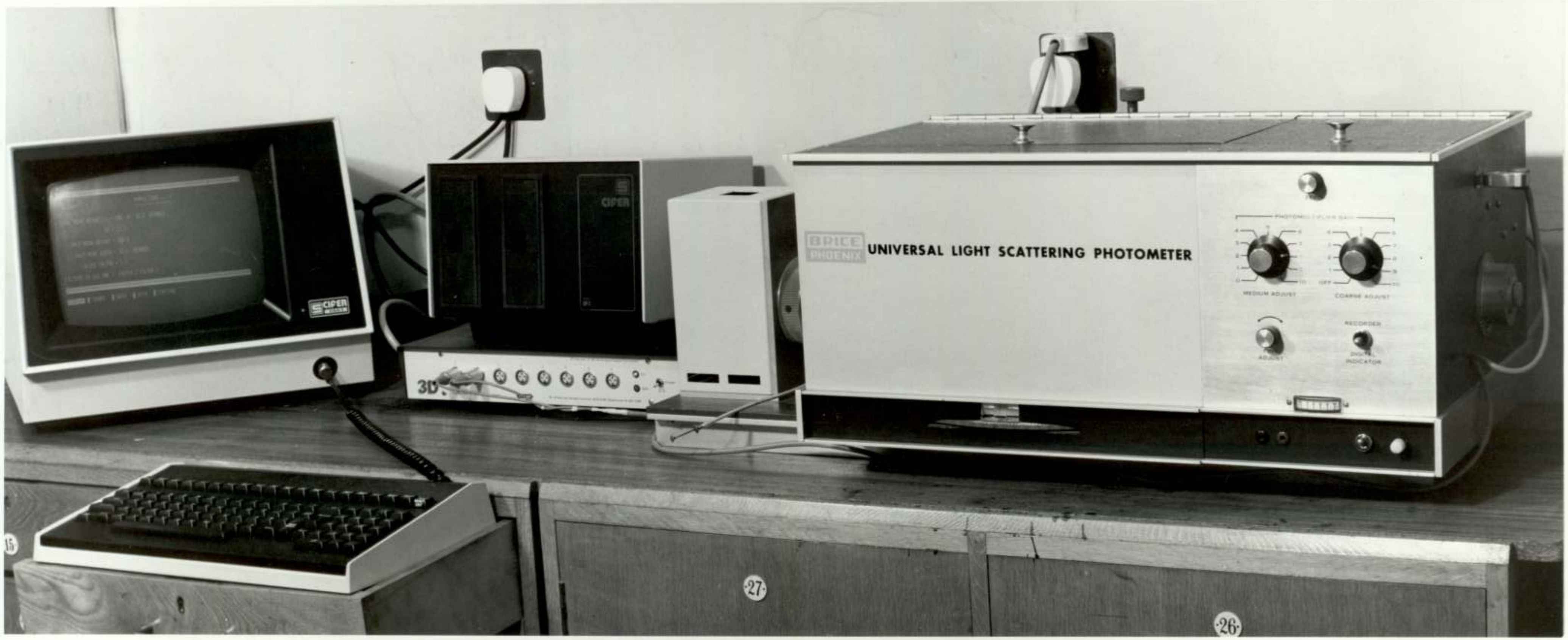
The availability of a 64K byte memory and disc system provided the facilities which allowed a drastic rethink and reformation of the original programme to be undertaken.

4.4.1 Cifer and A/D Interfacing

The availability of the Cifer with its larger memory and IEEE 488 input part provided the opportunity to use a twelve bit A/D converter. The A/D converter was purchased from 3D, Digital Design and Development of London. It is a twelve bit, eight channel, five volt full scale successive approximation converter, which is IEEE compatible.

The IEEE 488 General Purpose Interface Bus (GPIB) is an input/output

<u>Plate 4.1</u>:   Cifer Microcomputer, A/D Convertor and Goniophotometer



port on the computer which is capable of communicating with other computers and controlling auxiliary equipment simultaneously. The handshaking routines used on the GPIB are specified in the IEEE standard 488-1978 and are adhered to by a large number of instrument manufacturers (44). A summary of the basic principles of the GPIB are given below.

The GPIB consists of two groups of lines. One group consists of eight data lines, each carrying one bit of data. The other group has eight control/management lines. The eight bidirectional GPIB data lines carry parallel simultaneous bits transferred between the computer and a selected device on the GPIB. The eight GPIB control/management lines supply information as necessary immediately before, during or after the transmission of data. A maximum of fifteen devices of four types can be connected to this party line bus structure. The four types are:-

1) The Controller
2) Devices that talk only
3) Devices that listen only
4) Devices that talk or listen depending on how they are programmed.

In the present system the Cifer is the controller and the A/D converter is a talker.

The eight control/management lines are described as follows:-

1) Data Valid	DAV	Transfer Control Lines
2) Not Ready for Data	NRFD	
3) Not Data Accepted	NDAC	
4) End or Identify	EOI	Interface Management Lines
5) Interface Clear	IFC	
6) Service Request	SRQ	
7) Attention	ATN	
8) Remote Enable	REN	

All devices on the bus are identified by a primary address which is unique to each device. The 3D A/D converter waits until it recognises its own primary address (PA), which at present is set at 7, and then responds to a command specified by a secondary address (SA). Five addresses are required by the A/D converter for each conversion. They are listed below:-

1) PA = 7, SA = 0 - 7 Set multiplexer channel

2) PA = 7, SA = 16 Start conversion

3) PA = 7, SA = 20 Send 8 MSB

Cifer reads the 8 most significant bits

4) PA = 7, SA = 24 Send 4 LSB

Cifer reads the 4 least significant bits

5) PA = 7, SA = 31 Universal Untalk

Each primary and secondary address handshake is as follows:-

1) Typical idle state.
2) Cifer sets ATN line low (true), indicating it is ready. ATN is low for 190 µs minimum.
3) A/D converter responds by pulling NDAC low. Device has up to 14 µs to respond. Error if no response.
4) Cifer places primary address on DIO lines. Data is allowed 11 µs to settle.
5) Cifer assets DAV low as data valid indicator.
6) A/D converter responds by pulling NRFD low at the beginning of the read.
7) A/D converter pulls NRFD high (false) when read is complete.
8) Cifer pulls DAV high to indicate that the address data is no longer valid.
9) A/D converter sets NDAC low.
10) A/D converter sets NRFD high when it is ready for the next data byte. This ends the handshake sequence.
11) Cifer places secondary address on the DIO lines.
12) Cifer issues the data valid signal by pulling DAV low.
13) Cifer pulls DAV high to remove data valid indication after 28 µs.
14) Cifer resets ATN high, terminating the address timing.
15) Cifer reads first data byte on DIO lines.

The handshaking routines are contained in the subroutine which starts at line 120 in the listing "GONIO" in appendix 2.

4.4.2 Cifer Interfacing Software

The software which is used to address the IEEE 488 controller is supplied by Cifer as machine code library routines. These routines are loaded into memory below the CP/M operating system and are called as required by the programme. This means that any programme which addresses the IEEE 488 controller must be complied and run as a machine code file before the routines can be accessed. As a result designing and debugging a programme becomes difficult and time consuming as every alteration requires the whole programme to be recompiled before it can be checked.

Once the technique of compiling had been mastered it was discovered that the CP/M - IEEE 488 software supplied by Cifer was on the wrong system format, and in addition was faulty. The updated version of the software appeared to function correctly, but the A/D converter responded with faulty data. Eventually this was found to be caused by the Cifer handshaking being too fast for the A/D converter to respond correctly, despite the fact that both manufacturers claimed that their machines conformed to the IEEE 488 standard. The fault was rectified by wiring a 2 µf capacitor across the DAV line inside the A/D converter. This holds the DAV true for a few extra microseconds allowing time for the A/D converter to respond correctly.

4.4.3 Cifer Data Processing Software

As it was impossible to transfer the programme directly to the Cifer from the Sharp it was necessary to retype the programme in its entirety. This provided the opportunity to restructure the programme. The original programme had been developed step by step, each successive unit built onto the proceeding one, with many routines duplicated or subsequently made obsolete. Now that the aims and main features of the programme were known it was possible to design the programme as a whole from scratch. The first stage of this reformatting was redefining the main subroutines. These included the display commands, graphic display of data, data file loading and the main data processing. These subroutines were positioned at the top of the programme (see appendix 2), to speed up the access time, as a subroutine search starts at the top of the listing. The restructuring of a programme in this manner also aids future development, as new facilities can be created by calling up subroutines which are already present.

As mentioned previously, the Cifer possesses a separate graphics display memory, unlike the Sharp which overwrites the displayed text with graphic characters. This added facility allows the graphic representation of a curve to be retained in the memory whether on display or not, while user instructions or questions are being displayed. The edit facilities are further improved by the use of cross hair cursors for on screen editing.

When the programme was restructured it was decided to dispense with the multiple arrays. The original method of calculating the results read the data from the collection array into a second array, using flags to indicate the calculated peak height and background intensity. A third array was then used to plot the data. This system was replaced by a single data array and a plot array. The peak values are loaded into variables and the raw data left untouched in the main array. The raw data is then used for the graphics display and the variables for the calculations. This method uses less memory, runs quicker and allows more sophisticated editing.

While programming with the Cifer, it was realised that because of the more sophisticated nature of the computer it was more susceptible to system crashes due to operator error. This is particularly true of the disc operating system. To safeguard against the loss of data through a system crash, the programme dumps the raw data to a temporary file shortly after it has been collected. This data can easily be recovered after the system has been re-booted. The temporary file is also used to transfer data and variables between the four programmes which are chained together to make up the total goniophotometric data analysis package.

Perhaps the most important advantage of the Cifer over the Sharp is the disc operating system. This allows data files to be saved and retrieved instantly without the operator having to load and position a tape. The disc system also provides a directory of all the files on an individual disc. This simplifies the routines that are required to retrieve a particular file. The rapid file access time also allows the programme to call up the calibration data as required from the disc, saving the operator the need to recalibrate every time the programme is run. Despite this, it is recommended that the calibration routines are selected whenever the goniophotometer is first switched on.

A further difference in the format between the Cifer and the Sharp version of the programme is the use of a menu by the Cifer version. This allows the operator to jump straight to the routine required without waiting for a particular option to be offered by the programme. The menu is displayed after the completion of each selected section. The graphics display is also kept in the memory allowing the curve to be displayed or superimposed on the text whenever required.

4.5 Conclusion

In use, the two programmes, one for the Sharp MZ80K and the other for the Cifer 2683 microcomputers, have greatly reduced the average time required for a sample analysis and calculation of results. Additionally, the opportunities for operator error have been greatly reduced. The facilities for data comparison, display and storage have made the interpretation of results considerably easier than the earlier system which employed a chart recorder.

CHAPTER 5

MODIFICATIONS TO THE GONIOPHOTOMETER

The basic goniophotometer, together with the nature of the information produced by this technique have been described in Chapter 2. At the outset of this work a simple motor drive instrument which was essentially, in terms of electronic components, a Brice Phoenix Series 2000 light scattering photometer was available. Although this was reasonably satisfactory for use in conjunction with a chart recorder, its performance was inadequate for use in conjunction with the microcomputer system described in the previous chapter. For this reason, it was necessary to redesign the electronic circuitry. At the same time the opportunity was taken to modify some aspects of the mechanical performance of the instrument. This chapter describes the redesign and construction of a goniophotometer suitable for interfacing with the microcomputer system described in Chapter 4.

5.1 Initial Modifications

The most important mechanical modification was concerned with the provision of a more sophisticated motor drive mechanism which could rotate the turntable and hence the photocell at a constant rate through the scanning angle. The drive was originally provided by a high torque Citenco electric motor manufactured by Griffen and George Ltd. The output shaft of the motor was connected to a worm drive reduction gear with a flexible drive coupling. The reduction gear assembly was mounted on the rear of the goniophotometer slightly above the turntable. A dog clutch mechanism was then used to transfer the drive to a rubber wheel which ran on the protruding serrated edge of the turntable. Control of the rotational speed of the turntable was achieved by the use of a Variac control, which permitted fine adjustment of the drive motor's speed. The combination of the Variac control and the reduction gears allowed the turntable's rotational speed to be varied over the range of 0.5 - 5 sec/degree.

As the turntable speed was uniform, it was possible to dispense with the conventional galvonometer normally used with this type of photometer, and replace it with a chart recorder.

Further modifications which improved the accuracy and reproducibility of results were carried out on the specimen mount. The original design of the mount enabled it to be positioned at any angle of incidence to the light beam. As no means of indicating the actual angle were provided, it was virtually impossible to relocate the sample mount at exactly the same angle for repeated measurements. The improved mount is provided with a locating pin which securely fits into slots machined around the edge of the sample holder. These slots are located at 15° intervals. Once a slot has been calibrated, the angle of incidence between the sample and the light beam is easily reproduced by simply locating the pin in the same slot for each measurement.

An additional facility which was provided at this time was a beam narrower. This consists of a blocking plate with a small aperture which when required is attached to the specimen table diaphragm mount. The beam narrower reduces the illuminated area of the sample from approximately 1.2 cm^2 to 0.2 cm^2. The advantages of this narrower beam are firstly that it increases the selectivity with which the sample area can be chosen, so avoiding surface scratches and blemishes caused by handling of the sample. Secondly, it minimises the errors caused by substrate non-planarity.

The original power supply and electronics associated with the photomultiplier were left unmodified at this stage of the work. The unit required a 115 volts, 60 cycle A.C. supply for both the light source and the photomultiplier. A voltage of up to 1000 volts D.C. was produced by a valve circuit which utilised high voltage D.C. peak to peak regulation. This regulated voltage was supplied to the photomultiplier tube by a system of sensitivity controls. These controls could adjust the voltage continuously over the range of 0 volts through to 1000 volts. This was achieved firstly by fixed steps through a coarse sensitivity voltage control, secondly by a continuously adjustable medium sensitivity control which was designed to overlap the voltage settings obtained by the coarse sensitivity control. In the higher voltage settings of the coarse sensitivity control, the fine sensitivity control was used in conjunction with the medium sensitivity control to provide fine adjustment.

The output from the photomultiplier covered the range of 0 to 10 millivolts D.C. A dark current zero adjustment control supplied a bucking voltage from a mercury cell. This control allowed the recorder to be zeroed from the front panel of the goniophotometer in order to compensate for phototube dark currents.

The light source is a 85 watt high pressure mercury vapour lamp type AH-3. The lamp intensity was regulated by a lamp ballast transformer with an automatic current regulating unit, mounted in a separate shielded case. This unit was designed to regulate the voltage supplied to the lamp as the arc was struck, slowly reducing the voltage as the mercury vaporised. Additionally, the constant current unit regulated the lamp intensity after the initial warm-up period.

5.2 Interfacing to the Computer

When the decision was made to interface a computer to the goniophotometer it was initially intended to simply use the computer in a similar manner to the chart recorder, which was already in use. The main advantage of the computer over a chart recorder would have been the speed with which the various parameters could be calculated from the goniophotometric data, once it had been stored in the computer's memory. When the logistics of operating a computer with the goniophotometer were thoroughly studied it was soon realised that a simple system would be impractical to use. This was due to the difficulty of synchronizing the two machines during a goniophotometric scan. If the output from the goniophotometer was to be interpreted with any accuracy, the computer needed to be aware of the position of the turntable and hence the photomultiplier at any moment during a scan. The only feasible way to indicate the turntable's position to the computer was by having an electrical output from the goniophotometer which would vary linearly with the rotation of the turntable. This was achieved by mounting a multiturn potentiometer adjacent to the turntable drive mechanism at the rear of the goniophotometer. A small gear wheel attached to the potentiometer shaft was held against the turntable edge by a spring loaded lever, so that any rotation of the turntable altered the setting of the potentiometer. A small five volt stabilised power supply was wired across the potentiometer, the wiper of which was connected to one input of the analog to digital convertor. The resulting voltage at the wiper varied between 0 and 5 volts depending upon the position of the turntable. This output was totally isolated from the electronics associated with the goniophotometer and therefore could be monitored by the computer independently of the photomultiplier output.

In addition to the provision of a turntable output it was necessary to construct a buffer amplifier in order to interface the photomultiplier output with the analog to digital converter. This unit was required as the output from the photomultiplier needed to be loaded by an impedance that was similar to that of the original galvanometer. Another factor which necessitated the use of a buffer amplifier was that the output of the goniophotometer was negative with respect to ground, whereas the analog to digital converter requires a positive voltage. To solve these problems the buffer amplifier was constructed using two field effect transistor operational amplifiers. F.E.T. amplifiers were chosen so as to provide the necessary matching impedance. Two operational amplifiers were necessary because the maximum output from the goniophotometer which represented full scale deflection was only 10 millivolts, whereas the analog to digital converter required this maximum to be 5 volts. A single operational amplifier would be operating at its limits of stability to provide this much gain, so the first amplifier was wired in an inverting mode providing a positive output of a maximum of 0.25 volts. The second amplifier was non-inverting increasing the output to 5 volts maximum (see Figure 5.1). The amplifiers were powered by a small ± 15 volt stabilised supply.

5.3 Initial Operation of the Goniophotometer with the Computer

After the initial modifications described above had been completed and the interfacing amplifiers constructed, it was possible to use the goniophotometer in conjunction with the programme which had already been written for use on a Sharp MZ80K, 48k byte microcomputer. This early programme had been written and debugged using simulated goniophotometric data. As a direct result of this, when the programme was run in conjunction with the goniophotometer, numerous errors came to light. The majority of

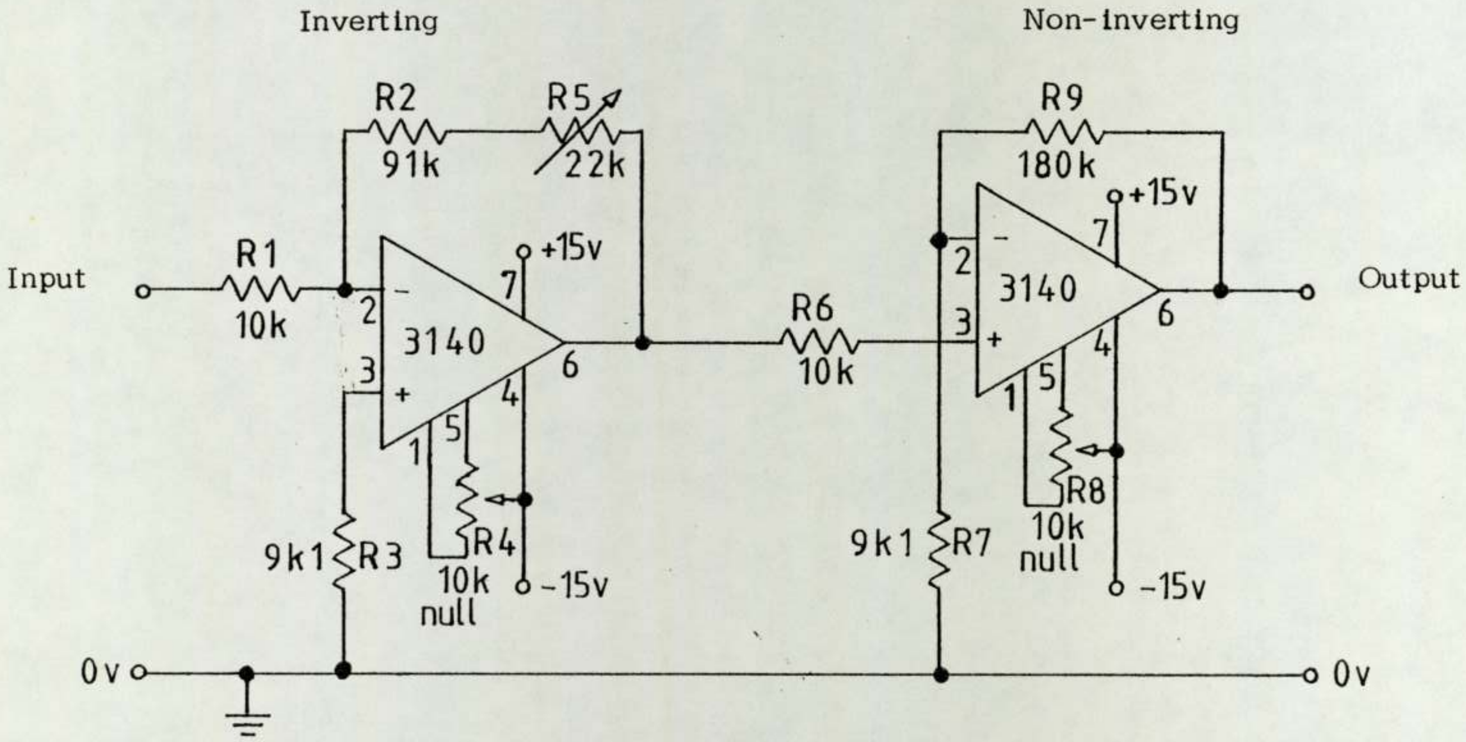


Figure 5.1: F.E.T. Buffer Amplifier: Design I

these errors were not due to bugs within the actual programme, but were in fact caused by previously undetectable faults with the goniophotometer output. At first, many of the faults were not recognised as originating from the goniophotometer since they appeared to be symptoms of faulty interfacing between the analog to digital converter and the computer. The faults appeared on the computer display as a noisy signal superimposed over the goniophotometric curve. The noise seemingly followed a rough sinasoidal pattern with occasional "spikes". This noise did not appear on the chart recorder trace of the output taken simultaneously with the computer data. Initially, it was believed to be interference generated by other equipment, picked up by the interconnecting leads in use with the computer system. This theory was strengthened by the continued presence of the interference on the computer data when the goniophotometer output was reduced to zero.

Unfortunately this noise frequently influenced the calculation of the peak height and the peak position by the computer. This was especially true if the voltage "spikes" were of greater amplitude than that of the goniophotometric peak. Furthermore, it was impossible to calculate the so-called diffuse intensity (Id - see Chapter 2), as this was of considerably lower amplitude than that of the noise present.

Eventually the interference was discovered to be a very high frequency alternating signal that was superimposed on the output of the photomultiplier. This signal was not detectable on the chart recorder due to the slowness of response of the pen servo system in comparison with the speed of data collection by the computer. To remove the noise a tuned resistor/capacitor network was constructed on the front end of the buffer amplifier to filter out the high frequency signal. The increased capacitance of this circuit unfortunately slowed down the response of the buffer amplifier to the photomultiplier's signal to approximately that of the chart recorder. In order to improve the response the turntable speed was subsequently reduced to allow for the damping effect of the electronics. At these slow speeds the turntable movement tended to be erratic and occasionally it would stop rotating altogether.

Further problems were discovered with the turntable output. This frequently went out of calibration if the photomultiplier was allowed to strike the end stops during a scan. Additionally when an occasion arose which required the photomultiplier to scan through a wider arc around the sample, the turntable would exceed the voltage range of the analog to digital convertor. Whenever this latter fault occurred the instrument had to be reset. This involved repositioning the gear wheel on the potentiometer shaft. This was a very cumbersome operation which had to be followed by careful re-calibration and alterations to certain constants within the computer programme.

At this stage of the work, even though the computer had greatly increased the rate of data analysis, it was taking considerably longer to collect the raw data from the goniophotometer than it did originally with the chart recorder. The calibration of the photomultiplier still required the use of a chart recorder, but due to the sensitivity of the computer it had to be checked after every scan as the computer programme indicated a steady base line drift which was present throughout every scan.

These difficulties and faults, combined with the inconvenience of having numerous add on units attached to the goniophotometer, led to the decision to construct from scratch an automated goniophotometer designed specifically for use with a computer.

5.4 Final Design and Modifications to the Goniophotometer

The main criteria which influenced this stage of the work were that the goniophotometer should be totally self-contained, possessing outputs that are compatible with standard analogue to digital converters. In addition it was required to be more versatile and quicker to use. This specifically applied to the photocell scan rates and the resolution of the turntable output. The original design of the high voltage power supply using valve circuitry needed replacing by a modern semiconductor circuit which would be inherently more stable and reliable. When all of these modifications were considered, it was decided to obtain a second Brice Phoenix Light Scattering Photometer as this represented a relatively inexpensive way of obtaining a suitable optical bench and light tight box. This photometer could be stripped down to its basic components and rebuilt more or less from scratch to the new specifications. The actual reconstruction can be divided into two main areas:-

(1) Mechanical

(2) Electrical

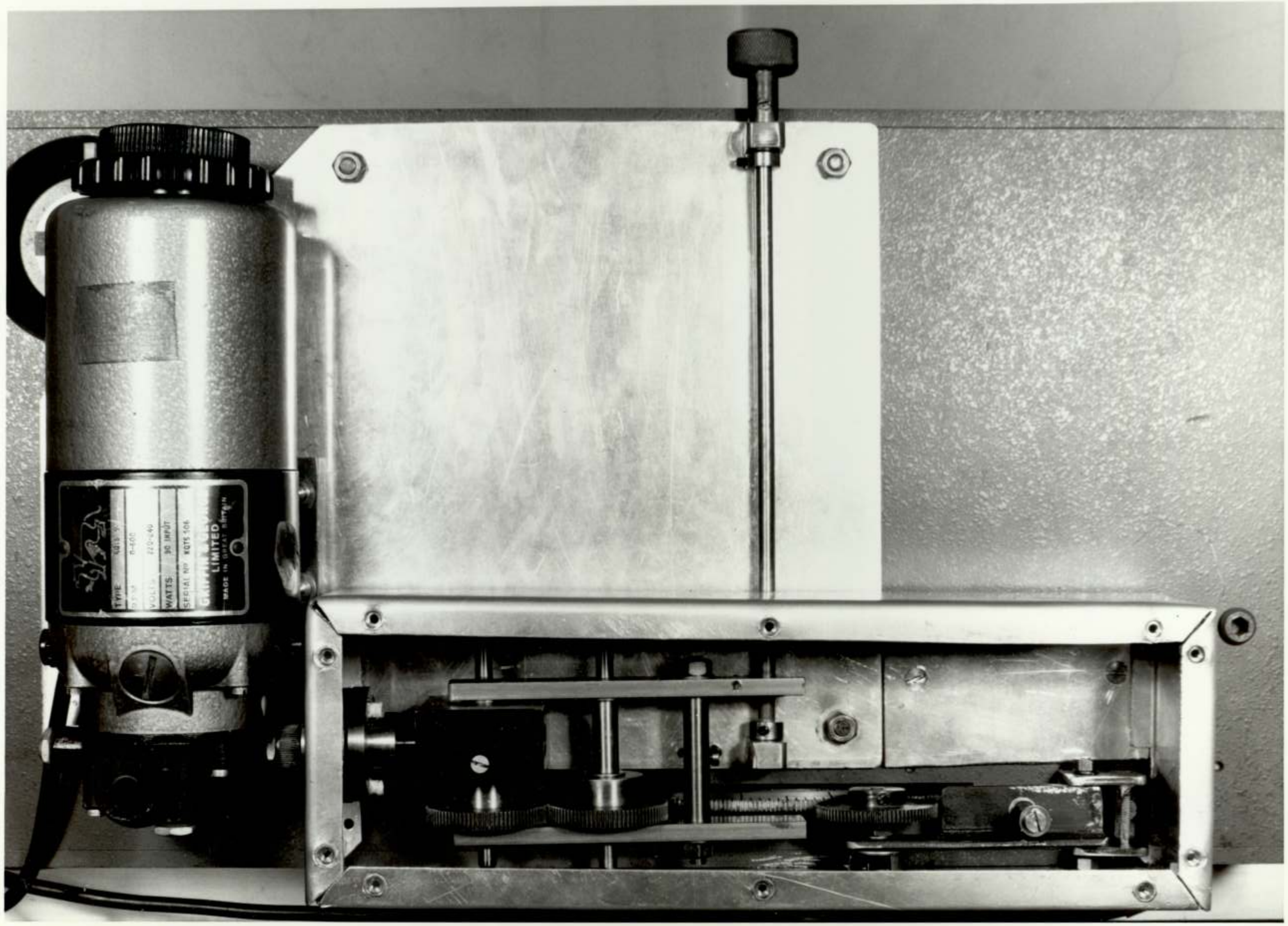
These are dealt with separately below.

5.4.1 Mechnical Modifications

After the photometer had been dismantled all moving parts were examined for wear. The two main bearings which support the turntable shaft were replaced due to the presence of excessive play. The turntable itself was dispatched to a gear cutters in order to have standard pitched gear teeth milled around its perimeter. All other components that were to be retained in the final goniophotometer, essentially the optical bench, the light source, the shutter, the filters and collimating tube, were cleaned and carefully stored. The light tight working compartment was dismantled in order to install the new gear system at the rear of the goniophotometer.

A Citenco high torque electric motor was retained as the drive source for the turntable. The difference between this and the earlier version is that the Variac control is dispensed with and the motor is mounted vertically, directly onto the back plate of the goniophotometer (see Plate 5.1). In this position both the motor ON/OFF switch and the speed control are easily accessible at the top of the goniophotometer. The motor is wired via a fuse to a 240 volt A.C. bus bar inside the goniophotometer. The drive from the motor is

Plate 5.1: Rear view of goniophotometer showing turntable drive mechanism



connected directly to a 25:1 worm drive reduction gear, dispensing with the flexible coupling and the dog clutch. Output from the worm drive is transferred by a gear train to the turntable. This gear train is mounted on a cam operated, spring loaded arm. Control of the cam is by a lever positioned next to the motor controls at the top of the goniophotometer. When this lever is operated the gears are meshed with the teeth on the turntable, giving a positive direct drive. Since the clutch and flexible drive are no longer used, the whiplash and erratic movements of the turntable have been corrected. The reduction gearing employed allows the Citenco motor to run at higher speeds with greater torque, hence giving a much steadier drive to the turntable. The rotational speed of the turntable is easily reproduced as the use of the cam to disengage the gear train allows the motor to be left running continuously. The whole of this assembly is protected by a metal casing bolted to the rear of the goniophotometer.

Within the actual light tight compartment which houses the photomultiplier only two modifications have been implemented. The first of these was the removal of the mounting brackets (which had become obsolete) attached to the rotating arm holding the photomultiplier housing. This has increased the angle through which the photomultiplier is capable of scanning from 185 degrees to 280 degrees. Unfortunately it is impossible to scan through a complete 360 degrees due to fouling of the collimating tube and the connecting wires to the photomultiplier. The second modification is the provision of a microswitch adjacent to the lower end stop for the rotating arm (see Plate 5.2). This facility proved to be necessary since the clutch mechanism had been dispensed with in the turntable drive. The switch disconnects the electrical supply from the drive motor immediately before the photomultiplier arm hits the end stop. The supply is restored once the drive gears are disengaged and the turntable rotated away from this stop.

The turntable output is still derived from a low voltage D.C. power supply by the use of a multiturn potentiometer, driven by the turntable. A lower gear ratio has been used with this version ensuring that the potentiometer does not exceed its designed operating travel when the turntable is rotated towards either extreme of its scanning range. Coarse mechanical calibration is allowed by the provision of a spring loaded arm which tensions the potentiometer gear against the turntable. This permits the gear to be disengaged from the turntable and rotated without the need to dismantle the assembly holding the potentiometer.

The final mechanical modifications consisted of providing mounting brackets for the new circuits plus the provision of an edgewise meter, which indicates the output voltage from the photomultiplier. This meter is required as an aid to calibration and filter selection, since other than the computer display there is no means of monitoring

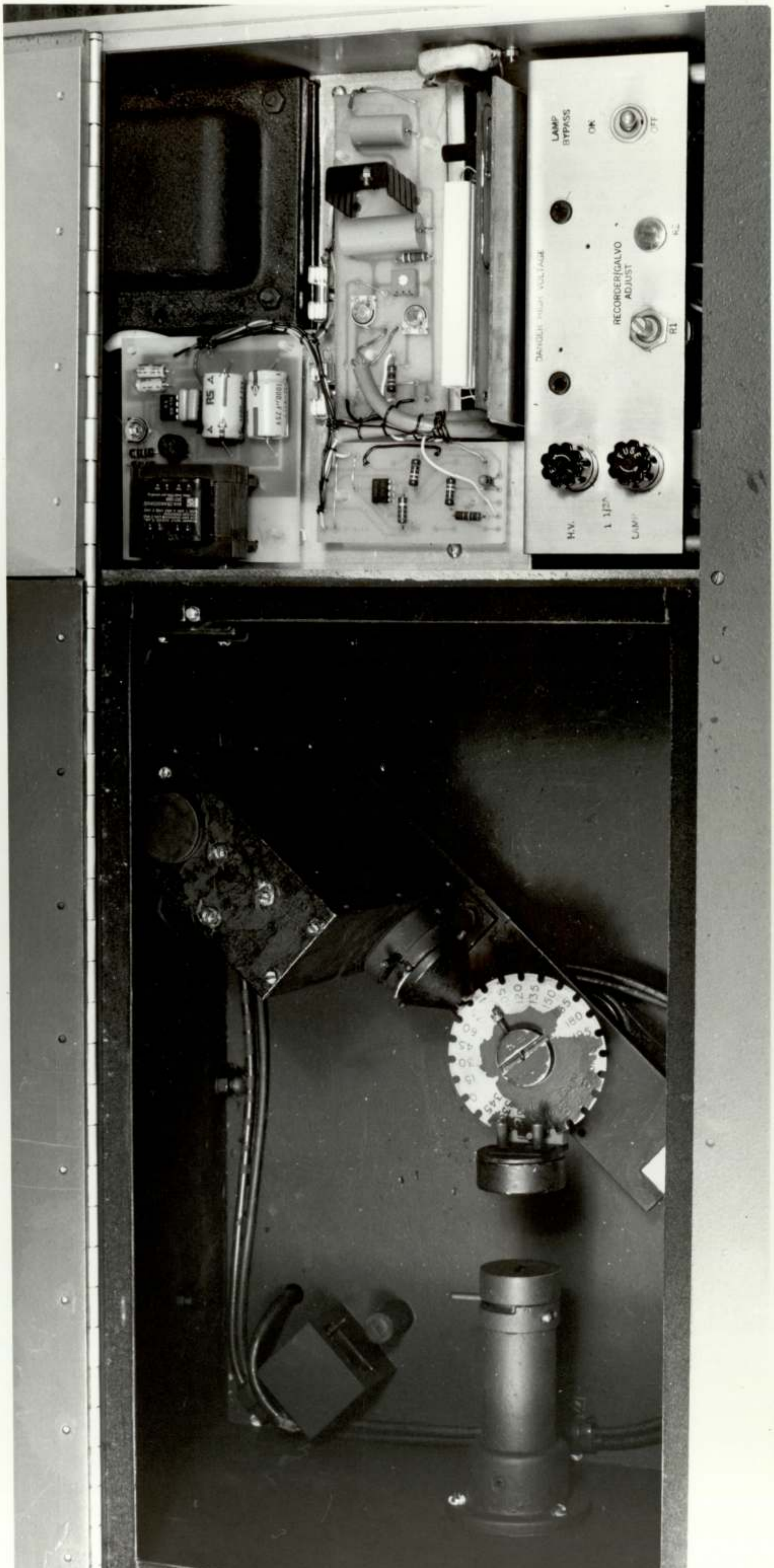


Plate 5.2: Interior of goniophotometer

the photomultiplier output, as the chart recorder has been dispensed with.

5.4.2 Electrical Modifications

The simplest but perhaps the most essential electrical modification to the basic light scattering photometer was the conversion which enables the machine to operate on a 240 volt A.C. supply as opposed to the original design which used a 115 volt A.C. supply. This was achieved by installing an auto transformer inside the electrical compartment which lowers the mains voltage to 115 volts A.C. The output from this transformer supplies both the lamp control circuitry and the high voltage circuits for the photomultiplier. The supply for the computer interface buffer circuits is derived from the original 240 volt A.C. supply.

The original design for the lamp control circuit was retained, but the power factor correction capacitor was replaced, along with the bleed resistor in order to ensure the future reliability of the circuit. In addition a bypass switch was installed in the lamp supply circuit. This was provided in order to improve the lamp life, by allowing the high voltage supply to be switched off if the machine is to be left unattended for short periods without extinguising the mercury vapour lamp.

As mentioned previously, the original valve-controlled high voltage supply was completely dispensed with. This was replaced by a comparatively simple semi-conductor circuit. The new circuit was designed to provide a stabilised output of approximately 1200 volts without any voltage spikes or drift. It was possible to utilize a conventional basic high-voltage circuit since it was not necessary to include any load regulation as the photomultiplier tube provides a constant load. The simplicity of the circuit has the advantage of improving the reliability of the supply as there are fewer components subjected to the high voltages and therefore fewer connections to fail.

The 110 volt A.C. supply is connected to the primary of a high ratio transformer together with a 3 µf power factor correction capacitor (see Figure 5.2). The two secondary windings are series connected and feed a bridge rectifier consisting of four BYX 10 high voltage diodes. A 50 H swinging choke is series connected to a 2 µf capacitor and a 125 K ohm bleed resistor to provide the smoothing and regulation of the power supply. The positive rail is grounded while the negative rail feeds the original calibration controls via a 1 meg. ohm preset resistor. The ouput from the calibration controls is connected to the photomultiplier tube via a microswitch, which interrupts the supply when the light tight compartment lid is opened. This serves two purposes, firstly to minimise the risk of an electric shock to the operator and secondly to protect the photomultiplier tube when it is exposed to bright room lights.

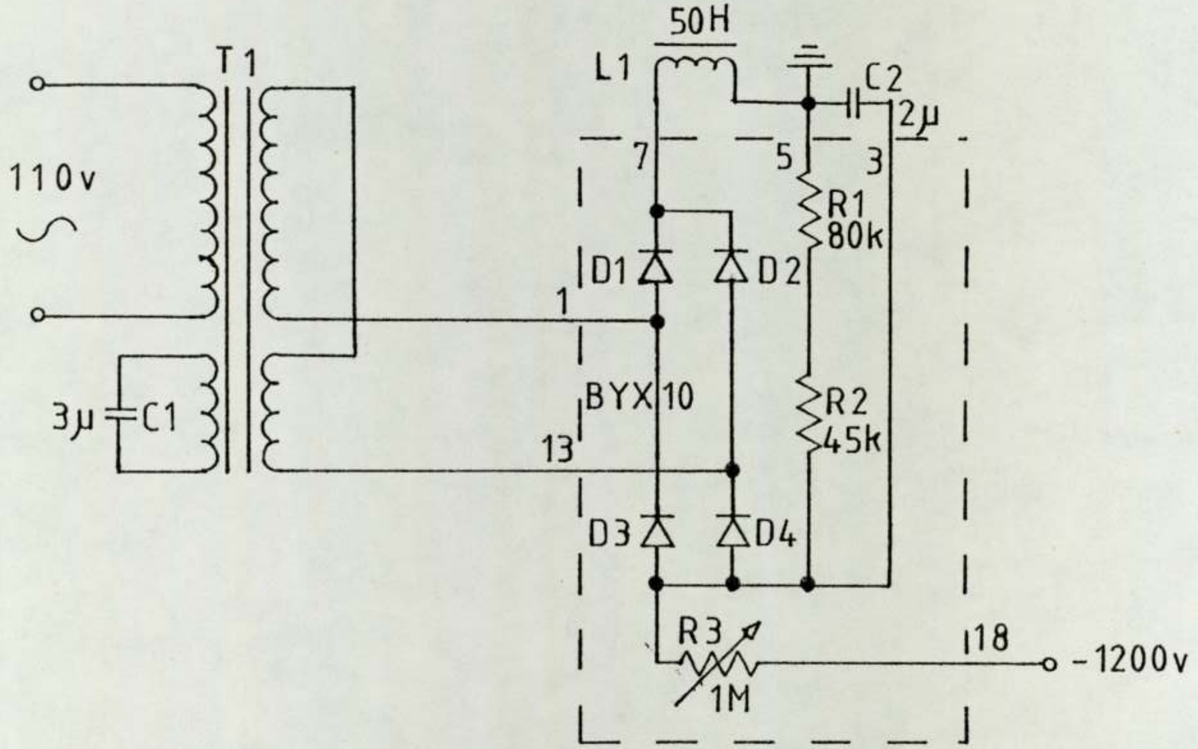


Figure 5.2: High voltage supply circuit

In order to facilitate maintenance and repairs the components which are most likely to fail in the high voltage power supply (the diodes and the bleed resistor (see Figure 5.2)) are mounted on a plug in circuit board. This printed circuit board was made from epoxy glass copper-clad board to ensure that the circuit can withstand the heat and high voltages generated by this section of the power supply. The method by which this and the other printed circuit boards were produced is described later in this chapter.

The output from the photomultiplier is negative with respect to ground, with a typical maximum value of 0.5 volts. A three pole, two way switch, centre off, is used to select matching impedances to suit either a chart recorder or a digital indicator such as a computer interface. This switch should be set to the recorder position if a chart recorder is to be used in addition to the computer. Zero adjustment of the signal is provided for by an adjustable bucking voltage which is applied to photomultiplier output. This voltage is supplied by the same circuit as the turntable output and is described later in this section.

The photomultiplier output is inverted and amplified ten fold by a single F.E.T. operational amplifier. Only a single amplifier is required as the new high voltage supply enables the photomultiplier tube to give a much higher output than did the previous valve supply. A F.E.T. amplifier was chosen because of its high input impedance which reduces the current load on the photomultiplier tube. The buffer amplifier (see Figure 5.3) containing the F.E.T. amplifier also incorporates a filter circuit, at the front end, to remove any voltage spikes which may be present.

The supply for the buffer amplifier is provided by a 15-0-15 volt stabilised power supply (see Figure 5.4 and Plate 5.2). This power supply uses a dual monolithic regulator to provide up to 50 milliamps per rail. It also provides an unregulated output of 18 volts D.C. for the turntable output and the black light zero circuit. This circuit (see Figure 5.5) uses a one amp fixed voltage regulator to supply the potentiometer connected to the turntable. The two variable resistors R2 and R3 enable the voltage to be adjusted for calibration purposes. R2 sets the voltage range and hence the resolution of the output, while R3 adjusts the zero position of the turntable output. The preset R4 sets the voltage available at the black light zero control. It is normally set to give approximately 1.5 volts.

The output from the buffer amplifier is wired to a nine pin subminiature 'D' type socket along with the turntable output, for connection to the computer. An edgewise 100 µA meter is also connected in parallel with the buffer amplifier output. This gives an instant visual indication of the photomultiplier output, which is useful during the calibration of the photomultiplier and the selection of the filters.

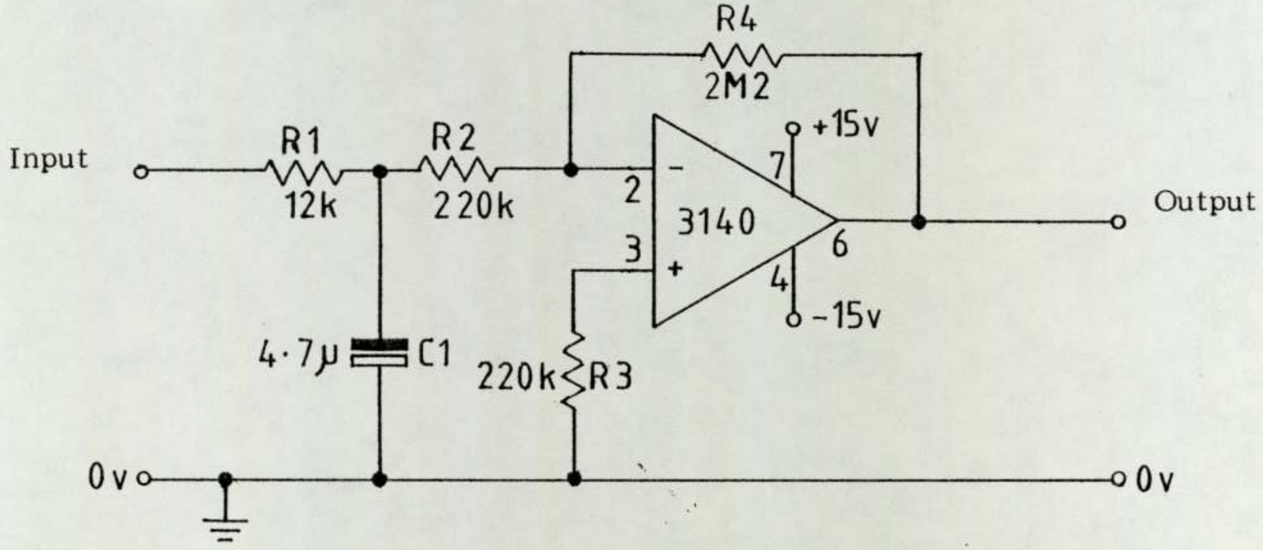


Figure 5.3: F.E.T. Buffer amplifier: Design II

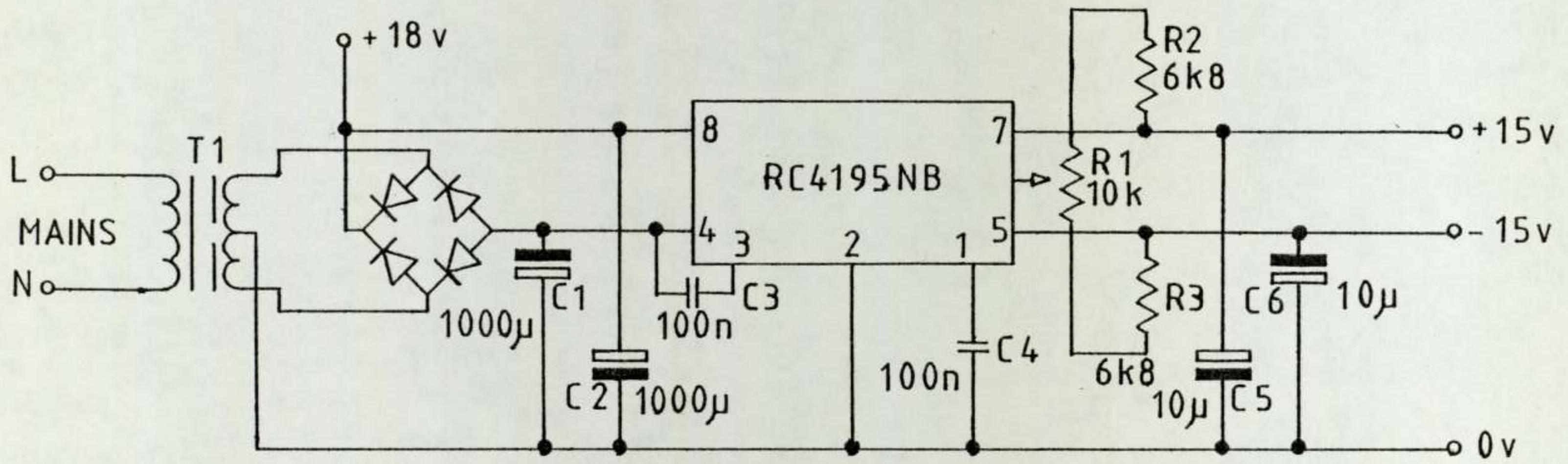


Figure 5.4: Low voltage supply circuit

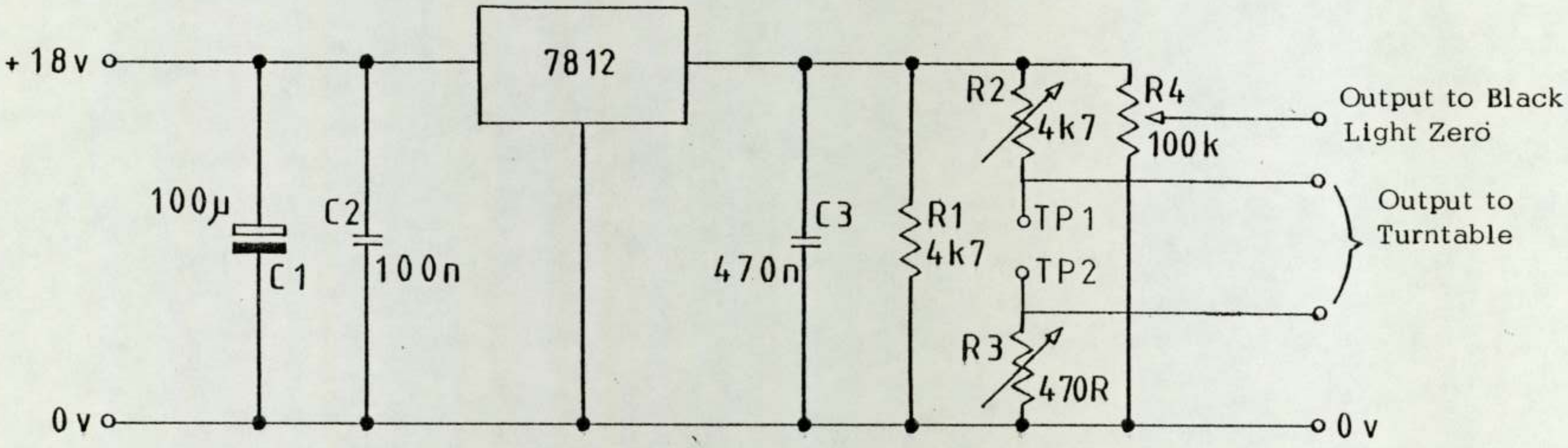


Figure 5.5: Turntable and Black Light Zero Supply Circuit

5.5 Preparation of Printed Circuit Boards

Since the circuits described in this Chapter were specifically designed for use in the goniophotometer, the few commercial circuit boards which were available were not entirely suitable, nor would they fit into the space available within the electronics compartment of the machine. These facts combined with the critical layout required by the high voltage circuits necessitated the individual production of high quality circuit boards.

The first stage in the production of these boards was designing the layout for the components which were to be mounted and planning the routes of the circuit tracks. Once a suitable layout had been achieved it was transferred onto Melinex sheets using an etch resistant transfer system.

The copper clad epoxy glass boards which were to be etched were thoroughly degreased and dried. A thin coat of AZ-1300 series positive photo-resist manufactured by the Shipley Co. Ltd, Irvine, U.S.A., was spun onto the copper surface. After checking that the surface was free from dust, the boards were placed in an oven and the resist baked at 90°C for 15 minutes. When the boards had cooled the Melinex transfer was placed over the copper and the resist exposed under a mercury vapour lamp for approximately 30 minutes. After exposure the boards were placed in MF-312 developer, also manufactured by the Shipley Co. Ltd, for precisely 40 seconds at exactly 20°C. The temperature and duration of development are critical as excessive time or a lower temperature may result in some attack on the unexposed photo-resist. Once developed the boards were immediately rinsed in distilled water and then baked again at 100°C for 40 minutes.

The boards were etched in a solution of 500 g of ferric chloride hexahydrate per litre of water at 40°C. The remaining etch resist was removed by cleaning with acetone and finally the boards were drilled to take the electronic components.

5.6 Operating Procedure for the Modified Goniophotometer

The following instructions describe the method of calibration and operation of the modified goniophotometer. The instructions are divided into two sections. The first section deals with the calibration of the optical system and the turntable computer output. These only need recalibration if the machine is moved or if it is to be used over a different turntable scanning range. The second section covers the daily calibration of the output and general use of the machine. The instructions in this section assume that the goniophotometer is being used in conjunction with the computer programme described in Chapter 4.

5.6.1 Procedure for Optical and Turntable Calibration

1) Check that both the mains switch and the lamp bypass switch are OFF.
2) Connect the machine to the mains supply.

3) Position the turntable at 136°.

4) Remove the cover plate from the motor drive unit at the rear of the machine.

5) Disengage the turntable potentiometer and rotate it anticlockwise to the limit of its travel. Re-engage the gears and replace the cover.

6) Rotate the turntable to 136° - 2x (where x = lowest angle to be scanned).

7) Using a voltmeter adjust R2 to give 10 volts at TP1 (see Figure 5.5).

8) Check that the voltage at TP2 (see Figure 5.5) is approximately 4 millivolts. Adjust R3 to correct it.

9) Switch on the mains on/off switch on the front panel.

10) Allow the lamp to warm up for 30 minutes.

11) Remove sample holder and select all neutral filters.

12) Select recorder O/P on front panel.

13) Rotate the turntable to approximately zero degrees.

14) Open the shutter and carefully adjust the turntable until the meter indicates a maximum value. Note the angle of the turntable (A).

15) Position a glass slide in the specimen holder at the angle of incidence to be used for the analysis.

16) Rotate the turntable clockwise to approximately twice the angle of incidence and adjust to give a maximum reading on the meter. Note the angle (B).

17) Close the shutter.

18) The true angle of incidence of the sample to the light beam is $90^\circ - (\frac{B - A}{2})$.

19) The angle at which the photomultiplier is normal to the surface is $3(\frac{B - A}{2}) + A$ degrees.

5.6.2 General Calibration and Sample Analysis

1) Connect to the mains supply.
2) Switch on the mains on/off switch on the front panel.
3) Allow 2 hours for the photomultiplier to stabilise.
4) Switch on the A to D converter.
5) Load and run the computer programme.
6) Follow the displayed instructions for the turntable and gain calibration.
7) Load the sample and rotate the turntable to approximately twice the angle of incidence.
8) Open the shutter and select the appropriate filters to give a full scale reading on the output meter.
9) Close the shutter and adjust the zero control to give a zero reading on the output meter.
10) Switch on the drive motor and engage the turntable drive.
11) Adjust the motor speed to give the desired rate of rotation.
12) Disengage the turntable drive.
13) Continue with the computer programme instructions.
14) When computer produces warning bleeps close the light shutter, disengage the turntable drive and remove the sample.

15) Continue with the computer programme instructions.

5.7 Conclusion

The modifications to the goniophotometer have produced an analytical machine which is relatively simple to operate, self contained and reliable. The facilities which enable it to be directly interfaced with a computer have reduced the average sample run and calculation time from 2 hours to 5 minutes. In addition, the data is stored by the computer allowing rapid access and easy comparison of results.

CHAPTER 6

THE INTERACTION OF NITRIC OXIDE WITH POLY (VINYL CHLORIDE) SURFACE COATINGS: A PRELIMINARY STUDY

6.1 Introduction

As was stated in Chapter 1, little work has been reported on the interaction of nitric oxide on polymeric surface coatings. This is especially the case in situations where nitric oxide is present in an environment as an atmospheric pollutant, where there is no recorded work.

Since little is known about the interaction of nitric oxide with surface coatings, a preliminary investigation was undertaken. At the outset it was not known whether NO has a detrimental or stabilising effect on the polymer, nor was it clear whether this interaction is a bulk or surface effect. Additionally it was not known whether or not the stabilisers and pigmentation present in the surface coatings would influence these interactions. The aim of this initial investigation was to attempt to provide an indication of the effect and nature of the interaction of NO with polymeric surface coatings.

In this limited exploratory study the relative effects of nitric oxide and ultra-violet light, both separately and taken together, have been examined using a series of poly (vinyl chloride) (PVC) based coatings. PVC was selected for this initial work as it is chosen for use in many industrial environments, since it combines excellent chemical resistance with flexibility. There are various stabilisers available for use with PVC. It was hoped that by examining different formulations, which incorporate these stabilisers in various combinations, it would be possible to isolate their effects. Once these effects have been isolated it was also hoped that it would be possible to see if the stabilisers are involved in the interaction of NO with PVC.

This work was carried out in a basic manner using the apparatus described in the previous chapters, but without the sophistication of temperature cycling, gas flow or humidity control. No attempt was made to duplicate an urban or industrial environment. The ageing techniques were chosen simply to indicate the types of effects involved with NO, and polymeric surface coatings.

6.2 Methods and Materials

Three batches, each of seven samples, were prepared. These batches were comprised of detached, primed, unprimed and unpigmented poly (vinyl chloride) films. The films were coded 6, 7, 6P, 7P, 6NP, 7NP and PVC (UP). The details of the nature of the ageing techniques applied, and the nature of each sample, are given in Table 2.3. The samples with prefix (6) contain a uv stabiliser, while samples with prefix (7) contain a thermal stabiliser. Both types of film contain white pigmentation. The samples coded PVC (UP) contain no stabilisers, pigmentation or plasticisers. This last formulation was included to act as a reference in order to indicate the influence, if any, of the various additives, such as stabilisers, on the reactions of NO with the PVC films.

Each batch of seven samples was either exposed to uv radiation, nitric oxide, or to uv radiation and nitric oxide simultaneously. The methods employed are described in Chapter 2, section 2.2.

6.3 Results

The results obtained from the initial experiment are described under the three following headings, goniophotometry, colorimetry and micro-indentation.

6.3.1 Goniophotometry

The goniophotometry terms referred to in this section are described in Chapter 2, section 2.3.2.2.

The first noticeable change likely to occur on a goniophotometric curve, due to the deterioration of a coating, is usually a reduction in the specular intensity (Is) with no discernible change in the diffuse intensity (Id). There is no increase in the surface rugosity of the sample, both in terms of an increased population of imperfections and in increased size. At this stage the imperfections are small compared to the wavelength of the incident light ($\approx 0.5\,\mu m$). As the mean size of the imperfections approaches the wavelength of the light beam, peak broadening is observed. This is usually detected, at this stage, by an increase in width at half peak height ($W\frac{1}{2}$). Both the Is and the $W\frac{1}{2}$ values are incorporated in the gloss factor (GF). This quantity gives the best indication of the overall degree of degradation that has occurred on the surface of a polymer film.

Since the Is and GF between them indicate the overall state of the polymer surface, they are the two values that are discussed in this section. The results referred to are shown in Figures 6.1 and 6.2 as a percentage increase or decrease on the original value for the unaged sample.

In all cases there was a decrease in the Is value after exposure to nitric oxide. The combined exposure to ultra-violet light and nitric oxide simultaneously apparently had less effect than ultra-violet light or nitric oxide alone, on the Is value of most samples. In fact, in some cases a slight increase has occurred. The particular examples of this are the detached films (7) and PVC (UP). Samples (6NP) and (7P) show the largest decrease in Is after NO/uv exposure.

The effect of the ultra-violet light was substantial on all samples of formulation (7), with a large decrease in Is occurring in each case.

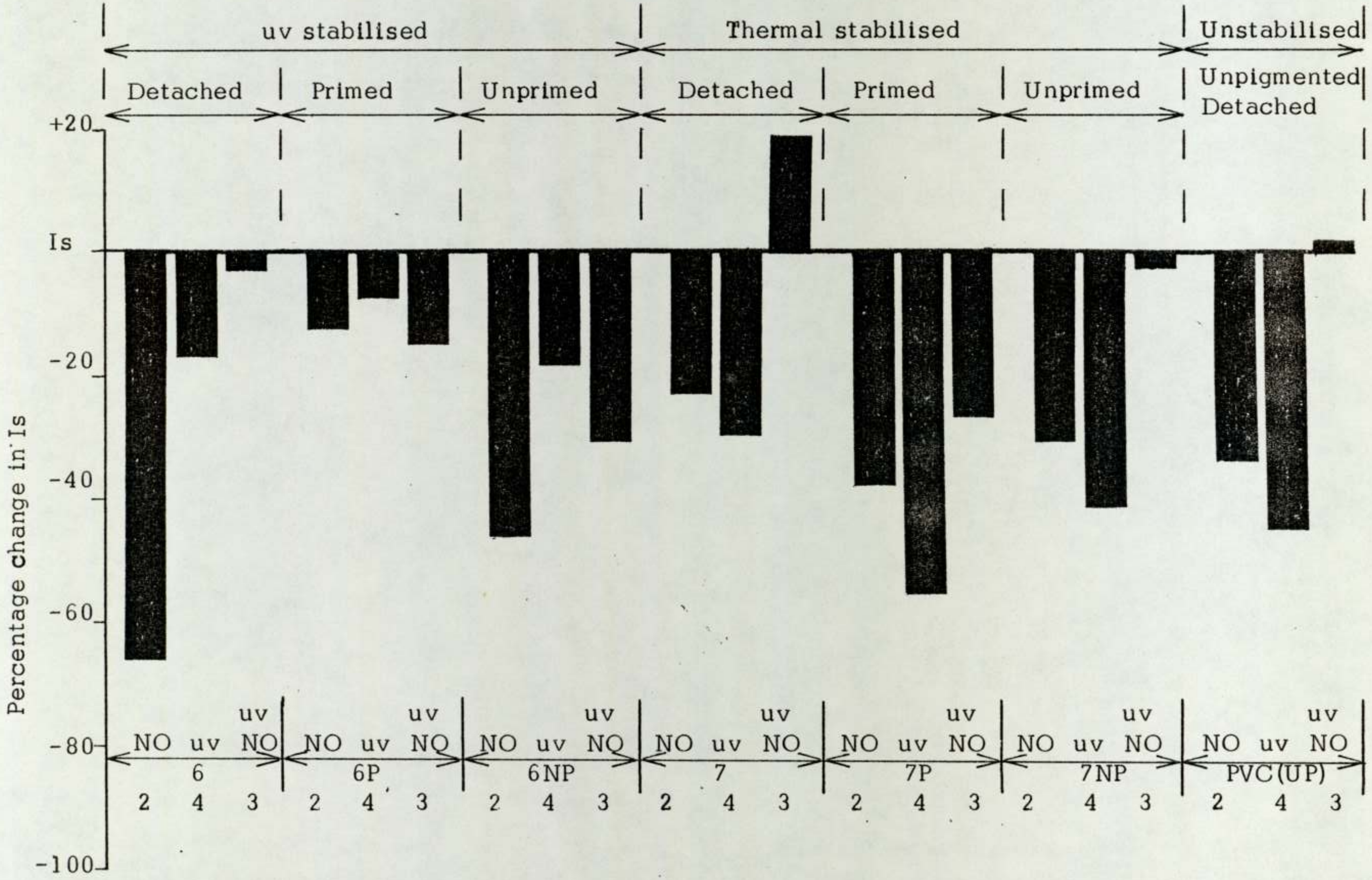


Figure 6.1: PVC coatings - Change in Is after ageing

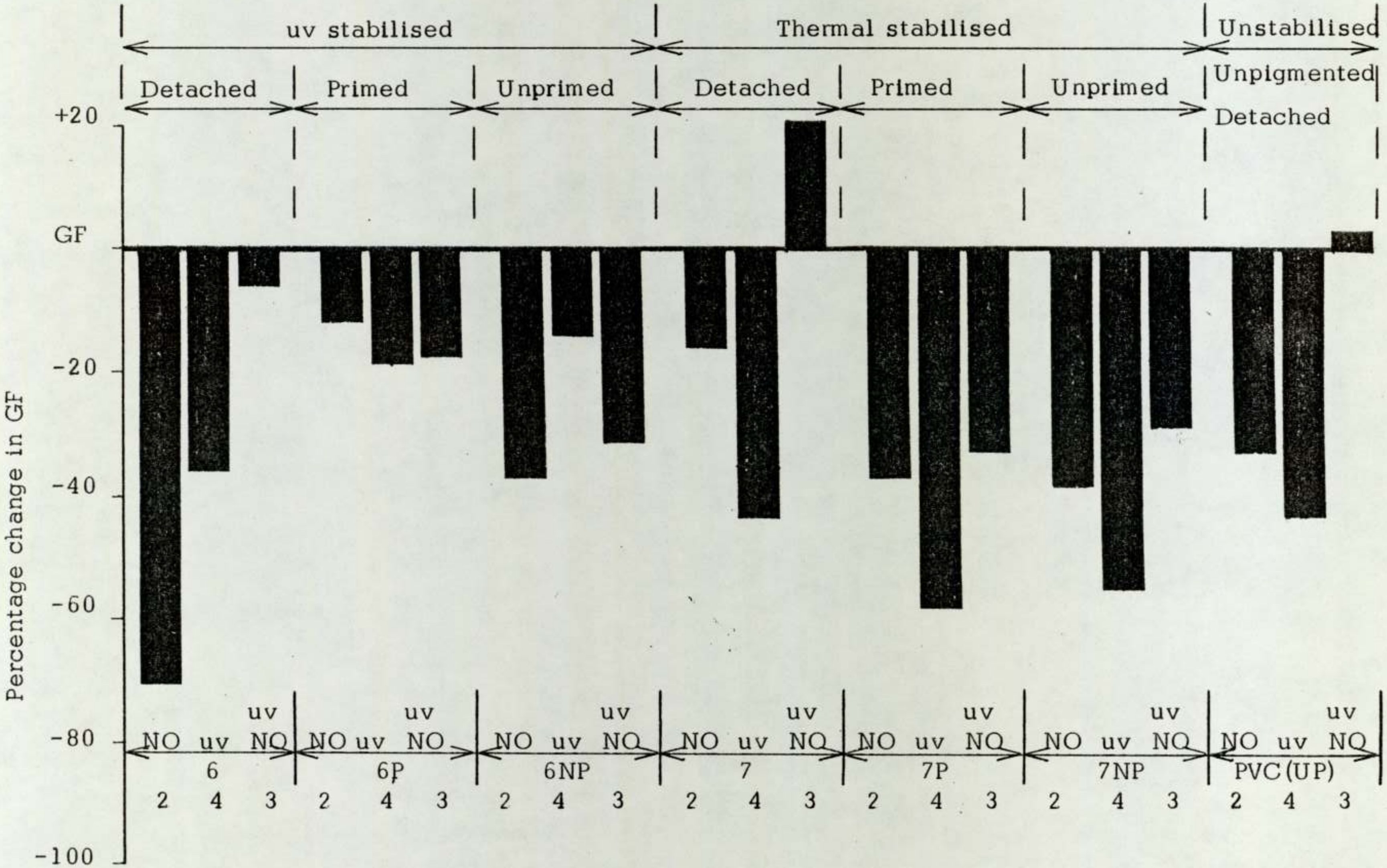


Figure 6.2: PVC coatings - Change in GF after ageing

However, with formulation (6) the decrease in Is is considerably less than that of formulation (7). The effects of the ultra-violet light were apparently independent of the presence or absence of a substrate in all cases.

In all cases the gloss factor (GF) fell substantially after exposure to nitric oxide (see Figure 6.2). The detached film of formulation (6) showing the largest decrease. The change in value of the gloss factor for samples exposed to NO and uv light simultaneously was less in all cases, except for samples coded (6P), than the change after exposure to NO alone. After exposure to uv light there was a large decrease in gloss factor in the case of PVC (UP) and with all samples of formulation (7). This decrease does not occur with formulation (6).

6.3.2 Colorimetry

The colorimetry results referred to in this section are shown in Tables 6.1 - 6.4. The results were not converted to CIE X, Y, Z values at this stage of the work, as comparisons were only required between samples directly involved in this work.

In all cases there was very little change in the percentage reflectance of the red and green light. With the PVC (UP) samples the slight increases indicated are most likely due to errors in the calibration of the colorimeter. Since the instrument is very sensitive to stray

SAMPLE	SPECIMEN NO.	AGEING TREATMENT	PERCENTAGE REFLECTANCE		
			R	G	B
6	1	-	79.60	80.12	77.62
	2	-	80.05	80.65	79.47
		NO, 2 hours	79.26	78.05	60.25
	3	-	80.02	80.41	77.49
		NO + uv, 2hrs	79.19	78.12	60.05
	4	-	80.17	80.60	77.96
		uv, 2 hours	79.74	80.19	76.90
7	1	-	77.04	76.90	69.76
	2	-	76.49	76.46	69.94
		NO, 2 hours	77.92	76.82	60.00
	3	-	76.67	76.59	68.78
		NO + uv, 2 hrs	78.21	77.34	60.49
	4	-	77.20	77.88	72.52
		uv, 2 hours	77.53	77.67	71.66

Table 6.1: Tristimulus Colorimeter Values for PVC Films

SAMPLE	SPECIMEN NO.	AGEING TREATMENT	PERCENTAGE REFLECTANCE		
			R	G	B
6P	1	-	83.54	82.87	75.81
	2	-	83.82	83.26	76.24
		NO, 2 hours	81.90	79.69	58.98
	3	-	83.64	83.64	79.53
		NO + uv, 2 hrs	81.30	79.04	57.50
	4	-	83.14	82.75	76.84
		uv, 2 hours	83.12	82.75	76.36
7P	1	-	81.98	81.96	71.21
	2	-	82.23	81.93	73.56
		NO, 2 hours	81.72	80.13	62.77
	3	-	82.54	82.37	76.06
		NO + uv, 2 hrs	82.16	80.99	65.10
	4	-	80.93	81.53	72.88
		uv, 2 hours	81.86	81.28	72.26

Table 6.2: Tristimulus Colorimeter Values for PVC Films

SAMPLE	SPECIMEN NO.	AGEING TREATMENT	PERCENTAGE REFLECTANCE		
			R	G	B
6NP	1	-	81.52	82.11	83.10
	2	-	82.50	82.98	83.66
		NO, 2 hours	82.14	81.17	66.88
	3	-	82.27	82.88	83.74
		NO + uv, 2 hrs	81.48	80.30	67.57
	4	-	82.12	82.71	83.82
		uv, 2 hours	82.03	82.74	83.58
7NP	1	-	81.05	81.71	82.79
	2	-	81.20	81.47	82.22
		NO, 2 hours	81.50	81.57	77.25
	3	-	81.95	82.18	82.64
		NO + uv, 2 hrs	82.21	82.63	79.33
	4	-	81.29	81.87	82.56
		uv, 2 hours	80.65	81.28	81.78

Table 6.3: Tristimulus Colorimeter Values for PVC Films

SAMPLE	SPECIMEN NO.	AGEING TREATMENT	PERCENTAGE REFLECTANCE		
			R	G	B
PVC (UP)	1	-	3.0	3.01	3.36
	2	-	2.53	2.63	3.07
		NO, 2 hours	2.81	2.87	2.88
	3	-	2.76	2.89	3.34
		NO + uv, 2 hrs	3.22	3.26	3.47
	4	-	3.41	3.46	3.86
		uv, 2 hours	3.44	3.48	3.79
			PERCENTAGE TRANSMITTANCE		
			R	G	B
PVC (UP)	1	-	87.14	86.70	85.49
	2	-	88.15	88.35	85.68
		NO, 2 hours	87.98	87.03	78.09
	3	-	87.66	87.70	85.60
		NO + uv, 2 hrs	88.11	87.67	82.87
	4	-	82.04	82.13	80.04
		uv, 2 hours	84.81	84.52	83.15

Table 6.4: Tristimulus Colorimeter Values for PVC Films

light, it tends to be inaccurate below 15-20% reflectance. As all the other values obtained are well above 50% reflectance it is safe to assume that these results are not influenced by stray light reflections.

All of the samples which had been exposed to nitric oxide appeared to have yellowed when assessed visually.* This condition was also indicated by the results obtained from the colorimeter. In each case the reflectance of the blue wavelength had decreased and hence the absorption of blue light had increased. When this occurs the colour of the coating becomes a desaturated yellow. The samples exposed to uv light alone showed little change in the reflectance of red, green and blue light. Also, there was no significant difference between the change in reflectance values for the samples exposed to NO and those exposed to NO and uv light simultaneously. The difference in formulation between sample types (6) and (7) did not appear to influence the colorimeter results.

Transmittance values were also obtained for the unpigmented PVC (UP) samples (see Table 6.4). These values showed no significant change after ageing, except for a few slight increases in readings for all three colours.

* See Plate 6.1 - Appendix 3

6.3.3 Micro-indentation

The results obtained from the micro-identation test, completed before and after ageing, did not show any significant change in the bulk properties of any of the samples. This was partly due to the inherent softness of the coatings. The only films with any rigidity were the unplasticised PVC films coded PVC(UP), but there was no discernible change in the hardness of these films after ageing.

6.4 Discussion

The most striking result of this initial experimentation was the obvious discoloration which has occurred with all of the samples exposed to nitric oxide. In order for the colorimetry results to be influenced, some form of chemical or physical reaction must have taken place to a substantial depth into the surface layers of the polymer. The sample of unpigmented, unplasticised polymer, PVC (UP), is the exception (see Table 6.4). This particular set of films do not show any significant change in their colour coordinates. This is most likely due to the lack of pigmentation in the films. The main component of a film which causes diffuse reflection of the light beam is the pigmentation. It is the diffuse intensity which has the greatest influence on the results obtained by colorimetry, as opposed to the specular intensity in the case of goniophotometry. Even if the polymer film is substantially altered, there will be no indication of this unless the light is reflected back to the photocell.

Despite the lack of any indication of ageing by the colorimeter, the goniophotometer did show a decrease in gloss factor and Is for PVC (UP), see

Figures 6.1 and 6.2. These changes in GF and Is occur with every sample exposed to nitric oxide. The decreases are not as large as would be expected with the degree of yellowing indicated by the colorimeter results. The exception to this is sample 6.2 in which the decrease is substantial. A possible explanation is that since this film was detached it is far more susceptible to mechanical damage through handling, also, due to the lack of rigidity, difficulty was encountered in ensuring that the specimen was mounted in exactly the same position for each goniophtometric analysis.

These results show that there is some form of reaction between the PVC films and nitric oxide. It is unlikely that the NO is simply diffusing into the film, which would still cause yellowing of the sample, for two reasons. Firstly, diffusion of the NO into the PVC would not lower the Is value as no surface degradation would occur. Secondly, as NO is a radical it is unlikely to diffuse into the polymer structure without some form of raaction occurring.

The lack of any evidence of a charge in hardness, as indicated by the micro-indentor, implies that the reaction of NO with PVC films is predominantly a surface effect. These particular measurements are only influenced by changes in the bulk properties of a polymer. According to the goniophotometric results, of the three different ageing systems employed, the exposure of the samples to ultra-violet light, without the presence of nitric oxide, seems to have caused the greatest degree of degradation. It is interesting to compare the effects of ultra-violet light on formulations (6) and (7).

The effect on the samples of formulation (7) is indicated by a substantial decrease in the gloss factor (see Figure 6.2). There is also a decrease in the gloss factor with samples of formulation (6), but nowhere near as large. The only difference between (6) and (7) is the type of stabiliser present, as shown in Table 2.1. Sample (6) contains an ultra-violet stabiliser.

It has been shown by DeCoste and Howard$^{(45)}$, that PVC begins to show signs of degradation when exposed to wavelengths between 373 and 350 μm, with a marked change occurring between 350 and 307 μm. Even above 455 μm some change has been observed. As the source of uv provided radiation with a wavelength of 350 μm and above, it would appear that there is a high probability that the degradation, in the case of formulation (7), is directly due to the uv radiation. Formulation (6) was affected to a lesser degree because of the action of the uv stabiliser. The mechanism of the breakdown of PVC is, even now, a controversial matter, though it is generally agreed that as a result of the action of ultra-violet radiation hydrogen chloride is evolved and oxidation then takes place, along with concurrent formation of conjugated unsaturation with some cross-linking and chain scission.

The presence or absence of the uv stabiliser does not appear to influence the reaction between NO and PVC. This indicates that the stabiliser is of the screening or absorption type, which effectively shields the polymer from the uv radiation and does not involve any radical reactions.

The decrease in Is and GF for the sample of PVC (UP) exposed to NO is of a similar magnitude to that of the other samples which contain pigmentation. It therefore seems to be unlikely that the pigmentation is involved in the reaction of NO with PVC.

From the above information it appears that there is a definite reaction between NO and PVC. This reaction does not, apparently, involve the stabilisers or pigmentation present within the polymer film. This implies that the NO must, in some way, react with the polymer chain. It is interesting to note that in the majority of results the combined effect of NO with uv light is less than the individual effects of these ageing elements.

6.5 Infrared Spectroscopy Investigations

Having verified that some form of reaction does occur when PVC is exposed to NO, it was decided to make use of an infrared spectrophotometer and the available expertise(46) to examine various unpigmented PVC films. It was hoped that the results from this technique would help to indicate the possible nature of the interaction of NO and uv/NO with PVC.

Four types of clear samples were available for this i.r. study. They are coded 1-4 and are described in Table 2.1. Each type of sample was exposed to NO at 100°C, uv light and NO, and finally heated to 100°C in a nitrogen environment. Spectra were obtained from each sample over varying periods of ageing. The range of conditions was chosen in order to produce interactions of a nature that are likely to occur in environmental conditions. It was necessary to raise the temperature in order to produce a pronounced effect which would create groups in reasonable concentrations so as to be detected by the i.r. spectroscopy. The third set of samples were heated to 100°C so that it would be possible to identify the effect of high temperature on the polymer films, in the i.r. spectra obtained from the samples exposed to NO and heat.

6.6 Infrared Results

Transmission i.r. spectroscopy was used to examine PVC clear films which were thermally aged in a nitrogen atmosphere and a nitric oxide/nitrogen atmosphere at 100°C. Analysis of the samples was carried out after intervals of 0, 5, 10, 20, 35, 50 and 60 hours. This technique was also used to examine films exposed to uv ageing in a nitric oxide/nitrogen environment for 250 hours.

A differential infrared "compensation" technique as used. This essentially entailed subtracting the spectrum of the same unaged control sample in the instrument's reference beam from that of the continuously exposed sample in the sample beam. Spectra obtained in this manner were substantially free from the previously dominating sample peaks. The technique therefore allows peaks which change in magnitude, or are newly formed, to be instantly identified and hence allowing the relatively small ageing effects to be easily followed. Two representative figures (6.3) and (6.4) are included which indicate the relative growth rates of the i.r. absorption peaks studied during this work.

6.6.1 Infrared Results - Thermal Ageing in N_2

Infrared spectra of the unstabilised, unpigmented PVC film coded (1) showed peaks centred at $2920cm^{-1}$, 1735-$1750cm^{-1}$, $1420cm^{-1}$, and at 735-$750cm^{-1}$ before it was exposed to any ageing elements. These initial small peaks were due to differences in the thickness of the sample and the reference films. The peaks centred at $2920cm^{-1}$, $1745cm^{-1}$, $1425cm^{-1}$, $1220cm^{-1}$ and $1170cm^{-1}$ increased during the first 20 hours of exposure (see Figure 6.3). The growing $-CH_2-$ stretching peak centred at $2920cm^{-1}$ broadened and developed a shoulder at $2865cm^{-1}$. The rate of growth of the carbonyl peak centred at $1745cm^{-1}$ was relatively faster than the growth rate of the $-CH_2-$ stretching band at $2920cm^{-1}$ for the first 20 hours of exposure.

The growth of the peak at $2920cm^{-1}$ changed trend after 35 hours, becoming a negative peak with respect to the reference sample. A slight decrease in the negativity occurred after 50 hours which was followed by the peak tending to revert to its former positive nature after 60 hours, although it was actually very close in absorbance to that of the unaged reference sample. In contrast, however, a

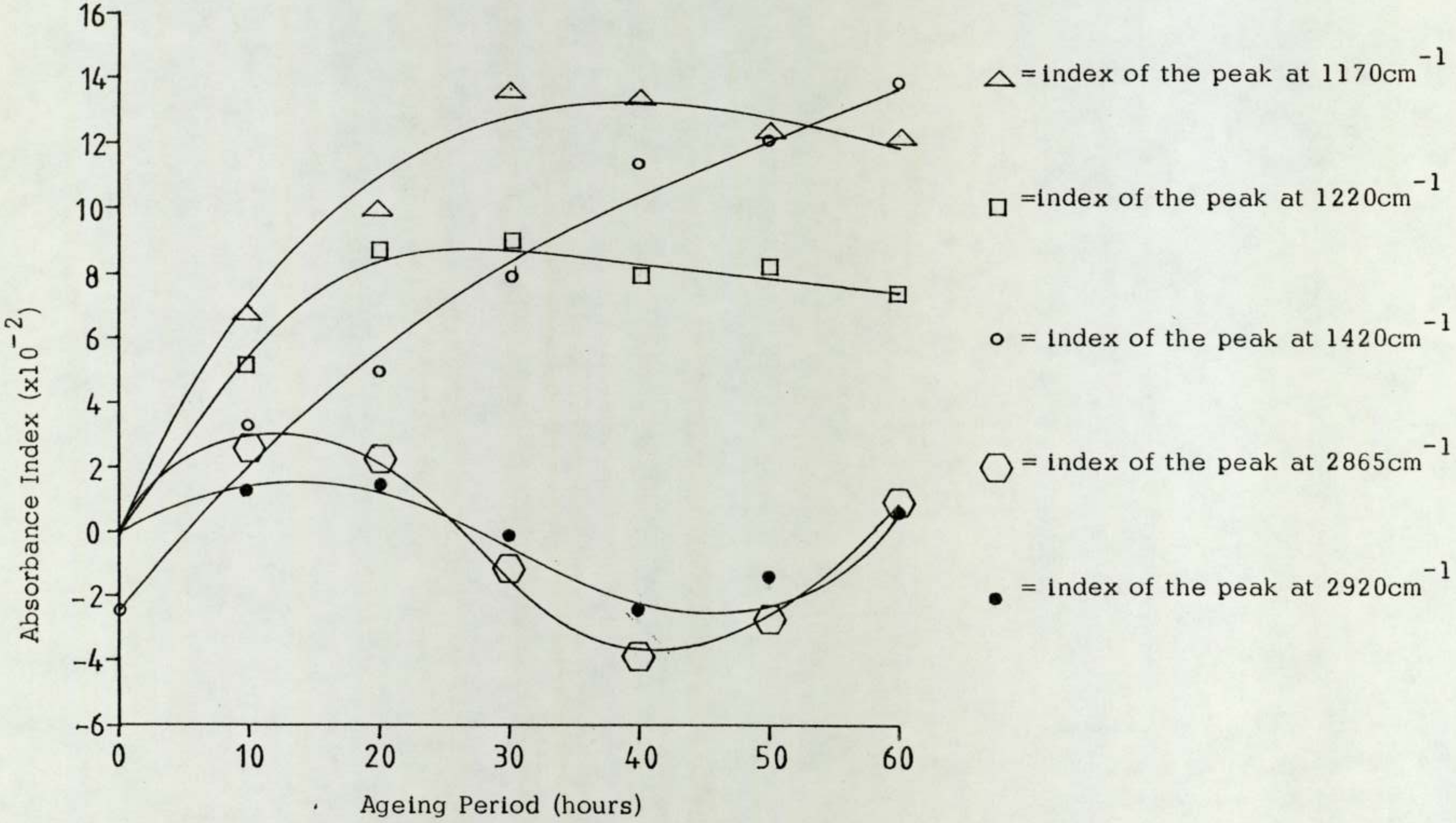


Figure 6.3: Absorption Indices of i.r. peaks: PVC (1) Thermally aged in N_2 at 100°C

continual decrease of the peak at 1745cm^{-1} was maintained until the end of the exposure. The increase of the -CH$_2$- bending peak at 1420cm^{-1} continued progressively while the peak centred at 1200cm^{-1} appeared to decrease after 20 hours.

Thermal ageing of sample (4), which is the PVC film containing both uv and thermal stabilisers, showed results similar in nature to those indicated in the i.r. transmission compensation spectra of sample (1) with a few small variations. Peaks centred at 2920cm^{-1}, 1740-1745cm^{-1} 1420cm^{-1} and 1200cm^{-1} showed a marked increase during the first 20 hours, then they tended to decrease with the exception of the -CH$_2$- bending peak at 1420cm^{-1} which continued growing for the first 35 hours. The peak centred at 2920cm^{-1} developed a shoulder at 2880cm^{-1} after 10 hours and the carbonyl peak at 1740cm^{-1} shifted to 1745cm^{-1} during exposure. The growth rate of the carbonyl peak centred at 1745cm^{-1} was faster than that of the carbonyl peak at 2920cm^{-1}. Both of these peaks were believed to be attributed to the plasticiser. The appearance of a shoulder at 1460cm^{-1} was observed after 5 hours. This shoulder remained until after 50 hours of exposure, at which time it diminished.

6.6.2 Infrared Results - Thermal Ageing in NO/N$_2$

In order to follow the thermal degradation of the PVC sample coded (1) the -CH$_2$- stretching peak centred at 2920cm^{-1}, the carbonyl (-C=O) peak at 1720-1750cm^{-1}, the -CH$_2$- bending peak at 1420cm^{-1} and the bands at 1245cm^{-1} amd 1120cm^{-1} were monitored. An additional peak centred at 1550cm^{-1} appeared after 10 hours of exposure (see Figure 6.4). The appearance of this peak may well be attributed to the formation of nitrogen-oxygen bonds on the surface of the polymer during ageing. The subsequent growth of this peak occurred in an almost linear fashion.

In the case of the i.r. transmission spectra for the film of sample (4) some slight differences from the spectra of sample (1) were noticed. Although the general ageing pattern was similar in trend, the development of certain specific peaks differed slightly when compared at various times during the exposure period. For example, the methylene stretching peaks, which were observed at 2920cm^{-1} and 2860 cm^{-1}, also exhibited a similar diminishing trend to that observed with sample (1), but this was not until after a slightly longer period of initial increase. Also, prior to subsequently decreasing, the initial growth rate of the carbonyl peak at 1720cm^{-1} was greater than that of the $-CH_2-$ stretching peak at 2920cm^{-1}. As before a peak started to appear at around 1550cm^{-1} after 5 hours of exposure and subsequently developed two shoulders at 1545cm^{-1} and 1560cm^{-1} after 20 hours. The growth of this peak, centred at 1550cm^{-1}, is more pronounced with the sample (4), containing uv and thermal stabilisers, than with the previous unstabilised sample (1).

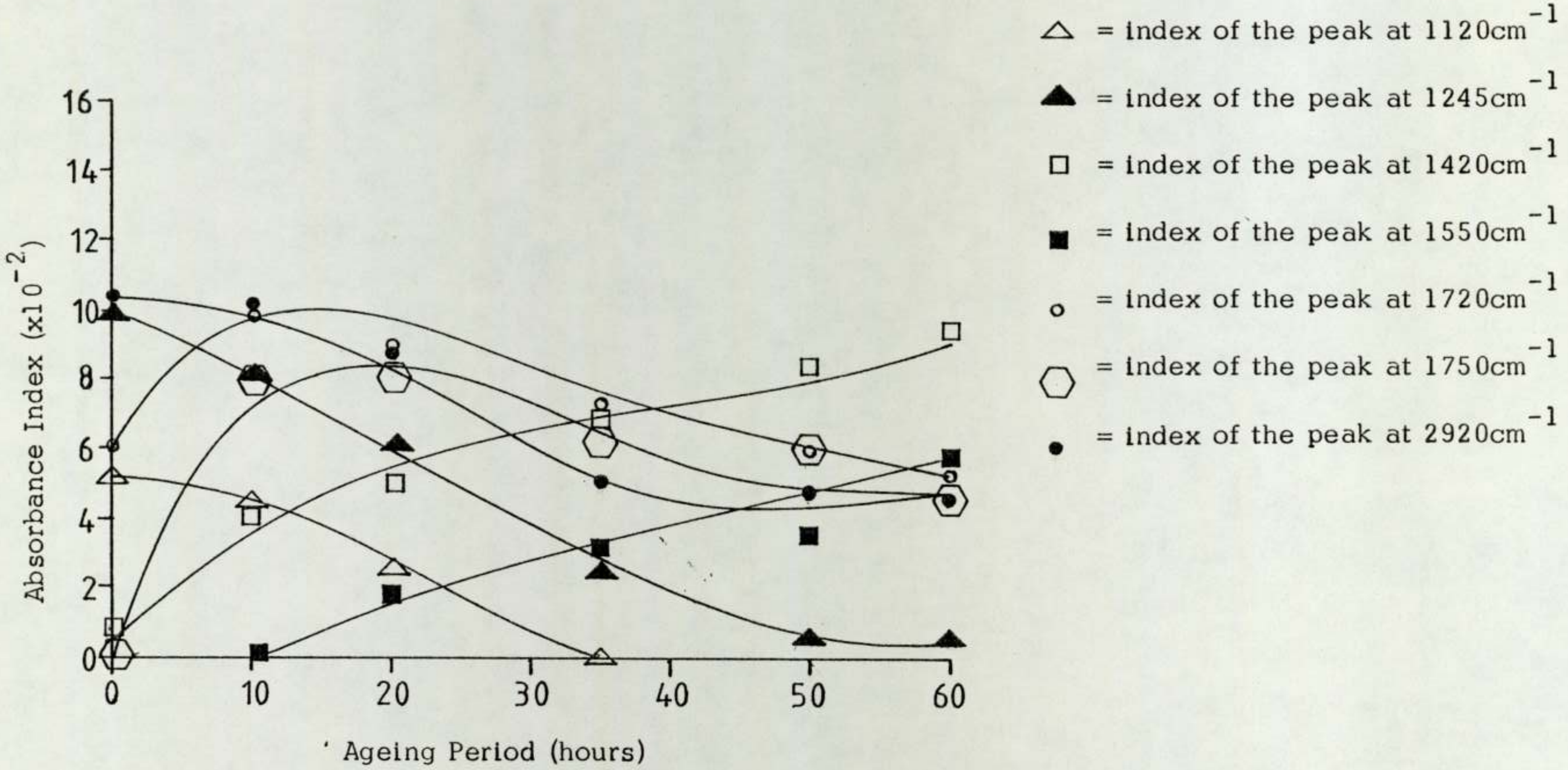


Figure 6.4: Absorption Indices of i.r. peaks: PVC (1) Thermally aged in NO/N_2 at 100°C

6.6.3 Infrared Results - uv ageing in NO/N_2

The film of sample (1) when analysed after 0, 100, 150, 200 and 250 hours exposure showed peaks centred at $3160cm^{-1}$, $2900cm^{-1}$, 1710-$1735cm^{-1}$, 1425-$1445cm^{-1}$, $1240cm^{-1}$, $1100cm^{-1}$, $950cm^{-1}$, $735cm^{-1}$ and $690cm^{-1}$.

The $-CH_2-$ stretching peak centred at $2900cm^{-1}$ with a shoulder at $2845cm^{-1}$, and the carbonyl peak centred at $1735cm^{-1}$, incorporating a shoulder at $1710cm^{-1}$ both increased in absorbance up to 100 hours exposure, although at varying rates. The growth of the carbonyl peak was faster, which may be an indication of oxidation having taken place.

After 100 hours a peak started growing centred at $1635cm^{-1}$. This peak developed a shoulder which seemed to decrease in subsequent stages. A hydroxyl peak centred at $3160cm^{-1}$ also started growing after 100 hours of exposure and continued increasing up to the end of the exposure period, also giving rise to a shoulder at $3060cm^{-1}$. Both peaks grew at relatively slow rates.

There appears to be little difference between the ageing characteristics of samples (1) and (4). After a concurrent increase of the carbonyl peaks at 1700-$1740cm^{-1}$ and the methylene stretching band at $2920cm^{-1}$ during the first 150 hours of ageing, a gradual decrease was observed for all the recorded peaks followed during ageing. The decreasing and increasing of the carbonyl and methylene stretching peaks took place almost in parallel.

Changes in the $-CH_2-$ bending band at $1420cm^{-1}$ were closely followed by changes in the peak at $2860cm^{-1}$. Additionally, the peak at $1240cm^{-1}$, being due to the C-H stretching in H-C-Cl, had a similarity in trend to the $1700cm^{-1}$ carbonyl development although with a difference in magnitude. Even though these samples were aged for 250 hours, the growth of peaks in the regions of $1530-1640cm^{-1}$ and $3060-3160cm^{-1}$ was at a considerably slower rate than the remaining peaks.

6.7 Discussion of Infrared Results

With all of the samples the peaks centred at $2920cm^{-1}$ (methylene stretching) and $1700-1750cm^{-1}$ (carbonyl peak) show an initial increase which would not normally be expected as a chemical variation. This may be explained in terms of plasticiser flow. The volatisation of the plasticiser from the surface of the polymer film, under the effect of the high temperature, would then account for the subsequent decrease in magnitude of these peaks. However, rather than these spectral changes being interpreted solely in terms of a plasticiser migration effect, the fact the $1423cm^{-1}$ PVC peak also varies along similar lines suggests that we are observing the added effect of film thickness variations. These physical processes serve to detract from the quantifiability of whatever genuine chemical changes may be spectrally measurable. However, even from a purely qualitative angle, the spectra fail to show any significant change in the C=C double bond region of the spectrum (around $1650cm^{-1}$) despite the discoloration of the samples. None the less these findings now form a basis upon which to compare the nitric oxide in nitrogen experimental results.

On ageing a new growing multi-peak absorbance appeared in the spectrum of each of the clear films in the $1500\text{-}1550cm^{-1}$ region which could clearly be assigned(47,48) to the formation of nitroso (-N=O) groups in the polymer. However, in the light of this positive evidence of an 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.

From the spectra of both the unstabilised and stabilised clear films, aged in uv light and NO/N_2, 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 is indicated by the progressive and parallel development, on uv/nitric oxide exposure, of the low frequency O-H stretching peak centred at $3160cm^{-1}$ and the C=N stretching band in the $1620\text{-}1650cm^{-1}$ region of the spectrum. Whilst there is also a suggestion of an accompanying N=O stretching absorbance in the $1500\text{-}1550cm^{-1}$ region, it is less definite than in the spectra of the previous thermally aged samples 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.

The results described in this chapter are seen to be in agreement with the findings of previous workers(36,37) that nitric oxide does chemically interact with poly (vinyl chloride) in a degradative (radical producing) environment. 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 as restricted in PVC as solid or liquid inhibitors with bulky molecules are likely to 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 nitric oxide has been reported(36 to accelerate, leading to the formation of polyene structures to which nitric oxide has been shown(37) to add.

The slower rate of the photolytic degradation in the presence of NO/N_2, may partially explain the low level of degradation of the samples exposed to uv and NO simultaneously, as indicated by the previous goniophotometric analysis.

CHAPTER 7

THE INTERACTION OF NITRIC OXIDE WITH POLYMER SURFACE COATINGS: AN INSTRUMENTAL INVESTIGATION

7.1 Introduction and Rationale

The initial work, which was described in Chapter 6, has indicated that, in high concentrations of nitric oxide, a reaction does occur between PVC and NO. It also verified that PVC coatings undergo photolytic degradation in the presence of uv light. The conditions employed in the preliminary study did not directly mimic the actual weathering situation present in an urban or industrial environment. This chapter describes the extension of this study to a more direct evaluation, by accelerated ageing techniques, of the role of NO in surface coating deterioration. The aim of these experiments was to produce reactions between NO and PVC of a nature that are likely to be encountered with a PVC surface coating exposed to NO in a natural weathering environment.

The initial experiments had simply exposed the samples of PVC to high concentrations of nitric oxide in two sets of sealed vessels. One set were irradiated with uv light along with a third set, which did not contain any nitric oxide. This technique possibly produced synergistic effects which could, in fact, differ drastically from those produced by natural weathering. Three factors which could have so influenced the reactions are, firstly, the exceptionally high concentration of pollutant gas employed, secondly, the lack of gas flow over the sample surface and thirdly, the static nature of the test, in as much as no cyclic variations occurred.

In an attempt to avoid synergistic effects unrepresentative of those occurring in the environment, the second series of experiments were conducted over a longer period of 450 hours, using low concentrations of nitric oxide. The techniques employed were closer to natural weathering conditions than those used in the initial experiments, but they still must be classed as accelerated ageing and not weathering, as no attempt was made to mimic naturally occurring conditions.

The long period of continuous ageing required the use of the automated ageing cabinet, the development of which is described in Chapter 3. The facilities provided by the chamber allowed the samples to be aged automatically without any attendance, but it still provided constant monitoring of the ageing elements being employed, by means of a multipoint chart recorder.

The ultra-violet source employed in the automated test chamber is rated at 125 watts. This energy is dissipated over a surface area of approximately $0.2m^2$. When the spectral energy distribution of the source and the periods for which it is switched on during a cycle are taken into account, this represents a two hundred fold increase in relative energy in comparison with solar radiation according to published figures(49). In order to increase the ageing potential of the nitric oxide by a similar factor, it was decided that a concentration in the region of 2000 ppm of NO in N_2 was required. This concentration of nitric oxide would effectively be reduced after allowing for possible reactions of the nitric oxide with any residual oxygen in the system, and possibly with the interconnecting PVC pipes. In addition, while the gas was not actually flowing, it would slowly diffuse through the non-return valve into the atmosphere.

Temperature cycling was employed during the ageing in order to allow for the diurnal variations which occur with natural weathering. The temperature cycling was synchronised with the switching of the uv source, the upper temperature occurring when the source was on and the lower when the source was off.

Due to the relatively high intensity of the uv source it was felt that it would be advisable to avoid the injection of fresh NO/N_2 gas into the vessels whilst the uv source was on. The intensity of the source may have substantially altered the ratio of NO to NO_2 present at the sample surface, especially as it was difficult to guarantee that all traces of oxygen had been flushed from the system. To avoid this problem, the gas was injected immediately after the uv source was extinguished and as the temperature started to drop towards the lower setting. Once the temperature of the chamber had stabilised at the lower setting, the system was replenished by a further injection of gas. It was assumed that when the point was reached in the cycle at which the uv source was switched on, the concentration of NO had dropped to a level which would not cause any substantial synergistic effects. Due to the injection of gas at these points in the cycle, the variations in concentration of the gas in the system roughly followed the variations monitored at industrial sites(6) That is, high concentrations occurring in the late afternoon which decline overnight until early morning, when the concentrations start to rise again.

It was decided to limit the analysis of the samples to colorimetry and goniophotometric techniques. The evidence from the previous experimentation had indicated that the micro-indentor was unlikely to show any change in properties, since this technique is only sensitive to changes in the bulk properties of the samples.

The availability of the goniophotometer interfaced to the computer allowed very rapid analysis of the samples with an immediate display of the results. The advantage of this was that the deterioration of the samples' surface could be assessed instantly, thus minimising the delay to the ageing programme. This permitted more frequent monitoring of the degradation of the samples than normally would be practical with a non-automated system. A further advantage was the ability of the computer to record the details of individual goniophotometric curves. These could be recalled as required and overlaid in order to compare the surface of a sample before and after ageing. This technique proved to be very useful for comparing the various degrees of deterioration that occurred with the different ageing elements employed.

The surface coatings studied in this experimentation were taken from the same family of coatings as the PVC coatings used in the experimentation described in Chapter 6. It was decided that it would not be necessary to compare different combinations of stabilisers, since it had been shown that the stabilisers and plasticisers used in these coatings did not influence the reaction of NO with PVC. This enabled samples to be used that were more representative of formulations that are employed in actual commercial PVC surface coatings.

7.2 Experimental Procedure

Four sets of samples were prepared. All the samples were of a similar formulation, comprised of white pigmented PVC, containing uv and thermal stabilisers along with a plasticiser, and were coded as number eight (see Table 2.1).

The samples were analysed using the automated goniophotometer and the colorimeter before being aged. The four sets of samples were respectively aged in the presence of heat alone, heat and uv light, heat and dilute NO and heat with uv light and NO simultaneously (see Table 7.1). All of the samples undergoing ageing were housed in glass vessels, (see Plate 3.5), located inside the accelerated ageing cabinet. The samples which were exposed to heat alone were used as reference samples in order to

SAMPLE CODE	AGEING TREATMENT	PERCENTAGE REFLECTANCE		
		RED	GREEN	BLUE
8.0	Reference	71.8	69.86	64.64
8.1	HT	81.38	77.85	66.67
8.2	HT + NO/N_2 + uv 450 hours	79.74	75.41	57.12
8.3	HT + NO/N_2 450 hours	81.15	77.43	59.30
8.4	HT + uv 450 hours	81.15	78.02	69.57

TABLE 7.1: Details of ageing conditions and colorimetry results

isolate the effects of heat from those of the other ageing elements. The accelerated ageing cabinet was programmed to operate in the following manner during each cycle. Over a period of two hours the temperature inside the chamber was raised to 60°C. Once it had stabilised at this temperature the uv source was switched on. These conditions were maintained for 40 hours. At the end of this period the uv source was switched off and the chamber slowly cooled over 4 hours, until a lower temperature of 25°C was attained. As the temperature started to drop NO/N_2 was released into the gas distribution manifold at 5 p.s.i. for approximately two minutes. This was repeated, again for two minutes, once the temperature had stabilised at 25°C. The lower temperature of 25°C was maintained for a further 40 hours before repeating the cycle. The details of the cycling conditions are represented graphically in Figure (7.1). Only one set of samples was subjected to the complete ageing system. The other samples were only subjected to heat, or heat plus the uv or NO elements of the cycles.

Whenever the test chamber was switched on, the system was automatically flushed through with nitrogen in order to displace the oxygen initially present. In addition nitrogen was flushed through the system whenever the test chamber was switched off or disconnected from the mains. This was done so as to purge the NO out of the system as a safety precaution.

After approximately 100 hours the ageing cycle was interrupted and the samples were removed. Each sample was subjected to colorimetry and

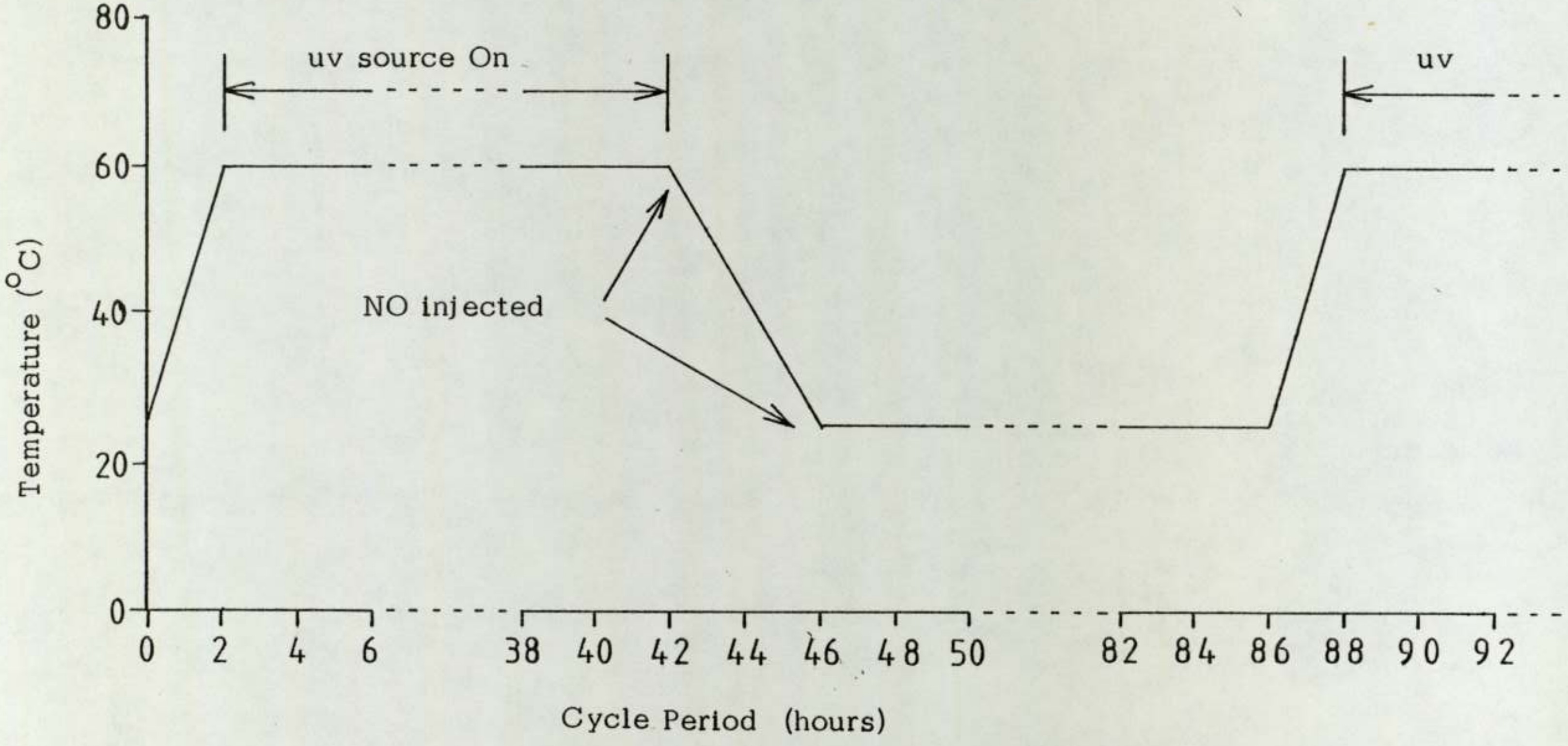


Figure 7.1: Details of cabinet cycling conditions

goniophotometric analysis, before being replaced in the test chamber and subjected to a further 100 hours of ageing. The samples were aged for a total of 450 hours.

7.3 Results of PVC Studies

The three colorimeter readings for the samples exposed to heat alone each show an increase in reflection after 450 hours of ageing (see Table 7.1). A similar increase was also observed with the samples exposed to heat and uv light. Both sets of samples which were exposed to NO/N_2, with or without uv light (8.2, 8.3), show a decrease in the percentage reflectance of blue light. The red and green reflectance values show an increase of a similar magnitude to those for the samples exposed to heat alone, sample (8.2) being slightly lower than sample (8.3). These colorimeter results agreed with a visual assessment of the films, which appeared to be slightly yellowed after exposure to NO.

None of the goniophotometric results indicated any significant change in the Id or $W\frac{1}{2}$ values. For this reason only the specular intensity (Is) is discussed in this section.

The sample (8.1) which was only subjected to the temperature cycling in a nitrogen environment, showed a steady increase in Is during the ageing. This was presumably due to the surface of the plasticised PVC flowing under the influence of heat. The figures obtained from this sample were used as a reference to correct the results obtained for the remaining samples. These corrected results are represented graphically in Figure 7.2.

All of the samples show a steady decrease in the corrected Is values during ageing, although sample (8.2), which was exposed to NO/N_2 and uv light simultaneously, tended to stabilise after 150 hours at a value which was approximately 10% below the original Is value. The sample exposed to uv light (8.4) showed the largest decrease in Is, dropping by 23.5% of its original Is value after 450 hours of ageing, which included approximately 210 hours of exposure to uv light.

7.4 PVC Studies: Discussion of Results

Again, as in the previous experiments, even though the colorimetry results were sensitive to the effects of ageing in a NO environment, only the goniophotometric results indicated the effect of uv light on the PVC coatings.

When the goniophotometric results were first examined, it was realised that the upper temperature of 60°C attained during the ageing cycles had the greatest influence on the surface of the samples. It is believed that a certain degree of flow had occurred in the plasticised films at this temperature. This flow tended to mask the deterioration caused by the other ageing elements. In order to overcome this problem the goniophotometer computer programme was used to superimpose the individual curves for each type of ageing element, see Figure 7.3. Once this had been done,

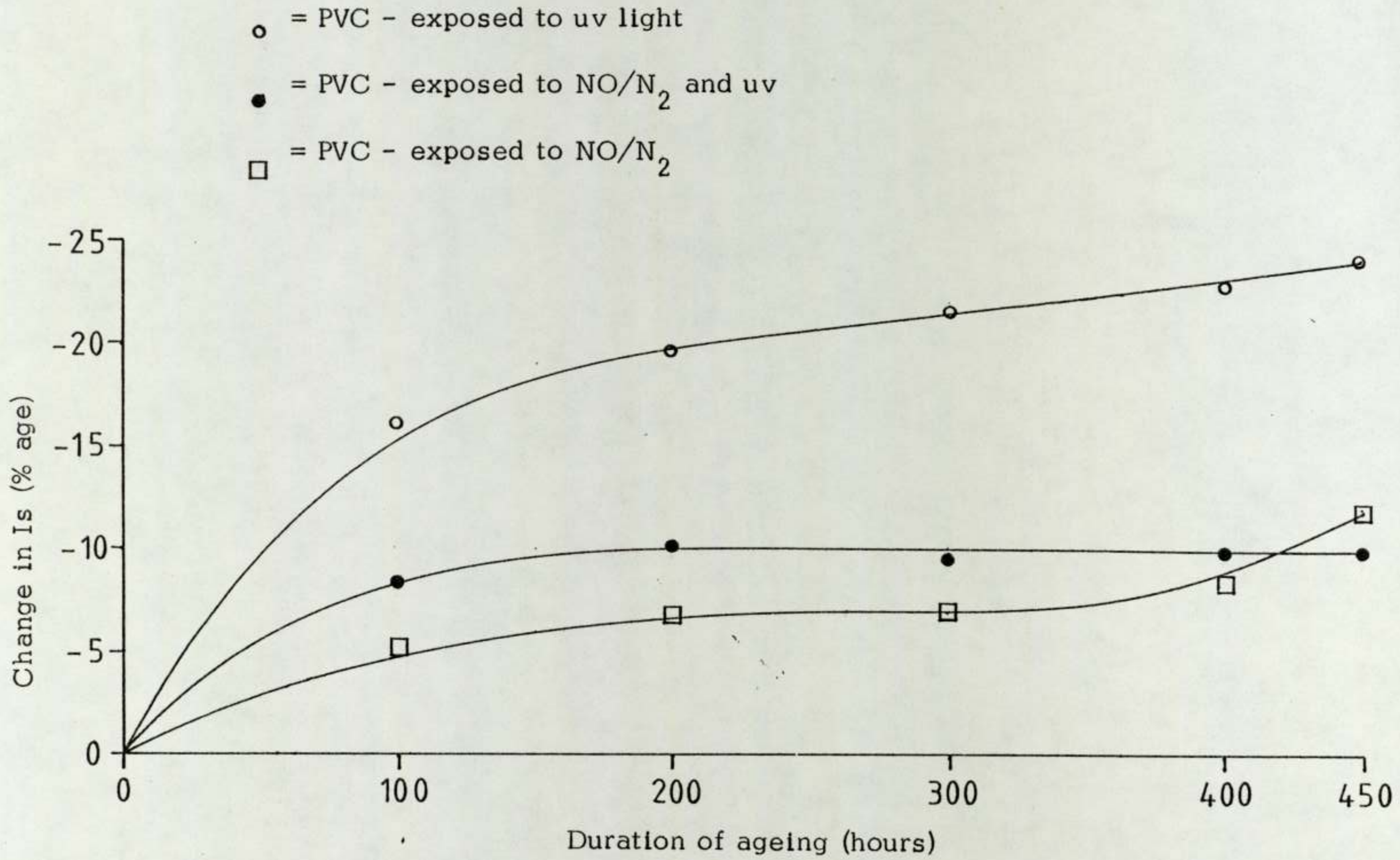


Figure 7.2: PVC coatings - Percentage change in Is on ageing

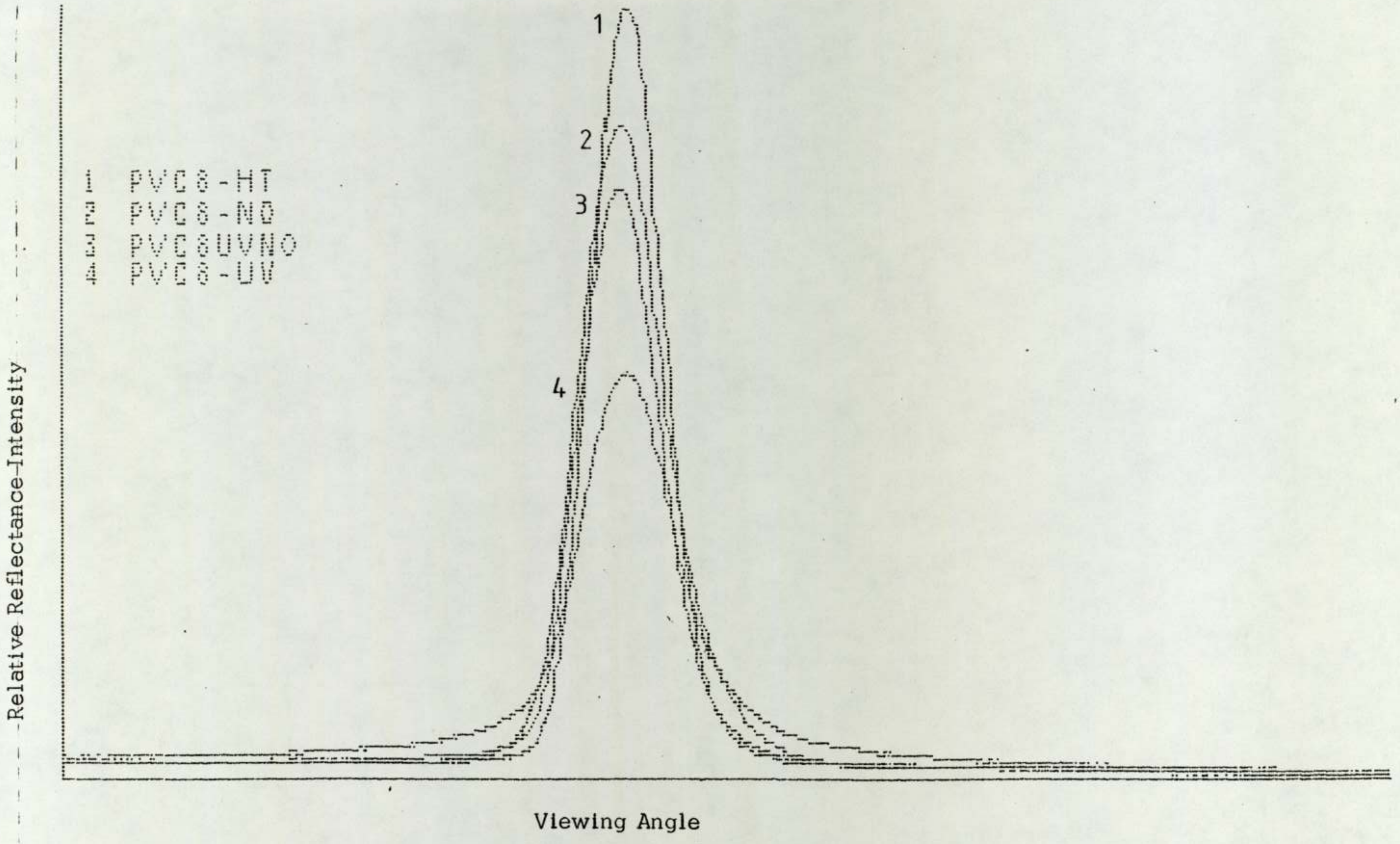


Figure 7.3: PVC coatings - Superimposed goniophotometric curves for different ageing environments after 300 hours ageing

it was possible to isolate the effect of the temperature cycling on the surface deterioration caused by the other ageing elements. When the corrected results, as shown in Figure 7.2, are compared, the different degrees of deterioration caused by uv light and NO became apparent.

When these results are compared with those of samples(6) from the previous experiments (see Figure 6.1), the decrease in Is of sample (8.3), which was exposed to NO/N_2, would be expected to be greater than that of sample (8.2), which was exposed to uv light and NO/N_2. This is not the case, not only has the NO/N_2 had less effect than the uv light with NO/N_2 ageing combination, it has had considerably less effect than uv light alone (sample 8.4). This difference in deterioration is even more pronounced when one considers that all of the samples contain a uv stabiliser.

When the trends of the results from the two experiments are compared, it appears that high concentrations of NO produce an acceleration in deterioration that is not in proportion with the increase in NO concentration. Assuming that the uv light in the previous experiment may have caused a degree of photo-oxidation of the NO, the concentration of NO at the polymer surface would have been lowered. This may explain the fact that uv light and NO was less detrimental than NO alone. In these later experiments, firstly the lower concentration of NO would mean that the NO/NO_2 equilibrium would favour the NO, and secondly the NO was only present in any substantial concentration when the uv source was switched off. In this situation the effect of the combined uv light and NO would tend to be similar to that of NO alone.

Again, in these later experiments, as in the previous experimentation, the difference in the effect of uv light in comparison with NO is very noticeable. The uv caused a much greater deterioration in the coating than the NO. In fact, when the results from the NO/uv sample (8.2) are taken into account, the NO apparently has a stabilising effect on the actions of the uv light with PVC. Both of these samples were exposed to uv light for the same duration and under similar conditions, apart from the presence of the NO.

7.5 PVC Studies: Conclusion

The accelerated ageing studies described in this chapter taken together with the information on chemical interactions (see Chapter 6), provide a basis for understanding the effect of NO on PVC coatings under simulated environmental conditions.

From the evidence it is clear that under the conditions in the test chamber, the reaction of nitric oxide on the surface layers of the PVC coatings is less detrimental than that of the uv light. This does not mean that the NO does not react to any substantial degree with the coating, but rather that the production of the nitroso groups in the polymer chain have little degradative influence on the surface properties. In comparison the dechlorination of the films, followed by oxidation along with conjugated unsaturation, crosslinking and chain scission, which occurs on exposure to uv light, does have a substantial degradative effect on the surface of the coating.

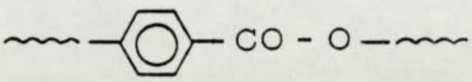
When the coatings are exposed to uv light in the presence of NO, it appears that the radical nature of NO results in the inhibition of the degradation of the PVC. The NO forms oxime groups by radical combination with the radicals produced by the uv light. This stabilises the deterioration caused by the uv light.

The slightly elevated temperatures which were employed, along with the uv light, in order to produce similar effects to those caused by sunlight, did not apparently cause any thermal degradation to the surface of the coating. The only discernible effect was a slight flow of the surface of the polymer.

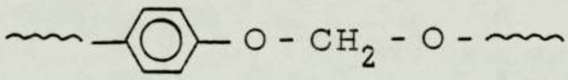
7.6 Further Ageing Studies Involving NO and uv light with Powder Coatings

The experimental work undertaken using PVC films has indicated the nature of the reactions between NO and the surface of a PVC coating. In these experiments it was discovered that the main backbone of the polymer was involved in the reaction, and not the stabilisers, pigmentation or plasticisers , which are additionally incorporated in a surface coating. Against the background of this information it was decided to investigate other surface coatings which are based on different polymers. It was hoped that the results from these further studies would indicate if NO has a greater or lesser deleterious effect than uv light on other chemical structures, and if it was also capable of acting as an inhibitor of the deterioration caused by uv light.

The samples chosen for this study were from the powder coating family of coatings. Specifically epoxy, polyester and epoxy/polyester coatings. The polymer backbone in these coatings is of a hetro-chain nature as opposed to the vinyl backbone of PVC, i.e.

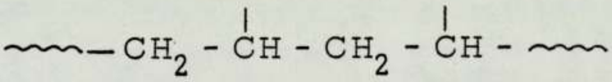


Polyester



Epoxy

rather than



$$\sim\!\sim - CH_2 - \overset{|}{C}H - CH_2 - \overset{|}{C}H - \sim\!\sim$$

vinyl

In addition these three types of coating were chosen because of their widespread use in industry.

The materials used in the preparation of the samples are described in Chapter 2, sections 2.1.3 - 2.1.5. Four sets of samples were prepared and subjected to goniophotometric analysis before being aged. The method of ageing employed was identical to the methods used for the experiments involving PVC, described earlier in this chapter. The test chamber was programmed to produce the cycling conditions previously described and depicted in Figure 7.1.

Table 2.3 gives details of the coding and the combinations of ageing elements that were applied to each sample. It must be remembered that in addition to the elements listed, each sample was subjected to thermal cycling. Goniophotometric readings were taken after every 100 hours up to a total of 450 hours of ageing.

7.7 Powder Coating Studies: Results and Discussion

As with the previous ageing experiments, involving PVC coatings, no substantial change in the Id or $W\frac{1}{2}$ values were observed with the different samples of powder coatings. For this reason this discussion only deals with the change in specular intensity for the various samples. This is the parameter which closely corresponds to the visually perceived image brightness at the sample surface. The computer was used to overlay the goniophotometric curves, allowing the influence on the results of the temperature cycling to be easily isolated from the effects of the other ageing techniques. These curves are shown in Figures 7.4, 7.5, 7.6. The advantage of this analytical technique is that the overall shapes of the light scattering envelopes may be compared. This gives a better indication of the nature and degree of degradation, than simply comparing the calculated results.

The change in Is values for these experiments are represented graphically in Figures 7.7, 7.8, 7.9. In the case of the epoxy samples the temperature

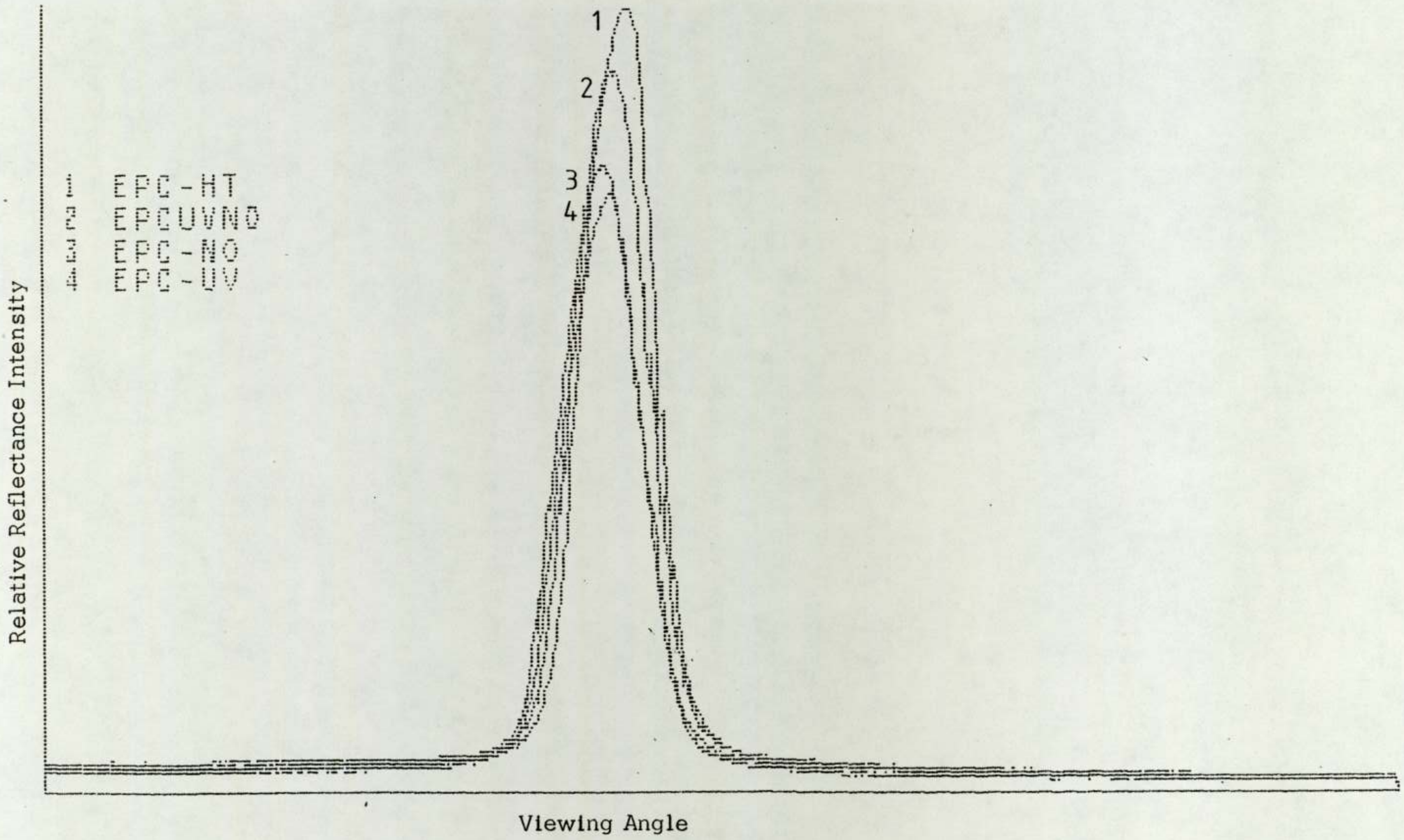


Figure 7.4: Epoxy Powder Coatings - Superimposed goniophotometric curves for different ageing environments after 300 hours ageing

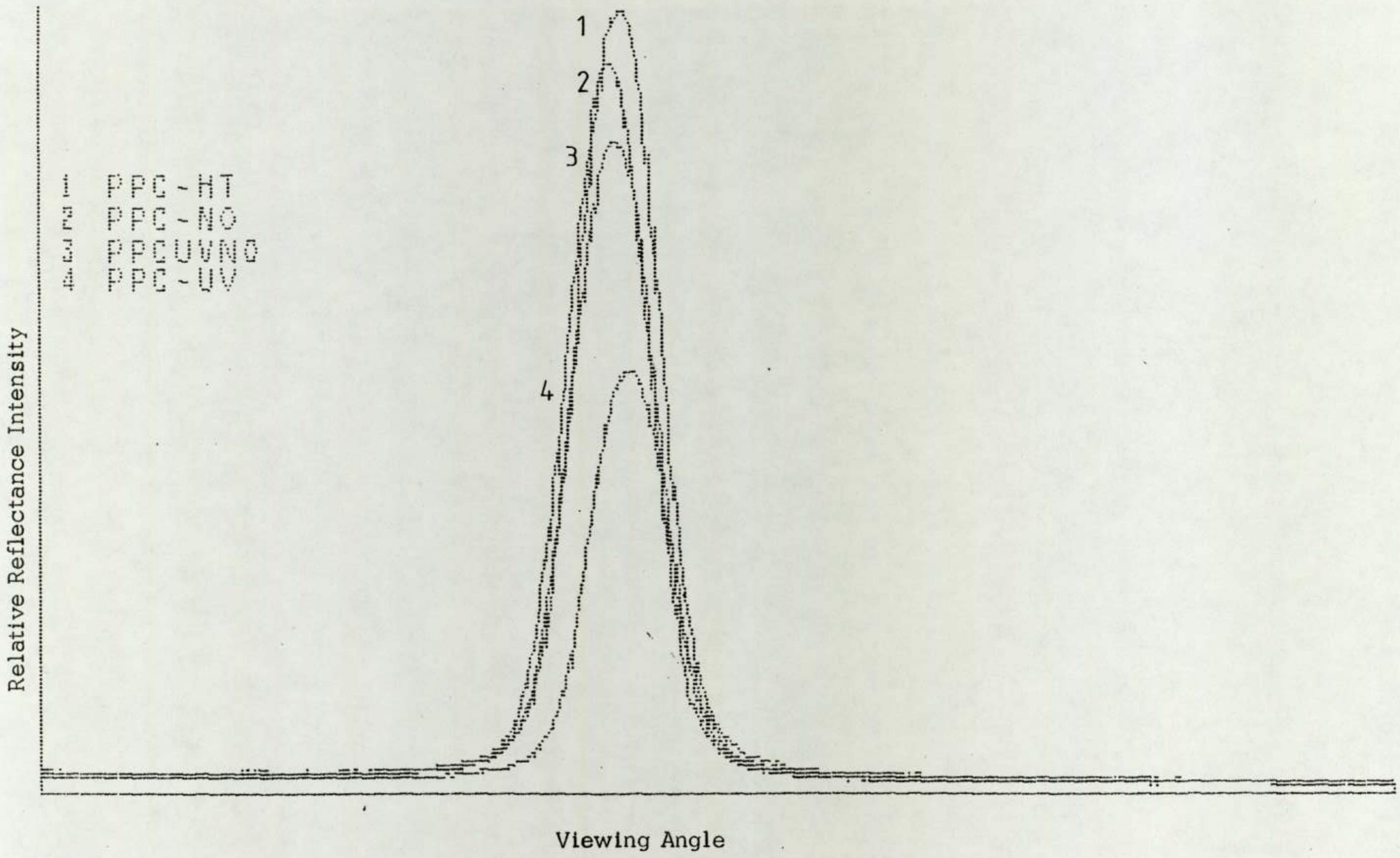


Figure 7.5: Polyester powder coatings - Superimposed goniophotometric curves for different ageing environments after 300 hours ageing

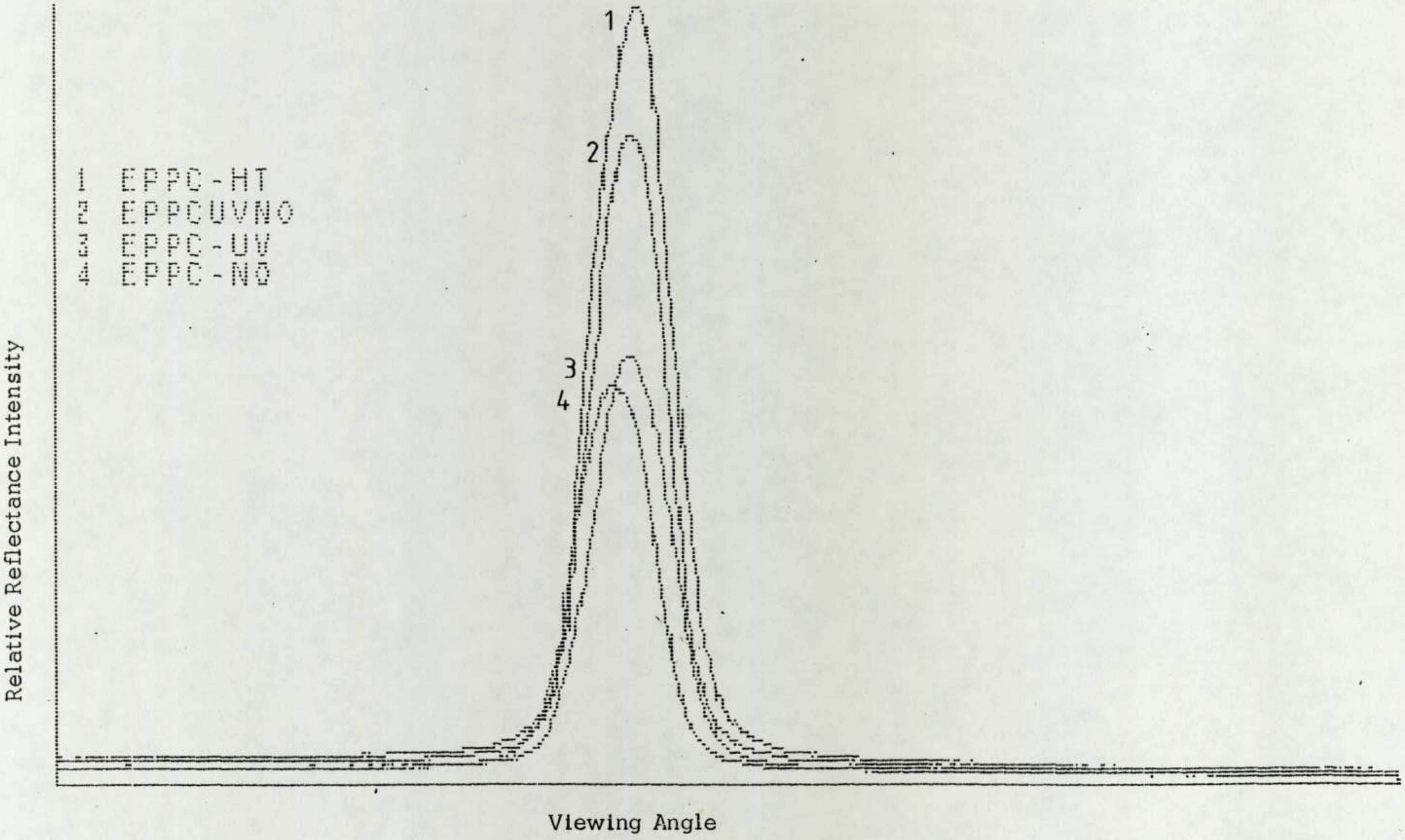


Figure 7.6: Epoxy/polyester powder coatings - Superimposed goniophotometric curves for different ageing environments after 300 hours ageing

cycling caused a drop in Is, as can be seen in Figure 7.7. This was indicated by the reference sample (EPC 1) which was only subjected to the temperature cycling. The drop in Is is probably due to the fact that the epoxy resin continues to "cure" by cross-linking under the influence of heat. Epoxy polymers are the only polymers which were studied that can do this. Additionally, oxidation may have occurred as it was difficult to remove all traces of oxygen from the sample vessels.

The remaining ageing elements, uv light, NO and NO/uv light, all caused similar degrees of degradation. If the drop in Is caused by the temperature cycling is taken into account when assessing the degree of deterioration of the remaining epoxy samples, it can be seen that these three ageing elements had little effect on the samples over the ageing period studied. Up to 300 hours the uv light and NO had a slightly greater effect than NO combined with uv light. After 450 hours the trend had changed, but the degree of ageing was so slight compared with the PVC samples, that it is difficult to predict the overall influence of these three ageing techniques. In summary therefore, the most important ageing process for epoxy resins, in the time scale studied, appears to originate in the thermal cross-linking process.

The polyester powder coating samples deteriorated at a similar rate to that of the PVC samples. It is much easier in this case to separate the ageing trends caused by the different techniques. Again, as with PVC, heat caused an overall increase in Is, due to the surface flow of the samples. Once the

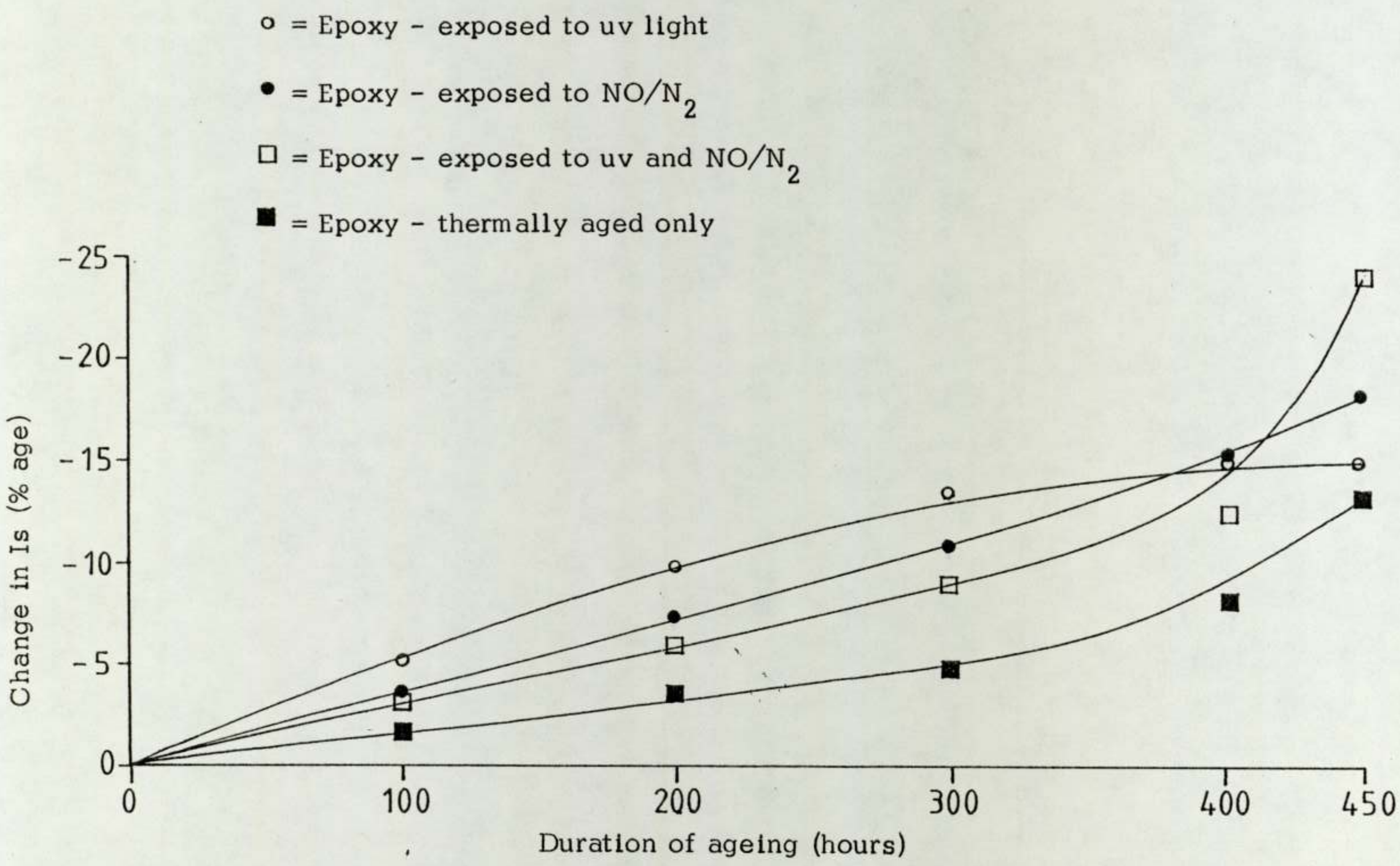


Figure 7.7: Epoxy powder coatings - Percentage change in Is on ageing

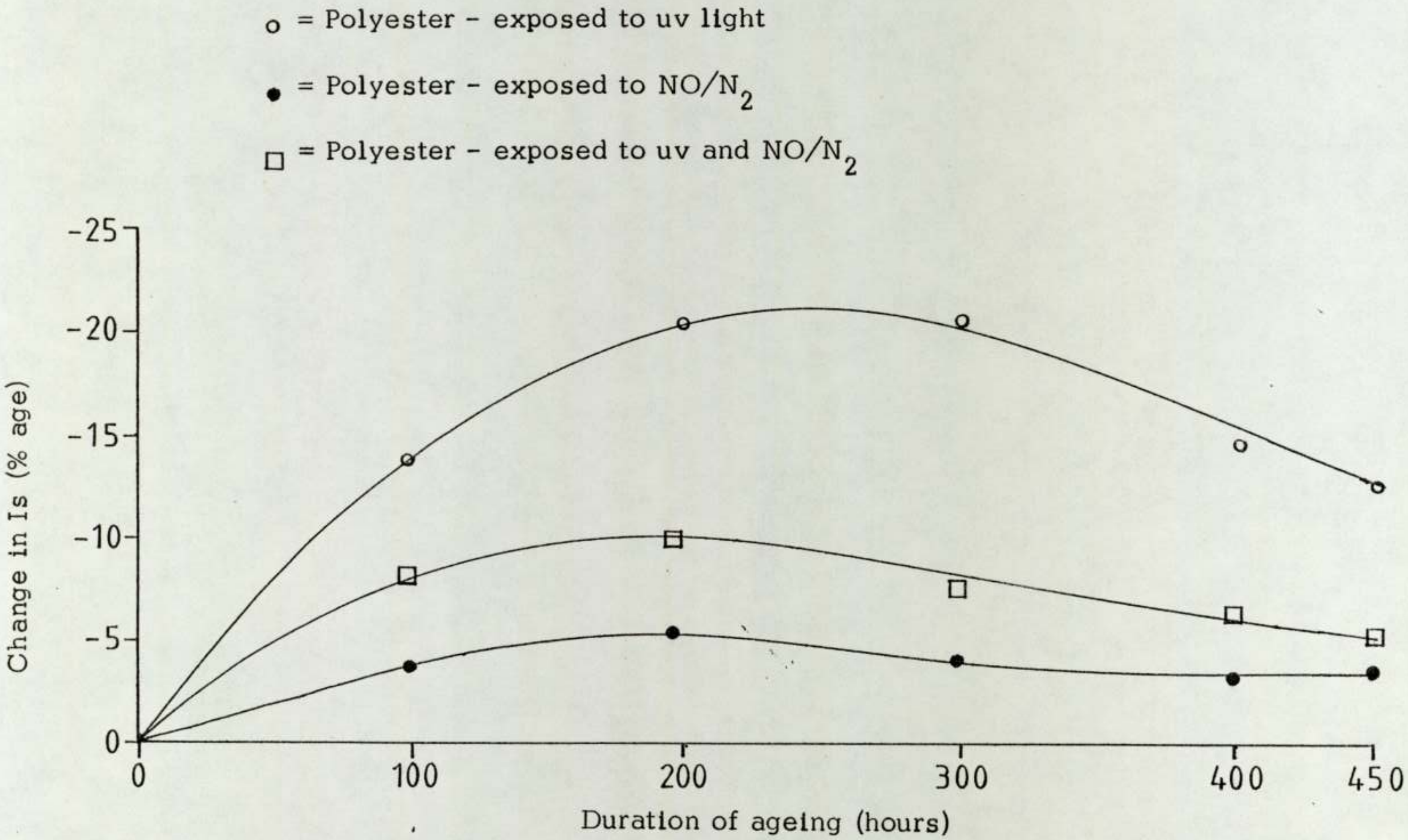


Figure 7.8: Polyester powder coatings - Percentage change in Is on ageing

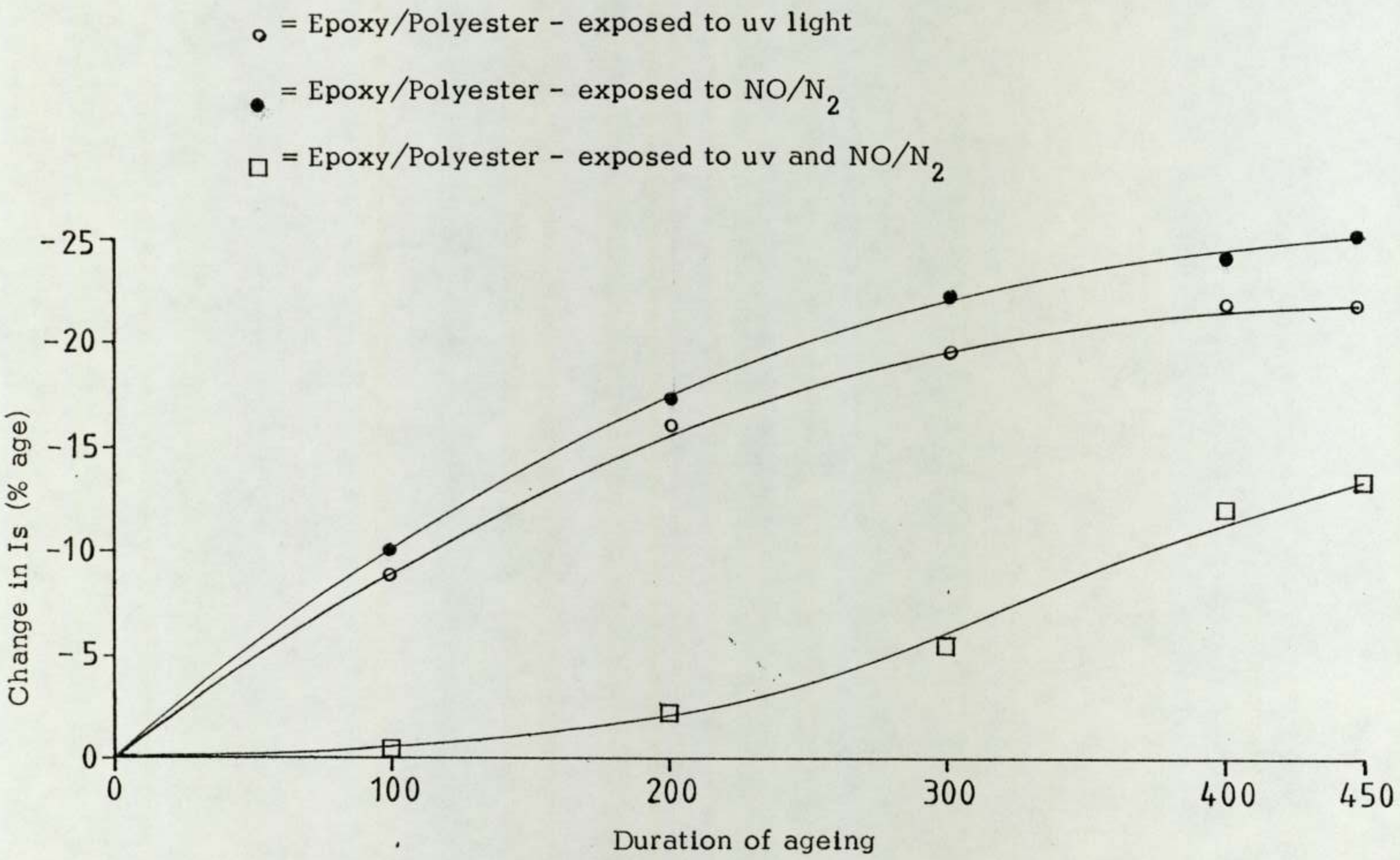


Figure 7.9: Epoxy/Polyester powder coatings - Percentage change in Is on ageing

influence of this flow on the results had been taken into account, the different rates of ageing became apparent (see Figure 7.8), with uv light causing the greatest decrease in specular intensity. The drop in Is for the polyester sample exposed to nitric oxide was considerably less than the decrease for the sample exposed to uv light. The action of NO in the presence of uv light, again, seems to be that of a stabiliser. This is indicated by the smaller decrease in Is of the polyester samples exposed to NO/uv light, than occurs with those exposed to uv light alone.

The surface of the epoxy/polyester samples also tended to flow due to the temperature cycling. The results shown in Figure 7.9 indicate the effects of the three ageing techniques after the influence of the temperature cycling had been taken into account.

The results for the epoxy/polyester samples exposed to NO or uv light show a trend which matches that of the epoxy samples, in that the drop in peak height due to the effects of NO and uv light are comparable. This decrease in peak height is of a similar magnitude to that of the polyester samples, being considerably greater than the decrease in Is of the epoxy samples. Yet again, the presence of NO has stabilised the degradation caused by uv light, although the epoxy/polyester coatings appear to be much more susceptible to degradation by NO alone, than the other systems studied.

It was noticed that the results for the powder coatings indicate that the rate of deterioration is non-linear over the period of ageing studied. This is especially the case with the polyester coatings which tended to show a slight increase in Is between 300 hours and 450 hours of ageing. In order to obtain a clearer indication of the relative rates of deterioration under different ageing conditions, the samples require ageing for a longer period than that used in this work. Despite this, the results from these experiments show that NO inhibits the degradation of powder coatings exposed to uv light. The polyester coatings degraded at similar rates to those of the PVC coatings. The epoxy coatings degraded at a considerably lower rate, which was comparable when exposed to uv light or NO. This trend was still apparent in the epoxy/polyester coatings.

The most interesting fact to emerge from this series of experiments, is that with all four systems, PVC, epoxy, polyester and epoxy/polyester, NO when present simultaneously with uv light, stabilises the degradation caused by the uv light. This appears to be a reflection of the situation which occurs in a natural weathering environment. The presence of nitric oxide at a polymer surface will normally be accompanied by the uv element of sunlight. The radicals produced by photolytic degradation within the surface of the coating will be absorbed by combining with the NO, due to its free radical nature, thus stabilising the degradation.

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1 Conclusions

The major initial object of the work described in this thesis was the establishment of an array of techniques to enable the effect of the interaction of nitric oxide with surface coatings to be examined. Two distinct constructional aspects were involved. One of these was concerned with a rapid non-destructive technique for the assessment of surface deterioration. The other involved an accelerated ageing technique to enable controlled exposure of samples to various combinations of degradative agents, (uv light, nitric oxide).

Without doubt the major single achievement has been the construction of an automated goniophotometer interfaced to a micro-computer data handling system. The broad aspects of the capability of this instrument can best be appreciated by considering the problem of subjective and objective assessment of surfaces.

The term "gloss" (sometimes referred to as sheen or lustre) is used to describe the result of a visual appraisal of a surface. No precise definition is possible to describe what is in fact a complex subjective phenomenon although various attempts have been made to define it and its various angular qualities. Figure 8.1a illustrates some of the relevant terms used in this field together with the representation in Figure 8.1b of the idealised diffuse or matt reflection, which in practice is extremely rare, and in Figure 8.1c the shape of the polar curve for a matt surface having a greater intensity of reflected light in the direction of specular reflection. When an individual makes a subjective visual assessment of the characteristics of a surface he does so using both eyes in a fairly arbitrary and (perhaps surprisingly) independent movement. In doing so he forms an impression based both on the sharpness and contrast of the images reflected to the eye from the surface, and the diffuse reflectance of the film. The point about a subjective impression of this type is that it contains a great deal of information and is virtually instantaneous, making it difficult to use instrumental techniques to assess a coating in this manner. On the other hand, although an individual can repeat his ranking of surfaces fairly well, his judgement may differ sharply from that of another observer. Thus the storage and transfer (as from one individual to another) of the information is, in any absolute and quantitative sense, impossible. It is in the use of a micro-computer, to store and recall in a precise fashion the complex light scattering data collected by the goniophotometer, that this project has gone some way towards mimicking and yet improving, the recall capacity of subjective human assessment.

The original decision to interface the goniophotometer with a computer was taken with two aims in mind. Firstly, to improve the accuracy and resolution of the data collected. Secondly, to utilise the speed of the computer to

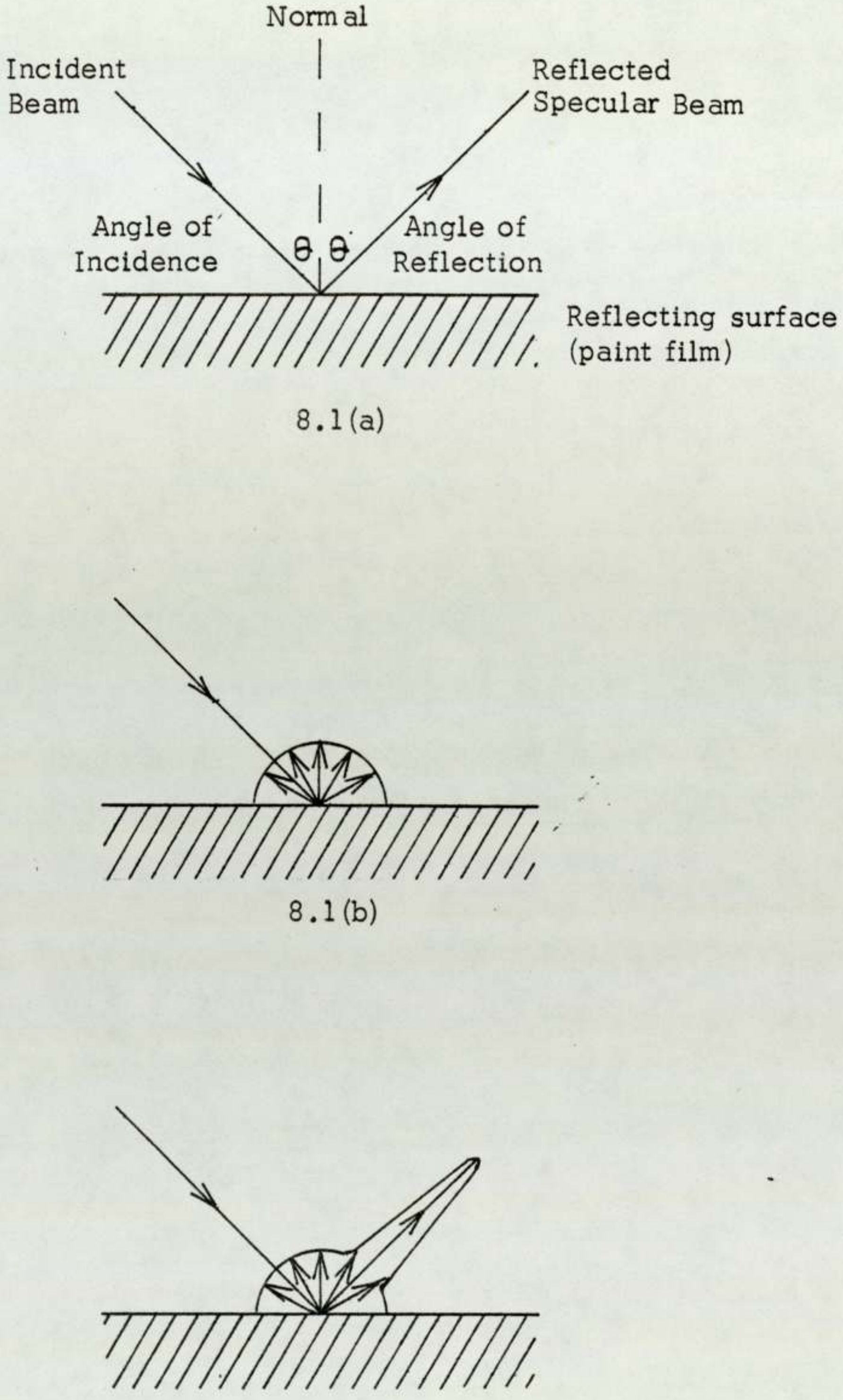


Figure 8.1: (a) Definition of terms
(b) Representation of matt reflection
(c) Representation of combined matt and specular reflection

rapidly calculate the various parameters required from the data, and to instantly display the results. Initially the computer was being used as a high speed calculator to convert the large quantities of goniophotometric data, which are obtained from each analysis, into simplified numerical parameters. These figures represent, in a quantitative manner, the nature of the light scattering envelope. The use of the computer changed this highly sensitive technique from a cumbersome, tedious procedure into a useful, rapid, non-destructive method of analysing a surface.

Once the initial development problems had been overcome and the technique mastered, it was soon realised that the data collected and subsequently recorded, could be analysed in many different ways by the computer. Perhaps the most important fact about the computerised system is that once the data has been collected, it is then held in the computer's memory in its "raw" state. This allows the computer to display the data in the form of a goniophotometric curve at any time after the actual sample analysis using the goniophotometer has been completed. During the initial studies carried out with surface coatings the facility to display the complete curve proved to be more useful than the original method of comparing the individual values derived from the curves.

Once the capabilities of the computer interfaced goniophotometer had been fully realised,the subsequent modifications to the programme have provided facilities to edit, expand, compress or to home in on individual details of a curve. These facilities are combined with the ability of the programme to superimpose separate curves on the same display. This technique allows the relative reflective nature of different samples to be rapidly compared. Figure 8.2 shows the overlaid curves for a high gloss paint, a matt paint and a sample of paper similar to that used in this thesis. The relative intensities of the light reflected from each surface can be clearly seen.

The technique of superimposing curves is very useful for studying the degree of ageing that has occurred on a surface, but it can be taken one step further. By using the computer to rescale the data in addition to superimposing the curves, it can be seen, as shown in Figure 8.3, that not only does the intensity of the reflected light vary for the different surfaces, but that the shape of the light scattering envelopes are vastly different. The differences between a glossy surface, a non-glossy but reflective surface and a matt surface are easily recognisable. The use of the goniophotometer and computer in this way provides a method of analysing a surface and representing the results both qualitatively and quantitatively.

By using the facilities of the computer to handle the goniophotometric data, the comparison of the light scattering envelopes provides a technique which can represent the "gloss" of a surface, in a manner which is close to the method by which an individual visually and subjectively assesses a surface. In fact, goniophotometric data analysed in this way has many advantages over a visual assessment of a surface. The sensitivity of the goniophotometer can indicate the most subtle of surface changes, even above and beyond visual perceptability. The individual visual assessment of a

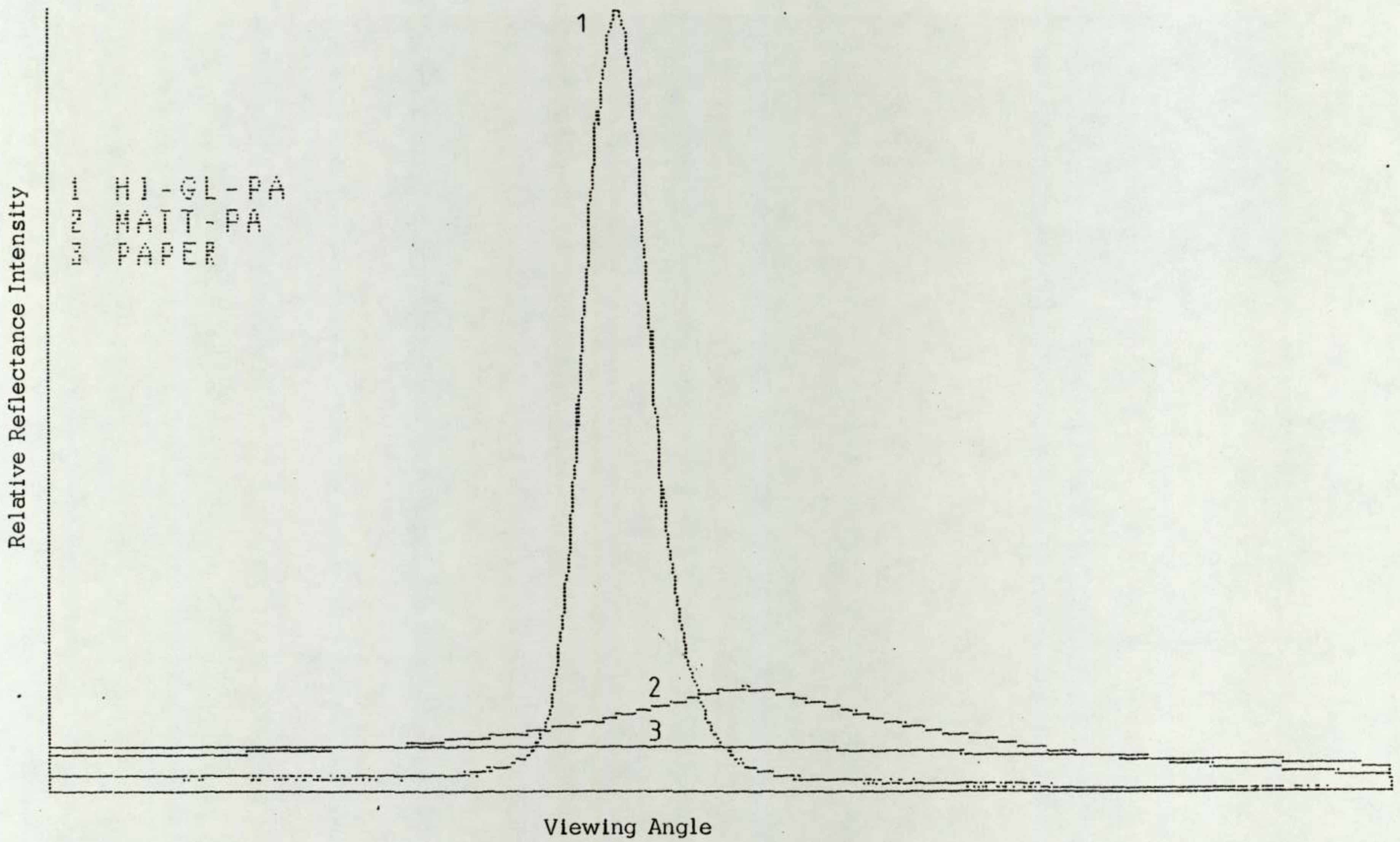


Figure 8.2: Superimposed goniophotometric curves for (1) High Gloss Paint, (2) Matt Paint and (3) White Paper

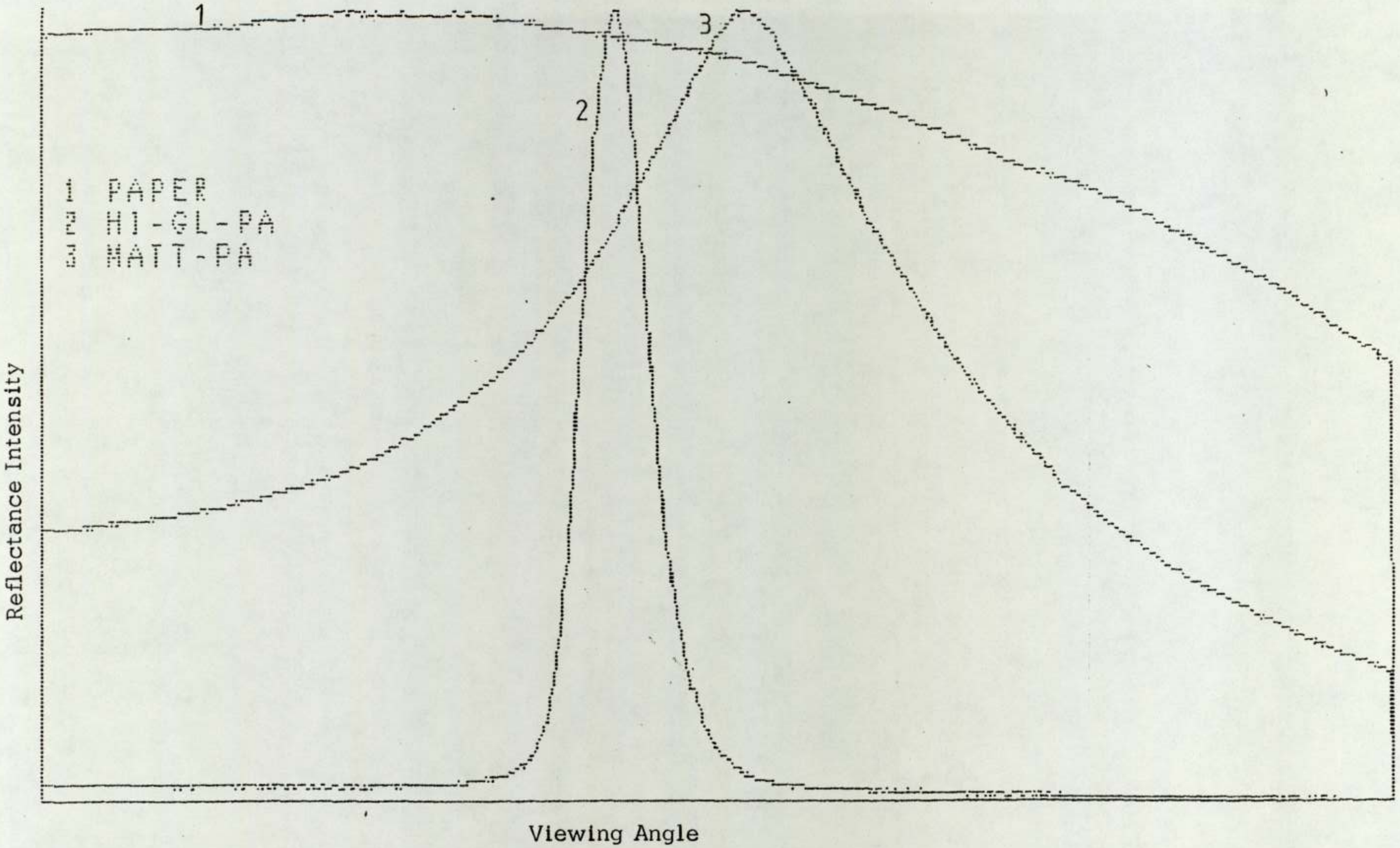


Figure 8.3: Rescaled superimposed goniophotometric curves for (1) White Paper, (2) High Gloss Paint and (3) Matt Paint

surface is difficult to recall if required for comparison after ageing. Additionally it is impossible to communicate ones visual assessment to another individual. The date held in the computer can be recorded onto disk or cassette and as a result is easily recalled for future analysis or can be passed on to another individual as an accurate record of the state of the surface.

The second area of development undertaken in this work was the construction of an accelerated ageing cabinet. The production of this cabinet was relatively inexpensive and has resulted in a versatile unit which, unlike commercial cabinets, is not dedicated to one particular ageing system. It is easily programmed to provide any combination of ageing techniques and is capable of operating over a wide range of temperatures, including subambient. The modular design allows additional units, providing different ageing facilities, to be added or substituted in the future. The cabinet has been designed specifically to facilitate the use of pollutant gases. Since some of these gases are high toxic, various devices have been incorporated in the cabinet to ensure that it fails safe in the event of operator error or equipment malfunction.

In use, the most important advantage of the cabinet is its ability to expose samples to different combinations of ageing elements simultaneously. This facility allows the individual effects of the ageing elements to be studied in conjunction with the combined effects. During the ageing studies undertaken with nitric oxide, this facility was employed to expose samples to the thermal cycling in isolation from the other ageing elements. Thus, it was possible to identify the effect of heat on the overall ageing of the samples. This technique of simultaneously ageing samples reduces the time required for an ageing study and ensures greater reproducibility as the samples are subjected to identical overall conditions.

The computer interfaced goniophotometer and the automated ageing cabinet have both been used extensively in the study of the reaction of nitric oxide with various surface coatings. These techniques used in conjunction with the i.r. spectroscopy studies described in Chapter 6, have shown that nitric oxide does chemically react with the surface coatings examined in this work.

The conclusions drawn from the results of these studies can be presented quite simply. In the case of poly (vinyl chloride) coatings, the i.r. spectroscopy studies have shown the reaction of nitric oxide with the surface of the samples follows different routes depending upon whether it occurs in conjunction with photolytic or thermal degradation. Thermal degradation in the presence of nitric oxide gives rise to the formation of nitroso groups (-N=O) attached to the polymer chain. Photolytic degradation of PVC in the presence of nitric oxide produces oxime groups (=N-OH) within the polymer.

The goniophotometric studies have shown that with all of the coatings investigated, whether based on the vinyl or hetro-chain types of polymer, nitric oxide inhibits the degradation caused by exposure to uv light. This is due to the free radical nature of this gas. The nitric oxide combines with the radicals produced by the exposure to uv light, thus stabilising the degradation of the coating.

Despite the fact that nitric oxide definitely reacts with a surface coating, its presence in a natural weathering environment must be regarded as beneficial for a coating, in that it retards degradation. It is unlikely that in such an environment the availability of nitric oxide at the surface would occur without the exposure of the same surface to uv light. The capability of nitric oxide to behave as a free radical sets it apart from the majority of pollutant gases. This is especially the case as this work has shown that the presence of nitric oxide in an environmental weathering situation is beneficial in the inhibition of the deterioration of a surface coating.

8.2 Suggestions for Further Work

In conclusion to this thesis the following suggestions for further work are made. These can be coveniently divided into two areas. The first of these is concerned with the exploitation and development of the goniophotometer interfaced with a micro-computer data handling system. The second area is related to the extension of the use of the ageing cabinet and studies involved with the deterioration of surface coatings.

In the first area of suggested work, further useful refinements to the goniophotometer could include the replacement of the valve photomultiplier and the bulky high voltage supply, by a semiconductor photocell of suitable sensitivity with a compact low voltage supply. This would allow a smaller, lighter unit to be designed, which would be more transportable than the present machine. The use of smaller semiconductor photocells would permit the installation of a second photocell together with a beam splitter, thus providing facilities for the computer to constantly and automatically control the calibration of the light source and amplifiers. This would effectively dispense with the need to allow the light source and electronics to stabilise prior to data collection.

The increasing availability of components for use in the opto-electronics field gives rise to the possibility of using a fibre optic system within the goniophotometer. An array of carefully positioned fibres, with individual detectors, could replace the present rotating photocell and turntable. The computer would read the light intensity at the end of each fibre and thus record the shape of the light scattering envelope for the surface. A goniophotometer designed on this basis could be constructed for use in applications where it is necessary for the instrument to be taken to the sample, for example held against a car body panel, as opposed to a small sample being placed inside the light tight compartment.

As regards the present design of goniophotometer, a future method of use might involve obtaining goniophotometric data by rotating the sample, keeping the light beam and photomultiplier stationary in relation to each other. This method of analysis would be closer to the actual technique with which an individual assesses the reflective properties of a surface. That is by holding the sample and slowly tilting the surface in order to assess the gloss. The use of a coloured filter system would allow the goniophotometer to be employed in colorimetry studies. The X, Y, Z co-ordinates being calculated by the computer from the respective reflected intensities for red, green and blue light.

As an analytical instrument the goniophotometer is not restricted to use with surface coatings. The technique can be applied to any situation where an assessment of the reflective properties of a surface are required. The wide range of applications could include the assessment of the effectiveness of various polishes used for improving the gloss of a surface, or for examining the appearance of foodstuffs. For example, one company is interested in using goniophotometry to assess the appearance of margarine.

In the second area of suggested work, the experimental programme, which involved the ageing cabinet and the goniophotometer, could be extended to include a wider range of surface coatings. As stated in Chapter 1, it was initially intended to include a range of automobile finishes in this study. Further work could additionally include an investigation into the effects on surface coatings of other atmospheric pollutants. A possible choice would be sulphur dioxide, since this gas is present in relatively high concentrations as a pollutant in industrial environments.

The versatility of the ageing cabinet means that its use is not limited to surface coatings. It has ready applications to other aspects of polymer ageing or weathering processes, in fact the broad field of polymer deterioration in general. The wide operating temperature range combined with the easily interchanged auxiliary units would allow the cabinet to be used for many accelerated studies. Examples of these are, the investigation of the shelf life of contact lens solution, the investigation of the photolytic degradation of polymers under the influence of different wavelengths of uv light, and for studying the effects of various temperatures on the curing of thermoset polymers.

Appendix 1

```
1 LIMIT MAX:GOTO4
2 IFPS=29/PITHENTI$=0:RETURN
3 TR$=TI$:RETURN
4 GRAPH 1:GRAPH 4
9 GRAPH 0:Z=49151:LIMITZ
10 REM CALCULATION OF GONIOPHOTOMETRIC
20 REM RESULTS, BY R.E.Raistrick.
50 DIMA(1,159),AV(255),BV(255),CV(255),DV(255),D(5,255):CA=1:AG=134
60 GOSUB370:GOTO530
70 REM*******************************
80 REM**A/D SUBROUTINE**
90 POKEZ+1,14
100 USR(Z+3)
110 IN=PEEK(Z+2)
120 POKE Z+1,15
130 USR(Z+3)
140 PS=PEEK(Z+2)
150 RETURN
160 REM*******************************
170 REM**DATA COLLECTION SUBROUTINE**
180 PR=500
190 FORX=0TO5
200 FORY=0TO255
210 D(X,Y)=500
220 NEXTY:NEXTX
230 PRINT"▩▩▩▩▩START TURNTABLE DRIVE "
240 PRINT"▩PRESS ANY KEY WHEN STARTED"
250 GETA$:IFA$=""THENGOTO250
260 PRINT"▩I N P U T I N G  D A T A
265 PRINT"▩PRESS B TO OVERRIDE DATA INPUT"
270 GOSUB80:REM**A/D**
280 IFPS=PRTHENCO=CO+1:GOTO300
290 CO=0:GOTO310
300 IFCO>5THENCO=5
310 D(CO,PS)=IN
320 PR=PS
330 IF(PS=255)*(CO>=5)THENRETURN
340 GETA$:IFA$="B"THENRETURN
342 IF(PS=29/PI)+(PS=79/PI)THENGOSUB2
350 GOTO270
360 REM*******************************
370 REM**A/D MACHINE CODE***
400 FORE=Z+3TOZ+37
410 READF:POKEE,F:NEXTE
420 C=(Z+1)/256:D=(Z+2)/256
430 G=INT(C):H=Z+1-G*256
440 I=INT(D):J=Z+2-I*256
450 POKE(Z+8),H:POKE(Z+9),G
460 POKE(Z+35),J:POKE(Z+36),I
470 RETURN
480 DATA62,152,211,191,58,0,0,211
490 DATA189,62,14,211,190,62,15,211
500 DATA190,62,12,211,190,227,227,219
510 DATA190,230,16,40,250,219,188,50
520 DATA0,0,201
530 REM*******************************
550 PRINT"▩"
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560 PRINT"▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒"
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620 PRINT"▒▒▒▒▒▒  GONIPHOTOMETRIC RESULTS          ▒▒▒▒▒▒"
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680 PRINT: PRINT"This program plots the goniophotometric"
690 PRINT"curve from the data inputed and
700 PRINT"calculates  :-
710 PRINT"▣   1, The Specular Intensity-- Is"
720 PRINT"   2, The Diffuse Intensity--- Id"
730 PRINT"   3, The Width At Half Peak"
740 PRINT"                           Height- W/2"
750 PRINT"   4, The Gloss Factor-------- Gf"
760 PRINT" ▣   PRESS ANY KEY TO CONTINUE"
770 GET A$:IF A$="" THEN GOTO 770
780 PRINT"▣"
790 PRINT"▣▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀"
800 PRINT"   ▒ ▒▒▒ ▒▒▒ ▒▒▒ ▒ ▒▒ ▒ ▒ ▒▒ ▒▒▒"
810 PRINT"   ▒▒▒ ▒▒▒ ▒▒▒ ▒▒▒ ▒ ▒▒▒ ▒ ▒▒"
820 PRINT"   ▒▒▒ ▒ ▒ ▒ ▒ ▒▒ ▒ ▒ ▒▒ ▒ ▒ ▒▒ ▒▒▒"
830 PRINT:PRINT"▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀"
840 PRINT"THIS PROGRAM RUNS IN GRAPHICS BASIC.
850 PRINT"                     ▔▔▔▔▔▔▔▔ "
860 PRINT"▣  IF RUN IN SHARP BASIC SP5025 THE "
870 PRINT"▣COMPUTER MAY CRASH WITH THE SUBSEQUENT"
880 PRINT"▣LOSS OF DATA"
890 PRINT"▣ IF YOU ARE NOT SURE WHICH BASIC IS"
900 PRINT"LOADED, EXIT THE PROGRAM NOW AND LOAD"
910 PRINT"GRAPHICS BASIC"
915 PRINT"──────────────"
920 PRINT" DO YOU WISH TO CONTINUE? Y/N"
930 GET A$:IF A$="" THEN GOTO 930
940 IF A$="Y" THEN GOTO960
950 END
960 GOSUB1010:REM**TEXT FILE?**
970 IFF$="Y"THENGOTO1660
980 GOTO1060
990 REM*****************************
1000 REM**TEXT FILE ?**
1010 PRINT"▣DO YOU WISH TO LOAD A TEXT FILE ?"
1020 PRINT"Y/N"
1030 GETF$:IFF$=""THEN1030
1040 RETURN
1050 REM*****************************
1060 IFCA=1THENGOTO1120
1070 PRINT"▣DOES THE TURNTABLE O/P REQUIRE"
1080 PRINT"▣CALIBRATION? Y/N "
1090 GETCA$:IFCA$=""THENGOTO1090
1100 IFCA$="Y"THENGOTO1120
1101 PRINT"▣IS THE Id ANGLE STILL ";DP;" DEGREES ?  Y/N"
```

```
1102 GETA$:IFA$=""THENGOTO1102
1103 IFA$="Y"THENGOTO1500
1104 INPUT"▒WHAT IS THE NEW Id ANGLE ?";DP
1110 GOTO1500
1120 PRINT"▒T U R N T A B L E   C A L I B R A T I O N"
1130 PRINT"▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬"
1140 PRINT"IF THIS IS NOT REQIRED BREAK THE PROG."
1150 PRINT"AND GOTO 1500"
1160 PRINT"========================================"
1170 PRINT"▒▒REMOVE THE SAMPLE HOLDER & SELECT ALL"
1180 PRINT"NEUTRAL FILTERS."
1190 PRINT"▒▒SWITCH ON THE LAMP AND ALIGN THE "
1200 PRINT"TURNTABLE TO GIVE A MAX. VALUE AS SHOWN"
1210 PRINT"BELOW.CHECK ON CHART REC."
1220 PRINT"▒PRESS ANY KEY WHEN DONE"
1230 IA=0
1240 FOR LN=0TO29
1250 GOSUB80:IA=IA+IN:NEXTLN
1260 CB=INT(IA/30):POKE4466,20:PRINTCB;"   "
1270 GETO$:IFO$=""THEN1230
1280 POKE4466,7:PRINT"▒ADJUST O/P TO GIVE AV 170 BELOW,54 ON   CHART REC."
1290 PRINT"▒PRESS ANY KEY WHEN DONE"
1300 IA=0
1310 FORLN=0TO99
1320 GOSUB80:IA=IA+IN:NEXTLN
1330 CB=INT(IA/99):POKE4466,20:PRINTCB;"   "
1340 GETO$:IFO$=""THEN1300
1350 PRINT"▒N O T E   T H E   T U R N T A B L E"
1360 PRINT"▒P O S I T I O N ."
1370 PRINT"▒This value has to be subtracted from all"
1380 PRINT"future direct turntable readings.
1390 PRINT:PRINT"CLOSE THE SHUTTER
1400 PRINT"▒▒▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬"
1410 PRINT"▒ROTATE THE TURNTABLE TO APPROX."
1420 PRINT"▒45 DEGREES.TYPE IN THE CORRECTED ANGLE"
1430 INPUT T2:GOSUB 80:P2=PS
1440 PRINT"▒REPEAT FOR A TURNTABLE POSISTION NEAR"
1450 PRINT"▒130 DEGREES"
1460 INPUTT3:GOSUB80:P3=PS
1470 INPUT"▒ENTER CALCULATED Id ANGLE ";DP
1480 FORP=0TO500:NEXT P
1490 PI=(T3-T2)/(P2-P3)
1500 REM
1505 PRINT"▒":PRINT"▒▒LOAD SAMPLE INTO GONIOPHOTOMETER AND"
1510 CA=0
1520 PRINT"SELECT FILTERS TO GIVE FULL SCALE"
1530 PRINT"DEFLECTION AT THE ANGLE OF MAXIMUM Is.
1540 PRINT" ▒▒ IF MANUAL CALCULATION OF Is AND/OR Id"
1550 PRINT"IS REQUIRED IT SHOULD BE DONE NOW."
1560 PRINT"▒▒WHEN COMPLETED RETURN THE TURNTABLE"
1570 PRINT"TO 137 DEGREES AND ENGAGE THE DRIVE"
1580 PRINT"CLUTCH":GOTO1590
1590 PRINT"  ▒▒     PRESS ANY KEY TO CONTINUE"
1600 GETA$:IFA$=""THENGOTO1602
1601 GOTO1619
1602 GOSUB80:POKE4466,20:PRINT"O/P.","POS."
1603 PRINTIN,PS:GOTO1600
```

```
1619 PRINT"▣"
1620 PRINT"CLEARING DATA INPUT ARRAYS
1630 PRINT"PLEASE WAIT"
1640 GOSUB160:REM**DATA COLLECTION**
1650 GOTO1770
1660 INPUT"▣ENTER NAME OF TEXT FILE ";CS$
1670 PRINT"▣LOAD TEXT FILE CASSETTE & PRESS"
1680 REM READ DATA INTO DV(Y)
1690 ROPEN CS$
1700 INPUT/T SC$
1710 INPUT/T PI
1720 INPUT/T DP
1730 FOR Y=0TO255
1740 INPUT/T DV(Y)
1750 NEXT Y
1751 INPUT/T CC
1752 INPUT/T PH
1753 INPUT/T DM
1754 INPUT/T FV
1755 INPUT/T L1$
1756 INPUT/T L2$
1757 INPUT/T L3$
1758 INPUT/T L4$
1760 CLOSE:RS=1:DD=1:DQ=DM+1:AG=134
1770 PRINT"▣ End of data input."
1771 PRINT:PRINT"DO YOU REQUIRE A PRINT-OUT OF THE RESULT  Y/N ?"
1772 GET P$:IF P$="" THEN 1772
1773 IF P$="Y" THEN PRINT "YES":GOTO 1775
1774 PRINT"NO"
1775 IFCC=1THENGOTO1900
1780 PRINT"▣▣":INPUT"WHAT IS THE SAMPLE CODE NUMBER..?";SC$
1785 PRINT"▣Processing data- ";SC$
1800 FORY=0TO255
1810 TT=0:NU=0
1820 FORX=0TO5
1830 TT=TT+NU:NU=D(X,Y):CU=X
1840 IFNU=500THENGOTO1860
1850 NEXTX
1860 IFCU<=0THENCU=1
1870 AV(Y)=INT((TT/CU)/255*199)
1880 IFAV(Y)>199THENAV(Y)=199
1890 NEXTY
1900 Y=0:PRINT"▣▣LOADING DATA INTO PLOT ARRAY"
1910 FORS=0TO1
1920 FORI=0TO159
1930 IFCC=1THENA(S,I)=DV(Y):Y=Y+1:GOTO1950
1940 A(S,I)=AV(Y):Y=Y+1
1950 IFY>255THENY=255:A(S,I)=0
1960 NEXTI
1970 NEXTS
1975 IFCC=1THENGOTO2080
1980 GRAPH 0:GOSUB2780:REM*PLOT DATA*
1990 GOSUB3030:REM**DATA OVERLAY**
2000 IFA$="Y"THENGOTO2015:GRAPH 0
2010 GRAPH 0:GOTO1500
2015 PRINT"▣▣CALCULATING PEAK HEIGHT"
2020 PH=0
```

```
2030 FORI=0TO255
2040 IFF$="Y"THENPJ=DV(I):GOTO2060
2050 PJ=AV(I)
2060 IFPJ>=PHTHENPH=PJ:DM=I:DQ=DM+1:DN=DQ
2070 NEXTI
2080 PS=(134-DP)/PI
2090 IV=0
2100 FORI=(PS-1)TO(PS+16)
2110 IFF$="Y"THENIV=IV+DV(I):GOTO2130
2120 IV=IV+AV(I)
2130 NEXT I
2140 IW=INT(IV/18+.5)
2145 PRINT"▣▣LOADING WORKING FILES WITH DATA"
2150 FORI=0TO255
2160 IFF$="Y"THENBV(I)=DV(I):GOTO2180
2170 BV(I)=AV(I)
2180 NEXTI
2190 FORI=(PS-1)TO(PS+16)
2200 BV(I)=IW:NEXTI:Y=0:IFCC=1THENSR=1:GOTO5000
2210 RS=1:GOSUB2250:REM**RESCALE**
2220 GOTO2340
2230 REM*******************************
2240 REM **RESCALE SUBROUTINE**
2250 FORS=0TO1
2260 FORI=0TO159
2270 O=INT(Y)
2280 A(S,I)=BV(O):Y=(Y+RS)
2290 IFY>255THENY=255
2300 NEXTI
2310 NEXTS
2320 RETURN
2330 REM*******************************
2340 GOSUB 2399:IF A$="Y" THEN GOSUB 2230 :GRAPH 0: GOSUB 2780
2350 FORI=PHTO0STEP-1
2360 SET(DM+1),(199-I):NEXTI
2365 SR=1:RS=1
2370 GOSUB3020:REM**DATA VERIFICATION**
2380 IFA$="Y"THENGOTO2391
2390 GOTO4000
2391 GOSUB2400:GOTO2440
2398 REM******************************
2399 REM**RESCALE???***
2400 POKEK,26:POKEL,1:PRINT"DO YOU WISH"
2410 POKEK,26:POKEL,2:PRINT"TO RESCALE?"
2415 POKEK,26:POKEL,3:PRINT"OR REDRAW?"
2420 POKEK,26:POKEL,4:PRINT"  Y/N
2430 GETA$:IFA$=""THENGOTO2430
2435 RETURN
2439 REM****************************
2440 IFA$="N"THEN DM=INT(DM):PH=BV(DM):DQ=DM+1:GOTO5000
2450 PH=BV(DM):GOSUB3120:REM*RESCALE PAR
2455 GOTO3200
2460 REM*****FILTER SUBROUTINE*******
2469 IFF$="Y"THENPRINT"▣":GOTO2710
2470 PRINT"▣     WHICH FILTERS ARE IN USE?"
2480 PRINT"     _________________________
2485 IFF$="Y"THENPRINT"▣":GOTO2710
```

```
2490 PRINT"▒        ENTER Y OR N AFTER EACH"
2500 PRINT"                -    -"
2510 PRINT"            RESPECTIVE FILTER"
2520 PRINT:PRINT"FILTER No 1..."
2530 F1$="":F2$="":F3$="":F4$=""
2540 POKE4465,16:POKE4466,7:GETF1$:IFF1$=""THENGOTO2540
2550 PRINTF1$
2560 PRINT"FILTER No 2..."
2570 POKE4465,16:GETF2$:IFF2$=""THENGOTO2570
2580 PRINT"▒";F2$
2590 PRINT"FILTER No 3..."
2600 POKE4465,16:GETF3$:IFF3$=""THENGOTO2600
2610 PRINT"▒";F3$
2620 PRINT"FILTER No 4..."
2630 POKE4465,16:GETF4$:IFF4$=""THENGOTO2630
2640 PRINT"▒";F4$
2650 F1=1:F2=1:F3=1:F4=1:L1$="":L2$="":L3$="":L4$=""
2660 IFF1$="Y"THENF1=0.497:L1$="FILTER 1"
2670 IFF2$="Y"THENF2=0.255:L2$="FILTER 2"
2680 IFF3$="Y"THENF3=0.113:L3$="FILTER 3"
2690 IFF4$="Y"THENF4=0.0543:L4$="FILTER 4"
2700 FV=F1*F2*F3*F4
2710 PRINT:PRINT"FILTERS IN USE ARE :-"
2720 PRINT"▒";L1$;" ";L2$;" ";L3$;" ";L4$
2730 PRINT"▒TOTAL FILTER VALUE = ";FV
2740 RETURN
2750 REM******************************
2760 END
2770 REM******************************
2780 REM PLOT DATA
2790 POKE57372,1:PRINT"▒"
2800 FORS=0TO1
2810 FORI=0TO159
2820 DI=I-1:DS=S
2830 IF(I=0)*(S=0)THENDI=0
2840 IF(I=0)*(S=1)THEN DI=159:DS=0
2850 LI=A(S,I)-A(DS,DI)
2860 IFLI>0THENIC=-1
2870 IFLI<0THENIC=1
2880 IFLI=0THENIC=0
2890 TC=0
2900 FORZL=1TOABS(LI)
2910 TC=TC+IC
2920 SET(I+(159*S)),(199-(A(S,I)+TC)):NEXT ZL
2930 NEXTI
2940 NEXTS
2960 LINE 0,0,0,199
2990 LINE 0,199,319,199
3010 RETURN
3020 REM******************************
3030 REM DATA VERIFICATION OVERLAY
3035 K=4465:L=4466
3040 POKEK,26:POKEL,1
3050 PRINT"SAMPLE ";SC$;"   "
3060 POKEK,26:POKEL,2:PRINT"IF DATA IS  "
3070 POKEK,26:POKEL,3:PRINT"CORRECT,PRESS"
3080 POKEK,26:POKEL,4:PRINT"Y TO CONTINUE"
```

```
3085 POKEK,26:POKEL,5:PRINT"                "
3090 GETA$:IFA$=""THENGOTO3090
3091 FOR I=1TO7
3092 POKEK,26:POKEL,I:PRINT"                "
3093 NEXT I
3100 RETURN
3110 REM****************************
3119 REM**RESCALE PARAMETERS**
3120 GRAPH 0:INPUT"BY WHAT FACTOR DO YOU WISH TO EXPAND THE X AXIS ? ";SR
3122 PRINT"▨▨▨▨▨▨ ← 134 ——————————————————————— 0 → ▨▨▨▨▨▨"
3130 INPUT"▨FROM WHICH ANGLE DO YOU WISH TO PLOT ?  ";AG
3135 PRINT"▨▨▨PROCESSING DATA"
3140 Y=(134-AG)/PI:RS=1/SR:IFY<0THENY=0
3150 DN=(DQ-Y)*SR:IF(DN<0)+(DN>319)THENDN=0
3155 IFM=1THENRETURN
3160 GOSUB2250:REM**RESCALE**
3170 GRAPH 0:GOSUB2780:REM**PLOT
3180 FORI=PHTOOSTEP-1
3190 SETDN,(199-I):NEXTI
3194 RETURN
3195 REM*****************************
3200 GOSUB3030:REM**VER
3210 IFA$="Y"THENGOTO3225
3220 GOTO4000
3225 GOSUB2400:GOTO2440
4000 POKEK,26:POKEL,1:PRINT"DO YOU WISH"
4005 POKEK,26:POKEL,2:PRINT"TO ALTER THE"
4010 POKEK,26:POKEL,3:PRINT"THE ID VALUE "
4020 GETA$:IFA$=""THENGOTO4020
4023 GOSUB 3091
4025 IFA$="N"THENGOTO4100
4030 GOSUB2400:REM**??RESCALE
4035 IFA$="N"THENGOTO4045
4040 GOSUB3120
4045 POKEK,26:POKEL,1:PRINT"TO ALTER THE"
4046 POKEK,26:POKEL,2:PRINT"ID VALUE,KEY"
4047 POKEK,26:POKEL,3:PRINT"D. TO LOWER  "
4048 POKEK,26:POKEL,4:PRINT"U. TO RAISE "
4049 POKEK,26:POKEL,5:PRINT"F. TO FINISH"
4051 FORI=1TO9
4052 POKEK,26:PRINT"              "
4053 NEXTI
4055 GETA$:IFA$=""THENGOTO4055
4059 DJ=0
4060 IFA$="D"THENDJ=-1
4065 IFA$="U"THENDJ=1
4070 IFA$="F"THENGOTO4096
4075 IX=IW+DJ:PS=(134-DP)/PI
4076 JY=INT((PS-3)*SR):JX=INT((PS+16)*SR)
4080 FORI=JYTOJX
4085 RESETI,(199-IW):SETI,(199-IX)
4090 NEXTI
4095 IW=IX:GOTO4055
4096 FORI=(PS-1)TO(PS+16)
4097 BV(I)=IW:A(0,I)=IW:NEXTI:GOSUB3091
4100 POKEK,26:POKEL,1:PRINT"DO YOU WISH"
4105 POKEK,26:POKEL,2:PRINT"TO ALTER THE"
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```
4110 POKEK,26:POKEL,3:PRINT"PH ANGLE Y/N "
4120 GETA$:IFA$=""THENGOTO4120
4122 GOSUB 3091
4125 IFA$="N"THENGOTO2370
4130 GOSUB2400:REM**??RESCALE**
4135 IFA$="N"THEN4145
4140 GOSUB3120
4145 POKEK,26:POKEL,1:PRINT"TO ALTER THE"
4146 POKEK,26:POKEL,2:PRINT"PH ANGLE,KEY"
4147 POKEK,26:POKEL,3:PRINT"L.TO INCREASE";
4148 POKEK,26:POKEL,4:PRINT"R.TO DECREASE"
4149 POKEK,26:POKEL,5:PRINT"F. TO FINISH"
4151 FOR I=1TO9
4152 POKEK,26:PRINT"              "
4153 NEXTI
4155 GETA$:IFA$=""THENGOTO4155
4159 Q=0
4160 IFA$="L"THENQ=-1*SR
4165 IFA$="R"THENQ=1*SR
4170 IFA$="F"THENGOTO2370
4172 IFDN<=0THENGOTO4155
4175 EN=DN+Q:IF(EN<1)+(EN>319)THENGOTO4155
4180 FORI=(PH-1)TO1STEP-1
4185 RESETDN,(199-I):SETEN,(199-I)
4187 NEXTI
4190 DN=EN:DM=DM+(Q*RS):DQ=DM+1:GOTO4155
5000 HP=BV(DM)/2
5010 FORI=5TO255
5020 IFBV(I)>HPTHENW1=I:GOTO5040
5030 NEXTI
5040 FORI=255TO0STEP-1
5050 IFBV(I)>HPTHENW2=(I+1):GOTO5065
5060 NEXTI
5065 YI=(134-AG)/PI
5067 IF (F$="Y")*(CC=1)THEN GRAPH 0:GOSUB 2780
5070 FORI=((W1-YI)*SR)TO((W2-YI)*SR)
5075 IFI<0THENI=0
5080 SETI,(199-HP)
5090 NEXTI
5095 FH=(W2-YI)*SR:FG=(W1-YI)*SR:IFFG<0THENFG=0
5097 IFFH>319THENFH=319
5100 FORI=HPTO0STEP-1
5110 SETFG,(199-I):SETFH,(199-I)
5120 NEXTI
5125 IFCC=1THENDN=DM+1
5130 FORI=PHTO0STEP -1
5140 SETDN,(199-I):NEXTI
5144 IF P$="Y" THEN GRAPH 6
5145 GOSUB3030:REM**VER**
5150 IFA$="N"THENCC=0:GOTO4000
5152 GRAPH 0:IF(F$="Y")*(CC=0)THENGOTO5154
5153 GOTO5160
5154 PRINT"▩DO YOU WISH TO CHANGE THE SAMPLE CODE ?   Y/N"
5155 GETA$:IFA$=""THENGOTO5155
5156 IFA$="Y"THENINPUT"NEW CODE ? ";SC$
5160 IFCC=1THENGOTO5195
5161 GOSUB2469
```

```
5170 PRINT"▣ARE THESE FILTERS CORRECT ?..Y/N"
5180 GET A$:IF A$=""THEN GOTO5180
5190 IFA$="N"THENF$="":GOTO5160
5195 TS=INT((((BV(DM)/FV)/199)*10)+.5):TD=INT((((BV(PS)/FV)/199)*10)+.5)
5200 TP=TS-TD:TH=TS/2
5210 PW=(INT(((W2-W1)*PI*100)+.5))/100:PA=(INT(100*((134-(DM*PI)))+.5))/100
5220 GF=(INT(((TP/PW)+.5)*100))/100
5225 PRINT"▣▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒"
5230 PRINT"▣    G O N I O P H O T O M E T R I C"
5240 PRINT"     ━━━━━━━━━━━━━━━━━━━━━━━━━━━━━━"
5250 PRINT"     C U R V E -- C O D E  N O., ";SC$
5260 PRINT"     ━━━━━━━━━━━━━━━━━━━━━━━━━━━━━━"
5270 PRINT"▣▣▣▣Is = ";TS;" UNITS AT ";PA;" DEGREES"
5280 PRINT"▣▣▣▣Id = ";TD;" UNITS AT ";DP;" DEGREES"
5290 PRINT"▣▣▣▣PEAK HEIGHT = ";TP;" UNITS"
5300 PRINT"▣▣▣▣HALF PEAK WIDTH = ";PW;" DEGREES"
5310 PRINT"▣▣▣▣GLOSS FACTOR = ";GF
5312 PRINT"▣   ";L1$;" ";L2$;" ";L3$;" ";L4$
5315 PRINT"▣▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒"
5320 IF P$="Y" THEN GRAPH 6
5329 IFCC=1THENGOTO6000
5330 PRINT"▣DO YOU WISH TO SAVE THIS DATA ? Y/N "
5335 GETA$:IFA$=""THENGOTO5335
5340 IFA$="Y"THENGOTO5345
5343 GOTO6000
5345 CC=1:PRINT"▣LOAD CASSETTE AND PRESS"
5400 WOPEN SC$
5410 PRINT/T SC$
5420 PRINT/T PI
5430 PRINT/T DP
5440 FOR Y=0 TO 255
5450 PRINT/T BV(Y)
5460 NEXT Y
5465 PRINT/T CC
5467 PRINT/T PH
5469 PRINT/T DM
5471 PRINT/T FV
5473 PRINT/T L1$
5475 PRINT/T L2$
5477 PRINT/T L3$
5479 PRINT/T L4$
5490 CLOSE
6000 PRINT"▣DO YOU WISH TO COMPARE THIS DATA WITH   ▣ANOTHER FILE ? Y/N"
6010 GETA$:IFA$=""THENGOTO6010
6020 IFA$="Y"THENGOTO7000
6030 PRINT"▣▣DO YOU WISH TO RUN ANOTHER SAMPLE/FILE ?Y/N"
6040 GETA$:IFA$=""THENGOTO6040
6050 IFA$="N"THENGOTO6200
6060 M=0:CC=0:F$="":DD=0:GOTO960
6200 PRINT"▣PROGRAM FINISHED":END
7000 INPUT"▣ENTER NAME OF TEXT FILE ";CS$
7002 PRINT"LOAD TEXT FILE CASSETTE & PRESS"
7005 ROPEN CS$
7009 INPUT/T SD$
7010 INPUT/T PK
7020 INPUT/T DR
7030 FOR Y=0TO255
```

```
7040 INPUT/T CV(Y)
7050 NEXT Y
7051 INPUT/T CC
7052 INPUT/T PG
7053 INPUT/T DL
7054 INPUT/T FW
7055 INPUT/T L5$
7056 INPUT/T L6$
7057 INPUT/T L7$
7058 INPUT/T L8$
7060 CLOSE:Y=0:RS=1:SR=1
7070 M1=PH/FV:M2=PG/FW:IFM2>M1THENM1=M2
7072 SS=0
7074 PRINT"▧PROCESSING DATA"
7075 B=Y:PT=PH:DQ=DM+1
7076 DN=(DQ-Y)*SR:PH=INT(PH/FV/M1*199)
7078 IFDN>255THENDN=0
7080 FORI=0TO255
7090 IFDD=1THENBV(I)=INT(DV(I)/FV/M1*199):GOTO7109
7095 IFSS=0THENAV(I)=BV(I)
7100 BV(I)=INT(AV(I)/FV/M1*199)
7109 NEXTI:SS=1:GRAPH 0:GOSUB2240:GOSUB2780
7110 GOSUB3180
7115 Y=B:DQ=DL+1:DN=(DQ-Y)*SR:PH=INT(PG/FW/M1*199)
7116 IFDN>255THENDN=0
7129 FORI=0TO255
7130 BV(I)=INT(CV(I)/FW/M1*199)
7131 NEXTI:GOSUB2240:GOSUB2780
7135 GOSUB3180
7140 PH=PT:POKE4466,23:POKE4465,(DN/8):PRINTSD$;"▥"
7159 GOSUB2399:IFA$="Y"THENM=1:GOTO7180
7160 GRAPH 0:GOTO6000
7180 GOSUB3119
7190 GOTO7075
60000 GOSUB 80:PRINTPS,IN:GOTO60000
```

Appendix 2

GONIO

```
10 FL1=0:FL2=0:FL3=0:DIM CURVE%(4095),SCALEX%(1023)
20 ESC$=CHR$(27):PLON$=CHR$(29):PLOFF$=CHR$(31):HLON$=ESC$+"
N":HLOFF$=ESC$+"O"
30 GRON$=ESC$+CHR$(94)+CHR$(18):GROFF$=ESC$+CHR$(94)+CHR$(84
):HLHOF$=ESC$+"Y"
40 HLDON$=ESC$+"E":ERASGR$=ESC$+CHR$(12):UNBLNKGR$=ECS$+CHR$
(90):UNBLSCR$=ESC$+"Z"
45 HLHON$=ESC$+"X":HLION$=ESC$+"L":HLDOF$=ESC$+"I":HLIOF$=ES
C$+"M"
50 SOH$=CHR$(25):DEFSOH$=ESC$+"*V19":PRINT DEFSOH$
80 CLR$=ESC$+"J":BLSTL$=ESC$+"V":UNBLSTL$=ESC$+"W":CURH$=ESC
$+"H"
100 GOSUB 200:GOSUB 1070:IF (FLI=1) + (FL1=2) THEN GOTO 1120
 ELSE  GOSUB 1470
110 GOSUB 1640:GOSUB 1790:GOTO 1120
120 REM*************a/d**************
122 P%=0:I%=0:FOR I=1 TO 3
123 CH%=0
124 PRIMARY%=&H47
126 SECONDARY%=&H60+CH%
128 GOSUB 172
130 CALL IEEERX(Z%)
132 SECONDARY%=&H70
134 GOSUB 172
136 CALL IEEERX(Z%)
138 GOSUB 162
140 SECONDARY%=&H74 : GOSUB 172
142 CALL IEEERX(Z%)
144 A%=Z%
146 SECONDARY%=&H78 : GOSUB 172
148 CALL IEEERX(Z%)
150 GOSUB 162
152 C%=Z%
154 B%=A%*16+C%/16
156 IF CH%=0 THEN P%=B%+P%:CH%=1:GOTO 124
158 I%=B%+I%
160 NEXT I
```

```
161 I%=I%/3:P%=P%/3:RETURN
162 U%=&H5F
164 CALL GETATN
166 CALL IEEETX(U%)
168 CALL RELATN
170 RETURN
172 CALL GETATN
174 CALL IEEETX(PRIMARY%)
176 CALL IEEETX(SECONDARY%)
178 CALL LISTEN
180 CALL RELATN
182 RETURN
200 REM*****resets everything************
210 PRINT GRON$;PLOFF$;ERASCR$;UNBLNKCR$;WHITE$;SOH$;GROFF$
220 PRINT UNBLSCR$;CLR$;UNBLSTL$
230 RETURN
240 REM**********load data from file**********************
250 PRINT CLR$:PRINT HLION$;HLON$;"DATA FILE ACCESS ROUTINE"
;HLOFF$ :PRINT
260 ON ERROR GOTO 370
270 INPUT "ENTER SAMPLE CODE NO.  or  FILE NAME ";FILE$
280 CAT$="B:" + FILE$
290 OPEN "I",#1,CAT$
300 INPUT#1,CODE$,Z,HP,W1,W2,IS,ID,FL1,FL2,FL3,MY,SX
310 INPUT#1,F1$,F2$,F3$,F4$,FV,T,TC,XP,AN,CA1,CA2,CA4,CA5
320 FOR I = 0 TO 4095
330 IF EOF(1) THEN GOTO 360
340 INPUT#1,CURVE%(I)
350 NEXT I
360 CLOSE#1:SC=I-1:ON ERROR GOTO 0:RETURN
370 IF (ERR=53)  AND (ERL=290) THEN PRINT"FILE NOT FOUND; TR
Y AGAIN":PRINT:CLOSE#1:FILES "B:*.*":PRINT:PRINT:RESUME 270
380 CLOSE#1:RESUME 240
390 PRINT GRON$;PLOFF$;UNBLNKCR$;ERASCR$;SOH$;GROFF$
400 RETURN
410 PRINT BLSCR$;BLSTL$:RETURN
420 PRINT GRON$;BLNKCR$;SOH$;GROFF$
430 RETURN
```

```
440 PRINT GRON$;UNBLNKGR$;SOH$;GROFF$
450 RETURN
460 PRINT GRON$;ERASGR$;SOH$;GROFF$
470 RETURN
480 PRINT CLR$;UNBLSTL$;UNBLSCR$
490 RETURN
500 PRINT UNBLSCR$:RETURN
510 PRINT CLR$;UNBLSCR$
520 RETURN
530 REM*************Sample Code*************
540  PRINT:PRINT:INPUT "ENTER SAMPLE CODE ";CODE$
550 IF LEN(CODE$)> 8 THEN 570
560 RETURN
570 PRINT"CODE TOO LONG, PLEASE REENTER,  MAX.8 CHAR.":GOTO
530
580 REM*****************Filter Selection********************
*********
590 GOSUB 480
600 PRINT:PRINT"                    WHICH FILTERS ARE IN USE
 ?"
610 PRINT"                    ---------------------------"
620 PRINT
630 PRINT"         PRESS Y OR N AFTER EACH RESPECTIVE FILTER
"
640 PRINT"               ~   ~":PRINT"FILTER No. 1 ...? ";
650 F1$=INKEY$:IF F1$="" THEN 650
660 A=ASC(F1$):IF (A=89) + (A=78) THEN PRINT F1$ ELSE 650
670 PRINT"FILTER No. 2 ...? ";
680 F2$=INKEY$:IF F2$="" THEN 680
690 A=ASC(F2$):IF (A=89) + (A=78) THEN PRINT F2$ ELSE 680
700 PRINT"FILTER No. 3 ...? ";
710 F3$=INKEY$: IF F3$="" THEN 710
720 A=ASC(F3$):IF (A=89) + (A=78) THEN PRINT F3$ ELSE 710
730 PRINT"FILTER No. 4 ...? ";
740 F4$=INKEY$:IF F4$="" THEN 740
750 A=ASC(F4$):IF (A=89) + (A=78) THEN PRINT F4$ ELSE 740
760 F1=1:F2=1:F3=1:F4=1:L1$="":L2$="":L3$="":L4$=""
770 IF F1$="Y" THEN F1=.5:L1$="FILTER 1"
```

```
780 IF F2$="Y" THEN F2=.245:L2$="FILTER 2"
790 IF F3$="Y" THEN F3=.113:L3$="FILTER 3"
800 IF F4$="Y" THEN F4=.0373:L4$="FILTER 4"
810 FV=F1*F2*F3*F4
820 PRINT:PRINT"FILTERS IN USE ARE >
830 PRINT"                    ";L1$;" ";L2$;" ";L3$;" ";L4$
840 PRINT:PRINT"TOTAL FILTER VALUE = ";FV
850 PRINT:PRINT:PRINT: PRINT:PRINT"                    ARE THESE F
ILTERS CORRECT ? (Y/N) ";
860 A$=INKEY$:IF A$="" THEN 860
870 IF (A$="Y") + (A$="N") THEN PRINT A$ ELSE 860
880 IF A$="N" THEN 580
890 RETURN
900 REM***************data dump*************
910 PRINT HLION$;HLON$;" TRANSFERING DATA ";HLOFF$
920 OPEN "O",#1,"TEMP.DAT"
930 PRINT#1,CODE$;",";Z;HP;W1;W2;IS;ID;FL1;FL2;FL3;MY;SX
940 PRINT#1,F1$;",";F2$;",";F3$;",";F4$;",";FV;T;TC;XP;AN;CA
1;CA2;CA4;CA5
950 FOR I = 0 TO SC
960 PRINT#1,CURVE%(I);
970 NEXT I
980 CLOSE #1
990 RETURN
1000 REM***********calibration************
1010 CHAIN"GPCAL"
1020 OPEN "O",#1,"CALIB.DAT"
1030 PRINT#1,CA1;CA2;CA3;CA4;CA5;MY;T;FL1;SC
1040 CLOSE #1
1050 RETURN
1060 REM**********read calib file*********
1070 OPEN "I",#1,"CALIB.DAT"
1080 INPUT#1,CA1,CA2,CA3,CA4,CA5,MY,T,FL1,SC
1090 CLOSE#1
1100 TC=CA3:RETURN
1110 REM**********************************************
1120 REM
1130 PRINT CLR$;HLION$;HLON$;" PRESS ";HLOFF$;"    ";HLON$;"
```

```
 1 ";HLOFF$;" To calibrate."
1140 PRINT:PRINT"                    ";HLON$;" 2 ";HLOFF$;" To load a
 data file."
1150 PRINT:PRINT"                    ";HLON$;" 3 ";HLOFF$;" To run sa
mple."
1155 PRINT:PRINT"                    ";HLON$;" 4 ";HLOFF$;" To compar
e data."
1160 PRINT:PRINT"                    ";HLON$;" 5 ";HLOFF$;" To exit p
rogramme."
1170 A$=INKEY$:IF A$="" THEN GOTO 1170
1180 IF (ASC(A$)>53) + (ASC(A$)<49) THEN GOTO 1170
1190 ON (ASC(A$)-48) GOTO 1010,1210,1230,1980,1220
1200 GOTO 1130
1210 GOSUB 250:FL3=3:GOSUB 910:CHAIN"GPMAIN
1220 FL1=0:GOSUB 1020:END
1230 IF FL1<>1 THEN GOTO 1010
1240 GOSUB 1910
1250 GOSUB 510:PRINT"CLEARING INPUT ARRAYS"
1260 FOR I=0 TO 4095
1270 CURVE%(I)=5000
1280 NEXT I
1290 GOSUB 1840:GOSUB 510:PRINT"ENGAGE TURNTABLE DRIVE":PRIN
T:PRINT:PRINT"I N P U T I N G  D A T A"
1300 GOSUB 120
1310 CURVE%(P%)=I%
1320 IF P%>=SC THEN 1340
1330 GOTO 1300
1340 FOR I=1 TO 10
1350 PRINT CHR$(7)
1360 FOR PAUSE=1 TO 500:NEXT PAUSE
1370 NEXT I
1380 FL2=0:FL3=0
1390 GOSUB 510
1400 SX=1023/SC
1410 GOSUB 540
1420 GOSUB 510
1430 GOSUB 580
1440 GOSUB 510
```

```
1450 GOSUB 900
1460 CHAIN"GPMAIN"
1470 REM**************Title Page**********************
1480 PRINT CLR$:PRINT:PRINT HLDON$;HLION$;HLHON$;HLON$
1490 PRINT"***************************************"
1500 PRINT"*";HLOFF$;SPC(74);HLON$;"*"
1510 PRINT"*";HLOFF$;SPC(74);HLON$;"*"
1520 PRINT"*";HLOFF$;SPC(74);HLON$;"*"
1530 PRINT"*";HLOFF$;SPC(22);HLHOF$;HLON$;"GONIOPHOTOMETER";
HLOFF$;HLHON$;SPC(22);HLON$;"*"
1540 PRINT"*";HLOFF$;SPC(74);HLON$"*"
1550 PRINT"*";HLOFF$;SPC(24);"D A T A    A N A L Y S I S";SP
C(24);HLON$;"*"
1560 PRINT"*";HLOFF$;SPC(24);"~~~~~~~    ~~~~~~~~~~~~~~~";SP
C(24);HLON$;"*"
1570 PRINT"*";HLOFF$;SPC(74);HLON$;"*"
1580 PRINT"*";HLOFF$;SPC(74);HLON$;"*"
1590 PRINT"*";HLOFF$;SPC(74);HLON$;"*"
1600 PRINT"***************************************"
1610 PRINT:PRINT:PRINT:PRINT:PRINT:PRINT:PRINT HLOFF$
1620 FOR PAUSE = 1 TO 5000:NEXT PAUSE
1630 RETURN
1640 REM************Prog. Description********************
1650 PRINT CLR$;HLDON$;HLIOF$;HLHOF$
1660 PRINT:PRINT HLON$;"GONIOPHOTOMETER ------ DATA ANALYSIS
,"
1670 PRINT "~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~";HLOFF$
1680 PRINT:PRINT"This programme loads data from the GONIOPHO
TOMETER or from a data file,"
1690 PRINT:PRINT"and then plots INTENSITY against ANGLE of R
EFLECTION."
1700 PRINT:PRINT"The following are calculated :-"
1710 PRINT:PRINT "       1, The Specular Intensity ---------
---- Is"
1720 PRINT:PRINT "       2, The Diffuse Intensity  ---------
---- Id"
1730 PRINT:PRINT"       3, The Width At Half Peak Height ---
--- W/2"
```

```
1740 PRINT:PRINT"       4, The Gloss Factor -----------------
--- Gf"
1750 PRINT:PRINT:PRINT;SPC(10);HLION$;HLDON$;HLON$;"Press Sp
ace Bar To Continue"
1760 PRINT HLOFF$;HLDOF$
1770 A$=INKEY$:IF A$ <> " " THEN 1770
1780 RETURN
1790 PRINT CLR$:PRINT:PRINT:PRINT" THIS PROGRAMME ASSUMES TH
AT THE SOURCE DISK IS IN DRIVE A."
1800 PRINT:PRINT"AND THAT THE DATA DISK IS IN DRIVE B."
1810 FL1=2:GOSUB 1020
1820 GOSUB 1750
1830 RETURN
1840 REM*****************
1850 B%=1:CALL SYSCON(B%)
1860 CALL ISTART:CALL ISSIFC
1870 B%=0:CALL SETADD(B%)
1880 B%=&H30:CALL SETMSK(B%)
1890 CALL RELATN
1900 RETURN
1910 GOSUB 510
1920 PRINT:PRINT" 1,     LOAD SAMPLE INTO GONIOPHOTOMETER"
1923 PRINT:PRINT"        Do You Wish To Enter The Id Manually
 ? (Y/N)":GOSUB 1990
1926 IF A$="Y" THEN GOSUB 2020
1930 PRINT:PRINT" 2,     SELECT APPROPIATE FILTERS FOR Is"
1940 PRINT:PRINT" 3,     SET TURNTABLE RATE OF ROTATION"
1950 PRINT:PRINT" 4,     POSITION TURNTABLE AT 136 DEGREES
1960 PRINT:PRINT" 5,     OPEN LIGHT SHUTTER
1970 GOSUB 1750:RETURN
1980 GOSUB 510:FL2=2:GOSUB 910:CHAIN "GPEDIT"
1990 A$=INKEY$:IF A$=""THEN GOTO 1990
2000 A=ASC(A$):IF (A=89)+(A=78) THEN RETURN
2010 GOTO 1990
2020 PRINT:PRINT"             ROTATE TURNTABLE TO Id ANGLE"
2030 PRINT:PRINT"             SELECT APPROPIATE FILTERS FOR Id
"
2035 PRINT:PRINT"             OPEN LIGHT SHUTTER"
```

```
2040 GOSUB 1750:GOSUB 1840:GOSUB 120
2050 IDM%=I%
2060 GOSUB 580
2070 HP=5000:ID=IDM%:IS=FV
2080 GOSUB 510:RETURN
Ok
```

GPCAL

```
10 WIDTH 100:DIM AF$(5)
20 ESC$=CHR$(27):PLON$=CHR$(29):PLOFF$=CHR$(31):HLON$=ESC$+"
N":HLOFF$=ESC$+"O"
30 GRON$=ESC$+CHR$(94)+CHR$(18):GROFF$=ESC$+CHR$(94)+CHR$(84
):HLHOF$=ESC$+"Y"
40 SOH$=CHR$(25):DEFSOH$=ESC$+"*V19":CLRSOH$=ESC$+"V99":HLDO
N$=ESC$+"E"
45 HLHON$=ESC$+"X":HLION$=ESC$+"L":HLDOF$=ESC$+"I":HLIOF$=ES
C$+"M"
50 ERASGR$=ESC$+CHR$(12):BLNKGR$=ESC$+CHR$(81):UNBLNKGR$=ESC
$+CHR$(90)
60 PRNTON$=ESC$+"(":PRNTOF$=ESC$+")"
70 GIN$=ESC$+CHR$(26):BLACK$=ESC$+CHR$(16):WHITE$=ESC$+CHR$(
1)
80 CLR$=ESC$+"J":BLSTL$=ESC$+"V":UNBLSTL$=ESC$+"W":CURH$=ESC
$+"H"
90 BLSCR$=ESC$+"Q":UNBLSCR$=ESC$+"Z":PRNTGR$=ESC$+CHR$(23):R
MFS$=ESC$+"=":RML$=ESC$+"7":PRINT DEFSOH$
100 GOSUB 120:GOTO 4000
120 REM******resets everything************
130 PRINT GRON$;PLOFF$;ERASGR$;UNBLNKGR$;WHITE$;SOH$;GROFF$
140 PRINT CLR$;UNBLSCR$;UNBLSTL$
150 RETURN
160 REM*************a/d**************
162 P%=0:I%=0:FOR I=1 TO 3
163 CH%=0
164 PRIMARY%=&H47
166 SECONDARY%=&H60+CH%
168 GOSUB 212
170 CALL IEEERX(Z%)
172 SECONDARY%=&H70
174 GOSUB 212
176 CALL IEEERX(Z%)
178 GOSUB 202
180 SECONDARY%=&H74 : GOSUB 212
182 CALL IEEERX(Z%)
184 A%=Z%
```

```
186 SECONDARY%=&H78 : GOSUB 212
188 CALL IEEERX(Z%)
190 GOSUB 202
192 C%=Z%
194 B%=A%*16+C%/16
196 IF CH%=0 THEN P%=B%+P%:CH%=1:GOTO 164
198 I%=B%+I%
200 NEXT I
201 I%=I%/3:P%=P%/3:RETURN
202 U%=&H5F
204 CALL GETATN
206 CALL IEEETX(U%)
208 CALL RELATN
210 RETURN
212 CALL GETATN
214 CALL IEEETX(PRIMARY%)
216 CALL IEEETX(SECONDARY%)
218 CALL LISTEN
220 CALL RELATN
222 RETURN
300 REM*****************
310 B%=1:CALL SYSCON(B%)
320 CALL ISTART:CALL ISSIFC
330 B%=0:CALL SETADD(B%)
340 B%=&H30:CALL SETMSK(B%)
350 CALL RELATN
360 RETURN
380 REM*********plot data*******************************
390 GOSUB 420:GOSUB 450
400 PRINT GRON$:GOSUB 470
410 PRINT SOH$;GROFF$:RETURN
420 REM********clear graphics*******************
430 PRINT GRON$;PLOFF$;UNBLNKGR$;ERASGR$;SOH$;GROFF$
440 RETURN
450 REM******************blank screen & status line*********
******
460 PRINT BLSCR$;BLSTL$:RETURN
470 REM*************draw axis*************************
```

```
480 XX=0:YY=780:GOSUB 620
490 VECTOR1$=VECTOR2$
500 XX=0:YY=0:GOSUB 620:GOSUB 730
510 XX=1023:YY=0:GOSUB 620:GOSUB 730
512 XX=512:YY=700:GOSUB 620:VECTOR1$=VECTOR2$:XX=512:YY=0:GO
SUB 620:GOSUB 730
520 RETURN
530 REM***************draw data*****************
540 PRINT GRON$
542 IF BL=2 THEN GOTO 550
543 IF I1%>700 THEN GOTO 7400
545 IF I1%>YM THEN GOSUB 575
546 IF DL=1 THEN GOTO 550
547 IF I1%<YMI THEN GOSUB 590
550 XX=1:YY=I1%:GOSUB 620
555 VECTOR1$=VECTOR2$
560 XX=511:GOSUB 620:GOSUB 730
570 RETURN
575 XX=513:YY=YM: GOSUB 620:VECTOR1$=VECTOR2$
580 XX=1023:GOSUB 620:PRINT BLACK$:GOSUB 730:PRINT WHITE$
585 GOSUB 550:XX=1023:GOSUB 620:GOSUB 730
588 YM=I1%:RETURN
590 XX=513:YY=YMI:GOSUB 620:VECTOR1$=VECTOR2$
595 XX=1023:GOSUB 620:PRINT BLACK$:GOSUB 730:PRINT WHITE$
600 GOSUB 550:XX=1023:GOSUB 620:GOSUB 730
610 YMI=I1%:RETURN
620 REM************puts (xx,yy,) into a vector format*******
****
630 IF XX<0 THEN XX=0
632 IF XX>1023 THEN XX=1023
634 IF YY<0 THEN YY=0
635 HX=INT(XX/32)
636 IF YY>780 THEN YY=780
640 LX=(XX MOD 32)
650 HY=INT(YY/32)
660 LY=(YY MOD 32)
670 HX=(HX OR &H20)
680 LX=(LX OR &H40)
```

```
690 HY=(HY OR &H20)
700 LY=(LY OR &H60)
710 VECTOR2$=CHR$(HY)+CHR$(LY)+CHR$(HX)+CHR$(LX)
720 RETURN
730 REM*************draw to a point***************
740 PRINT PLON$;VECTOR1$;VECTOR2$
750 VECTOR1$=VECTOR2$
760 PRINT PLOFF$
770 RETURN
780 REM*************blank graphics****************
790 PRINT GRON$;BLNKGR$;SOH$;GROFF$
800 RETURN
810 REM*************unblank graphics***************
820 PRINT GRON$;UNBLNKGR$;SOH$;GROFF$
830 RETURN
840 REM*************erase graphics********************
850 PRINT GRON$;ERASGR$;SOH$;GROFF$
860 RETURN
870 REM*************clear screen,unblank screen & status lin
e************
880 PRINT CLR$;UNBLSTL$;UNBLSCR$
890 RETURN
900 REM*********unblank screen*****************************
***
910 PRINT UNBLSCR$:RETURN
920 REM***********clear screen & unblank screen*************
***
930 PRINT CLR$;UNBLSCR$
940 RETURN
1700 REM*************Plot line****************
1710 REM
1720 PRINT GRON$:GOSUB 620
1730 VECTOR1$=VECTOR2$:REM
1740 GOSUB 620:GOSUB 730
1750 PRINT SOH$;GROFF$:RETURN
2496 REM***********gin mode************
2497 GOSUB 2510:GOSUB 670
2499 RETURN
```

```
2500 REM************x,y coord. cursor************
2510 PRINT GIN$;
2520 VALUE$=INPUT$(6)
2530 HX=(ASC(MID$(VALUE$,2,1)) AND &H1F)
2540 LX=(ASC(MID$(VALUE$,3,1)) AND &H1F)
2550 HY=(ASC(MID$(VALUE$,4,1)) AND &H1F)
2560 LY=(ASC(MID$(VALUE$,5,1)) AND &H1F)
2570 X=HX*32+LX
2580 Y=HY*32+LY
2590 RETURN
2829 REM*************data check****************
2830 GOSUB 120:PRINT:PRINT" DO YOU WISH TO KEEP THIS EDIT (Y
/N) ?"
2840 A$=INKEY$:IF A$ ="" THEN 2840
2850 A=ASC(A$): IF (A=89) + (A=78) THEN GOTO 2860 ELSE GOTO
2840
2860 RETURN
2950 REM************graphic cursOr****************
2955 YY=600
2960 GOSUB 630
2965 PRINT GRON$;PLON$;VECTOR2$;
2970 PRINT PLOFF$;GRATXT$;SOH$;GROFF$
2975 RETURN
2980 REM*******scale***************
2985 XX=4:REM
2990 GRATXT$=STR$(AF):GOSUB 2955
2995 XX=800:AF%=(CAZ-((((1023/SX)+XP)-CA1)*TC))*10:AF=INT(AF
%)/10
3000 GRATXT$=STR$(AF):GOSUB 2955:RETURN
3800 REM*************write calib file**********
3810 OPEN "O",#1,"CALIB.DAT"
3820 PRINT#1,CA1;CA2;CA3;CA4;CA5;MY;T;FL1;SC
3830 CLOSE #1
3840 RETURN
3900 REM*********read calib file*********
3910 OPEN "I",#1,"CALIB.DAT"
3920 INPUT#1,CA1,CA2,CA3,CA4,CA5,MY,T,FL1,SC
3930 CLOSE#1
```

```
3940 RETURN
3950 REM****************************************
3999 REM*************************************************
4000 GOSUB 3910
4010 IF FL1=1 THEN 5000
4030 MY=4095:FL1=1
4035 GOSUB 7100:GOSUB 7260:GOSUB 7700:GOSUB 7800:GOTO 5000
5000 REM *****menu***********
5010 GOSUB 120
5020 PRINT HLINON$;HLDON$;CLR$;"                       ";HLO
N$;"CALIBRATION";HLOFF$;"    ";HLON$;"MENU";HLOFF$
5030 PRINT:PRINT HLON$;" 1 ";HLOFF$;"  CAL. TURNTABLE":PRINT
5040 PRINT HLON$;" 2 ";HLOFF$;"  CAL. GAIN":PRINT
5050 PRINT HLON$;" 3 ";HLOFF$;"  CAL. Id":PRINT
5060 PRINT HLON$;" 4 ";HLOFF$;"  CAL. END OF PLOT":PRINT
5070 PRINT HLON$;" 5 ";HLOFF$;"  FINISH THIS MENU":PRINT
5080 PRINT" OPTION NO."
5090 A$=INKEY$:IF A$="" THEN 5090
5100 IF (ASC(A$)>53)+(ASC(A$)<49) THEN 5090
5110 ON (ASC(A$)-48) GOSUB 7090,7250,7700,7800,7000
5120 GOTO 5000
7000 PRINT HLDOF$:GOSUB 3810:CHAIN"GONIO"
7090 REM*************t/c************
7100 GOSUB 870:FL1=1
7110 PRINT:PRINT SPC(17);HLION$;HLDON$;HLON$;"TURNTABLE";HLO
FF$;"     ";HLON$;"CALIBRATION";HLOFF$
7120 GOSUB 300
7130 PRINT:INPUT" 1,     POSITION TURNTABLE AT APPROXIMATELY
130 DEGREES & ENTER EXACT ANGLE ";CA2
7140 GOSUB 160:CA1=P%
7150 PRINT:INPUT" 2,     POSITION TURNTABLE AT APPROXIMATELY
30  DEGREES & ENTER EXACT ANGLE ";CA5
7160 GOSUB 160:CA4=P%
7170 PRINT HLDOF$:RETURN
7250 REM************intensity*****************
7260 GOSUB 870:GOSUB 300
7270 PRINT SPC(15);HLION$;HLDON$;HLON$;"P.M.";HLOFF$;"     ";
HLON$;"GAIN";HLOFF$;"     ";HLON$;"CALIBRATION";HLOFF$
```

```
7280 PRINT:PRINT" 1,     SELECT ALL FILTERS"
7290 PRINT:PRINT" 2,     REMOVE SAMPLE"
7300 PRINT:PRINT" 3,     ROTATE TURNTABLE TO '0' DEGREES"
7310 PRINT:PRINT" 4,     OPEN SHUTTER"
7320 GOSUB 9000
7330 GOSUB 380
7340 GOSUB 920:PRINT SPC(5);"ROTATE TURNTABLE TO GIVE MAX. R
EADING BELOW.-PRESS SPACE BAR WHEN DONE"
7345 YM=5:YMI=700:DL=1
7350 GOSUB 160
7355 I1%=INT(I%/4095*780):GOSUB 540
7360 A$=INKEY$:IF A$=" " THEN 7500
7370 GOSUB 160:IF INT(I%/4095*780)=I1% THEN 7355
7380 PRINT BLACK$:BL=2:GOSUB 540:PRINT WHITE$:BL=0:GOTO 7355
7400 GOSUB 120:PRINT"REDUCE GAIN":YM=0
7410 FOR PAUSE = 1 TO 2000:NEXT PAUSE
7420 GOSUB 380:GOSUB 920:RETURN
7500 GOSUB 160:GOSUB 120:TCF=P%
7510 AN=CA2-((TCF-CA1)*(CA2-CA5)/(CA4-CA1))
7520 PRINT "        TURNTABLE CORRECTION FACTOR = ";AN;" DEGRE
ES"
7530 PRINT:PRINT"  DO YOU WISH TO ALTER THIS ? (Y/N)"
7540 A$=INKEY$:IF A$="" THEN 7540
7550 A=ASC(A$):IF (A=89)+(A=78) THEN GOTO 7560 ELSE GOTO 754
0
7560 IF A$="Y" THEN INPUT "ENTER NEW ANGLE ";AN
7570 CA2=CA2-AN:CA5=CA5-AN
7580 CA3=(CA2-CA5)/(CA4-CA1)
7590 GOSUB 380:XX=513:YY=390
7600 PRINT GRON$:GOSUB 620:VECTOR1$=VECTOR2$
7610 XX=1023:GOSUB 620:GOSUB 730:PRINT SOH$;GROFF$
7620 GOSUB 920:PRINT SPC(8);" ADJUST GAIN TO ALIGN THE TWO L
INES- PRESS SPACE BAR WHEN DONE"
7624 PRINT SPC(8);"PRESS  D  TO CHECK DRIFT"
7630 GOSUB 160:BL=2
7640 I1%=INT(I%/4095*780):GOSUB 540
7650 A$=INKEY$:IF A$=" " THEN GOSUB 120:RETURN
7652 IF A$="D" THEN YM=393:YMI=387:BL=0:DL=0
```

```
7660 GOSUB 160:IF INT(I%/4095*780)=I1% THEN 7640
7670 PRINT BLACK$:GOSUB 540:PRINT WHITE$:GOTO 7640
7700 REM*********************id********
7710 GOSUB 870
7720 PRINT"                             ";HLDON$;HLON$;"Id";
HLOFF$;"    ";HLON$"CALIBRATION";HLOFF$
7725 PRINT:PRINT:PRINT HLDOF$
7730 INPUT"  ENTER CALCULATED Id ANGLE  ";AN
7740 T=CA4-((AN-CA5)*(CA4-CA2)/(CA2-CA5))
7750 RETURN
7800 REM*************plot limit******************
7810 GOSUB 870
7820 PRINT"                       ";HLDON$;HLON$;"LIMIT";HLO
FF$;"  ";HLON$;"OF";HLOFF$;"   ";HLON$;"PLOT";HLOFF$
7830 PRINT:PRINT:PRINT
7840 INPUT "ENTER ANGLE";AN
7850 XC=T:GOSUB 7740:SC=T:T=XC
7855 IF SC>4095 THEN SC=4095
7857 IF SC<0 THEN SC=0
7860 PRINT HLDOF$:RETURN
8999 END
9000 PRINT:PRINT:PRINT;SPC(10);HLION$;HLDON$;HLON$;"Press Sp
ace Bar To Continue"
9010 PRINT HLOFF$;HLDOF$
9020 A$=INKEY$:IF A$ <> " " THEN 9020
9030 RETURN
OK
```

GPMAIN

```
10 DIM CURVE%(4095),SCALEX%(1023)
20 ESC$=CHR$(27):PLON$=CHR$(29):PLOFF$=CHR$(31):HLON$=ESC$+"
N":HLOFF$=ESC$+"O"
30 GRON$=ESC$+CHR$(94)+CHR$(18):GROFF$=ESC$+CHR$(94)+CHR$(84
):HLHOF$=ESC$+"Y"
40 SOH$=CHR$(25):DEFSOH$=ESC$+"*V19":CLRSOH$=ESC$+"V99":HLDO
N$=ESC$+"E"
45 HLHON$=ESC$+"X":HLION$=ESC$+"L":HLDOF$=ESC$+"I":HLIOF$=ES
C$+"M"
50 ERASGR$=ESC$+CHR$(12):BLNKGR$=ESC$+CHR$(81):UNBLNKGR$=ESC
$+CHR$(90)
60 PRNTON$=ESC$+"(":PRNTOF$=ESC$+")"
80 CLR$=ESC$+"J":BLSTL$=ESC$+"V":UNBLSTL$=ESC$+"W":CURH$=ESC
$+"H"
90 BLSCR$=ESC$+"Q":UNBLSCR$=ESC$+"Z":PRNTGR$=ESC$+CHR$(23):R
MFS$=ESC$+"=":RML$=ESC$+"7"
100 PRINT DEFSOH$:GOSUB 130:GOTO 4000
130 PRINT GRON$;PLOFF$;ERASGR$;UNBLNKGR$;WHITE$;SOH$;GROFF$
140 PRINT CLR$;UNBLSCR$;UNBLSTL$:RETURN
161 PRINT CLR$:PRINT HLION$;HLON$;" LOADING DATA ";HLOFF$ :P
RINT
180 OPEN "I",#1,"TEMP.DAT"
182 INPUT#1,CODE$,Z,HP,W1,W2,IS,ID,FL1,FL2,FL3,MY,SX
185 INPUT#1,F1$,F2$,F3$,F4$,FV,T,TC,XP,AN,CA1,CA2,CA4,CA5
188 FVD=IS
190 FOR I = 0 TO 4095
200 IF EOF(1) THEN GOTO 230
210 INPUT#1,CURVE%(I):NEXT I
230 CLOSE#1:SC=I-1:RETURN
250 PRINT:PRINT"Clearing Arrays"
260 SY=780/MY
270 FOR I = 0 TO 1023
280 SCALEX%(I)=1000:NEXT I
320 PRINT:PRINT"Scaling Data"
330 FOR I = 0 TO SC
340 S=INT(I*SX):IF S>1023 THEN S=1023
345 FI=I+XP:IF FI>SC THEN FI=SC
```

```
347 IF CURVE%(FI)=5000 THEN GOTO 355
350 SCALEX%(S)=INT(CURVE%(FI)*SY)
355 NEXT I:RETURN
390 GOSUB 430:GOSUB 460
400 PRINT GRON$:GOSUB 480:GOSUB 540
410 PRINT SOH$;GROFF$:RETURN
430 PRINT GRON$;PLOFF$;UNBLNKGR$;ERASGR$;SOH$;GROFF$:RETURN
460 PRINT BLSCR$;BLSTL$:RETURN
480 XX=0:YY=780:GOSUB 630
490 VECTOR1$=VECTOR2$
500 XX=0:YY=0:GOSUB 630:GOSUB 740
510 XX=1023:YY=0:GOSUB 630:GOSUB 740:RETURN
540 XX=0:YY=0:GOSUB 630
550 VECTOR1$=VECTOR2$
560 FOR I = 0 TO 1023
570 IF SCALEX%(I)=1000 THEN GOTO 600
580 YY=SCALEX%(I):XX=I
590 GOSUB 630:GOSUB 740
600 NEXT I
610 PRINT PLOFF$:RETURN
630 IF XX<0 THEN XX=0
632 IF XX>1023 THEN XX=1023
634 IF YY<0 THEN YY=0
636 IF YY>780 THEN YY=780
638 HX=INT(XX/32)
640 LX=(XX MOD 32)
650 HY=INT(YY/32)
660 LY=(YY MOD 32)
670 HX=(HX OR &H20)
680 LX=(LX OR &H40)
690 HY=(HY OR &H20)
700 LY=(LY OR &H60)
710 VECTOR2$=CHR$(HY)+CHR$(LY)+CHR$(HX)+CHR$(LX):RETURN
740 PRINT PLON$;VECTOR1$;VECTOR2$
750 VECTOR1$=VECTOR2$:PRINT PLOFF$:RETURN
790 PRINT GRON$;BLNKGR$;SOH$;GROFF$:RETURN
820 PRINT GRON$;UNBLNKGR$;SOH$;GROFF$:RETURN
850 PRINT GRON$;ERASGR$;SOH$;GROFF$:RETURN
```

```
880 PRINT CLR$;UNBLSTL$;UNBLSCR$:RETURN
910 PRINT UNBLSCR$:RETURN
930 PRINT CLR$;UNBLSCR$:RETURN
990 IS=0
991 FOR I= 1 TO SC
995 IF CURVE%(I)=5000 THEN 1010
1000 IF CURVE%(I)>IS THEN IS=CURVE%(I):Z=I
1010 NEXT I
1030 AN%=(CA2-((Z-CA1)*TC))*10:AN=AN%/10:RETURN
1060 IF HP=5000 THEN ID=ID/FVD*FV:GOTO 1100
1062 IDA=0:IDD=100:FOR TA=T TO (T+99)
1065 IF CURVE%(TA)=5000 THEN IDD=IDD-1:GOTO 1075
1070 IDA=IDA + CURVE%(TA)
1075 NEXT TA
1080 ID=INT(IDA/IDD)
1100 SI=IS-ID
1110 HP =(SI/2)+ ID:RETURN
1230 F1=1:F2=1:F3=1:F4=1:L1$="":L2$="":L3$="":L4$=""
1240 IF F1$="Y" THEN F1=.5:L1$="FILTER 1"
1250 IF F2$="Y" THEN F2=.245:L2$="FILTER 2"
1260 IF F3$="Y" THEN F3=.113:L3$="FILTER 3"
1270 IF F4$="Y" THEN F4=.0373:L4$="FILTER 4"
1280 RETURN
1360 IRS=INT(IS/FV/409.5)+INT((((IS/FV)-INT(IS/FV))*10)+.5)/
10
1370 RID=INT(ID/FV/409.5)+INT((((ID/FV)-INT(ID/FV))*10)+.5)/
10
1380 RSI =IRS -RID
1390 RHP=INT((RSI/2)+RID)+INT(((((RSI/2)+RID)-INT((RSI/2)+RI
D))*10)+.5)/10:RETURN
1420 FOR D = 1 TO SC
1425 IF CURVE%(D)=5000 THEN 1440
1430  IF CURVE%(D)>= HP THEN 1450
1440 NEXT D
1450 W1=D
1460 FOR D = SC TO 1 STEP -1
1465 IF CURVE%(D)=5000 THEN 1480
1470 IF CURVE%(D)>= HP THEN 1490
```

```
1480 NEXT D
1490 W2=D
1500 WIX=(W2-W1)/4095*(CA2-CA5)
1505 WI=INT(WIX)+INT(((WIX-INT(WIX))*10)+.5)/10
1507 RGF=INT(RSI/WI)+INT((((RSI/WI)-INT(RSI/WI))*10)+.5)/10:
RETURN
1525 PRINT HLION$;HLON$
1530 PRINT"*************************************************
*****************************"
1535 PRINT HLOFF$
1540 PRINT"                              SAMPLE CODE ...."
;CODE$
1543 INE$="                              -----------------
------------------"
1545 INES$=LEFT$(INE$,LEN(CODE$)+48)
1550 PRINT INES$
1560 PRINT:PRINT"TOTAL PEAK HEIGHT(Is)=";IRS;" AT ";AN;" DEG
REES"
1570 PRINT:PRINT"                  Id =";RID
1580 PRINT:PRINT"    HALF PEAK HEIGHT =";RHP
1590 PRINT:PRINT"     HALF PEAK WIDTH =";WI;" DEGREES"
1610 PRINT:PRINT"        GLOSS FACTOR =";  RGF
1611 PRINT:PRINT"FILTERS IN USE ARE > ";L1$;" ";L2$;" ";L3$;
" ";L4$
1615 PRINT HLON$
1620 PRINT"*************************************************
*****************************"
1625 PRINT HLOFF$;HLIOF$:RETURN
1650 GOSUB 930
1660 PRINT HLION$;HLON$;"DO YOU WISH TO CONTINUE WITH THIS D
ATA (Y/N) ?":PRINT HLOFF$
1665 PRINT CHR$(7)
1670 A$=INKEY$:IF A$="" THEN 1670
1680 A=ASC(A$):IF (A=89) + (A=78) THEN RETURN
1690 GOTO 1670
1710 XX=INT((Z-XP)*SX):YY=INT(IS*SY)
1720 PRINT GRON$:GOSUB 630
1730 VECTOR1$=VECTOR2$:YY=0
```

```
1740 GOSUB 630:GOSUB 740
1750 PRINT SOH$;GROFF$:RETURN
1755 XX=INT((T-XP)*SX):YY=INT(ID*SY):PRINT GRON$:GOSUB 630
1760 VECTOR1$=VECTOR2$:YY=0:GOSUB 630:GOSUB 740
1765 PRINT SOH$;GROFF$:RETURN
1770 XX=INT((W1-XP)*SX):YY=0
1780 PRINT GRON$:GOSUB 630
1790 VECTOR1$=VECTOR2$:YY=INT(HP*SY)
1800 GOSUB 630:GOSUB 740
1810 VECTOR1$=VECTOR2$:XX=INT((W2-XP)*SX)
1820 GOSUB 630:GOSUB 740
1830 VECTOR1$=VECTOR2$:YY=0
1840 GOSUB 630:GOSUB 740
1850 PRINT SOH$;GROFF$:RETURN
1860 PRINT HLION$;HLHOF$;HLON$;"DISPLAY";HLOFF$;" ";HLON$;"1
";HLOFF$;" GRAPH   ";HLON$;"2";HLOFF$;" DATA   ";HLON$;"3";HL
OFF$;" BOTH   ";HLON$;"4";HLOFF$;" CONTINUE":RETURN
1890 A$=INKEY$:IF (A$ <> "1") * (A$<>"2") * (A$<>"3") * (A$<
>"4") THEN 1890
1900 A=ASC(A$)-48:PRINT RMFS$:ON A GOTO 1920,1910,1930,1940
1910 GOSUB 790:GOSUB 910:GOTO 1890
1920 GOSUB 460:GOSUB 820:GOTO 1890
1930 GOSUB 820:GOSUB 910:GOTO 1890
1940 PRINT RML$:GOSUB 790:GOSUB 880:RETURN
1960 PRINT HLION$;CLR$:PRINT:PRINT
1970 PRINT HLON$;" 1 ";HLOFF$;" Copy Results & Graph to Prin
ter":PRINT
1980 PRINT HLON$;" 2 ";HLOFF$;" Copy Graph to Printer":PRINT
1990 PRINT HLON$;" 3 ";HLOFF$;" Copy Results to Printer":PRI
NT
2000 PRINT HLON$;" 4 ";HLOFF$;" Copy Data to Disk":PRINT
2010 PRINT HLON$;" 5 ";HLOFF$;" Edit Data":PRINT
2020 PRINT HLON$;" 6 ";HLOFF$;" Display Results":PRINT
2030 PRINT HLON$;" 7 ";HLOFF$;" New Sample":PRINT
2040 PRINT HLON$;" 8 ";HLOFF$;" Compare Sets of Data":PRINT
2050 PRINT HLON$;" 9 ";HLOFF$;" Exit Programme":PRINT
2060 PRINT "OPTION NO.?"
2070 A$=INKEY$:IF A$="" THEN GOTO 2070
```

```
2075 IF (ASC(A$)>57) + (ASC(A$)<49) THEN GOTO 2070
2080 ON (ASC(A$)-48) GOTO 6110,6210,6310,6410,6510,6600,6700
,6800,6900
2090 GOTO 1960
2110 GOSUB 930:PRINT TAB(36) "WARNING"
2120 PRINT:PRINT TAB(17) "The data will be lost unless copie
d to a disc"
2130 PRINT TAB(17);:GOSUB 1660:RETURN
2160 XX=4:YY=772:GOSUB 630
2170 PRINT GRON$;PLON$;VECTOR2$;
2180 PRINT PLOFF$;GRATXT$;SOH$;GROFF$:RETURN
2210 GRATXT$="DISPLAY   1 GRAPH   2 DATA   3 BOTH   4 CONTIN
UE":RETURN
2240 GOSUB 880:PRINT:PRINT:PRINT:PRINT:PRINT:PRINT:PRINT "
                    Check that printer is ON LINE"
2250 PRINT:PRINT:GOSUB 9280:RETURN
2280 GOSUB 460:GOSUB 930:PRINT:PRINT:PRINT
2290 PRINT"Press RETURN when complete":RETURN
2315 PRINT HLION$;HLON$;" COPYING DATA ";HLOFF$
2320 OPEN "O",#1,"TEMP.DAT"
2330 PRINT#1,CODE$;",";Z;HP;W1;W2;IS;ID;FL1;FL2;FL3;MY;SX
2335 PRINT#1,F1$;",";F2$;",";F3$;",";F4$;",";FV;T;TC;XP;AN;C
A1;CA2;CA4;CA5
2340 FOR I = 0 TO SC
2350 PRINT#1,CURVE%(I);:NEXT I:CLOSE #1:RETURN
4000 GOSUB 161:GOSUB 250:GOSUB 390: IF (FL2=6) + (FL3=3) THE
N GOSUB 1100:GOSUB 1230: GOTO 4080
4025 GOSUB 1650:IF A$="N" THEN GOSUB 850:CHAIN"GONIO"
4030 GOSUB 930:PRINT:PRINT"Calculating Is.":GOSUB 990:GOSUB
1060:GOSUB 1230
4080 GOSUB 1360:GOSUB 1420:GOSUB 1710:GOSUB 1755:GOSUB 1770:
GOSUB 460:GOSUB 9150
5017 GOSUB 790:GOSUB 930:GOSUB 1525:GOSUB 1860:GOSUB 2160:GO
SUB 2210:GOSUB 2160:GOSUB 1890:GOTO 1960
6110 GOSUB 2240:GOSUB 930:PRINT PRNTON$:GOSUB 1525:PRINT PRN
TOF$:GOTO 6220
6210 GOSUB 2240
6220 GOSUB 390 :GOSUB 1710:GOSUB 1755:GOSUB 1770:GRATXT$=COD
```

```
E$:GOSUB 2160:GOSUB 2280:PRINT GRON$;PRNTGR$;
6280 LET A$=INPUT$(1)
6290 PRINT SOH$;GROFF$:GOSUB 790:GOTO 1960
6310 GOSUB 2240:GOSUB 930:PRINT PRNTON$:GOSUB 1525:PRINT PRN
TOF$:GOTO 1960
6410 CAT$="B:"+CODE$
6412 ON ERROR GOTO 6450
6415 GOSUB 930:PRINT:PRINT "COPYING DATA "
6420 OPEN "O",#1,CAT$
6430 GOSUB 2330
6440 ON ERROR GOTO 0:IF R=1 THEN RETURN ELSE GOTO 1960
6450 IF (ERR=61)+(ERR=67) THEN PRINT"DISC FULL, PLEASE LOAD
A NEW DISC ":GOSUB 9280
6460 GOSUB 2315:PRINT:PRINT"REBOOT THE DISK (WARM START) AND
 RUN 'GPMAIN' ":END
6510 FL2=0:GOSUB 930: GOSUB 2315:CHAIN"GPEDIT"
6600 GOSUB 390:GOSUB 1710:GOSUB 1755:GOSUB 1770:GOTO 5017
6700 GOSUB 2110:IF A$="Y" THEN GOTO 1960
6710 CHAIN"GONIO"
6800 GOSUB 930:R=1:GOSUB 6410:R=0:FL2=2:GOSUB 930:GOSUB 2315
:CHAIN "GPEDIT"
6900 GOSUB 2110:IF A$="N" THEN GOTO 6902 ELSE GOTO 1960
6902 OPEN "O",#1,"CALIB.DAT"
6904 FL1=0:PRINT#1,CA1;CA2;CA3;CA4;CA5;MY;T;FL1;SC
6905 CLOSE#1
6906 END
9150 FOR PAUSE =1 TO 5000:NEXT PAUSE:RETURN
9280 PRINT:PRINT:PRINT;SPC(10);HLION$;HLDON$;HLON$;"Press Sp
ace Bar To Continue"
9290 PRINT HLOFF$;HLDOF$
9300 A$=INKEY$:IF A$ <> " " THEN 9300
9310 RETURN
Ok
```

GPEDIT

```
10 WIDTH 100:DIM CURVE%(4095),SCALEX%(1023),AF$(5)
20 ESC$=CHR$(27):PLON$=CHR$(29):PLOFF$=CHR$(31):HLON$=ESC$+"
N":HLOFF$=ESC$+"O"
30 GRON$=ESC$+CHR$(94)+CHR$(18):GROFF$=ESC$+CHR$(94)+CHR$(34
):HLHOF$=ESC$+"Y"
40 SOH$=CHR$(25):DEFSOH$=ESC$+"*V19":CLRSOH$=ESC$+"V99":HLDO
N$=ESC$+"E"
45 HLHON$=ESC$+"X":HLION$=ESC$+"L":HLDOF$=ESC$+"I":HLIOF$=ES
C$+"M"
50 ERASGR$=ESC$+CHR$(12):BLNKGR$=ESC$+CHR$(81):UNBLNKGR$=ESC
$+CHR$(90)
60 PRNTON$=ESC$+"(":PRNTOF$=ESC$+")"
70 GIN$=ESC$+CHR$(26):BLACK$=ESC$+CHR$(16):WHITE$=ESC$+CHR$(
1)
80 CLR$=ESC$+"J":BLSTL$=ESC$+"V":UNBLSTL$=ESC$+"W":CURH$=ESC
$+"H"
90 BLSCR$=ESC$+"Q":UNBLSCR$=ESC$+"Z":PRNTGR$=ESC$+CHR$(23):R
MFS$=ESC$+"=":RML$=ESC$+"7":PRINT DEFSOH$
100 GOTO 4000
120 REM*****resets everything***********
130 PRINT GRON$;PLOFF$;ERASGR$;UNBLNKGR$;WHITE$;SOH$;GROFF$
140 PRINT CLR$;UNBLSCR$;UNBLSTL$
150 RETURN
160 REM*********load data from file********************
161 PRINT CLR$:PRINT HLION$;HLON$;" LOADING DATA ";HLOFF$ :P
RINT
180 OPEN "I",#1,"TEMP.DAT"
182 INPUT#1,CODE$,Z,HP,W1,W2,IS,ID,FL1,FL2,FL3,MY,SX
185 INPUT#1,F1$,F2$,F3$,F4$,FV,T,TC,XP,AN,CA1,CA2,CA4,CA5
190 FOR I = 0 TO 4095
200 IF EOF(1) THEN GOTO 230
210 INPUT#1,CURVE%(I):NEXT I
230 CLOSE#1:SC=I-1:RETURN
240 REM******rescale data for plot****************
250 PRINT:PRINT"Clearing Rescale Arrays"
260 SY=780/MY:XP=0
270 FOR I = 0 TO 1023
```

```
280 SCALEX%(I)=1000
310 NEXT I
320 PRINT:PRINT"Rescaling Data"
330 FOR I = 0 TO SC
340 S=INT(I*SX):IF S>1023 THEN S=1023
345 FI=I+XP:IF FI>SC THEN FI=SC
347 IF CURVE%(FI)=5000 THEN 360
350 SCALEX%(S)=INT(CURVE%(FI)*SY)
360 NEXT I
370 RETURN
380 REM*********plot data*******************************
390 GOSUB 420:GOSUB 450
400 PRINT GRON$:GOSUB 470:GOSUB 530
410 PRINT SOH$;GROFF$:RETURN
420 REM********clear graphics******************
430 PRINT GRON$;PLOFF$;UNBLNKGR$;ERASGR$;SOH$;GROFF$
440 RETURN
450 REM******************blank screen & status line*********
******
460 PRINT BLSCR$;BLSTL$:RETURN
470 REM*************draw axis**************************
480 XX=0:YY=780:GOSUB 620
490 VECTOR1$=VECTOR2$
500 XX=0:YY=0:GOSUB 620:GOSUB 730
510 XX=1023:YY=0:GOSUB 620:GOSUB 730
520 RETURN
530 REM***************draw data*****************
540 XX=0:YY=0:GOSUB 620
550 VECTOR1$=VECTOR2$
560 FOR I = 0 TO 1023
570 IF SCALEX%(I)=1000 THEN GOTO 600
580 YY=SCALEX%(I):XX=I
590 GOSUB 620
597 GOSUB 730
600 NEXT I
610 PRINT PLOFF$:RETURN
620 REM************puts (xx,yy,) into a vector format*******
****
```

```
630 IF XX<0 THEN XX=0
632 IF XX>1023 THEN XX=1023
634 IF YY<0 THEN YY=0
635 HX=INT(XX/32)
636 IF YY>780 THEN YY=780
640 LX=(XX MOD 32)
650 HY=INT(YY/32)
660 LY=(YY MOD 32)
670 HX=(HX OR &H20)
680 LX=(LX OR &H40)
690 HY=(HY OR &H20)
700 LY=(LY OR &H60)
710 VECTOR2$=CHR$(HY)+CHR$(LY)+CHR$(HX)+CHR$(LX)
720 RETURN
730 REM*************draw to a point***************
740 PRINT PLON$;VECTOR1$;VECTOR2$
750 VECTOR1$=VECTOR2$
760 PRINT PLOFF$
770 RETURN
780 REM*************blank graphics*****************
790 PRINT GRON$;BLNKGR$;SOH$;GROFF$
800 RETURN
810 REM*************unblank graphics***************
820 PRINT GRON$;UNBLNKGR$;SOH$;GROFF$
830 RETURN
840 REM*************erase graphics*********************
850 PRINT GRON$;ERASGR$;SOH$;GROFF$
860 RETURN
870 REM*************clear screen,unblank screen & status lin
e************
880 PRINT CLR$;UNBLSTL$;UNBLSCR$
890 RETURN
900 REM*********unblank screen*******************************
***
910 PRINT UNBLSCR$:RETURN
920 REM***********clear screen & unblank screen*************
***
930 PRINT CLR$;UNBLSCR$
```

```
940 RETURN
1700 REM*************Plot Is*****************
1710 XX=INT((Z-XP)*SX):YY=INT(IS*SY)
1720 PRINT GRON$:GOSUB 620
1730 VECTOR1$=VECTOR2$:YY=0
1740 GOSUB 620:GOSUB 730
1750 PRINT SOH$;GROFF$:RETURN
1760 REM*************Plot Half Peak Width*****************
1770 XX=INT((W1-XP)*SX):YY=0
1780 PRINT GRON$:GOSUB 620
1790 VECTOR1$=VECTOR2$:YY=INT(HP*SY)
1800 GOSUB 620:GOSUB 730
1810 VECTOR1$=VECTOR2$:XX=INT((W2-XP)*SX)
1820 GOSUB 620:GOSUB 730
1830 VECTOR1$=VECTOR2$:YY=0
1840 GOSUB 620:GOSUB 730
1850 PRINT WHITE$;SOH$;GROFF$:RETURN
2310 REM***************data dump*************
2315 PRINT HLION$;HLON$;" TRANSFERING DATA ";HLOFF$
2320 OPEN "O",#1,"TEMP.DAT"
2330 PRINT#1,CODE$;",";Z;T;HP;W1;W2;IS;ID;FL1;FL2;FL3
2335 PRINT#1,F1$;",";F2$;",";F3$;",";F4$;",";FV
2340 FOR I = 0 TO SC
2350 PRINT#1,CURVE%(I);
2370 NEXT I
2380 CLOSE #1
2390 RETURN
2400 REM*****************plot id position************
2410 XX=INT((T-XP)*SX):YY=INT(ID*SY):PRINT GRON$:GOSUB 630
2420 VECTOR1$=VECTOR2$:YY=0:GOSUB 630:GOSUB 740
2430 PRINT SOH$;GROFF$:RETURN
2440 REM***********edit mode*************
2450 PRINT CLR$; HLION$;HLON$" Position & "HLOFF$"  "HLON$"
R "HLOFF$" Rescale  "HLON$" S "HLOFF$" Change Is.  "HLON$" D
 "HLOFF$" Change Id.  "HLON$" E "HLOFF$" Exit "
2451 GOSUB 2985:PRINT GRON$;PLON$;
2452 GOSUB 2497
2453 X$=CHR$(&H5F AND ASC(MID$(VALUE$,1,1)))
```

```
2454 IF X$="R" THEN GOTO 2600
2455 IF X$="S" THEN GOTO 2700
2456 IF X$="D" THEN GOTO 2800
2457 IF X$="E" THEN PRINT PLOFF$;SOH$;GROFF$;:RETURN
2458 PRINT SOH$;GROFF$:GOTO 2450
2460 RETURN
2496 REM************gin mode************
2497 GOSUB 2510:GOSUB 670
2499 RETURN
2500 REM***********x,y coord. cursor************
2510 PRINT GIN$;
2520 VALUE$=INPUT$(6)
2530 HX=(ASC(MID$(VALUE$,2,1)) AND &H1F)
2540 LX=(ASC(MID$(VALUE$,3,1)) AND &H1F)
2550 HY=(ASC(MID$(VALUE$,4,1)) AND &H1F)
2560 LY=(ASC(MID$(VALUE$,5,1)) AND &H1F)
2570 X=HX*32+LX
2580 Y=HY*32+LY
2590 RETURN
2595 REM*****************edit routines************
2600 GOSUB 780:GOSUB 920:GOSUB 840
2602 PRINT"                      RESCALE OPTIONS"
2604 PRINT"                      ~~~~~~~~~~~~~~~"
2606 PRINT:PRINT HLON$;" PRESS ";HLOFF$;"   ";HLON$;" 1 ";HL
OFF$;"  To enter X axis expansion factor e.g. 0.25,0.5,1,2 et
c.
2608 PRINT:PRINT "          ";HLON$;" 2 ";HLOFF$;"  To enter
 highest turntable position to be plotted e.g.";" < 135
                       -- 0  --                             -1
35>"
2609 IF FL2=2 THEN GOTO 2612
2610 PRINT:PRINT "          ";HLON$;" 3 ";HLOFF$;"  To enter
 Y axis expansion factor e.g.";"               0, Is = Full s
cale      >  10, 100% reflection = Full scale"
2612 PRINT:PRINT "          ";HLON$;" 4 ";HLOFF$;"  To resca
le"
2613 IF FL2=2 THEN GOTO 2616
2614 PRINT:PRINT "          ";HLON$;" 5 ";HLOFF$;"  To reset
```

```
 & finish this menu":PRINT
2616 A$=INKEY$:IF A$="" THEN GOTO 2616
2618 IF (ASC(A$)>53) + (ASC(A$)<49) THEN GOTO 2615
2620 ON (ASC(A$)-48) GOTO 2630,2635,2640,2644,2680
2622 GOTO 2616
2630 PRINT HLON$;" 1 ";HLOFF$;:INPUT" 'X' Expansion Factor "
,X:SX=SX*X
2631 GOTO 2616
2635 PRINT HLON$;" 2 ";HLOFF$;:INPUT" Turntable Position ",T
P:XP=INT(CA4-((TP-CA5)/TC)):IF XP>SC THEN XP=SC
2637 GOTO 2616
2640 PRINT HLON$;" 3 ";HLOFF$;:INPUT" 'Y' Expansion factor "
,MSY:YC=2.63677E+06/10*FV
2642 MY=MSY*YC:IF MSY=0 THEN MY=IS+120
2643 SY=780/MY:GOTO 2616
2644 IF FL2=2 THEN RETURN
2645 PRINT HLON$;" 4 ";HLOFF$:GOSUB 270:GOSUB 820:GOSUB 390:
GOSUB 1710:GOSUB 1770: GOSUB 2410:GOSUB 910:GOTO 2450
2680 PRINT HLON$;" 5 ";HLOFF$:SX=SX1:SY=SY1:MY=MY1:XP=0:GOSU
B 810:GOTO 4020
2699 STOP
2700 PRINT GRON$;BLACK$:GOSUB 1710:PRINT GRON$;BLACK$:GOSUB
1770:PRINT GRON$;WHITE$;
2710 Z=INT((X/SX)+.7+XP)
2712 IS=CURVE%(Z)
2713 IF IS=5000 THEN Z=Z-1:GOTO 2712
2714 GOSUB 1710
2715 AN%=(CA2-((Z-CA1)*TC))*10:AN=INT(AN%)/10
2720 W1=0:W2=0:HP=0:GOTO 2450
2800 PRINT GRON$;BLACK$:GOSUB 2410:PRINT GRON$;WHITE$
2810 T=INT((X/SX)+.7+XP):ID=INT((Y/SY)+.7):GOSUB 2410
2820 GOTO 2450
2829 REM************data check***************
2830 GOSUB 120:PRINT:PRINT" DO YOU WISH TO KEEP THIS EDIT (Y
/N) ?"
2840 A$=INKEY$:IF A$ ="" THEN 2840
2850 A=ASC(A$): IF (A=89) + (A=78) THEN GOTO 2860 ELSE GOTO
2840
```

```
2860 RETURN
2870 REM**********data dump*****************
2875 PRINT CLR$;HLION$;HLON$;" COPYING DATA ";HLOFF$
2880 OPEN "O",#1,"TEMP.DAT"
2885 PRINT#1,CODE$;",";Z;HP;W1;W2;IS;ID;FL1;FL2;FL3;MY;SX
2890 PRINT#1,F1$;",";F2$;",";F3$;",";F4$;",";FV;T;TC;XP;AN;C
A1;CA2;CA4;CA5
2895 FOR I= 0 TO SC
2900 PRINT#1,CURVE%(I);:NEXT I:CLOSE#1:RETURN
2905 REM***********sample code check***********
2910 PRINT CLR$:PRINT:PRINT"SAMPLE CODE IS '";CODE$;"'  DO Y
OU WISH TO CHANGE THIS (Y/N) ?"
2915 GOSUB 2840:IF A$="Y" THEN GOSUB 2930
2920 RETURN
2925 REM*********sample code*********
2930 PRINT:PRINT:INPUT "ENTER SAMPLE CODE ";CODE$
2935 IF LEN(CODE$)> 8 THEN 2945
2940 RETURN
2945 PRINT"CODE TOO LONG, REENTER,  MAX.8 CHAR.":GOTO 2930
2950 REM***********graphic curs0r****************
2955 YY=600
2960 GOSUB 630
2965 PRINT GRON$;PLON$;VECTOR2$;
2970 PRINT PLOFF$;GRATXT$;SOH$;GROFF$
2975 RETURN
2980 REM*******scale***************
2985 XX=4:AF%=(CA2-((XP-CA1)*TC))*10:AF=INT(AF%)/10
2990 GRATXT$=STR$(AF):GOSUB 2955
2995 XX=800:AF%=(CA2-((((1023/SX)+XP)-CA1)*TC))*10:AF=INT(AF
%)/10
3000 GRATXT$=STR$(AF):GOSUB 2955:RETURN
3999 REM**********************************************
4000 GOSUB 130:GOSUB 161
4010 IF FL2=2 THEN GOTO 6000
4020 GOSUB 250:GOSUB 390:GOSUB 1710:GOSUB 1770:GOSUB 2410
4030 GOSUB 930
4040 SX1=SX:SY1=SY:MY1=MY:GOSUB 2450
4050 GOSUB 2830:IF A$="N" THEN FL3=3:CHAIN"GPMAIN"
```

```
4060 GOSUB 2910:FL2=6:GOSUB 2875:CHAIN "GPMAIN"
6000 GOSUB 840:PRINT:PRINT :INPUT "ENTER NUMBER OF SETS OF D
ATA TO BE COMPARED (MAX 5 )",C
6005 PRINT:PRINT:FILES"B:*.*":PRINT:PRINT
6010 GHA=0:SCA=0:SCB=0:X=1:SXA=4095:TPA=135:FL4=0:FOR LO=1 T
O C
6015 PRINT "SAMPLE CODE No. ";LO;"    ";:INPUT AF$(LO)
6016 NEXT LO
6017 PRINT CLR$,"Checking Maximum Intensity Value":FOR LO= 1
 TO C
6018 PRINT AF$(LO)
6020 ON ERROR GOTO 7050
6021 CATE$="B:"+ AF$(LO)
6022 OPEN "I",#1,CATE$
6023 INPUT#1,CODE$,Z,HP,W1,W2,IS,ID,FL1,FL2,FL3,MY,SX
6024 INPUT#1,F1$,F2$,F3$,F4$,FV,T,TC,XP,AN,CA1,CA2,CA4,CA5
6025 CLOSE#1
6026 TP%=(CA2-((XP-CA1)*TC))*10:TP=INT(TP%)/10
6030 GH=IS/FV:IF GH>GHA THEN GHA=GH
6032 IF TP<TPA THEN TPA=TP
6034 IF SX<SXA THEN SXA=SX
6040 IF SC>SCA THEN SCA=SC
6050 NEXT LO
6055 GOSUB 9400
6060 FOR LO=1 TO C
6065 PRINT CLR$,"LOADING ";AF$(LO)
6070 GOSUB 7000
6072 IF FL4=1 THEN XTE=IS
6074 IF FL4=2 THEN FD=FV
6080 MY=(XTE+15)*FD:SX=1023/SCB*X
6084 XP=INT(CA4-((TPA-CA5)/TC)):IF XP>SC THEN XP=SC
6086 SY=780/MY
6090 GOSUB 270
6100 GOSUB 450:GOSUB 400:GOSUB 900
6101 FOR I=0 TO SCA
6102 CURVE%(I)=0 :NEXT I
6103 GRATXT$=CHR$(LO+48)+" "+AF$(LO):YY=600-(20*LO):XX=15:GO
SUB 2960
```

```
6110 NEXT LO
6200 PRINT CLR$,"Do You Wish To Print This ? (Y/N)
6210 GOSUB 2840
6220 IF A$="N" THEN GOTO 6300
6230 GOSUB 880:PRINT:PRINT:PRINT:PRINT:PRINT:PRINT:PRINT"
                          CHECK THAT PRINTER IS ON LINE"
6240 GOSUB 9280
6250 PRINT CLR$,"Press RETURN when complete"
6260 PRINT GRON$;PRNTGR$;
6270 LET A$=INPUT$(1)
6280 PRINT SOH$;GROFF$:GOTO 6300
6300 PRINT CLR$;"Do You Wish To Compare More Results ? (Y/N)
"
6310 GOSUB 2840
6320 IF A$="N" THEN FL2=6:CHAIN "GPMAIN"
6330 GOTO 6000
6999 STOP
7000 REM*******data access************
7010 ON ERROR GOTO 7050
7020 CATE$="B:"+ AF$(LO)
7030 OPEN  "I",#1,CATE$
7040 GOSUB 182
7045 RETURN
7050 IF (ERR=53) AND (ERL=7030) THEN PRINT"FILE NOT FOUND; T
RY AGAIN":PRINT:CLOSE#1:FILES "B:*.*":RESUME 6010
7060 CLOSE#1:RESUME 6000
9280 PRINT:PRINT:PRINT;SPC(10);HLION$;HLDON$;HLON$;"Press Sp
ace Bar To Continue"
9290 PRINT HLOFF$;HLDOF$
9300 A$=INKEY$:IF A$ <>" " THEN 9300
9310 RETURN
9400 PRINT CLR$:PRINT:PRINT HLON$;" PRESS ";HLOFF$;"   ";HLO
N$;" 1 ";HLOFF$;" To plot each Is at full scale."
9410 PRINT:PRINT"            ";HLON$;" 2 ";HLOFF$;" To plot al
l data on the same vertical scale."
9420 A$=INKEY$:IF A$="" THEN GOTO 9420
9430 IF (ASC(A$)>50) + (ASC(A$)<49) THEN GOTO 9420
9440 IF A$="1" THEN FL4=1:FD=1
```

```
9450 IF A$="2" THEN XTE=CHA+100:FL4=2
9460 PRINT:PRINT HLON$;" PRESS ";HLOFF$;"   ";HLON$;" 1 ";HL
OFF$;" To display all data collected for each curve."
9470 PRINT:PRINT"          ";HLON$;" 2 ";HLOFF$;" To display
 data including last retained edits."
9480 PRINT:PRINT"          ";HLON$;" 3 ";HLOFF$;" To set 'X'
 scale position and expansion factor."
9490 A$=INKEY$:IF A$="" THEN GOTO 9490
9500 IF (ASC(A$)>51) + (ASC(A$)<49) THEN GOTO 9490
9510 ON (ASC(A$)-48) GOTO 9520,9550,9570
9520 TPA=135
9530 SCB=SCA
9540 RETURN
9550 SCB=1023/SXA
9560 RETURN
9570 FL2=2
9580 GOSUB 2600
9590 GOSUB 820
9600 TPA=TP
9610 SCB=SCA
9620 RETURN
Ok
```

GPDATA

```
10 DIM IS(50),AN(50),ID(50),W(50),GF(50),CODE$(50),N(50)
20 PRINT CHR$(27)+"J"
30 PRINT"No."TAB(11)"Code"TAB(22)"Is"TAB(33)"Angle"TAB(44)"I
d"TAB(55)"W1/2"TAB(66)"G/f"
40 I=1:F=0:PRINT
50 PRINT I;
60 PRINT TAB(8):INPUT " ";CODE$(I)
61 ON ERROR GOTO 300:OPEN "I",#1,"B:"+CODE$(I)
62 INPUT#1,CODE$,Z,HP,  W1,W2,IS,ID,FL1,FL2,FL3,MY,SX
63 INPUT#1,F1$,F2$,F3$,F4$,FV,T,TC,XP,AN,CA1,CA2,CA4,CA5
64 CLOSE#1
70 IS(I)=INT(IS/FV/409.5)+INT((((IS/FV)-INT(IS/FV))*10)+.5)/
10
80 ID(I)=INT(ID/FV/409.5)+INT((((ID/FV)-INT(ID/FV))*10)+.5)/
10
90 WIX=(W2-W1)/4095*(CA2-CA5)
100 W(I)=INT(WIX)+INT(((WIX-INT(WIX))*10)+.5)/10
110 RSI=IS(I)-ID(I)
120 GF(I)=INT(RSI/W(I))+INT((((RSI/W(I))-INT(RSI/W(I)))*10)+
.5)/10
130 AN%=(CA2-((Z-CA1)*TC))*10
140 AN=AN%/10
150 AN(I)=AN
200 PRINT CHR$(27)+"H"
210 PRINT:FOR L=1 TO (I-F)
220 PRINT
230 NEXT L
240 PRINT I TAB(11) CODE$(I)TAB(22)IS(I)TAB(33)AN(I)TAB(44)I
D(I)TAB(55)W(I)TAB(66)GF(I)
250 I=I+1:IF I=20 THEN GOSUB 500
260 GOTO 50
300 IF ERR=53 THEN PRINT"FILE NOT FOUND":I=I-1:CLOSE#1 :RESU
ME 200
310 END
500 FOR X=1 TO 20
510 PRINT:NEXT X
520 F=19: PRINT CHR$(27)+"H":PRINT:PRINT:RETURN
```

Appendix 3

Free Radical and Other Chemical Reactions involving the Ox, HOx and NOx species

Abstracted from - A Computer Modelling Study of the Relationship between Urban Exposure to Nitrogen Dioxide and Motor Vehicle Exhaust Emissions during the Summer Months.

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October 1981

AERE - R10273

The O_x, HO_x and NO_x Reactions Included in the Photochemical Column Trajectory Model

	Process	Rate Coefficient, cm^3 molecule^{-1} s^{-1}	
1	$O(^1D) + N_2 = O(^3P) + N_2$	4.5×10^{-11}	A**
2	$O(^1D) + O_2 = O(^3P) + O_2$	4.6×10^{-11}	A**
3	$O(^1D) + H_2O = OH + OH$	2.8×10^{-10}	A**
4	$NO + O_3 = NO_2 + O_2$	$2.3 \times 10^{-12} \exp(-1450/T)$	A
5	$NO_2 + O_3 = NO_3 + O_2$	$1.2 \times 10^{-13} \exp(-2450/T)$	A
6	$HO_2 + O_3 = OH + O_2 + O_2$	2.0×10^{-15}	A
7	$NO + NO_3 = NO_2 + NO_2$	2.0×10^{-11}	A
8	$NO + HO_2 = NO_2 + OH$	8.4×10^{-12}	A
9	$NO_2 + NO_3 = N_2O_5$	2.7×10^{-12}	A
10	$NO_2 + OH = HNO_3$	1.1×10^{-11}	A
11	$NO_2 + HO_2 = HO_2NO_2$	5.0×10^{-12}	A
12	$HO_2NO_2 = HO_2 + NO_2$	$1.4 \times 10^{14} \exp(-10420/T)$	A*
13	$N_2O_5 = NO_3 + NO_2$	$1.24 \times 10^{14} \exp(-10317/T)$	A*
14	$HO_2 + HO_2 = H_2O_2 + O_2$	2.3×10^{-12}	A
15	$OH + CO = H + CO_2$	2.8×10^{-13}	A
16	$O + O_2 = O_3$	2.8×10^{-12}	A**
17	$H + O_2 = HO_2$	1.4×10^{-12}	A**
18	$OH + SO_2 = HOSO_2$	1.1×10^{-12}	B
19	$HOSO_2 + O_2 = HOSO_2O_2$		**
20	$HOSO_2O_2 + NO = NO_2 + HSO_4$		**
21	HSO_4 = sulphate aerosol		**

NOTES

* First order rate coefficient in s^{-1} quoted

** Reaction pathway not explicitly modelled since photochemical equilibrium assumed

A Baulch et al. (1981)

B Calvert et al. (1978)

Photochemical Processes and Photolysis Rate Coefficient Parameters used in the Photochemical Column Trajectory Model

Process			Photolysis Rate Coefficient Parameter*	
			a_i	b_i
50	$O_3 + hv$	$= O(^1D) + O_2$	8.6×10^{-5}	-2.5
51	$NO_2 + hv$	$= NO + O$	1.0×10^{-2}	-0.3
52	$NO_3 + hv$	$= NO + O_2$	3.5×10^{-2}	-0.1
53	$NO_3 + hv$	$= NO_2 + O$	8.9×10^{-2}	-0.1
54	$N_2O_5 + hv$	$= NO_2 + NO_3$	3.3×10^{-5}	-0.6
55	$HCHO + hv$	$= H + HCO$	4.9×10^{-5}	-0.8
56	$HCHO + hv$	$= H_2 + CO$	7.7×10^{-5}	-0.5
57	$CH_3CHO + hv$	$= CH_3 + HCO$	6.8×10^{-5}	-0.7
58	$C_2H_5CHO + hv$	$= C_2H_5 + HCO$	3.0×10^{-5}	-0.8
59	$CH_3CO\ CH_3 + hv$	$= CH_3 + CH_3CO$	8.9×10^{-6}	-0.9
60	$C_3H_7CHO + hv$	$= C_3H_7 + HCO$	2.8×10^{-5}	-0.8
61	$CH_3COC_2H_5 + hv$	$= CH_3 + C_2H_5CO$	2.4×10^{-5}	-0.9
62	$(CH_3CO)_2 + hv$	$= CH_3CO + CH_3CO$	1.8×10^{-8}	-0.1

NOTE

* $J_i = a_i \exp(b_i \sec\theta)$

Unaged PVC Sample

PVC Sample
after exposure to NO

Plate 6.1: A Typical example of the effect of NO on the appearance of PVC coatings

REFERENCES

1. CARTMELL, E., and FOWLES, G., "Valency and Molecular Structure", 3rd Edn., (Butterworths, London, 1966).

2. REES, Y., and WILLIAMS, G. H., Adv. Free Radical Chem., 4, 111, 199, (1968).

3. LEIGHTON, P.A., "Photochemistry of Air Pollution", Vol. IX of "Physical Chemistry. A Series of Monographs", (Academic Press, New York, 1971).

4. BUTLER, J.D., "Air Pollution Chemistry", (Academic Press, London, 1979).

5. BUTLER, J.D., MACMURDO, S.D., and MIDDLETON, D.R., Environmental Health, 83, 1, 24, (1975).

6. APLING, A.J., POTTER, C.J., and WILLIAMS, M.L., "Air Pollution from Oxides of Nitrogen, Carbon Monoxide and Hydrocarbons", (Warren Spring Laboratory, Dept. of Industry, 1979).

7. WEISMANTEL, G.E., "Paint Handbook", (McGraw-Hill, London, 1981).

8. WHITELEY, P., and ROTHWELL, G.W., Xth FATIPEC Congress, Montreux, Switzerland, 375, (1970).

9. CARLY, C.R., and RHEINECK, A.E., Off. Dig. Fed. Soc. Paint Technol., 37, 481, 129, (1965).

10. FULLARD, J.E., J. Oil. Col. Chem. Assoc., 52, 334, (1969).

11. BRAND, B.G., NOWACKI, L.J., MIRICK, W., and MUELLER, E.R., J. Paint Technol., 40, 524, 396, (1968).

12. HOEY, C.E., and HIPWOOD, H.A., J. Oil Col. Chem. Assoc., 34 43, (1951).

13. CAPRON, E., CROWDER, J.R., and SMITH, R.G., Polymer Age, 4(54), 3, 97, (1973).

14. CAMPBELL, G.B., Materials Quality Assurance Directorate (MQAD) Memorandum No. 219, Ministry of Defence, London SE18.

15. "XENOTEST WL and 450" manufactured by Quartz Lampen Gassellschaft GmbH, Hanu (U.K. suppliers, John Godrich, Ludford Mill, Ludlow, Shropshire).

16. STEIG, F.B., J. Paint Technol., 38, 192, 29, (1966).

17. MONK, C.J.H., and WRIGHT, T.A., J. Oil Col. Chem. Assoc., 48, 6, 520 (1965).

18. CHATFIELD, H.W., "The Science of Surface Coatings", (Ernst Benn Ltd., London, 1962).

19. ALLEN, E., J. Paint Technol., 45, 584, 65, (1973).

20. JONES, L.A., J. Opt. Soc. Amer., 6, 213, (1921).

21. LOOF, H., J. Paint Technol., 38, 501, 632, (1966).

22. COLLING, J.H., CRAKER, W.E., and DUNDERDALE, J., J. Oil Col. Chem. Assoc., 51, 524, (1968).

23. LOOF, H., 1st AIC Congress, Color 69, Stockholm, (1969).

24. BILLMEYER, F.W., Jr., and DAVIDSON, J.G., J. Paint Technol., 41, 539, 647, (1969).

25. QUINNEY, P.S., and TIGHE, B.J., Br. Polym. J., 3, 274, (1971).

26. EDWARDS, J.B., Paint Res. Assoc. Tech. Report, TR/6/74, (1974).

27. TAHAN, M., J. Paint Technol., 46, 590, 35, (1974).

28. TAHAN, M., and TIGHE, B.J., J. Paint Technol., 46, 590, 48, (1974).

29. TAHAN, M. J. Paint Technol, 46, 597, 52, (1974).

30. TAHAN, M., MOLLOY, R., and TIGHE, B.J., J. Paint Technol., 47, 602, 52, (1975).

31. JELLINEK, H.H.G., and TOYOSHIMA, Y., J. Polym. Sci., A-1, 5, 3214, (1967).

32. JELLINEK, H.H.G., and FLAJSMAN, F., J. Polym. Sci., A-1, 7, 1153, (1969).

33. JELLINEK, H.H.G., and FLAJSMAN, F., J. Polym. Sci., A-1, 8, 711, (1970).

34. JELLINEK, H.H.G., and HRDLOVIC, P., J. Polym. Sci., A-1, 9, 1219 (1971).

35. JELLINEK, H.H.G., FLAJSMAN, F., and KRYMAN, F.J., J. Appl. Polym. Sci., 13, 107, (1969).

36. MLADENOV, Iv., and SLAVOV, G., Int. Symp. on Degradation and Stabilisation of Polymers, Preprints Booklet, 11-13th September 1974.

37. GEDDES, W.C., Eur. Polym. J., <u>3</u>, 747, (1967).

38. LEE, H., and NEVILLE, K., "Handbook of Epoxy Resins", (McGraw-Hill, London, 1967).

39. HARRIS, S.T., "The Technology of Powder Coatings", (Portcullis Press, London, 1976).

40. "Encyclopaedia of Chemical Technology", 3rd Edn., Vol, 19, (John Wiley and Sons, Chichester).

41. AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) E42 (1964), "Recommended Practice for Operating Light and Water Exposure Apparatus (carbon arc type) for Artificial Weathering Test".

42. GROSSMAN, G.W., J. Of Coating Technol., <u>38</u>, 192, 29, (1966).

43. HOESCHELE, D.F., Jnr., "Analog to Digital/Digital to Analog Converstion Techniques", (John Wiley and Sons, London, 1968).

44. FISHER, E., and JENSEN, C.W., "Pet and the IEEE 488 Bus (GPIB)", (Osbourn, McGraw-Hill, 1980).

45. DECOSTE, J.B., HOWARD, J.B., and WALLDER, V.T., Ind. Eng. Chem. and Eng. Data Series, <u>3</u>, 131, (1958).

46. ÜNLÜ, M., Private Communication.

47. SILVERSTEIN, R.M., and BASSLER, G.L., "Spectrometric Identification of Organic Compounds", 2nd Edn., (Wiley, New York, 1967).

48. FEUER, H., (Ed.), "The Chemistry of the Nitro and Nitroso Groups", Part 1, (Interscience, New York, 1969).

49. Atlas Electric Devices Co., Data Sheet No. 1360B, (Chicago, U.S.A.).