A STUDY OF THE FACTORS AFFECTING THE DETERIORATION OF OLD PAINT MEDIA

by

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A Thesis submitted for the Degree of
Doctor of Philosophy of the University of
Aston in Birmingham.

October 1979

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This thesis is concerned with the factors which cause old paint media to deteriorate over a long period of time.

The first part of study is concerned with the development of techniques for evaluating the changes occurring during photo-oxidation and two have been found to be particularly useful. The first involves a measurement of the decrease in IR absorbance of the $-CH_2-$ stretching vibration at 2930 cm^{-1} which correlates with weightloss. The second monitors the formation of scission product (dicarboxylic acids).

The second part of the investigation is concerned with the mechanism of action of some of the common pigments used in old paint-media. Verdigris (basic copper acetate) was found to be an effective photo-stabiliser due to the ability of copper acetate to behave as a regenerative antioxidant in the paint film. This leads to the formation of conjugated unsaturation during ageing which is the reason for the discolouration associated with this pigment. Vermilion on the other hand is an effective sensitiser for photo-oxidation due to the formation of hydroperoxides. The probable intervention of singlet oxygen and hydrogen peroxide via radical intermediates in this process is indicated.

Vermilion pigmented paint film is considered to be a useful monitor of photo-oxidation. It is highly active in the wavelength range 300-365 nm and it is considered unlikely that physical screening of incident light over that already employed in art galleries will achieve significant additional protection. The study suggests that chemical protectants may provide a long-term solution to the problem of paint deterioration.

Paint
Photo-oxidation
Pigments
Copper acetate
Mercuric sulphide

This is to certify that the work contained in this Thesis was carried out between October 1975 and September 1978. It has been done independently and submitted for no other degree.

F Rasti

ACKNOWLEDGEMENT

The author wishes to thank the following:

Professor G. Scott for his encouragement, supervision and constructive criticism.

Department of Environment and National Gallery of London for their financial help given for this project.

The staff and technician at the University of Aston.

Last but not least to my sister Mrs. N. Attarzadeh for her encouragement and for her patience in typing this Thesis.

To my mother and father

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CHAPTER 1

THE PAINT MEDIA

1.1. INTRODUCTION

The significance of a painting is much more than the representation on canvas of what the artist actually sees. Art reveals much more than can be expressed in words, is more than just the portrayal of beauty or a demonstration of the skill of the artist. Many pages of the written word may be expended in describing only one canvas.

Tolstoy(1) one of the greatest writers of all time gave the following definition of the art of painting. 'To evoke in oneself a feeling one has experienced, and having evoked it in oneself, then by means of movement, lines, colour, sound, or forms expressed in words so to transmit that feeling that others experience the same feeling - this is the activity of art.

Art is a human activity consisting in this, that one man consciously, by means of certain external signs, hands on to others feelings he has lived through, and that others are infected by these feelings and also experiences them'.

Matisse(2) discribes his actual procedure in painting On the following words;

'If, on a clean canvas, I put at intervals patches of blue, green, and red, with every touch that I lay on, each of those put there previously loses in importance. Say I have to paint an interior: I see before me a wardrobe; it gives me very vividly a sensation of red, and so I put on a red which satisfies me. A relation is established between this red and the white of the canvas. When I put on besides a green, when I represent the floor by a yellow, between this green and this yellow and the canvas there will be still further relations. But these different tones mutually diminish each other. It is necessary that the various notes which I use should be balanced in such a way that they do not destroy one another. I must imply in my work of art a harmony of every thing together'. Hence we may induce from the above that the artist wants to stress feeling in harmony of colours or some colour intensities of precise hue and tone, a certain blue or a certain green, a brown of mixtures of pigments which they express in visual experience, These are the colours which have meaning for them corresponding to their emotional and symbolic requirements.

Opacity, translucency, weight, brilliance, dullness, darkness and brightness all are the governing features and secrets of the art of painting. Each one of them has its own merit and integrity which in our day it is our duty to respect through the skill of preservation.

No artist wants to see his masterpiece changing or fading. What he hopes for is that they will be looked after by subsequent generations, his work of art may continue to please those who will follow after. In order to maintain and preserve our cultural heritage, the cooperation of every individual involved in the world of art conservation is necessary.

Throughout the ages, paintings have suffered all manner of insult. Smoke, dampness, heat and lighting have all taken their toll. Sometimes pictures went out of favour and were then put down in a dungeon or up in the garret and forgotten.

As long ago as the middle of eighteenth century the Trustees of the National Gallery of London flirted with science as a possible way to solve their problem of picture preservation. They asked Michael Faraday (3) how they might tackle the question of the damage the dirt and grime of London caused to their paintings. Faraday replied that, whilst he himself could not take on the task, he had 'no doubt that a person of competent chemical knowledge and a little aquainted with paintings in ancient and modern times might be valuably employed in ascertaining such points'. Regrettably Faraday's advice went unheeded for 80 years.

The biggest threat of all to the Gallery's pictures was yet to come in the shape of a World War II. Strangely, the threat of war led to a major discovery and was a turning point in the preservation of works of art. On the outbreak of war and with the evacuation of the National Gallery's collection to a slate quarry in North Wales, air conditioning which some had thought to be a luxury became a prime necessity. The relative humidity in the slate quarry was close to 100 per cent all the year round. Heating alone brought the relative humidity down to 58 per cent, and as a result of this, a dramatic reduction in all problems associated with the detachment of paint, gave strong impetus to the introduction of air conditioning in exhibition rooms after the war.

It is not only temperature and humidity and a heavily polluted atomosphere which are important in influencing the detachment of works of art; lighting is also crucial since it not only affects the colours but also accelerates the process of ageing of the medium.

Neglect can also be as devastating to a painting as a poor environment. Failure of the collector to observe and understand the process of deterioration can lead to a shortened existence for a work of art and unless signs of deterioration are noted and corrected the paints's future will be in jeopardy and its value will depreciate.

We all assess paintings in different ways. The layman views a painting with perhaps the greatest detachment, usually basing his assessment on often repeated cliche' 'I don't know much about art, but I know what I like'. In some ways this is what we all do, no matter how knowledgeable we are about art. The critic views through the perspective of accepted standards; the historian looks for clues to periods and events through dress or significant detail. Artists view with an appraisal of the technique and the harmony of the colours.

Not only art historians and art lovers have made paintings the subject of study, scientists too, have subjected them to detailed examination. Using new techniques undreamed of in the days of Rembrandt and Titian, scientists have unlocked many secrets "laying" hidden for centuries below the yellowing varnish. New methods of examination have enabled scientists to see more clearly than ever before exactly how pictures were built up in those far off days and restore them to their original magnificence. Scientific technique have also been put to good use in monitoring the changes that occuring in colours with the passage of time as the painting has hung in a Gallery. The application of the scientific method has caused a revolution in the way pictures are cared for and preserved. The complexity of the problems have prompted scientists to do considerable research into the fascinating chemistry of pigments and varnishes and into the chemical reactions of specific paint media.

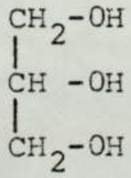
The National Gallery today is equipped with the latest air conditioning i.e. constant temperature, humidity, clean air and diffuse lighting, and yet there is still relatively little known about the relative importance of the interaction between light, the paint medium, the pigment and atomospheric pollutants.

1.2. NATURE OF PAINT MEDIA

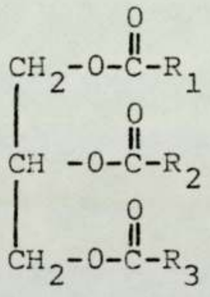
The main binding media used in easel paintings are drying oils, resins, egg and glue and/or possible combination of these(4). The majority of paintings produced since the fifteenth century were executed in an oil medium. Generally speaking, as far as fine art is concerned, only three of them were used to any great extent, these are linseed oil, poppy oil and walnut oil.

Because of different drying properties or yellowing properties, sometimes artists have traditionally blended more than one type of oil in the same picture.

The main constituents of natural oil(4), whether drived from plant or animals, are triesters of glycerol formed by the combination of glycerol (I) with three molecules of a variety of possible fatty acids. These are usually straight chain saturated or unsaturated fatty-acids. The structure of the triglycerides may be represented therefore by the general formula (II) where R_1, R_2, R_3 represents possible carbon-hydrogen chains varying in length and number of double bonds.



(I)



(II)

the principal of fatty acids encountered in drying oils are shown in Table 1.1. (4).

Drying oils contain a large portion of the three unsaturated acids listed in Table 1.2. with smaller proportions of stearic and palmitic acid. Very little myristic and lauric acids are present.

Table 1.1. The Common Fatty Acids

Name	No of carbon atoms	No of double bonds	Formula
Lauric	12	-	$HOOC(CH_2)_{10}CH_3$
Myristic	14	-	$HOOC(CH_2)_{12}CH_3$
Palmitic	16	-	$HOOC(CH_2)_{14}CH_3$
Stearic	18	-	$HOOC(CH_2)_{16}CH_3$
Oleic	18	1	$HOOC(CH_2)_7CH{=}CH(CH_2)_7{-}CH_3$
Linoleic	18	2	$HOOC(CH_2)_7{-}CH{=}CH{-}CH_2{-}CH$ $={CH}{-}(CH_2)_4{-}CH_3$
Linolenic	18	3	$HOOC(CH_2)_7{-}CH{=}CH{=}CH_2{-}CH$ $={CH}{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3$

A typical fatty acid composition for the three drying oils is shown in Table (1.2.)

Table 1.2. Fatty acid composition of drying oils(5)

Name	Linseed	Walnut	Poppy seed
Palmitic	6%	8	10
Stearic	4	3	2
Oleic	22	15	11
Linoleic	15	61	76
Linolenic	52	12	-

1.3. THERMAL OXIDATION

Drying oils spontaneously "cure" by an oxidative process under relatively mild conditions of temperature, oxygen pressure and day light. Subsequent degradation which leads to the deterioration of physical properties, however, is an extension of the same process in which light plays an important part. There is therefore no point at which curing ends and degradation begins.

The general subject of oxidative polymerisation and film formation is normally presented in the literature by specific examples of the more general phenomenon of autoxidation and polymerisation$^{(6-10)}$. With few exception, the oxidation of organic compounds proceeds via a free radical chain mechanism, which may be described by the following general scheme$^{(11-13)}$.

$\text{Initiator} \longrightarrow \dot{R}$ (1)

$ROOH \longrightarrow R\dot{O} + \dot{O}H$ (2) Initiation

$2ROOH \longrightarrow RO\dot{O} + H_2O + R\dot{O}$ (3)

$\dot{R} + O_2 \longrightarrow RO\dot{O}$ (4)

$RO\dot{O} + RH \longrightarrow ROOH + \dot{R}$ (5)

$RO\dot{O} + C{=}C \longrightarrow ROO{-}C{-}C\cdot$ (5a)

$H\dot{O} + RH \longrightarrow H_2O + \dot{R}$ (6) Propagation

$R\dot{O} + RH \longrightarrow ROH + \dot{R}$ (7)

$R\dot{O} + C{=}C \longrightarrow RO{-}C{-}C.$ (7a)

$2\dot{R} \longrightarrow$ (8) Termination

$RO\dot{O} + \dot{R} \longrightarrow$ (9)

$$\left.\begin{array}{l} 2ROO^{\cdot} \longrightarrow \\ R + RO^{\cdot} \longrightarrow \\ 2RO^{\cdot} \longrightarrow \end{array}\right\} \text{Non radical products} \quad \begin{array}{l} (10)\ \text{Termination} \\ (11) \\ (12) \end{array}$$

These are frequently subjected to autocatalysis by products (i.e., hydroperoxides, peracids, etc.). At normal oxygen pressures, the radical present in highest concentration is the alkylperoxy $ROO^{\cdot}$(14). The alkylperoxy radical play a vital role in both propagation and termination processes. Hydroperoxides, RO_2H, are primary products of autoxidation (15,16) and have been isolated in high yields in many cases(17). In the propagation step alkylperoxy radicals can either add to the double bond or abstract a hydrogen from the olefin exclusively at the reactive allylic position. Abstraction and addition are competing processes in olefin autoxidation. The ratio of addition to abstraction **is** strongly dependent on the structure of the olefin(18). Table 1.3 compares the heat of reaction for hydrogen abstraction ΔH_5 and double bond addition reaction ΔH_{5a}.(11)

Table 1.3.

Olefin	ΔH_5 KJ/mol	ΔH_{5a} KJ/mol
$R-CH_2CH=CH-CH_2-R'$	-62.7	-38.4
$R-CH=CH-CH=CH-R'$	-79.4	-83.6
$R-CH=CH-CH_2-CH=CH-R'$	-108.68	-38.4

In many liquid phase oxidants$^{(20,21)}$, at partial pressure of oxygen greater than 100 Torr, chain termination occurs via the mutual destruction of two alkylperoxy radical equation(10). Under these conditions the cross termination reaction equation (9) may be neglected and the predicted rate expression, under steady state condition, is then given by

$$-\frac{d(RH)}{dt} = -\frac{d(O_2)}{dt} = K_p(RH)\left(\frac{Ri}{2K_t}\right)^{\frac{1}{2}} \quad (13)$$

The susceptibility of any particular hydrocarbon to autoxidation is determined by the ratio $K_p/(2K_t)^{\frac{1}{2}}$. Table 1.4. lists the maximum rate of oxidation of the most important double bond activated methylenic compounds at 37°C. It can be seen that whereas the introduction of a second$^{(22)}$ α, β double bond (B) increases the oxidation rate of an olefinic ester (A) by a factor of about 40 the existence of two such structure in the molecule (C) leads only to a further increase of activity of approximately 2.

Table 1.4.

Structure	Relative oxidation rates	
	R=H	R=Et
A. $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH=CH(CH_2)_7COOR$	1	1
B. $CH_3CH_2CH_2CH_2CH_2CH=CHCH_2CH=CH(CH_2)_7COOR$	28	41
C. $CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOR$	77	98

Chain initiation is readily accomplished by the deliberate addition of initiators; that is compounds yielding free radicals on thermal decomposition. Typical initiators are aliphatic azo compounds, dialkyl peroxides, diacylperoxides and peresters. Initiation by direct reaction of the organic substrate with molecular oxygen, namely

$$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot} \qquad (14)$$

is thermodynamically and kinetically unfavourable for most hydrocarbon, although it has been observed in few cases (23,24). A third mechanism for initiation is the reaction of carbanions with molecular oxygen(25,26)

$$R^{-} + O_2 \longrightarrow R^{\cdot} + O_2^{\dot{-}} \qquad (15)$$

However, except for highly acidic hydrocarbons, this pathway is not a common one.

Thermal decomposition of alkyl hydroperoxides presents a major source of free radicals in autoxidation reaction. Therefore the bimolecular breakdown of hydroperoxide may dominate the initiation once hydroperoxides are present.

1.4. PHOTO-OXIDATION

It is now generally believed that similar free radical mechanism occur in both thermal and photo oxidation (27), however, although the mechanism of photo-oxidation is similar, the breakdown products are generally different since most of the breakdown during thermal oxidation occurs via hydroperoxides whilst photolysis of carbonyl compounds is also involved in U.V. degradation. Fig 1.1. relates the energy content of visible and U.V. light to its wavelength, and shows the double bond dissociation energies and double bond activation energies of some chemical grouping present in some oxidising media(28). Because of the screening effect of the upper atmosphere, no radiation of wave length shorter than 290nm reaches the earth's surface.

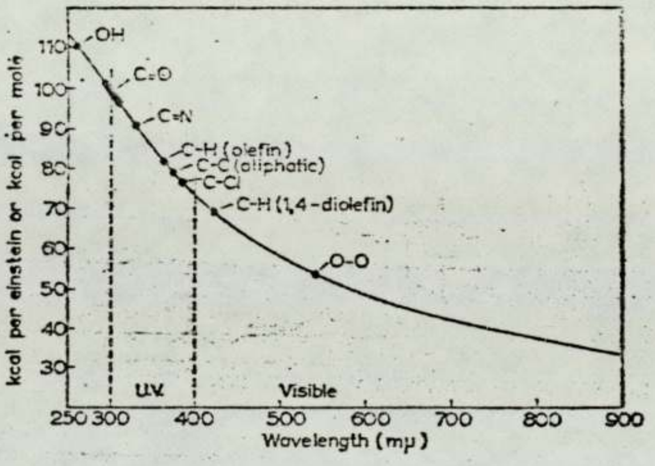


Fig 1.1.

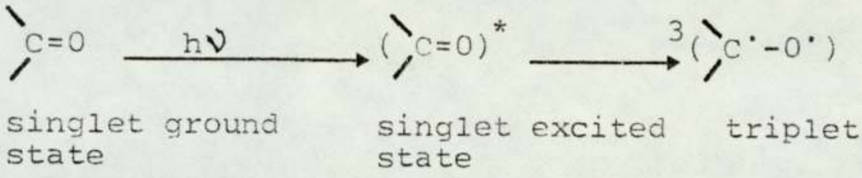
U.V. has the greatest energy of sun light. It consists 5% of sun light and is in the range of 300-400nm.

Alkyl hydroperoxides have a continuous absorption spectrum that extends from the far U.V. to about 300nm in the near U.V.(29). They are, therefore, capable of absorbing energy from sun light and undergo cleavage at the peroxide bond. The slow bimolecular breakdown of hydroperoxide in autoxidation is replaced by a much faster photolysis in the presence of light

$$ROOH \xrightarrow{h\nu} RO^{\cdot} + O^{\cdot}H \qquad (16)$$

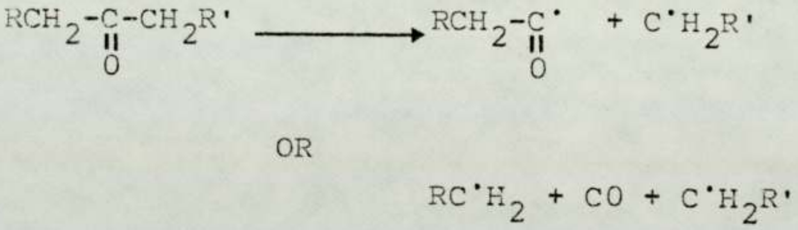
giving rise to a shorter chain length. The presence of hydroperoxide during photo-oxidation has been confirmed for(30) methyl oleate, 1-methyl cyclohexene, ethyl linolenate, rubber(31), and polymers in general. Carlsson and Wiles(32), studied the photolysis of polypropylene hydroperoxide generated by thermal oxidation of the polymer. They found a quantum efficiency of about four. According to Scott and co workers(33) hydroperoxides formed during processing are the main photo initiators in the early stages of photo initiation of commercial polyolefins.

Similarly carbonyl groups whose absorption maxima occur at 270-320nm are known to undergo chemical reactions leading to formation of free radicals(34). Carbonyl compounds are therefore capable of absorbing sun light energy the absorption arises from promotion of a non-bonding, π-orbital electron localised on the oxygen to a delocalised anti bonding, π-orbital, delocalised over the carbonyl group. The excited singlet state, $^1(n-\pi^*)$ may, by intersystem crossing, change to the excited triplet state, $^3(n-\pi^*)$, both of which may lead to chain scission reaction(36)



(17)

The photo chemical reactions of excited carbonyl groups in organic compounds are classified as Norrish reaction type I and II(37); the excited triplet state can lead to the formation of free radicals by Norrish I type mechanism in which the bond between the carbonyl group and an adjacent α - carbon is homolytically cleaved.

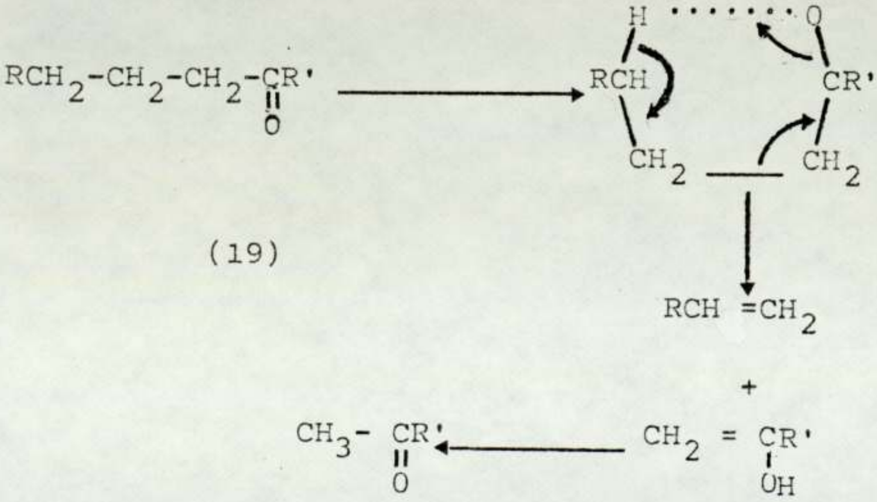


$$RCH_2-\underset{O}{\underset{\|}{C}}-CH_2R' \longrightarrow RCH_2-\underset{O}{\underset{\|}{C^{\bullet}}} + C^{\bullet}H_2R'$$

OR

$$RC^{\bullet}H_2 + CO + C^{\bullet}H_2R'$$

When the ketone possesses at least one hydrogen atom on the γ-carbon with respect to the carbonyl group, the Norrish II process can occur. It is a non radical, intramolecular process which occurs via a six membered cyclic intermediate.



(19)

Triplet carbonyl can hydrogen abstract to form a macro radical in the chain(38)

$$^{3}(\mathrm{>C^{\cdot}-O^{\cdot}}) \xrightarrow{\mathrm{RH}} \mathrm{>C^{\cdot}-OH} + \mathrm{R^{\cdot}} \qquad (20)$$

Photo-initiation by a radical formed from Norrish I will only be significant after an appreciable amount of carbonyl has built up in the substrate. It has been shown that U.V. excited carbonyl groups in the triplet state may transfer their excitation energy to molecular oxygen, forming singlet oxygen (39). In accordance with this it has been shown that triplet carbonyl is not initially important as a photo initiator in aliphatic saturated and olefincally unsaturated polymers(40).

CHAPTER 2

THE EFFECT OF PIGMENTS ON OXIDATION

2.1. EFFECT OF PIGMENTS IN AUTOXIDIZING MEDIA

Colourants are additives which impart colour by virtue of the manner in which they absorb light. Classically they are divided into two catagories, pigments and dyes. Pigments are insoluble and dyes are soluble in the medium in which they are incorporated. However, this definition is ambiguous for many materials since it is frequently impossible to determine where solubility ends and colloidal dispersion begins. Therefore in this project the term "pigment" is used throughout the course irrespective of their physical characteristics. Two major processes are important in studying the effects of pigments in any organic substrate. In the first process interest centres around the physical interaction of the colourant with light; in the second with the chemical and physical interactions with the substrate. The interaction of practical significance between pigment and light consists of five basic types: absorption, scattering, reflection, interference and emission.

The physical interaction of a pigment/medium blend with light determines its appearance However, pigments are chemicals and as such can also undergo chemical and physical interactions with the substrate or other ingredients of the formulation. These interactions may affect not only the initial colour but also the long term performance of the system.

Pigments can absorb or scatter actinic radiation, thus interfering with the initiation step or photolytic chain reactions. In this case, they are analogous to U.V. absorbers. Their effectiveness is determined by their ability to shield inner layers of the substrate from the damaging effects of light and by their proficiency in absorbing U.V. light, and dissipation of the energy absorbed in a harmless manner.

Iron oxide (Fe_2O_3 and Fe_2O_4) protects polyolefins but rapidly catalyses the decomposition of polyvinyl alcohol on exposure to U.V. light. Chromic oxide (Cr_2O_3), Red Lead oxide (Pb_3O_4), Zinc oxide (ZnO), Titanium dioxide (TiO_2), Titanium sulphide are widely used in the plastics and paint (41) industries. Powdered metals, e.g. aluminium are excellent reflectors of U.V. light, and therefore they improve the outdoor stability of such plastics as ABS resins and other polymers when applied to the surface. On the other hand metal powders in a plastics matrix may act as randomly placed mirrors and cause repeated light reflection throughout the solid and hence accelerate the rate of degradation.

Coloured pigments show on the whole poorer U.V. reflectance than white pigments. Absorption of U.V. is more important than reflection, particularly if the pigment absorbs those wavelength which are essentially damaging to to the polymer matrix.

Because of the presence of metal ions in some pigments, they may participate in catalysing the autoxidation of the substrate. The most common pathway for catalysis of liquid phase autoxidation undoubtedly involves the metal catalysed decomposition of alkyl hydroperoxides. The rapid decomposition of alkyl hydroperoxide in hydrocarbon solution in the presence of trace amounts of iron manganese, cobalt and copper naphthenates is well known$^{(42-43)}$.

$$RO_2H + M^{(n-1)+} \longrightarrow RO^{\cdot} + M^{n+} + HO^{-} \quad (21)$$

$$RO_2H + M^{n+} \longrightarrow RO_2^{\cdot} + M^{(n-1)+} + H^{+} \quad (22)$$

When a particular metal ion is capable of effecting only one of these reactions, a stoichiometric but not a catalytic decomposition of alkyl hydroperoxide would be expected. However, a catalytic decomposition reaction is feasible if there is a regenerative pathway for the metal complex when allows it to react again with the alkyl hydroperoxide.

The relative rates of reaction (21) and (22) are roughly correlated with the redox pontential of the particular $M^{n+}/M^{(n-1)+}$ couple $^{(44-45)}$, as shown in Table 2.1. When the metal complex is a strong oxidant, reaction (22) predominates. For example, Pb(IV) reacts stoichiometrically with 2 moles of alkyl hydroperoxide to afford alkylperoxy radicals$^{(46)}$.

$$Pb(OAC)_4 + 2ROOH \longrightarrow Pb(OAc)_2 + 2RO_2^{\cdot} + 2HOAC$$

TABLE 2.1.

REDOX POTENTIAL (AQUEOUS SOLUTION)

M^{n+} + e		$M^{(n-1)+}$	F_o(ev)
Ag(II) + e	$\longrightarrow$	Ag(I)	1.98
Co(III) + e	$\longrightarrow$	Co(II)	1.82
Mn(III) + e	$\longrightarrow$	Mn(II)	1.51
Fe(III) + e	$\longrightarrow$	Fe(II)	0.77
Cu(II) + e	$\longrightarrow$	Cu(I)	0.15
Cr(III) + e	$\longrightarrow$	Cr(II)	-0.41

When the metal ion is a strong reducing agent, reaction (21) predominates (non catalytic). Chromous ion, Cr(II), reduces alkyl hydroperoxides to the corresponding alcohol$^{(47)}$.

$$RO_2H + Cr(II) \longrightarrow R\dot{O} + Cr(III)OH \quad (24)$$

$$R\dot{O} + Cr(II) \longrightarrow ROCr(III) \quad (25)$$

Copper (I) similarly reduces hydroperoxides to the corresponding alcohols. The reaction of the Cu(I)/Cu(II) couple with peroxides has been studied$^{(48-49)}$. In contrast to the reaction with Cr(II), alkyl hydroperoxides can react by a catalytic process with Cu(I), since there are several routes available for regeneration of Cu(I). Thus, in the copper catalysed reduction of tert-amyl hydroperoxide$^{(50)}$. The Cu(I) is regenerated via electron transfer oxidation$^{(51)}$

of the ethyl radical, formed by the rapid fragmentation of tert-amyloxy radical

$$CH_3CH_2C(CH_3)_2O_2H + Cu(I) \longrightarrow Cu(II)OH + CH_3CH_2C(CH_3)_2\dot{O} \qquad (26)$$

$$CH_3CH_2C(CH_3)_2\dot{O} \longrightarrow (CH_3)_2\underset{\overset{\|}{O}}{C} + C_2H_5^{\bullet} \qquad (27)$$

$$C_2H_5^{\bullet} + Cu(II) \longrightarrow C_2H_4 + H^+ + Cu(I) \text{ etc.} \qquad (28)$$

When the metal has two oxidation state of comparable stability, reaction (21) and (22) occur concurrently. Cobalt and manganese compounds are among the most effective catalysts for autoxidation since they are able to induce the efficient catalytic decomposition of alkyl hydroperoxide and overall reaction is formation of alkoxy and alkylperoxy radicals

$$2RO_2H \xrightarrow{M^n/M^{n+1}} R\dot{O}_2 + R\dot{O} + H_2O \qquad (29)$$

Another route that may be possible for chain initiation involves direct oxygen activation, whereby the complexation of molecular oxygen by transition metal lowers the energy of activation for direct reaction with the substrate. For example, oxygen coordination to a metal might be expected to possess properties similar to alkylperoxy radicals and undergo hydrogen transfer with a hydrocarbon

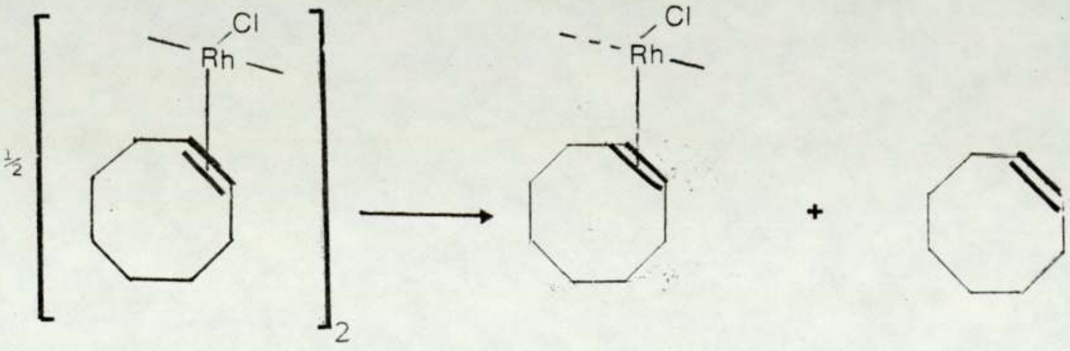
$$M\text{-}O\text{-}\dot{O} + RH \longrightarrow M\text{-}O\text{-}OH + \dot{R} \qquad (30)$$

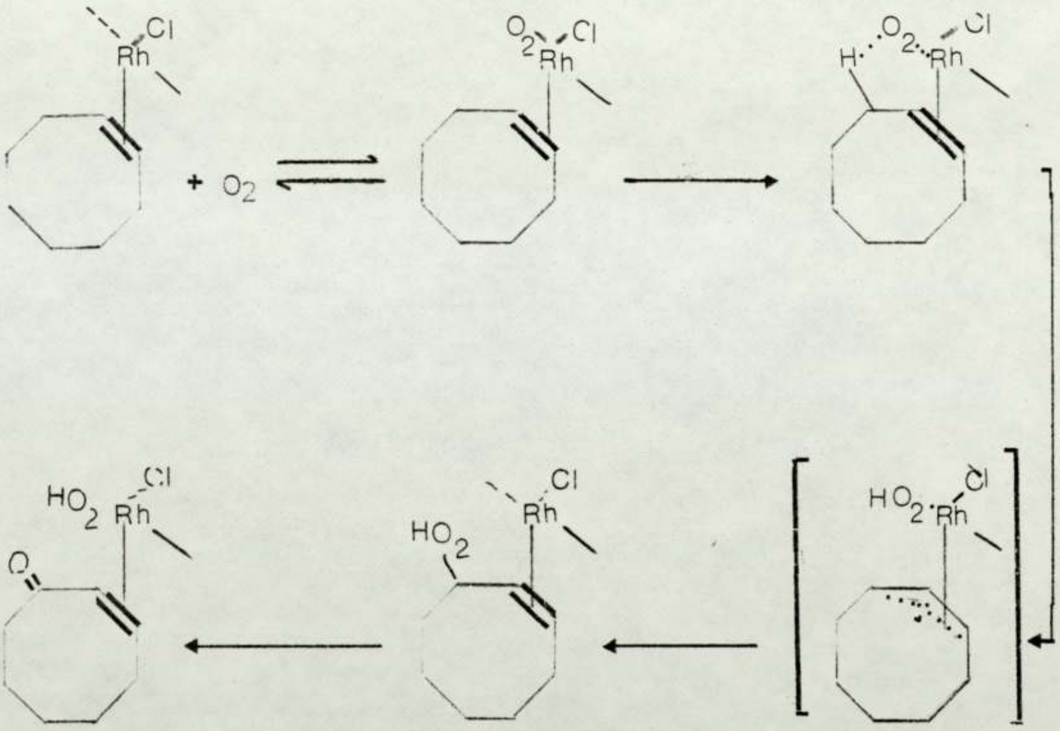
Many authors have proposed (52-53) reaction (30), or a variant of it, in an attempt to explain kinetic data. For example(53), Uri proposed the following mechanism for the initiation of cobaltous stearate catalysed autoxidation of methyl linoleate in benzene.

$$Co(II) + O_2 \rightleftharpoons CO(II)O_2 \qquad (31)$$

$$CO(II)O_2 + CO(II)XH \longrightarrow CO(II) + Co(III)X + H\dot{O}_2 \qquad (32)$$

In the last few years, numerous stable, diamagnetic(32) oxygen complexes of other group V111 elements (Ir, Rh, Ru Os, Ni, Pd, Pt) have been prepared(54-55). Many of these complexes have 0-0 bond length that corresponds closely to those of the peroxide (O_2^{2-}) or superoxide ($O_2^{\cdot -}$) anions and, hence, may be regarded as inorganic peroxides(56). Some of these complexes form hydrogen peroxide on protonation. Collman et al(57) reported that dioxygen complexes of Ir(I), Rh(I) and Pt(0) catalysed the autoxidation of cyclohexene at 25°C to 60°C in benzene or methylene chloride. Cyclohexene-3-one is the major product (together with water) and cyclohexene oxide a minor product. Another situation has been(58,59) reported in which hydrogen abstraction from a coordinated olefin by coordinated dioxygen occurred. The following mechanism was proposed.





It should be bornein mind, however, that the foregoing reaction is a stoichiometric one. More recent investigation have shown that these reactions involve metal catalysed decomposition of hydroperoxide via the usual redox cycle and such autoxidation processes would be readily masked by one involving metal catalysed decomposition of the hydroperoxide(59,60). Further evidence against initiation by direct oxygen activation in the oxidation of olefins is provided by Sheldon(61).

Inhibition of autoxidation by transition metal in low oxidation states, such as Co(II) or Mn(II), has often been observed (52,42,43).

Since alkylperoxy radicals are relatively strong oxidants, they can react with the reduced form of the catalysts:

$$R\dot{O}_2 + M^{(n-1)+} \rightleftharpoons RO_2M^{n+} \qquad (34)$$

In the early stages of autoxidation , hydroperoxide concentrations are low and chain initiation is inefficient. Under these conditions, Mn(II) and Co(II) can act as inhibitors by scavenging alkylperoxy radicals. Bernhard and Marr(62) have found that cupric sulphate markedly inhibits the autoxidation of α-limonene and propose that the metal ions remove alkoxy radicals.

$$Cu^{2+} + R\dot{O} \longrightarrow \left[Cu^{2+}.OR\right] \qquad (35)$$

There are also recent findings to indicate that metallic ions could effect the rate termination if they form a complex with the $R^{\cdot}$ radical as proposed by Kochi and Rust(63).

Russian workers(64) have reached the same conclusion when they found that copper acetyl acetonate stabilizes polyamides against light. However no mechanistic evidence was presented.

Tranistion metal complexes often behave as catalysts at low concentrations but as inhibitors at high concentration (52,43). There has been some suggestions and questions as to the cause of this phenomenon but still the detailed mechanism of the inhibiting action of these metal complexes are not very well understood.

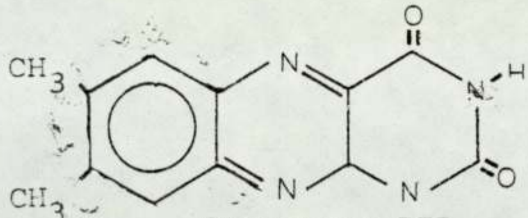
2.2. PHOTOSENSITIZATION

The photosensitized oxidation of organic substrates in the presence of some pigments has been known for a long time. Some soluble pigments, such as methylene blue and eosin, etc. are able to absorb the low energy photons of visible light and convert this energy in some way to effect a chemical change in the neighbouring non-absorbing molecules.

Although the light which it absorbs is of long wave length and of very low energy in photochemical terms, Methylene blue is well known for its destructive reactions in the presence of oxygen in a wide variety of organic substrates.

The absorption of light results in the electronic excitation of the molecules - that is the absorption of this quantum will elevate one electron from its ground state energy level into one of higher energy, the difference in energy between these corresponding to the energy of the quantum. The molecule is then said to be in an excited state.

The excited states of organic molecules fall into two main classes, the 'singlet' and 'triplet' excited states, which are not necessarily interconvertible and behave in quite different ways. Absorption of light almost invariably leads to the generation of a singlet excited states.



Structure III

The energy level diagram of this process for lumiflavin (structure III) is shown in Fig 2.1.$^{(65)}$.

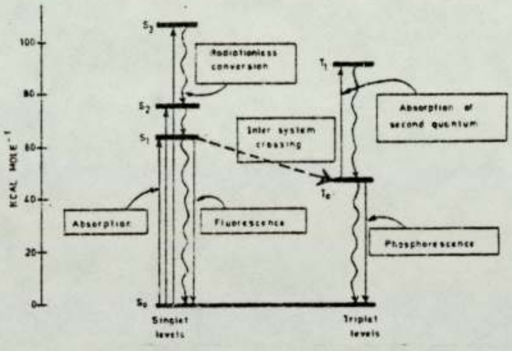


Fig. 2.1. The energy level diagram for lumiflavin.

This is a typical diagram for a conjugated organic melecule. Light of wavelength about 400nm will excite the molecule into the lowest singlet level (S_1), the molecule acquiring the corresponding excitation energy of 63 Kcal/mole. Light of shorter wavelength, with quanta of greater energy, can excite the molecule into higher levels, but this extra energy is rapidly lost by radiationless conversion (the wavy arrows) so that the molecule returnes to the S_1 level, which is therefore the only singlet excited state of importance to this discussion.

There are four main processes which the singlet state can undergo:

(i) it can lose its energy by a further radiationless conversion, the molecule returning to the ground state;

(ii) it can emit a quantum of the same or slightly lower energy, seen as fluorescene;

(iii) it can undergo 'inter-system crossing' to excite the lowest triplet state of the molecule; or

(iv) it can undergo a bimolecular reaction with a second molecule and so lose its excitation energy.

These processes compete with one another and the dominant one will depend on the molecule and its environment. They are all fast reactions and so the lifetime of the S_1 state is about 1ns. In fluid solution, the singlet-excited molecule is unlikely to encounter a second molecule during this brief lifetime and so few photochemical reactions directly involve the singlet state. On the other hand, the triplet excited state is of considerably longer lifetime - up to 1 ms in fluid solution - and far longer in a rigid matrix. This means that if sufficient inter-system crossing takes place, the triplet is more likely to be involved in photochemistry and, in most sensitized reactions, it is the triplet state of the sensitizer which brings about the reaction. The excitation energy of the triplet can also be dissipated in various ways;

(i) by radiationless conversion;

(ii) by emission of a quantum of phosphorescene - the long lifetime of the phosphorescene indicating the persistence of the triplet or

(iii) in a reaction with a second molecule.

A combined effect of sensitizer, light and atmospheric oxygen were shown to be important in the

(1) inactivation of enzymes, proteins, nucleic acid and other biological system(66),

(2) oxygenation of low molecular weight organic compounds(67),

(3) photodegradation of polymers(68),

(4) chalking of pigments(69),

(5) phototendering of Vat dyes(70),

(6) atmospheric processes especially in the chemistry of polluted urban atmosphere(71),

Gollnick(72) has classified reactions which are open to sensitizer as Type I and Type II.

IN TYPE I, the sensitizer interacts with another molecule directly, usually with hydrogen-atom or electron transfer. The radical formed react further with oxygen or other organic molecules.

IN TYPE II, sensitizer will transfer its energy to oxygen molecule to give singlet oxygen which reacts further with various acceptors.

Foote and Denny(73) found that the oxidation of

2 methyl-2-pentene photosensitized by methylene blue involves a singlet oxygen intermediate, while Knowles(74) concludes that the methylene blue oxidation of nucleotides operates via a hydrogen abstraction mechanism.

The photochemistry of the Vat-dye-sensitized photodegradation of cotton and other cellulosic fibres has been reviewed by McKellar(75). No satisfactory mechanism to explain the many complex facts has yet been made. However two mechanisms have emerged that explain the main features.

The first, proposed by Egerton(76) in 1947, who postulates the formation of activated oxygen which reacts with substrate or water forming hydrogen peroxide as shown (A = pigment, cell-H = cellulose)

$$\begin{array}{llll}
A + h\nu & \longrightarrow & A^* & (1) \\
A^* + O_2 & \longrightarrow & A + O_2^* & (ii) \\
O_2^* + \text{cell-H} & \longrightarrow & \text{oxidation products} & (iii)\ \text{dry condition}
\end{array}$$

$$\left.\begin{array}{lll}
O_2^* + 2H_2O & \longrightarrow & 2H_2O_2 \\
H_2O_2 + \text{cell-H} & \longrightarrow & \text{Oxidation products}
\end{array}\right\}\begin{array}{l} (iv) \\ (v) \end{array}\ \text{moist condition}$$

Later Egerton(77) postulates that reaction (ii) results in the formation of excited singlet state oxygen.

The second mechanism proposed by Bamford and Dewar(78) in 1949, postulates initial interaction between the photoactive dye and the substrate by a process of hydrogen abstraction. The work of Davies et al(79) provided a rational explanation for this apparently anamalous behaviour in terms of the hydrogen-atom abstraction theory.

Clays(80) has reviewed some of the photochemical effects of a number of inorganic pigments including titanium dioxide. The photosensitising effects of titanium dioxide on surrounding polymers(81-82) has been discussed by many authors. Some workers suggested that the polymer degradation is related to the formation of superoxide ion (or oxygen radical anion), $O_2^{\dot{-}}$ produced by electron transfer from excited state of TiO_2 to molecular oxygen and generating strong oxidising site on the TiO_2 and leaving positive hole in the crystal lattice.

$$TiO_2 + O_2 \xrightarrow{h\nu} TiO_2^{+} + O_2^{-\cdot}$$

An additional photolysis effect is the ejection of oxygen from the crystal lattice leaving Ti^{3+} defects, reoxidation to Ti^{4+} by molecular oxygen occurs readily(81-82).

However, evidence has been obtained for the formation of metal peroxides(83), atomic oxygen(81), and other radical (84), non radical, and ionic oxygen species on metal oxide surface by the both thermal and photolytic paths. Some workers(85) have suggested that the initiation polymerisation of vinyl monomers, crosslinking of polypropylene, and the oxidation of a species, such as isopropyl alcohol(86), is due to hydrogen abstraction ability of U.V. irradiated titanium dioxide/oxygen system. Pappas and Fischer(87), have demonstrated that singlet oxygen and hydrogen peroxide are important in the degradation of polymer substrates, whereas Kaemph and co-workers(88) conclude from their work that both $O^{\cdot}H$ and $HO_2^{\cdot}$ radicals which are precursors to hydrogen peroxide are responsible for the degradation of polymer. The above results indicate the complexity of the mechanism involved.

Spectroscopic studies(89) have identified singlet-oxygen in both of its excited singlet states which are described symbolically in Table 2.2.

TABLE 2.2.

ELECTRONIC STATES AND CONFIGURATION OF OXYGEN MOLECULE

STATE	OCCUPANCY OF HIGHEST ORBITAL		ENERGY KJmol^{-1}
$^1\Sigma_g^+$	↑	↓	159.6
$^1\Delta_g$	↑↓		94.1
$^3\Sigma_g^-$	↑	↑	ground state

The sigma singlet ($^1\Sigma_g^+$) which possess 159.6 KJ mol^{-1} is predicted to have free radical reactivity, and the delta singlet state ($^1\Delta_g$) which possess 94.1 KJ mol^{-1} above the ground state has characterised as a reactive dienophile.

The sigma state has a higher energy, and is considerably shorter lived and is in fact rapidly deactivated to delta state, which has been identified or implicated in many important chemical processes.

Kautsky(90) was the first to report the involvement of singlet oxygen in sensitized photo-oxygenation of variety of low molecular weight organic compounds. Foote and co-workers(91), have shown that singlet oxygen is the intermediate in the dye-sensitized photo-oxidation of a number of monoenoic and dienoic compounds. Khan and Rawls(92) and Van Santan(93) have presented evidence for the participation of singlet oxygen in the sensitized photo-oxidation of linoleic and oleic acid. Although the photosensitized singlet oxygen oxidation of low molecular weight organic compounds is well known and has been studied extensively in past, there is still considerable divergence of opinion about the importance of singlet oxygen in a more complicated system like polymers(94).

2.3. OBJECTIVE OF THE PRESENT WORK

Paintings deteriorate with time due to a complex interaction between the oil medium, the pigment and oxygen of the atmosphere in a process which is catalysed by light. Every pigment differs in the way in which it affect the photochemical reaction; very few have no effect at all.

The physical manifestation of deterioration of a polymerised linseed oil, are many. They include loss of gloss, erosion, yellowing, embrittlement, loss of adhesion and cracking, but all are the consequences of the same oxidation sequence.

In this project attempt will be made to achieve the following objectives.

(1) To establish a simple procedure which could be used in any art galleries for monitoring the deterioration of paint media

(2) to establish that the technique correlated with the actual experience of old paint media

(3) to elucidate the photochemical changes occurring with some of the more important artists pigments.

Once a satisfactory procedure is identified, the technique will be applied to a study of the wavelength sensitivity of paint media. Any old master usually consists of several pigments, however, all the pigments are not equally stable towards light. The pigment which is the most sensitive towards light will determine the rate of overall degradation process. In order to find the least stable pigment in the paint media several pigments will be studied under the condition of light exposure. This study will provide a rapid screening test regarding photo-stability of pigment. In this context, pigments used by artists thought to be the generators of singlet oxygen will be particularly studied in details in view of the known harmful photochemical effects of this species.

CHAPTER 3

EXPERIMENTAL

3.1. MATERIALS

The oil used was refined linseed oil (Winsor and Newton Limited, Batch No. (060404).

The pigments used are recommended by the National Gallery of London and are listed in Table 3.1.

Table 3.1.

Pigment	Colour	Chemical Composition	Source
Lead white	White	Basic lead carbonate $PbCO_3,Pb(OH)_2$	Conservation department of National Gallery
Light red	Reddish Brown	An anhydrous ferric oxide Fe_2O_3	" "
Verdigris	Light blue	Basic copper acetate $Cu(CH_3COO)_2.Cu(OH)_2.5H_2O$	" "
Vermilion	Brick red	Complex of mercuric sulphide (dry ground)	Winsor & Newton Batch No.289MS
Cadmium yellow	Pale yellow	Complex of cadmium sulphide(dry ground)	Winsor & Newton Batch No.289MS
Cadmium red	red	" "	John Malthey No.P844
Cadmium marron	marron	" "	No.P625
Cadmium red	red	" "	No.624
Oppiment	light yellow	As_2S_3	B.D.H.
Realgar	yellow orange	As_2S_2	B.D.H.

3.2. PURIFICATION OF REAGENTS

CUMENE HYDROPEROXIDE

Cumene hydroperoxide stablized with 6% of 15% W/W slurry of aqeous Na_2CO_3 was purified by a modification of Karasch's method(95) as follows.

50gm (1.25 mole) of caustic soda in 100ml of water was added to 152gm (1.0 mole) of hydroperoxide in ligorin at 0^oC. The sodium salt was filtered, washed with 25% caustic soda solution, then with petroleum ether, and suspended in 500ml of water. A stream of carbon-dioxide was bubbled through the suspension and when all the hydroperoxide has been reliberated the solution became opaque, and separated into two layers. The lower layer was extracted three times with pet ether and the combined ethereal fraction was washed with dilute sodium carbonate solution and dried over anhydrous sodium carbonate. The product was vaccum distilled and the fraction boiling at $52/54^oC/0.1mm$ Hg was collected. Iodometric titration(96) showed a purity higher than 98.5% (B.P. $60^oC/0.2mm$ Hg)(97).

G.L.C. STANDARDS

A.R. grade acetic acid and isopropanol were used without further purification.

CHLOROBENZENE

General purpose reagent (B.D.H.) was fractionally distilled over phosphorus pentoxide and the fraction distilling at 130°C being collected (131.7°C/760mm Hg)(98).

ACETONE

A.R. grade was used without further purification.

ACETOPHENONE

Redistilled fractionally and the fraction boiling between 201-202°C was collected (202/760mm Hg)(98).

α-CUMYL ALCOHOL (2-PHENYL PROPAN 2-OL)

This was recrystallised from petroleum ether (60/80°C) M.P. 34°C (Lit.(95) 36°C).

α METHYL STYRENE (2- PHENYL PROPENE)

This was fractionally distilled under nitrogen. Fraction boiling at 165°C was collected.

PHENOL

Fractionally distilled. The fraction boiling at 182°C was collected.

The methyl esters of following acids were obtained from SUPELCO Chromatography Supplier with 99% purity.

1. C_7 dicarboxylic acid (Pimelic acid)
2. C_8 dicarboxylic acid (Suberic acid)
3. C_9 dicarboxylic acid (Azelaic acid)
4. C_{10} dicarboxylic acid (Sebacic acid)
5. C_{14} saturated acid (Myristic acid)
6. C_{15} saturated acid
7. C_{16} saturated acid (Palmitic acid)
8. C_{17} saturated acid
9. Stearic acid
10. Oleic acid
11. Linoleic acid
12. Linolenic acid

N-METHYL, N-NITROZO-PARATOLUENE SULPHONAMIDE

This reagent obtained from Aldrich Chemical Co. and used without further purification.

METHANOL, DIETHYL ETHER AND ETHYLDIGOL

A.R. grade (Fisons laboratory reagent) were used without further purification.

3.3. SPECTROSCOPY

3.3.1. INFRA RED SPECTROSCOPY

Since the 1940's infra red spectroscopy has been as important tool for the study of linseed oil and the changes that it undergoes in the course of drying(99). In addition to its use in the characterisation and monitoring of the processes of oxidation and drying, infra red instrumentation has been used in attempts to study the yellowing which occurs almost invariably in the process of ageing(100-101). It has also been applied to the identification of individual products after chromatographic separation, especially in conjunction with mass spectroscopy (102), and to attempt to characterize the dried film(103). Infra red spectroscopy(104) has been used on sample taken from surfaces of paintings on canvas in effort to identify paint media and pigments.

All the infra red spectra were recorded using a Perkin-Elmer grating infra red spectrophotometer model 257. The spectra from 4000cm^{-1} to 625cm^{-1} were recorded at medium scan speed.

Three region of infra red-spectrum, which are likely to provide the most information about the progress of the degradation of paint media are; the carbonyl, the hydroxyl and the double bond.

3.3.1.1. SAMPLE PREPARATION

In order to follow the progress of oxidation for a long time a free-unsupported film was desirable.

3.3.1.1.1. PREPARATION OF UNSUPPORTED FREE FILM

Known amounts of ground pigment and oil were mixed and applied to the tin foil, polyethylene and teflon sheets and air dried at normal room temperature and humidity for one week. Before drawing films, strips of cellulose tape were placed around the edges of substrate sheets to prevent retracting of wet coating composition. Dried paint sticks to polyethylene and tin foil wrinkles, but because of low surface energy of teflon sheets, paint films could easily be stripped off. Unpigmented films, could be most easily removed by cooling them to minus 10°C in a freezer and stripping them while they were warming to room temperature. After stripping films were attached to 3 x 4cm sheets for use in spectrophotometer. An unsatisfactory result was obtained by using unsupported free film see Fig. 3.1. because of the thickness of the films. Many attempt was made to prepare thinner films without any improvement.

3.3.1.1.2. SODIUM CHLORIDE DISC TECHNIQUE

Liquid films of linseed oil, approximately 0.02mm, thick, in the presence (1% based on the weight of the oil) and absence of pigment were spread on a sodium chloride disc. Every disc were allowed to stand for a week in a horizontal position under normal conditions of temperature and relative humidity in an artificially lighted room. The disc was placed in an appropriate holder and the spectrum was taken. The exposed area was marked in order to follow the changes of the functional group during

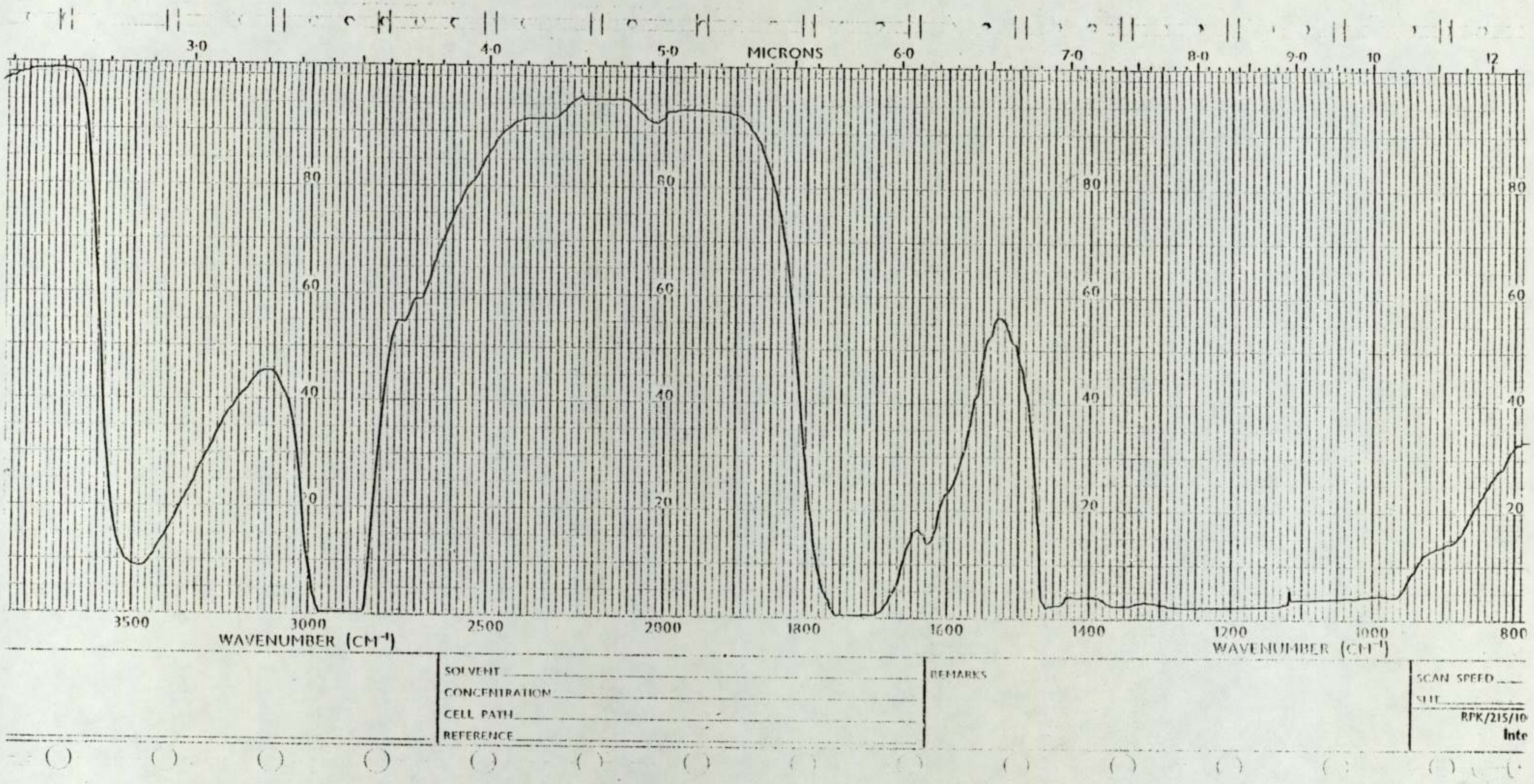
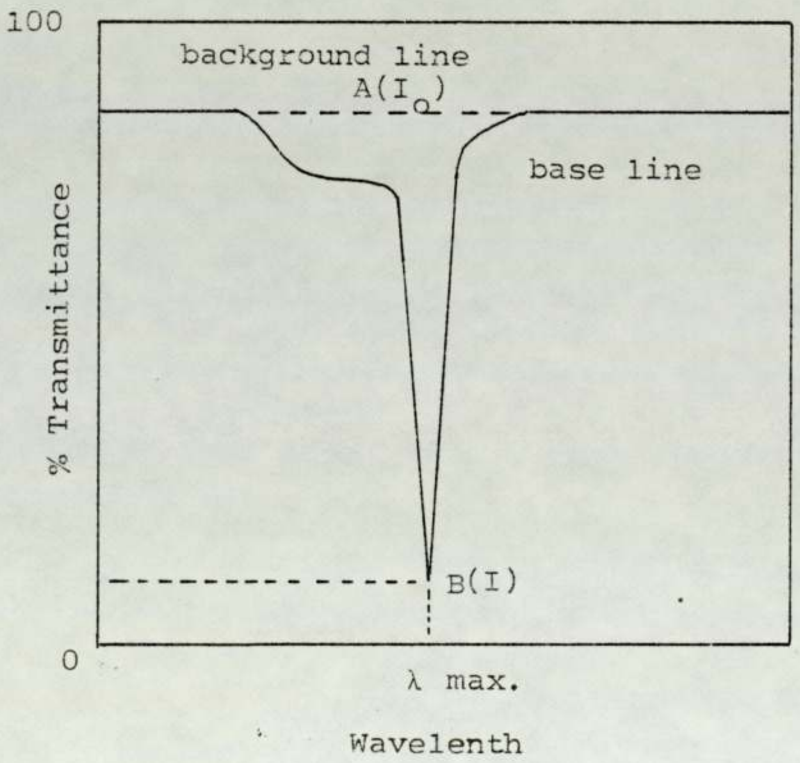


Fig 3.1. IR spectra of dried unsupported film

different stages of U.V. and non U.V. irradiation.

The base line technique was used to calculate the optical density or absorbance due to various functional groups. This was done as shown in Fig 3.2. by drawing a straight line (base line) tangential to adjacent absorption maxima or shoulder, then erecting a perpendicular through the analytical wave length until it intersects with base line. At 'A' the concentration of the functional group to be determined is zero at 'B' there appears an absorption peak whose height serves to calculate the concentration. Before scanning, the spectraphotometer was adjusted to read 100% transmission and this was known as back-ground line.



3.4. ULTRAVIOLET SPECTROSCOPY

Ultra Violet and visible spectra were recorded on a Perkin Elmer 137 spectrophotometer.

3.5. CHROMATOGRAPHY

3.5.1. GAS-LIQUID CHROMATOGRAPHY (G.L.C.)

A Pye 104 gas chromatograph with a flame ionisation detector was used for;

3.5.1.1. QUALITATIVE ANALYSIS OF PRODUCTS FROM DECOMPOSITION OF CUMENE HYDROPEROXIDE

The following conditions were used.

GASES

Gases were purified by passing through molecular sieves. (U.C. 13X)
Nitrogen gas was used as the mobile phase flowing at a rate of 40ml/minute.

TEMPERATURE

The following temperature programming gave a good separation of products.

Initial temperature	100°C
Rate of increase	12°C/minute

Final temperature 160°C for 5 minutes

The detector temperature 200°C

The retention distances for the compounds analysed by G.L.C. appears in the Table 3.2.

Table 3.2.

RETENTION DISTANCES OF COMPOUNDS ANALYSED BY G.L.C.

COMPOUND	RETENTION DISTANCE/CM
Acetone	2.2
Chlorobenzene	8.0
2 Chloroethane	11.7
α Methyl styrene	13.1
Acetophenone	29.5
Cumyl alcohol	33.0
Phenol	39.6

The column used was 10-12% polyethyleneglycol adipate supported on 80-100 mesh celite. The column material used, dissolved in chloroform was mixed with the celite. The solvent was removed using a rotary evaporator so that the column material was easily coated on the support. The column was 5 feet long made of glass with an outside diameter 0.6 cm. The column material was packed into the column under vacuum. The column was then conditioned by placing it in the column oven and temperature programmer was used to raise the oven temperature from 20°C to 160°C over a period of four hours. The maximum operating temperature of the column was 180°C.

3.5.1.2. QUALITATIVE AND QUANTITATIVE ANALYSIS OF PRODUCTS FORMED DURING THE AGEING OF PAINT FILM

Two column were prepared and used for this purpose;

(a) A 5 feet long glass column with 2% each of E-301 silicone elastomer and epizone-L grease on 80-100 mesh acid washed silanized celite. Maximum operating temperature was 300°C. Column was conditioned for about 30 hours before being used.

Flow rate	40ml/minute
Initial temperature	150°C
Rate of increase	4°C/minute
Final temperature	210°C
Chart speed	20mm/minute

Since this packing gave a base line drift at higher temperature the second column was packed. This is described as follow;

(b) A five feet column of 3% OV-1 (Dimethyl silicone gum) on 80-100 mesh Diatomite CQ was prepared and used. The following combination gives a good separation of products and the drift in the base line at higher temperature was almost negligible.

Maximum operating temperature	325-375°C
Initial temperature	150°C
Rate of increase	4°C/minute
Final temperature	230°C
The detector temperature	300°C
Gas flow rate	15ml/minute
Chart speed	40 inches/hour

3.5.1.2.1. SAMPLE PREPARATION

Linseed oil was spread in duplicate on glass plate of similar thickness as unpigmented and pigmented films. One set of film was kept in the diffuse day light and artificial light of the laboratory, while the other, when touch-dried after a week was placed in the U.V. cabinet, in this position the films were subjected to rather severe conditions of radiation energy and fairly high temperature. At different time intervals about $0.25cm^2$ of the paint film was removed from the plates and was warmed with an estimated 0.2-0.5ml of 10% methanolic potassium hydroxide(3) solution in a 5ml centrifuge tube. The sample disintegrated even after few minutes. The tube was then corked and allowed to stand over night at room temperature. The contents were then diluted with water, mixed well and centrifuged. The solution of potassium soap-was decanted from pigment into another centrifuge tube and acidified by addition of a few drops of 3M hydrochloric acid. 2ml of ether was added, then tube shaken well and then centrifuged for about 1 minute to aid the separation of the phases. As much as possible of the ether layer was pipetted off and the remainder diluted with fresh ether without shaking and also pipetted off. This procedure was repeated at least three times. The ether extracts was then evaporated on the steam bath at atmospheric pressure. The liberated acids were isolated. No significant effects were observed on the amount of the liberated fatty acids with change of time, temperature of saponification or pH of solution.

3.5.1.2.1.1. METHYLATION OF FATTY ACID

The separation of fatty acids by G.L.C. for several reasons is not satisfactory, but they can be separated provided they are converted to more volatile, non-ionized derivatives; conveniently their methyl ester.

The methylation apparatus consists of three test tubes as described by Schlenk and Gellerman(105). The first contained ether, the second diazomethane generating mixture, and the third the sample which was dissolved in a small volume of ether/methanol (9:1). The test tubes were interconnected by suitable tubing so that a slow stream of nitrogen from a cylinder bubbled through each in turn and carried the diazomethane (which is a yellow gas) over into the sample. According to Schlenk and Gellerman diazomethane is a particularly effective reagent for methylation and reacts almost instantaneously with carboxylic acids to yield their methyl esters and nitrogen, thus

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

As well as being poisonous, diazomethane is also explosive, and in apparatus for its preparation it is often recommended that ground-glass joints be avoided. The diazomethane was generated by adding a few milligrams of N-methyl-N-nitroso-para-toluene-sulphonamide (sufficiently stable for storage) to a mixture of about equal volumes (5ml) of ethyldigol (diethylene glycol monoethyl ether), ether and 60% aqueous potassium hydroxide contained in a second tube. The function of the ether in the first tube is to saturate the nitrogen stream with ether vapour. Methylation was deemed complete when the sample solution turned distinctly yellow from excess diazomethane. This operation takes about five minutes or perhaps a little more with a large sample. The solution of ester was then evaporated on the steam bath. This needs rather more care than when evaporating the solution of free acids since the esters are distinctly more volatile.

$$CH_3C_6H_4.SO_2N(CH_3).NO + KOH$$

$$\longrightarrow CH_2N_2 + CH_3.C_6H_4.SO_3K + H_2O \quad (80\text{-}90\%)$$

3.6. KINETIC EXPERIMENTS

The rate of decompostion of hydroperoxide in the absence and presence of pigment was followed iodometrically. Though various method(96) including spectroscopic methods are available for the determination of hydroperoxide, isopropanol-acetic acid method was chosen due to the simplicity of the procedure. A blank experiment (in the absence of hydroperoxide) was carried out after each run to increase the reliability of the experiment.

1 -Methyl-1-phenylethyl hydroperoxide, (cumene hydroperoxide) was used in this study because

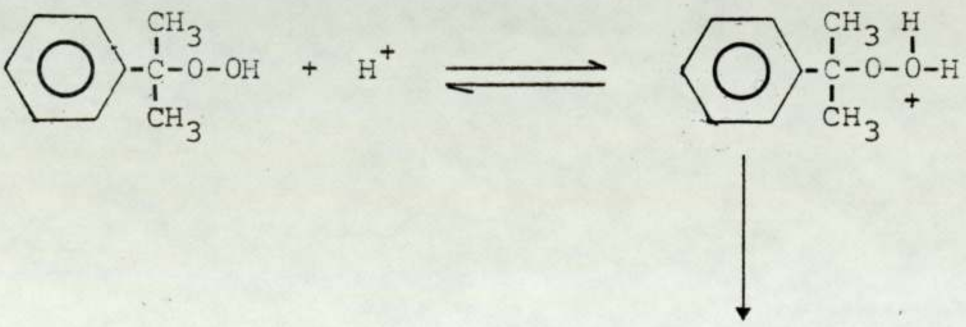
(1) It is readily available and can be easily purified.

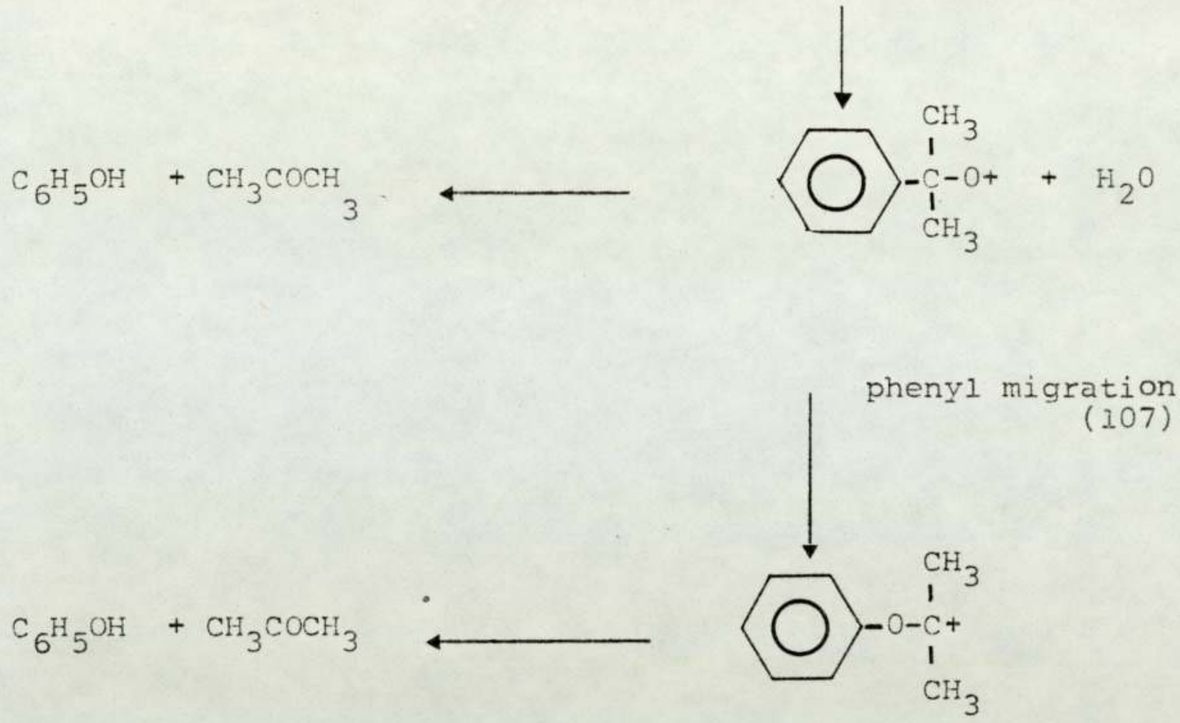
(2) Reaction can be carried out safely at elevated temperature (up to about 100°C) without it being thermally decomposed.

(3) The product formed during decomposition can be easily characterised by G.L.C.

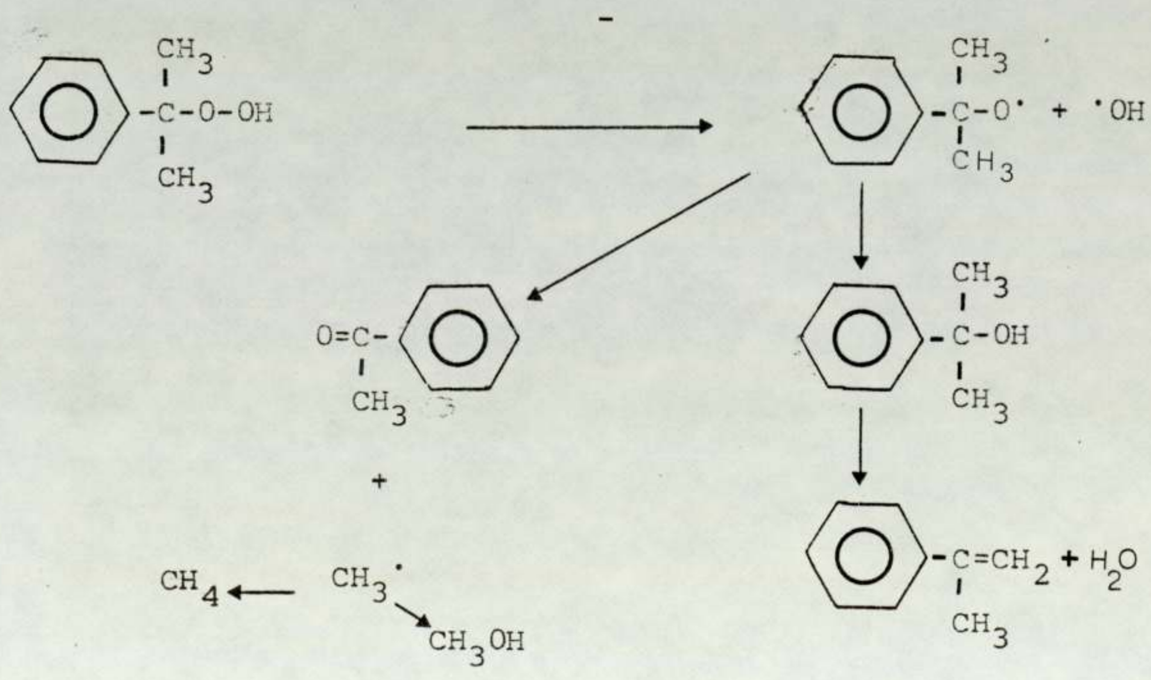
(4) A completely different set of products is obtained under different conditions so indicative of different reaction mechanism involved(95,106).

(a) Lewis acids react rapidly with cumene hydroperoxide forming acetone and phenol by an ionic mechanism(106).





(b) Reaction involving one electron donors (and thermal decomposition) proceeds through cumyloxy radicals and the product include cumyl alcohol, acetophenone, α-methyl styrene, dicumyl peroxide and in certain cases methane and methanol(106).



3.6.1. EXPERIMENTAL PROCEDURE

peroxid Estimation

25ml of a solution containing 10% (V/V) of glacial acetic acid in isopropanol was taken into a conical flask and 1.00ml of reaction mixture was pipetted in. To this a 10 ml of sodium iodide (10%) in isopropanol was added. This was then kept in the dark for 3 hours and the liberated iodine titrated against standard sodium thiosulphate.

Sodium iodide is soluble in isopropanol and hence the determination of hydroperoxide by this method can be done in anhydrous non-aqueous solvent. The solution of sodium iodide in isopropanol was flushed with nitrogen to exclude air so that the aerial oxidation of sodium iodide is prevented.

Due to the presence of excess I^-, liberated iodine is converted to I_3^-. All I_2 is therefore retained in isopropanol solution.

$$2H^+ + 2I^- + ROOH \longrightarrow I_2 + ROH + H_2O$$

$$I_2 + I^- \longrightarrow I_3^-$$

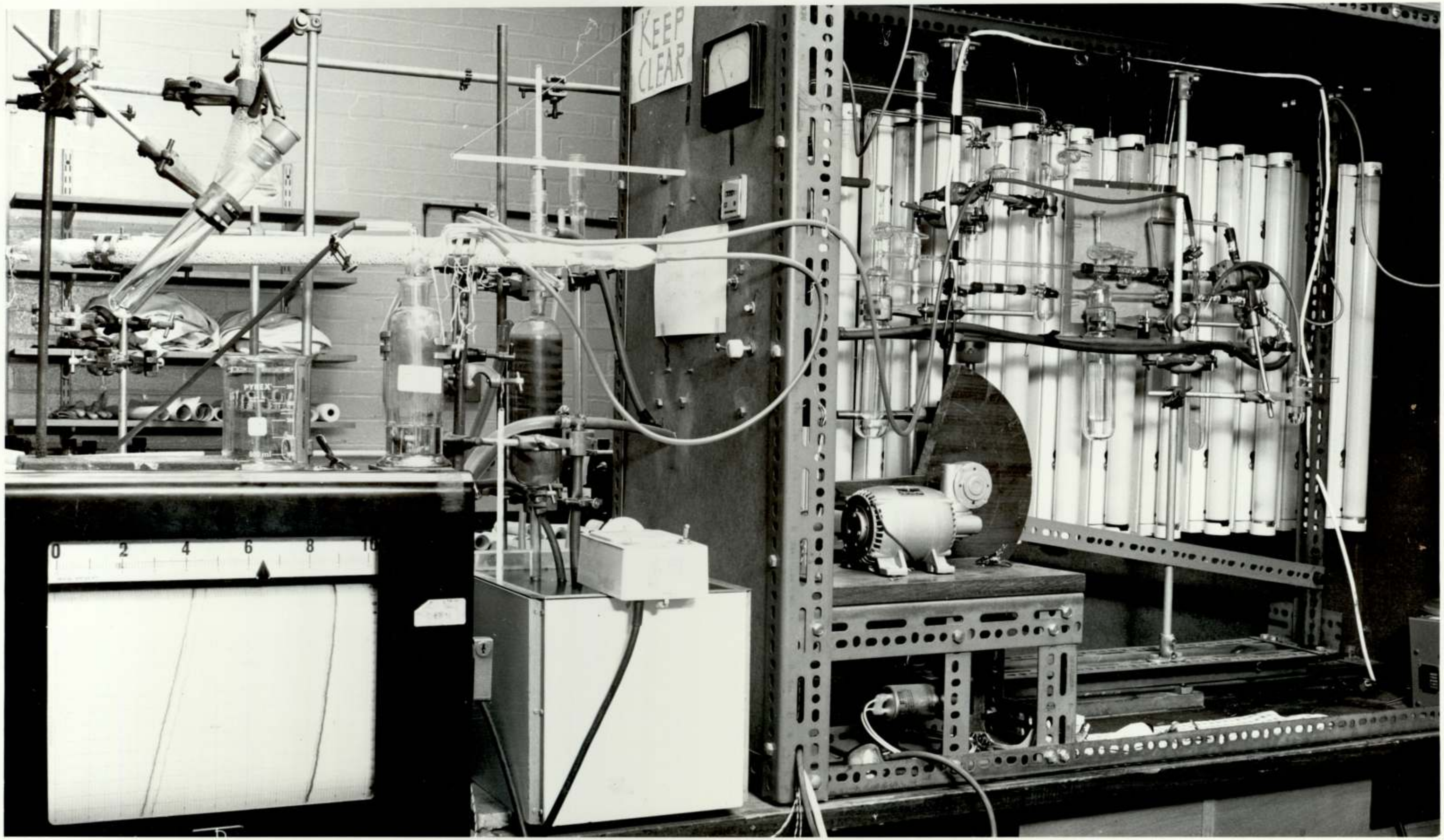
$$I_3^- + 2S_2O_3^{--} \longrightarrow 3I^- + S_4O_6^{--}$$

A three-necked 100ml round bottom flask was used as the reaction vessel. This was fitted with a drying tube and the contents were stirred by a magnetic follower. The hydroperoxide of the required concentration was allowed to reach the intended temperature in an oil (Risella oil) bath. The pigment under investigation was carefully added and the concentration of the hydroperoxide in the reaction vessel was estimated at pre-determined time interval.

3.7. OXYGEN ABSORPTION

The apparatus used for measurement of autoxidation (in the dark) and photo-oxidation of oil with and without pigment is shown in photograph1. This contained two identical sets of tubes, arranged on the reciprocating rack (10cm) in front of alternate Westinghouse/Atlas fluorescent sun lamps, the intensity of which approximate to a normal distribution centred at a maximum intensity of 317nm and 350nm with a cut off at 280nm and 300nm respectively(108). The atomosphere of the cavity (126cm^3) containing the sample was purged with oxygen, via a drying tube, the change in volume of oxygen, absorbed by the oil during autoxidation, and photo-oxidation, and hence pressure was recorded automatically and continuously on a chart recorder via a pressure transducer (maintained at 2.0 volts) Pye Ether Ltd., Stevenage, Hertfordshire, type UP-3TC$\pm$ 34.5KNm^{-2} (which was internally temperature compensated). The liquid in the reaction tube was stirred continuously, to facilitate oxygen diffusion, during autoxidation and photo-oxidation by very small inert magnetic stirrer and motor mounted on the rack directly below the sample tube.

Photograph No.1



Rate of stirring could be controlled by a Variac unit. Calibration of the chart recorder was attained by extracting a known volume of gas from the sample vessel and reading the corresponding value on the recorder. Zero suppression was set at a reading of 'one' on the chart.

3.8. ULTRA VIOLET CABINET

U.V. irradiation of the samples were carried out in the ultra-violet cabinet which comprised a metal cylinder of about 110cm in outer diameter and having a concentric circular rotating sample drum whose circumference was 15cm from the periphery of metal cylinder (Photograph No.2) 32 fluorescent tube lamps were mounted on the inside face of the cylinder. The rotating arrangement of the samples allows an indentical amount of total radiation to fall on every sample. The cylindrical cabinet was open to the atomosphere on both, the lower and upper sides, and the circulation of the air in the cabinet was assured by the driven ventilator situated under the rotating frame.

The samples were attached to a separately made hard brown paper board with aluminium foil backing which was mounted vertically on the circumference of the rotating wheel fixed inside the cabinet. In this position the light beam fell perpendicularly on the surface of the films. The temperature recorded inside the cabinet with the lamps on was 29 $\pm 1^{o}$C.

Photograph No.2.

The radiation source consisted of the cylindrical array of 20W fluorescent tube lamps, positioned on the inner side of the cabinet. 24 lamps type C(Phillips actinic blue 05) and 8 lamps type A1 (Westinghouse sun lamps FS20) were used and these were symmetrically distributed so that the combination was one lamp type A1 for every three lamps of type C. The spectral distribution of both types of lamp used is shown in Fig. 3.3. and 3.4. for the lamp A1 and lamp C respectively.

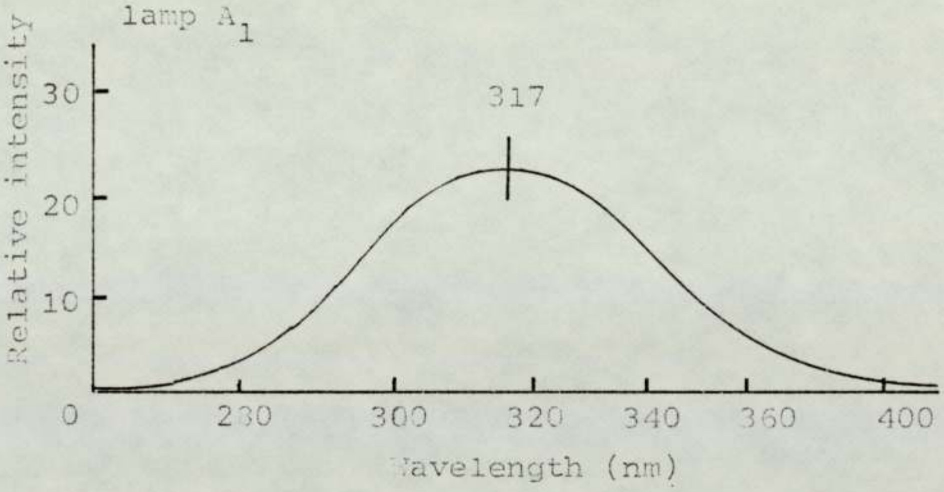


Fig. 3.3.

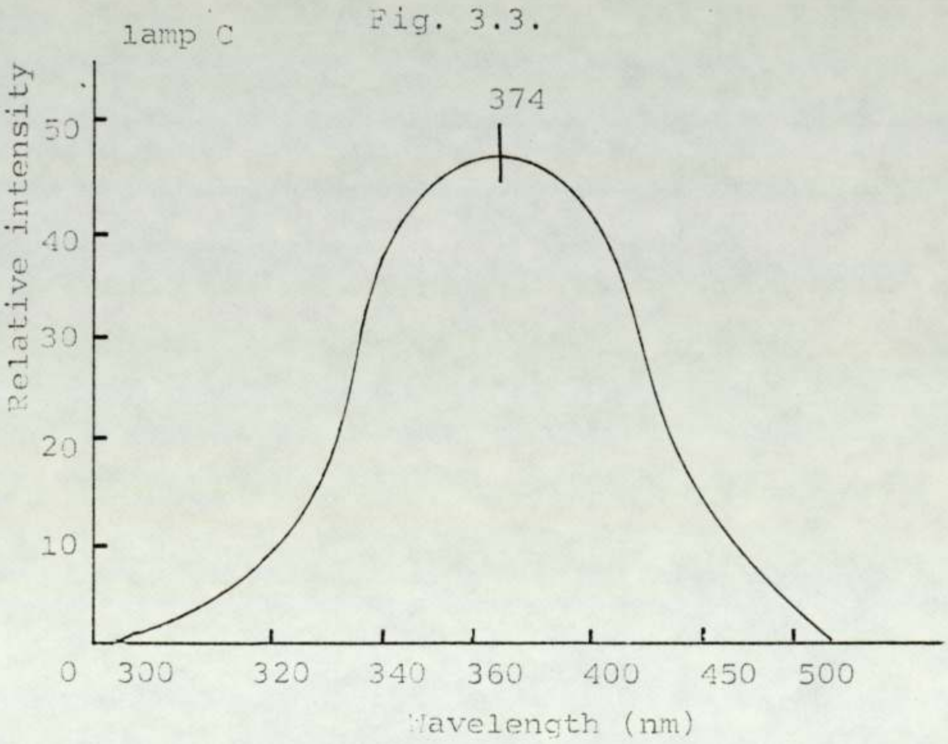


Fig. 3.4.

The maximum in the relative intensity of the lamp A1 is at 317nm and of the lamp C at 374nm. The available wave length with the above combination of lamps was between 280nm-500nm and the radiation intensity I_o at the surface was $I_o = 44.3\ W/m^2$.

To minimise the problem of decline in lamp output the tubes were replaced sequentially every 2000 hours of exposure.

CHAPTER 4

THE CHEMISTRY OF LINSEED OIL OXIDATION

Spectral changes in drying film of linseed oil

4.1. U.V. SPECTRAL CHANGES

The change in ultra violet spectrum of the linseed oil during very early stages of drying was recorded on a Perkin-Elmer 137 spectrophotometer and is shown in Fig 4.1. The oil was smeared on a quartz, microscopic slide, size 1.5 x 3cm and exposed to U.V. light of the U.V cabinet. The first apparent change is the increase in the U.V. light absorption at 235nm. At this wavelength, non irradiated oil had an absorption of 0.5. The formation of this band was slow during the first 15 minutes of U.V. exposure, but increased relatively rapidly in a linear manner, up to 60 minutes of U.V. exposure Fig 4.2. After 1 hour the maximum absorption in this absorption fell to give an almost asymmetric profile. After an induction period of 15 minutes two absorption bands at 285 and 275nm developed. The rate of formation of the band at 275nm was slower than that at 235 nm and reached a maximum after 75 minutes of U.V. exposure. This is followed by a decay of these functional groups to a level almost undetectable after 2 hours. The absorption maxima (λmax) at 235 and 275nm have been attributed to conjugated diene and α, β, γ, δ unsaturated carbonyl(109) respectively. The difference

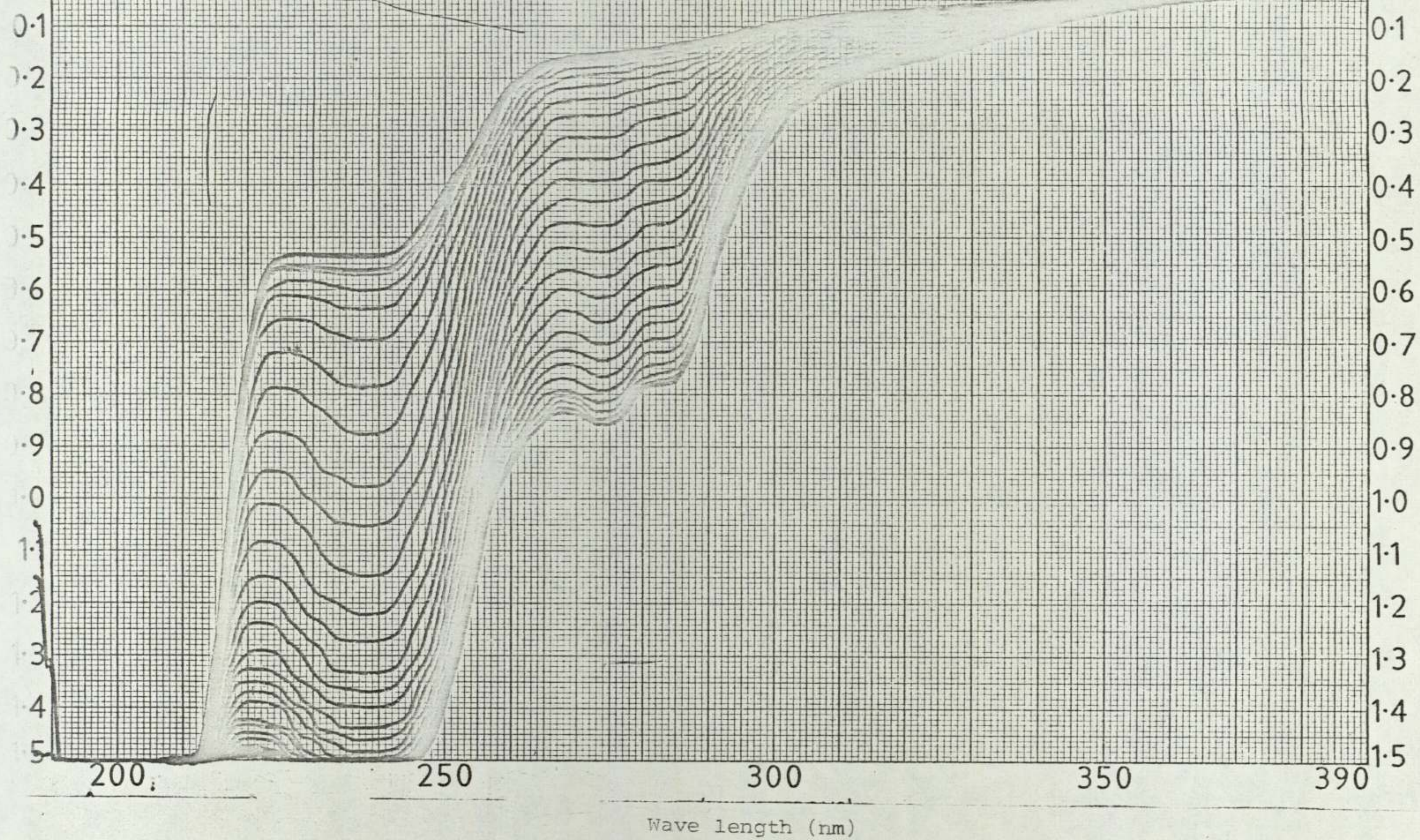


Fig 4.1. The UV spectral changes during the photo oxidation of linseed oil

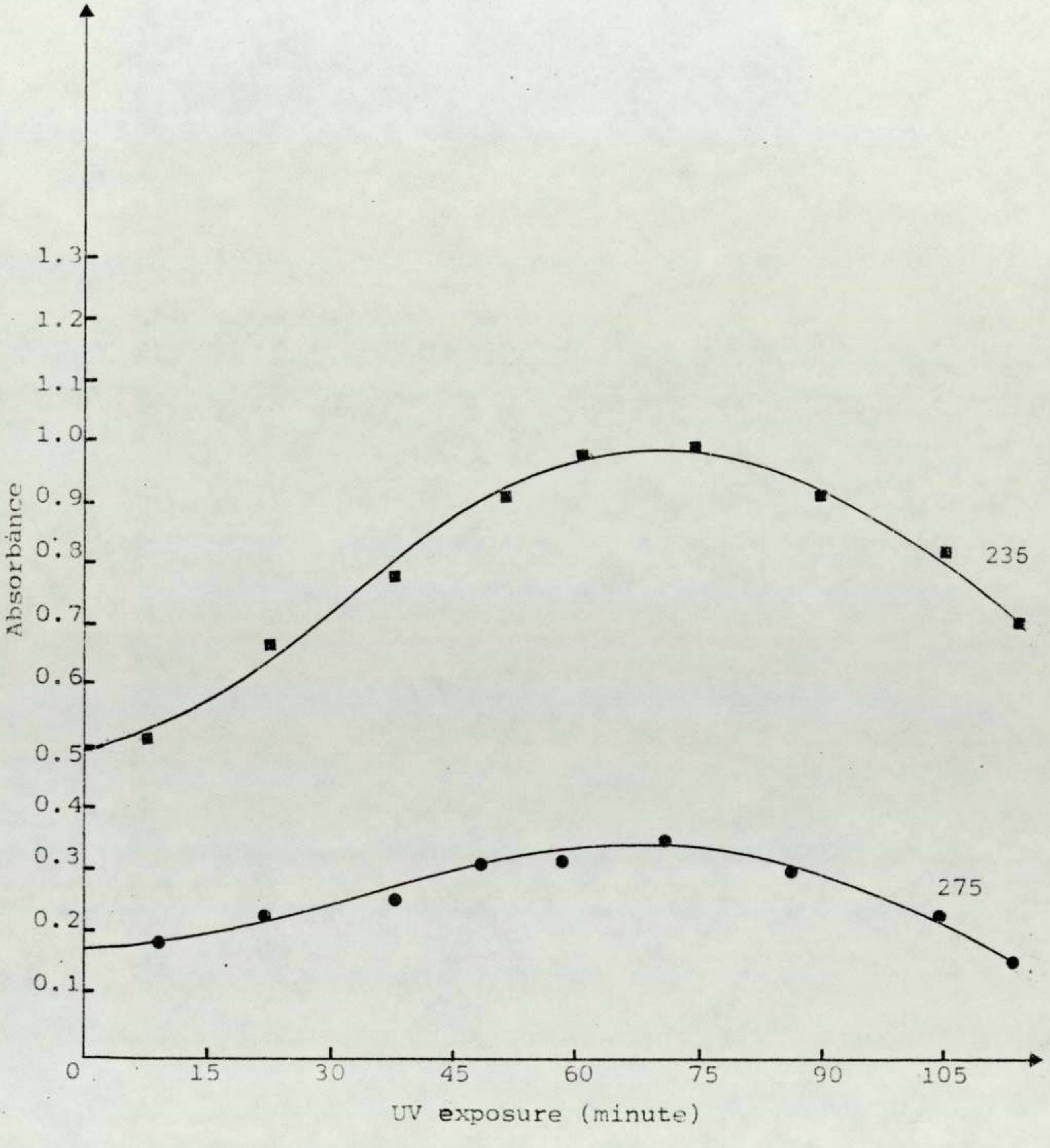


Fig 4.2. Development of conjugation (235nm) and conjugated carbonyl (275nm) during the drying of linseed oil

between the two maxima is probably accounted for by the fact that conjugated hydroperoxide steadily decomposes to give conjugated ketone, aldehyde and ethers which themselves removed during the later stages of the photo oxidation. The U.V. spectral changes of the autoxidized linseed oil revealed similar changes.

4.2. IR SPECTRAL CHANGES

The change in the IR spectrum of the linseed oil smeared on sodium chloride disc as described in Section 3.3.1.1.2. was recorded on a Perkin-Elmer spectrophotometer. The IR examination revealed the changes in a number of significant functional groups during the very early stages of drying process and is shown in Fig 4.3. The sample was exposed to U.V. light in the U.V. cabinet. The cis(116) configuration of initial unsaturated present in the oil is measured by an absorption at 910cm^{-1}. With the onset of the drying process, conjugated unsaturation of cis-trans configuration appears at 952cm^{-1} and this is subsequently transformed to the more stable trans-trans conjugated structure at 988cm^{-1} (111). Further drying leads to the gradual disappearance of the latter peak leading to the formation of isolated trans unsaturation at 967cm^{-1}(112). These changes are also accompanied by rapid disappearance of the band at 3020cm^{-1} and formation of hydroperoxy and hydroxy groups as evidenced by the band around 3450cm^{-1}. The absorption band at 3020cm^{-1} has been assigned to

Fig 4.3. IR spectral changes during photo oxidation of oil film

a methylene group α to a double bond by some workers$^{(113)}$, whereas it has been assigned to C-H of C=C-H by another worker. Privett et al$^{(114)}$ in a study of the structures of hydroperoxides obtained from autoxidised methyl linoleate have assigned 3020cm^{-1} band to the alpha methylenic group. In this report, the 3020cm^{-1} band is also assigned to alpha methylene group from comparison of IR spectra of various olefins. The formation of trans unsaturation was accompanied by a broadening of the peak at 1100cm^{-1} attributed to formation of ether linkages$^{(115)}$. Unsaturated carbonyl formation at 1640cm^{-1} was also observed during the drying process. The apparent width of the band at 1740cm^{-1} (original esteric carbonyl) also increased on film exposure. As the film dries and undergoes deterioration the band peak shift to 1745cm^{-1}. The IR spectral changes of the autoxidized linseed oil revealed similar changes. Fig 4.4. shows the infra-red spectra of the film after having passed through the initial stages of drying. The spectra were taken after periods of irradiation and show a general decrease in absorption bands of the different functional groups. The decrease is particularly evident for the bands at 3450, 2930 and 1740cm^{-1} assigned to the OH, CH_2 and C=O groups respectively. Fig 4.5. shows the plot of % loss of CH_2 at 2930cm^{-1} corresponding to stretching vibration of $-CH_2-$ group, versus U.V. irradiation time in days. A uniform curve is obtained which begins to level off at longer period of exposure.

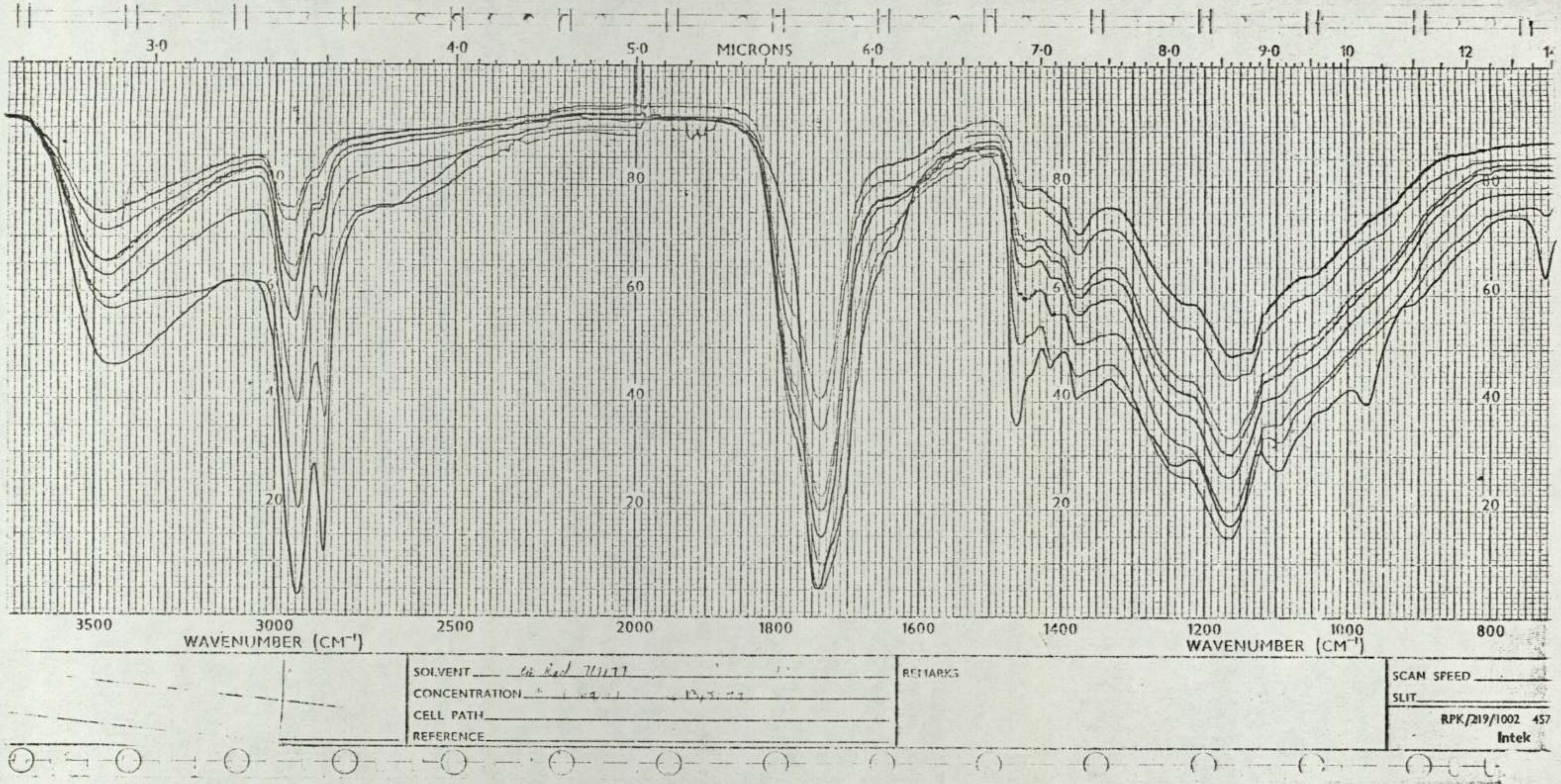


Fig 4.4. IR spectral of the linseed oil spread on the NaCl disc during the UV irradiation

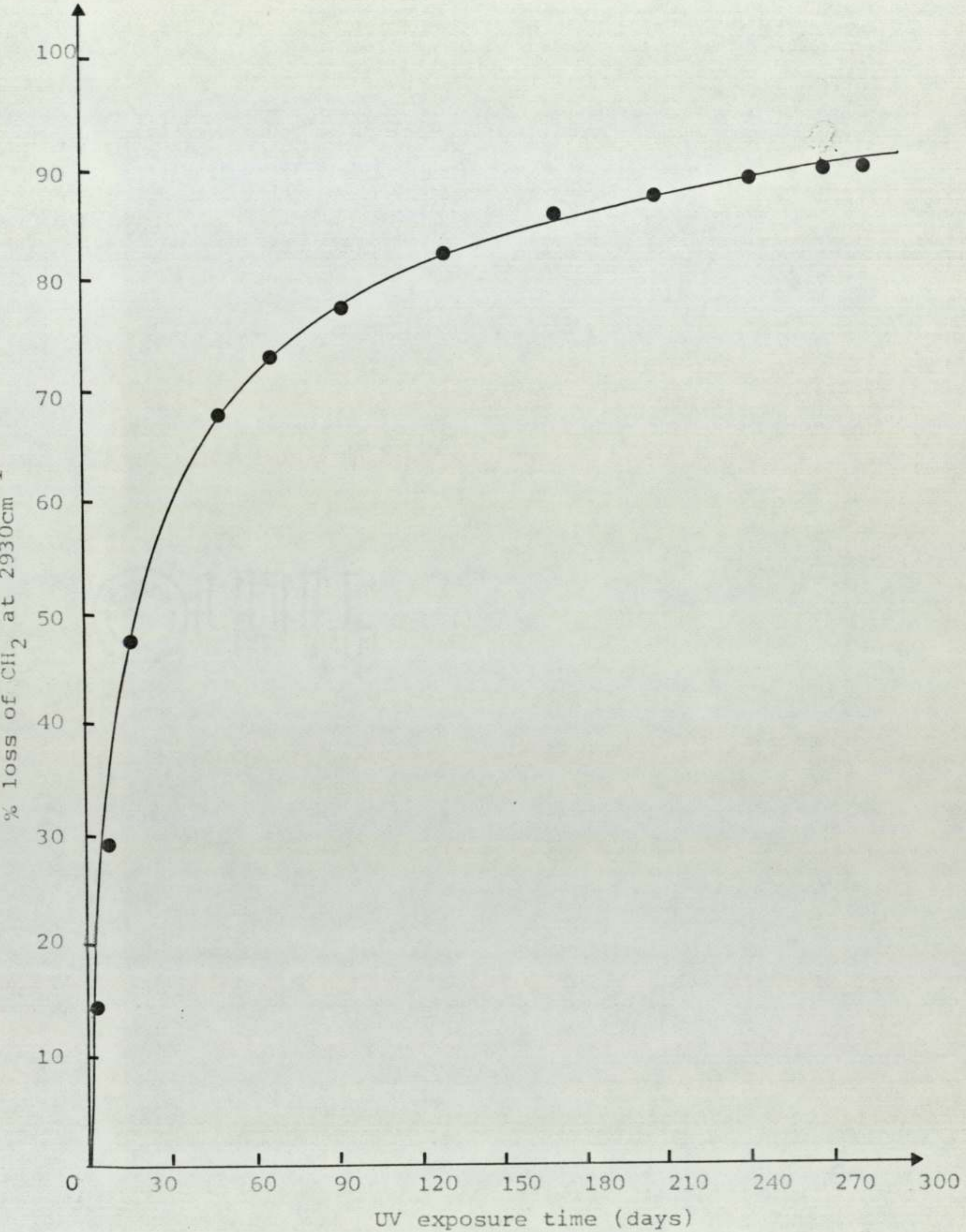


Fig 4.5. Disappearance of CH_2 group at 2930 cm^{-1} of dried linseed oil resulting from exposure to UV light

The decay of the functional group, may indicate the volatilisation of gases such as CO_2, CO and water vapour or low molecular weight acids or aldehydes such as formic acid as a result of successive chain scission(116). Overholt and Elm(117) also reported weight losses of oil films on prolonged exposure to U.V. light. The work of Creceluis(118) and co-workers provide strong additional evidence to confirm that the % decay rate of $-CH_2-$ group is related to the rate of errosion of the dried oil surface. Fig 4.6. shows the plot of log $(\frac{A_o}{A_t})_{2930cm^{-1}}$ i.e. logΔCH_2, versus time where A_o and A_t represent the absorbance of $-CH_2-$ group at $2930cm^{-1}$ at time 0 and time t respectively. It is seen that at long U.V. irradiation time, the decay become linear with respect to time. This allows the rate of errosion to be calculated for pigmented and unpigmented sample under different conditions such as wavelength of light and etc.

4.3. CHROMATOGRAPHIC (G.L.C.) STUDIES OF HYDROLYSED FILM

The chromatographic procedure has been described in 3.5.1.2.1. Fig 4.7. shows a typical chromatograph of the product formed during the later stages of photo oxidation of dried linseed oil in the absence of pigment. Table 4.1. indicates the relative retention distances of methyl esters of various mono and dicarboxylic acid present initially or formed during the ageing of linseed oil. The major product of photo-oxidation is shown to be azelaic acid (C_9 dicarboxylic acid), while smaller quantities of C_7, C_8 and C_{10}

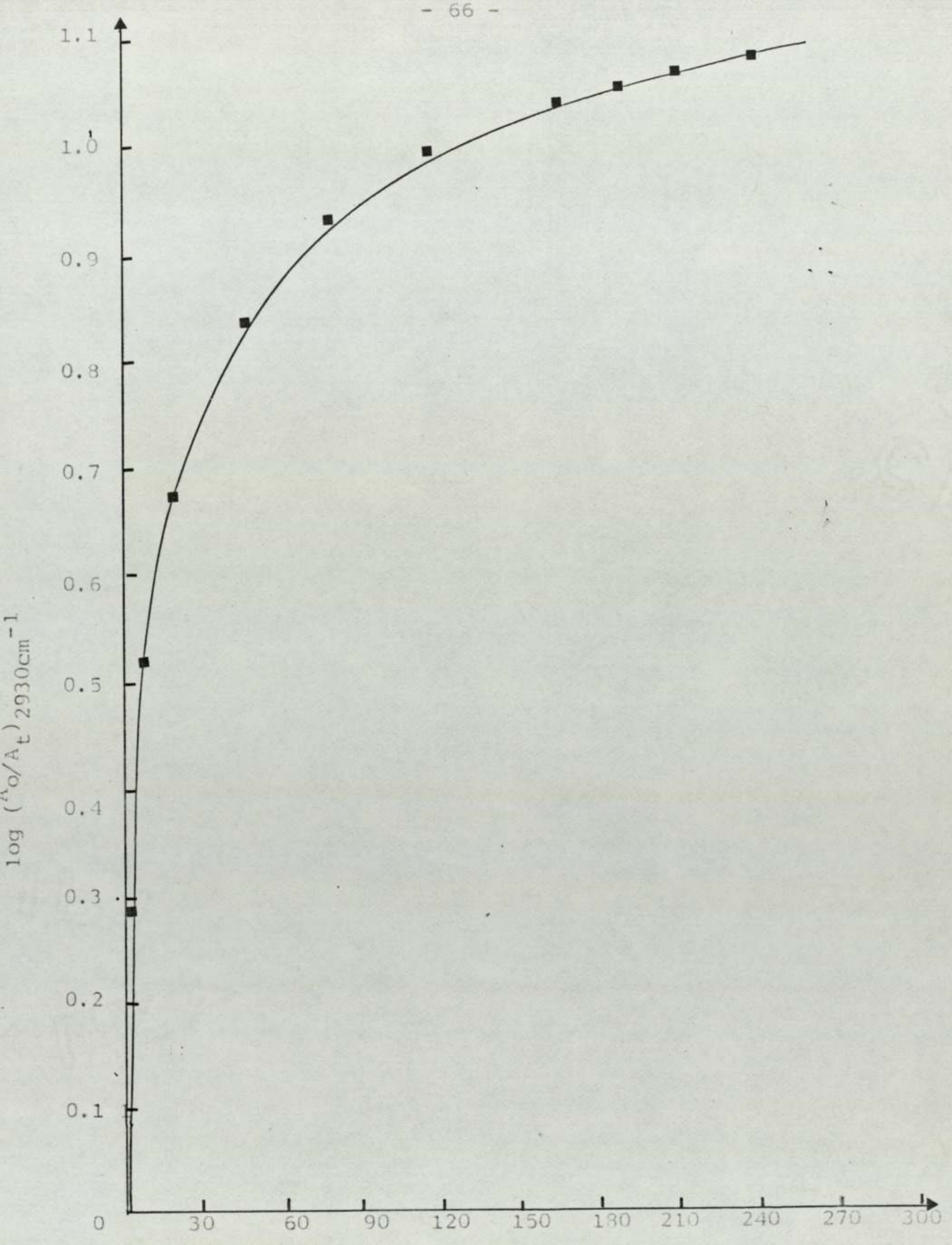


Fig. 4.6. change in logΔCH_2 group at 2930cm^{-1} of dried linseed oil resulting from exposure to UV light.

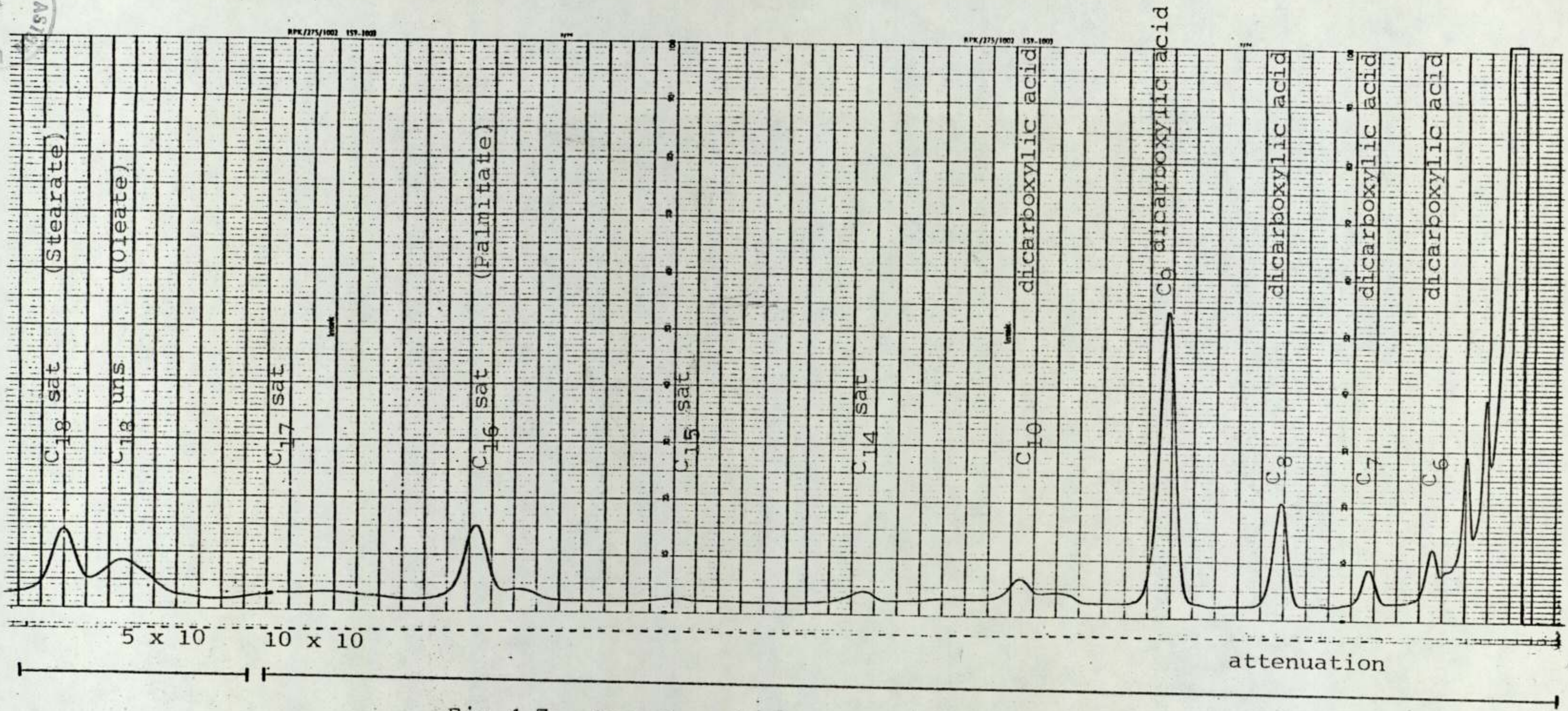


Fig 4.7. Gas chromotogram of methyl esters formed during photo degradation of dried linseed oil

Table 4.1.

COMPOUND	RETENTION DISTANCE/CM
C_7 dicarboxylic acid(Pimelic acid)	10.1
C_8 dicarboxylic acid(Subesic acid)	15.2
C_9 dicarboxylic acid(Azelaic acid)	21.7
C_{10} dicarboxylic acid(Sebacic acid)	29.6
C_{14} saturated acid (Myristic acid)	37.9
C_{15} saturated acid	48.9
C_{16} saturated acid(Palmitic acid)	58.9
C_{17} saturated acid	69.5
C_{18} mono unsaturated acid (Oleic acid)	77.5
C_{18} saturated (Stearic acid)	80.0

Retention distance of compounds analysed by G.L.C.

dicarboxylic acids were also detectable. Similar scission products were detected in a non U.V. aged linseed oil.

4.4. DISCUSSION OF MECHANISM OF DRYING AND PHOTO-OXIDATION OF LINSEED OIL

The chemical changes that occur during the initial stages of the photo-oxidation of linseed oil can be deduced from the results shown in Fig 4.1., 4.2. and 4.3. The most significant changes that occur can be summarised as follows:

(1) The formation of conjugated unsaturation by rearrangement of the initially present isolated cis-cis unsaturation, as evidenced by the formation of a U.V. absorption band at 235nm Fig 4.1. and IR peak at 952cm^{-1} (cis-trans conjugation) and 998cm^{-1} (trans-trans conjugation) Fig 4.3.

(2) The disappearence of activated methylenic group adjacent to the double bond as shown by the decay of the 3020cm^{-1} absorption Fig 4.3. and the concommitant formation of hydroperoxides and hydroxyl functional groups at 3450cm^{-1}.

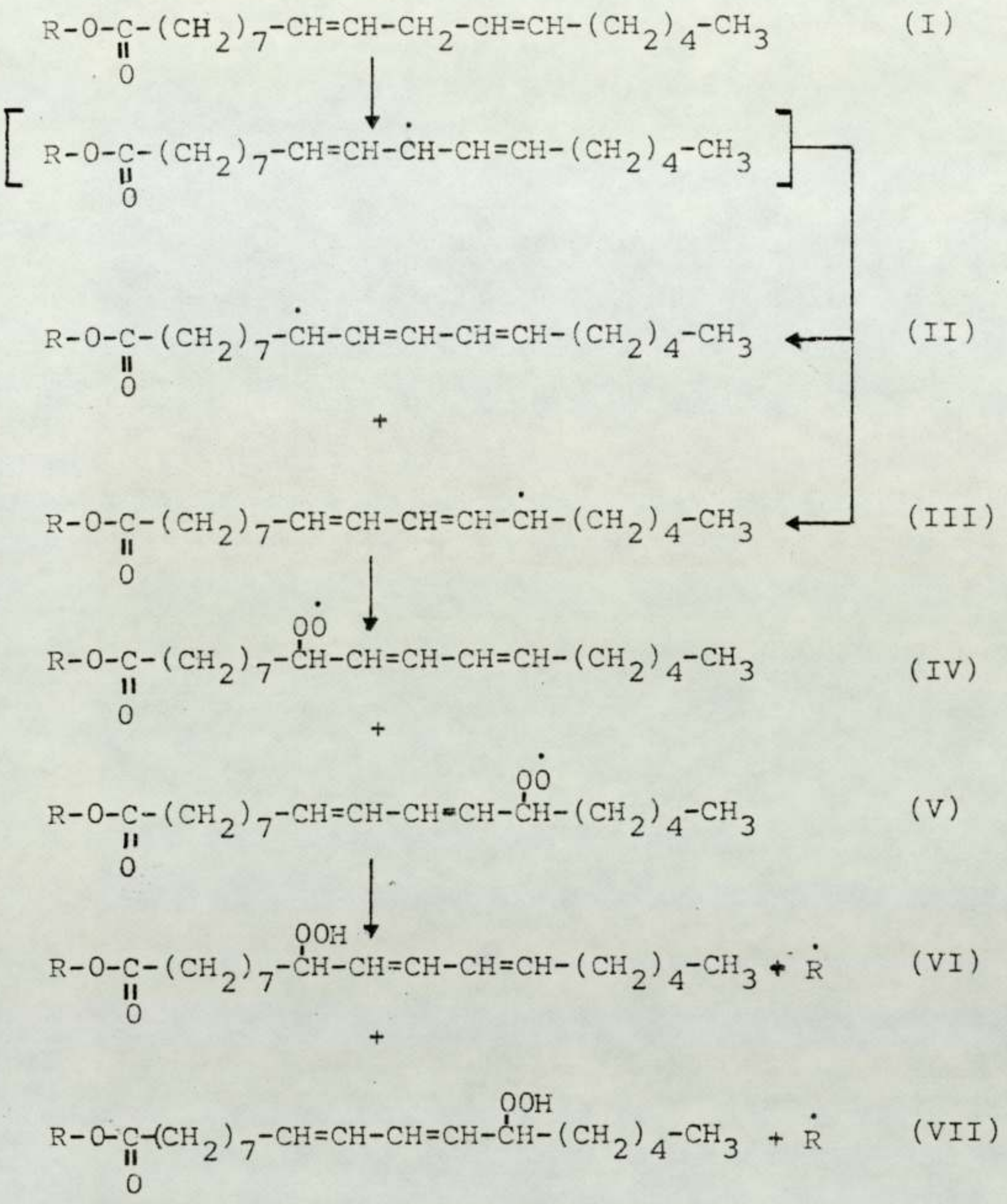
(3) The simultaneous formation of an ether group at 1100cm^{-1} provides additional evidence for the cross linking reaction. The analysis of linseed oil has shown that the initial unsaturation present is of the cis configuration$^{(119)}$. The band at 910cm^{-1} Fig 4.3. confirms this observation.

The reaction can be initiated by the attack of any free radical. However the radicals most likely to initiate the reaction are those formed by decomposition of a peroxide. The latter may be formed in trace quantities as a result of mild refining conditions(120). Subsequent exposure to U.V. will cleave the oxygen-oxygen bond with a quantum efficiency of approaching unity(121) with production of active alkoxy and hydroxyl radicals capable of hydrogen abstraction. In purified methyl linoleate, an oxygen-linoleate complex has been suggested to be an initiator for the reaction(122). Hydrogen abstraction will occur at the doubly activated methylenic position of the linoleate part of the glyceride (I) owing to the low dissociation energy of the carbon-hydrogen bond(123) producing two mesomeric conjugated allylic radicals (II) and (III). These are stabilized by resonance with an equal liklihood of further reaction taking place from either radical centre. Atomospheric oxygen reacts with the two mesomeric conjugated allylic radicals leading to the formation of the corresponding alkylperoxy radicals (IV) and (V), these are capable of several immediate reactions of which only the most important will be considered here.

A:

Hydrogen abstraction of a labile hydrogen from another chain will produce the corresponding conjugated hydroperoxides (VI) and (VII) as evidenced by the U.V. spectral measurement at 235nm Fig.4.1. and growth of the band at 3540cm^{-1} Fig 4.3

Equal amounts of C_9 and C_{13} conjugated isomeric hydroperoxides have been reported(124,125).



$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_4{-}CH_3} \qquad (I)$$

$$\downarrow$$

$$\left[\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}\dot{C}H{-}CH{=}CH{-}(CH_2)_4{-}CH_3}\right]$$

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}\dot{C}H{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3} \leftarrow \qquad (II)$$

$$+$$

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}CH{=}CH{-}\dot{C}H{-}(CH_2)_4{-}CH_3} \leftarrow \qquad (III)$$

$$\downarrow$$

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}\overset{\dot{O}O}{\overset{|}{C}}H{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3} \qquad (IV)$$

$$+$$

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}CH{=}CH{-}\overset{\dot{O}O}{\overset{|}{C}}H{-}(CH_2)_4{-}CH_3} \qquad (V)$$

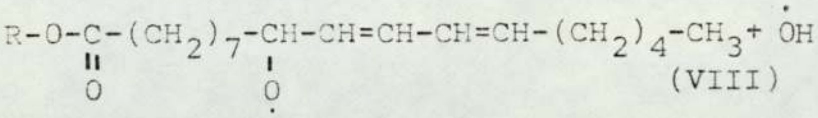
$$\downarrow$$

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}\overset{OOH}{\overset{|}{C}}H{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3 + \dot{R}} \qquad (VI)$$

$$+$$

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}CH{=}CH{-}\overset{OOH}{\overset{|}{C}}H{-}(CH_2)_4{-}CH_3 + \dot{R}} \qquad (VII)$$

The autocatalytic nature of the oxidation process is confirmed by the initial relatively slow formation of conjugated unsaturation at 235nm followed by a significantly more rapid accumulation of this species Fig 4.2. The difference between the time to reach the two maxima at 235and 275nm corresponding to conjugated hydroperoxide and conjugated (126) carbonyl is probably accounted for by the fact that conjugated diene carbonyl (XVI) is formed through a possible cage intermediate or it may undergo homolysis producing an alkoxy (VIII) and a hydroxy radical. Conjugated carbonyl

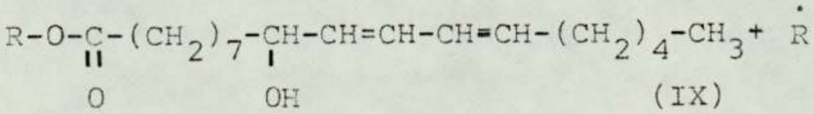


$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}\underset{\underset{\underset{\cdot}{O}}{|}}{C}H\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3 + \dot{O}H$$

(VIII)

itself is removed during the later stages of the autocatalytic reaction.

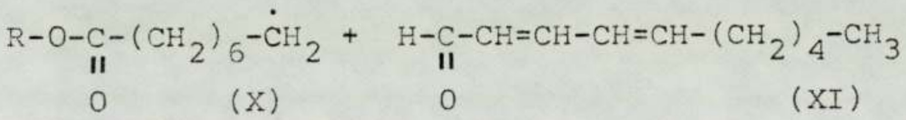
The alkoxy radical (VIII) may in turn either abstract a hydrogen forming the corresponding alcohol (IX) or



$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}\underset{\underset{OH}{|}}{C}H\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3 + \dot{R}$$

(IX)

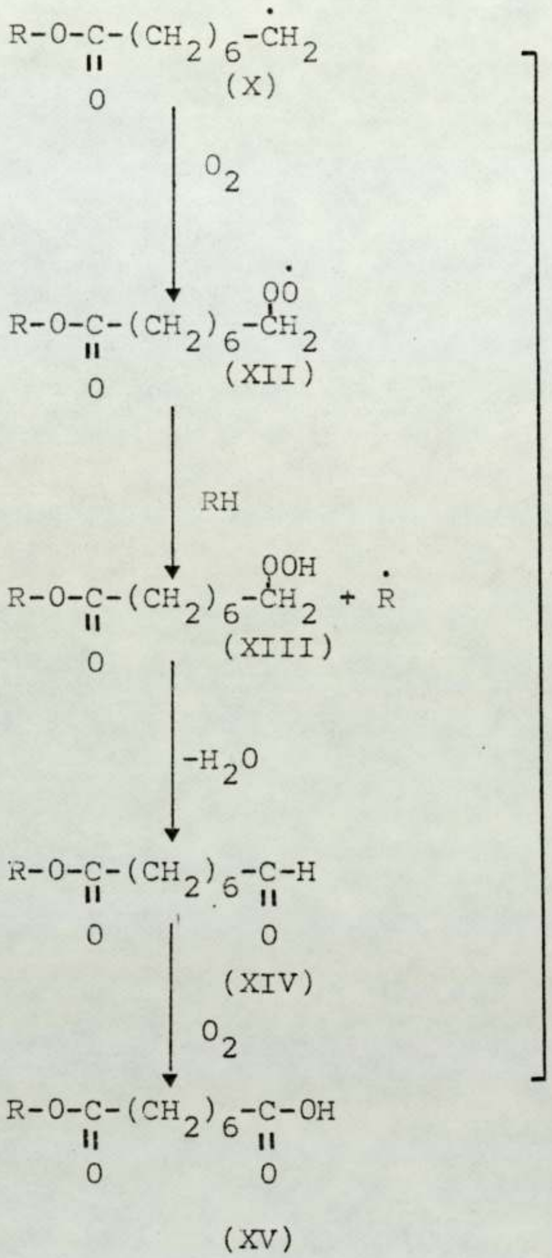
undergo β-scission forming an alkyl radical (X) and conjugated diene aldehyde(XI)$^{(127)}$



$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_6\text{-}\dot{C}H_2 + H\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$$

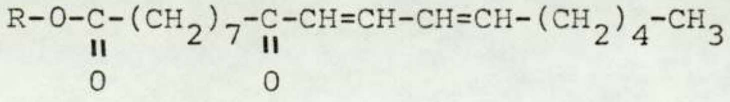
(X) (XI)

The alkyl radical (X) according to the scheme (a) leads to the formation of product (XV). Hydrolysis and methylation of product (XV) leads to the formation of the methyl ester of C_8 dicarboxylic acid detected in the dried oil evidenced in Fig 4.7.



Scheme a

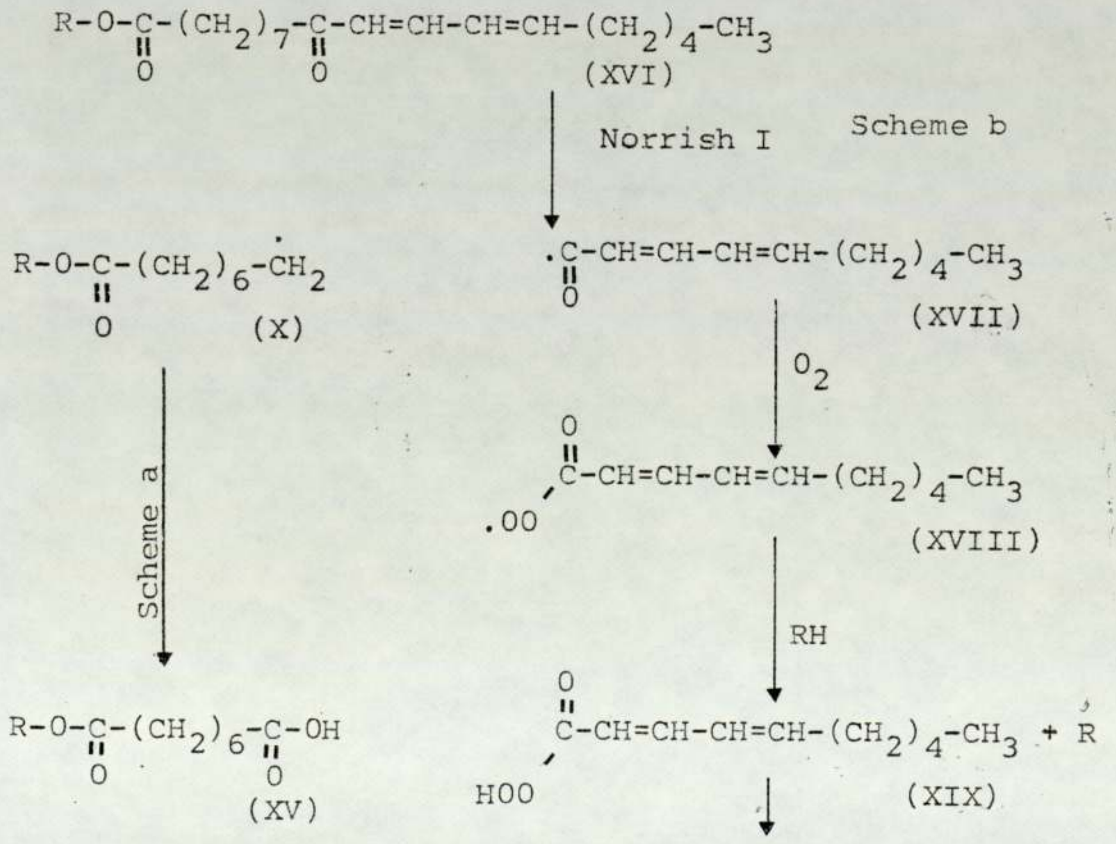
Disproportionation of alkoxy radical (VIII) may also take place with another alkoxy radical to produce equimolecular mixture of alcohol and ketone (XVI)

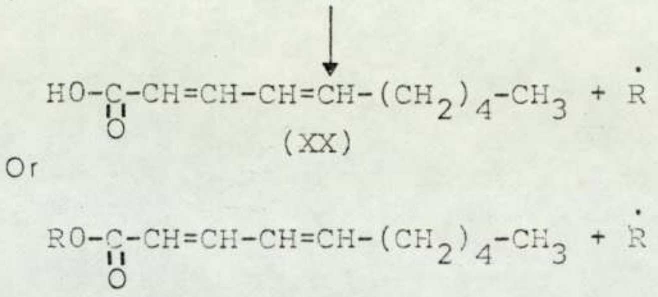


$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$$

(XVI)

Complementary to β scission, other chain cleavage reactions may involve Norrish I or II photolysis of carbonyl. Norrish I cleavage of conjugated carbonyl (XVI) may readily occur producing both alkyl radical (X) and an acyl radical (XVII). The alkyl radical (X) according to scheme a leads to the formation of (XV). However the acyl radical may also undergo various reactions with radicals to produce different functional groups. An illustrative reaction involves the addition of triplet oxygen followed by hydrogen abstraction from another chain leading to a conjugated peroxide (XIX). Homolysis of the oxygen - oxygen bond results in an alkoxy radical capable of abstracting a hydrogen to produce conjugated carboxylic acid (XX) or cross linking with an alkyl radical forming conjugated ester XXI.





$$\mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3 + \dot{R}}$$

(XX)

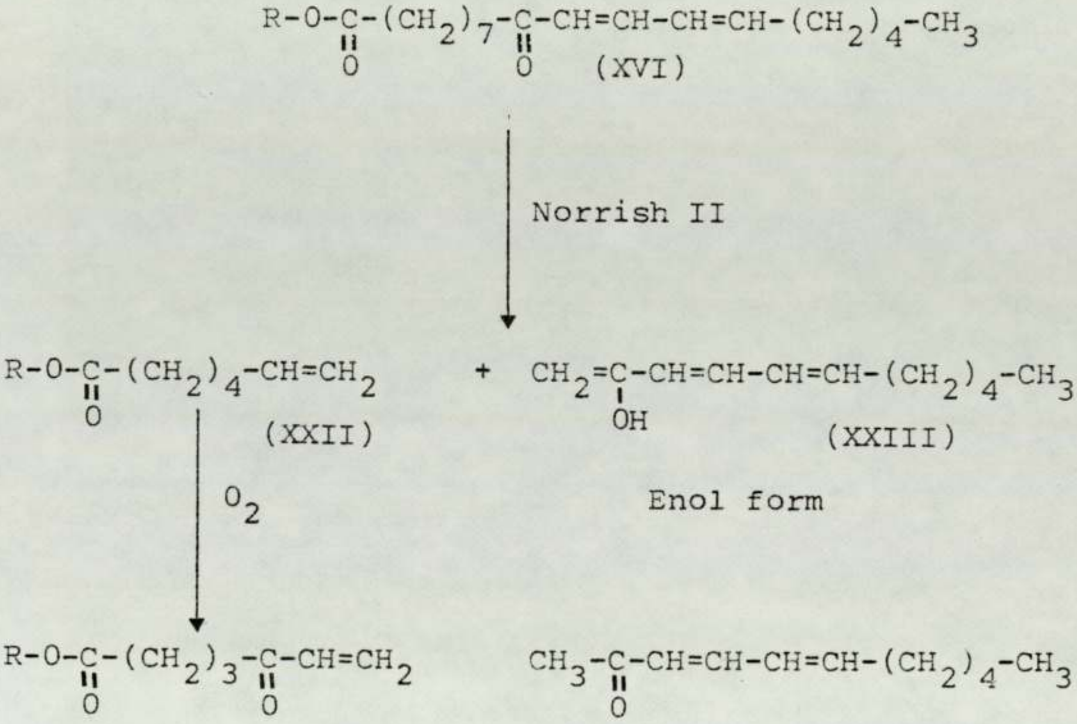
Or

$$\mathrm{RO{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3 + \dot{R}}$$

(XXI)

Scheme b

Norrish II scission of (XVI) may also occur leading to the formation of end chain conjugated carbonyl (XXIV) and compound (XXIII) and (XXV).



$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_7{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3}$$

(XVI)

Norrish II

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_4{-}CH{=}CH_2 \quad + \quad CH_2{=}\underset{\underset{OH}{|}}{C}{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3}$$

(XXII) (XXIII)

O_2

Enol form

$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_3{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2 \qquad CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_4{-}CH_3}$$

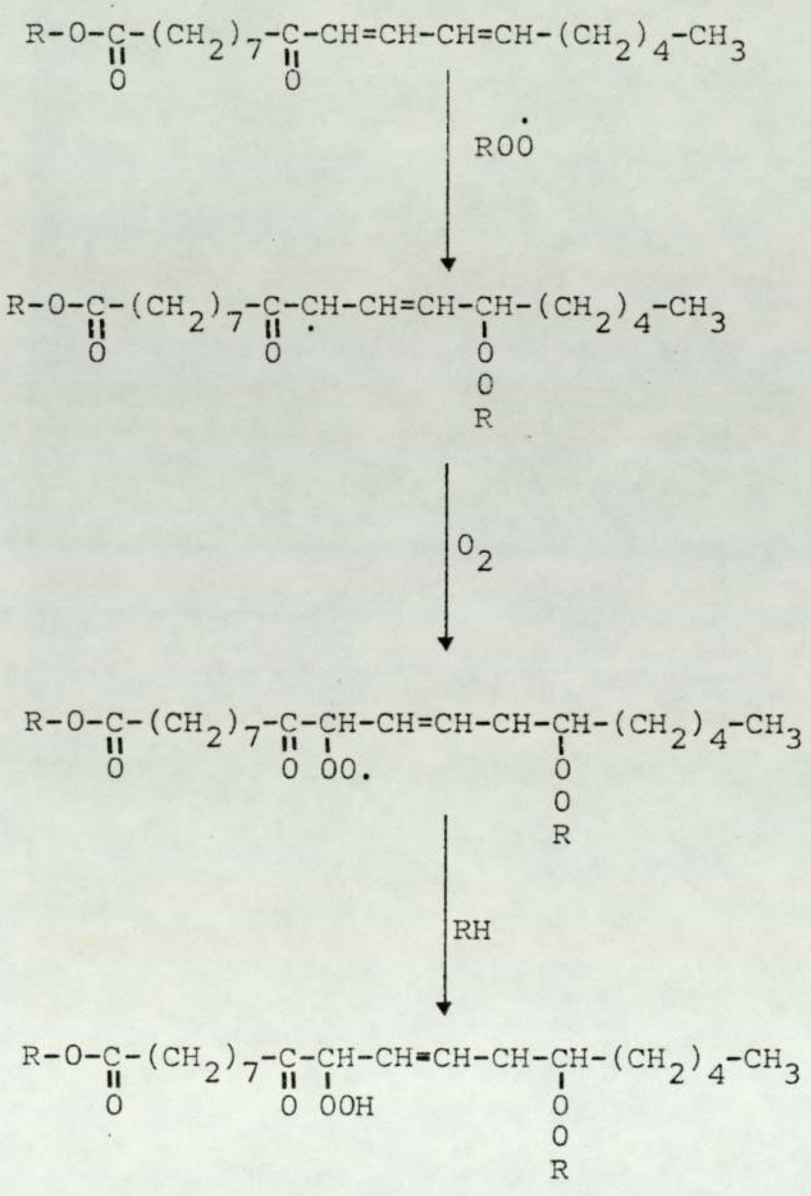
(XXIV) (XXV)

Keto form

B:

The alkylperoxy radical can remove conjugated carbonyl (XVI) by 1,4 addition to the conjugated system. This leads to the formation of cross linked structures via a labile peroxidic linkage 150KJmol$^{-1(128-129)}$. If the attack takes place at carbon 13, then the resulting stable radical (XXVI) through the sequence of reaction shown in scheme c leads to the compound (XXXI).

Scheme c



$$R\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$$

(XVI)

$$R\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}\underset{\overset{\|}{O}}{C}\text{-}\dot{C}H\text{-}CH{=}CH\text{-}\underset{\overset{|}{OOR}}{CH}\text{-}(CH_2)_4\text{-}CH_3$$

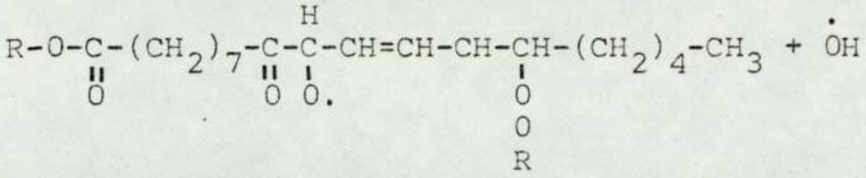
(XXVI)

$$R\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{\overset{|}{OO\cdot}}{CH}\text{-}CH{=}CH\text{-}CH\text{-}\underset{\overset{|}{OOR}}{CH}\text{-}(CH_2)_4\text{-}CH_3$$

(XXVII)

$$R\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{\overset{|}{OOH}}{CH}\text{-}CH{=}CH\text{-}CH\text{-}\underset{\overset{|}{OOR}}{CH}\text{-}(CH_2)_4\text{-}CH_3$$

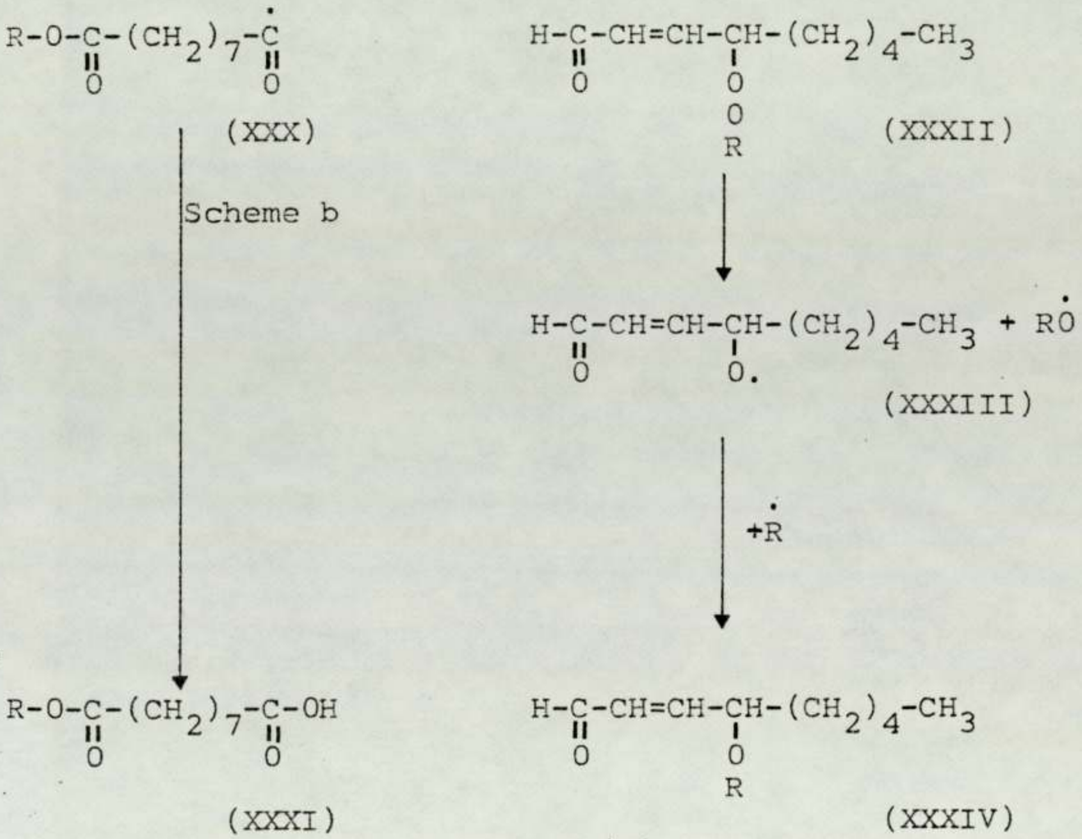
(XXVIII)



$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}\underset{\underset{O}{\|}}{C}\text{-}\overset{H}{\underset{\underset{O\cdot}{|}}{C}}\text{-}CH{=}CH\text{-}CH\text{-}\underset{\underset{\underset{\underset{R}{O}}{O}}{|}}{CH}\text{-}(CH_2)_4\text{-}CH_3 + \dot{O}H$$

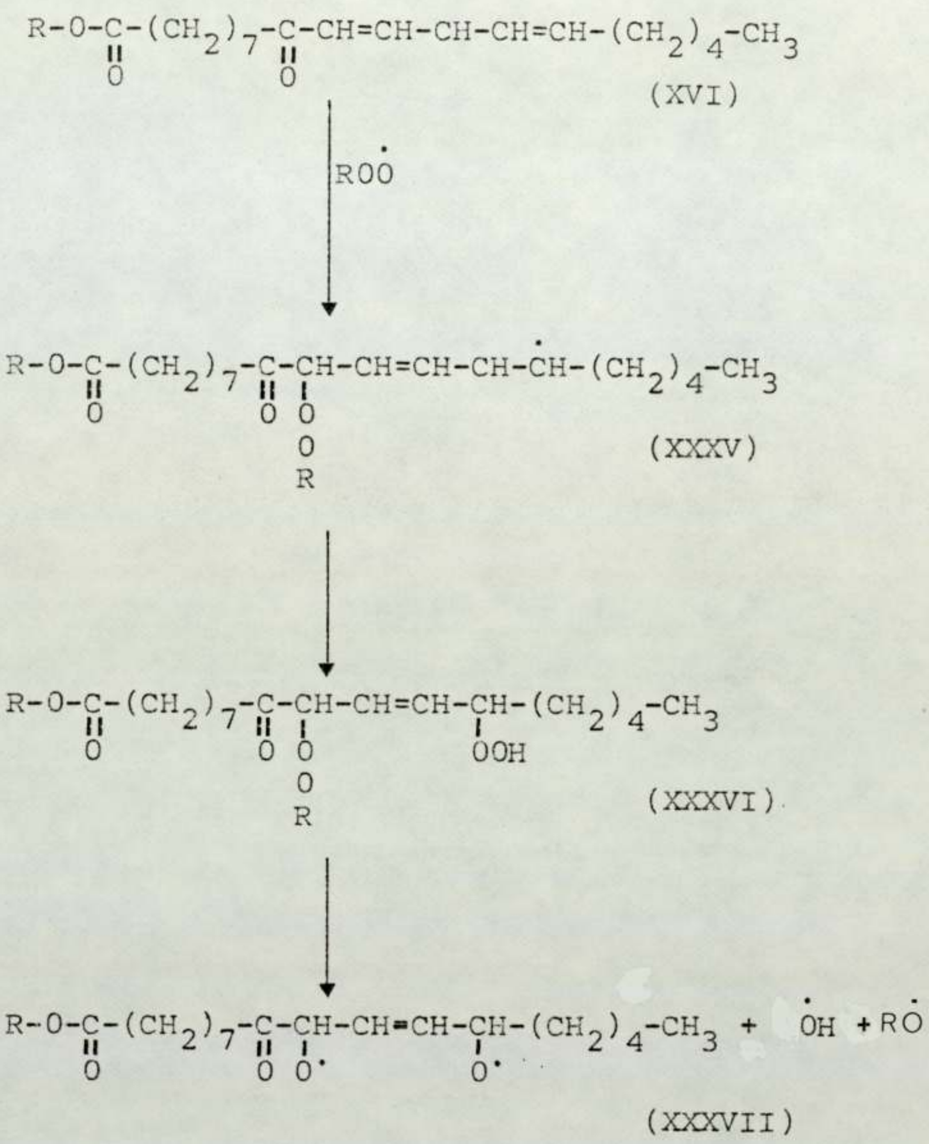
(XXIX)

Homolysis of the peroxidic linkage results in the formation of a secondary alkoxy radical which can attack a conjugated double bond to form a secondary ether linkage (XXXIV) which is more stable towards U.V. ($360KJmol^{-1}$) (128-129).



If attack takes place at carbon 10 of (XVI), then the following reactions occur via scheme d.

Scheme d



$$R-O-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{O}{\|}}{C}-CH=CH-CH-CH=CH-(CH_2)_4-CH_3 \quad (XVI)$$

$$\Big\downarrow\, RO\dot{O}$$

$$R-O-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{O}{\|}}{C}-\underset{\underset{\underset{R}{O}}{\underset{O}{|}}}{CH}-CH=CH-CH-\dot{C}H-(CH_2)_4-CH_3 \quad (XXXV)$$

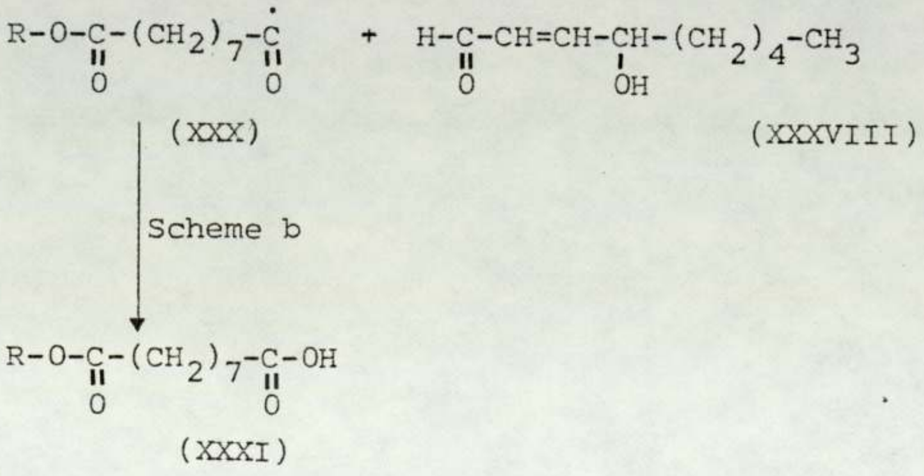
$$\Big\downarrow$$

$$R-O-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{O}{\|}}{C}-\underset{\underset{\underset{R}{O}}{\underset{O}{|}}}{CH}-CH=CH-\underset{\underset{OOH}{|}}{CH}-(CH_2)_4-CH_3 \quad (XXXVI)$$

$$\Big\downarrow$$

$$R-O-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{O}{\|}}{C}-\underset{\underset{O^{\cdot}}{|}}{CH}-CH=CH-\underset{\underset{O^{\cdot}}{|}}{CH}-(CH_2)_4-CH_3 + \dot{O}H + R\dot{O} \quad (XXXVII)$$

Compound (XXXVII) may break down to give (XXXI)



$$\underset{(XXX)}{R-O-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{O}{\|}}{\dot{C}}} + \underset{(XXXVIII)}{H-\underset{\underset{O}{\|}}{C}-CH=CH-\underset{\underset{OH}{|}}{CH}-(CH_2)_4-CH_3}$$

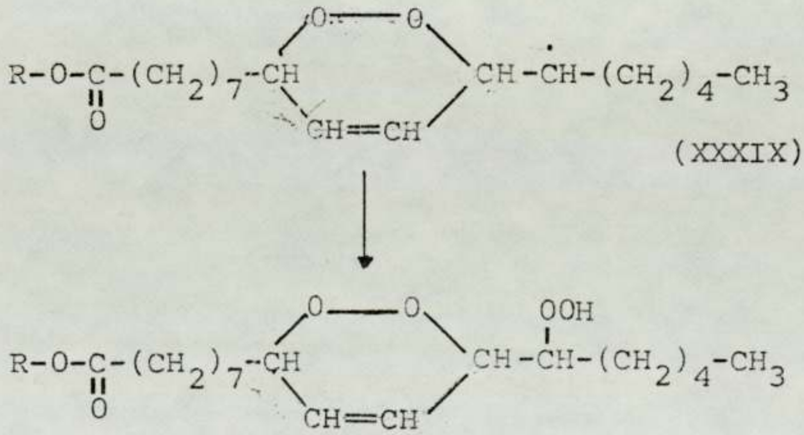
$$\Big\downarrow\, \text{Scheme b}$$

$$\underset{(XXXI)}{R-O-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{O}{\|}}{C}-OH}$$

An alkoxy radical in a similar manner to the alkylperoxy radical can remove conjugated carbonyl (XVI) via Scheme c and d to form eventually compound (XXXI) and an ether cross linked structure. Hydrolysis and ultimate methylation of compound (XXXI) leads to the formation of methyl esters of azelaic acid detected by G.L.C.

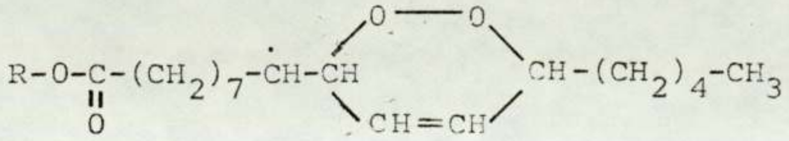
C:

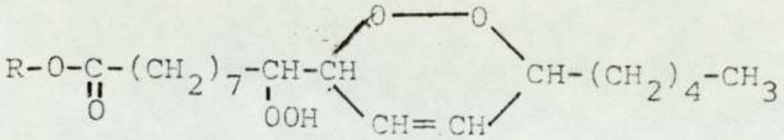
The alkylperoxy radicals (IV) and (V) can internally cyclize to form the corresponding unconjugated monomeric diperoxide(130-131). The alkylperoxy radical (IV) through the cyclization would give the corresponding structures (XXXIX) and (XL).


(XXXIX)

(XL)

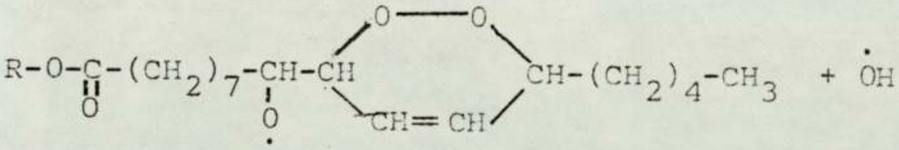
whereas the alkylperoxy radical (V) would lead to the formation of compound (XLII).


(XLI)



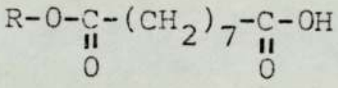
(XLII)

Homolysis of compound (XLII) leads to the formation of alkoxy radical (XLIII) and the hydroxyl radical



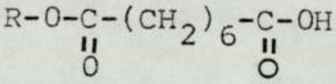
(XLIII)

Break down of the above alkoxy radical can then lead to the formation of compounds (XXX1) and (XV).



$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH$$

(XXXI)



$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_6\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH$$

(XV)

which were both detected by G.L.C.

In addition to the above reactions leading to ether and peroxide linkages between molecules, reaction leading to carbon-carbon bond may also occur, particularly in cases of low oxygen availability. Firstly two alkyl radicals may couple, though this is probably a rather rare event.

Secondly an alkyl radical may attack a double bond, the newly formed radical then carrying on in the same way.

To sum up the overall results of the above processes, it can be said that the initial drying of an oil film will be due largely to the formation of polyperoxide; that, as these peroxy linkages themselves undergo scission to alkoxy radicals, formation of ether linkages will built up. Carbon-carbon bond formation will only occur to significant extent in the lower levels of rather thick films or if other special factors exist to keep the concentration of oxygen in the film low. Simultaneously with the above polymerization reactions there occurs degradation reactions resulting in breaking of the cross links and scission of the fatty acid chain. In the last case, of course saturated acids, remains of the oleic acid, and one of the two fragments of unsaturated fatty acids will still be connected to the glyceride molecule while the other become a short-chain free fatty acid, which if it is volatile enough, may be lost by evaporation, or it may combine with basic pigment which happens to be present.

The useful information which can be extracted from such an analysis is that the plot of the ratio of the concentration of the fragment (calculated by measuring the area under the peak) which is connected to the glyceride molecule to originally present saturated acid in linseed oil versus time of ageing would indicate the rate of degradation of paint film (the fragments and saturated acid can easily be isolated by saponification of the dried paint film with alkali at ester linkages). The ratio of methyl esters of azeläic acid to palmitic acid is taken for the above purpose,

$$\frac{\Delta AC_9 \text{ dicarboxylic acid}}{A \text{ palmitic acid}}$$

A = Peak area

and Fig 4.8. shows this plot. The above statement is based on the assumption that the concentration of the saturated fatty acid (palmitic acid) remains constant throughout the ageing.

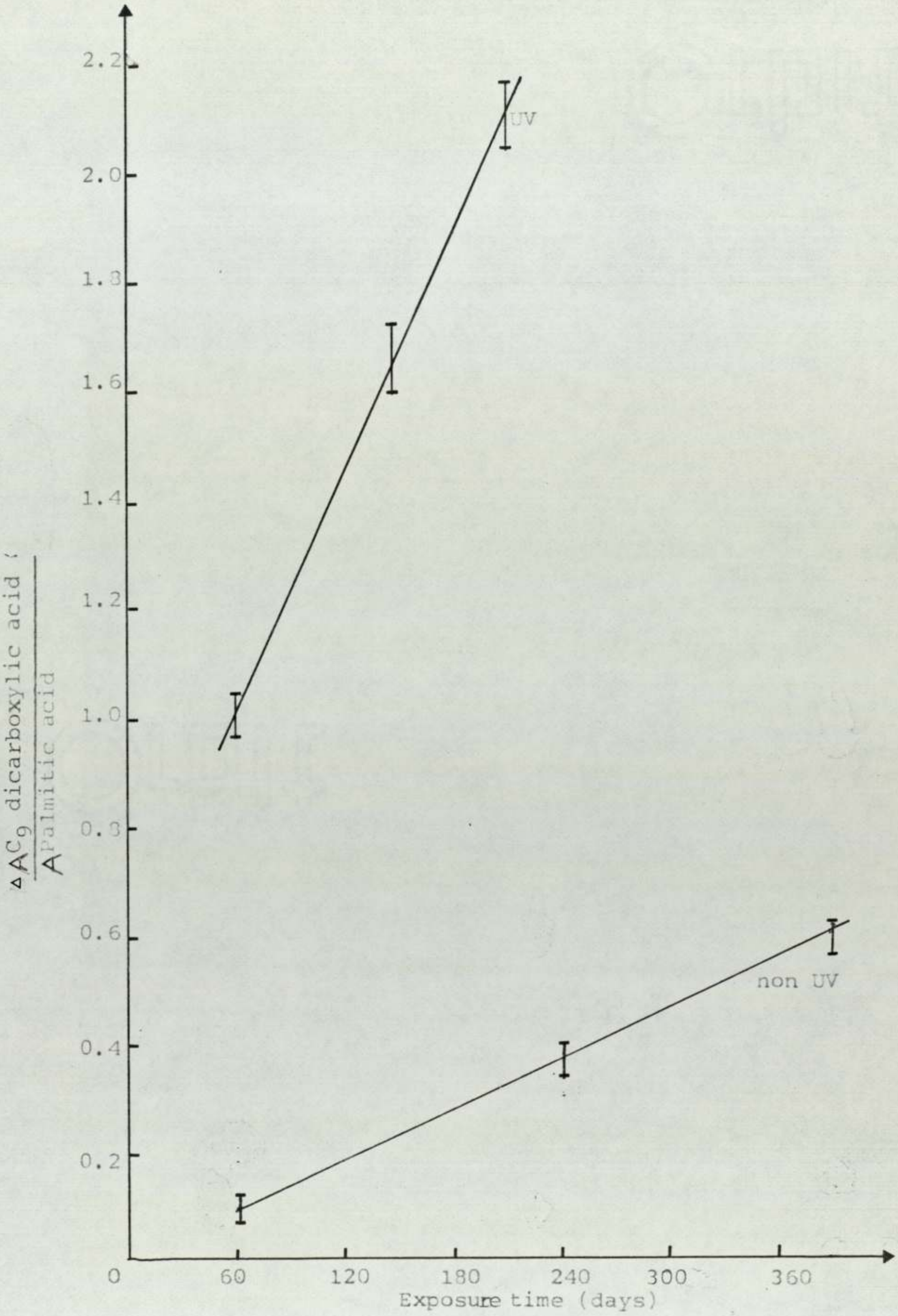


Fig 4.8 Formation of scission product of dried oil in the presence and absence of UV light.

CHAPTER 5

EFFECT OF VERDIGRIS ON OXIDATION OF LINSEED OIL

5.1. INTRODUCTION

Verdigris is a collective term used to describe blue, blue-green, green-blue and green copper salts of acetic acid.

Pliny, in Natural Historia$^{(132)}$, mentioned that verdigris was often used as pigment in antiquity. Although Raehlnann$^{(133)}$ found copper in numerous green and greenish-green paint of samples of paintings from Rome and Pompeii, he could not establish whether these samples contained verdigris or malachite. In colour lists and in the literature on the technique of painting through the Middle ages and the Renaissance and Barogue periods, verdigris is often mentioned. Examination of paintings has confirmed that verdigris was employed as a pigment by European painters from the thirteenth to nineteenth centuries. Verdigris is most found on easel paintings of the fifteenth to the seventeenth centuries. In the Italian, early Dutch and early German paintings, verdigris was almost exclusively used as the green pigment, to produce intense pure green tones, since neither mixtures of blue and yellow pigments nor the other green pigments known at the time, i.e. malachite and green earth, possessed such strong colour. However, it is rarely found in eighteenth and early nineteenth paintings. This may be due to the fact that there was no longer any special need for this bright green in the eighteenth century, and further that Emerald (Schweinfurt) green, a pigment hardly surpassable in its brightness, was available as early as the nineteenth century.

The composition, preparation and properties of the various copper acetates have been extensively described by Gauthier(134) on the basis of their chemical composition. The numerous kinds of verdigris can be divided into two groups; basic and neutral verdigris. According to Gauthier, basic verdigris may contain the following copper acetate basic salts.

1.	$\left[Cu(CH_3COO)_2\right]_2 \cdot Cu(OH)_2 \cdot 5H_2O$	blue
2.	$Cu(CH_3COO)_2 \cdot Cu(OH)_2 \cdot 5H_2O$	blue
3.	$Cu(CH_3COO)_2 \cdot \left[Cu(OH)_2\right]_2$	blue
4.	$Cu(CH_3COO)_2 \cdot \left[Cu(OH)_2\right]_3 \cdot 2H_2O$	green

Verdigris can be composed of any one of these acetates alone or of mixtures with acetate 1. and 2. or 3. and 4. Acetic acid dissolves basic verdigris with the formation of a dark green colour, the product being neutral copper acetate hydrate, $(CH_3COO)_2^{Cu} \cdot H_2O$, after removal of acetic acid.

5.2. EFFECT OF VERDIGRIS ON INITIAL AUTOXIDATION OF LINSEED OIL

5.2.1. RESULTS

When verdigris was added to linseed oil the initial blue colour of the pigment changed to yellow green. The colour change was accompanied by a rapid oxygen absorption. Fig 5.1. shows that in the absence of verdigris, the oil absorbs slowly over 2 hours in the dark. After this period, the rate of oxygen absorption autoaccelerates and became nearly a linear function with time. A total of 4.6 ml oxygen/ml of oil was consumed during the 20 hours period. When the same experiment was conducted in the presence of 1% of verdigris the rate of oxygen absorption relative to the control increased. The oxygen consumed during nineteen hours was 10.5 ml/ml of oil. However, after 20 hours when the samples were irradiated with UV light, the relative rates of oxidation of the control and the sample containing verdigris were reversed.

Infra red spectral examination of the verdigris film showed that similar changes to those in unpigmented film occurred Fig 5.2.

Fig.5.3. shows that verdigris accelerates the decomposition of cumene hydroperoxide in chlorobenzene at 69°c. Fig.5.4. shows that the main products formed from decomposition of cumene hydroperoxide by verdigris are cumyl alcohol, acetophenone and α methyl-styrene.

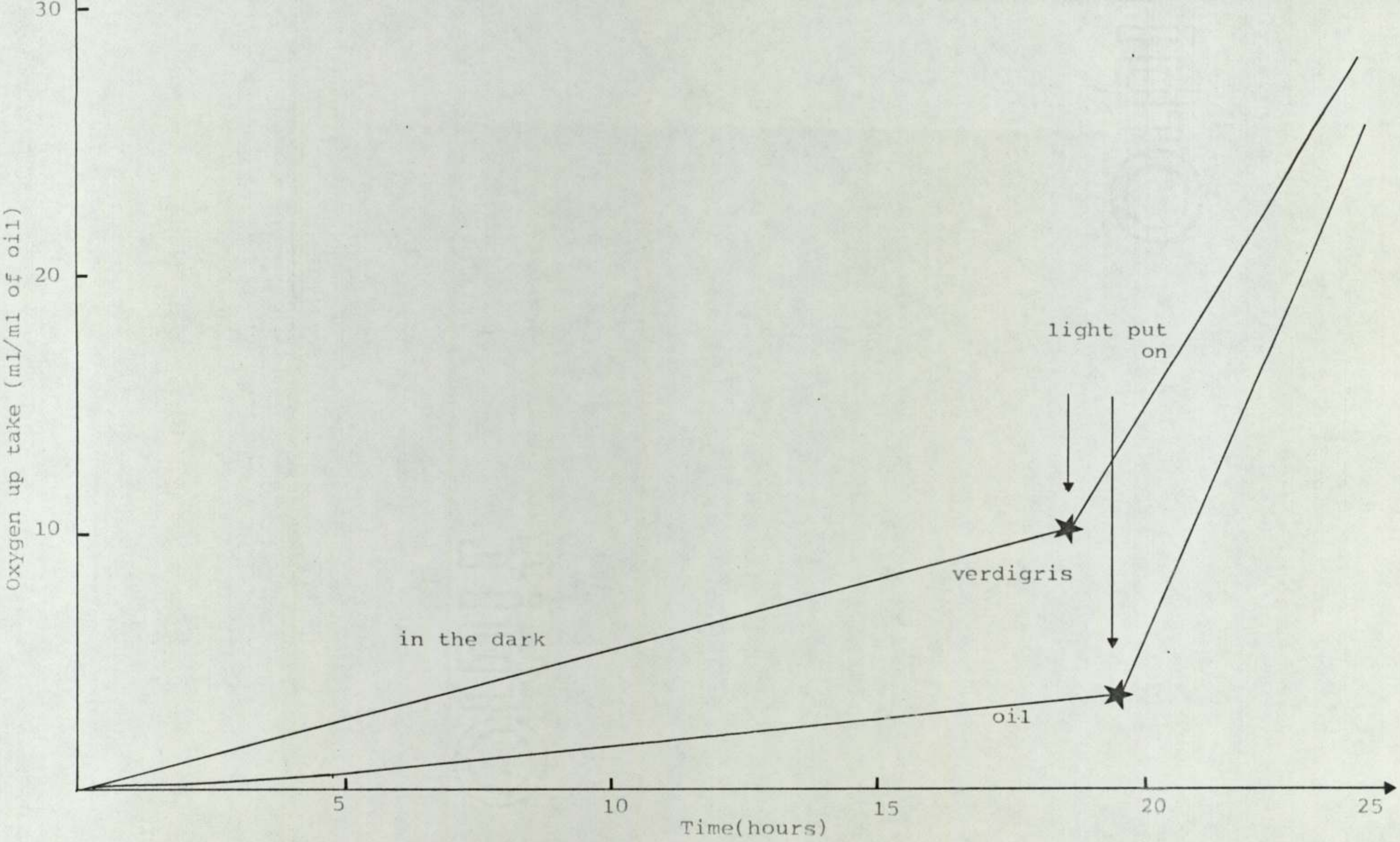


Fig 5.1. Effect of verdigris on the rate of oxygen absorption in the absence and presence of light

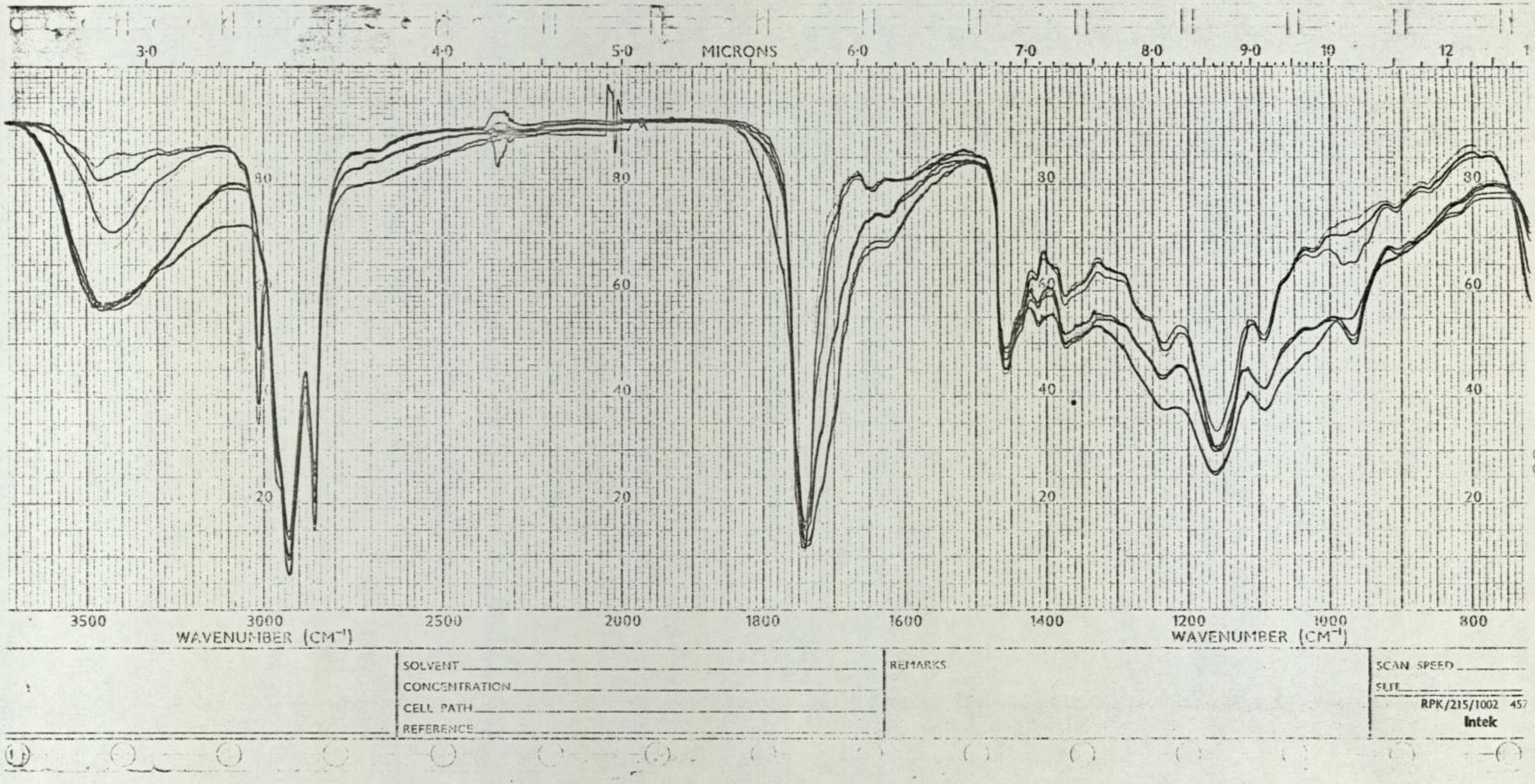


Fig. 5.2. IR spectral changes occurring during the initial drying of linseed oil containing 1% verdigris.

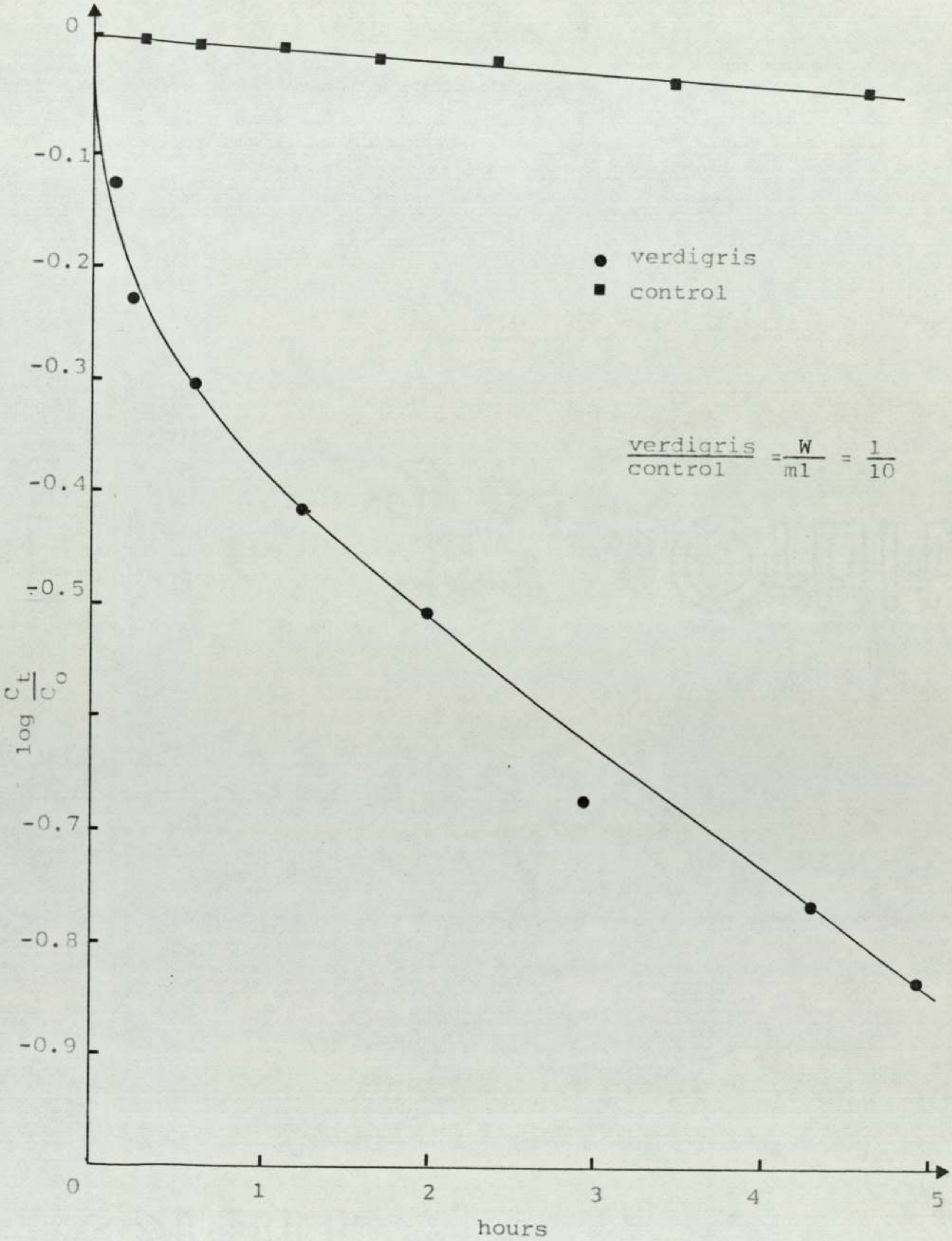
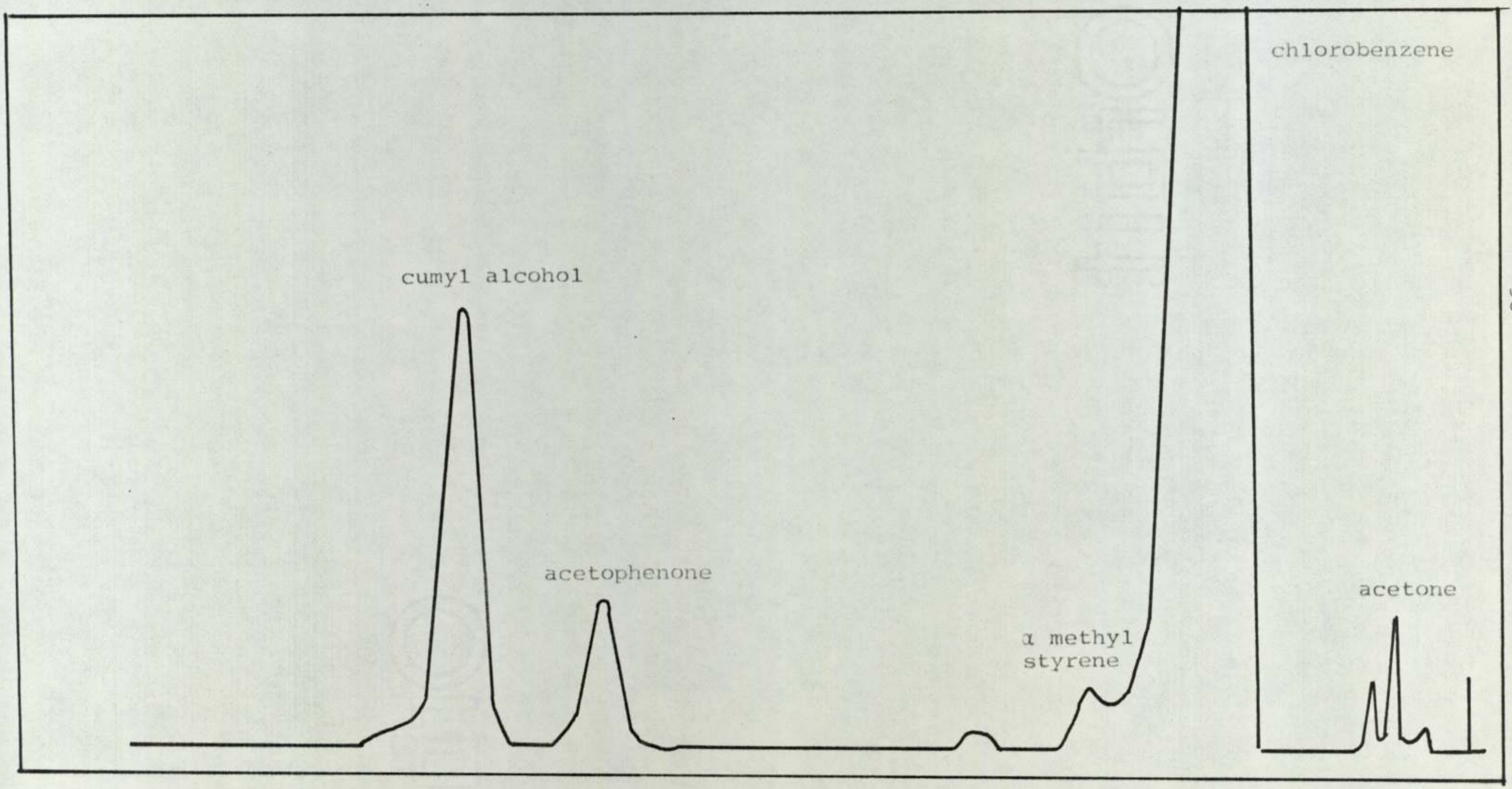


Fig 5.3. First order plot of the decomposition of cumene hydroperoxide by verdigris in chloroform at 69°C.

Fig 5.4. G.L.C. trace of the decomposition products of cumene hydroperoxide by verdigris



5.2.2. DISCUSSION

The immediate colour change observed when verdigris was added to linseed oil may be attributed to the presence of free fatty acid in the oil, since the same colour change was observed when verdigris was added to pure oleic, linoleic and linolenic acids, whereas no colour change was observed when the corresponding methyl esters were used. The presence of fatty acids in the oil may solubilize the copper hydroxide part of the pigment leading to the formation of the soluble copper salt in which the hydroxy ligands are exchanged for the corresponding acids present. From Fig.5.1. it is evidenced that verdigris accelerates the up-take of the oxygen relative to control and hence promotes the autoxidation reaction. However after 20 hours in the dark, when the UV light was put on, the rates of oxidation were reversed. This suggests that the verdigris has slight UV stablizer activity.

Copper compounds are particularly efficient catalysts for the decomposition of hydroperoxide as evidenced by Fig.5.3 and work of Richardson(135). Decomposition is believed to be due to the lowering of the activation energy of -0-0- bond to the formation of two free radicals $\dot{R}O$ and $\dot{O}H$ (the mechanism and products formed were discussed in Section 3.6.). Fig.5.4. adds additional support to this view since nearly all the products formed are those expected from homolytic break down of the hydroperoxide.

The changes that occur in the oil during the initial stages of autoxidation in the presence of verdigris compared withthe control, suggest that verdigris changes the rate of the drying process but not the mechanism by which these occur.

5.3. EFFECT OF VERDIGRIS ON DRIED PAINT MEDIA

It was concluded in Chapter 4 that the main process responsible for the autoxidation of linseed oil is a free radical chain reaction. Verdigris accelerates these processes due to its ability to catalytically decompose the hydroperoxides in a free radical mechanism leading to more rapid cross linking of the oil film.

5.3.1. IR STUDIES OF DRIED VERDIGRIS PIGMENTED FILM

The rate of photo-degradation of pigmented and unpigmented film was followed using a sodium chloride disc technique (see Section 3.3.1.1.2.). Sodium chloride discs were coated with pure linseed oil and linseed oil containing 1% of verdigris. Before UV irradiation the films were allowed to stand for a week in the laboratory in normal day light, humidity and temperature. The rate of errosion of paint surface is related to the loss of the $-CH_2-$ of dried film (see Section 3.3.1.1.2) Fig.5.5. compares the loss of CH_2 of dried oil and pigmented films. This figure clearly demonstrates that after 15 days irradiation only 13% of the paint medium was lost in the film pigmented with verdigris, whereas the unpigmented film lost about 50% of its $-CH_2-$ in the same time. After 60 days the verdigris

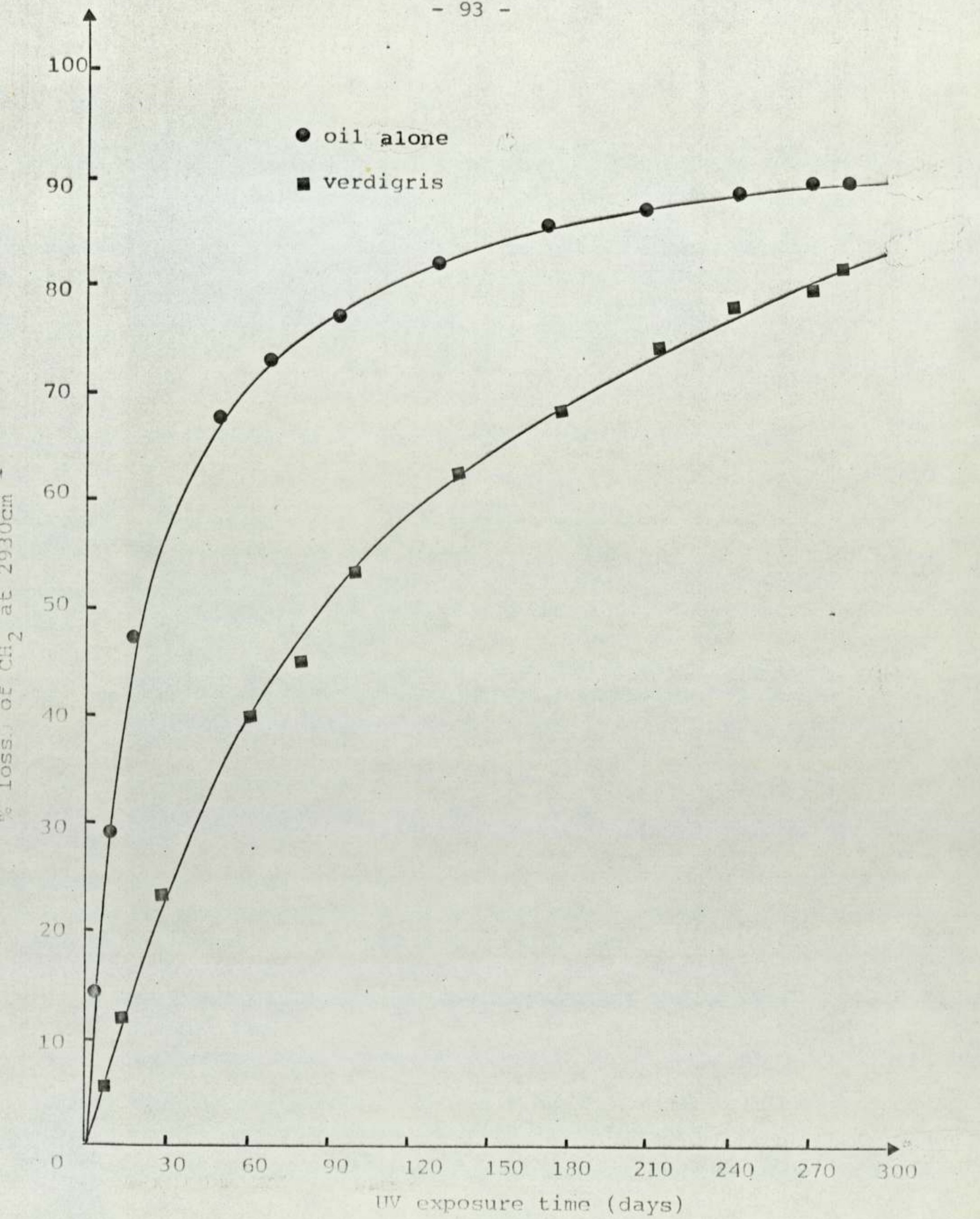


Fig 5.5 Disappearance of $-CH_2-$ at $2930\ cm^{-1}$ of dried oil with and without verdigris

pigmented film had lost 42% whereas the control lost over 70%. However, after 280 days of UV irradiation the difference in $-CH_2-$ between pigmented and unpigmented was not appreciable. Fig 5.6. compares the first order plot for the decay of $-CH_2-$ groups of verdigris pigmented and unpigmented films. It can be seen that after 90 days of UV irradiation log ΔCH_2 becomes linear with time. Fig 5.7. shows the decay of esteric carbonyl at 1740 cm^{-1} in verdigris pigmented and in unpigmented film. The decay of esteric carbonyl of the pigmented film is much slower compared to the control during the initial of 45 days of UV irradiation and it auto-retards to give almost complete inhibition. The control film on the other hand shows a linear decay with time after about 90 days. However, the pigmented film shows a higher decay rate of ester carbonyl after about 240 days. Fig 5.8. shows the change in the IR spectra occuring during the 240 days of UV irradiation after the initial period of drying. After 60 days there is very little absorption in the region 1640 cm^{-1}, however, from 70 days to 120 days an absorption in the region 1640 cm^{-1} becomes evident and starts to grow. After 150 to 180 days two peaks at 1640 cm^{-1} and 1620 cm^{-1} become quite pronounced due to formation of unsaturation groups.

5.3.2. UV SPECTRAL EXAMINATION OF VERDIGRIS PIGMENTED FILM

Fig 5.9. shows the UV spectral changes during UV irradiation of the same sample used for IR spectral

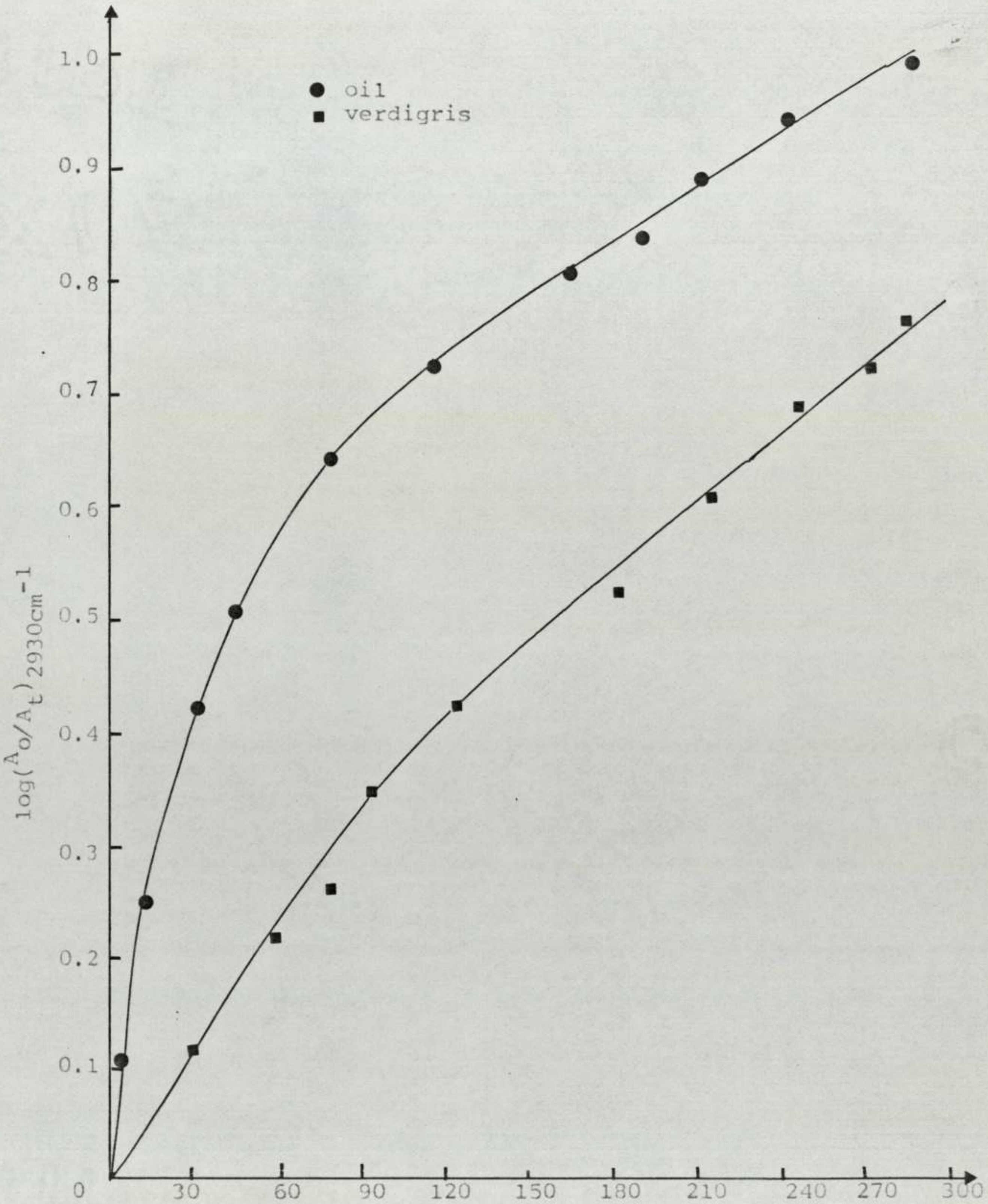


Fig 5.6. Disappearance of log CH_2 group at 2930cm^{-1} of dried oil with and without verdigris

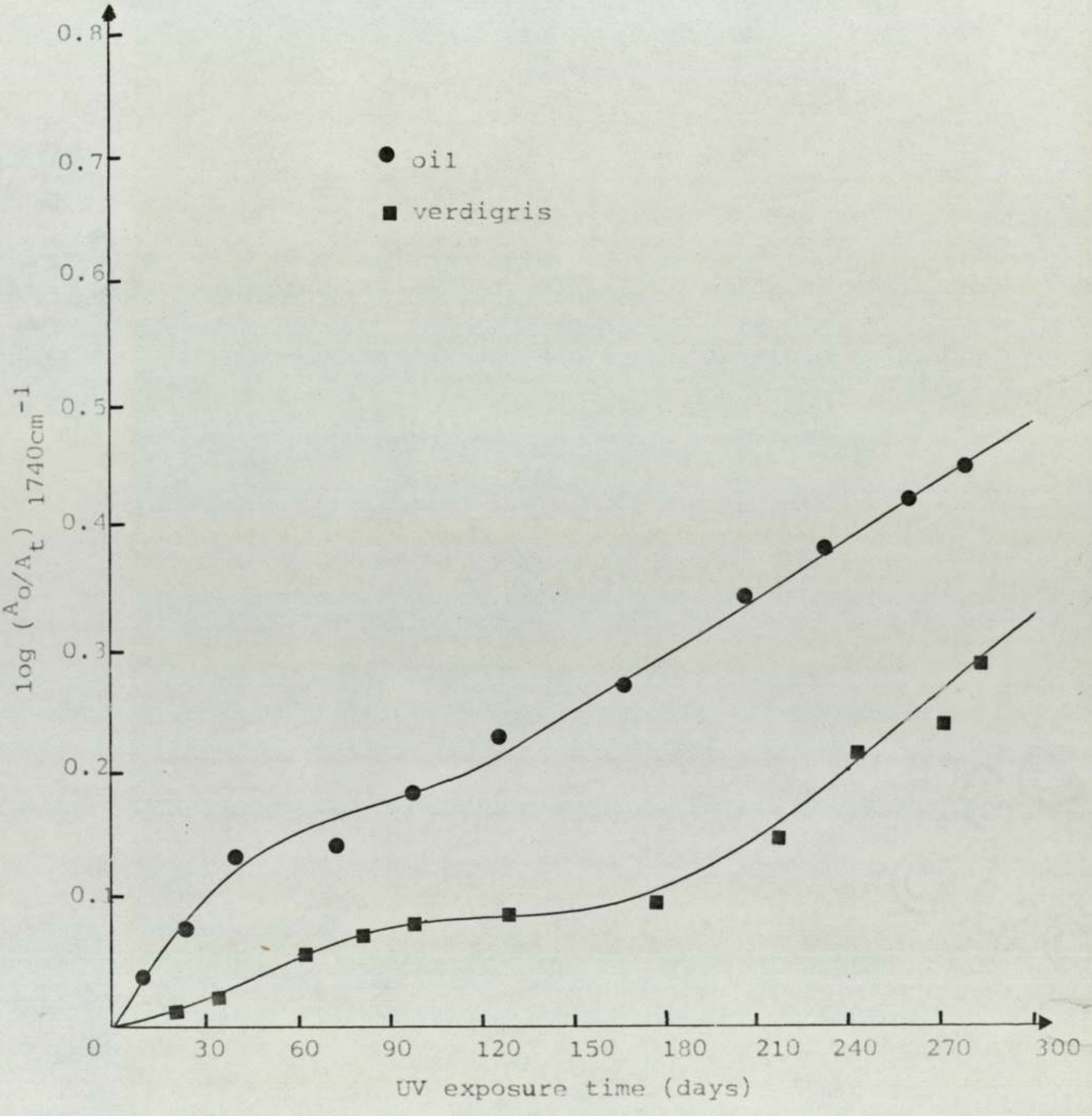


Fig 5.7. Disappearance of log CO group at 1740 cm^{-1} of dried oil with and without verdigris

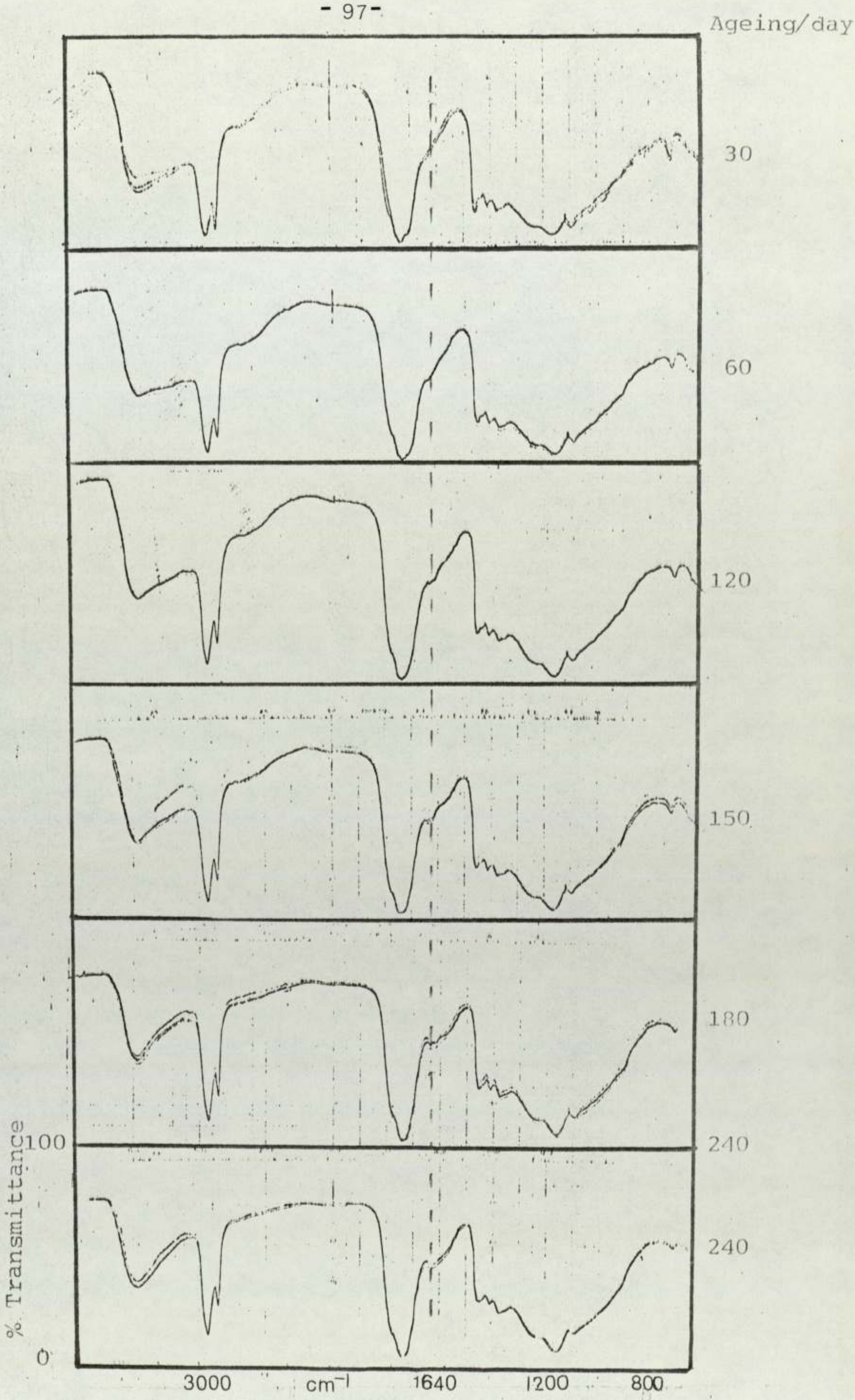


Fig 5.8. IR spectra changes occurring during the UV exposure of dried verdigris pigmented film.

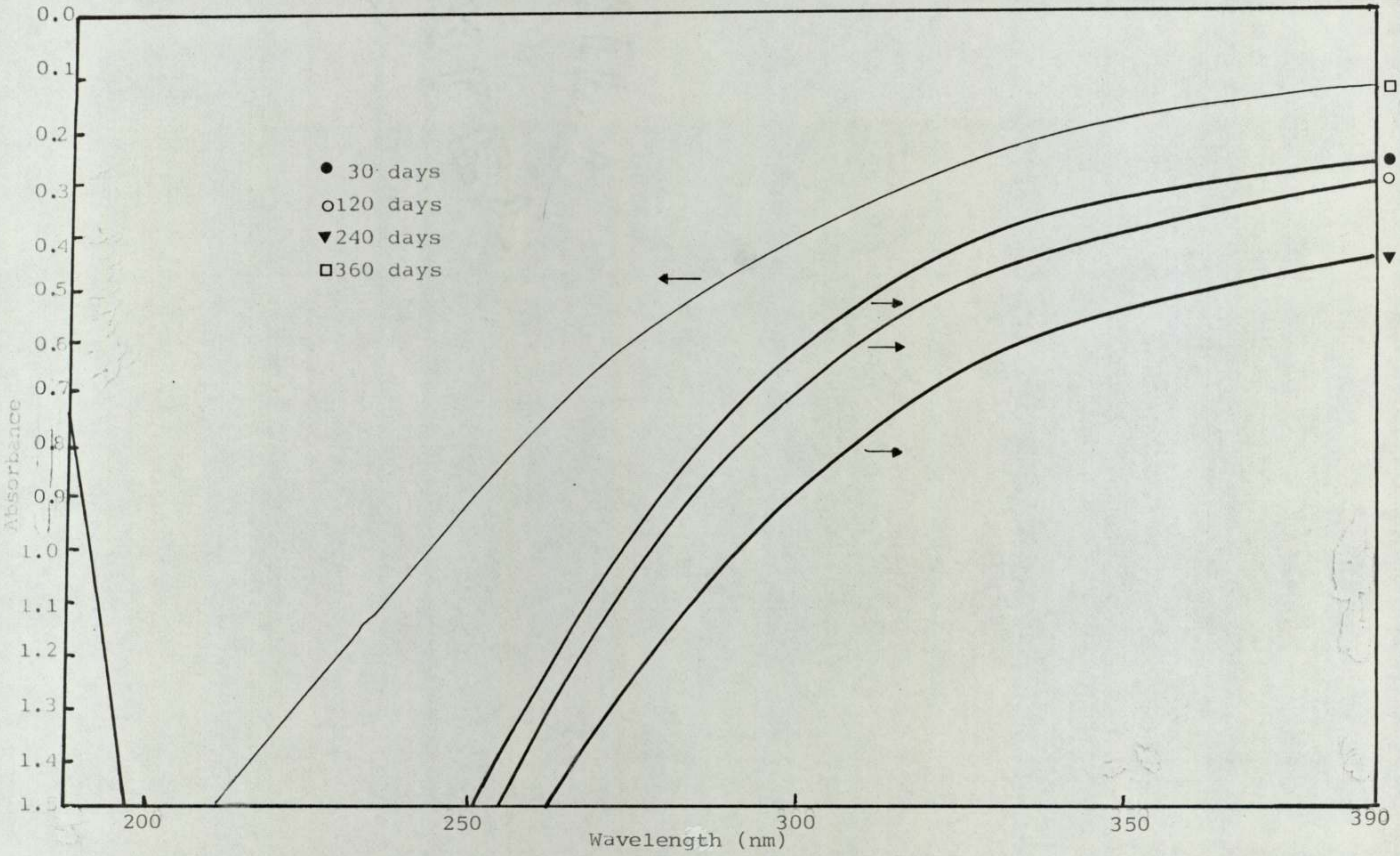


Fig. 5.9. The UV spectral changes of dried verdigris thin pigmented film during UV irradiation

examination Fig 5.8. These spectra show that during photo-oxidation from 30 days to 240 days a chromophore is forming which shifts the wave length from UV towards the visible region. After 240 days however the absorption of this functional group started to decrease.

5.3.3. G.L.C. EXAMINATION OF DRIED VERDIGRIS PIGMENTED FILM

Linseed oil with and without pigment were spread in duplicate on glass plates. The verdigris paint contained 60% of pigment. One set of films was kept in the diffuse light of the laboratory, while the other, when touch dry after a week, was placed in the UV cabinet.

Fig 5.10 and Fig 5.11 show the G.L.C. chromatograph (see Section 3.5.1.2.) of dried pigmented film and non-pigmented film of which had been kept in diffuse light for 60 days. It is however evidenced from these chromatographs that the pigmented film contain s a higher concentration of the original unsaturated fatty acids than the control and hence a lower amount of scission products. The amount of scission product was estimated by dividing the concentration of scission products by that of palmitic acid (palmitic acid is a saturated long chain fatty acid which oxidizes very slowly and hence can be used as a reference peak). It is evident that the distribution of the scission products is different. Figs 5.12 and 5.13 show the G.L.C. Chromatographs of the UV irradiated verdigris paint film after 397 days and of verdigris paint film kept 15 years in the

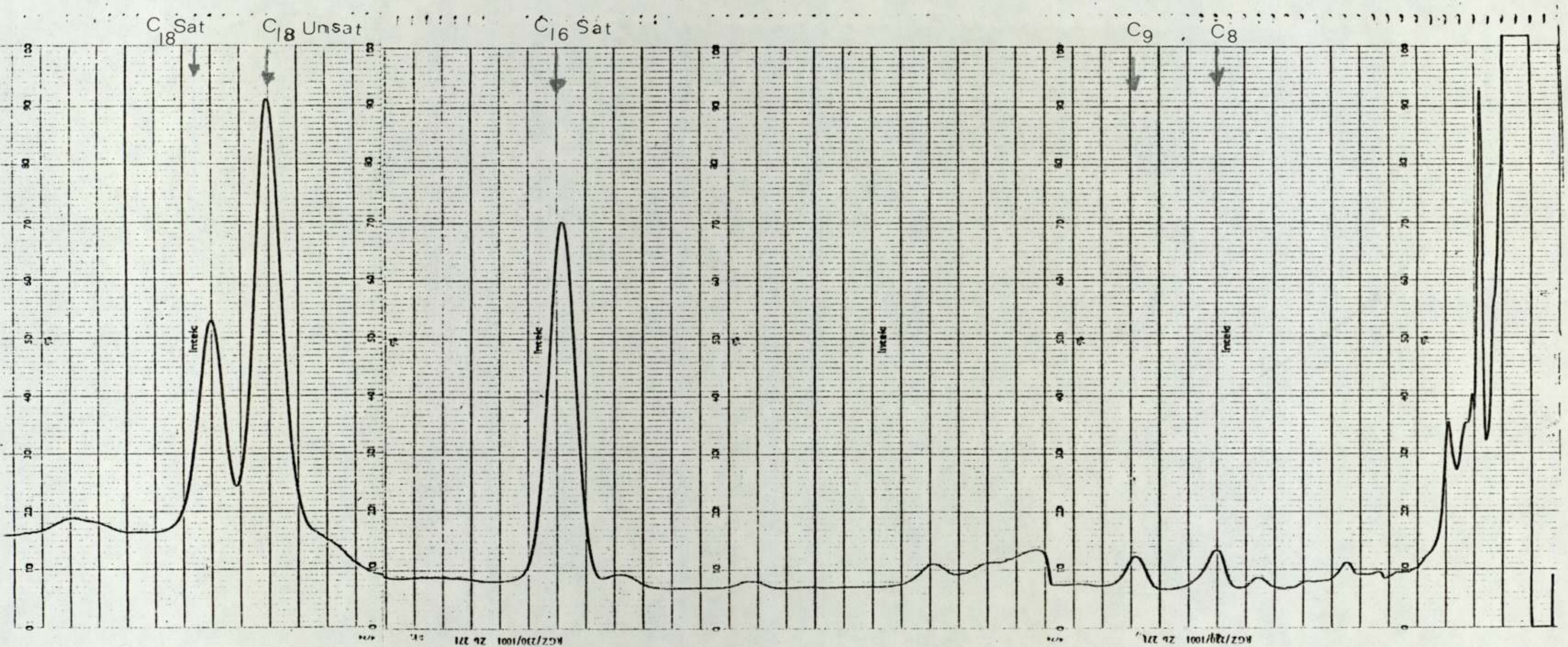


Fig 5.10 Gas chromatograph trace of verdigris pigmented paint kept in the laboratory for 60 days.

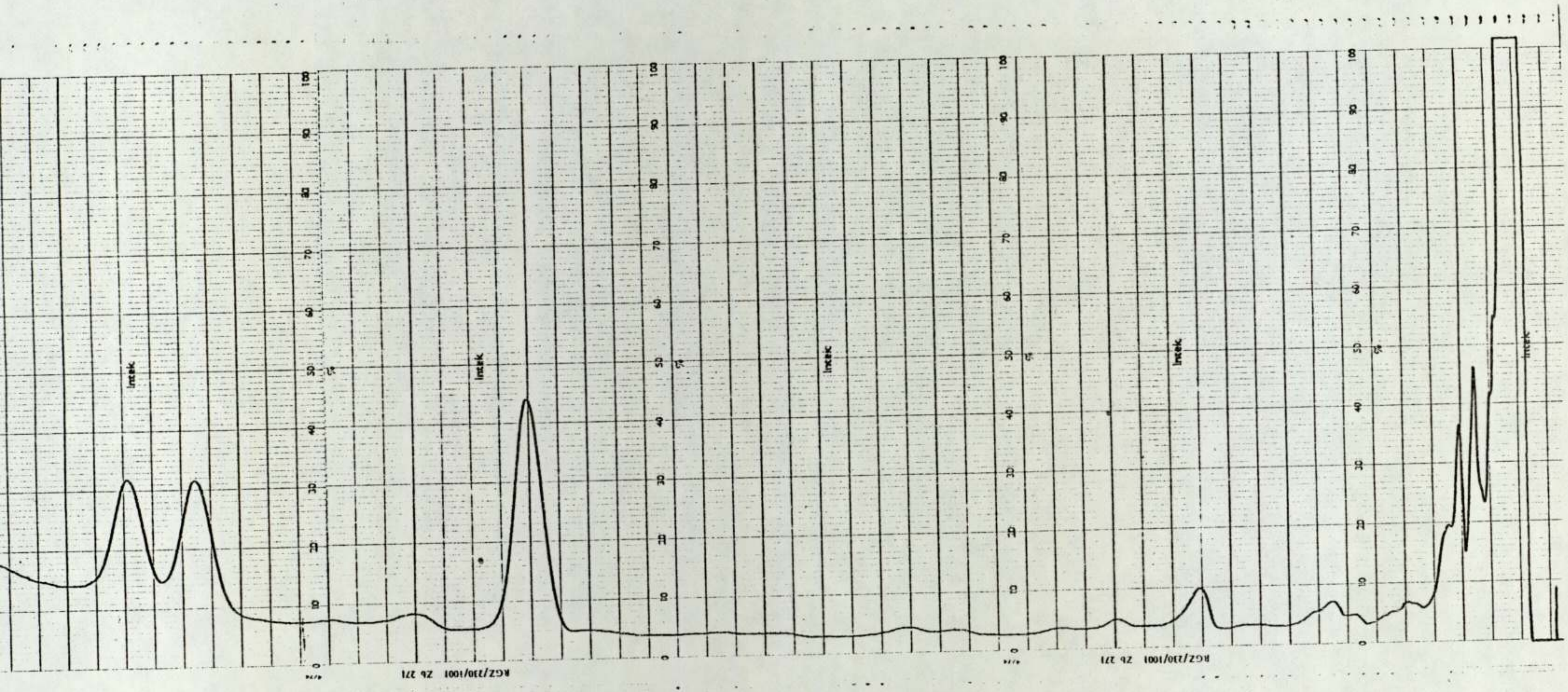


Fig 5.11. Gas chromatograph trace of dried linseed oil aged in laboratory for 60 days.

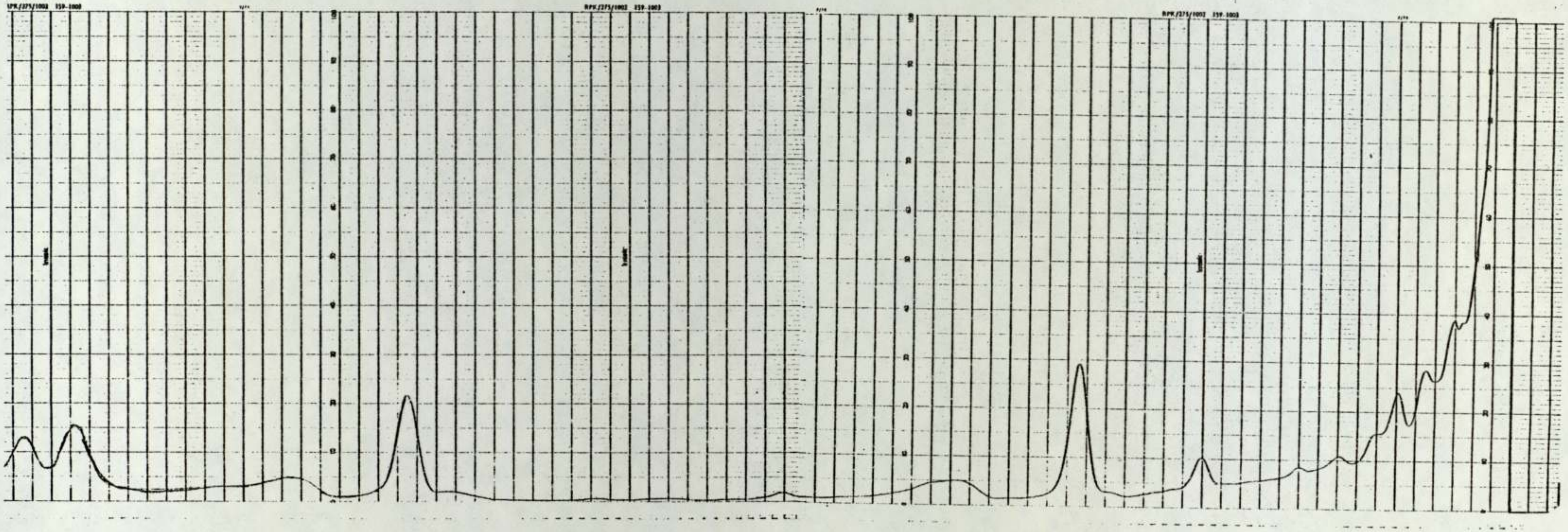


Fig 5.12 Gas chromatograph trace of verdigris pigmented paint film irraidated in UV cabinet for 13 months.

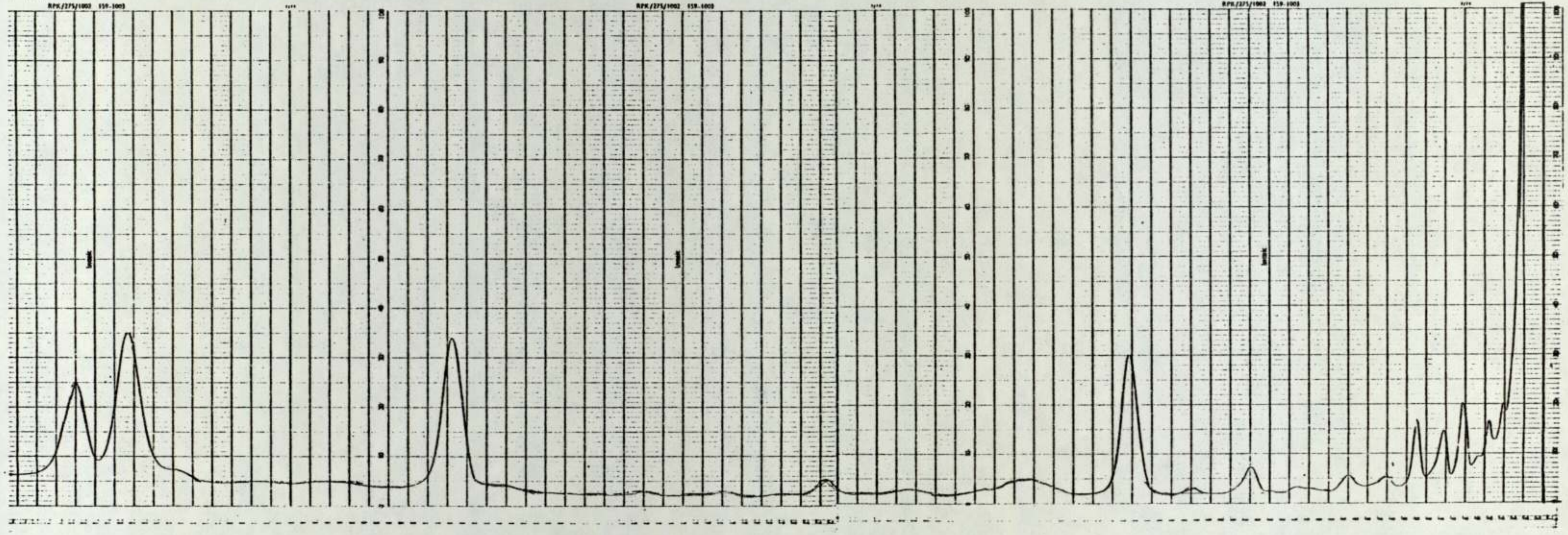


Fig 5.13 Gas chromatograph trace of verdigris pigmented paint film kept for 15 years in the National Gallery

National Gallery. By comparing the two chromatographs it is evident that the distribution of scission products are essentially similar. Fig 5.14 compares the rate of formation of scission products (C_9 dicarboxylic acid) of pigmented and unpigmented aged film. It is quite clear that verdigris slows down the rate of degradation of the aged film under UV and day light conditions. Fig 5.15 compares the rate of formation of C_9 dicarboxylic acid of unpigmented film and verdigris pigmented film including the paint sample obtained from National Gallery. Fig 5.16 shows that as the concentration of the original unsaturation decreases, the concentration of the scission product increases. Concentration of the original unsaturation was found by dividing the concentration of the initially present in the oil to that of saturated acid palmitic acid.

5.3.4. EFFECT OF PHOTO-OXIDATION ON PHYSICAL PROPERTIES OF VERDIGRIS PIGMENTED PAINT FILM

5.3.4.1. DISCUSSION

It was concluded in Chapter 4 that the drying of linseed oil proceeds via a free radical chain mechanism. The spontaneous 'curing' by the above mechanism, under relatively mild conditions of temperature, oxygen pressure and daylight, leads to the formation of a tight net-work and a hard film with low flexibility. If it were possible to stop the reaction at this point, all would be well. However, this is not possible since the process which is

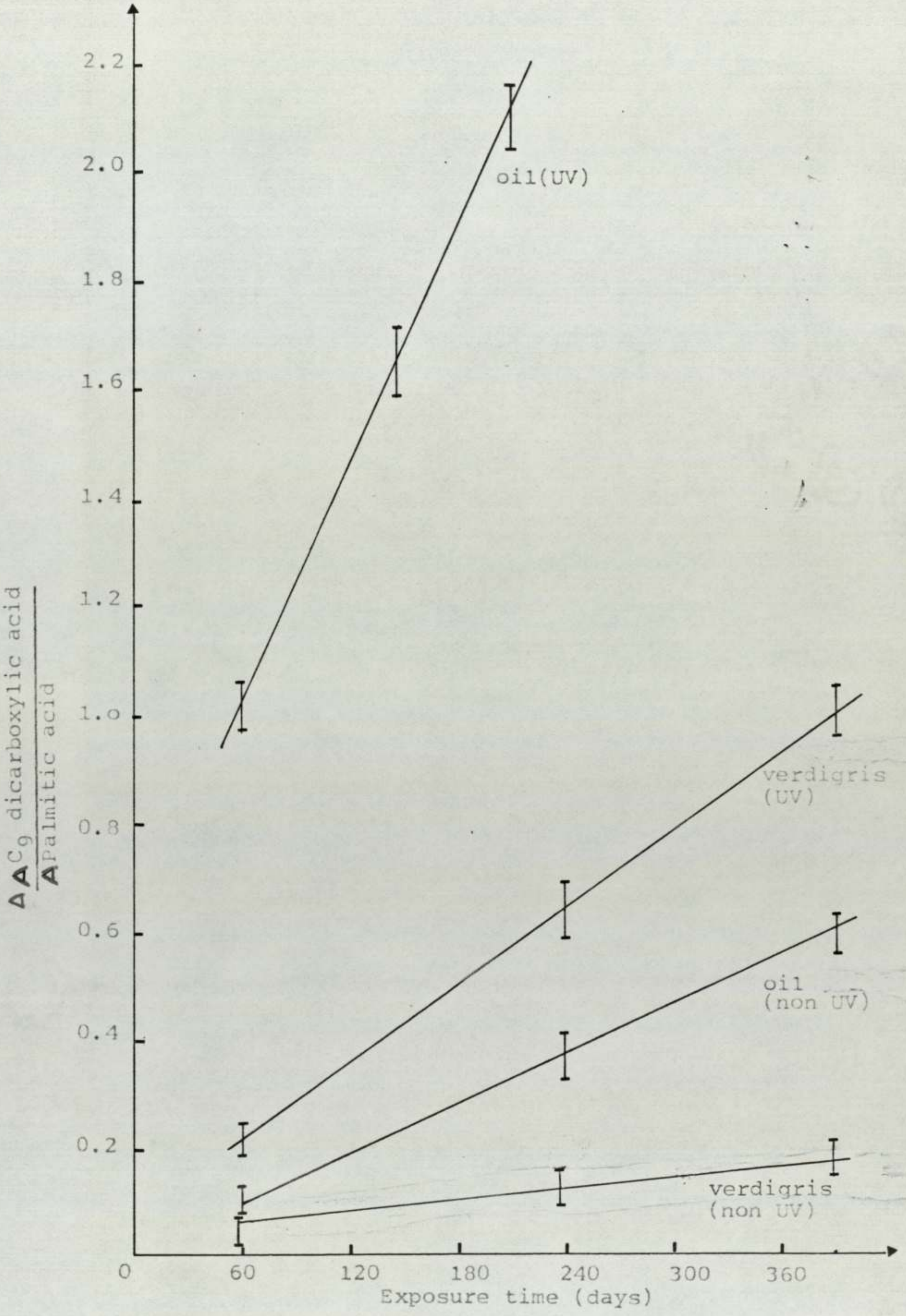


Fig. 5.14 Effect of verdigris on the rate of formation of scission product of dried oil in the presence and absence of UV light

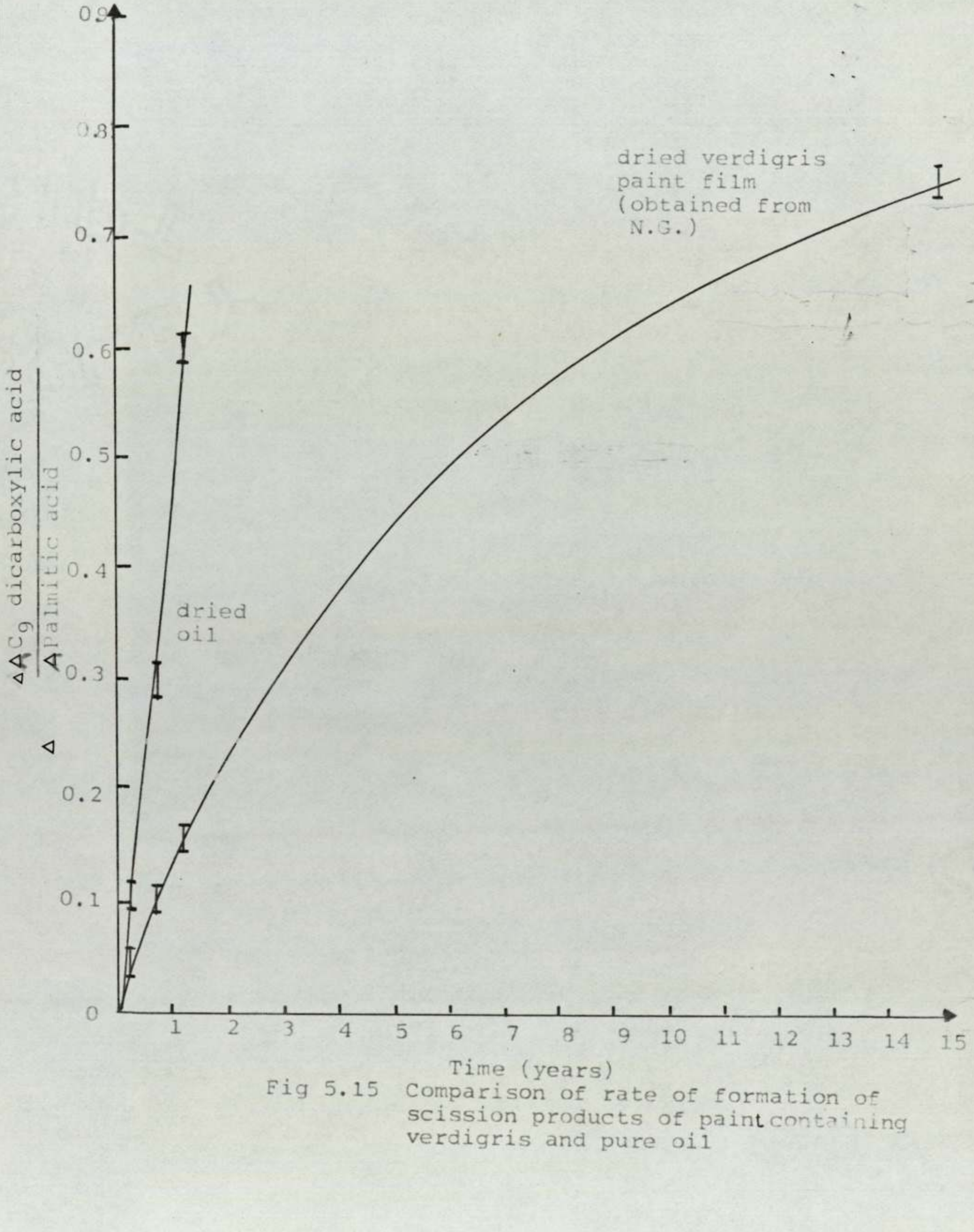


Fig 5.15 Comparison of rate of formation of scission products of paint containing verdigris and pure oil

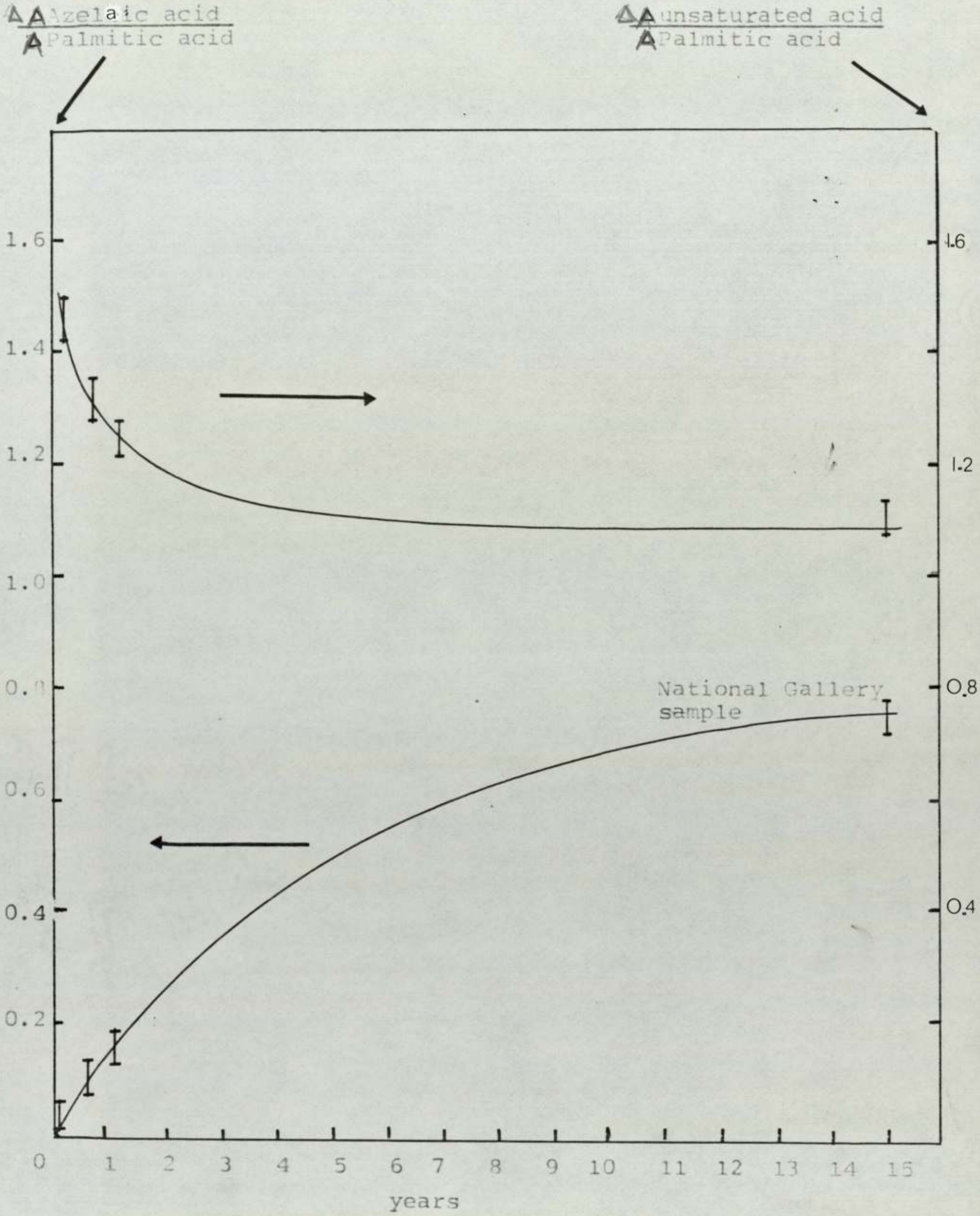


Fig 5.16. Variation of the initially present unsaturation and scission product formed during diffuse light ageing

essentially oxidative continues though at a much reduced rate see Fig 5.15 and a loss rather than a gain of weight is observed. The weight loss may be monitored by the decay of the $-CH_2-$ stretching absorption at 2930 cm^{-1} and is found to correlate with the formation of scission product Figs 5.5. and 5.14. This indicates that the greater the main-chain scission, the greater will be the weight loss, The chain scission will have a severe effect on the physical properties of the paint such as loss of gloss, loss of adhesion, cracking, loss of film strength, loss of elasticity etc. The physical appearance of verdigris paint films are therefore of interest. All the verdigris pigmented paint films are hard, glossy and dry. This is reflected in the low formation of scission products and low weight loss of the paint with respect to the control Figs 5.5. and 5.14.

The concentration of oxygen within the surface of the film is equal to its solubility in the film. At greater depth, the concentration of oxygen will be related to its rate of depletion by oxidation and the rate of diffusion of oxygen. This in tern limits the rate of oxidation. The rate of diffusion of oxygen obeys Fick's Law(136) which states that, if we mount a film so that there is more oxygen on one side of it than on the other, the amount of oxygen diffusing through the film to the side of lower concentration is proportional to the area of the film, the time, and the concentration gradient of oxygen across the paint. Fick's Law can be usually written as;

$$Q = DA_t\ (C_1 - C_2)/h$$

where

Q = quantity of oxygen passing through the film of area A in time t,

A = area of the film

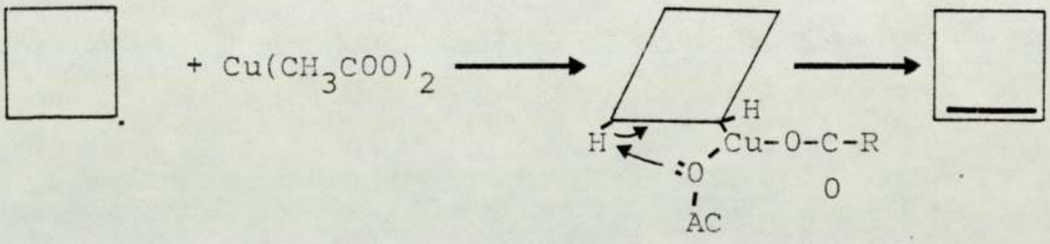
D = the diffusion constant,

and C_1 and C_2 are the concentrations on either side of a film of thickness h, so that $(C_1-C_2)/h$ is the concentration gradient. The possibility of complete oxygen starvation in the depth of a normal stable mature oil or tempera paint under ambient conditions has been recently rejected(136), although generally it is accepted that the concentration of oxygen decreases along the depth of the paint. It is known that in many oxidisable media, the rate of oxidation is dependent on oxygen pressure (20) and that such dependence will limit the oxidation rate due to slow diffusion of oxygen. This may in part be an important factor in determining the stability of verdigris pigmented film towards ageing. However, these factors alone can not explain the change in the photo and autoxidation mechanism of paint containing verdigris as evidenced by the dissimilarity of the scission products of pigmented films Fig 5.10 and non-pigmented films Fig 5.11. Similarly the formation of unsaturation during the ageing as evidenced from Fig 5.8 indicates a more specific chemical mechanism.

Another finding is that the distribution of carboxylic acids of the paint containing verdigris irradiated in an accelerated UV exposure test Fig 5.12. is identical to that found in verdigris pigmented film aged for 15 years in diffuse day light in the National Gallery Fig 5.13. This indicates that the mode of break-down is the same in spite of the higher energy distribution of the lamps of the UV cabinet. This is considered to be sufficient justification for concluding that newly dried film can be used to model the long term behaviour of paint containing this pigment. The inhibiting effect of metal catalysts have been described in literature; Cu^{II} in particular has been reported as having an inhibitory effect on the oxidation of hydrocarbons(138), lipids(139), and polyamides(64). However, no mechanistic evidence has been presented to explain its antioxidant activity.

5.4. PHOTO-STABLISATION MECHANISM INVOLVING COPPER ACETATE

Ingold(141) and Kochi(63) have demonstrated the rapid reactions of Cu^{II} with alkyl radicals and this process, in which Cu^{II} ions compete with oxygen for alkyl radicals is likely in a system in which oxygen diffusion is limited. This is particularly likely in photo-oxidation since the rate of radical generation is high. It is to be anticipated that the lower the oxygen pressure, the greater will be the contribution of the reaction of alkyl radical with the metal and the greater will be influence of the metal ion terminating reaction. Direct evidence for copper alkyl intermediate has been obtained by studying the E.S.R. spectra of 2-butyl radicals produced by reaction 2-butyl lithium with copper(II) salts(143). It has been shown that the exclusive product of oxidation of cyclobutyl radical by copper (II) acetate is cyclobutene(150).



The production of unsaturation and the anti-oxidative properties of copper in paint film is clearly demonstrated in Figs 5.7 and 5.8. The first sign of the formation of unsaturation after 70 days Fig 5.8. corresponds to the begining of the auto inhibitive part of the curve in Fig 5.7. Moreover, the antioxidative portion of the curve continued as long as double bond formation continued (until 270 days) when the second prooxidant stage occurred.

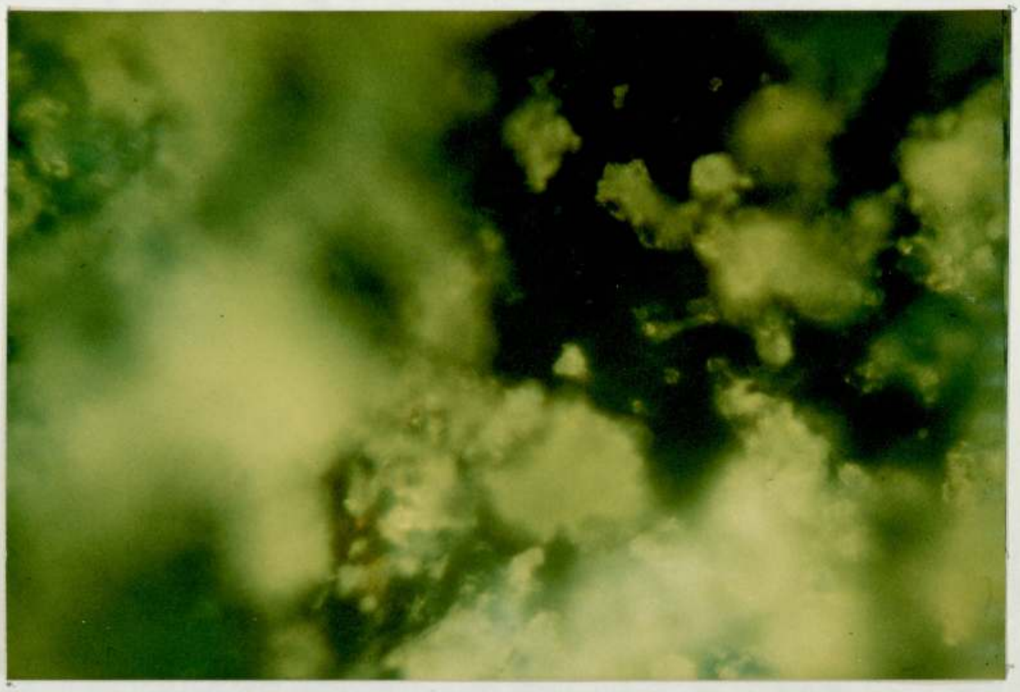
5.5. STUDY OF BROWNING OF VERDIGRIS PIGMENTED FILM

It is often seen in paintings from earlier centuries, that certain areas of green (leaves of trees, etc.) show a strong brown discolouration. The reason for such discolouration has so far been a matter of speculation. It has however been established that the discolouration is not due to decomposition of verdigris under the influence of light(146). Photograph 5.1. shows the cross section of an old paint containing verdigris(146) and clearly demonstrate the formation of dark brown colour on the surface of the paint. Photograph 5.2. was taken from the surface of an aged verdigris pigmented film kept in UV cabinet for 150 and 240 days and indicate the presence of brownish patches.

The foregoing discussion suggested that under certain circumstances (low oxygen pressure due to low diffusion rate) thealkyl radical may react with Cu^{II} to produce an alkene. This fact and other factors prompted the use of oleic acid as a model compound for studying the discolouration observed in verdigris paintings.

The following pigment oil ratio (POR) of 0.001, 0.01 and 0.1g/cc were made up and added to three 25ml beakers so that the solution depth at the bottom of each beaker was about 0.20cm. The beakers were placed in the laboratory under ambient condition for 720 days. Of the three, only the first sample of 0.001g/cc (POR) was converted to a dark brown mass whereas the other two, were showing relatively less browning possibly because the blue colour of the pigment

Photograph 5.1.
Cross-section of a paint layer containing verdigris. Lucas Cranach Elder, c.1540 'Winged house-altar of the Passion of Christ', Bayerische Staatsgemaldesammlungen, Inv. No.695.



(a)

Photograph 5.2. Photographs of the surface of the verdigris pigmented film irradiated by UV after

(a) 150 days (b) 240 days

(b)

itself will mask the brown colour. Therefore the first sample was chosen for further investigation.

About 2ml of 10% methanolic sodium hydroxide was added to the brown mass in a test tube. The sodium salts were neutralised by addition of an excess of hydrochloric acid. A few drops of ether were added to the mixture which was well shaken. A three phase mixture was obtained; an aqueous solution remained at the bottom of the test tube, a viscous dark brown gel (designated as D) separated in the middle and the ether extract rose to the top. The extract was removed by means of syringe, and extraction was repeated three times to remove any scission product and excess acid originally present.

Fig 5.17 shows the IR spectra of the gel (D), the bands at 910 and 960 cm^{-1} indicates the presence of isolated cis and trans unsaturation respectively and the presence of conjugated unsaturation. The broad absorption band between 1700 and 1740 cm^{-1} and the presence of shoulder between 1620-1680 cm^{-1} may also indicate the presence of conjugated carbonyl. A relatively broad band between 1500 to 1550 cm^{-1} is evident. Fig 5.18 shows IR spectra of 10- undecenoic acid, $CH_2=CH-(CH_2)_8-COOH$ the peak at 1640 is due to vinylene double bond. Fig 5.19 shows the IR spectra of the mixture of above acid with verdigris, the acid being in excess. Comparison of the above two spectra indicates the presence of three extra peaks at 1510 and 1590 and 1610 cm^{-1}. The band at 1510 Cm^{-1} is in the region, where we might expect to find a coordinated double bond. Avakyan$^{(147)}$, observed

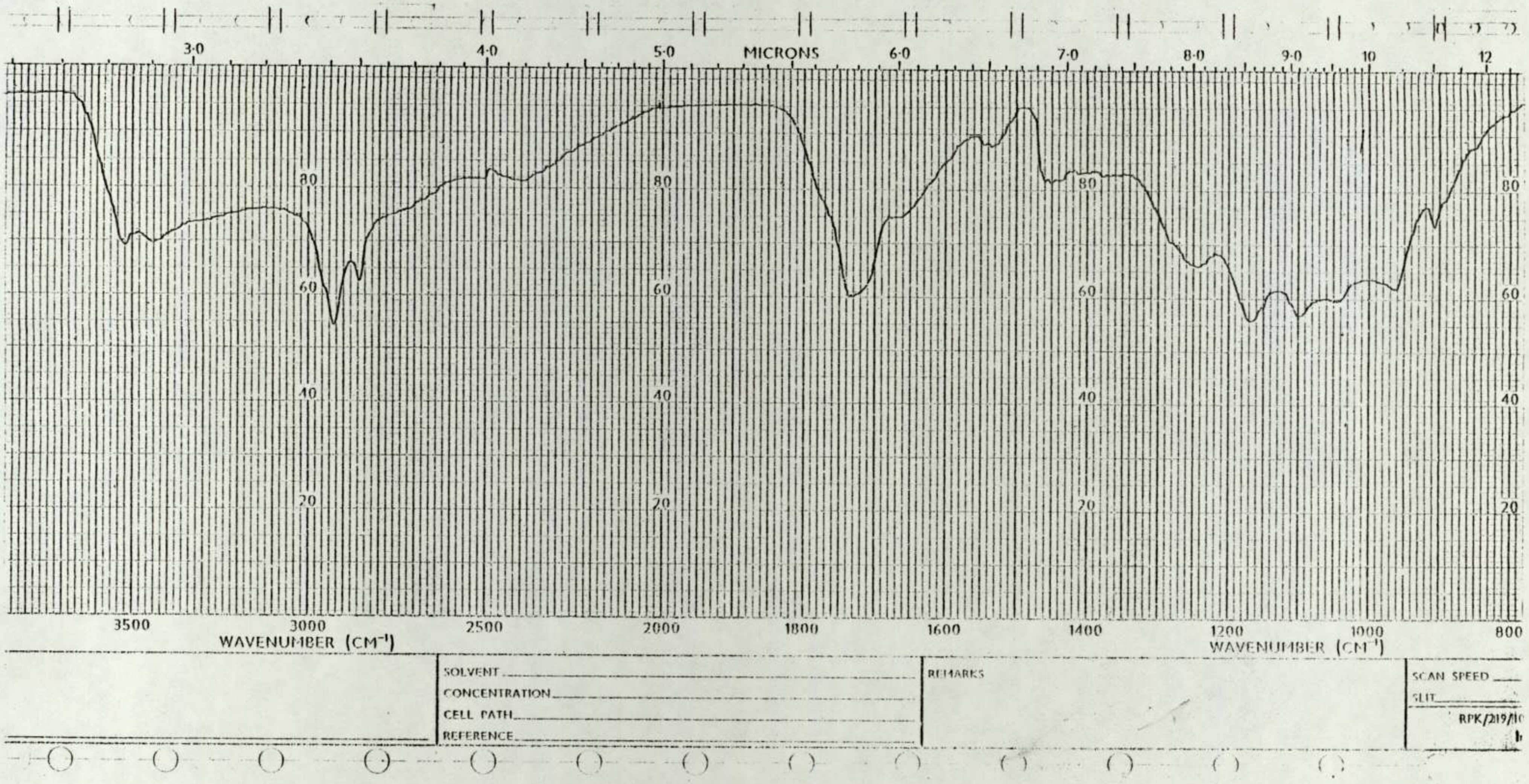


Fig 5.17 The IR spectra of the brown gel D

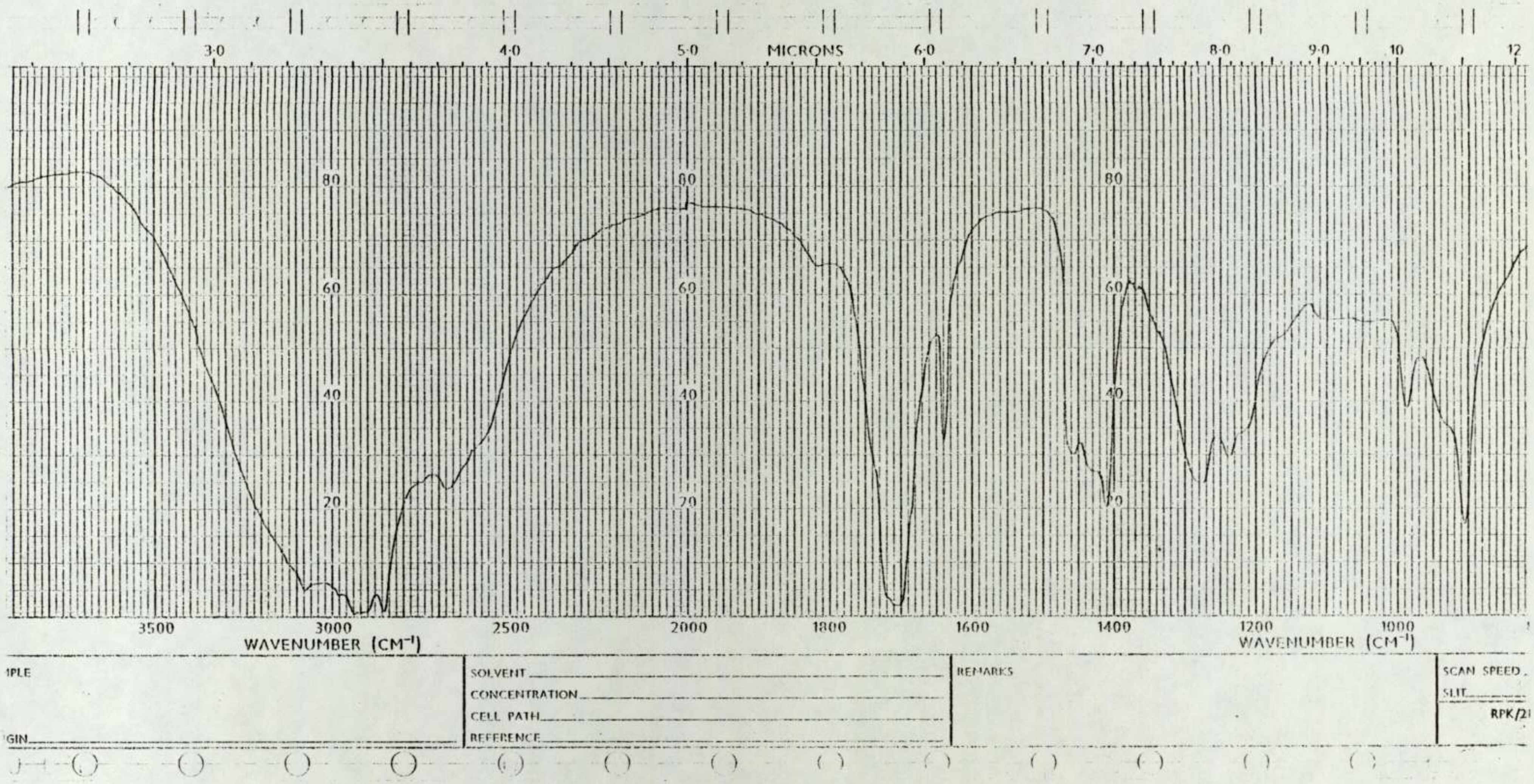


Fig 5.18 The IR spectra of the 10-undecenoic acid

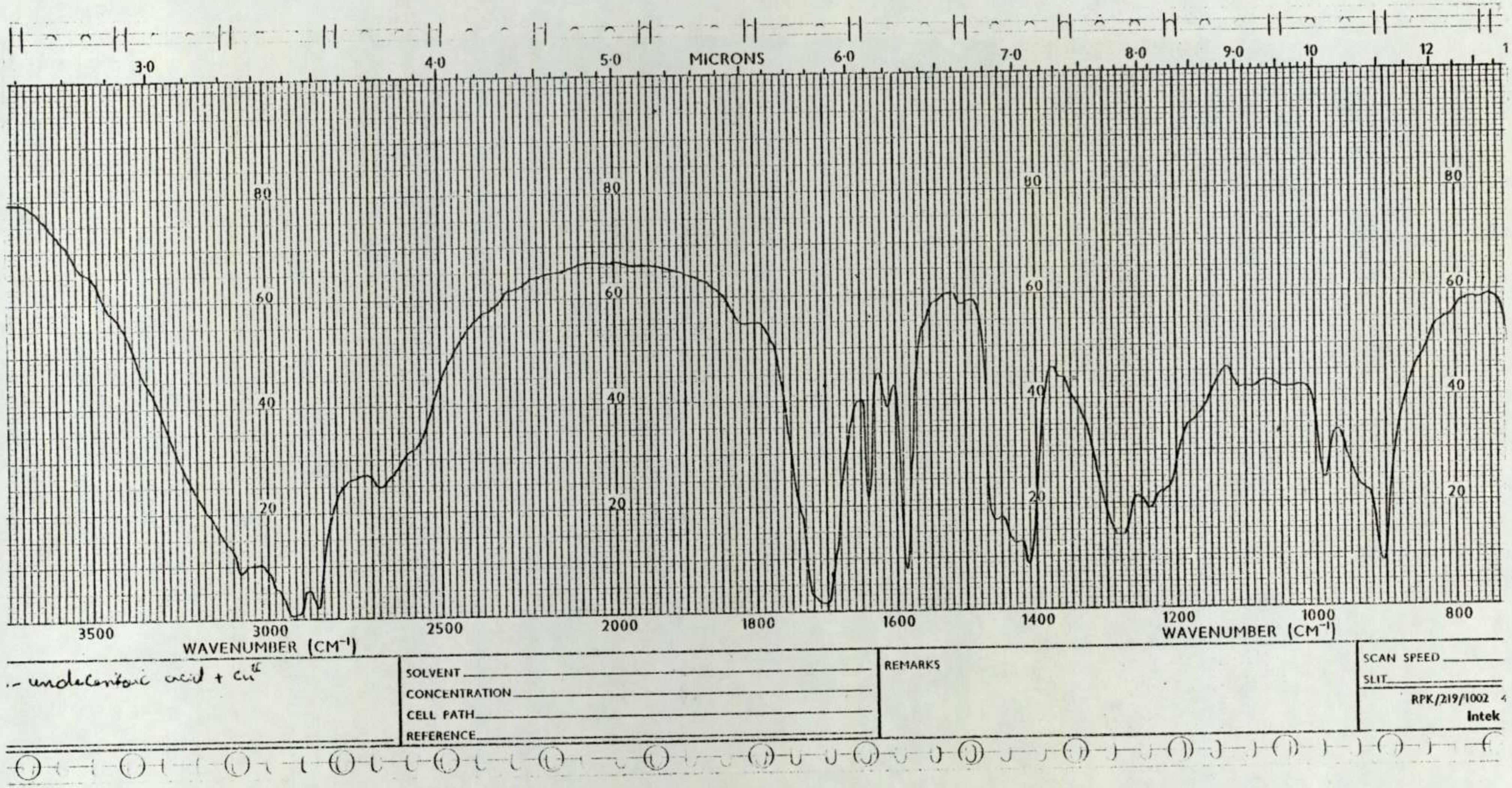


Fig 5.19 The IR spectra of the 10-undecenoic acid containing verdigris

a shift of the double bond from 1620 to 1585 , when he made a complex of 2-chloro-but-1,3-diene ($CH_2=CCl-CH=CH_2$) with copper (II) sulphate. He attributed this shift to the effect of coordination. Another worker(148), made a complex between copper (I) chloride and acrolein ($CH_2=CH-CHO$). The IR spectra of this complex also showed a peak at 1530 cm^{-1}, a shift of almost 90 cm^{-1} to the longer wave length. This suggests that the broad band between 1500 and 1550 cm^{-1} which was observed in the IR spectra of gel (D) is due to the coordination of the double bonds to the copper salt. The peak at 1590 cm^{-1} is also undoubtedly due to the asymetric stretching vibration of CO_2^- of the copper salt. The viscous gel (D) was not soluble in the ether layer. However it was soluble in chloroform. The UV spectra of the gel (D) dissolved in chloroform Fig 5.20 shows a succession of maxima from the region 250 to 380nm. The following chromophores can exist in the aged film of oleic acid and copper acetate which are able to absorb below 300nm ; hydroperoxides, carbonyl compounds and isolated ethylenic groups.

Carbonyl compounds, when they are not conjugated with a double bond, give an absorption which has a maximum near 280nm and then decreases smoothly towards longer wavelength without showing any other peak. In the case of hydroperoxide also, the absorption tail is structureless beyond 300nm. It is therefore unlikely that these two groups could be the cause of the maxima identified in Fig 5.20. Isolated unsaturation is also very unlikely to

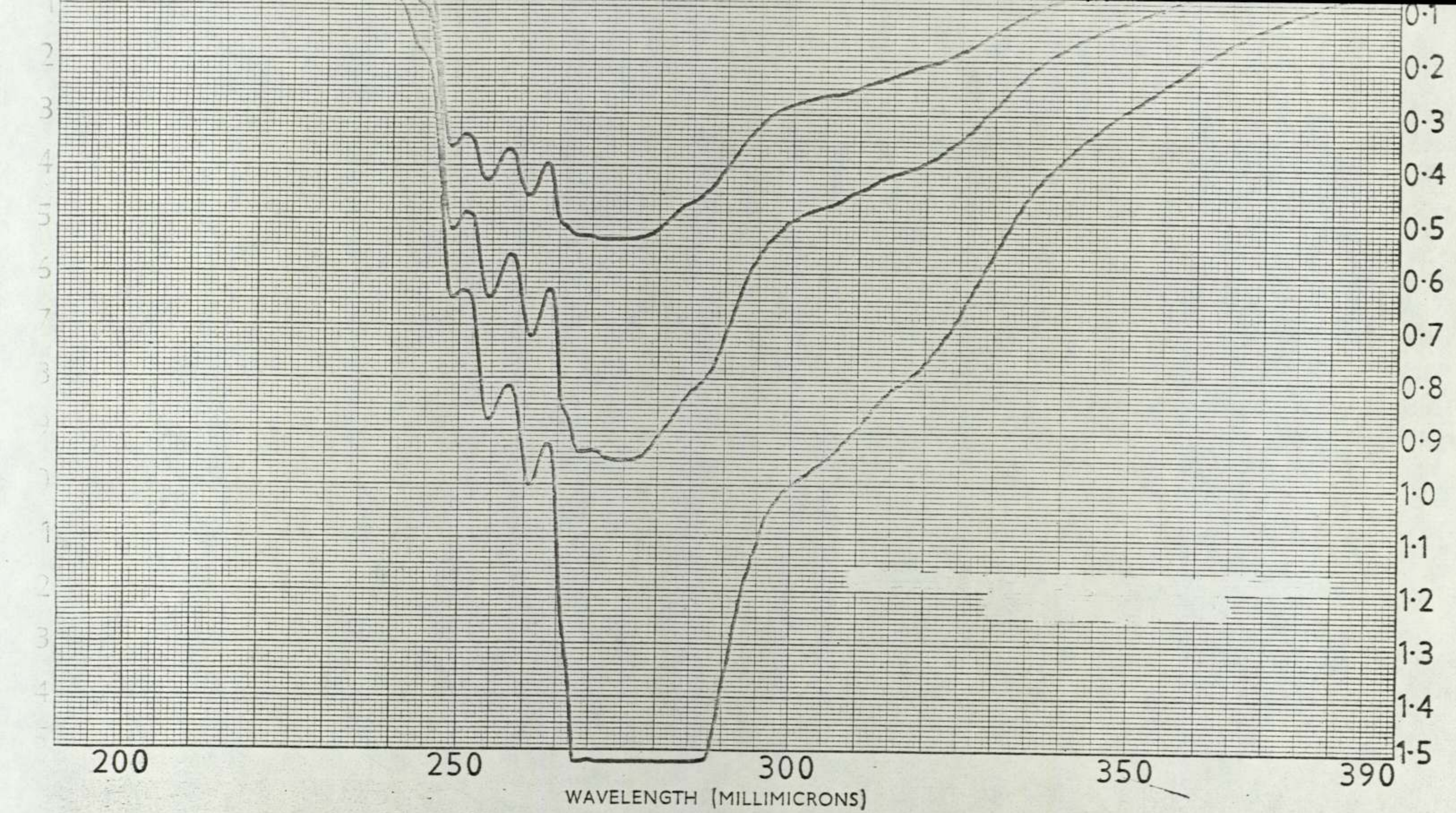


Fig 5.20 UV spectra of dark brown gel in choloroform

absorb in this region. However, the situation becomes different for sequences of conjugated double bonds. These show a succession of absorption maxima in the UV, the spectral position of which shifts towards the red with increasing conjugation. Spectrographic analysis carried out by various authors on unsubstituted aliphatic polyenes show that four conjugated double bonds gave peaks in the solar spectral region (see Table 5.1.).

TABLE 5.1.

Ultra Violet Maxima of conjugated polyene of type $H\text{-}(CH{=}CH)_n\text{-}H$

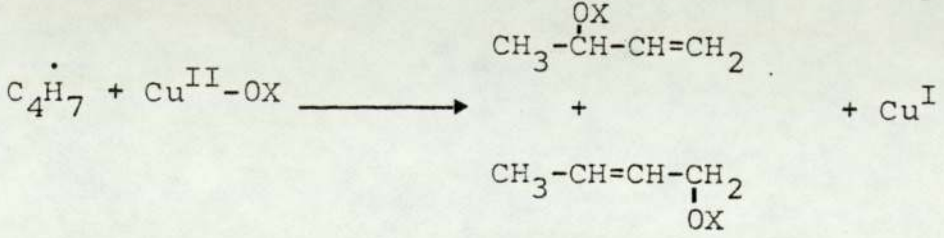
Spectral position of the maxima, in nm (from Sodenheimer)(149)

n									
3 Trienes	240	248	257	268					
4 Tetraenes				267	278	290	304		
5 Pentaenes					279	290	304	317	334

Such sequences exist in the UV spectrum of the brown gel (D). This therefore suggests that the humps and shoulders observed in UV spectra of gel (D) are due to conjugated carbon-carbon double bonds. Absorption maxima at 243, 249, 254, 267, 268, 275, 286 and 305nm 320 see Fig 5.20 indicate presence of trienic and tetraenic unsaturation. Other humps above 300nm may indicate the presence of highly unsaturated carbonyl compounds. An extra absorption band centred at 261nm is also evident which may be attributed to the coordinated double bond in agreement with the IR spectra of the gel (D) Fig 5.17.

5.5.1. DISCUSSION

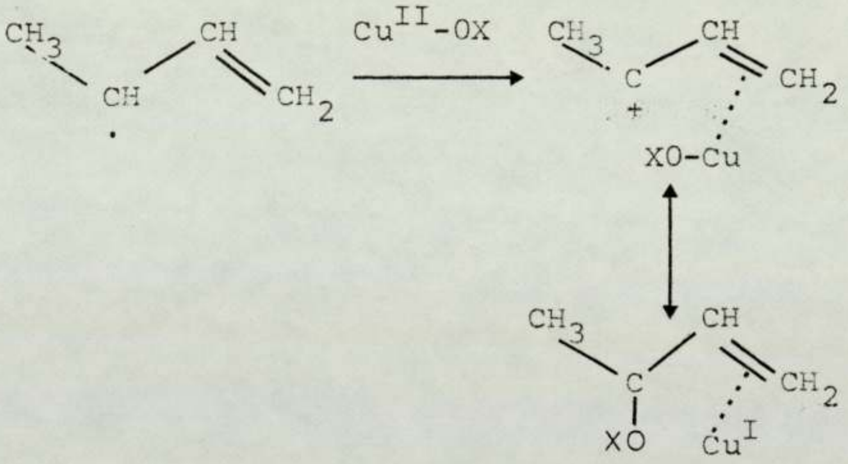
The UV spectrum of the dark brown gel dissolved in chloroform , indicates the presence of mixtures of triens and tetraenes. These functional groups absorb strongly in the UV region which tails into the visible region of the spectrum. The browning of the paint containing verdigris may therefore be considered to be due mainly to the formation of highly unsaturated double bonds and in part to the formation of a Cu^{I}- double bond complex similar to that reported by Kochi(150). Kochi found that alkyl radicals such as n-butyl, sec butyl and tertiary-butyl radicals which all contain a readily available β - hydrogen atom, give alkene as the principle (and often exclusive) products. He also reported that allylic radicals, on oxidation yielded substitution products. For example



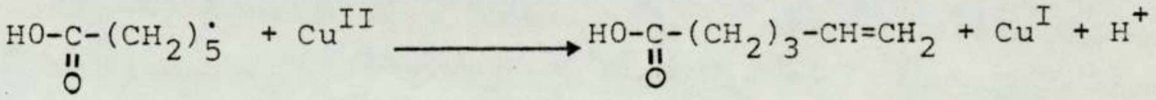
$$\dot{C}_4H_7 + Cu^{II}\text{-}OX \longrightarrow \begin{array}{c} CH_3\text{-}\overset{OX}{CH}\text{-}CH{=}CH_2 \\ + \\ CH_3\text{-}CH{=}CH\text{-}\underset{OX}{CH_2} \end{array} + Cu^{I}$$

where OX can be RCO, H.

The butenyl radical gives a 95% yield of α methyl allyl substituted isomers. The composition is independent of temperature or solvent. He postulated that the formation of high yields of the latter is due to the ability of Cu^{I} to coordiate to the end chain double bond. The following transition state, comprising electron transfer and a ligand transfer through carbonium ion was postulated.

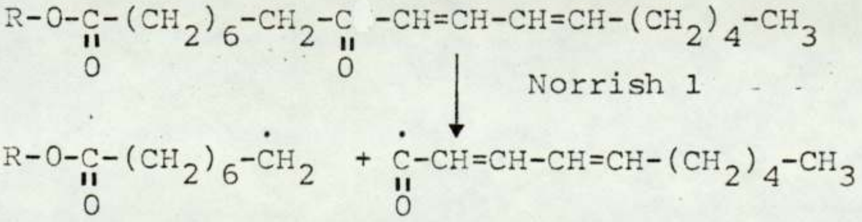


It has been shown that the 5-carboxypentyl radical can be directly intercepted by Cu^{II} to give ω-hexanoic acid



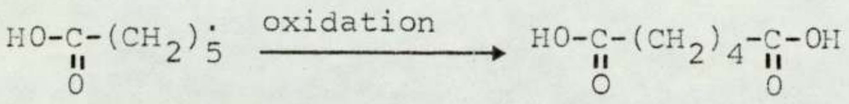
$$HO-\underset{\overset{\|}{O}}{C}-(CH_2)_5^{\bullet} + Cu^{II} \longrightarrow HO-\underset{\overset{\|}{O}}{C}-(CH_2)_3-CH=CH_2 + Cu^{I} + H^{+}$$

Such alkyl radicals are very abundant during the photo-oxidation of drying oils, and in the absence of Cu^{II}



$$\begin{gathered}R-O-\underset{\overset{\|}{O}}{C}-(CH_2)_6-CH_2-\underset{\overset{\|}{O}}{C}-CH=CH-CH=CH-(CH_2)_4-CH_3\\ \Big\downarrow\ \text{Norrish 1}\\ R-O-\underset{\overset{\|}{O}}{C}-(CH_2)_6-\dot{C}H_2 + \underset{\overset{\|}{O}}{\dot{C}}-CH=CH-CH=CH-(CH_2)_4-CH_3\end{gathered}$$

and presence of oxygen 2-hexanoic acid would lead to the formation of corresponding acid



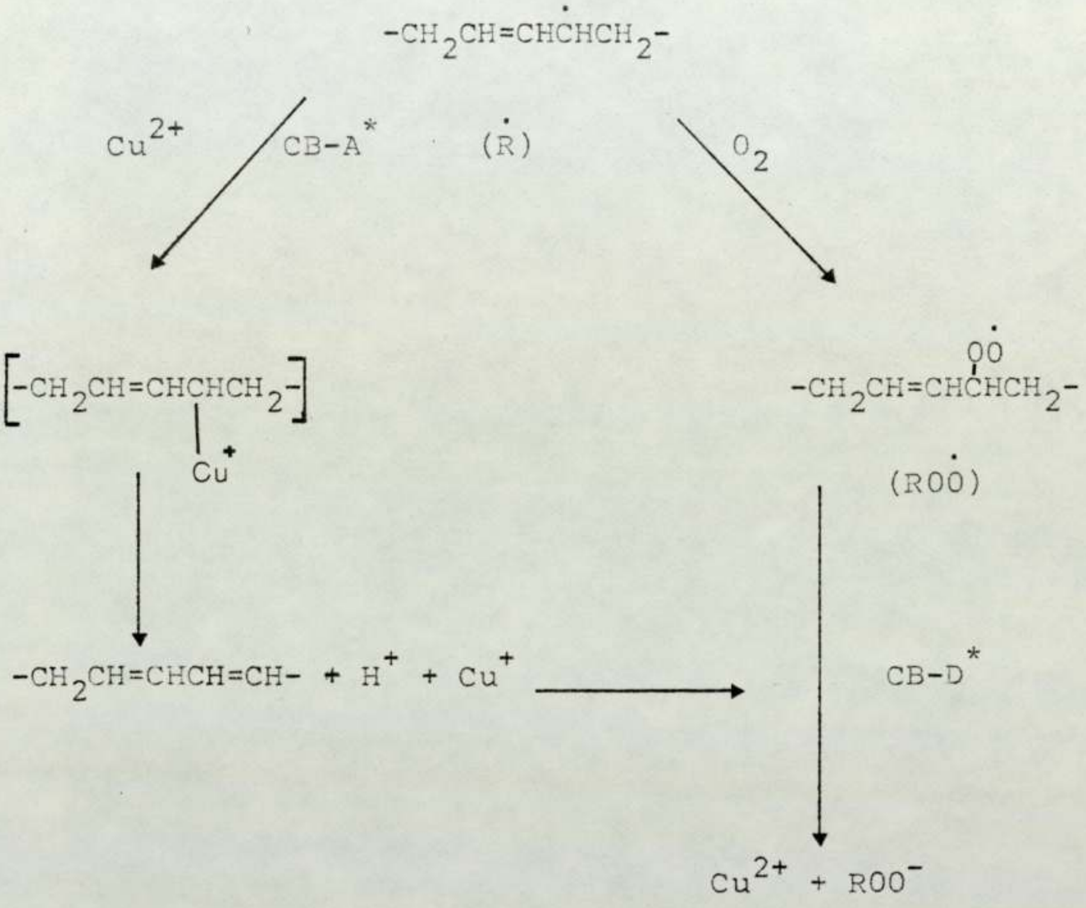
$$\mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_5^{\bullet}} \xrightarrow{\text{oxidation}} \mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}(CH_2)_4{-}\underset{\underset{O}{\|}}{C}{-}OH}$$

The dissimilarity of the scission products of verdigris pigmented film with the control as observed in Figs 5.10 5.11 is thus satisfactorily explained. It should be mentioned that the formation of conjugated unsaturation is evidenced for a high concentration of alkyl radicals during oxidation and hence diffusion control of oxygen migration. Alkylperoxy radicals are relatively strong oxidants, and are able to react with the reduced form of the metal complex. Cu^{I} may also react with alkylperoxy radical to form a non-radical product.

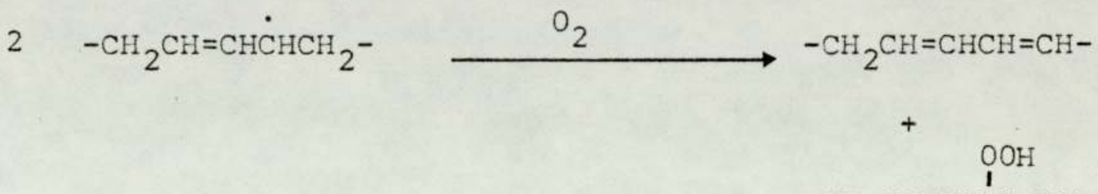
$$\mathrm{RO\dot{O}} + \mathrm{Cu^{+}} \longrightarrow \mathrm{RO\bar{O}} + \mathrm{Cu^{2+}}$$

This reaction may be competing with the normal bimolecular termination step involving peroxy radicals which in turn effects the chain lenth of the autoxidation.

The following cyclic mechanism may be involved in the photo stabilisation of paint films by copper ions. This process is also the cause of the brown discolouration occurring in paintings containing the pigment verdigris which results from the formation of extended conjugation in the polymer film.



<u>Overall</u>



$$2\quad -CH_2CH=CH\dot{C}HCH_2- \xrightarrow{O_2} -CH_2CH=CHCH=CH- + -CH_2CH=CH\overset{OOH}{C}H-CH-$$

* CB-A = chain-breaking (acceptor mechanism)
CB-D = chain breaking (donor mechanism)

CHAPTER 6

EFFECT OF VERMILION ON OXIDATION OF LINSEED OIL

6.1. INTRODUCTION

Vermilion is the standard name given in England and the United States to the red artists' pigment based on artificially made mercuric sulphide, HgS. The mineralogist and crystallographer have given the common red crystalline form of mercuric sulphide the name cinnabar, which is reserved for the specific crystal structure of the natural mineral. The name cinnabar is reputedly of Indian orgin, and was sometimes used to designate "dragon's blood", a red resin. Cinnabar, is the principal ore of the metal mercury and is distributed fairly widely, but not abundantly. Cinnabar is mentioned by the 4th century Greek writer, Theophrastus, the author of De Lapidibus, but Caley and Richards, the translators, say(151) that cinnabar was known in Greece as early as the sixth century B.C. and perhaps in Asia minor long before that.

Mercuric sulphide exists in two enantiomorphic modifications, the red cinnabar (α-HgS) and the black metacinnabar (α'-HgS). An unstable red form (β-HgS) has also been reported in laboratory synthesized material(152). The interrelationship between these crystalline forms is summarized in Scheme 6.1.

Scheme 6.1.

$$\underline{\chi'\text{-HgS}} \rightleftarrows \underline{\alpha\text{-HgS}}$$

Meta cinnabar	Cinnabar
Colour: Black	Colour: Red
Specific gravity: 8.176	Specific gravity: 7.71
Electrically conducting	Nonconductor
Formed principally from acid solution	Formed principally from solutions of alkali sulphide
Stable above 344±2°C	Sublimes at 580°C

$\underline{\beta\text{ - HgS}}$

Unstable form not found in nature

Colour: Red

Specific gravity: 7.20

Formed from thiosulphate and sodium mercuric chloride by Allen and Grenshaw(152) possibly also observed by Eibner(153).

Although it is the red form that is required by artists, most methods of synthesizing the compound first yield the black form, which must be sublimed or digested to produce the red variety. Detailed studies by Eibner(153) in 1912-18 showed that during digestion in alkali, polysulphides facilitated the transition of the black to the red, but that impurities in the digestion liquor, particularly thiosulphate, led to considerable instability of the red form. Both rubbing (trituration) and exposure to light promote the conversion to meta cinnabar. In controlled experiments darkening has been found to be more rapid in paints that allow the light to penerate below the surface. Plesters, however, states (private communication Miss J. Plesters, National Gallery) that most of the darkening of vermilion that she has encountered occurs in tempera rather than oil. One of the most striking examples she reported appeared in the red-painted borders of the interior decoration in a late Byzantine church in Cyprus, where the light coming from small windows was low. There was obvious darkening in the powdery distemper paint whereever the surface was turned toward the light, but it remained bright-red in the under cutting of the moulding. She also mentions that just perceptible darkening is found in one or two areas of vermilion in the Raphael cartoons in the Queen's collection. An extensive review of the darkening phenomenon has been prepared by Feller(154). In spite of the fact that vermilion is a sulphide, it is remarkably unreactive with other pigments. In oil medium, it was commonly used with lead white to produce flesh tints with no sign of formation of black lead sulphide.

Vermilion was considered to be a light-fast pigment by the German Society for promotion of Rational painting technique(155) and the United States commercial standard CS98-62(156), yet authorities today do not generally consider it to be a 'permanent' pigment, for it has been known since Roman times that speciments may darken in an apparently capricious manner. Numerous examples in paintings, nevertheless, testify to its essential stability, and samples have been observed to withstand exposure to sunlight for at least 10 years(153). Photograph numbers 6.1 and 6.2 show two examples of usage of HgS in old paintings.

In this work attempt will be made to examine the behaviour of HgS on the paint media under day light of the laboratory and the artificial lighting of the UV cabinet. In this connection attempts will also be made to elucidate the basic mechanism involved.

Photograph 6.2.
Oil painting, Bacchus and Ariadne by Titian.
Detail showing the vermilion red scarf of Ariadne.
Reproduced by courtesy of the Trustees of the
National Gallery, London.

Photograph 6.1.
An example of the use of vermilion in
a Chinese Handscroll, 'Tribute Horse
and Groom' by Chao Yung, 1289-c.1360.
Dated 1347.Detail. Courtesy Freer
Gallery of Art, 45.32.

6.2. EFFECT OF HgS ON THE RATE OF OXIDATION OF LINSEED OIL

6.2.1. EFFECT OF HgS ON THE INITIAL RATE OF FORMATION OF CONJUGATED DIENE HYDROPEROXIDE

The progress of UV accelerated oxidation can be followed by observing the increase in the UV absorption at about 235nm due to the formation of conjugated diene hydroperoxide. Fig 6.1. shows the variation of this absorbance with time of photo-oxidation, (UV cabinet S/B combination) in the presence and absence of HgS. The samples were thin films of unknown but similar thickness deposited on quartz microscopic slides. The initially slow rate of formation, and relatively low concentration of this absorption of pure oil was replaced by a faster rate and higher concentration when HgS was present.

6.2.2. EFFECT OF HgS ON THE RATE OF OXYGEN ABSORPTION OF OIL

The measurement of the relative degrees of autoxidation and photo-oxidation has been obtained from the rates of oxygen uptake whilst the light was switched on and off. The details of apparatus, recording and procedure is given in Section 3.7. It is seen in Fig 6.2. that after 19.5 hours oxidation (in the absence of UV light), linseed oil absorbs 4.6. oxygen/ml of oil, whereas it appears that no oxygen was absorbed when HgS was present. Similar observations were made under practical conditions. HgS pigmented paint film was touch-dry after 7 days of spreading, whereas unpigmented thin film spread on glass plate was dry in about

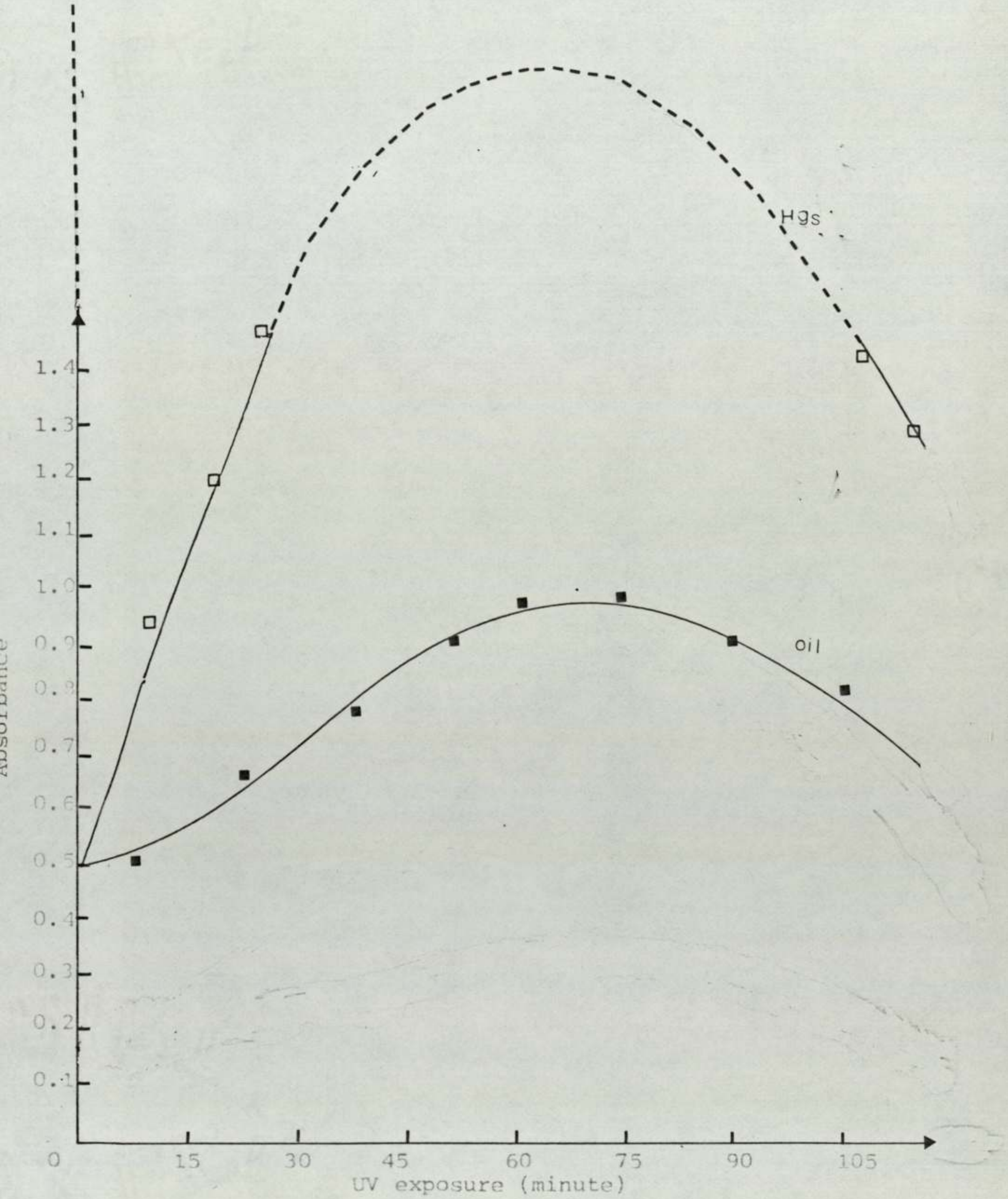


Fig 6.1. Variation of peak at 235 nm in the presence and absence of HgS

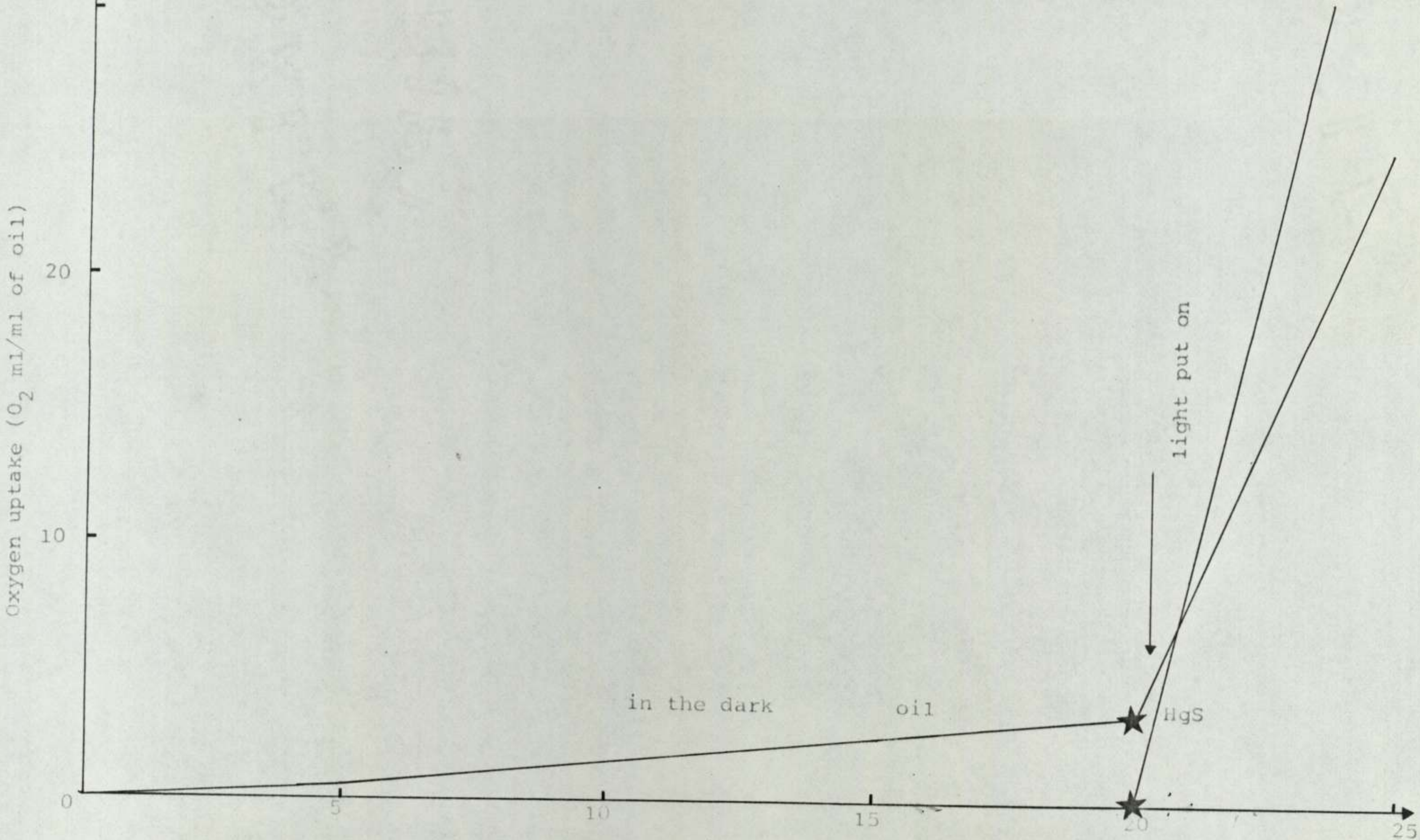


Fig. 6.2. Effect of vermilion on the rate of oxygen absorption in the presence and absence of light

3 days. Both glass plates were located in diffuse daylight of the laboratory. However, when the UV light was switched on after 20 hours, the relative rates of oxygen absorption were reversed, and the former became a powerful photo-sensitizer relative to the control. Fig 6.3. compares the rate of photo-oxidation of the oil with and without pigment immediately after mixing.

6.2.3. EFFECT OF HgS ON THE RATE OF PHOTODEGRADATION OF OIL AS MONITORED BY THE DECAY OF $^{-}CH_2$

The IR spectral changes of linseed oil with and without HgS was followed by the sodium chloride disc technique see Chapter 3.3.1.1.2. The IR spectra showed similar changes in functional groups. The rate of decay of $-CH_2-$of paint media is related to the rate of errosion of the dried oil surface see 3.3.1.1.2. This means that the faster the decay of this functional group, the faster will be the rate of physical destruction of paint media. Fig 6.4. shows the decay of CH_2 in the presence and absence of the pigment. It can be seen that HgS accelerates the rate of degradation of the paint medium. Fig 6.5. also shows the decay of $\log\Delta CH_2$ with respect to time.

6.2.4. EFFECT OF HgS ON THE RATE OF FORMATION OF SCISSION PRODUCTS

Linseed oil with and without pigment were spread in duplicate on glass plates. The vermilion paint contained 60% of pigment. One set of film was kept in the diffuse

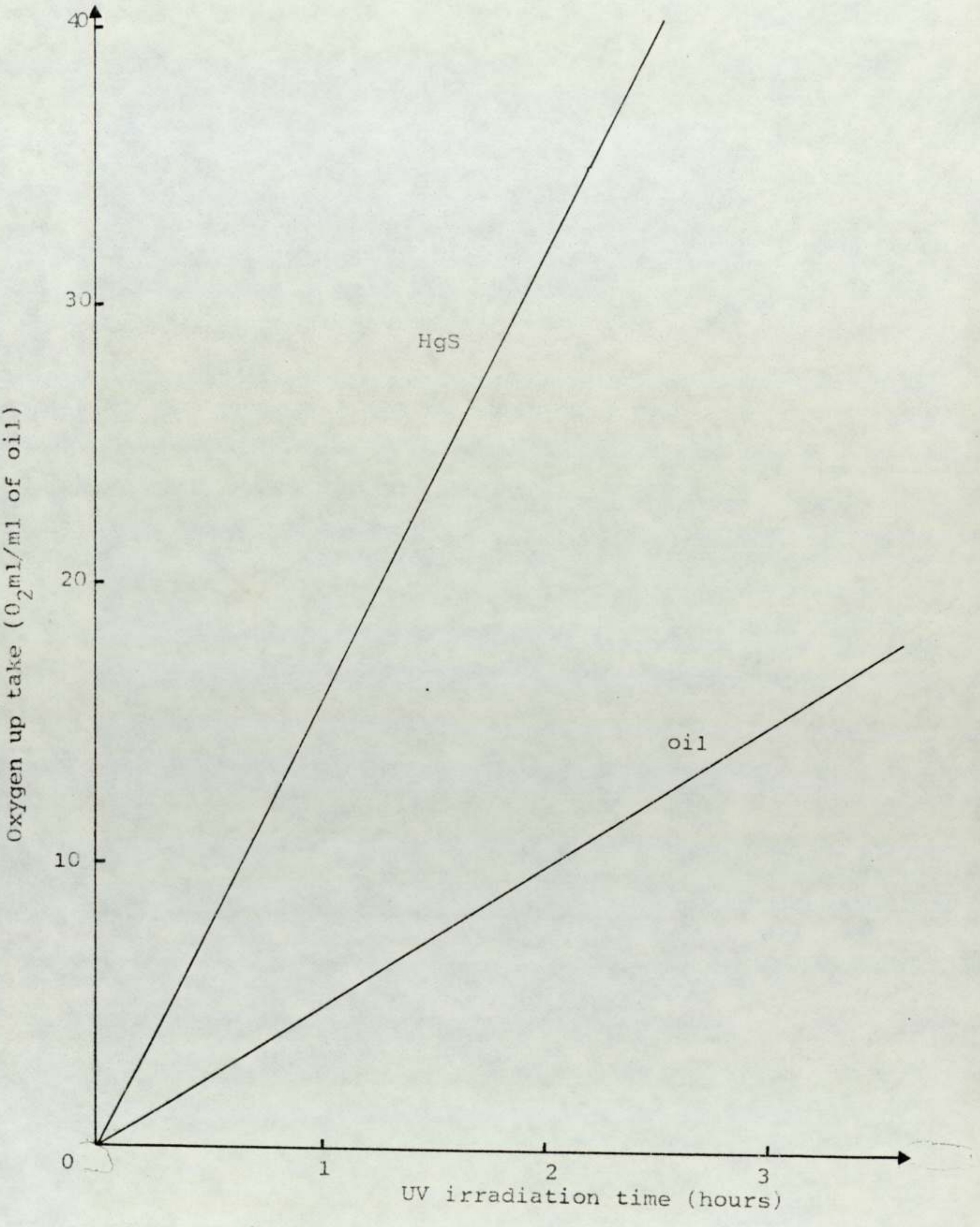


Fig. 6.3. Rate of absorption of oxygen for pure oil and oil + HgS in the presence of UV light

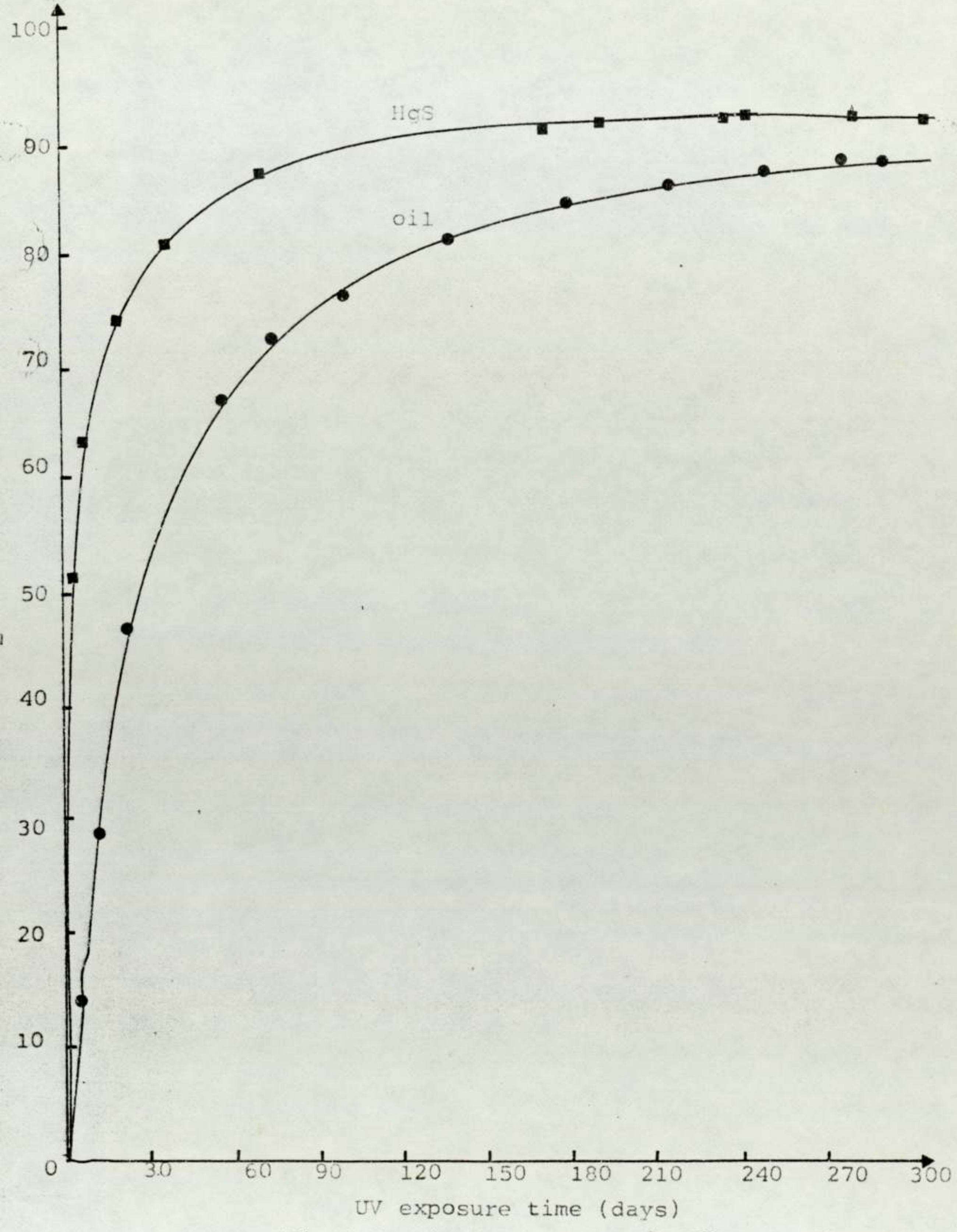


Fig 6.4 Disappearance of CH_2 at $2930cm^{-1}$ of dried oil with and without vermilion

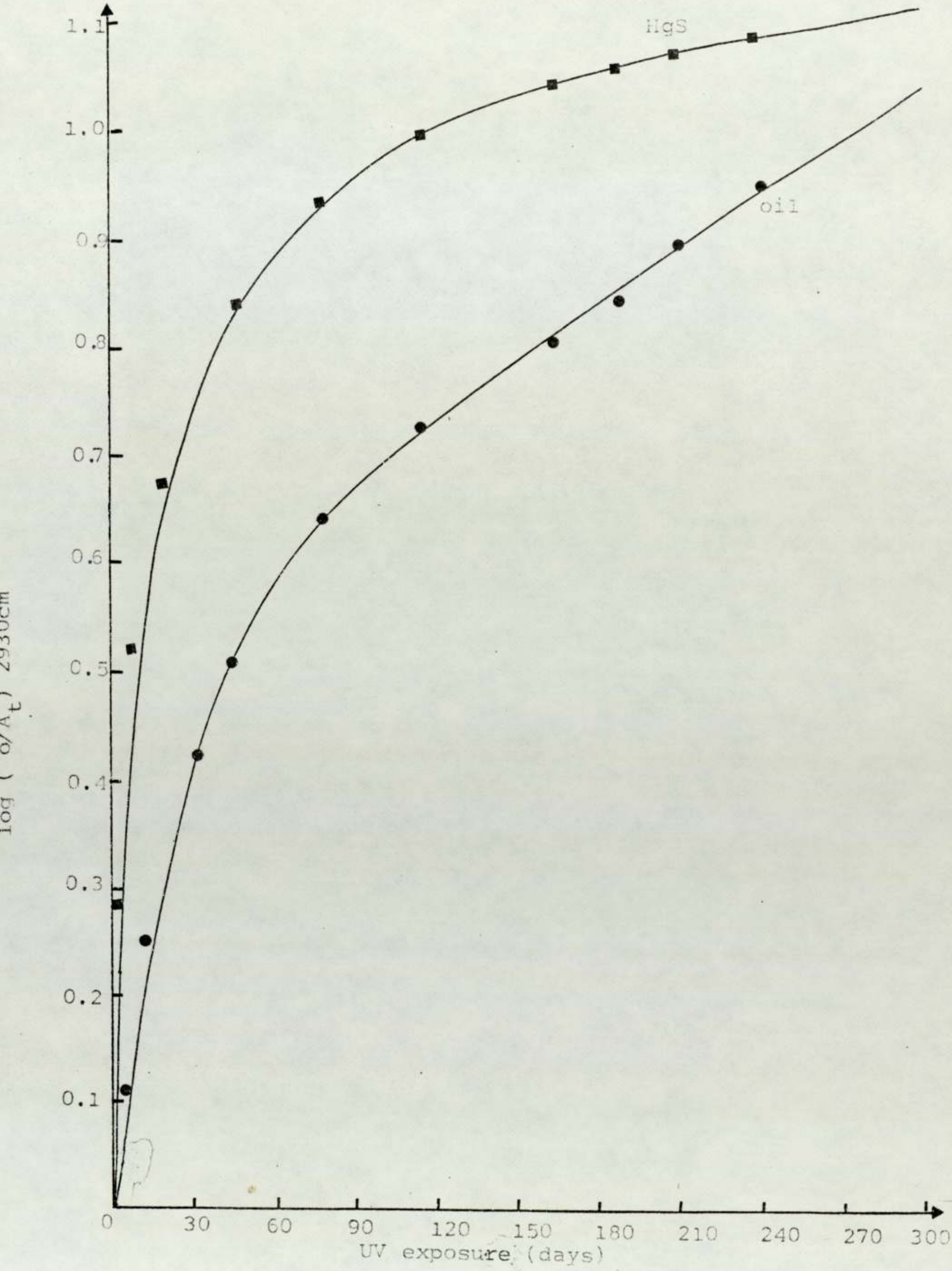


Fig 6.5. logΔCH_2 at 2930cm^{-1} of dried oil with and without mercuric sulphide

light of the laboratory, while the other, when touch dry after a week, was placed in the UV cabinet.

Fig 6.6. and Fig 5.11. compares the G.L.C. chromatograph of dried pigmented film and non-pigmented film of which had been kept in diffuse light in the laboratory for 60 days. It is clear that the main scission products are essentially similar. The G.L.C. chromatographs of pigmented and nonpigmented non UV irradiated paints are not only similar to each other but also similar to the UV irradiated pigmented film and dried oil sample Figs.6.7 and 4.7. The amount was estimated by dividing the concentration of scission product by that of palmitic acid. Fig 6.8. compares the rate of formation of the methyl ester of C_9 dicarboxylic acid with that of pure linseed oil in the presence and absence of UV light. It is seen that HgS accelerates the rate of formation of scission products of the samples kept in the UV cabinet and the one kept under the ambient condition of laboratory.

6.2.5. DEGRADATION PROCESS IN HgS - PIGMENTED PAINT FILMS ON EXPOSURE TO UV AND NATURALLY WEATHERING

So far the results show that HgS accelerates the degradation process under UV light as evidenced by rapid formation of conjugated diene hydroperoxide Fig 6.1. and rapid oxygen absorption Fig 6.3. This is associated with the rapid formation of scission products at a given time Fig 6.8. compared to unpigmented film and consequent rapid weight loss as a result of high scission product formation Fig 6.4.

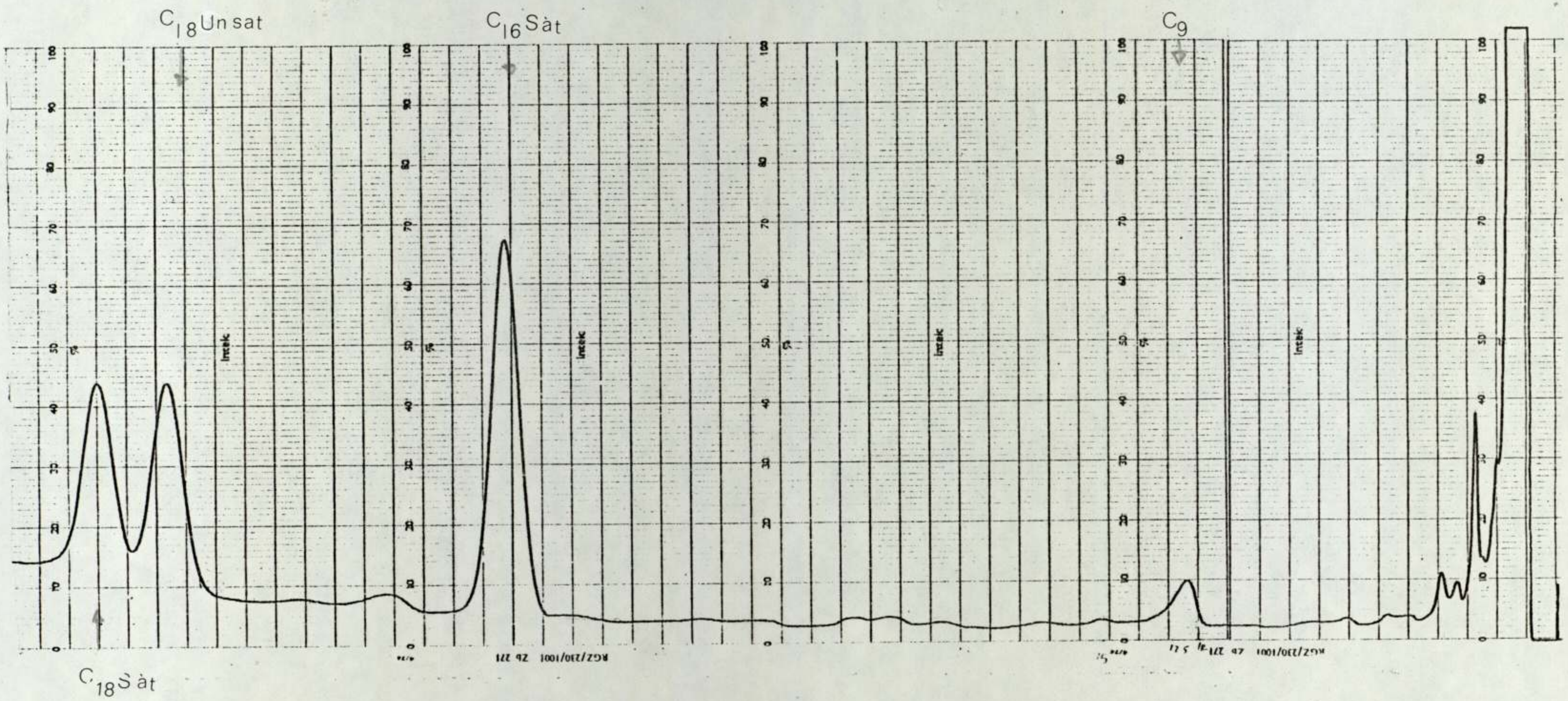


Fig 6.6. Gas chromatogragh of vermilion pigmented paint film placed in laboratory for 60 days.

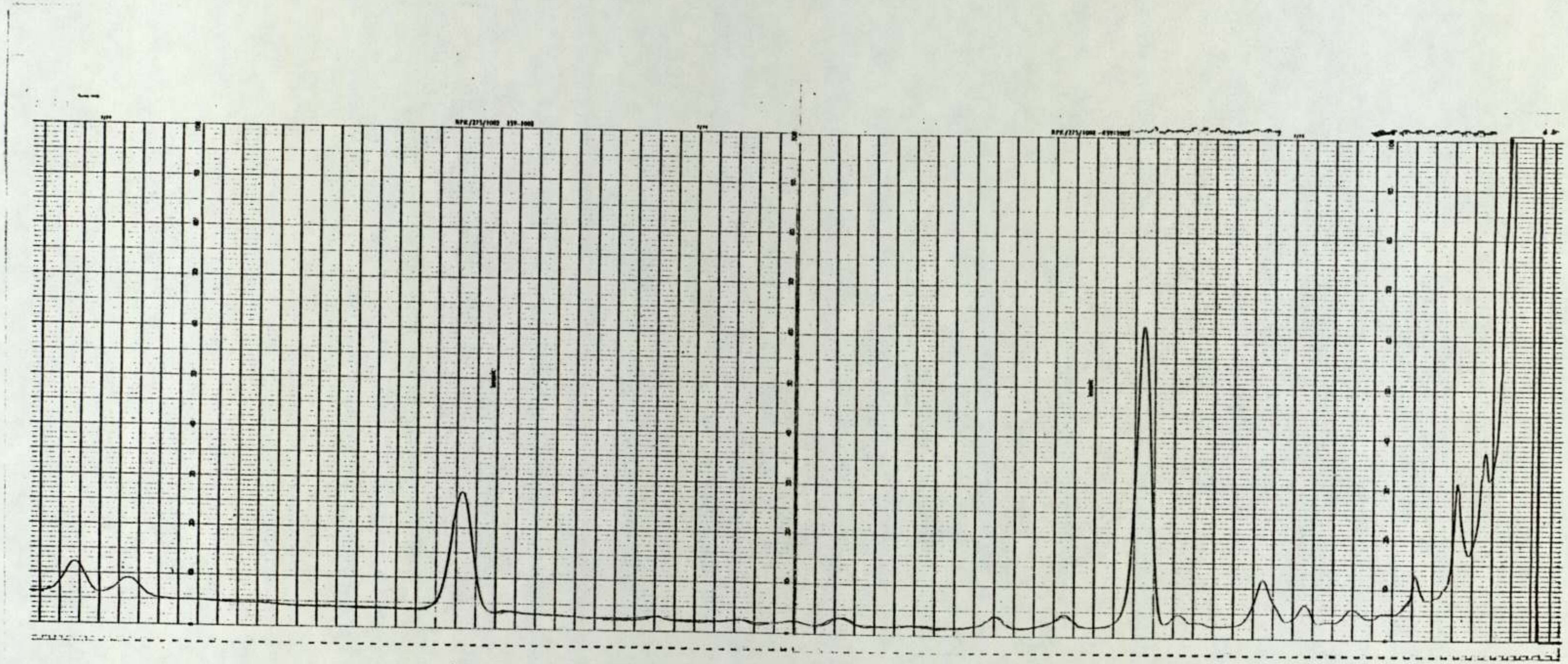


Fig 6.7. Gas chromatograph trace of vermilion pigmented paint film irradiated in UV cabinet for 105 days.

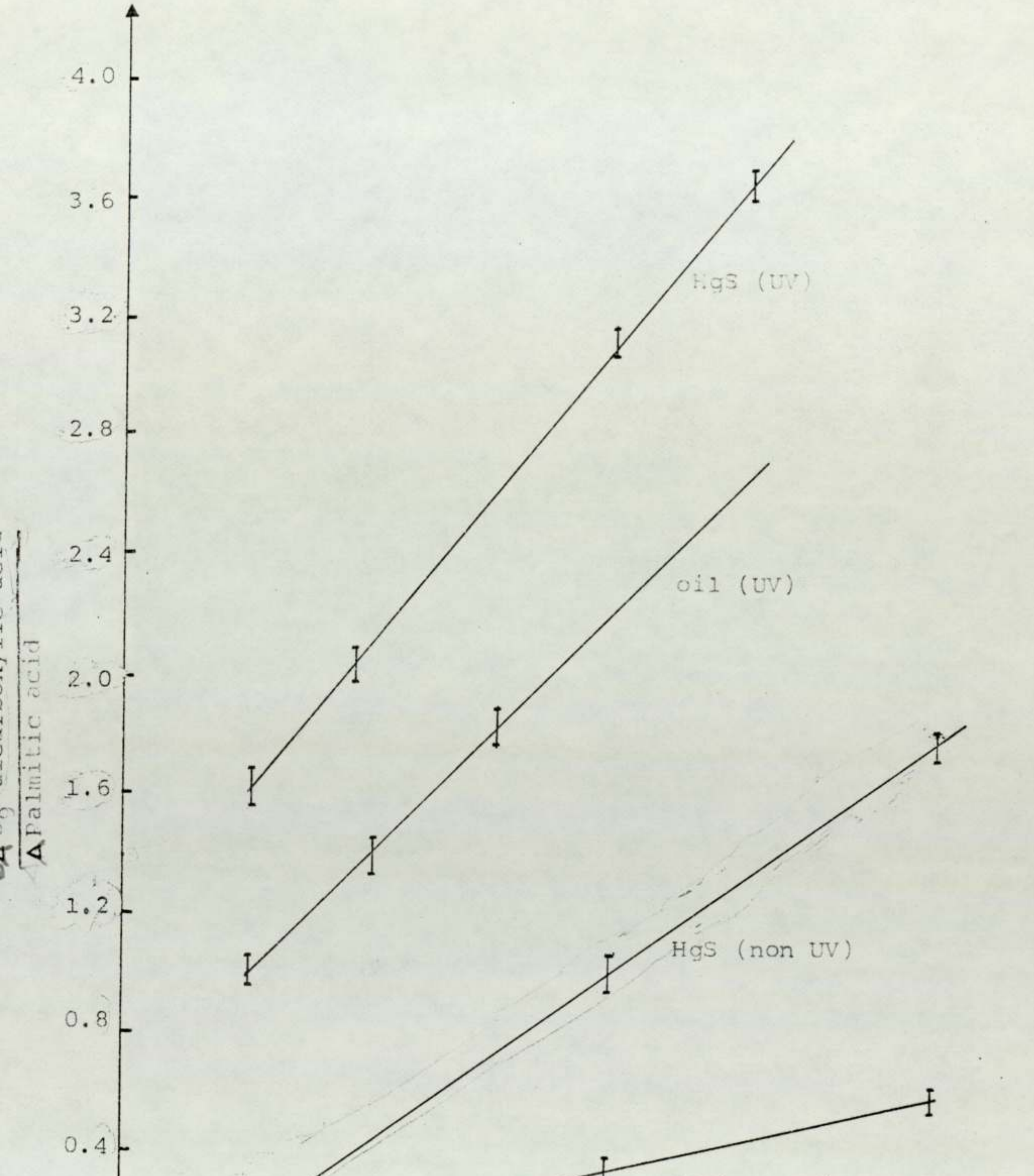
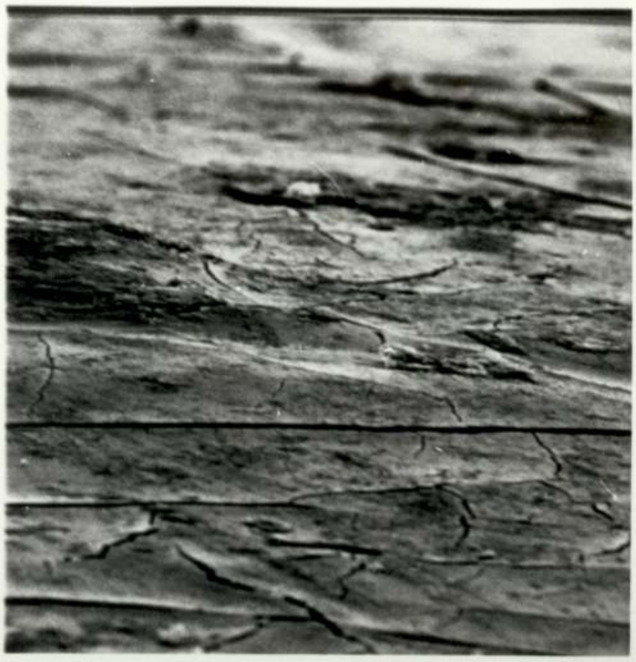


Fig 6.8. Effect of vermilion on the rate formation of scission product of dried oil in the presence and absence of UV light

These are all reflected in the physical appearence of the paint film, which is very soft and tacky probably due to the plastisizing effect of products. The scanning electron microscope of the paint surface also indicates the irregularity and cracking of the surface photograph 6.3. Some holes are also observed from the photograph 6.4.; the holes appear to be associated with the heavy degradation of the binder surrounding the HgS particles. There are therefore essentially two largely independent mechanisms which takes part in the degradation process.

1. Degradation of the binder by the short wave portion of the incident radiation.
2. Degradation of the binder due to the sensitization activity of the HgS.

Photograph 6.5. was taken of the surface of a paint film smeared on a glass plate. The plate was kept in the indoor laboratory under ambient conditions. The photographs were taken by an optical microscope after 60, 180, 360, 480 days of ageing. A white crystaline material is apparent in the left hand corner of the photographs which grows on ageing. Photograph 6.6. was also taken of the surface of paint exposed in the UV cabinet. The photographs were taken after 2, 120 and 240 days of UV irradiation. It is interesting to note that the white material which was present in the naturally weathered paint are not markedly apparent in UV irradiated paints, instead darkening of the pigment has occurred.



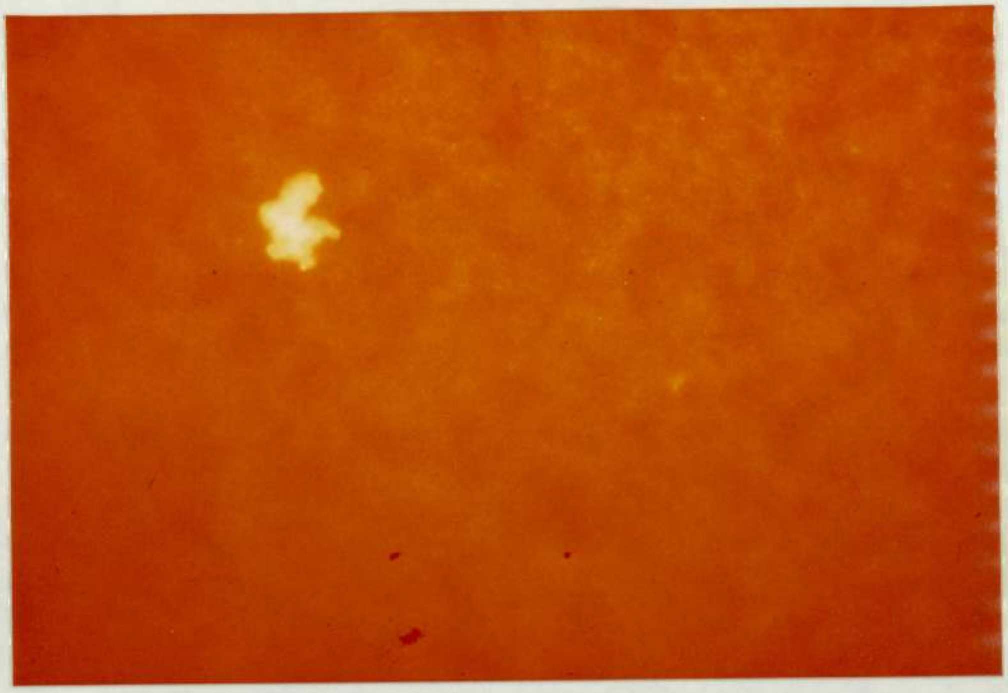
Photograph 6.3. The scanning electron micrograph of a paint sample containing vermilion.

x 2000

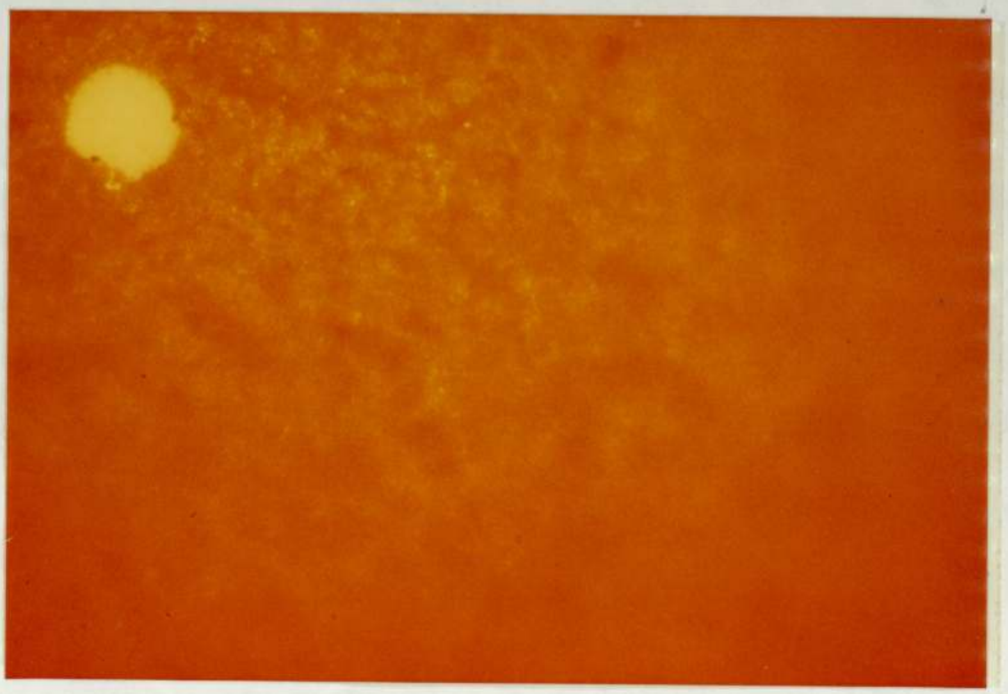
Photograph 6.4. The scanning electron micrograph of a paint sample containing vermilion

x 10,000

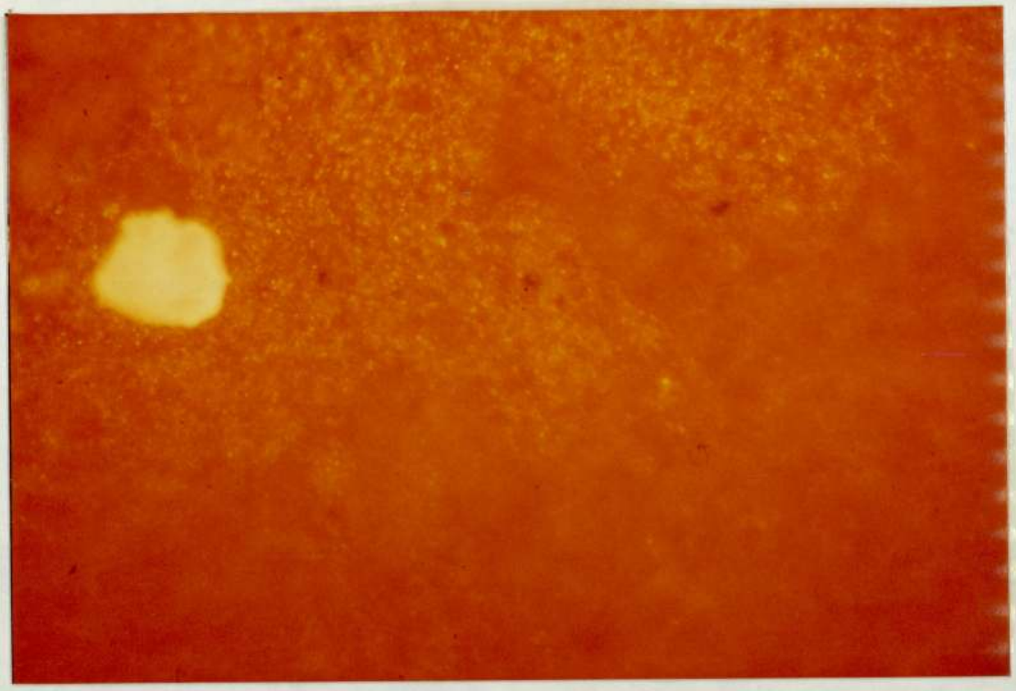
Photographs 6.5.
Taken from surface of paint film kept in diffused light of the laboratory after
Magnification = x 625



(a) 60 days



(b) 180 days

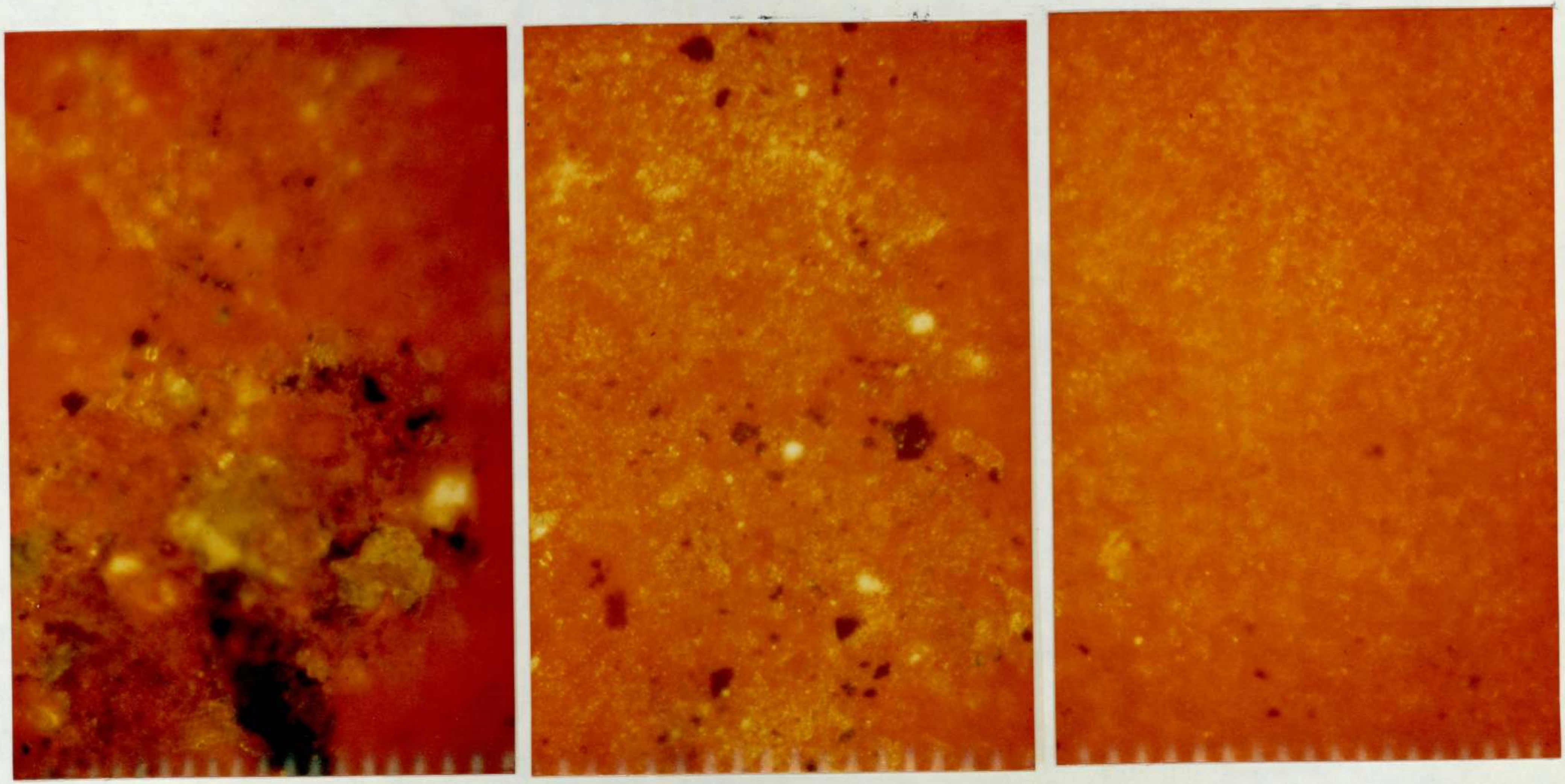


(c) 360 days

(d) 480 days

Photographs 6.6.

Taken from the surface of paint film after
(a) 2, (b) 120, (c) 240 days of UV irradiation



(c) (b) (a)

In conclusion so far, it can be said that this brilliant red coloured pigment appears to behave as an anti-oxidant in the absence of UV light during the drying (cross linking) of linseed oil as evidenced by oxygen absorption experiments Fig 6.2., and by direct observation of paint samples spread on a glass plate. However scission product examination of uncross-linked paint showed higher amount of scission product than the one in the absence of pigment.

In the presence of light HgS behaves as a pro-oxidant which leads ultimately to the rapid physical deterioration of the paint medium. The following specific conclusions can be drawn,

1. There is a good correlation between the decay of $-CH_2-$ of the binder (related to the weight loss) and the formation of scission products.

2. The techniques used suggest that the mechanism of the UV and laboratory aged paint are the same.

3. HgS acts as a strong photosensitizer.

6.3. FUNDAMENTAL STUDIES ON THE MECHANISM OF HgS

Studies on the photosensitizing activity of pigments in commercial polyolefins and paints have been mainly concerned with white pigment. Titanium dioxide (TiO_2) is the most widely studied of these, since it is technically outstanding in many respects as a pigment. It has been recently demonstrated by Pappas(87) and co-worker, that singlet oxygen and hydrogen peroxide are both important in the sensitization phenomena by titania pigments and in view of the similarity of their behaviour to that of mercuric sulphide, the possibility of their formation in this case was investigated.

6.3.1. HYDROGEN PEROXIDE FORMATION IN HgS/H_2O SYSTEM

6.3.1.1. EXPERIMENTAL

Irradiation were carried out in a 100ml two layer beaker, with an oxygen inlet. A General Electric par- 38, H 100PSP 38-4, 100W light sources was mounted above the beaker and the light was filtered through a 2mm pyrex cover glass place on the top of the beaker, to eliminate wavelengths shorter than 380nm. 0.5g of HgS was dispersed in 50ml doubly distilled water by a small plastic covered magnetic stirrer, and subsequently was allowed to settle on the bottom of the beaker. Oxygen was passed through the system by a narrow syringe at a flow rate of 10-15ml/minute. The reaction temperature was maintained at about 15°C by the continuous passage of tap water through the beaker jacket. During the irradiation, aliquots were removed periodically and filtered through a fine sintered glass filter tube to remove any suspended pigment particles. The aliquots were assayed for hydrogen peroxide content by the following method(158).

To a 2.0ml aliquot (placed in a quartz UV cell) was added:

1. 0.5ml of 0.3ml potassium phosphate buffer, PH 7.8
2. 0.5ml of 0.6mM 0-dianisidine dihydrochloride (caution: cancer suspect agent)
3. 0.1ml of a 0.01% aqueous solution of horse radish peroxidase, buffered with potassium phosphate.

The presence of hydrogen peroxide was qualitively indicated by the formation of reddish colour in the sample immediately after the addition of the peroxidase solution to the irradiated sample. Qualitative measurements were made with a UV spectrophotometer at 450nm as shown in Fig 6.9. A reference standard curve was plotted Fig 6.10. and the optical density at this wave length was converted into hydrogen peroxide concentration by reference to the reference standard curve.

6.3.1.2. RESULTS

Fig 6.11a indicates the rate of formation of H_2O_2 by HgS under conditions mentioned in experimental Section 6.3.1. The rate of formation of H_2O_2 was decreased by decreasing the oxygen flow rate (5ml/minute) through the system Fig 6.11b. Curve 6.11c indicates the rate of formation of H_2O_2 when the above system was placed in the day light of laboratory (i.e. absence of a UV source and no oxygen was bubbling through the system). Curve 6.11d indicates rate of formation of H_2O_2 under the condition 6.11c when 1.8×10^{-3}mol 1,4-diazabicyclo-2,2,2,-octane, (DABCO) was added to the system. Curve 6.11e represents the rate of formation of H_2O_2 under condition

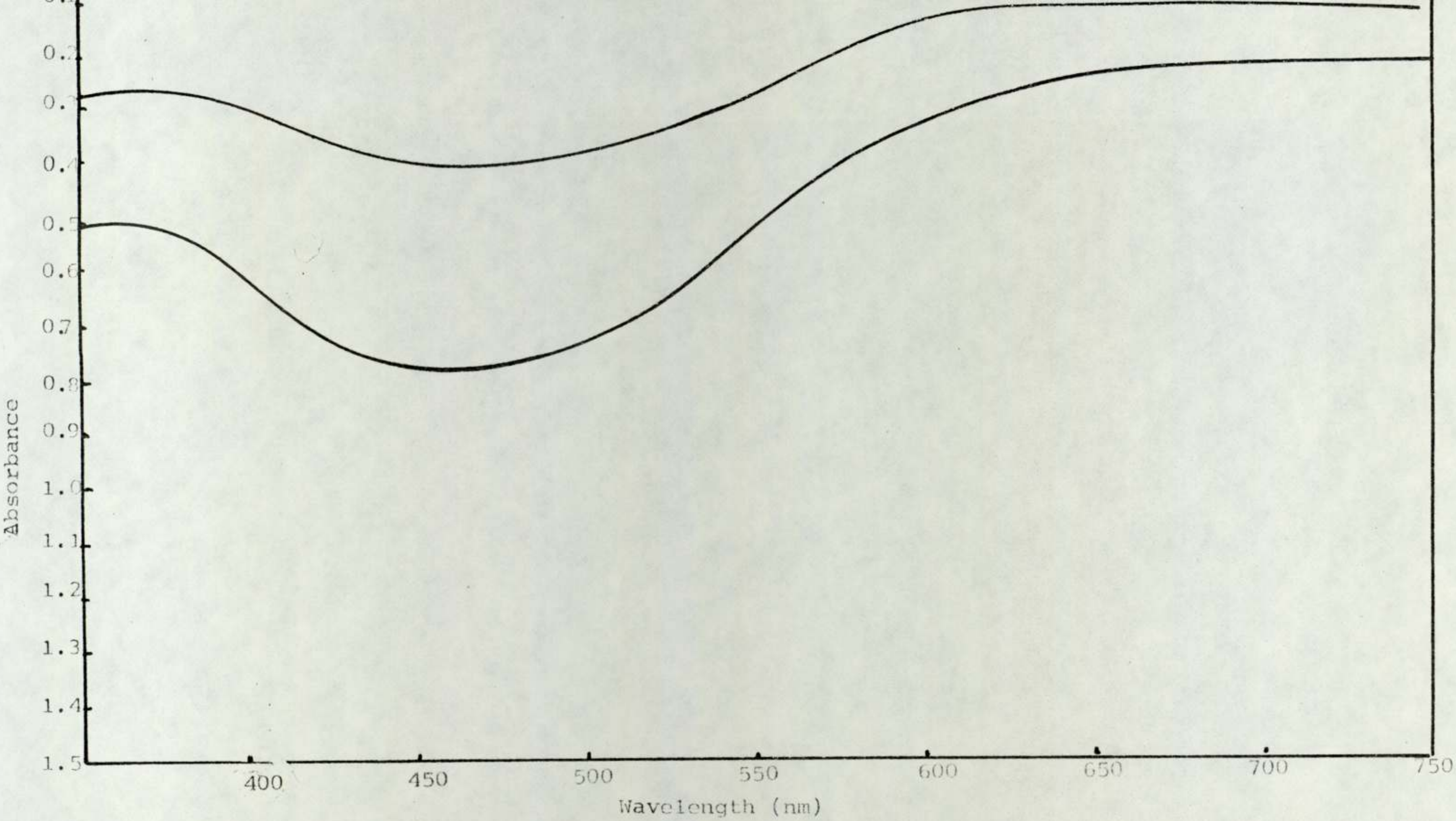


Fig 6.9. UV spectral of red solution indicating presence of hydrogen peroxide

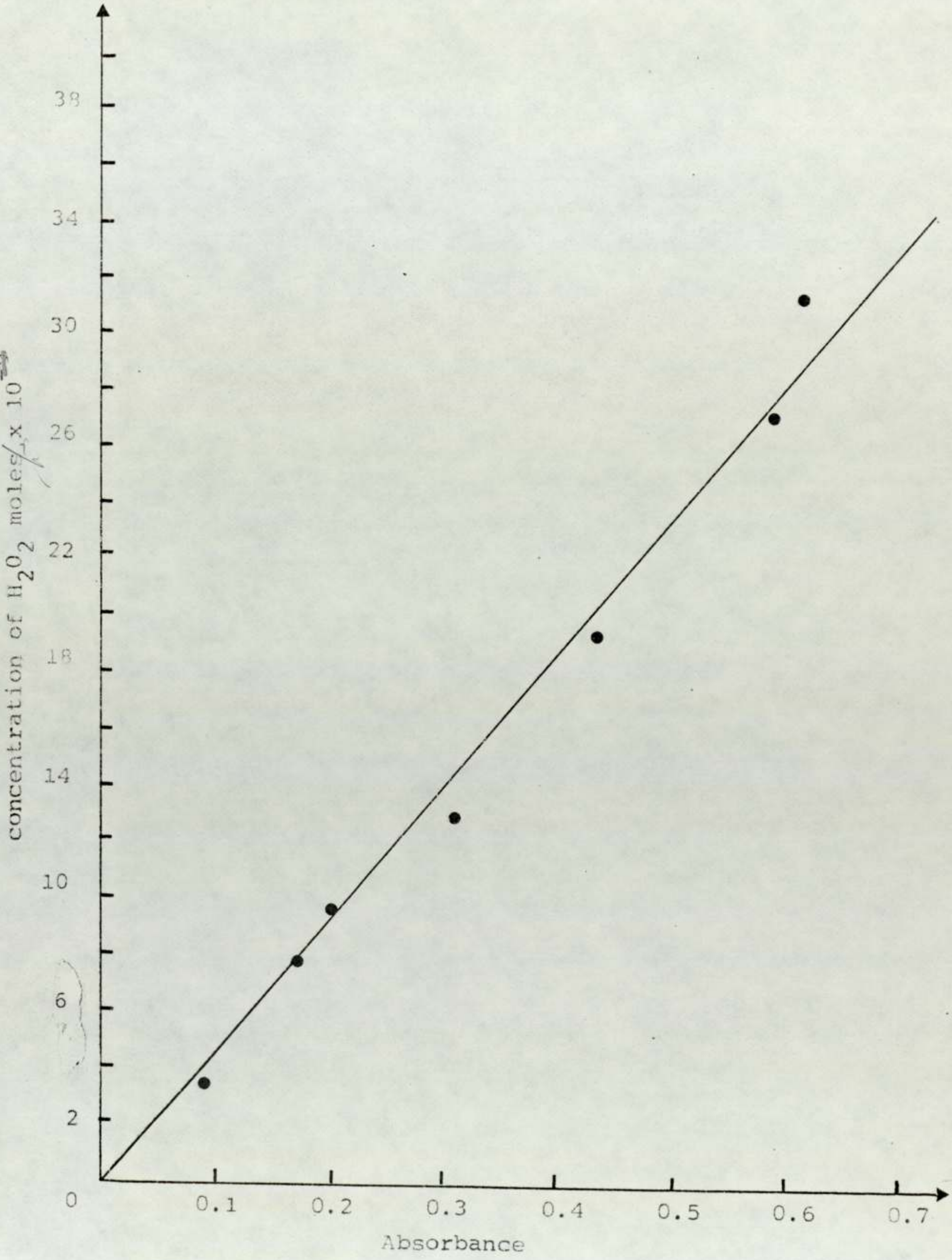


Fig. 6.10 Reference standard curve for converting optical density to the concentration of hydrogen peroxide.

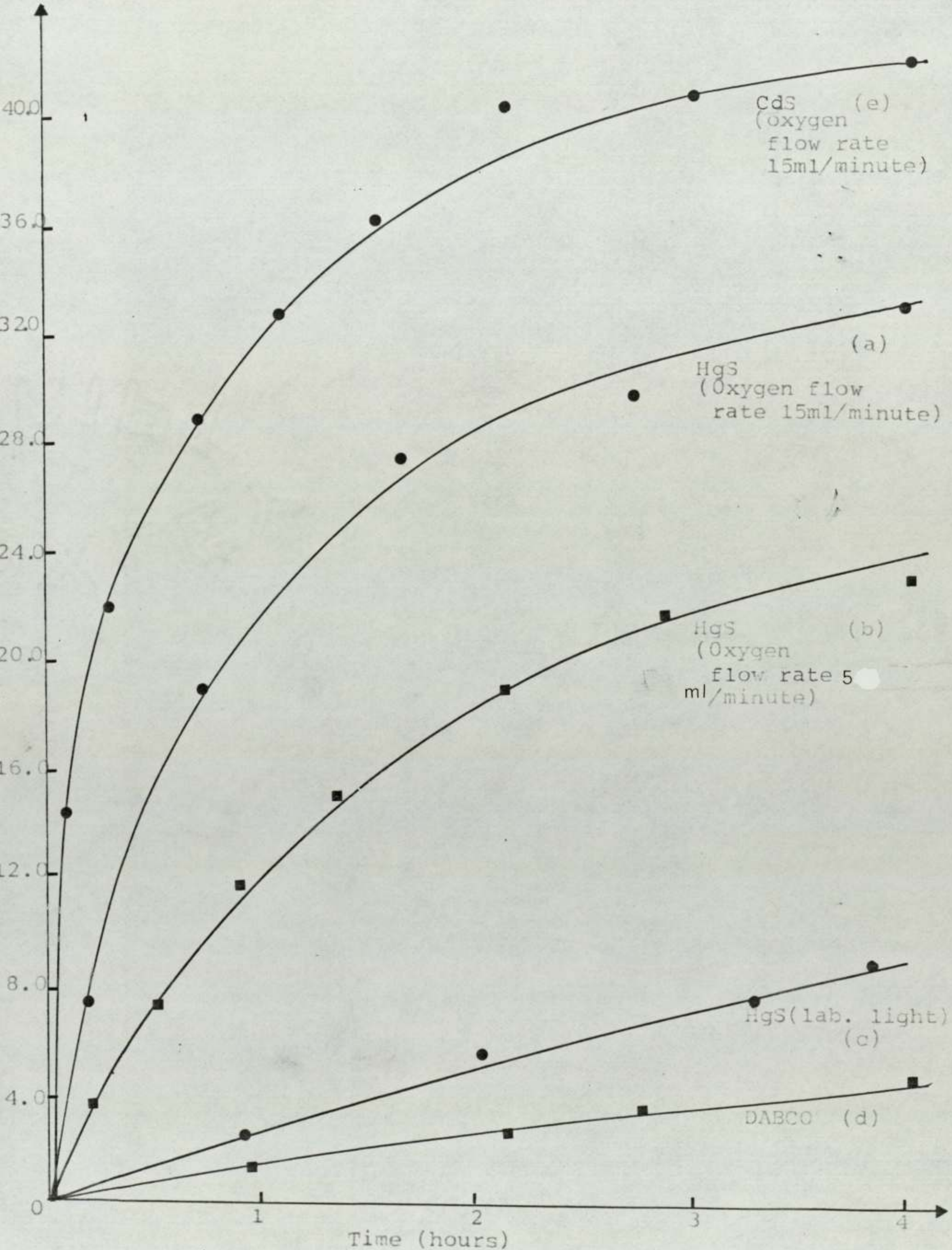


Fig.6.11 Formation of H_2O_2 under different conditions

6.11a when CdS (Cadmium yellow) obtained from National Gallery was used. All other pigments containing Cadmium sulphide i,e. Cadmium marron, Cadmium red, etc. showed similar formation of H_2O_2. No hydrogen peroxide was formed when As_2S_3 (OPPIMENT) and As_2S_2 (REALGAR) were used as pigments.

The results may be summarized as follows:

1. HgS produces hydrogen peroxide in the presence of light. This result is in agreement with those of Grossweiner (159).
2. CdS produces more hydrogen peroxide than HgS under similar conditions.
3. Reduction of the oxygen flow rate decreased the yield of hydrogen peroxide in the presence of HgS.
4. Diffuse daylight of a normal laboratory also produces hydrogen peroxide from a HgS/water system.
5. DABCO, a compound known to be singlet oxygen quencher(160), decreases the rate of formation of H_2O_2.

The threshold for photo-conduction in air of HgS is 630mμ(161). The extrapolated threshold for hydrogen peroxide formation is 613mμ(159). The coincidence of the wavelength thresholds for this reaction and photoconduction in HgS crystal suggests that the first step upon light absorption is the promotion of conduction electrons. The following reaction scheme has been suggested by Grossweiner(159).

$$(\overset{*}{HgS}) + \overset{-}{OH}\ (aq) \longrightarrow (\overset{-}{HgS}) + \overset{\bullet}{OH}\ (ad)$$

$$(\overset{-}{HgS}) + \overset{+}{H}\ (aq) \longrightarrow (\overset{+}{HgS}) + \overset{\bullet}{H}\ (ad)$$

$$(\overset{-}{HgS})\ldots\overset{+}{H} + O_2(aq) \longrightarrow (\overset{o}{HgS}) + \overset{\bullet}{HO_2}(ad)$$

$$\overset{\bullet}{HO_2}(ad) + H_2O_2 \longrightarrow H_2O\ (aq) + O_2(aq) + \overset{\bullet}{OH}\ (ad)$$

However electron transfer from HgS to atomospheric oxygen to form superoxide (radical anion oxygen) which has been reported for CdS (162) cannot be ruled out.

6.4. DECOMPOSITION OF CUMENE HYDROPEROXIDE BY HgS

Hydroperoxides play a prominent role in degradation of polymers. These are produced as a result of thermal oxidation during processing and either directly or indirectly by photo initiation process. As previously described in Chapter 1, hydroperoxides can be decomposed either by heat or UV radiation producing very reactive $\overset{\bullet}{OH}$ and alkoxy radicals $R\overset{\bullet}{O}$. Many metal salts are known to act as catalysts for free radical decomposition of hydroperoxides, whereas other compounds are known to decompose hydroperoxides by ionic decomposition Section 3.6.

6.4.1. EXPERIMENTAL

The rate of decomposition of cumene hydroperoxide by

HgS was carried out according to the experimental procedure mentioned in Chapter 3.6.1.

6.4.2. RESULTS

Fig 6.12a indicates the rate of decomposition of cumene bydroperoxide at 69°C under normal lighting of the laboratory. It is seen that HgS decomposes the cumene hydroperoxide in the first 70 minutes of the reaction. After this time the rate decreases relative to the first 70 minutes. However when the system was irradiated by the light source similar to that described in Section 6.3.1. , the rate of decomposition of cumene hydroperoxide increased very rapidly compared to the non-irradiated sample as shown in Fig 6.12b. The final products determined by G.L.C. indicate that in both cases acetophenone, cumylalcohol and α-methyl styrene are the main products. This may indicate the absence of formation of a Lewis acid (SO_2) since the latter is known to decompose cumene hydroperoxide by an ionic mechanism(163).

In conclusion it seems likely that the rapid decomposition of hydroperoxide in the presence of light is due to the formation of an excited state species which catalyses the decomposition. The leveling off of the curve may indicate that during decomposition of cumene hydroperoxide some water is formed which in the presence of HgS and visible light leads to the formation of hydrogen peroxide. It is therefore likely that there exists an equilibrium between decomposition

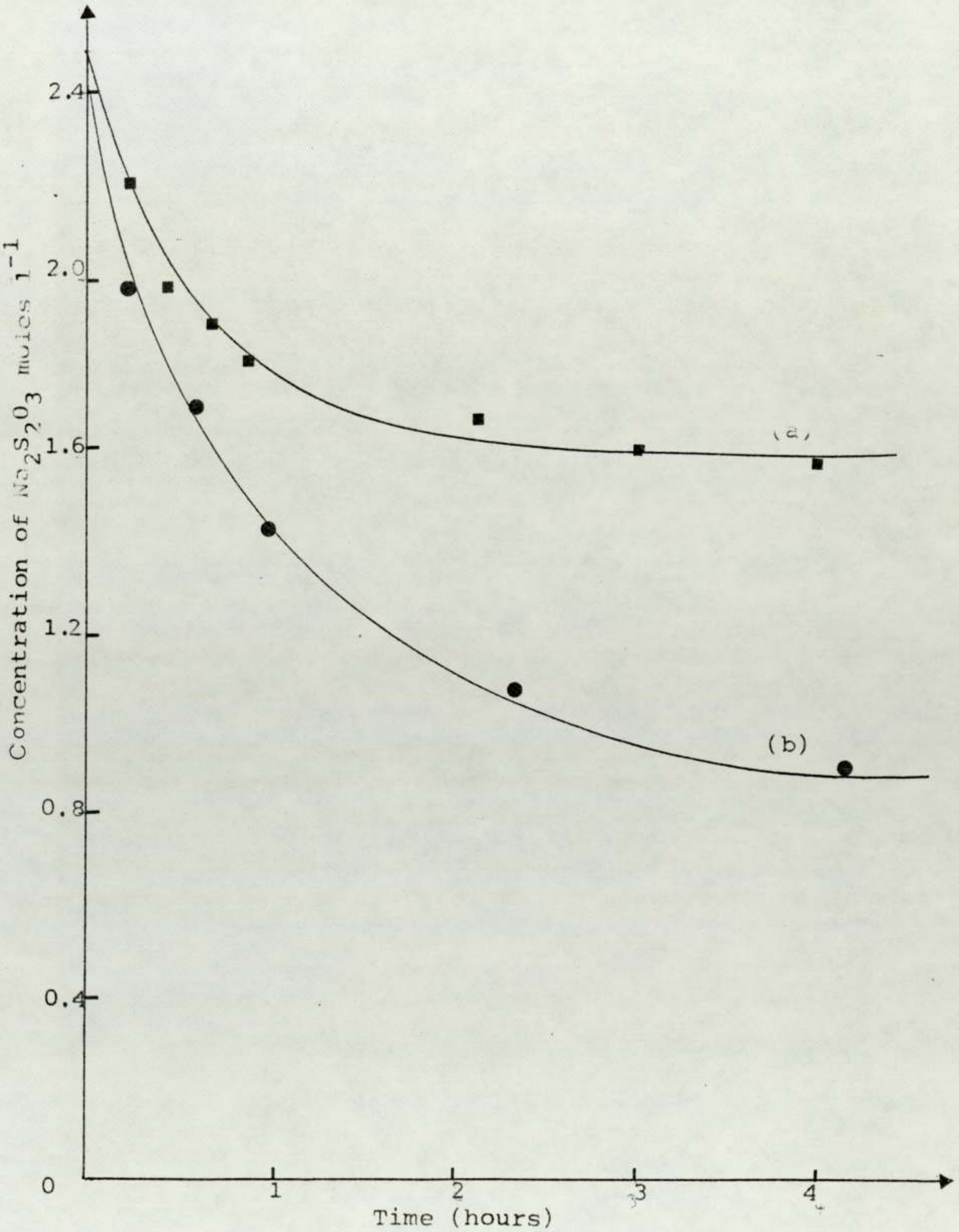


Fig 6.12 Decomposition of cumene hydroperoxide by HgS at 69°C in chloroform under different conditions

of cumene hydroperoxide and the formation of hydroperoxide by pigment under similar conditions.

6.5. FORMATION OF SINGLET OXYGEN

Singlet oxygen has recently been reported by Pappas and co-workers, to be an effective species in causing the deterioration of organic substrates. It appeared worthwhile to examine the possible participation of singlet oxygen in the present study. 1-Methyl-cyclohexene, which is known to produce products by dye senstized oxygenation different from those in normal autoxidation reactions, was chosen as the test substrate.

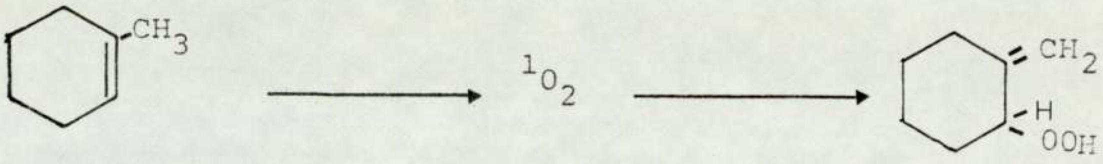
The established mechanism of this process is outlined in Scheme 6.2.(164). The critical feature being electronic energy transfer from the excited triplet state dye ($^3D^*$) to ground state oxygen ($^3O_2$), to produce ground state Dye (D_o) and excited singlet oxygen $^1O_2$. The singlet oxygen undergoes cyclic reaction to produce "ene" product I, which may be identified by IR spectroscopy since it contains an isolated vinylidine group which will absorb in a different position (C-H out of plane deformation of vinylidine absorbs around 898-885) from the in-chain double bond of the original 1-methyl-cyclohexene.

Scheme 6.2.

$$D_o \xrightarrow{h\nu} {}^1D^*$$

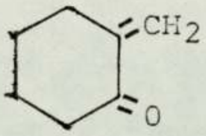
$$ {}^1D^* \longrightarrow {}^3D^*$$

$$ {}^3D^* + {}^3O_2 \longrightarrow D_o + {}^1O_2$$



I

However product I may not be stable under the experimental condition and might decompose to the corresponding conjugated ketone II.



II

6.5.1. EXPERIMENTAL

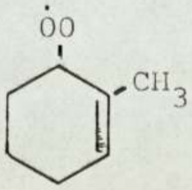
IRRADIATION OF THE 1-METHYL CYCLOHEXENE/MERCURIC SULPHIDE SYSTEM

The apparatus was identical to that utilized in the water-pigment system.

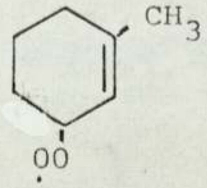
The pigment (0.1gm) was added to the beaker containing 5ml of pure 1-methyl-cyclohexene. The mixture was stirred very slowly with a small plastic covered magnet. The rate of flow of oxygen was reduced to 5ml/minute and the temperature of the reaction vessel was maintained at 15°C. The above procedure was used in order to prevent volatilazation of 1-methyl-cyclo-hexene. Samples were then removed periodically, filtered through a a fine sintered glass filter tube and examined by IR.

6.5.2. RESULTS

1-Methyl-cyclohexene has two labile hydrogens in the allylic position 6 and 3. In autoxidation the removal of these hydrogens and ultimate reaction of triplet oxygen will lead to the formation of alkylperoxy radicals III and IV.

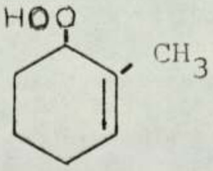


III

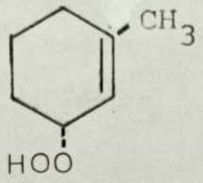


IV

the majority of products isolated (165) are V and VI.



V



VI

Fig 6.13 indicates the IR spectra of 1-methyl-cyclohexene after 2 minutes of irradiation in the presence of HgS. Three peaks are of particular importance in the starting methyl-cyclohexene (1) $3040cm^{-1}$ (2) $3000cm^{-1}$ and (3) $1670cm^{-1}$. The peak at $3040cm^{-1}$ may be attributed to the C-H stretching vibration of allylic hydrogen in the 3 and 6 position. The peak at $3000cm^{-1}$ can be assigned to the C-H stretching vibration of methyl group attached to cyclohexene ring. The peak at $1670cm^{-1}$ may be assigned to the C=C stretching of the internal double bond.
During irradiation peak at $3000cm^{-1}$ starts to decrease as evidenced from Fig 6.14 to Fig 6.16, and following peaks at

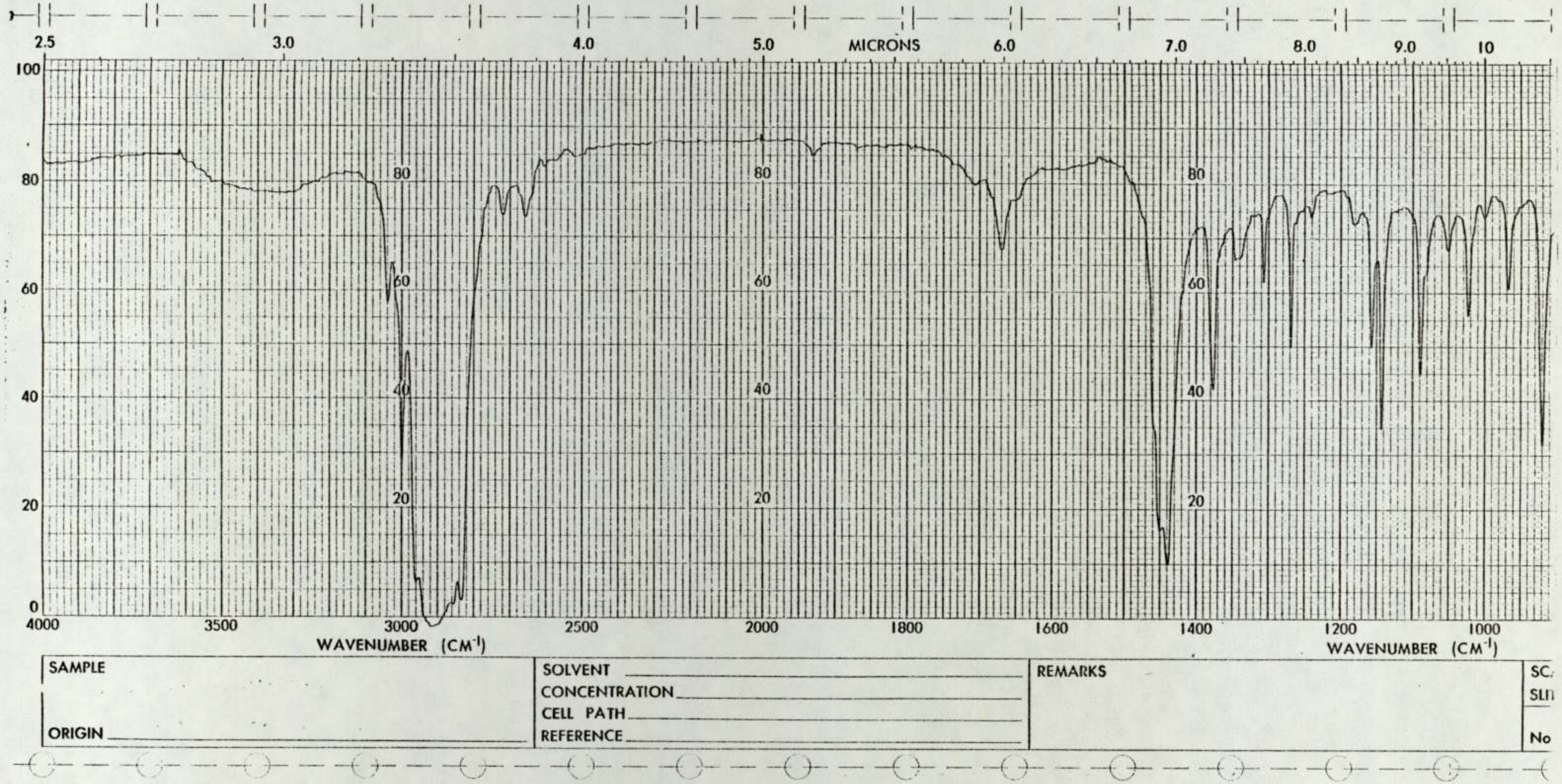


Fig.6.13. IR spectra of irradiated methyl cyclohexene containing mercuric sulphide after 2 minutes.

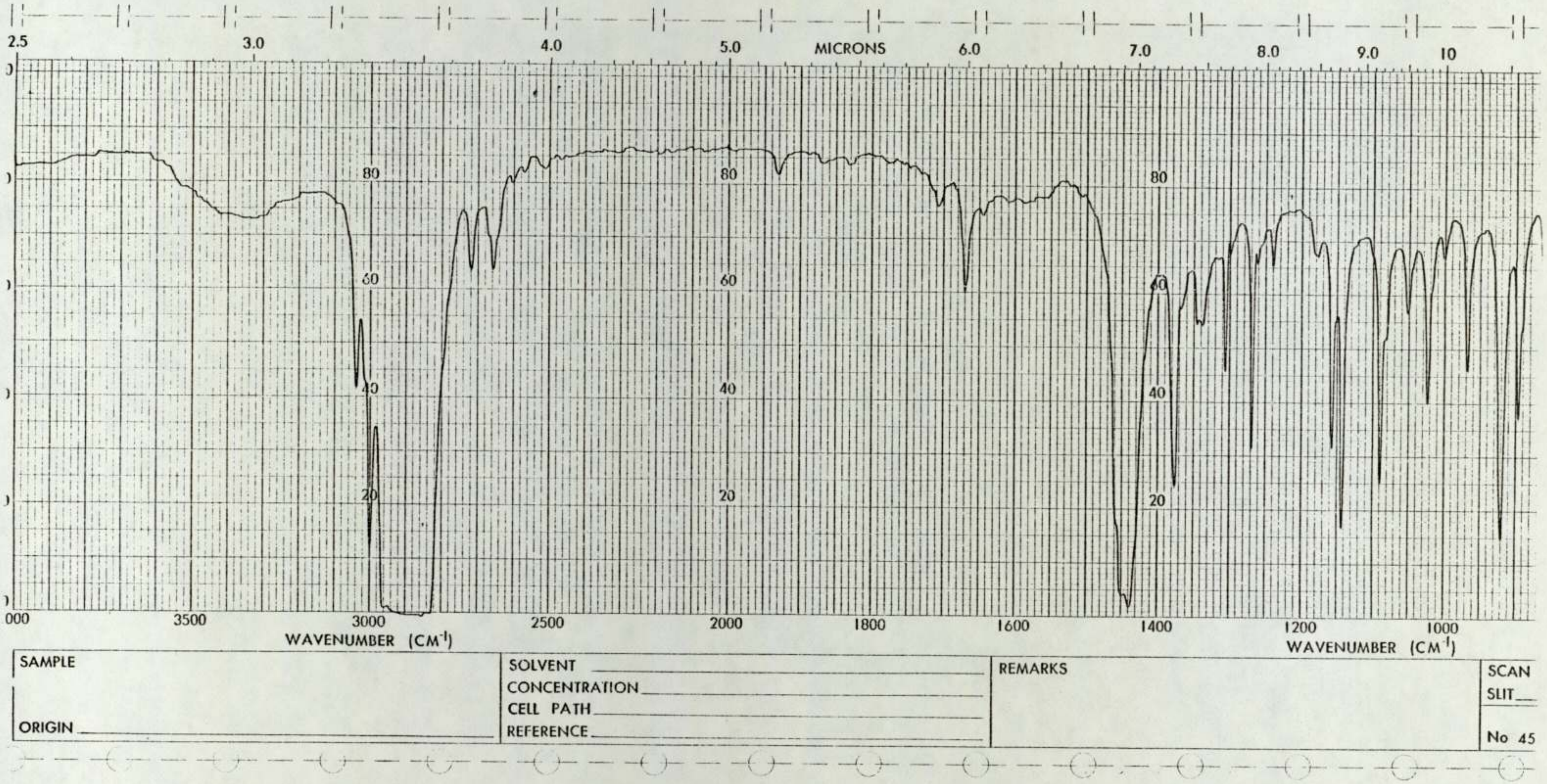


Fig.6.14 IR spectra of irradiated methyl cyclohexene containing mercuric sulphide after 15 minutes.

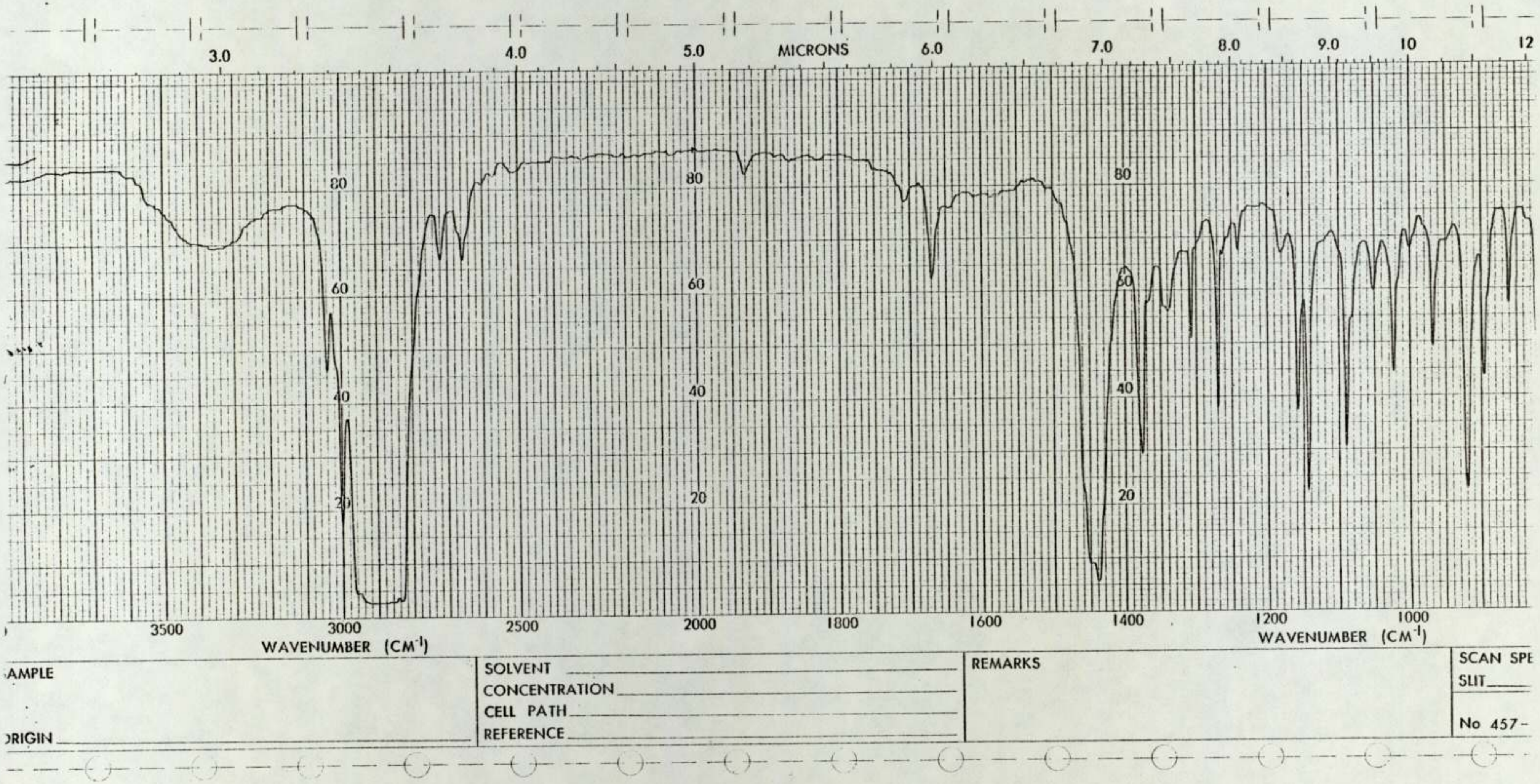


Fig. 6.15 IR spectra of irradiated methyl cyclohexene containing mercuric sulphide after 1 hour.

Fig 6.16 IR spectra of irradiated methyl cyclohexene containing mercuric sulphide after 2.30 hours.

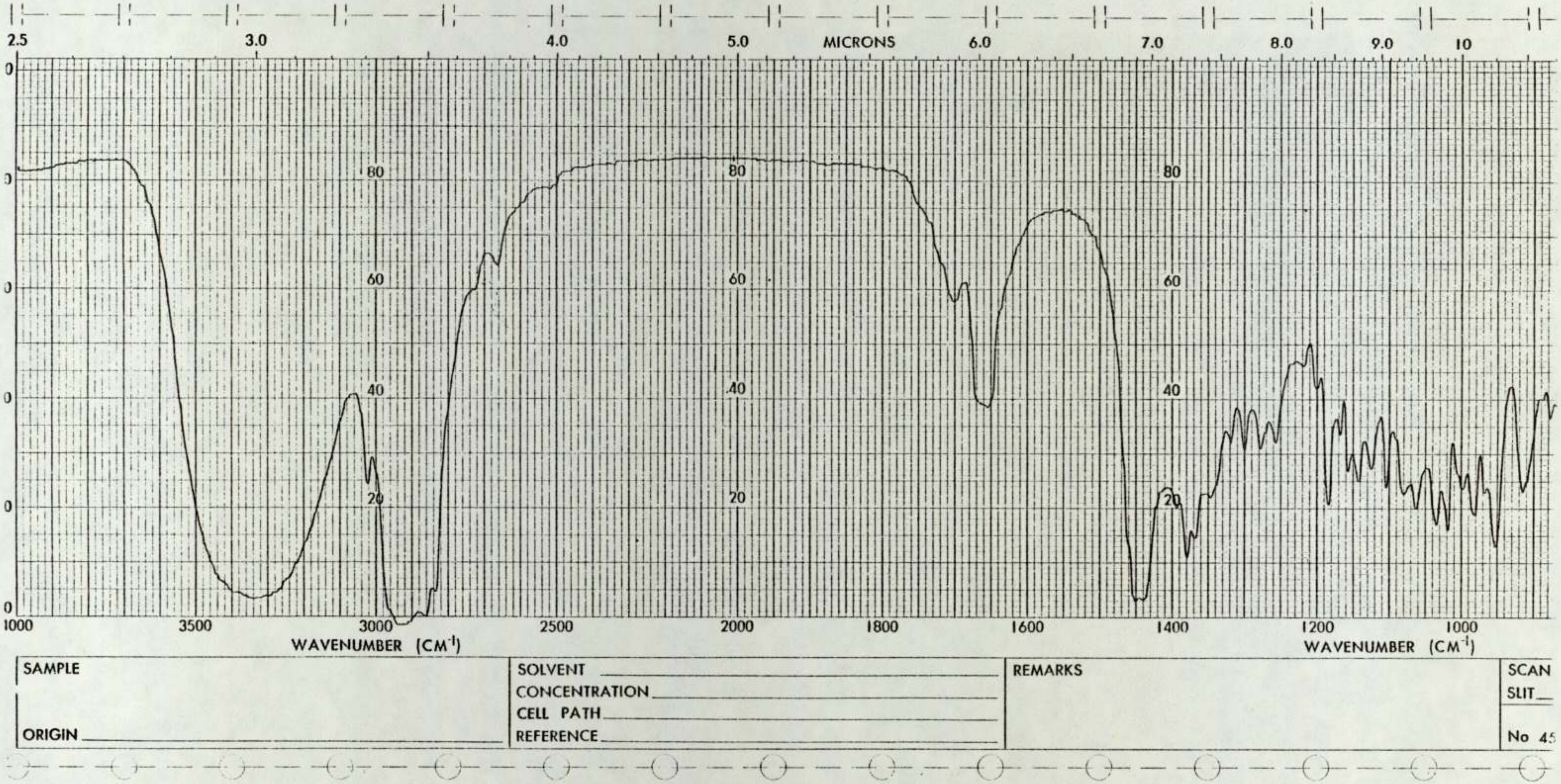


Fig. 6.17 IR spectra of irradiated methyl cyclohexene containing mercuric suphide after 5 hours.

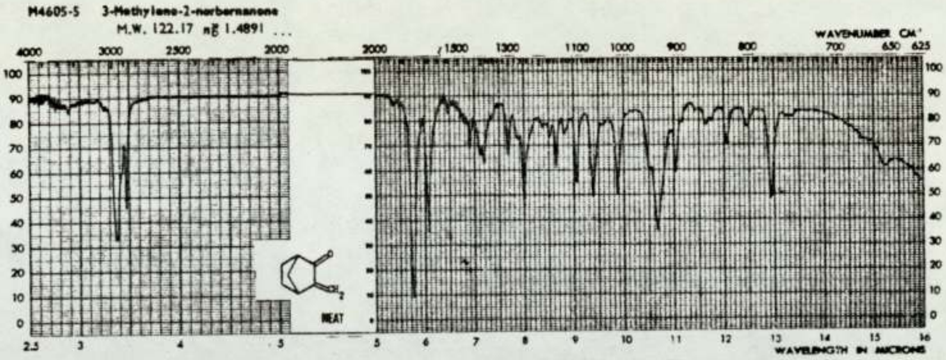
3350cm^{-1} attributed to hydroxyl groups, 1715cm^{-1} due to ketonic carbonyl, 1640 to 1670cm^{-1} due to formation of conjugated carbonyls, and a peak at 950cm^{-1} start to increase. Fig 6.17. indicates the position after 5 hours. It is interesting to see that the complete disappearance of peak at 3000cm^{-1} is accompanied to the broadening of the band in the region of 3200 to 3500cm^{-1}, formation of ketone at 1710cm^{-1}, formation of conjugated carbonyl at 1640 to 1660cm^{-1} and finally formation of a peak at 950cm^{-1}.

Table 6.1 indicates δ $=CH_2$ (out of plane deformation) in conjugated vinylidine compounds taken from the Aldrich Library of infra red spectra and references (137,140).

TABLE 6.1.

Types of conjugation	Frequency change	cm^{-1}
Unconjugated		895-885
Conjugated with C=C	Raised	910-895
Conjugated with acid C=O	Raised	950-935
Conjugated with ketonic C=O	Raised	930

The IR spectra of 3-methylene-2-norbornanone indicates presence of a sharp band at 940cm^{-1} which appears to be indentical to that observed in this study.

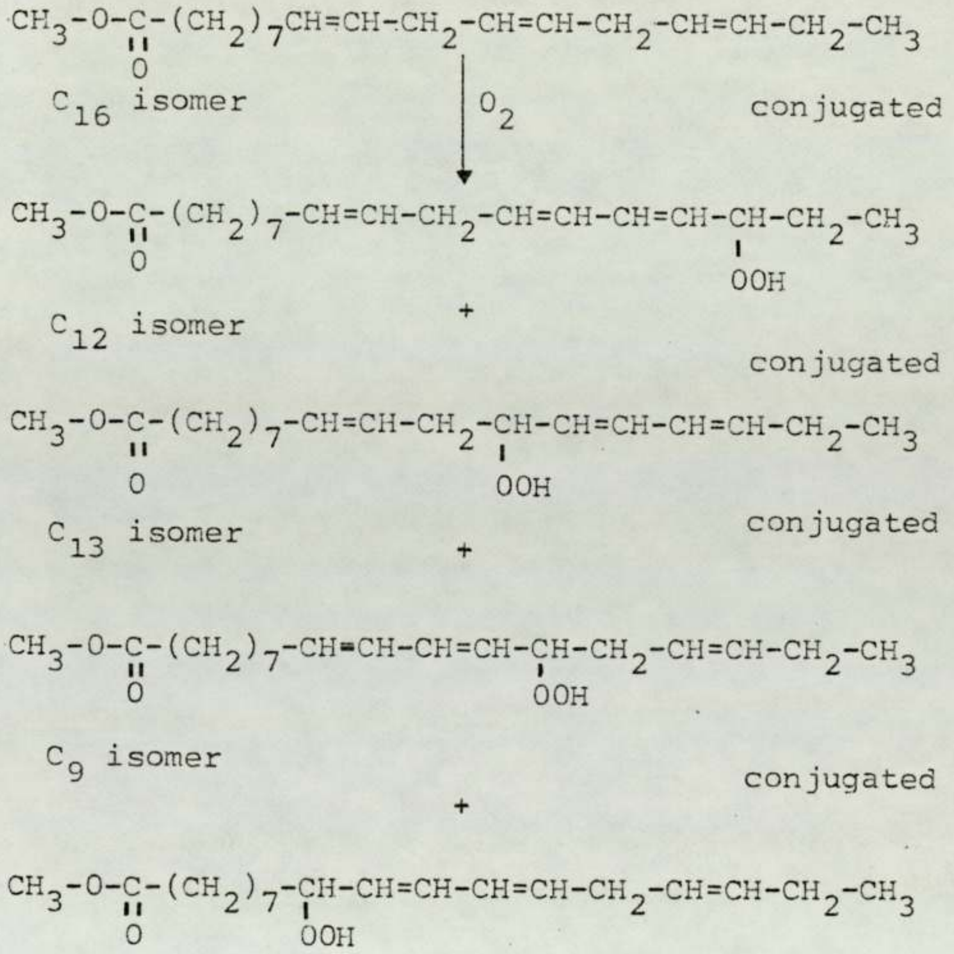


It seems likely therefore that during irradiation of the 1-methyl-cyclohexene/HgS system, product II is formed as well as the other products. Formation of product II indicates involvement of singlet oxygen in the intermediate stages.

DABCO is an oxidatively stable compound and does not react chemically with $^1O_2$. However it has been demonstrated that DABCO quenches $^1O_2$ in both solution and in gas phase$^{(166)}$ Therefore, it is widely used as a diagnostic test for the participation$^{(167)}$ or non- participation$^{(168)}$ of $^1O_2$ in oxygenation reactions. Further support of $^1O_2$ as intermediate in this study was also made by addition of 2.5×10^{-4} moles DABCO in the 1-methyl-cyclohexene/HgS system. No peak at 950cm^{-1} was appeared after 10 hours of irradiation.

6.6. DISCUSSION

The most common mode of attachment of an oxygen molecule to the hydrocarbon chain in the oxidation of unsaturated fatty acids is the reaction of molecular oxygen with a conjugated free radical as, for example, in the propagation step of autoxidation. Preferential attack occurs at the extremities on the longest possible conjugation such as the radicals formed at the ends of a 1,4-diene system. For a complex molecule such as linolenate, two separate 1,4-diene systems are present and autoxidation of linolenate has been shown(169) to give rise to a hydroperoxide mixture containing the 9, 12, 13, and 16 positional isomers:



$$CH_3\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$$

C_{16} isomer

$$\downarrow O_2$$

conjugated

$$CH_3\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH{=}CH\text{-}\underset{\overset{|}{OOH}}{CH}\text{-}CH_2\text{-}CH_3$$

$+$

C_{12} isomer

conjugated

$$CH_3\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}\underset{\overset{|}{OOH}}{CH}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$$

C_{13} isomer

conjugated

$+$

$$CH_3\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH{=}CH\text{-}\underset{\overset{|}{OOH}}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$$

C_9 isomer

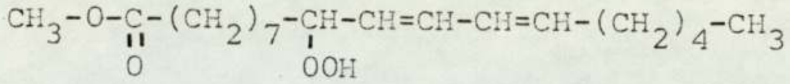
conjugated

$+$

$$CH_3\text{-}O\text{-}\underset{\overset{\|}{O}}{C}\text{-}(CH_2)_7\text{-}\underset{\overset{|}{OOH}}{CH}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$$

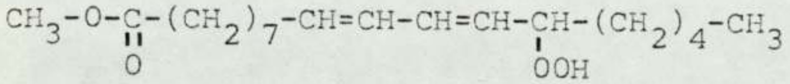
Methyl linoleate has also been shown to form two isomeric hydroperoxide namely 9 and 13 isomers in almost equal amount both of which are conjugated(124).

C_9 isomer



$$CH_3\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}\underset{\underset{OOH}{|}}{CH}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$$

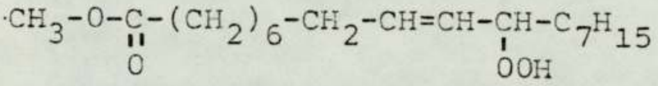
C_{13} isomer



$$CH_3\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH{=}CH\text{-}\underset{\underset{OOH}{|}}{CH}\text{-}(CH_2)_4\text{-}CH_3$$

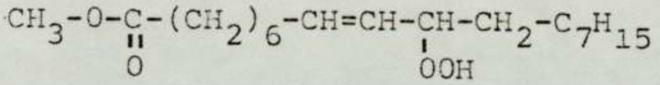
Similarly, methyl oleate which can, by hydrogen abstraction, give rise to allylic radicals between positions 8-10 and 9-11, is autoxidised to a mixture of 8, 9, 10 and 11 hydroperoxide isomers(170).

C_{11} isomer



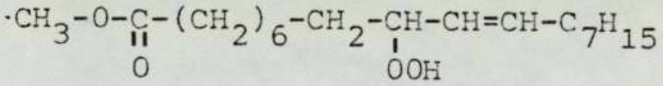
$$CH_3\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_6\text{-}CH_2\text{-}CH{=}CH\text{-}\underset{\underset{OOH}{|}}{CH}\text{-}C_7H_{15}$$

C_{10} isomer



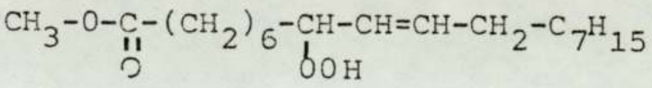
$$CH_3\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_6\text{-}CH{=}CH\text{-}\underset{\underset{OOH}{|}}{CH}\text{-}CH_2\text{-}C_7H_{15}$$

C_9 isomer



$$CH_3\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_6\text{-}CH_2\text{-}\underset{\underset{OOH}{|}}{CH}\text{-}CH{=}CH\text{-}C_7H_{15}$$

C_8 isomer



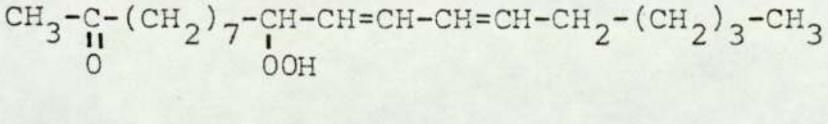
$$CH_3\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_6\text{-}\underset{\underset{OOH}{|}}{CH}\text{-}CH{=}CH\text{-}CH_2\text{-}C_7H_{15}$$

It was demonstrated that HgS decomposes the cumene hydroperoxide in the presence light by a free radical mechanism possibly via formation of an excited species as was suggested in Section 6.4. It is therefore likely that the same free radical homolytic breakdown takes place in the paint substrate to produce two free radicals namely alkoxy and hydroxy radicals, both of which can take part in hydrogen abstraction reactions to produce alcohol and water molecules, and hence accelerate the degradation. Furthermore, the formation of hydrogen peroxide (from the water formed during oxidation) via production of $\dot{O}H$ and $H\dot{O}_2$, the decomposition of hydrogen peroxide by HgS in the presence of light, and the possibility of forming superoxide radical (anion oxygen radical) from electron transfer process from HgS to atomospheric oxygen, may all be important in the sensitization reactions observed.

The formation of the above species cannot totally explain the predominate effect of scission process over the cross linking, and as a result initial slow curing of the oil; however a more clear understanding may be concluded from the following explaination.

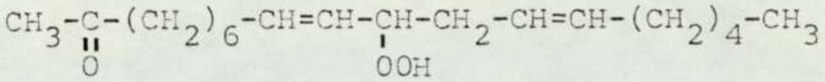
The reaction between singlet oxygen (which may be formed in intermediate stages in this study) and olefinic bonds does not totally involve conjugated free radicals, but proceeds via a spin allowed addition reaction, i.e. the "ene" reaction(142). This is a concerted reaction between singlet oxygen and a carbon-carbon bond in which the oxygen molecule is inserted at either carbon atom of the C=C bond, which is shifted to yield an allylic hydroperoxide. A good demonstration of these reactions is given for the methyl linoleate(157)

C_9 isomer



$$CH_3-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{OOH}{|}}{CH}-CH=CH-CH=CH-CH_2-(CH_2)_3-CH_3$$

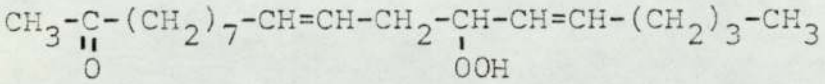
C_{10} isomer



$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-(CH_2)_6-CH=CH-\underset{\underset{OOH}{|}}{CH}-CH_2-CH=CH-(CH_2)_4-CH_3}$$

Non-conjugated

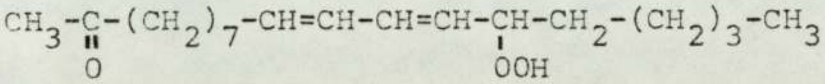
C_{12} isomer



$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-(CH_2)_7-CH=CH-CH_2-\underset{\underset{OOH}{|}}{CH}-CH=CH-(CH_2)_3-CH_3}$$

Non-conjugated

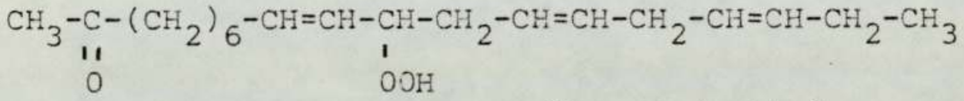
C_{13} isomer



$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-(CH_2)_7-CH=CH-CH=CH-\underset{\underset{OOH}{|}}{CH}-CH_2-(CH_2)_3-CH_3}$$

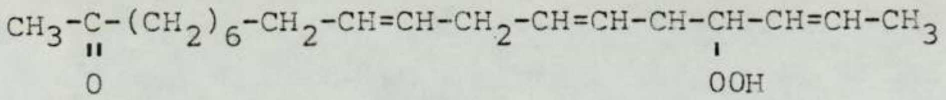
conjugated

and for methyl linolinate in addition to the four conjugated isomeric hydroperoxide two more non-conjugated hydroperoxides were also isolated(110).



$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-(CH_2)_6-CH=CH-\underset{\underset{OOH}{|}}{CH}-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3}$$

Non-conjugated



$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-(CH_2)_6-CH_2-CH=CH-CH_2-CH=CH-CH-\underset{\underset{OOH}{|}}{CH}-CH=CH-CH_3}$$

Non-conjugated

It follows that in singlet oxygen reactions with polyunsaturated, methylene-interrupted fatty acids, the reactive moieties in the hydrocarbon chains are the isolated olefinic bonds rather than the 1,4-diene system.

The main process of 'drying' in linseed oil is the attack of the $R\dot{O}$ or $RO\dot{O}$ on the conjugated double bonds. The rate of this reaction is much faster than the rate of attack of $R\dot{O}$ or $RO\dot{O}$ on isolated double bonds. It is therefore expected that in this particular system the rate of cross linking of linseed oil containing HgS will be lower than the control. It should be bornein mind, however, that the reaction between $^1O_2$ and poly-unsaturated, methylene-interrupted fatty acids, is a stoichiometric one and takes place in a minor amount. Subsequent decomposition of hydroperoxide group to free radicals may cause further degradation of the polymer by the usual free radical chain reaction.

CHAPTER 7

7.1. A COMPARISON OF PIGMENTS USED

7.1.1. INTRODUCTION

In Chapters 5 and 6 it was demonstrated that there is a good correlation between the weightloss of paint media as monitored by the decay of $-CH_2-$ group at $2930cm^{-1}$ (ΔCH_2) and the chain scission process.

In this Chapter the effect of each pigment on the rate of auto and photo-oxidation of paint media will be compared.

7.1.2. THE RATE OF DECAY OF $-CH_2-$ GROUP

Fig 7.1. compares the effect of the pigments, Fe_2O_3, $Cu(Ac)_2.Cu(OH)_2.5H_2O$, HgS and $PbCO_3$ on the rate of degradation of media. The order of stability in the first 3 months of UV exposure is as follows:

$Cu(AC)_2.Cu(OH)_2.5H_2O > Fe_2O_3 > PbCO_3 . Pb(OH)_2 >$ oil alone $>$ HgS.

However after 3 months, the effect of Fe_2O_3 and $Cu(Ac)_2.Cu(OH)_2.5H_2O$ are reversed i.e.

$Fe_2O_3 > Cu(Ac)_2.Cu(OH)_2.5H_2O > PbCO_3.Pb(OH)_2 >$ oil alone $>$ HgS.

Fig 7.2. shows that $\log\Delta CH_2$ of the paint substrates becomes linear for all the pigments in the later stages of oxidation. Similar order of stability as was observed in Fig 7.1. is also indicated.

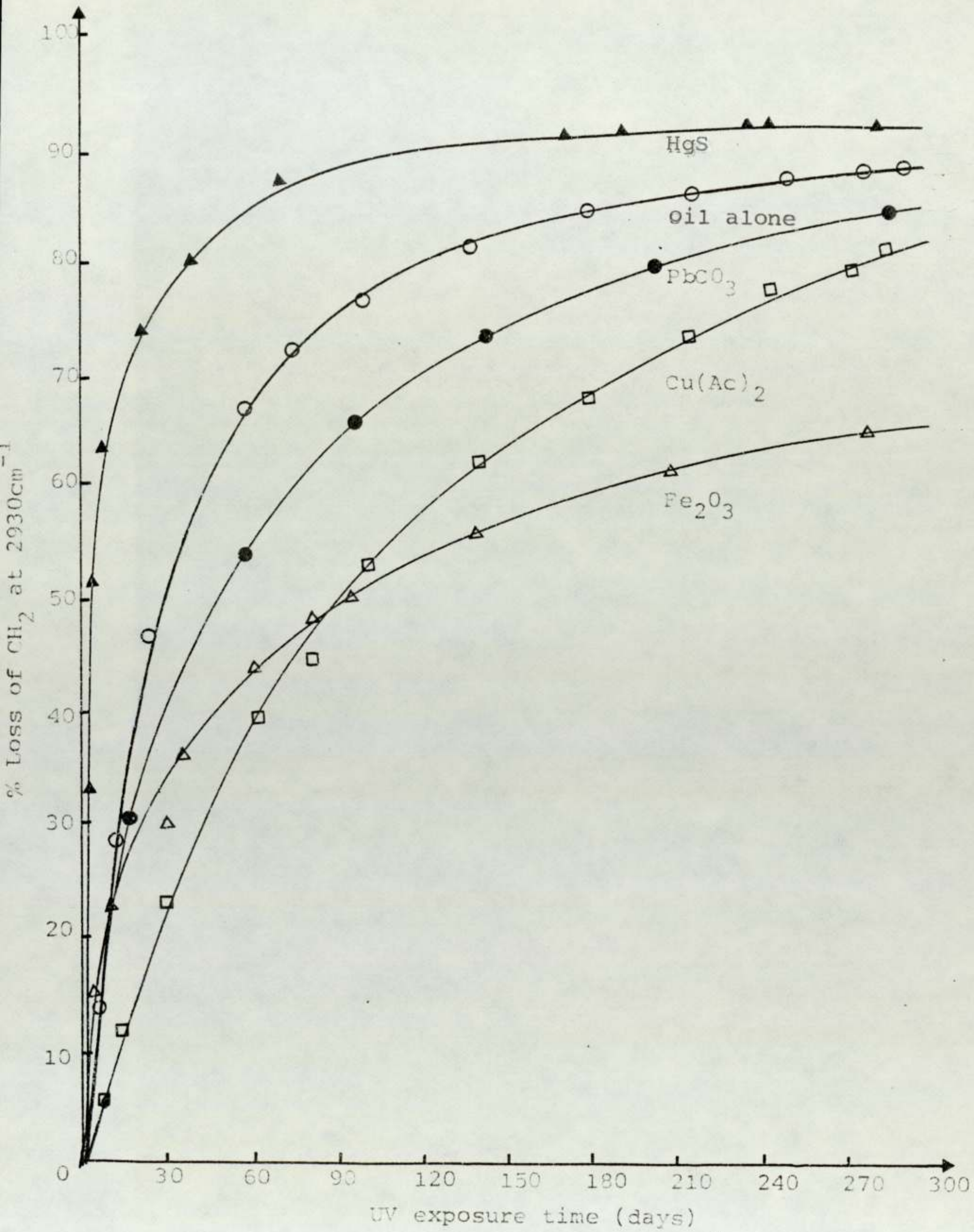


Fig 7.1. Decay of CH_2 at 2930cm^{-1} of dried oil with and without pigments.

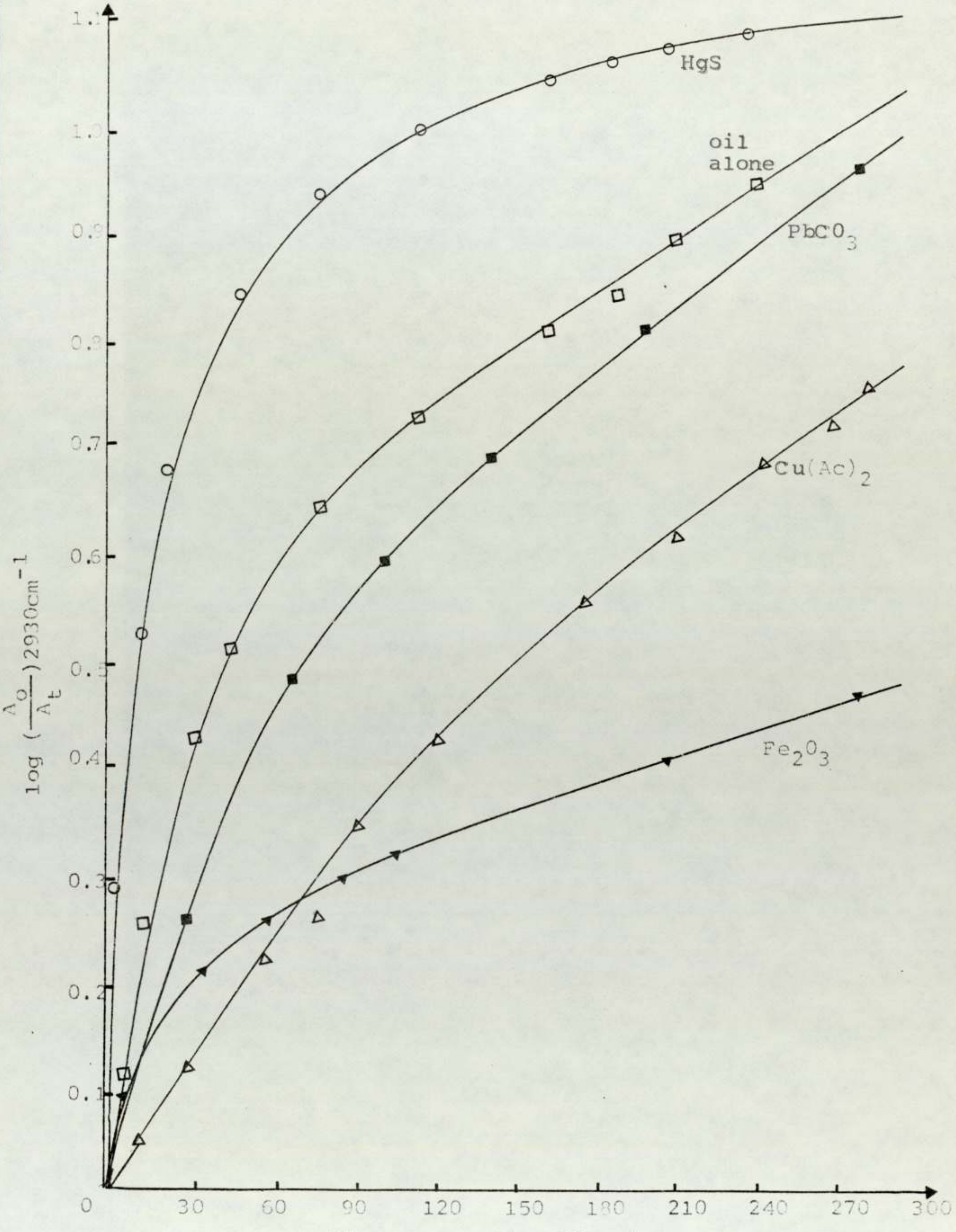


Fig 7.2. Log Δ CH_2 at 2930cm^{-1} of dried oil with and without pigments

7.1.3. THE RATE OF FORMATION OF SCISSION PRODUCTS

A 60% pigment to oil paste was prepared for each pigment and smeared in duplicate on glass plates. One set of each composition was placed in the UV cabinet and the other set was placed in the laboratory. The yield of scission products is a measure of the extent of film degradation. Fig. 7.3. shows the rate of formation of C_9 dicarboxylic acid, azelaic acid, of paint formulations under UV light. The order of stability as measured by chain scission is as follows:

$Cu(Ac)_2.Cu(OH)_2.5H_2O > PbCO_3.Pb(OH)_2$ >oil alone $> Fe_2O_3 >$ HgS.

Fig 7.4. shows the rate of formation of C_9 dicarboxylic acids of paints containing pigments under normal laboratory lighting. The order of stability as measured by chain scission is as follows:

$Cu(Ac)_2.Cu(OH)_2.5H_2O > PbCO_3.Pb(OH)_2$ >oil alone $> Fe_2O_3 >$ HgS.

7.1.4. CONCLUSION

The mechanism of behaviour of verdigris and vermilion observed has been studied in Chapter 5 and 6. No mechanistic studies have been done on lead white and light red, however the formation of lead salts may explain the observed stability$^{(144)}$. The function of pigments under UV cabinet condition and ambient condition as determined by scission product determination is identical. This is considered to be sufficient justification for concluding that newly dried film could be used to accurately reflect the behaviour of old paint containing the same pigment.

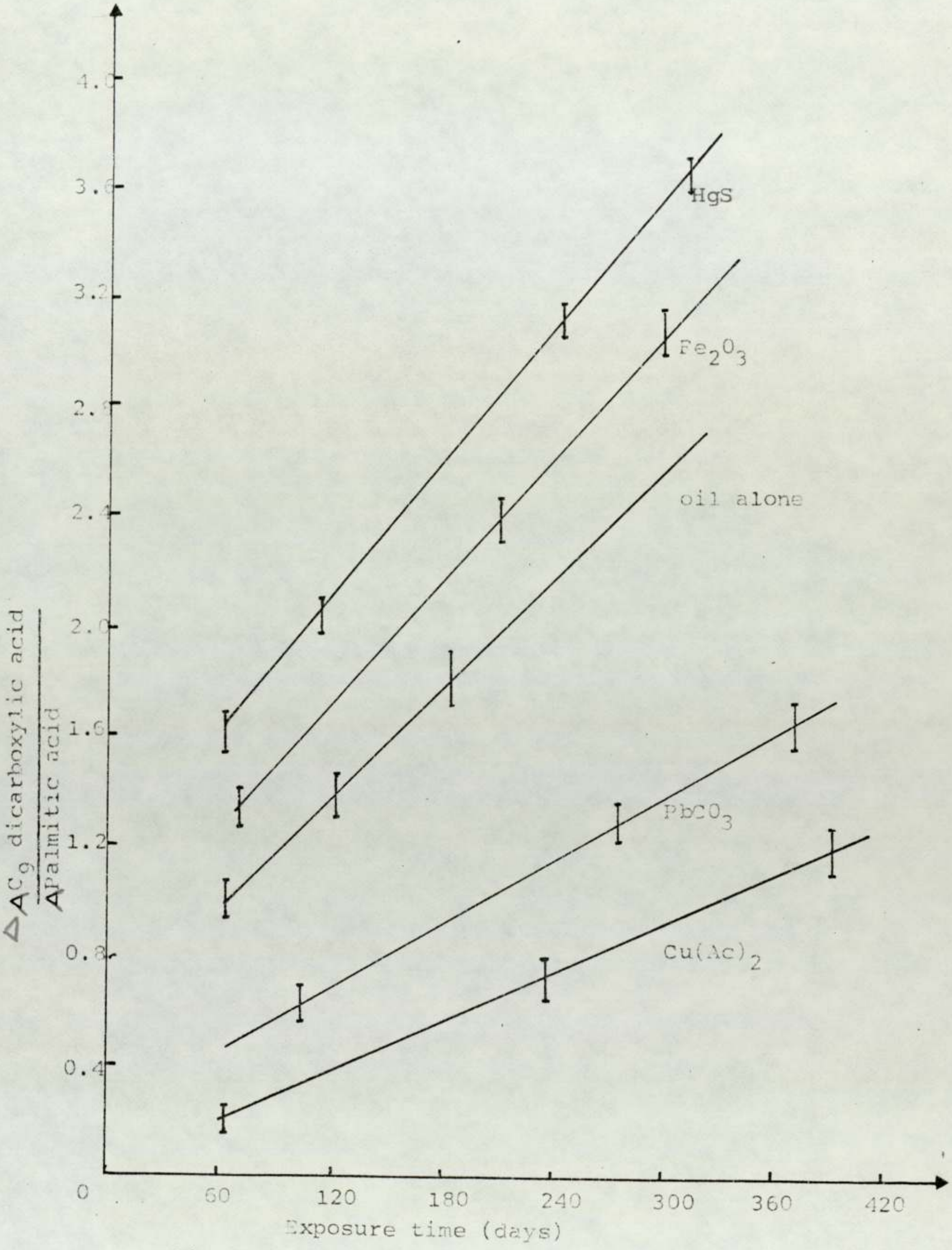


Fig 7.3. Effects of pigments on the rate of formation of scission product under UV light

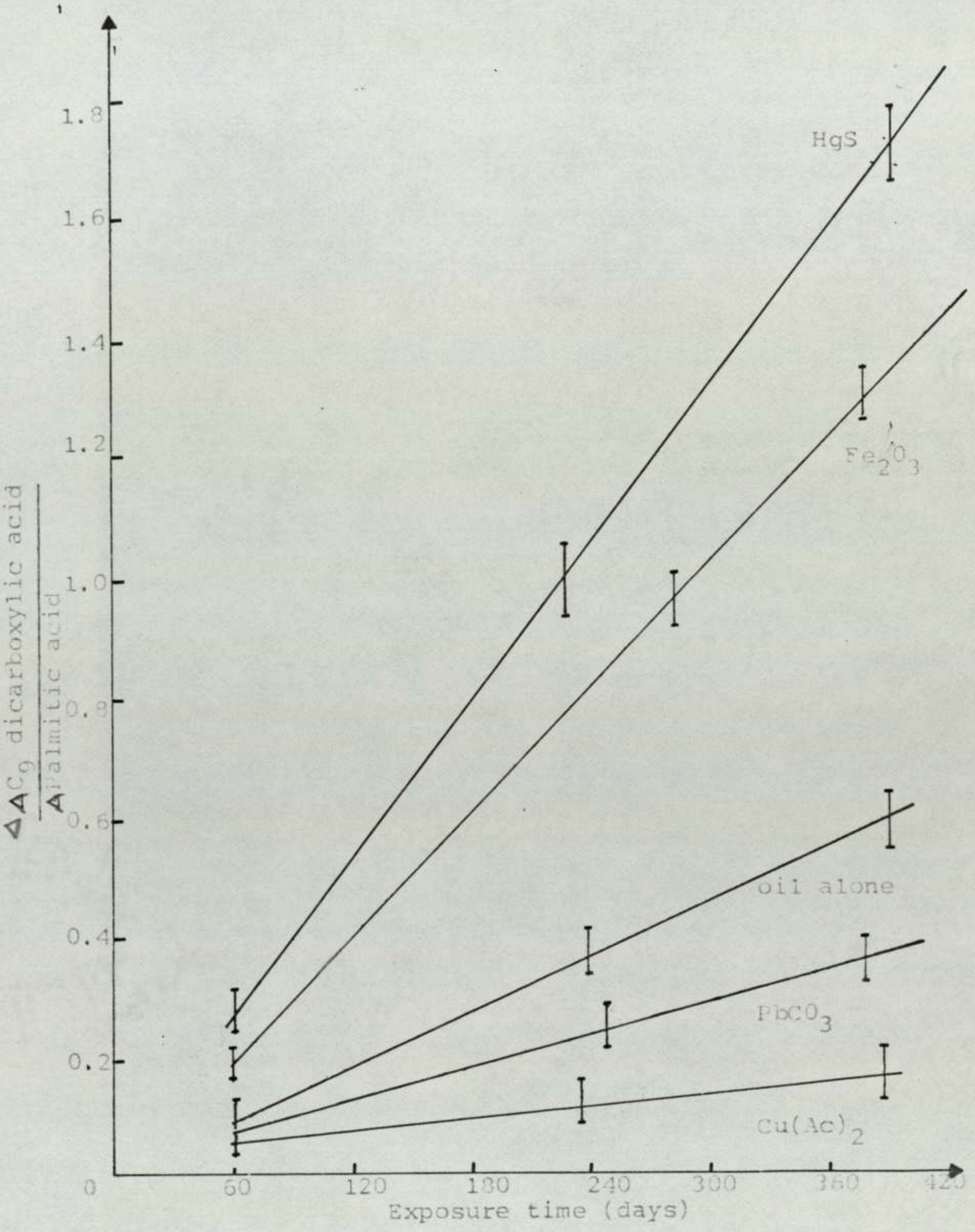


Fig 7.4. Effect of pigments on therate of formation of scission product kept under the diffuse light of laboratory

7.2. EFFECT OF WAVELENGTH OF THE LIGHT ON THE RATE OF DEGRADATION OF PAINTS

7.2.1. INTRODUCTION

Most picture galleries today are equipped with latest air conditioning (i.e. constant temperature, humidity, clean air and diffused lighting) and yet there is still relatively little known about the significance of the interaction between light, pigment, paint media and of atmospheric pollutants.

In previous Chapters, the effect of selected pigments on the rate of photo-oxidation of dried linseed oil was studied. It was found that vermilion HgS acts as a strong photo-sensitizer and causes damage to the paint substrate and verdigris $Cu(Ac)_2.Cu(OH)_2.5H_2O$ stabilizer the paint substrate in spite of the fact that this chemical stabilization lead to the browning of the paint.

In this Chapter the effect of the light on the rate of photo-oxidation of these particular pigments will be studied in view of their interesting behaviour in paint media.

7.2.2. EXPERIMENTAL

The UV cabinet was as described in Section 3.8. linseed oil was smeared on sodium chloride discs in the conventional manner, after incorporating 1% of the selected pigments. The films were allowed to dry to the touch stage for a week and the samples were mounted in an apparatus designed for UV irradiation at narrow wavebands.

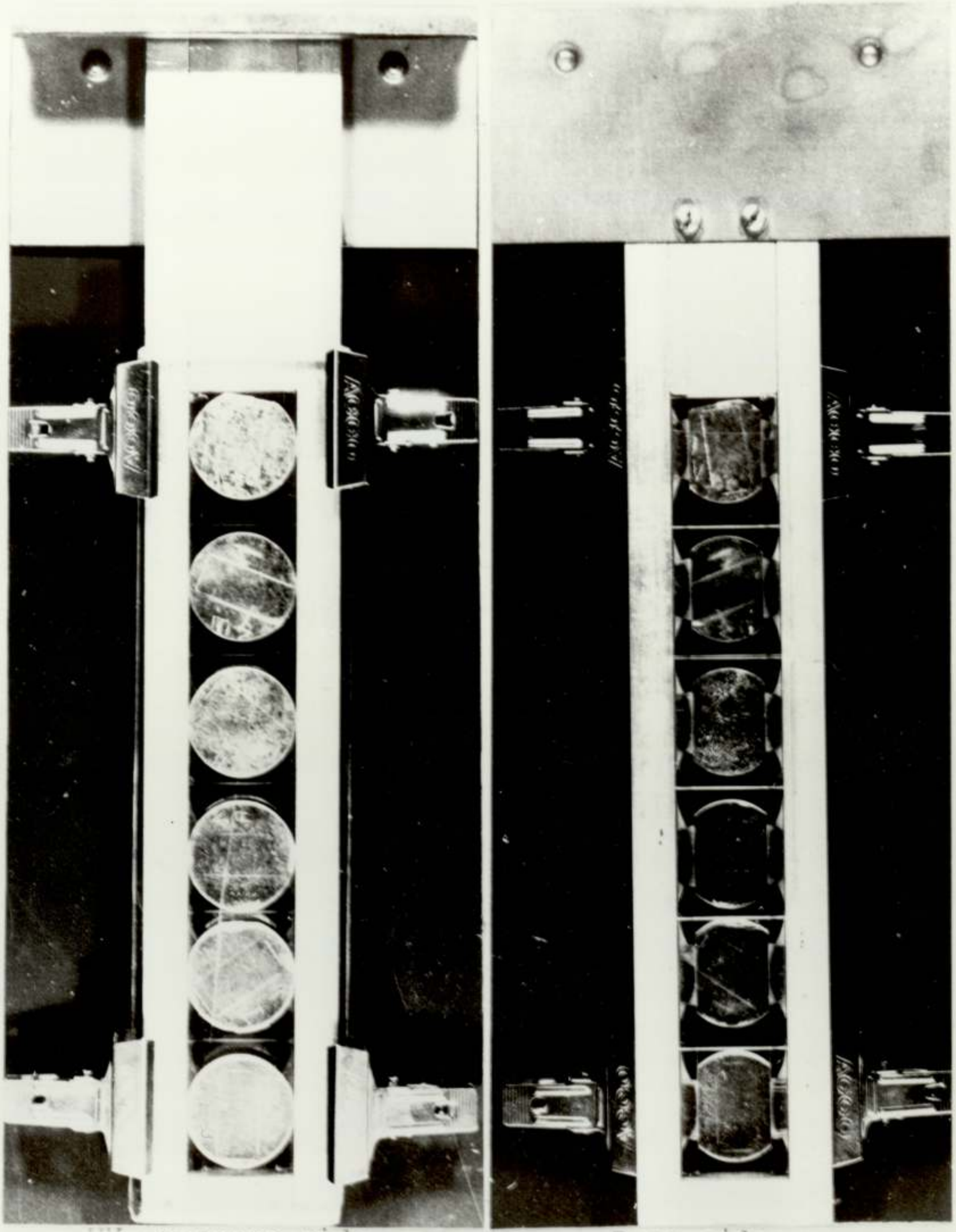
The apparatus consisted of two parallel and vertically placed aluminium colomns with 2mm thick reflectance glass windows ranging from 294 to 365nm mounted as a series of windows see Photograph 7.1.

Identical sodium chloride discs smeared with linseed oil samples, were placed behind each window. In order to facilitate a uniform flow rate of air over the samples and to prevent physical contact with filters, two glass rods were mounted along the aluminium column and the discs placed over the rods. This arrangement did not affect the exposed area of the sample under study. The samples were then securely fastened on to the frame by a glass plate that was placed over the discs. During UV exposure, the apparatus was placed in the UV cabinet in such a way as to expose the filter directly to the light and the same light intensity was received by each test sample enabling a comparison to be made of the effect of each filter on the rate of photo-oxidation of the sample under examination.

7.2.3. RESULTS

The decay of $-CH_2-$ was used to follow the rate of degradation of paint media in the presence of different light filters.

Figs 7.5 and 7.6 show $\log\Delta CH_2$ in the presence of



UV exposure side

II

Rear side

I

Fig 7.1.

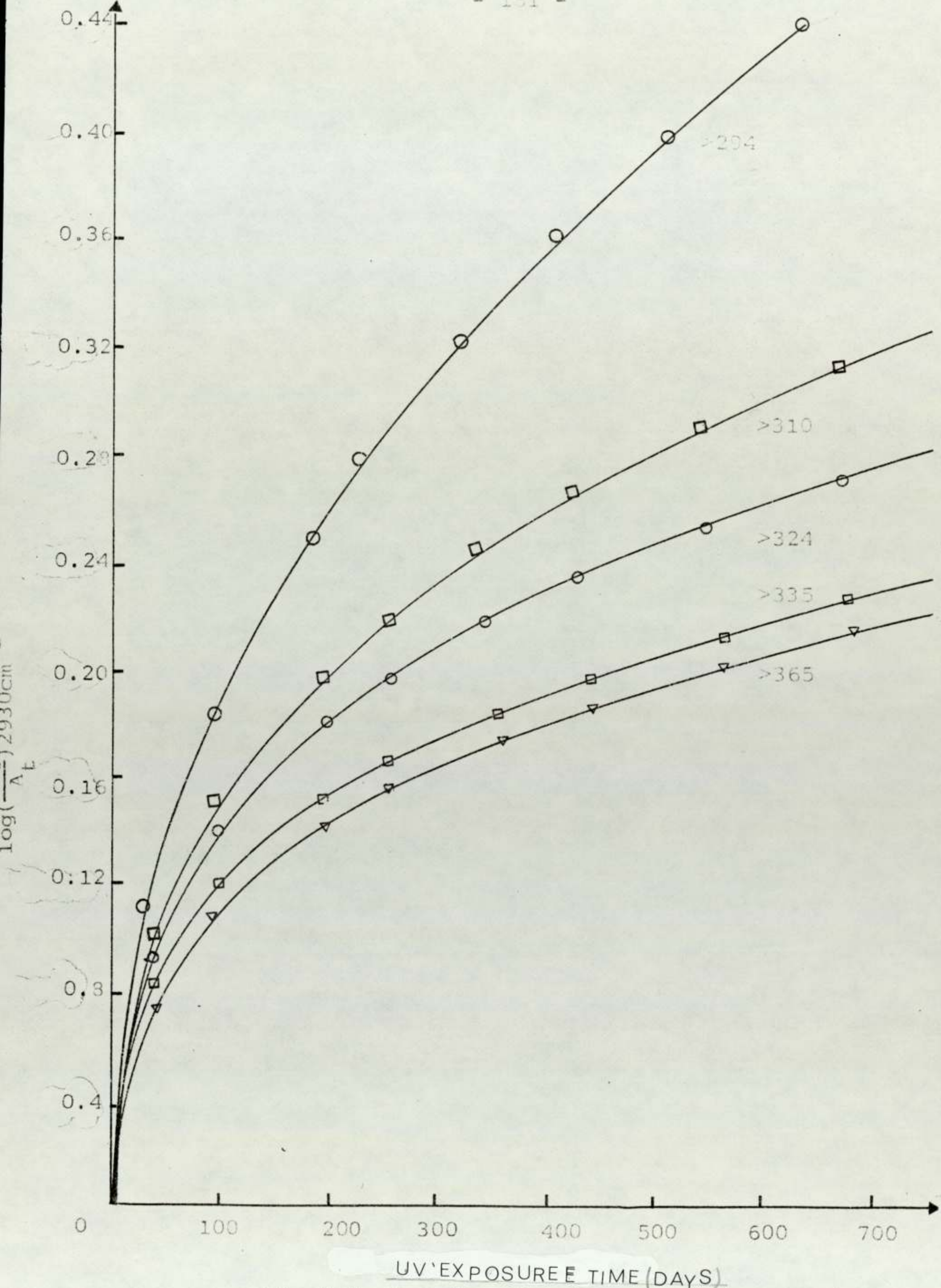


Fig 7.5. Log CH_2 of paint containing vermilion in the presence of different wavelengths

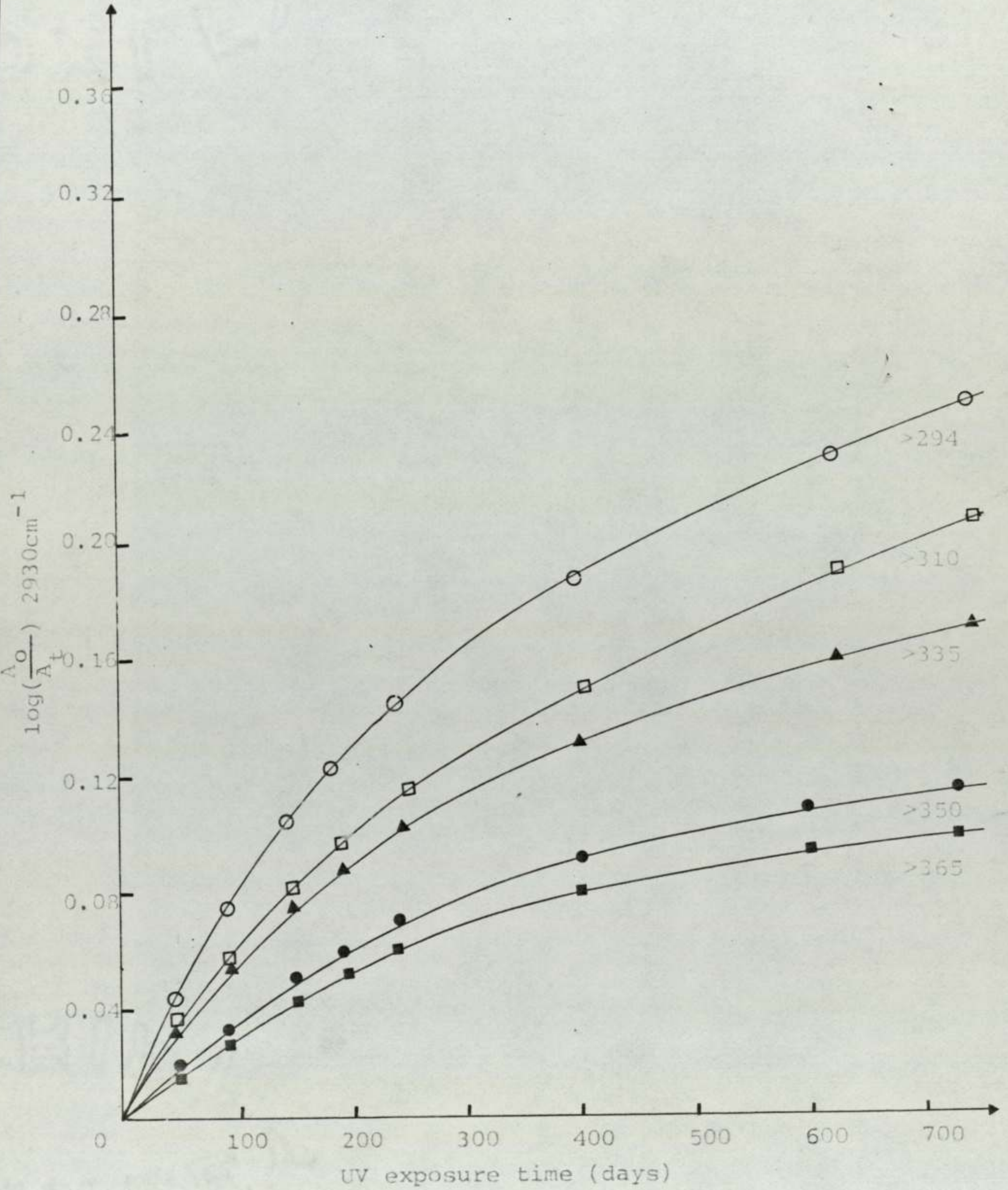


Fig 7.6. Log CH_2 of paint containing verdigris in the presence of different wavelength

filters for vermilion and verdigris pigmented films. It was found in the previous Chapters that the plot of logΔCH$_2$ versus time of exposure after an initial rapid decay gives a straight line plot. The gradient of each plot is calculated and plotted against the corresponding wavelength in Fig 7.7.

7.2.4. DISCUSSION

It is seen from Fig 7.7 that the rate of degradation of paints is highly dependent on the pigment and wavelength used.

In the case of verdigris the rate of degradation appears to be proportional to the wavelength at least up to 365nm. It follows from this, that one possible way of stabilizing the verdigris pigmented film is by using filters of higher cut off wavelength.

In contrast to verdigris, the rate of photo-oxidation of vermilion pigmented film does not change appreciably with wavelenth above 350nm. From this it may be concluded that it is not possible to reduce the rate of degradation of vermilion pigmented film by physical screening alone without affecting the aesthtic appreciation of paintings. An alternative approach to stabilization must therefore be sought in the chemical or physical removal of the degradative agents. Possible approaches are the use of antioxidants and singlet oxygen quenching agents by incorporation in the varnishes.

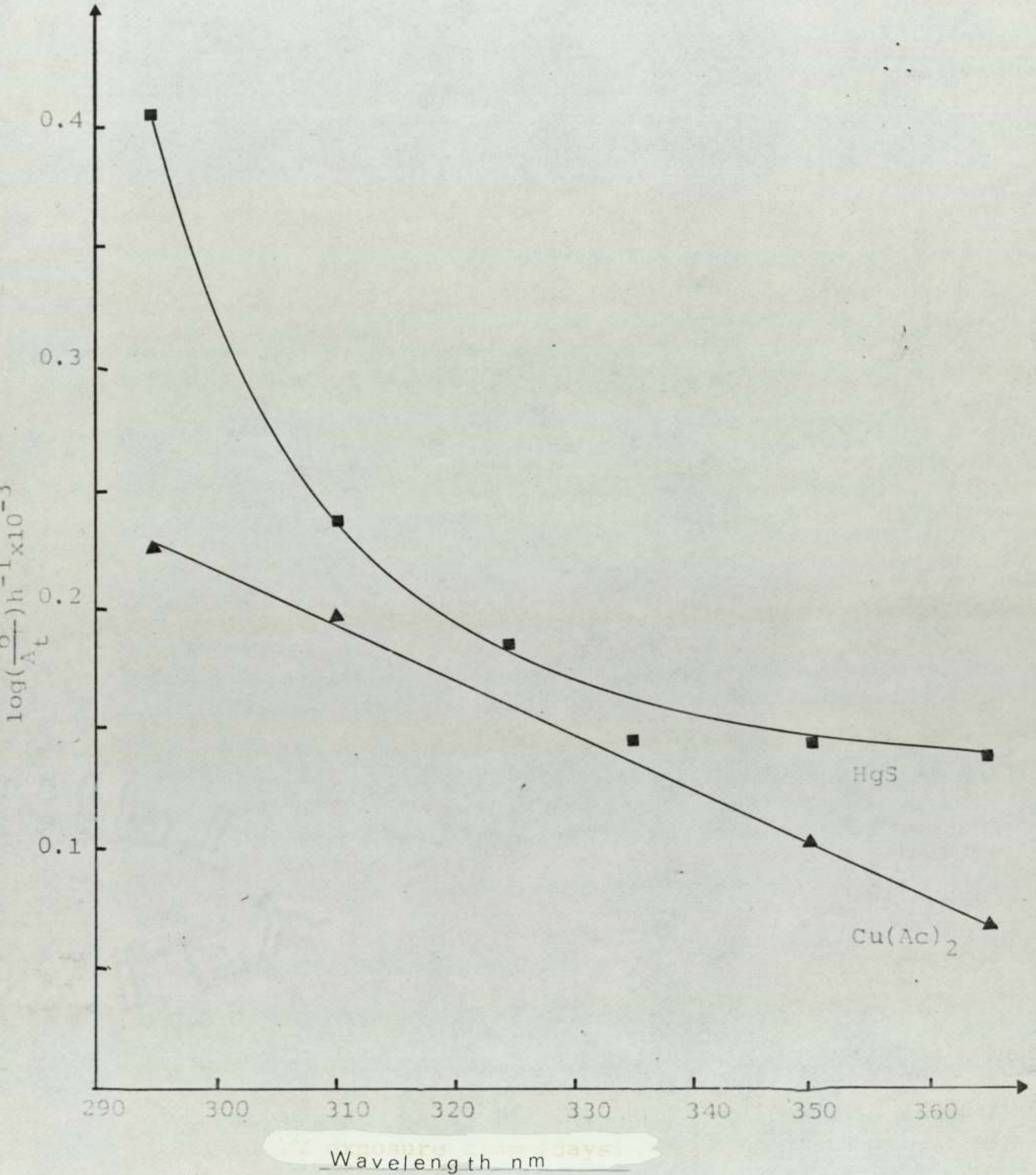


Fig 7.7. Dependence of rate of degradation on the wavelengths of light

CHAPTER 8

SIGNIFICANCE OF THE RESULTS OF THIS STUDY OF OLD PAINT MEDIA

1. Degradation can be conveniently followed by means of the decay of the methylene absorption ($-CH_2-$) at $2930cm^{-1}$ in both visible and UV light.
2. The use of new paint film appears to correlate with that of old media as indicated by the extent of scission product formation.
3. Vermilion (HgS) appears to be a convenient monitor for the effect of light on paint media.
4. The rate of degradation of vermilion pigmented film is insensitive to wavelength variation above 350nm, therefore there is no point in extending light screening in art galleries above 350nm.
5. Photo degradation of pigmented paint media involves a variety of highly active intermediates of which the most important are both alkyl and alkylperoxy radicals, hydroperoxides, and in the case of highly sensitising pigments, excited states of the pigment molecules with rapid generation of singlet oxygen and chain-propagating radicals. Preliminary experiments have shown that it is possible to incorporate UV stabilisers into drying paint media which effectively retard the rate of degradation during UV exposure without appreciably affecting the rate of the drying process.
6. A more practical approach to the protection of works

of art against the effects of environment damage is to incorporate antioxidants, excited state quenching agents etc into the protective laquers or even as a long-term possibility to attach them to the surface of the paint medium itself.

SUGGESTION FOR FURTHER WORK

1. EXTENSION OF THE MONITORING PROCEDURE TO OTHER PIGMENTS

Although an excellent correlation has been found between physical breakdown of the paint medium and the formation of chain scission products(carboxylic acids) in the case of sensitising pigments, it has been found that the mechanism of the oxidative degradation is quite different in the case of stabilising pigments. Some other common pigments used in old paintings should be examined by the sodium chloride disc technique and the hydrolysis /glc procedure over a range of selected wavelength between 285 and 400nm.

2. RELATION BETWEEN CHEMICAL PHOTO-OXIDATION AND PHYSICAL DETERIORATION OF PAINT FILMS

Although a satisfactory correlation has been observed between the rate of film deterioration and rate of photo-oxidation using the sodium chloride disc (weightloss) procedure, it has not been unequivocally demonstrated that there is a direct relationship between weightloss and paint film cracking. It is known that surface effects are of paramount importance in determining the rate of crack propagation and an attempt should be made to investigate this phenomenon using preformed films on a background similar to canvas. Surface examination techniques such as microscopy, goniophotometery and ATR are useful for such studies.

3. EXAMINATION OF POTENTIAL SURFACE PROTECTIVE TREATMENT FOR SENSITIVE PAINT MEDIA

Since it is already common practice to apply protective laquers to old paintings, this would appear to be the most accessible way of applying chemical protective agents to the paint media. This has the advantage that UV degradation begins in the surface of the medium and in the case of mobile sensitizers such as singlet oxygen which has been shown to be involved in some cases, there is a good possibility that they may be readily deactivated in this way. There are several associated problems involved in the use of protective films:

(a) Many films tend to yellow over extended periods of time and consequently need to be renewed with consequent risk to the painting. It is known that certain antioxidants and stabilizers retard this process.

(b) Commercial antioxidants and stabilizers are lost from the polymer films over the extended periods of time involved in conservation of works of art. This severely restricts their effectiveness.

There are potential solutions to both of these problems in the chemical binding of antioxidants and stabilizers in either the protective film or, even more interestingly, to the surface of the paint media itself(19,145,171,172).

These possibilities could lead to the effective protection of old paintings against environmental degradation but will required very thorough experimentation on new paint media in the first instance and on old paintings of no value before they could be even considered for old masters.

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