THE DEGRADATION AND STABILISATION OF EPOXIDE RESINS

to

ULTRAVIOLET RADIATION

by

MICHAEL JOSEPH DOYLE

A dissertation submitted for the degree of

Doctor of Philosophy

at the

University of Aston in Birmingham

March 1972

The Ultraviolet Degradation and Stabilisation of Epoxide Resins

Summary of a Thesis by M.J. Doyle

This thesis was an investigation of the chemical and physical changes which occurred on exposure of two epoxide resins, one amine and the other anhydride cured, to ultraviolet light.

The method of study was by investigation of the changes in both cured resins and the monomers from which they were synthesised. Also, because of the intractable nature of the cured structures, the degradation of a number of model compounds which were structurally similar to the cured systems were investigated.

The results showed that the monomer itself was susceptible to the radiation used. Monomer purity decreased the rate but it did not eliminate the degradation process. From quantum yields studied, the initiation was found to result in a non-chain reaction. The extent of degradation was proportional to the intensity of the light used. No "dark" chemical reactions were observed to occur with any of the compounds studied, although "dark" physical reactions by diffusion of degradation products did occur in the cured structures.

The wavelengths of light causing maximum degradation were contained in the short wavelength region of the lamp. In the anhydride cured resins the 365 nm band was also found to contribute to the overall degradation process.

The photo-oxidative degradation resulted in the formation of an oxidised surface layer of material from crosslinking reactions involving atmospheric oxygen. Volatile compounds were evolved during irradiation and their rate of concentration change confirmed the surface layer theory, as did measurement of the torsion modulus of the cured systems.

Complete stabilisation of the materials with existing stabilisers and new synergistic mixtures failed. However it was possible to decrease the rate of degradation in both the amine and anhydride cured polymers.

ABEUNT STUDIA IN MORES

Francis Bacon 1597.

Preface

This study was carried out during the period May 1968 to May 1971, at the Building Industry Division of the Institute for Industrial Research and Standards, Ireland, and at the Department of Chemistry of the University of Aston in Birmingham, under the supervision of Professor Gerald Scott.

I would like to thank my supervisor for his guidance and encouragement during the full period of the research. Also I would like to thank Dr. R. J. Nichol of the Institute of Industrial Research and Standards, and Dr. D. G. Smith and colleagues, Shell Research Ltd., Egham, Surrey for the useful discussions which I had with them. I am grateful to Mr. S. F. Dunleavy, Director, Building Industry Division, of the above named institute for permission to commence the work during my employment there, and for the financial assistance provided by the Division. Finally I thank Shell Research Ltd., for financial assistance during the final two years of the work, and for many of the materials used in this research.

To my wife for enduring discomfort during the tenure of the work an expression of thanks alone is not enough.

CONTENTS

CHAPTER I

INTRODUCTION

Materials suffer change on exposure to ultraviolet light. The temperature, atmosphere, pressure, wavelength, intensity and duration of the irradiation determine the type and extent of this change in all organic and inorganic matter. Even the evolution of life on our planet may have been partly caused by the interaction of high energy photons with such materials as methane, ammonia, hydrogen and water vapours to produce the first protein molecules (1).

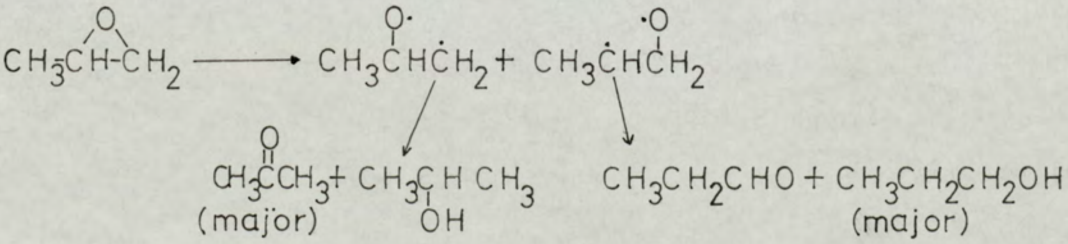
This thesis is concerned with the deleterious action of light on epoxide resins, (based on the reaction product of bisphenol - A and epichlorohydrin reacted with amine and acid anhydride curing agents). The ultimate aim of the work is the elucidation of the mechanism of solar light degradation of these materials, and with this information to formulate and test the effectiveness of suitable light stabilisers in these polymers. Due to the intractable nature of these cured, three-dimensional materials it was necessary to examine the mode of degradation of model compounds with structures similar to those found in the cured materials. The effect of resin impurities, surface changes in solid polymers, light intensity and wavelength were also investigated.

Solar radiation at sea level consists principally of long wavelength light (wavelength greater than 300 n.m.) and a fraction of short wavelength light (wavelength less than 300 n.m.). The absorption spectra of common polymers e.g. polyvinylchloride, polystyrene, polyolefins etc., do not contain absorption bands in the region above 300 n.m. and should not be appreciably affected by solar ageing. However these polymers break down rapidly in sunlight (2). Thus sunlight of wavelength less than 300 n.m. initiates some and in many cases all of the photodegradation processes in polymers e.g. the wings of the absorption bands attributed to carbonyl groups (acetone, wavelength maximum 280 n.m.) and conjugated polyene structures ($CH_3-(CH = CH)_4-CH_3$, wavelength maximum 290 n.m.) are in this region. These and similar groups may be regarded as initiation centres for light induced ageing in polymers whose monomers or curing agent units do not contain absorbing groups.

This chapter is concerned with the effects of light absorption of polymers. The current theories on degradation and stabilisation are reviewed briefly; for a more detailed discussion on photochemistry in the gaseous, liquid and solid state reference should be made to the book by Calvert and Pitts (3). Discussion of the phenomenon of degradation and stabilisation of polymers and related materials is available in texts (4-8).

1 - 1. Mechanism of Degradation in Irradiated Polymers

The initial reaction in the photodegradation of polymers is usually the absorption of light by a chromophoric group present in the polymer molecule, or by some impurity present. This gives rise to an excited singlet state which can return to its initial state by emission of light (fluorescence), or may give rise to an excited triplet state and a radiationless transition accompanied by dissociation. The excited state may undergo quenching of fluorescence (singlet-singlet energy transfer to an acceptor molecule). Other reactions that can occur are transformation of the triplet state, photodissociation, or the formation of photolytic products, and/or crosslinking. The reaction species is not normally the result of direct bond scission, although if light of wavelength less than 300 n.m. is used, bond scission can and does occur (9). In many photochemical studies unfiltered low pressure mercury arcs (strong band at 254 n.m.) are used. This band does in some cases lead to direct scission of bonds e.g. photolysis of propylene oxide (light source emitting 95% of its energy at 254 n.m.) was said to produce homolytic cleavage of a carbon - oxygen bond with formation of propanol and acetone as major products (10).



The use of radiation of wavelength greater than 350 n.m. did not produce similar results.

The normal nomenclature of initiation, propagation and termination is applicable to the free radical chain reaction occurring in irradiated polymers. Initiation may be due to light absorption by a chromophoric group such as carbonyl or by some impurity, which again may be a carbonyl or hydroperoxide whose presence may be due to processing conditions, as happens with unstabilised polyolefins. The sensitising action of the carbonyl group of acetone has been investigated (11) in the degradation of polyvinyl chloride. Another impurity sometimes found is the metal catalyst residue, which can catalyse the decomposition of hydroperoxides (12). Often the presence of these impurities cannot be determined by direct spectroscopic (or chemical) means because of their low concentration and indirect methods, such as the determination of quantum yield at different wavelengths of irradiation, must be used.

Once the initial radical is formed, propagation occurs. If oxygen is present the immediate reaction is the formation of peroxide radicals, which may react with the polymer substrate causing chain scission (13). This reaction is known to occur in the oxidation of rubber (14), where hydroperoxides and cyclic peroxides are formed, the latter giving rise to oxidative chain scission. However, since these reactions have activation energies of approximately 17 k.cals per mole, they should not proceed with noticeable velocity until a temperature of 100 ^{o}C is reached. In epoxide resins the curing temperatures are often in excess of 100 ^{o}C, also exotherms which occur during the crosslinking processes can produce, in the bulk of the material, temperatures greater than 100 ^{o}C. Thus photo-oxidative scission can proceed readily by reaction of the peroxides with the polymer chain.

The peroxide group may attach itself to other centres of unsaturation such as carbon - carbon double bonds which may still remain in the polymers. This occurs in the photo-oxidative degradation of styrene (15) to produce overall 1,2 addition

$$\mathrm{POO\cdot} + \mathrm{CH_2 = CH - C_6H_5} \longrightarrow \mathrm{POO{-}CH_2 - \dot{C}H - C_6H_5}$$

where POO· is a peroxide radical on the polymer chain

It has been suggested (16) that this may be the mechanism by which drying oils act. The termination reactions that occur are almost exclusively between two peroxide radicals, giving rise to stable products.

The Overall Scheme for Oxidative Degradation of Polymers

1. Initiation

$$RH + O_2 \longrightarrow ROO\cdot + H$$

2. Propagation

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

$$ROOH \longrightarrow RO\cdot + HO\cdot$$

$$ROOH + RH \longrightarrow R\cdot + RO\cdot + H_2O$$

3. Termination

$$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2$$

1 - 2. Stabilisation of Polymers

The most widely held view on the mechanism of light stabilisation of polymers reduces to the screening effect of a light stabiliser additive (17-20). It is suggested that a light stabiliser acts as a filter, weakening the flux of photons reaching the polymer. Unsuccessful attempts have been made to correlate the absorption spectra and efficiency of stabilisers (21). The most noteworthy is that of Hirt and Schmitt (22). They derived an expression for the protective effect of a stabiliser based on the ratio of energy absorbed by the polymer without additive, to the energy absorbed by the polymer with added light stabilisers. This ratio is always greater than unity because the energy absorbed by the polymer with additive is greater than that of the polymer alone. This suggests that any ultraviolet absorber, at a given wavelength, should exhibit a stabilising action on irradiation with light of this wavelength. However, experimental results show that this is not the case (21, 23). In general no correlation exists between the ultraviolet spectra of light stabilisers and their stabilising effect.

Comparison of the Hirt and Schmitt ratio for different polymers (22, 23) shows that the stabilisation effect cannot be explained merely by screening. Nor can the sensitising effect of some light stabilisers with certain polymers be explained in this way. Unsuccessful attempts have been made to develop a theory of the interaction of substrate and additive, to explain the mode of action of light stabilisers (18, 19).

Schmitt and Hirt (22) postulated a non radiative energy transfer between a donor and an acceptor as being the stabilising or sensitising effect in polymers.

The derivation of the Hirt/Schmitt ratio is based on this assumption i.e. the possibility of independent interaction of the reactive sites in a system. Some support for this theory has been found by studies of the quenching of luminescence of polymers by stabilisers (24, 25) as is the case of polypropylene with 4-hydroxybenzophenones. However, quenching may not be entirely due to energy transfer.

The thickness of the polymer sample is also of importance in stabilisation studies. Grassie (26) found that the stabilisation of polystyrene with 2-hydroxy-4-methoxy-benzophenone was completely retarded in thin films, and that the additive accelerated the rate of oxidation of the polymer. In thick specimens the outer layers break down on addition of the stabiliser, but the bulk of the polymer is protected by the screening effects of the additive. Similar effects were found by Fox and Rice (27) for the sensitisation of P M M A by 2, 4, dihydroxybenzophenone with light of wavelength 254 n.m. Stabilisation was observed with benzophenone, because of energy transfer from the P M M A molecule to the triplet levels of benzophenone.

1 - 3. Synergism

Synergism is the ability of a multi-component system to act as a stabiliser to an extent greater than the sum of the stabilising actions of the individual components. These systems consist of an ultraviolet absorber in combination with both chain breaking and peroxide decomposing antioxidants (6). The ultraviolet absorber prevents the injection of free radicals into an autoxidisable medium in part by protecting hydroperoxides from photolysis. Both peroxides and hydroperoxides are decomposed by ultraviolet radiation even at long wavelengths.

Absorption Wavelengths of Peroxides and Hydroperoxides (3)

Compound	Absorption Wavelengths (n.m.)
Dimethyl peroxide	350 - 200
Dicumyl peroxide	320 - 240, and less than 240
tert-Butyl hydroperoxide	320 - 200
Cumene hydroperoxide	320 - 230, and less than 230

The decomposition of hydroperoxides can be represented as

$$ROOH \longrightarrow RO\cdot + \cdot OH$$

The radical pair RO· and ·OH can then start a free radical chain. The more efficient peroxide decomposers have quite a high order of ultraviolet deactivating activity and suppress the decomposition of hydroperoxides to chain initiating fragments.

In some pigmented synergistic systems the effectiveness of phenolic and amine antioxidants can be reduced (28) e.g. carbon black pigment in polyolefins, where the adverse effect is attributed to absorption of the antioxidant on the carbon surface, followed by oxidation (29) of the antioxidant.

With complex systems such as epoxide resins and polyesters effective stabilisation by many of the known light screens, ultraviolet absorbers and antioxidants have failed. Successful stabilisation lies in developing new hitherto unknown stabilisers or in the use of synergistic mixtures.

REFERENCES

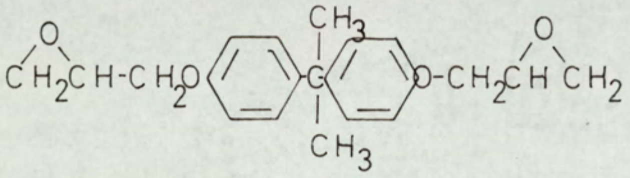
1. Miller, S.L., Science 117, 528, 1953
2. "Ageing and Weathering of Plastics", RAPRA 1970 Review of Literature
3. "Photochemistry", by Calvert, J.G., Pitts, J.N., J. Wiley and Sons, New York, 1966
4. "Ageing and Stabilisation of Polymers", Ed. Neiman M.B., Consultants Bureau, New York, 1965
5. "Stabilisation of Synthetic High Polymers" by Gordon G. Ya., Israel Program for Scientific Translations, 1964
6. "Atmospheric Oxidation and Antioxidants" by Scott, G., Elsevier, Amsterdam, 1965
7. "Die Stabilisiering der Kunstoffe gegen Licht und Wärme", von Voigt, J., Springer-Verlag, Berlin, 1966
8. "Autoxidation of Hydrocarbons and Polyolefins", Reich, L., Stivala, S.S., M. Dekker Inc., New York, 1969
9. Swanson, L.W., Volman, D.H., J.A.C.S. 82, 4141, 1960
10. Gritter, R.J., Sabatino, E.C., J. Org. Chem. 29, 1965, 1964
11. Kenyon, A.S., U.S. Nat. Bur. Stand, Rept. 525, 1953 p.81
12. Mercurion, A., Tobolsky, A.V., J.A.C.S. 81, 5535, 1959
13. Bolland, J.L., Quart. Rev. Chem. Soc. 3, 1, 1949
14. Bailey, H.C., Indus. Chem. 215, 1962
15. Mayo, F.R., Miller, A.A., J.A.C.S. 78, 1017, 1956
16. Mayo, F.R., Ind. Chem. Eng. 52, 614, 1960
17. Strobel, A.F., Cating S.C., Ind. Eng. Chem., Prod. Res. Dev. 1, 241, 1962
18. Balaban, L., Chem. Promysl. 13, 45, 1963
19. Balaban, L., Chem. Promysl. 14, 366, 1964
20. Maxim, L.D., Kuist, C.H., Am. Chem. Soc. Polym. Preps 4, 352, 1963
21. Wright, N., Plastics 28, 125, 1963
22. Schmitt, R., Hirt, R., J. Appl. Polym. Sci. 1, 1565, 1963
23. Takamatas, T., Kenichi, S., Chem. High Polymers (Japan) 21, 494, 1964
24. Pivovarov, A.P., Ershov, Yu. A., Plast. Massy No. 10, 7, 1966
25. Suppan, P., Ph.D. Thesis, University of Sheffield 1965
26. Grassie, N., Weir, N.A., J. Appl. Polym. Sci., 9, 987, 1965
27. Fox, R.B., Rice, T.R., Am. Chem. Soc. Polymer Preps 5, 390, 1964
28. Speckman, J.W.C., Chem. and Ind. (London) 1532, 1961
29. Hawkins, A.L., Winslow, F.H., Worthington, M.A., Proc 4th Conf. on Carbon, p. 63, 1959

CHAPTER 2

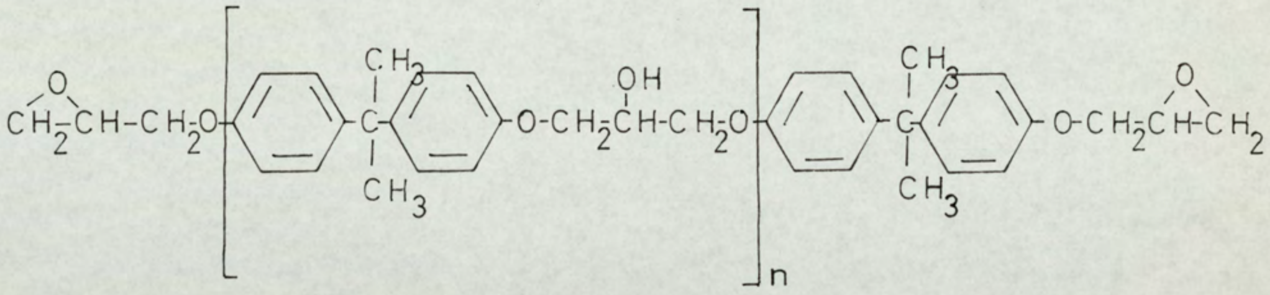
Introduction to the Chemistry of Epoxide Resins

Epoxide resins were first prepared commercially in 1936 by Caston in Switzerland (1) and by Greenlee in the United States (2). Their monomers were based on the reaction product of epichlorohydrin and bisphenol - A, and were the outgrowth of several decades of research by workers in the field of substituted ethylene oxide derivatives (3, 4, 5, 6).

The most commonly used epoxide monomer is the diglycidyl ether of bisphenol - A, prepared by reaction of epichlorohydrin and bisphenol - A in the presence of caustic soda, (7)

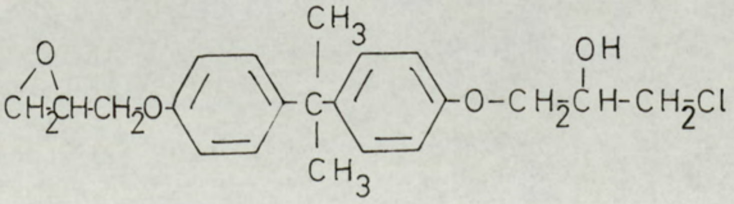


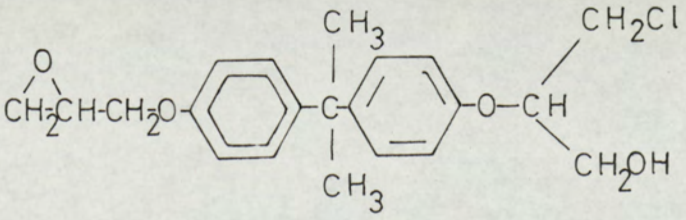
when pure it is a crystalline solid of melting point 40 °C. The monomer used in commercial resins consists of the following structure:



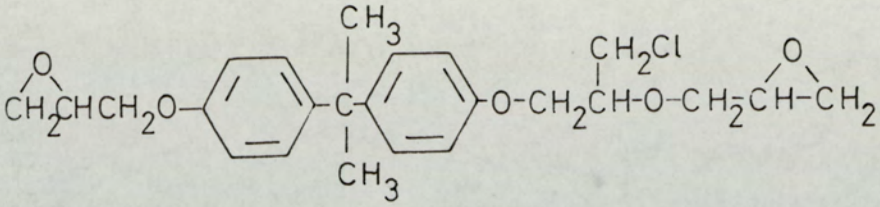
where $n = 0.5 - 12.0$

together with impurities present which may come from the sulphur in bisphenol - A, the solvent from the removal of caustic soda or chlorine ($<1\%$) from the excess quantities of epichlorohydrin, or from structures of the type

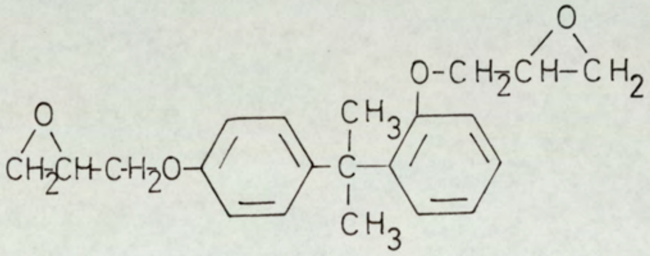




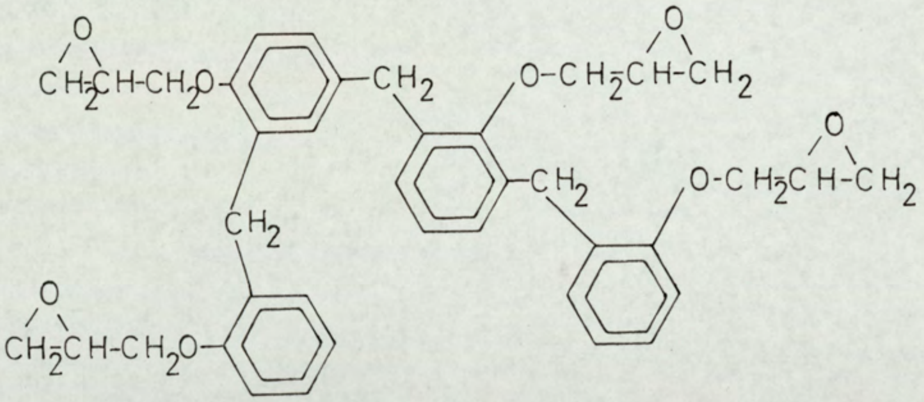
or



in which ring closure, to form one of the terminal epoxide groups during the synthesis, has not been successful (8). A 1, 2 addition product (1 - 2%) is also present (9)

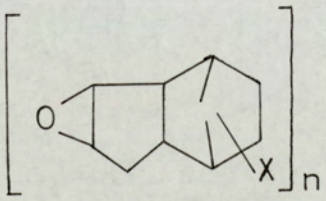


A number of other epoxide monomers are also used commercially including (i). Epoxide novolacs (10) having oxidation resistant structures



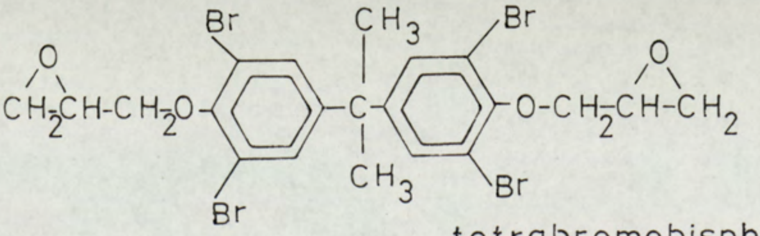
Epoxide phenol-formaldehyde novolac resin

(ii). Cycloaliphatic epoxides (10-15) such as tricyclodecene oxide group



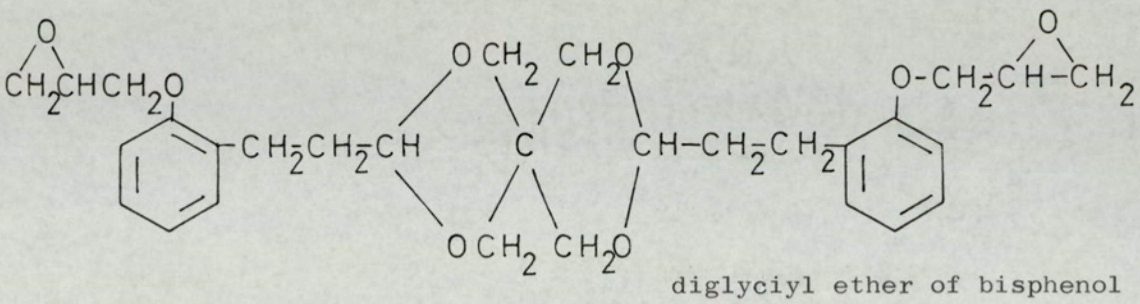
X = ester, ether, acetal etc., which have greater heat resistance and improved electrical properties

(iii). Halogenated bisphenol - A types which impart flame resistance (16)



tetrabromobisphenol-A

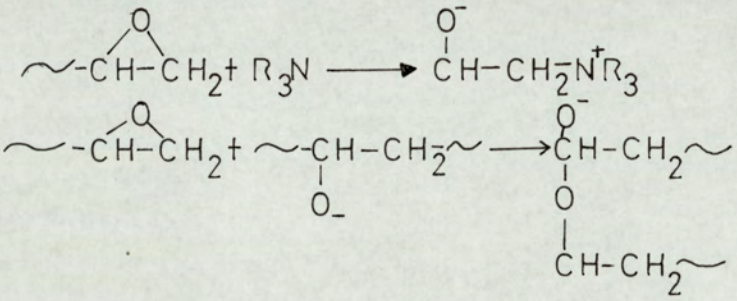
The use of long linear segments between epoxide groups gives greater toughness and flexibility e.g.



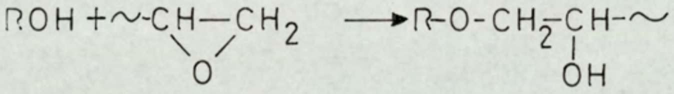
diglyciyl ether of bisphenol "PA" (17)

2-1.2 Polymerisation of Epoxide Monomers

Polymerisation is accomplished by the use of catalysts such as tertiary amines (18)



The epoxide groups can, in the presence of the tertiary amines, react with hydroxyl groups in the commercial monomer (19)



$$ROH + \sim CH{-}CH_2 \text{ (epoxide)} \longrightarrow R{-}O{-}CH_2{-}\underset{OH}{\underset{|}{C}}H{-}\sim$$

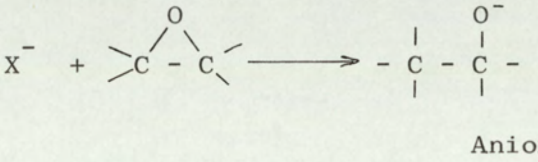
The tertiary amine approaches one of the carbon atoms of the epoxide group, and attaches itself generally from the rear. It has been suggested that the reaction then requires the presence of a hydroxyl group or equivalent, which provides hydrogen bonding for the epoxide oxygen. The transition state is three membered, and favours the creation of an alkoxide ion from the original hydrogen donor. Once available this ion reacts with the epoxy group, creating a new alkoxide ion.

Tertiary amines alone are normally required in high concentrations, indicating frequent chain termination. Also, the reaction of hydroxyl with epoxide is insignificant without amines, even at 200 °C (20).

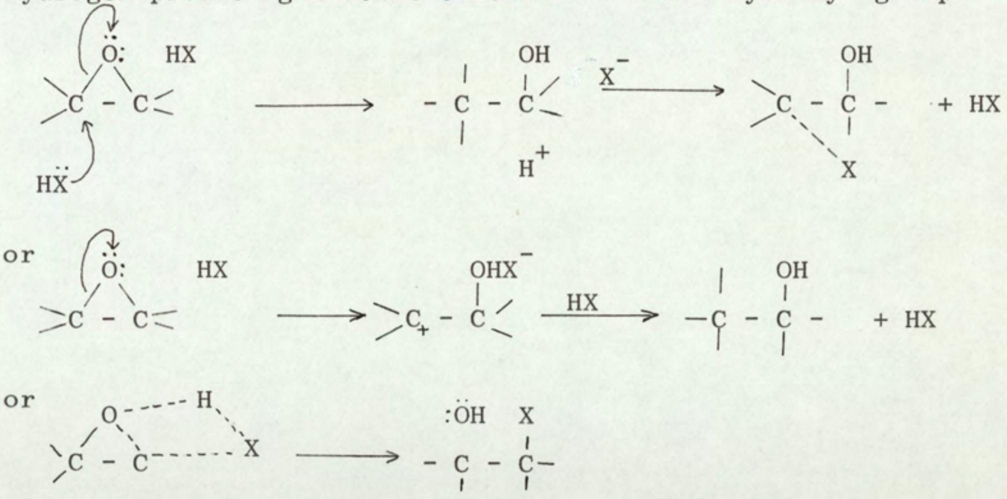
2-1.3 Crosslinking of Epoxide Monomers

The reactivity of the epoxide group is determined by its accessibility, and the electronic nature of the epoxide oxygen atom. The stereochemistry of bulky substituents on the reactive molecule may necessitate rearward or sidewise approaches. On the other hand if there is accessibility then the nature of the neighbouring substituents is important. Electron attracting groups increase the rate with nucleophilic curing agents and the same is true of electron withdrawing groups with electrophilic curing agents.

The epoxide group may react anionically



or cationically where ring opening may be accomplished by an active hydrogen producing a new chemical bond and a hydroxyl group



Normal curing agents are primary and secondary amines, amido polyamines, organic acids and acid anhydrides.

2 - 1. 4 Types of Amine Curing Agents

In order to form a three-dimensional structure, it is necessary for one of the reagents to be trifunctional and for the other to be at least bifunctional (21). The epoxide group normally used has only two reactive groups, thus the amine must have three. Therefore, polyamines must be used, since primary amines have a functionality of two.

Common aliphatic and aromatic polyamines include:

ethylene diamine

$H_2N - (-CH_2-)_2 -NH_2$

diethylene triamine

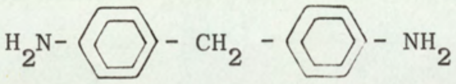
$H_2N - (-CH_2-)_2 -NH - (-CH_2-)_2 -NH_2$

triethylene tetramine

$H_2N- (-CH_2-)_2 -NH-(-CH_2-)_2 -NH- (-CH_2-)_2 -NH_2$

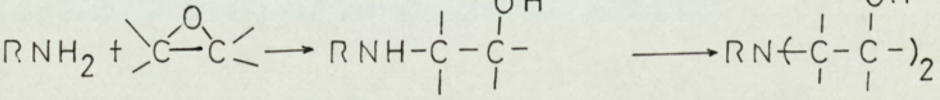
meta-phenylene diamine

p, p - di-amino-diphenyl methane

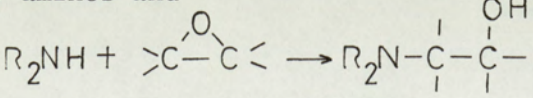


The latter gives increased heat resistance.

2 - 1. 5 Reaction of Epoxide Monomer with Primary and Secondary Amines (22).



for primary amines and



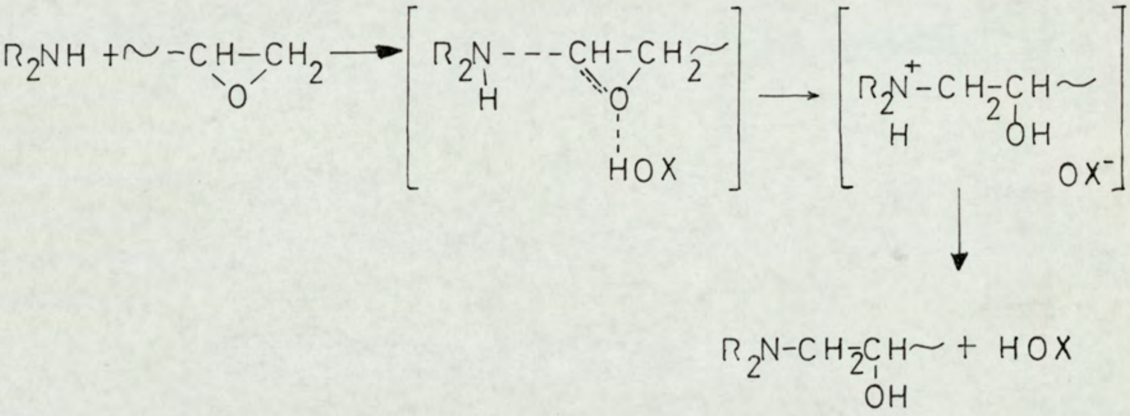
for secondary amines

Since primary amines have only one bulky substituent, they may approach the epoxide carbon atoms from other than an absolutely linearly rearward direction, making them suitable for use with ring situated groups.

Secondary amines approach from the rearward direction. Although the transition state is strained, some secondary amines are capable of sluggish reactivity with the ring substituted epoxide groups. Tertiary amines due to their size do not catalyse the epoxide-hydroxyl reaction.

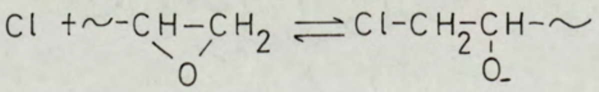
The reaction of epoxide with amines is second order, with an activation energy of 14-15 k.cal./mole (23).

The effects of solvents on epoxide/amine reactions have been investigated (18, 20 and 23). It was found that the solvent could to a large extent influence the reaction pattern as determined by the types of products obtained. Non-hydroxyl solvents retarded the reaction because of dilution effects. Alcoholic or phenolic solvents catalyse the reaction by aiding ring opening of the epoxide group by hydrogen bonding in the transition state (20)



2 - 1. 6 Effects of Chlorine on Amine Epoxide Reactions

Wynstra et al (20) whilst using potassium hydroxide as a catalyst for a glycidyl ether reaction found that the presence of chlorine caused precipitation of potassium chloride, and a gradual loss of catalytic power. No effect was noticed with the tertiary amine catalyst for phenol, or acid - glycidyl reactions. However, chlorine had an immediate effect on alcohol-glycidyl systems, producing acid conditions which prevented rapid reactions.



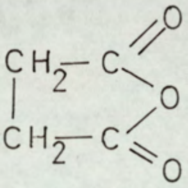
In the reaction the equilibrium lies to the left hand side of the equation. Insoluble chlorides would shift the equilibrium completely to the left. The presence of phenols and acids shift it to the right hand side by neutralising alkoxide ions, and generating more stable carboxylate or phenoxide ions, which then react with the epoxide. Chlorine however adversely affects the alcohol-glycidyl ether reaction, because there is no similar driving force to upset the equilibrium and produce the necessary degree of alkalinity to ensure a rapid reaction.

2 - 1. 7 Types of Acid Anhydride Curing Agents

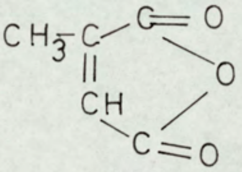
Acid anhydride curing agents crosslink by reaction with hydroxyl groups which are either initially present in the epoxide monomer, or formed by catalytic epoxide ring opening (24)

Common anhydride curing agents include:

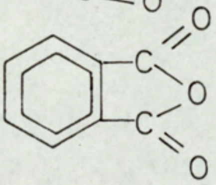
succinic anhydride



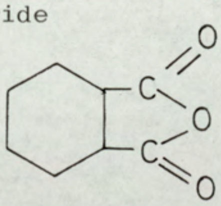
citraconic anhydride



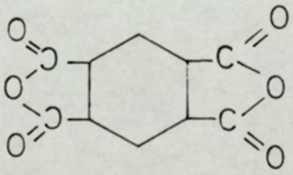
phthalic anhydride



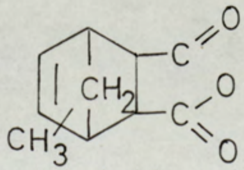
hexahydrophthalic anhydride



pyromellitic dianhydride



methyl nadic anhydride

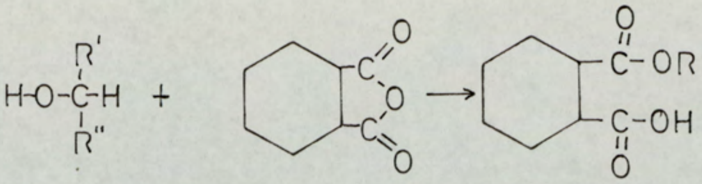


2 - 1. 8 Reaction of Epoxide Monomer with Acids and Acid Anhydrides

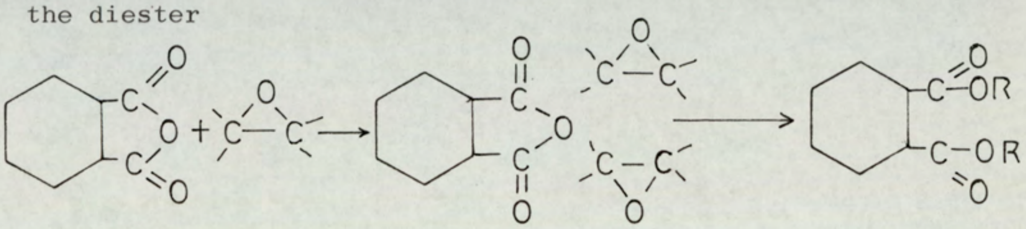
Fisch and Hofmann (25) showed that the uncatalysed reaction of anhydrides and acids proceeded by the following reactions:

1. Anhydrides

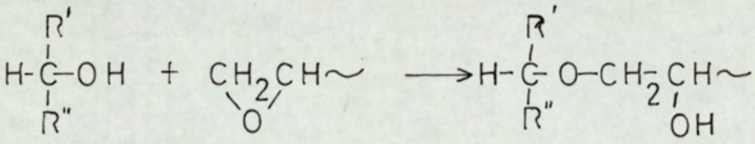
1. Ring opening of anhydride to form the monoester



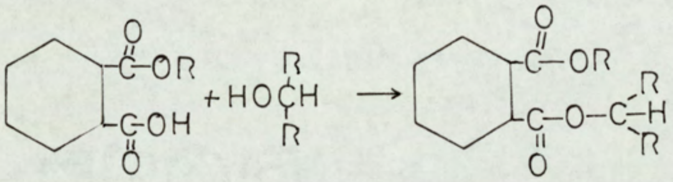
2. Reaction of carboxylic acid and epoxide groups to form the diester



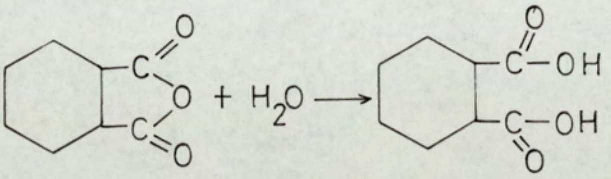
3. Epoxide alcohol esterification



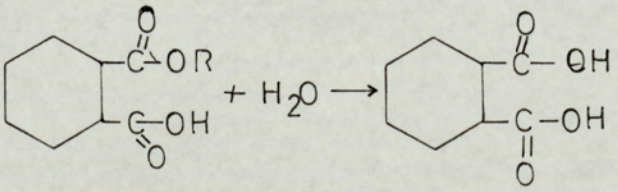
4. Diester formation between monoester and alcohol



5. Diacid formation from anhydride and water



6. Diacid formation from monoester and water

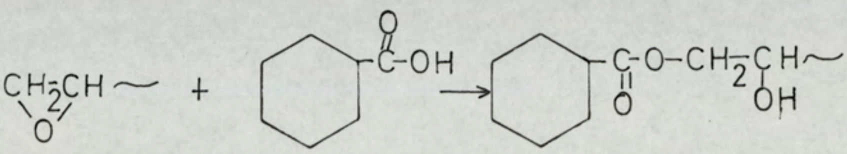


Reactions 1 - 3 inclusive are important reactions in the curing of epoxides by anhydrides, reaction 2 the diester formation being the most important.

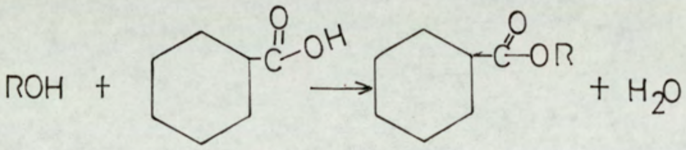
The formation of ethers from the epoxide alcohol reaction proceeds in the presence of acids as catalysts. An equal number of ether and ester linkages result from the catalytic cures of the epoxide monomers by anhydrides.

II. Acids (26)

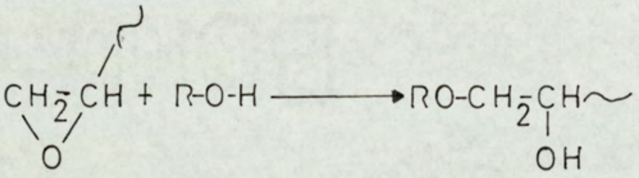
7. Epoxide - acid esterification



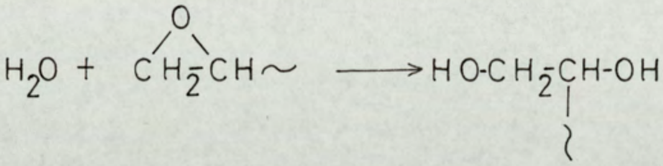
8. Hydroxyl - acid esterification



9. Epoxide - hydroxyl esterification



10. Hydration of epoxide groups

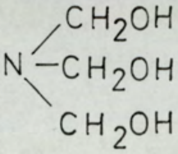


In practise reaction 8 is suppressed due to the reaction equilibrium, although some water might be removed through alcohol formation (reaction 10), or evaporation during elevated temperature cures (27). The esterification and etherification reactions (reactions 7, 8, 9) play a major role during cure and are temperature dependent, with higher temperature favouring increasing addition esterification. The latter is also dependent on the nature of the carboxyl group and the location of the epoxide group in the molecule (28).

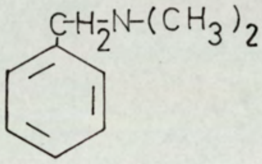
An important step in epoxide cures is the ring opening of the anhydride. This is achieved by active hydrogens present as water or hydroxyl groups, or by a Lewis base.

The common Lewis bases employed include:

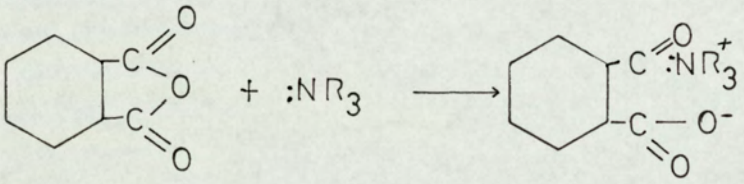
triethanolamine



benzyldimethylamine

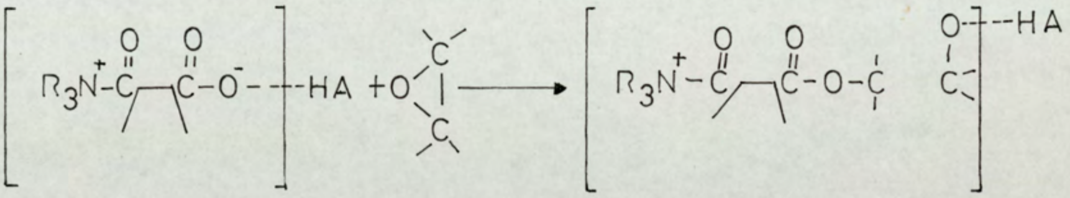


The Lewis base reacts with the epoxide group releasing an anion capable of continuing the reaction through other chain elements. The base reacts preferentially with an anhydride to generate a carboxyl ion



This carboxyl ion then reacts with an epoxide group, and a further ion is generated, which may then open a second anhydride ring.

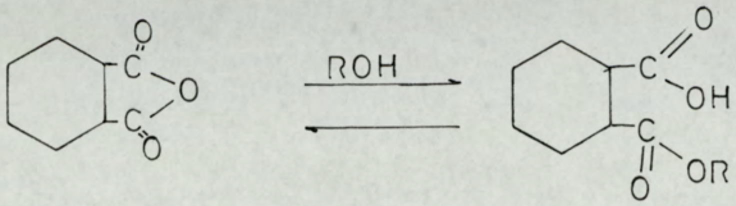
When active hydrogens are present the proposed initiation step is:



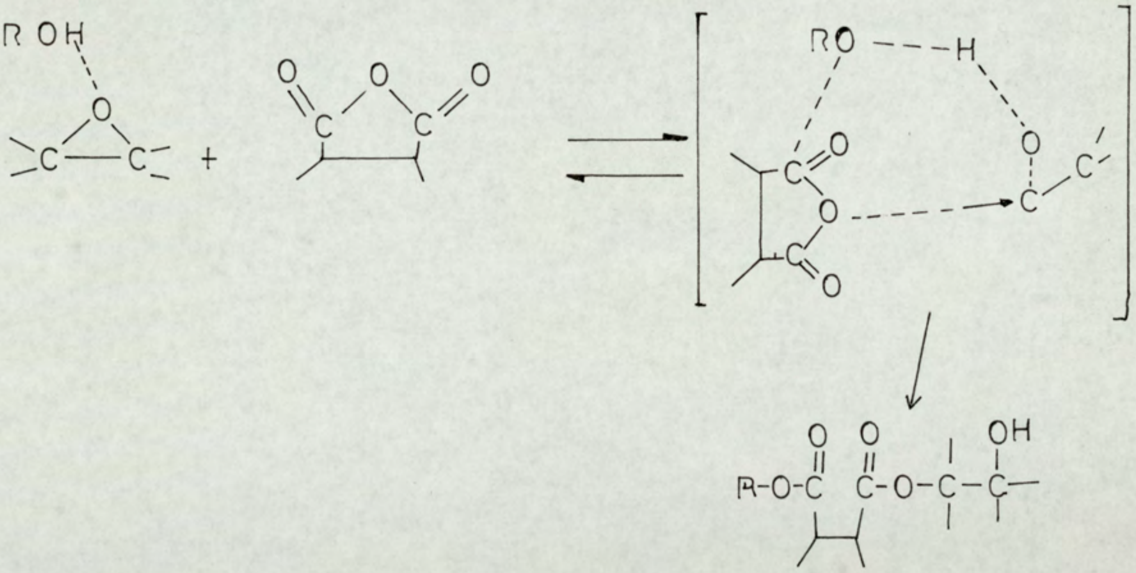
In support of this mechanism it was found that cocatalysts (amine/alcohol or amine/phenol) acted as synergists (29). After initiation the reaction continues in such a way as to introduce alcoholic residues into the system.

The reaction equilibrium of condensation esterification of anhydrides may be ignored, unless the water formed is removed. However preparatory to the carboxyl-epoxide reaction, a new reversible reaction is introduced when the monoester is formed.

Volatile compounds which are part of the equilibrium may be lost by evaporation from the surface. Much of the weight loss experienced with the anhydride systems at temperatures of 150 to 200 °C may be attributed to the splitting out of incompletely reacted anhydrides, initially present as monoesters, and to subsequent volatilisation of the anhydride.



Reaction rate studies on the ring opening indicate that in some cases a termolecular transition state is formed producing two ester linkages



2 - 2. Review of Literature on the Effects of Ultraviolet Radiation on Epoxide Resins (30)

The results reported to date may be divided into two categories:

(a) Effects of natural weathering on cured epoxide resins

(b) Effects of artificial weathering on cured epoxide resins

(a) The natural weathering of cured epoxide resins has been reported by Pschorr and Cianiurulo (31), who exposed amine cured specimens outdoors as specified by A S T M-D-1435-58 for up to five years.

Glaser and Floyd (32) reported on a five year exposure investigation of polyamide - epoxy coatings; Lebbink (33), and Werren and Lebbink (34) investigated amine paint systems, both pigmented with rutile titanium dioxide, and unpigmented, exposed to natural weathering. These investigations included studies of the effect of curing conditions, curing agents, resin, and filler type on the rates and extents of degradation.

2 - 2. 1 Effect of Curing Agents and Conditions

Pschorr et al (31) found a greater retention in mechanical and dielectric properties on irradiation with higher temperature cured systems. They found little difference between TETA and a "safety" hardener. Aromatic diamines and anhydrides were superior to the aliphatic amines.

Hebbink et al (33, 34) found that the quantity of curing agent was of importance in gloss retention on ultraviolet exposure. Smaller quantities than the theoretical amounts gave much better gloss retention. This was the case with diethylene triamine (DTA) and ethylene diamine (EDA), although the differences were greater with variation in the percentage of DTA. Equivalent amounts of DTA gave better gloss retention than EDA, which was equivalent to polyamines. The curing agent appeared to have no effect on the change in transmission, characteristic of the cured materials undergoing ultraviolet degradation. Glaser and Floyd (32) reported that polyamides were superior to amines and that epoxy esters were superior to both in gloss retention on irradiation. They also found for a series, including epoxy, vinyl and alkyd, that whiteness after exposure was of the order:

alkyd > polyamide/epoxy > amine/epoxy > epoxy ester > phenolic > oleo resins

Epoxy enamels were superior to alkyd enamels on long term exposure.

De Hoff (35) reported similar results for the natural weathering of Epon 828 with a variety of amine and anhydride cured systems. Based on flexural properties, the resistance to weathering of the various systems was rated:

HHPA > NMA > m-phenylenediamine > boron trifluoride monoethylamine > epon curing agent Z > TETA > chlorendic anhydride > DETA > DDSA > diaminodiphenyl sulfone.

2 - 2. 1. 1 Effect of Resin

Lebbink et al (33, 34) found that addition of epikote 828 to epikote 1001 (a higher molecular weight version of the 828 system) had a deleterious effect on the ultraviolet stability of the latter. They suggested that heterogeneous film formation occurred with monomers of different molecular weight (828, 1001). They also proposed that poor film formation was the reason for bad weathering of the 828 systems.

2 - 2. 1. 2 Effects of Fillers

Lebbink (33) found that certain combinations of solvents (e.g. cyclohexanone, xylene:MIBK) had a tendency to "sweat" out the curing agent, and that the addition of butyraldoxim resulted in a noticeable improvement.

Floyd and Glaser (32) found that the addition of corrosion inhibitors to the systems improved the ultra-violet resistance, evaluated in terms of the protective efficiency of paint films. The polyamide epoxy system, containing chrome green pigment, gave nearly as good a performance, as the same system with conventional corrosion inhibiting pigments (red lead and zinc oxide), which suggests that the polyamide/epoxy enamel should have superior weathering characteristics. However, they did not evaluate such systems.

Exposure of silica filled and unfilled epoxy resin systems was made by Rugger (36). He found no noticeable changes after six months, but after a year's natural exposure the unfiltered system darkened, while the silica filled system chalked. After eighteen months exposure the colour was much darker, and the chalking more severe. (Orange staining, and hazing with flexible systems). Less change was observed up to 24 months when the tests were discontinued. Addition of fillers, such as quartz and slate powder, have been reported to decrease deterioration due to weathering.

Matting and Ehrenstein (37) are currently evaluating the natural weathering characteristics of a variety of systems, including epoxide and glass reinforced plastics. No results have been reported for unreinforced systems.

(b) Artificial Weathering of Epoxide Resin Systems

A number of useful studies have been reported on the ageing of epoxide resin systems using artificial light sources. Unfortunately the authors used different sources, and no details of the light output were given. Also, as with natural weathering studies, a wide variety of curing agents have been used, and no details of cure schedules and conditions were reported. No quantifications were reported. No quantification of the results was attempted, though Lee and Watson (38) did attempt to correlate colour formation with other properties.

2 - 2. 1. 3 Effect of Curing Agents and Conditions

Christie (39) evaluated diglycidyl ether of bisphenol-A (DGEBA) cured with trimethoxyboroxine, and with HHPA, using a General Electric black light and Westing House sunlamp, and found that the trimethoxyboroxine system was more resistant than the HHPA cured system. Lemon's results (40) confirmed this and also showed the susceptibility of HHPA systems to degradation. He also found that aromatic polyamines were superior to boron trifluoride monoethylene complexes. He reported that, after exposure at 200°C for 100 - 1000 hours, considerable dimensional changes together with surface cracking and embrittlement occurred with amine cured systems.

Lee and Watson (38) investigated a large number of curing agents, using changes in ultraviolet/visible spectroscopy transmission characteristics as a measure of degradation. Their results showed that resins, cured with amine hardeners which gave the lightest initial colour, were most resistant to discolouration on exposure to ultraviolet light. Amines in which nitrogen atoms were not situated on aromatic rings, and were separated from each other by methylene or propylene groups rather than ethylene groups, resulted in colour stable resins. Similarly resins cured with amines of lower functionality showed low colour formation. The discolouration ranged from dark brown to faint yellow.

Using hydroxyethyldiethylene curing agent Wohl (41) found that a 10% reduction in strength occurred after five hundred hours exposure to radiation of wavelength 200 - 600 n.m. Also, a loss in weight of 1% in the form of plasticiser and other non polymerisable substances occurred during similar exposures, under a vacuum of 10^{-6} torr.

Schmitt and Hirt (42) carried out a major research project on numerous plastics, including high molecular weight bisphenol-A based epoxy resins cured with diethylene triamine and with alkylated melamine resins. The light source used was an unfiltered xenon lamp and the time of exposure was 250 hours. However, no results were reported for the epoxide systems used. Woelfel (43) reported in a less definite way on a similar system for use as denture material, as did Gaubart (44) using linoleic acid dimer, polyamide cured.

Khozin and Vaskresonski (45) studied the effect of natural and artificial weathering (twin mercury arc, energy output 0.27 cal/cm^2 min) in a polyethylenepolyamine cured epoxide resin based on DGEBA and furfural - acetone modified epoxide resins of the same type. A polyester based on diethylene glycol and adipic acid was used for comparison purposes. Thermo-mechanical methods, microscopy and soxhlet extraction were used to follow the degradation process. Both epoxide systems were found to undergo a further hardening process on ultra-violet irradiation as evidenced by the increase in molecular weight and Tg. This was attributed to undercure in the test pieces. Fully cured systems were found to react in the opposite way (reduction in Tm and Tg and an increase in high elastic deformation). Resins fully cured over long periods at room temperature, especially the unmodified ones, were most adversely effected, as shown by the increased quantity of soxhlet extracted material from the latter. 600 hours artificial ageing gave degradation similar to that obtained from six months outdoor ageing.

Microscopy studies of the degraded surfaces showed the presence of a network of micro cracks. Unmodified specimens, cured at room temperature and tested under atmospheric conditions, displayed wide cracking, while the surface of weatherometer aged samples showed a more dense network of narrow cracks. Samples subjected to heat treatment after curing had less dense networks of cracks. Furan/alcohol modified systems showed a dense network of wide cracks for naturally and artificially aged specimens.

The flexural and impact strength of all systems were diminished on ageing. There was little difference in the decrease of flexural strength (39-40%) for both types of ageing of the furan/alcohol modified specimens.

In the unmodified samples the decrease of flexural strength was much smaller for both types of ageing. The drop in impact strenth (crack dependent) was 20-30% for all samples. These results agreed with those reported by Pierce (46), Somerville (47) and Halsworth (48). However, the latter did not specify ageing conditions, and the difference in the rate of degradation of the epoxides used was partly due to this, and also to the composition and dimensional differences in the samples.

2 - 2. 1. 4 Effect of Resin

The ageing of three types of resin including liquid diphenyl propane based resin, solid diphenylol propane based resin, and a poly-functional novolak based resin, were studied by Lemon (40). The best resistance to ultraviolet irradiation was attained with the novolak materials and can be attributed to the highly aliphatic character of these materials.

Cyclo aliphatic resins have been prepared by Trigaux (49) which showed a superior resistance to weathering. Christie (39) evaluated bisphenol-A type epoxides, vinyl-cyclohexene dioxide (VDO) and 3, 4 - epoxy - 6 - methyl - cyclohexylmethyl - 3, 4 - epoxy - 6 - methylcyclohexene carboxylate (DDC), cured with HHPA. They were both found to be inferior to acrylic systems. However, the DDC resin showed only a 4 % decrease in light transmission properties after 500 hours exposure (sunlamp black-lamp) while the VDO/HHPA system showed a 9% decrease. A trimethoxyborine TMB/DGEBA resin proved to be superior in light transmission characteristics to all other systems.

Modification of epoxide resins was found by Pschorr (31) to affect their weathering properties. Modified liquid epoxide resins and low viscosity epoxide resins showed greater change in tensile and flexural properties, than the equivalent unmodified materials. Least change in dielectric constant occurred with the modified liquid epoxide resin.

Modification of epoxide resins by the addition of different amounts of aliphatic diepoxide diluent (1, 4 - butanediol diglycidyl ether) was studied in accordance with ASTM-D-1435 - 58(2). Less change in flexural and tensile strength occurred in diluent modified systems. The change in dielectric constant was more pronounced with the increased amount of diluent present. Kurz (50) compared bisphenol-A type epoxide resins with cyclo aliphatic epoxide resins, and found comparable flexural strength, lower heat distortion temperature and except for an aromatic diglycidyl ester all had superior track resistance.

Trigaux (49) evaluated cyclic aliphatic diepoxides and found them superior to conventional bisphenol-A epoxides in terms of ultra-violet resistance. The improved colour stability was probably due to the lack of phenolic nuclei in the resin. High heat deflection values were also found for these materials, which confirmed Pschorr's findings, that systems of highest deflection temperature show least surface change on ultra-violet exposure. This disagreed with the findings of Kurz (50).

2 - 2. 1. 5 Effect of Fillers

Hearst (51-53) using mercury and xenon light sources reported in a series of papers on the effect of fillers on amine and polyamide cured epoxide resins. The evaluation was made by the yields of gaseous degradation products found by infra-red spectroscopy. He found that the yields of volatiles were always less with pigmented, than with the corresponding clear films, but the addition of pigment had no uniform quantitative effect on the yields of individual volatile products. The yield of carbon dioxide (major product) was not always reduced by pigmentation. Pigmentation greatly reduced, or eliminated the production of ethylene and acetone (by mercury or xenon irradiation), but it had comparatively small effect on the yields of acetylene and methane obtained from mercury are irradiation. This relatively small effect of pigmentation on some of the mercury arc irradiation products may be due to lower penetration at shorter wavelength. This difference in the effect of pigmentation on the yields of some of the volatile products indicated differences in some of the photodegradation reactions that occur with the mercury and xenon arc irradiations.

Clauss et al (54) tested epoxy resins, (composition not reported) filled with titanium dioxide, using an argon filled high pressure mercury lamp (65,000 lumens). The lamp and the sampleng housing were water cooled to absorb infra-red radiations. He found that colour formation occurred in less than twenty six hours. In all cases "tinting" of titanium dioxide by pigments caused a deeper colour to be formed.

In the same study cured epoxide and epoxide/phenolic adhesives were evaluated by ultraviolet light and gamma rays (temperature 100 - 150 °C, and vacuum 10^{-6} torr). No results were reported.

2 - 2. 1. 6 Effect of Ultraviolet Light on Optical Properties

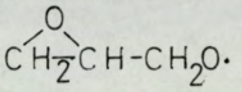
Work on the effect of ultraviolet light on optical properties was carried out by Lee and Watson (38) using the S - I sunlamp. Nelson (55) also used this light source in evaluating the effects of different stabilisers on the reaction product of DGEBA/DETA. Wiedmann (56) tested the same system under natural and S - I exposures, and found that after ten weeks marked yellowing occurred, the S - I lamp producing the greatest initial change. The rate of discolouration with the sunlamp and outdoor weathering was equal after 5 - 6 weeks, and the maximum discolouration occurred after 10 weeks regardless of the method of ageing. This disagreed with the work of Clauss (54). Schmitt (42) in his studies on the evaluation of ultraviolet stabilisers for plastics evaluated some epoxide resins cured with polyamines and melamines, using a Cary spectrophotometer for colour measurement. His results showed that unstabilised resins yellowed on ultravilolet exposure, and that some resins containing stabilisers yellowed during cure, others yellowed rapidly during the exposures. Lee and Watson (38), Christie (39), De Hoff (35), Woelfel (43), Crilly (57) and Smith (58) using a variety of light sources, reported that all systems tested yellowed on ultraviolet exposure. The use of tetrabromophthalic anhydride with epoxides resulted in rapid brown colour formation, due to light activated breakdown of the C - Br bond (59).

The change in optical characteristics of epoxy mirrors (828/m - phenylenediamine) was reported by Sexton and Kline (60), and correlation was made with subsequent changes in mechanical properties. Their work was concerned mainly with the production of optical flats by replica processes.

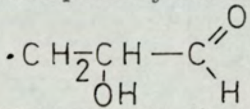
Tetreault (61) reported that laboratory ageing caused loss of gloss, and colour formation, but natural ageing resulted in chalking and loss of gloss.

A variety of epoxide monomers including DGEBA, butyl glycidyl ether, diepoxide cyclic aliphatics and epoxidised polycarbonate were investigated by Slowikowska et al (62) in terms of elasto-optical properties.

Voronkov et al (63) investigated the ultraviolet degradation of cured epoxide films by electron microscopy and infra-red spectroscopy. A mercury arc operating at 80 °C was used as the ultraviolet source. From their results, which reported changes in the original globular formation and the appearance of a carbonyl band (1658 cm^{-1}), they proposed a degradation scheme similar to that of Neiman i.e. formation of the radical



which subsequently isomerised to



$\cdot CH_2-\underset{OH}{CH}-C\begin{array}{l}/\!\!/O\\ \backslash H\end{array}$

They also proposed that ring opening of the unreacted epoxide groups, left from incomplete cure of the system, resulted in further curing initially, followed by breakdown later. The macromolecular structure of the films was broken down, and replaced by asymetrical structural elements, and complicated secondary macromolecular structures. The structural changes were accompanied by variation of mechanical and thermophysical properties, shown by change of moduli.

Artificial weathering tests have recently been reported on Araldite, bisphenol-A based epoxide systems, in terms of the changes in transmission characterised by ultraviolet/visible spectroscopy and by transmission infra-red spectroscopy using a xenon light source. Exposure times of up to 2,400 hours were used (66). A change in the transmission of 60% at 400 n.m. was found after 2,400 hours. No carbonyl groups were observed in the infra-red spectroscopy even after 18 days, however a broadening of all peaks was found on irradiation. This confirmed the earlier work of Hearst (51). From surface conductivity measurements, Hearst found that a steady state was reached in the degradation process. He assumed that the majority of broken bonds recombined and that only a few of the free radicals so formed combined with water and oxygen. When the irradiation source was turned off, the conduction fell exponentially, and plots on a log scale showed that two rates of recombination were present, suggesting that two types of bonds were broken in the original polymer. This is not in agreement with the work of Tetreault (61) who reported rapid chalking for bisphenol-A type epoxides.

Krapivin et al (64) investigated the kinetics of decay of cured epoxide films using laser pulses of 10^{-3} sec. duration, which generated crack formation and growth in the systems. He reported that on exposure to an impulse of light immediate structural changes occurred in the material, and a gas phase appeared, followed by cracks. Crack growth was quick at first, slowing down with the appearance of other cracks. The general plane of destructive growth varied linearly with time, in the beginning, because of the growing number of cracks, and finally because of the enlargement of existing cracks. The growth followed a step function from radii of 0.020 m.m. to 0.13 m.m. after 30×10^{-6} seconds. The area undergoing crack growth increased with time from 2 mm^2 at 15×10^{-6} sec to 16 mm^2 at 140×10^{-6} sec., and the number of cracks from 4 at 10×10^{-6} sec. to 18 at 100 to 140 $\times 10^{-6}$ seconds.

2 - 2. 1.7 Effects of Ultraviolet Light on Electrical Properties

A review of the work of Pschorr (31) has been presented by Rugger (36) which includes the effects of water and diluents on the dielectric constant of cured systems.

Kurz (50) evaluated a number of cycloaliphatic epoxide resins, cyclo aliphatic diglycidyl esters, aromatic diglycidyl esters, and bisphenol-A epoxide systems. No details of curing agents or schedules were given for any of the systems. The same filler (20% by weight alumina trihydrate, and 50% by weight silica) was used in all samples. No details of the weatherometer were given (type DMC twin arc, with water spray). Practically all systems gained weight up to 2,600 hours exposure, after which weight loss occurred. The bisphenol-A system began to lose weight at 100 hours, which increased more rapidly after 2,100 hours.

Tetreault (61) investigated the effect of weathering on epoxide insulators using natural (5 years) and artificial conditions, and found that on weathering, chain scission or hydrolysis occurred, the latter being more probable. No differentiation was made between the two types of ageing. On extraction with methyl ethyl ketone (MEK) similar extractables were found from control and weathered samples. It was suggested that weathering had little effect on the polymer. It is more likely that erosion of the weathered surface had occurred leaving a relatively fresh surface for the extraction procedure.

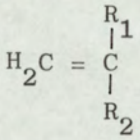
He did, however, find that the MEK extract from the weathered sample had a low pH value. The acid concentration was 2 milli equivalents/g. of starting polymer. On the basis of this and the infra red results, with no noticeable change recorded, he assumed that little oxidative degradation had occurred. His results from physical tests were more significant; an increase in surface hardness and the occurrence of deflection load on weathering. In terms of the electrical properties no change in tracking resistance, dissipation factor, dielectric constant or resistivity was observed on weathering.

2 - 3. Stabilisation of Epoxide Resins to Ultraviolet Light.

The patent literature abounds with references to the use of epoxide containing compounds as stabilisers (synergistic mixtures) for other polymers, in particular with PVC (63). However, on the stabilisation of the epoxide polymers themselves few publications exist (64 - 69), these include:

(i) benzophenones (concentration 0.01 - 10% by weight starting material)

(ii) unsaturated compounds of the type

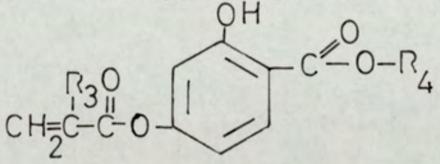


$$H_2C = C(R_1)(R_2)$$

(concentration 0.1 - 10 mole %)

where R_1 could be hydrogen or preferably an alkyl group with 1 - 4 carbon atoms, R_2 could be: H, X, allyl (1-4 C atoms), carboalkoxy, carboaryloxy, phenyl, acetoxy or cyano

(iii) esters



R_3 hydrogen or alkyl of 1-3 carbon atoms

R_4 alkyl group 1-4 carbon atoms

(iv) hydrogen peroxide and peroxides (dialkyl, dicyclo alkyl and hydrocarbon hydroperoxides 0.01 - 3% by weight based on the amount of diepoxide monomer.

A large number of the common ultraviolet stabilisers have been investigated for the stabilisation of epoxides by Lee and Watson (38), Hirt and Schmitt (42, Nelson (55) and Wahl (70). These are listed (Table 2-1). None of the stabilisers evaluated either prevented the initial yellowing on cure, nor did they prevent colour formation on ultraviolet ageing.

TABLE 2-1

Stabiliser	Effect	Reference
phenyl salicylate	cured clear, but yellowed under UV	38
4-tert butyl phenyl salicylate		42
p-octyl phenyl salicylate		
resorcinol monobenzoate	cured yellow	38
dibenzoyl resorcinol		42
2,4 - dihydroxybenzophenone	cured yellow	
2-hydroxy - 4 methoxy benzophenone	" "	38
2-hydroxy-4,4' - dimethoxy benzophenone	" "	55
2, 2'-dihydroxy-4,4' - dimethoxy benzophenone	" "	42
2, 2' - dihydroxy-4-methoxy benzophenone	" "	
2, 2' - dihydroxy-4-octyloxy benzophenone	" "	
4-dodecyloxy-2-hydroxy benzophenone	" "	
2-(2'hydroxy 5'-methyl phenyl) benzotriazole	cured yellow	38
dialkyl methylene malononitriles	cured clear, but yellowed under UV	38
benzoyl ferrocene	cured yellow	
2 hydroxy benzoyl ferrocene		
dibenzyl ferrocene		42
1' - ferrocene dicarboxylic acid		38
2-hydroxy-4-methoxy benzoyl ferrocene		
2-methoxy benzoyl ferrocene		
hexamethyl phosphoramide	cured clear, but yellowed under UV	38
hydroquinone monobenzyl ether	cured clear, but yellowed under UV	55
sym-bibetanaphthyl p-phenylenediamine		
pp' - dibenzoyl quinonedioxine		

REFERENCES

1. Caston, P., Swiss Pat. 211, 116, 1940

2. Greenlee, S.O., U.S. Pat. 2, 521, 911, 1940

3. Eisleb, E., U.S. Pat. 1, 790, 042, 1931

4. Schlack, I., U.S. Pat. 2, 136, 928, 1938

5. Mc Intosh, G., U.S. Pat. 1, 642, 079 1927

6. Blumer, F., Ger. Pat. 576, 177, 1933

7. Pezzaglia, G., U.S. Pat. 2, 840, 541, 1958

9. Patterson-Jones, C., Smith, D.A., Report CoA Note Mat No. 10, College of Aeronautics, Cranfield 1967

10. D'Alelio, A., U.S. Pat. 2, 658, 884, 1953

11. Zech, R., U.S. Pat. 2, 712, 000 1954

12. Grover, B., 15th ANTEC of SPE, 1959

13. D'Alelio, A., U.S. Pat. 2, 695, 894, 1954

14. Forester, G., U.S. Pat. 2, 868, 768, 1959

15. Applegath, R., S.P.E. J., January 1959

16. Sidlow, A., Williams, M., Brit. Pat. 953, 206, 1964

17. Norris, D.P., Sellers, R.F., Smith, S.G., U.S. Govt. Rept. A.D., 430360

18. Shechter, L., Wynstra, J., Ind. Eng. Chem. 48, 94, 1956

19. Sherr, A.E., Krupnik, A.A., J. Appl. Polym. Sci 9, 2707,1965

20. Shechter, L., Wynstra, J., Kurkjy, P., Ind. Eng. Chem., 43, 86, 1956

21. "Epoxy Resins" by Lee, H., Neville, K., Chapter 6. McGraw-Hill, New York, 1967

22. Issacs, N., Parker, R., J.C.S. 3497, September, 1960

23. Issacs, N., Parker, R., J.A.C.S. 84, 4277, 1961

24. Fisch, W., Hofmann, W., Koskikallio, J.J. Appl. Chem. 429, Oct., 1956

25. Fisch, W., Hofmann, W., Makromol. Chemie, 8, 1961

26. Fisch, W., Hofmann, W., FATIPEC Conference, May, 1962

27. Ref. 21 Chapter 5.

28. Fischer, E., Ind. Eng. Chem., 41, April, 1960

29. Tanaka, Y., Kakiuchi, H., J. Polyn. Sci 2A, 3405, 1964

30. "Ageing and Weathering of Plastics", RAPRA Literature review, 1970

31. Pschorr, F.E., Cianciarulo A.N., Polym. Eng. Sci 5, 166, 1965

32. Glaser, D., Floyd, D.E., J. Paint Technol 108, Jan. 1960

33. Lebbink, B.G., FATIPEC Conf. 177, 1957

34. Werren, F., Lebbink, B.G., WADC T - R - 55 - 319, 1956-61

35. DeHoff, R.L., 16th Ann. NACE Conf., March, 1960

36. Rugger, G.R., et al. U.S. Govt. Report A.D. 630987, 1966

37. Matting, A., Ehrenstein, G.W., p85 Conf. on High Voltage.
Application of Epoxide Resins, 1967

38. Lee, E.H., Watson, F.T., 20th ANTEC of SPE 1964, paper 1

39. Christie H., Medved, T., "High Temperature Resistant Plastics"
Midwest Res. Inst. T - R - 2491 - C, Oct. 1960

40. Lemon, R.H., Brit. Plast. 36, 336, 1963

41. Wohl, N., Plast. Technol 8, 23, 1962

42. Schmitt, R.G., Hirt, R.C., ACS, Symp, 314, 1961

43. Woelfel, J.B., J. Am. Dental Ass., 62, 643, 1961

44. Gaubart, L., SPE RECTEC, 126, October, 1960

45. Khozin, U.G., et al., Sov. Plast., 6, 48, 1969

46. Pierce, P.E., J. Paint Technol 38, 588, 1966

47. Somerville, G.R., Ind. Eng. Chem. 49, 1080, 1957

48. Holsworth, R.M., J. Paint Technol. 38, 688, 1966

49. Trigaux, G.A., Mod. Plast. 38, 147, 1960

50. Kurz, R.A., 28th ANTEC of SPE, 1970 p191

51. Hearst, P.J., U.S., NCEL - TR - 685, 1964

52. Hearst, P.J., U.S., - TR - Y - ROII - OI - OI - 021, 1964

53. Hearst, P.J., U.S., NCEL - TR - 729, 1965

54. Clauss, F.J., et al., Proc. Inst. of Environmental Sci.
p475, 1961

55. Nelson, J., U.S. Army P.R.L. - TR - No. 5814, 1958

56. Wiedmann, W., U.S. Army P.R.L. - TR - No. 5953, 1959

57. Crilly, R., U.S. N.C.E. 1 TR - N - 450, 1963

58. Smith, H.A., "Borden Award Symp. on Epoxy Resins", p244, 1969

59. Nelson, J., TR 5814, U.S. Prosthetics R.L., 1958

60. Sexton, J.H., Kline, D.E., J. Opt. Soc. Am., 50, 1103, 1960

61. Tetreault, R.J., Insulation, November, 37, 1965

62. Slowikowska, I., et al Polim. Tworz. Wielk. 15, 523, 1970

63. Voronkov, V.A., et al Koll. Zurnal (USSR) 32, 261, 1970

64. Krapivin, L.L., et al Mek. Polim. 3, 460, 1969

65. Yanovski, D.M., et al Zh. Prikl. Khim. 41, 1810, 1968

66. "High Voltage Applications of Epoxide Resins", CIBA (ARL), 1967

67. Smith, R.M., U.S. Pat. 3, 226, 358, 1965

68. Tocken, S., U.S. Pat. 3, 113, 907, 1963

69. Goldsmith, W.F., U.S. Pat. 3, 142, 687, 1964

70. Wahl, N.E., 15th ANTEC of SPI, RPD, 1960

CHAPTER 3

EXPERIMENTAL METHODS AND MATERIALS

3 - 1 Experimental Methods

This chapter is concerned with the irradiation apparatus, choice of light source, filters and sample holders used.
The methods of analysis including chromatography, mass spectrometry and spectroscopy are reviewed briefly.

3 - 1 - 1 Irradiation Apparatus

The apparatus for the irradiation studies is shown in figure 3 -1. The sample - source distance was varied from 10 to 30 cm. To minimise the effect of "light spots", polished aluminium reflector plates were used (The aluminium was not treated to maximise its reflecting power). The reflector ensured a more even distribution of photons in all of the samples. Black photographic paper was used as a liner at the back of the sample vessels, whilst investigating the effect of incident light on the surface of cured polymers.

The intensity of the light source was monitored during the warm up period. Light intensity for all of the sample positions used in the irradiation studies was measured. It was found that the inverse square law, $I = P/R^2$ (I - intensity of illumination, P - illuminating power and R - distance of sample from the source), held for distances up to 30 cm from the source (5).

3 - 1 - 2 Choice of Light Source

Since improvement of the weatherability of cured epoxide resins was the aim of this research, it was desirable to use a light source with a spectral energy distribution similar to that of sunlight. Other workers in the field of environmental ageing have claimed some success using filtered xenon, carbon arcs, and high pressure mercury lamps. The latter source, recommended by the A S T M, is an S-I sunlamp, manufactured by General Electric Company, U.S.A. has been discontinued. The filtered xenon lamp is now used by many authorities. The main disadvantage with all artificial light sources used for accelerated ageing studies is that they emit band spectra, while the sun's output is continuous. Recent devices developed to accelerate natural weathering (6,7) claim to avoid the extraneous effects of unnatural spectral distributions.

Natural sunlight is intensified by the use of mirrors. Details of results on polymers have been reported (8), for further information on artificial weathering reference should be made to the work of Kamal (9) and others(10, 11).

The light sources used were a 2 kw high pressure mercury arc (12) with a built-in filter to prevent ozone formation (now discontinued), and the combination fluorescent sunlamp and black lamp, 20 w rating (13). The latter was used in a commercially available cabinet (14). The combination lamps have a life of less than 1,500 hours compared to the mercury lamp 5,000 - 6,000 hours. The mercury lamp had a less erratic energy distribution, and a surface temperature of 300 - 500 °C during normal use. The energy output of the sources is shown in figure 3 - 2.

Water cooling (Vycor jacket) was necessary to control temperature of the mercury lamp at 25 - 30 °C. As tap water was used for cooling, the effects of metal salts had to be taken into account in the calculation of light intensity. Use of the cooling jacket caused solarisation of the built-in filter on the mercury lamp. This problem was noticeable with the pyrex sample vessels, when short wavelength radiation was used. Details of this effect are shown in Table 3 - 1. Heat treatment removed the colour from the affected glass in all cases, except the filter. The use of the lamp under normal service conditions in lightprinting would minimise this effect, and from the actinometry results it was found that the reduction in light intensity (20% after 1,000 hours) was proportional to the solarisation of the filter. The subsequent reduction in intensity up to 5,000 hours was due to mercury deposits on the wall of the quartz burner.

To optimise the use of the lamps a series of filters were used (Figure 3 - 3). The two cut off filters were supplied by Chance Pilkington Limited (15).

The shapes of sample vessels used are shown (figure 3 - 1) and their transmission characteristics are shown (figure 3 - 3).

TABLE 3 - 1

SOLARISATION OF GLASSES

Type of glass	Hours Irradiation	% Transmission at 300 nm	Heat Treatment (hours at 200 °C)	% Transmission at 300 nm
Pyrex	0	90	—	—
	100	65	1	80
Lamp Filter	0	25	-	-
	300	17	1	20
Quartz	0	98	-	-
	100	89	2	98
	400	82	2	97
Vycor	0	90	-	-
	500	85	3	86
Filter OXL	0	8	-	-
	700	7.4	6	8

3 - 1 - 3. Determination of Quantum Yields

In studies on the photolysis and photoxidative degradation of polymers reported, few authors (16, 17) have measured the variation in spectral output of the light source used. Most workers describe the type of source, sample source distance and the number of hours irradiation. This is not sufficient for the comparison of work from different laboratories, because errors arise from change in warm up time, blank spots on filters and progressive deterioration of the source during use.

The quantum yield of a photochemical reaction may be defined as the change in the number of molecules of a substance in the gaseous, liquid, or solid state per quantum of light absorbed by the molecules undergoing change. Since a molecule in an excited state can lose excess energy by various secondary processes (fluorescence, phosphorescence, etc.) and since differentiation is made between primary and secondary photochemical reactions, it is essential to indicate with which process the particular quantum yield is associated.

Consider the reaction:

$$A \ + \ \text{photons} \longrightarrow B + C$$

the quantum yield of A is

$$A = \frac{\text{No. molecules of A consumed}}{\text{No. quanta of light absorbed by A molecules}}$$

Similarly quantum yields may be written for B and C

The second law of photochemistry states that the absorption of light by a molecule is a one quantum process, such that the sum of the primary process quantum yields must be unity. If collision deactivation, fluorescence, radiationless transitions and other similar photophysical primary process are important, the sum of the primary quantum yields must be less than unity. Where secondary reactions are important the overall quantum yield need not be less than unity. Small quantum yields of all decomposition products indicate important deactivation, fluorescence or other processes leading to no net chemical change. Large product quantum yields indicate the importance of a chain reaction forming the products.

3 - 1 - 4. Chemical Measurement of Light Intensity

Systems for chemical measurements rely on an understanding of a photochemical reaction and an accurate knowledge of the quantum yield at the wavelength of interest. Both liquid and gaseous systems have been used, in particular the uranyl oxalate actinometer. Other systems include potassium ferrioxalate, acetone, nitrous oxide and hydrogen bromide. The potassium ferrioxalate is perhaps the most useful actinometer since the material is active over a wide wavelength range and can be used to monitor mono, and polychromatic radiation. Recently a solid state actinometer, using a cobalt complex, has been reported (18).

Potassium ferrioxalate Actinometer

The potassium ferrioxalate actinometer, developed by Parker and Hatchard (19, 20, 21, 22), was used in these studies for the measurement of light intensity, radiation outputs from the light source and quantum yields.

The actinometer solution was prepared by mixing three volumes of 1.5 molar potassium oxalate with one volume of 1.5 molar ferric chloride. The filtered green crystals were recrystallised from water and dried at 50 °C, giving a purity of 99.7%. Aqueous solutions of the crystals stored in stoppered bottles were stable for one week. All operations for the preparation of the actinometer solutions were performed in a dark room.

Exposure to light of the ferrioxalate ion in an acid medium (1 normal sulphuric acid) causes the following reaction to occur:

$$2\ \mathrm{fe}\,(C_2O_4)_3^{3-} \longrightarrow 2\ \mathrm{fe}^{2+} + 5\ C_2O_4^{2-} + 2CO_2$$

The amount of ferrous ions produced was determined using the complexing agent 1, 10-phenanthroline in aqueous solution.

The concentration of the actinometer used was 0.006 molar, and in 4 cm pathlength cells all incident quanta of radiation were absorbed. During exposure of the actinometer the solution was stirred by a stream of nitrogen to prevent air oxidation of the ferrous ions. During long exposures (4 - 10 hours) a neutral filter of gauze was superimposed on the front face of the actinometer to reduce the light intensity incident on the face of the cell. Decomposition of the actinometer was thus kept to level of 20%.

After exposure of a known volume of the solution was pipetted into a 25 ml volumetric flask, to which was added 2.5 ml of a 0.1% solution of 1,10 phenanthroline in water, followed by 1.5 ml of 0.3 molar sodium acetate/acetic acid buffer and made up to volume. An equal volume of unirradiated solution was used as blank. The actinomer and the blank solution were left in the dark for one hour to allow the development of the ferrous ion complex, the optical densities were then read at 510 nm. The optical density at this wavelength is independent of the amount of buffer, providing that the volume added is at least half the total volume of the 0.1 normal acid in the final solution. A solution of pH 3.5 is recommended as protonation of the phenanthroline cation occurs at a pH of less than 3.

The extinction coefficient (1.1×10^4 litre/mole/cm) for solutions of known ferrous ion concentrations was determined using a Perkin Elmer Model 350 spectrophotometer.

The number of ferrous ions (n) was then determined from the equation

$$n = \frac{6.023 \times 10^{20}\, V_1\, V_3 \log_{10} (I_o/I)}{V_2\, le}$$

where V_1 = volume of actinometer solution irradiated (ml)

V_2 = volume of aliquot used for analysis (ml)

V_3 = final volume to which aliquot was diluted (ml)

$\log_{10} (I_o/I)$ = measured optical density at 510 nm

l = path length of spectrophotometer cell used (cm)

e = molar extinction coefficient of ferrous ion complex

Using the value of n, calculated as shown, the value of the light intensity was read from the master tables of Parker(20). The light intensity incident inside the front window of the actinometer cell was calculated from the standard photochemical equation.

3 - 1 - 5. Chromatography

Thin layer (TLC) and gas liquid chromatography (GLC) were used in the irradiation studies. The former was used for the determination of molecular weight distribution of the epoxide monomers, employing the method of Weatherhead (23) using chloroform as the developing solvent. This technique was also used for separation and determination of the number of products in the solid or liquid phase. However, for quantification of product yields gas chromatography and wet chemical analysis were used. For preparative thin layer chromatography (TLC) work grooved plates (Burkard) and an applicator (Burkard TLC Preparative applicator, Model SA20) were used. The distribution of molecular species was determined by the relative area (Allbrit planimeter) of the spots on the plate as shown by the iodine technique (24). Product identification was made by spectroscopic techniques and mass spectrometry.

A Perkin Elmer GLC (Model FII) with a linear temperature programmer and duel flame ionization detector FID was used for most of the studies. A Pye (Model 104) instrument fitted with a katharometer was used for non ionisable species. GLC was used primarily for the analysis of the gaseous degradation products from all systems. Mass spectrometry was carried out on representative samples from each batch of products as a check on the method. A variety of columns including Porapak R and S, Carbowax silicone oil and fluorosilicone oil were used. The method for quantitative work was based on the use of internal standards (25).

3 - 1 - 6. Mass Spectrometry

An AEI (Model MS9) spectrometer was used throughout the work. Samples of solids, liquids and gases were analysed by the peak matching technique (26). The determination of molecular weights for some systems e.g. crosslinked polymers and model systems by mass spectrometry proved valueless due to the complex splitting patterns obtained. Gas analysis using the mass spectra of pure compounds proved to be the most useful application of the technique.

3 - 1 - 7. Spectroscopic Methods

Spectroscopic methods included (a) ultra-violet/visible measurements (Perkin Elmer, Model 350 or Model 137) for liquids and thin films of cured polymers, both stabilised and unstabilised,

(b) transmission infrared using the KBr pellet technique for granular solids, standard film holder for solid films, and KBr, Cs I, and Na Cl plates for liquid smears, and Nujol mulls on "wet" solids. The Perkin Elmer (Model 225) infrared spectrophotometer with slave recorder and polariser was used for quantitative work and for all reflectance work in the fundamental region. For pure identification purposes the Perkin Elmer (Model 457 or 237) infrared spectrophotometer was used. Peak assignment was made by reference to the texts of Hummel (27), Bellamy (28) and Nakiniski (29), and for gas analysis to these of Harms (30) and Hagen (31). The Perkin Elmer (Model 350) ultraviolet/visible, near - infrared spectrophotometer was used for near - infrared (NIR) work (1st overtones) to determine the degree of cure of amine cured epoxide resins, and to determine the extent of reaction with amine crosslinked model compounds. For further details of the application of the technique reference should be made to the review by Wetzel (32) and the text of Henniker (33).

3 - 1 - 8. Chemical Analysis

All monomers (commercial and purified), simple model compounds, curing agents, and crosslinked model compounds were analysed chemically. Details of the methods used are to be found in the texts of Lee and Neville (34), Potter (35), Skeist (36) Schrade (37), and Paquin (38). The chemical analysis of the anhydride cured monomer is also given by Fisch and Hofman, and others (1, 2, 3, 4).

3 - 1 - 9. Torsion Braid Analysis

Torsion Braid Analysis (TBA) is an extension of the torsion pendulum method (39) for examining materials. The method consists of impregnating a multi-filament glass braid substrate with the material under test. Polymers may be applied by solvent impregnation with subsequent removal of the solvent (40), by coating with a solution of monomer and curing agent, removing the excess material, and finally curing of the polymer system on the braid (41), or by coating a wetted braid with a granular polymer (42), and then careful fusion of the polymer onto the braid, while allowing the wetting agent to diffuse out of the system.

In contrast to torsion pendulum studies the TBA method requires less than 100 mg of polymer per experiment. Also, this technique allows study of materials which cannot support their own weight. Studies to date with TBA include investigations of the dynamic mechanical behaviour of thermosets during the curing process (43), antioxidant activity in elastomer systems (44), thermoplastics (45), degradation of a thermoset polysiloxane (46), evaluation of heat resistant polybenzimidazole polymer (47) and correlation with other thermal techniques (48). An excellent review of TBA has been given by Gillham (49).

The apparatus used was that described by Lewis and Gillham (50) shown in Figure 3 - 4. The torque head was detachable. The torque was induced by a spring rather than by the failing weight technique used in earlier studies, to enable measurements to be carried out at low temperatures in a liquid nitrogen cooled apparatus. A 15 cm diameter protractor with a movable pointer was fitted to the base of the sample tube in line with the graduated inertia disc for measurement of the decrement.

The method of sample preparation consisted of heat cleaning the loosely wound multifilament glass braid in lengths of 29 cms. (Turner Brothers Asbestos Co. Ltd., Grade 225-1/3) in oxygen at 250 °C for 2 hours to remove the coating size. Mass spectrometric analysis of the volatile products evolved during the cleaning process showed that the heat treatment was sufficient. The cleaned braid was allowed to cool and then dip coated with the epoxide resin system. The amine cured resin required two passes through the mixture for a 5% by weight uptake of polymer. It was found that this uptake optimised the visual determination of the period of oscillation on heating (below the Tg) and cooling the material. The acid anhydride systems required four passes for optimum results. Globular formation was prevented by rolling the coated braids with a Teflon rod before curing at elevated temperatures. A 2 cm length of glass tubing (melting point tubing) was fixed to the ends of the coated braids, to eliminate errors in measurement due to expansion of the pin vices at high temperature. The braids were suspended, in tension, in an oven at the required temperature and cured in a nitrogen atmosphere.

All torsion measurements were made in a nitrogen atmosphere to minimise surface oxidation during heating. The nitrogen atmosphere also prevented condensation of water vapour at low temperatures.

The braid sample under test was clamped in the apparatus by pin vices, the upper vice attached to the torsion head. The torsion head and release arm were rotated against the tension of the spring and held by a camera release mechanism.

Disengagement of the camera release arm caused oscillation of the pendulum, from which the period and the decay angle were measured.

The equation for the rigidity modulus described by Lewis and Gillham (51) was used.

$$G = 8\pi Lv^2 \, (I/R^4)$$

R - radius coated braid

L - length of coated braid

v - frequency of pendulum

I - moment of inertia of system

Since the specimen radius is raised to the fourth power its accuracy is imperative. The radius was measured at 1 cm intervals along twice the length of the braid and an average taken, this enabled a shape factor (52) to be introduced into the denominator of the above equation

$$G = 8\pi Lv^2 \, (I/R^4u)$$

The results obtained using the shape factor gave good correlation (5% difference) with the results obtained from the Nonius Torsion Pendulum (53).

The decrement was found from the magnitude of successive amplitudes of vibration.

$$\mathrm{Tan}\,\delta = \ln \left(\frac{An}{An+1}\right)$$

δ - decrement

An - amplitude of n^{th} vibration

An+1 - amplitude of $(n+1)^{th}$ vibration

Measurement of G and δ were made at varying degrees of irradiation over the temperature range -100 °C to +200 °C. Each braid was used once. This was necessary since the samples were heated above their Tg's for measurement of the rubbery modulus at 200 °C. The values of G and δ for different braid systems prepared from the same melt were found to be the same, within the limits of experimental accuracy. This allowed the construction of a curve over the temperature range from a number of braids during the irradiation period.

3 - 1 - 10. Experimental Technique for A T. R. Spectroscopy

A Perkin Elmer infra-red spectrophotometer (Model 225) with a slave recorder was used for all ATR measurements reported. The two ATR optical systems (RIIC Model TR9 and Wilkes Model TR 25) used are shown (Figure 3 - 5). A number of reflection elements were tried including a hemicylinder, a trapezoid plate and a vertical double pass plate (Figure 3 - 6). All plates for infra-red work were made of KRS-5, a suitable material for ATR work. The limiting factor of the ATR technique is the refractive index (2.38) of the KRS-5.

The experimental method consisted of first covering the crystal face with a film of slightly larger dimensions. Two faces were covered in the case of the trapezoid. Resilient rubber pads slightly smaller than the films were fitted to the back of the film and pressure applied. As ultraviolet degradation progressed it was necessary to use carbon disulphide as a wetting agent, due to the formation of surface irregularities on the polymer film. The sample holder was mounted on the ATR optical bench and fitted in the spectrophotometer. Infra-red runs were carried out from 4,000 to 400 cm^{-1}. The crystals were washed in benzene and acetone, and allowed to dry between successive spectra. Blank runs of the crystals were carried out at regular intervals to check for impurities from the materials under investigation or from the atmospheres.

3-1-11 Calculation of Quantum Yields

1. Determine incident light quanta on film surface.
2. " transmitted " " thro' " "
3. Calculate the number of absorbed quanta.
4. From the % by volume of gaseous products & the total volume of volatiles per cm^2 of polymer surface, calculate the number of molecules of each product(s) formed.
5. Calculate quantum yields from the number of molecules of each product formed divided by the number of light quanta absorbed to produce these molecules.

3 - 2 MATERIALS

3 - 2. 1. Resins

A commercial epoxide monomer "Epikote 828" was used for the bulk of the work. This material contains impurities (described previously Chapter 2). Three methods of purification were used (i) molecular distillation of the commercial '828' material giving the monomer '826' (18), (ii) fractional precipitation of resin '828' from a solvent by a non solvent giving monomer '816' (18), (iii) thin layer chromatography (23).

The resins were characterised by their epoxide and hydroxyl equivalent, defined as the weight of resin in grams which contains one gram equivalent of epoxide or hydroxyl respectively. The methods used for determining the epoxide included: fundamental infrared (34) and near infrared spectroscopy, chemical analysis, the addition of a hydrogen halide to the epoxide group using the pyridinium chloride method (34). The hydroxyl equivalent was determined by near infrared spectroscopy (34) and the acetyl chloride method(34). The hydrolysable chlorine content of the materials, present as 1, 2 chlorohydrin from incomplete dehydrogenation, was determined by titration with HCL (34). The analysis of the three monomers is shown (Table 3 - 2).

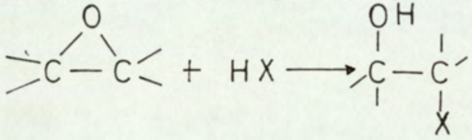


TABLE 3 - 2

Monomer	Epoxide Equivalent		Hydroxyl Equivalent		Chlorine	% Purity
	Near Infra Red	Chemical Analysis	Near Infra Red	Chemical Analysis		
Epikote '828'	185	185	0.014	0.015	0.021	91.8
Monomer '826'	174	175	0.014	0.014	0.020	97.5
Monomer '816'	170	170	-	-	-	100

3 - 2. 2. Curing Agents and Curing Process

Two of the common curing agents triethylene tetramine (TETA) and hexahydrophalic anhydride (HHPA) were used to crosslink monomers. The HHPA material required the presence of a catalyst, triethanolamine, to promote the reaction. The quantities of curing agent and catalyst used, together with the cure schedules recommended by the resin manufacturers are shown (Table 3 -3).

The prelimary results on vacuum and inert gas irradiated samples (cured in the presence of air) indicated that peroxide and hydroperoxide formation, due to the high temperatures encountered in the curing process, could have initiated the degradation reactions. To overcome this problem the samples were prepared by mixing the heated resin with the curing agent (and the catalyst when required) using a low speed stirrer. The mixture was transferred to a new container and stirred for a further period to avoid preferential wetting of the container surface by either component. The mixture was then degassed under vacuum for three minutes. The final curing reaction was performed in a nitrogen atmosphere.

TABLE 3 - 3

Formulations and cure schedules

Resin	Triethylenetetramine Systems			Hexahydrophthalic Anhydride Systems			
	TETA phr*	Temperature °C	Time hours	HHPA phr	TEAM phr	Temperature °C	Time hours
'828'	10-12	25	48	80	0.5-2.5	150	4
'826'							
'816'							

* phr - parts of curing agent per hundred parts of resin.

3 - 2. 3 Characterisation of Cured Systems

The amine cured systems were characterised for epoxide and hydroxyl content by the near infra-red technique of Dannenberg (34). The results are represented (Table 3 - 4 (A)).

TABLE 3 - 4 (A)

Amine Cured Systems

System	Epoxide Equivalent/litre	Hydroxyl Equivalent/litre
'828'/TETA	2.213	1.13
'826'/TETA	1.984	1.12
'816'/TETA	1.997	0.930

Anhydride cured systems were characterised by the swollen particle technique (1, 2, 3, 4). Typical results obtained are represented (Table 3 - 4 (B)).

3 - 2. 4 Model Compounds

The model compounds used have been divided into two classes:

(1) Simple model compounds, based on the commercial and pure monomer systems and their curing agents. The compounds are represented together with the preparative methods used (Table 3-5 (a)). The chemical properties are also represented (Table 3-5 (b)).

(2) Crosslinked model compounds, used to simulate the typical bonds formed in the cured three-dimensional epoxide resins. These compounds were prepared under reaction conditions similar to those used with the resin/curing agent systems. The extent of reaction was also determined by GLC, spectroscopic and chemical analysis. The methods of preparation are represented (Table 3-6 (a)).

TABLE 3 - 5 (a)

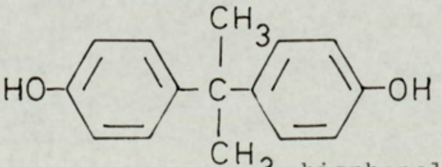
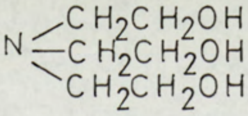
Compound	
 bisphenol-A	Commercial material (Shell Chemicals (UK) Ltd), purified by recrystallisation from ethanol
 triethanolamine	laboratory reagent

TABLE 3 - 4(B) ANHYDRIDE SYSTEMS

SYSTEM	EPOXIDE Equiv./kg		HYDROXYL Equiv./kg	MONOESTER Equiv./kg	DIESTER Equiv./kg	ANHYDRIDE Equiv./kg
	% (FIR)	Chemical Analysis				
HHPA/'828'	72	0.0575	1.862	0.509	1.431	0.024
HHPA/'826'	76	0.0491	1.972	0.492	1.327	0.027
HHPA/'816'	73	0.042	1.998	0.489	1.339	0.021

Table 3 - 5 (a) Continued

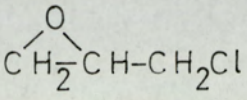
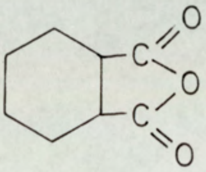
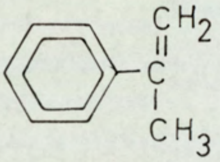
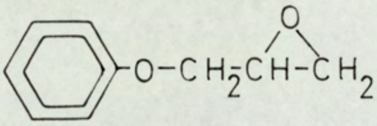
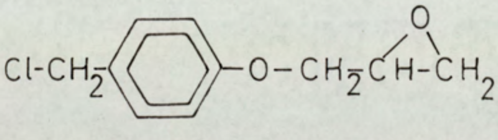
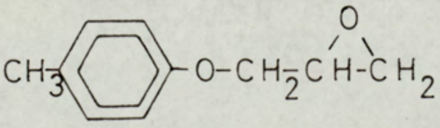
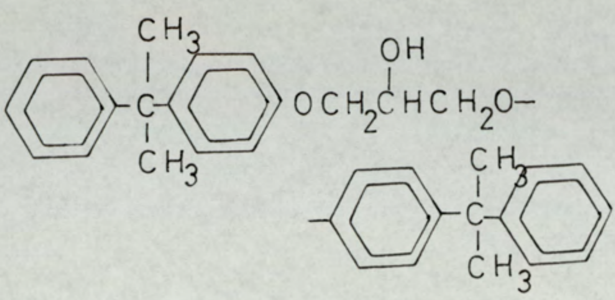
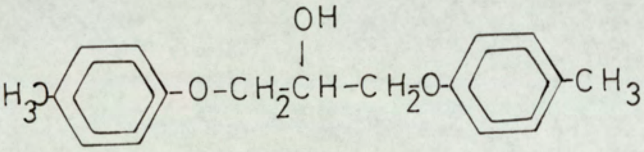
TETA	Laboratory reagent
 epichlorohydrin	Laboratory reagent, purified by vacuum distillation
 hexahydrophthalic anhydride	Commercial material (Shell Chemicals (UK) Limited)
 α- methyl styrene	Commercial material (BP Chemicals Ltd.) purified by vacuum distillation
 phenyl glycidyl ehter	Commercial material (Shell Chemicals (UK) Limited), purified by vacuum distillation
 chlorocresyl glycidyl ether	Commercial material (Shell Chemicals (UK) Limited)
 p-tolyl glycidyl ether	Prepared by the reaction of p-cresol with epichlorohydrin in the presence of sodium hydroxide, purification by vacuum distillation

Table 3 - 5 (a) Continued



glyceryl ether of diphenyl propane

Prepared by the reaction of α-methyl styrene with phenol in sulphuric acid giving 4-hydroxy phenyl propane, which was subsequently reacted with dichlorohydrin, purified by vacuum distillation and recrystallisation from ethanol



p p' - tolyl glyceryl ether

Prepared by the reaction of p-tolyl glycidyl ether with p-cresol in xylene, xylene removed by vacuum, purified by recrystallisation from ethanol

TABLE 3 -5(b)

Compound	Epoxide Equivalent /kg	Hydroxyl Equivalent /kg	% Purity	
			GLC	Chemical Analysis
epichlorohydrin	108	0.009	98.6	-
chlorocresyl glycidyl ether	208	0.012	92.0	-
phenyl glycidyl ether	150	-	99.9	-
tolyl glycidyl ether	168	0.002	99.0	-
ditolyl glycidyl ether	-	2.716	99.6	-
glyceryl ether of diphenyl propane	-	4.830	99.8	-
HHPA	-	-	-	98.28

TABLE 3 - 6

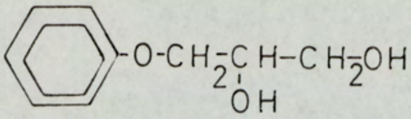
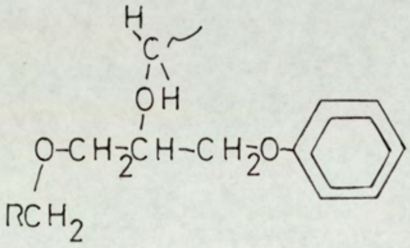
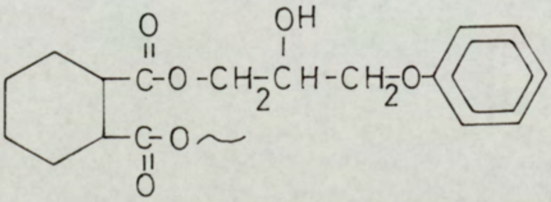
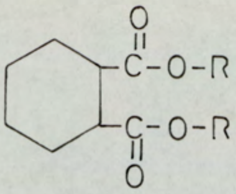
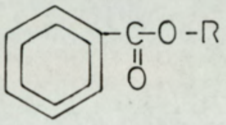
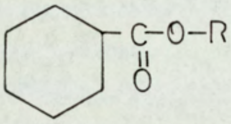
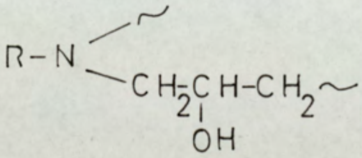
	Reflux (1:1 mole ratio of reactants) phenyl glycidyl ether and water at 120 °C for one hour. Colourless liquid.
	Reflux in the presence of 0.2% KOH by weight, for eight hours at 100 °C. Viscosity changes occurring during reaction gave an easy method for following the extent of the reaction. A 1:1 mole ratio of reactants was used. The alcohols used were ethylene glycol, propylene glycol (red brown liquids) and isopropanol. (colourless liquid) The latter caused self polymerisatio of the epoxide monomers.
	Reflux (1:1 mole ratio) phenyl glycidyl ether and hexahydrophthalic acid in the presence of 0.2% KOH for six hours at 150 °C. Further reaction occurred through the hydroxyl groups. Water was removed as formed to prevent reaction with the epoxide groups - colourless — grey viscous liquid.

Table 3 - 6 Continued

	Preparation as 3 except that hexhydrophthalic anhydride was used instead of its diacid - red thermoplastic solid.
	Reflux (1:1 mole ratio) phenyl glycidyl ether and benzoic acid in presence 0.2% KOH for six hours at 150 °C. - yellow crystalline solid
	Reflux (1:1 mole ratio) cyclohexane and carboxylic acid in the presence of 0.2% KOH for six hours at 150 °C. - viscous yellow liquid.
	Reflux amine and phenyl glycidyl ether. Ethylene diamine (1:2 mole ratio) for eight hours at 50 °C. Ethyl amine (1:1 mole ratio) for eight hours at 50 °C. Intensity of colour showed the extent of the reaction. - yellow crystalline solids.

REFERENCES

1. Fisch, W., Hofmann, W., Makromol Chemie 8, 1961
2. Fisch, W., Hofmann, W., Plast. Technol., 28, August 1961
3. Tanaka, Y., Kakiuchi, H., J. Appl. Polym. Sci., I, 1063, 1963
4. Fisch, W., Hofmann, W., Koskikallio, J., J.Appl. Chem. 6, 429, 1956
5. "Photometry", by Walsh, J.W.T., 3rd Ed. Chapter 5, Constable London, 1958
6. Caryl, C.R., Helmick, W.E., U.S. Pat. 2, 945, 417, 1960
7. Caryl, C.R., Rheineck, A.E., Offic. Dig, 34, 1017, 1962
8. Garner, B.L., Papillo, P.J., Ind. Eng. Chem. Prod. Res. Develop 1, 249, 1962
9. "Weatherability of Plastics", Ed. Kamal, M.R., Appl. Polym. Symp. No. 4, J. Wiley and Sons, New York, 1967
10. "Ageing and Weatherability of Plastics", a literature review, RAPRA, 1970
11. "Ultraviolet Radiation", by Koller, L.R., 2nd Ed., Chapter 2 and 3, J. Wiley and Sons, New York, 1967
12. Philips Lighting Catalogue, p.111, HOK I Light-Printing Lamps
13. Westinghouse Catalogue of Fluorescent Lamps and Equipment p.9
14. Mektron, Fridgistor Ltd., Slough, Bucks, England
15. Chance Pilkington Catalogue of Colour Filter Glasses, Chance Pilkington Ltd., St. Asaph, Flintshire, Wales.
16. Heacock, J.F., Mallory, F.B., Gay, F.P., J. Polym. Sci., A1, 6, 2921 1968
17. Fox, R.B., Stokes, M., N R L - T - C - 551, 1961
18. Simmons, E.L., Wendlandt, W.W., An. Chim. Acta, 53, 81, 1971
19. Parker, C.A., Hatchard, C.G., Proc. Roy. Soc. (London) A335, 518, 1958
20. Parker, C.A., Hatchard, C.G., J. Phys. Chem. 63, 22, 1959
21. Parker, C.A., Hatchard, C.G., Nature 182, 1002, 1958
22. Parker, C.A., Hatchard, C.G., A.M.L. Rept. A/42 (M), 1953
23. Weatherhead, R.G., Analyst 91, 445, 1966
24. "Thin Layer Chromatography", by Truter", by Truter, E.V., Cleaver Hume Press, London
25. "Gas Chromatography", Ed. Perry, E.S., and Weissberger, A., J. Wiley and Sons, New York, 1968
26. "Mass Spectrometry and its Applications to Organic Chemistry", by Beynon, J.H., Elsevier, Amsterdam, 1960
27. "Infra Red Analysis of Polymers, Resins and Additives", I by Hummel, D.O., Scholl, F., J. Wiley & Sons, New York 1969

28. "Infrared Spectra of Complex Molecules", by Bellamy, L.J.,
2nd Ed. Methuen, London, 1958

29. "Infrared Absorption Spectroscopy", by Nakanishi, K., Nankodo Co. Ltd., Tokyo, 1964

30. Harms, D.L., Anal. Chem. 25, 1140, 1953

31. Hagen, E., Plaste u Kaut, 15, 711, 1968

32. Whetsel, K.B., Appl. Spec. Reviews 2, 1, 1968

33. "Infrared Spectroscopy of Industrial Polymers", by Henniker, C.J., Academic Press, New York, 1967

34. "Epoxy Resins", by Lee, H., Nevill, K., McGraw Hill, New York, 1967

35. "Epoxide Resins", by Potter, W.G., Iliffe Books, London, 1970

36. "Epoxy Resins", by Skeist, L., Reinhold Publishing Corp. New York, 1958

37. "The Epoxy Resins", by Schrade, G., Dunod, Paris, 1957

38. "Epoxy Verbindingen und Epoxyhoiz", Paquin, I., Springer, Berlin, 1958

39. "Mechanical Properties of Polymers", by Nielson, L.E., Chapter 7, Reinhold, New York, 1967

40. Lewis, A.F., Tobin, M.C., S P E Trans. 177 Oct. 1961

41. Lewis, A.F., Gillham, J.K., J. Appl. Polym. Sci., 6, 422, 1962

42. Lewis, A.F., S P E Trans. 201, July, 1963

43. Lewis, A.F., Gillham, J.K., J. Polym. Sci. C, 6, 125, 1963

44. Lewis, A.F., Gillham, J.K., J. Appl. Polym. Sci., 1, 685, 1963

45. Lewis, A.F., Gillham, J.K., J. Appl. Polym. Sci., 1, 2293, 1963

46. Gillham, J.K., Polym. Eng. Sci., 225, Oct., 1967

47. Tobolsky, A.V., Du Pré, D.B., J. Polym. Sci., A-2, 6, 1177, 1968

48. Williams, B.L., Weissbein, L., J. Appl. Polym. Sci., 12, 1439, 1968

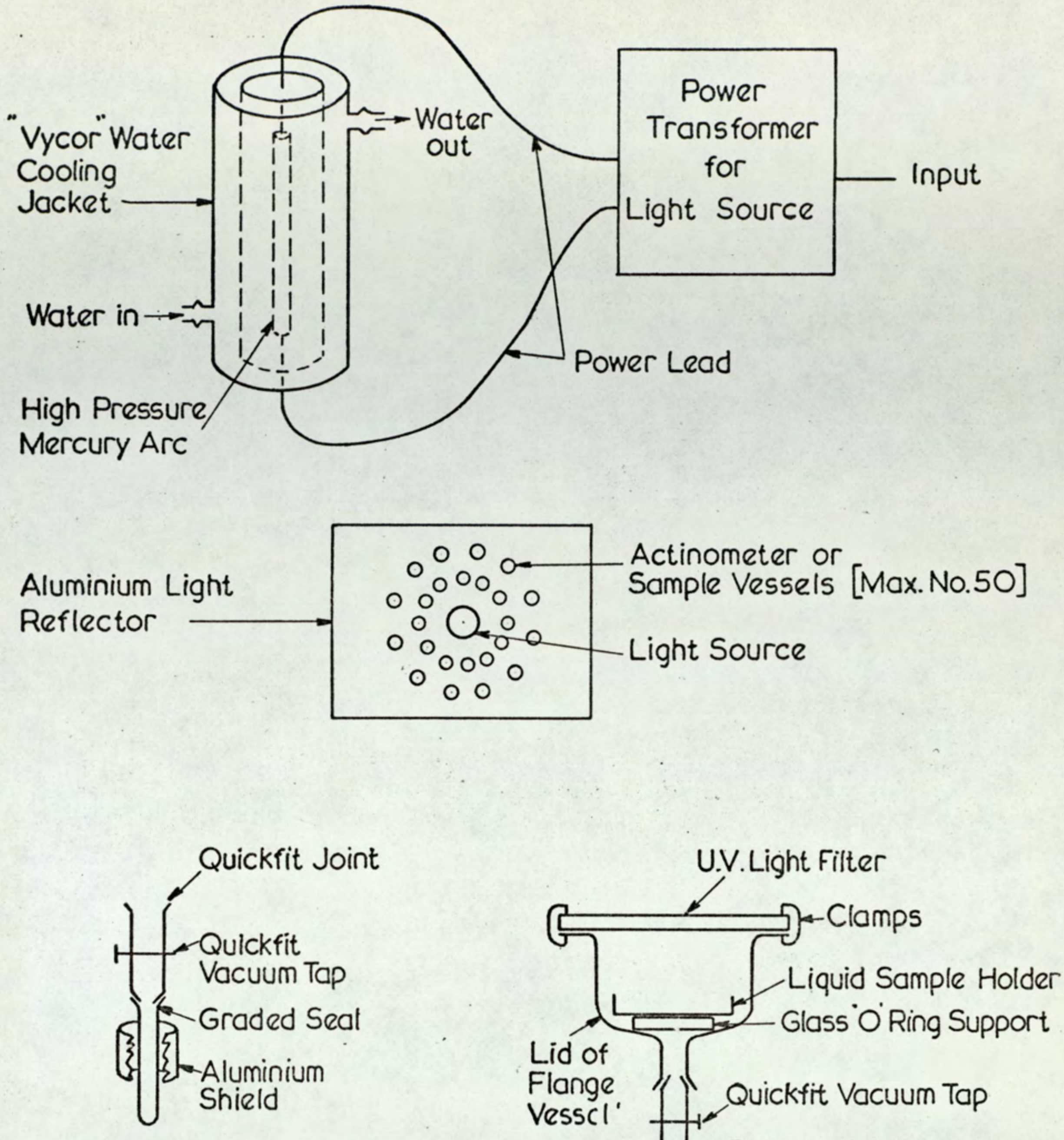
49. "Thermal Characterisation Techniques", Ed. Slade, P.E., Jenkins, L.T., Chapter 4, 2, Dekker, New York, 1970

50. Reference 49 p. 226

51. Reference 11 pages 227 - 229

52. Nielsen, L.E., ASTM Bulletin 48, April 1950

53. Nonius Torsion Pendulum, T N O, Holland



Sample Vessel for Liquids or Solid Films

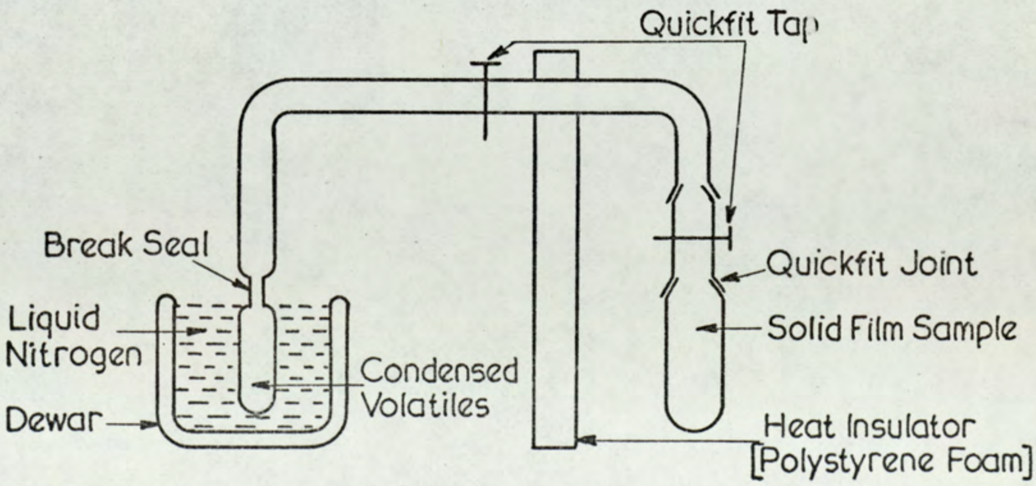


Fig. 3-1 IRRADIATION APPARATUS

FIG. 3-2 Spectral Output of Sources

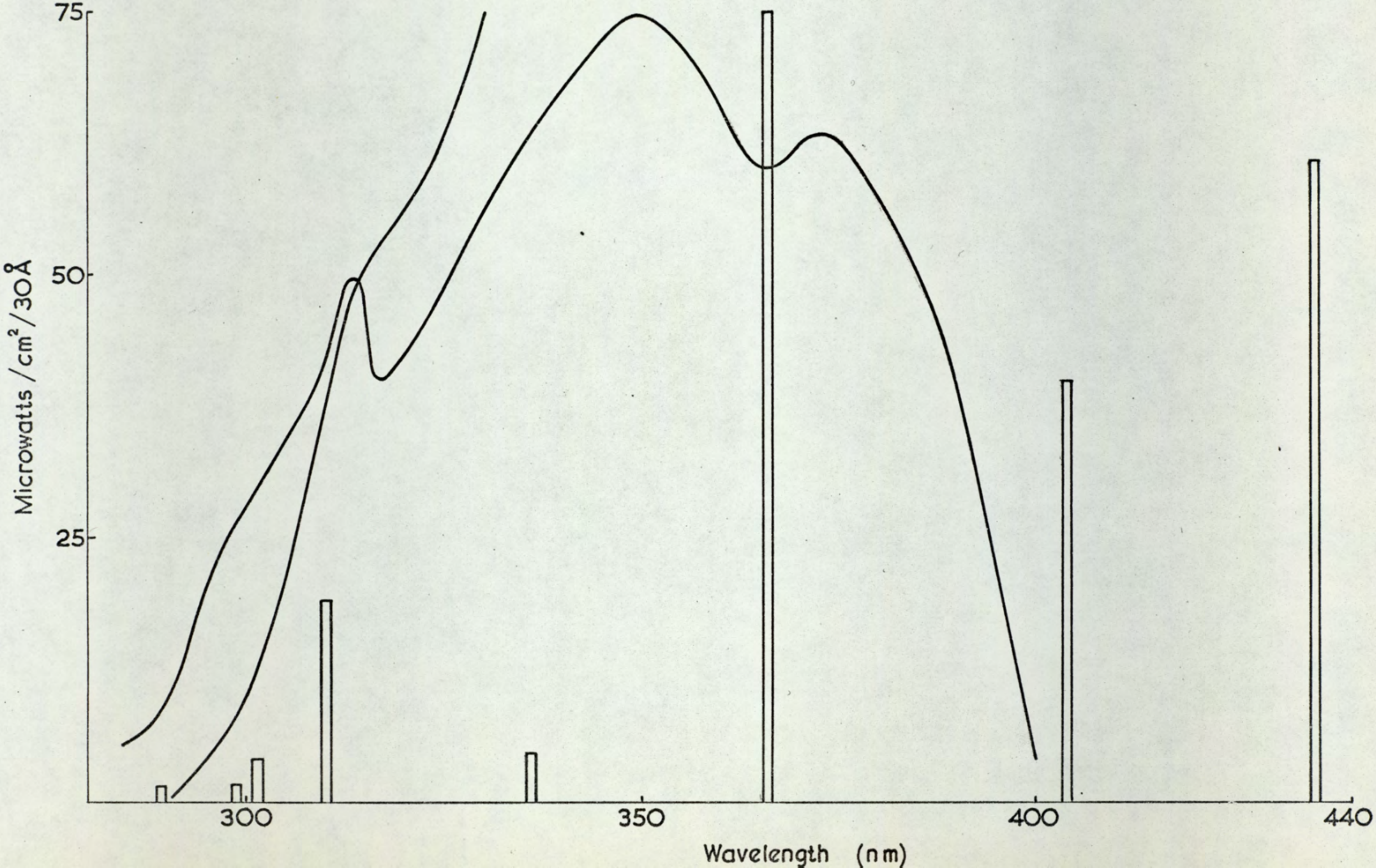
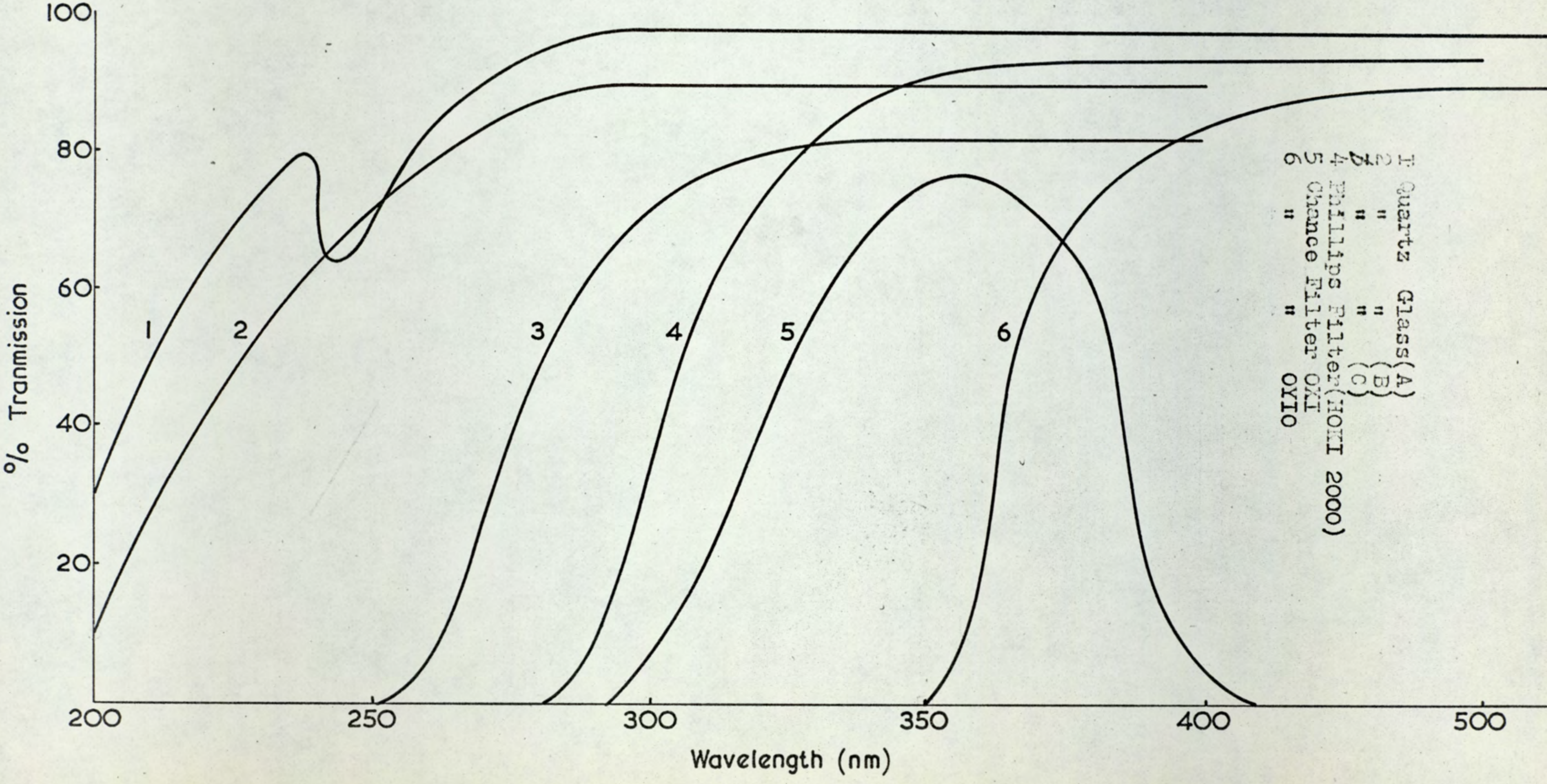


FIG. 3-3 Transmission Characteristics of Glasses



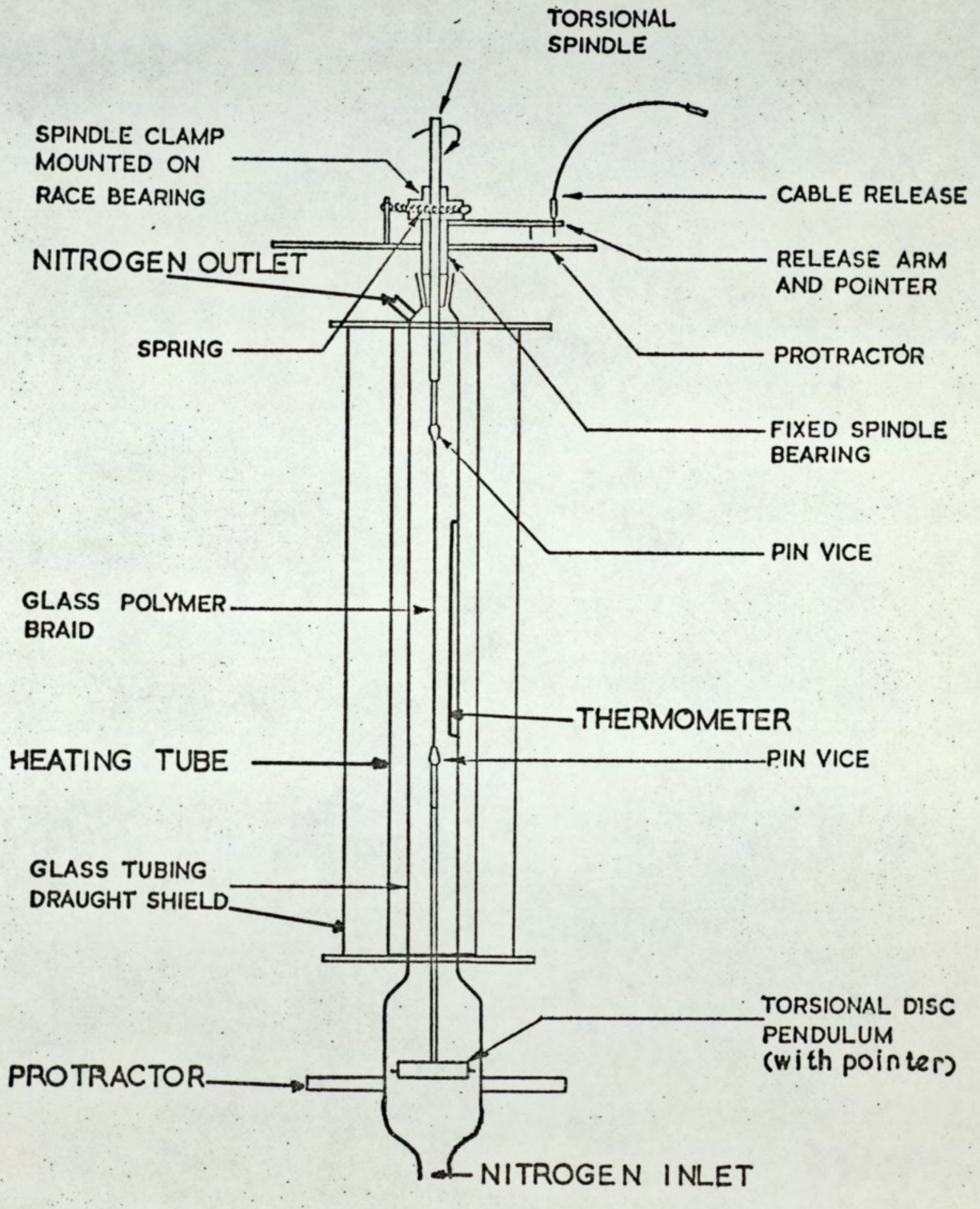
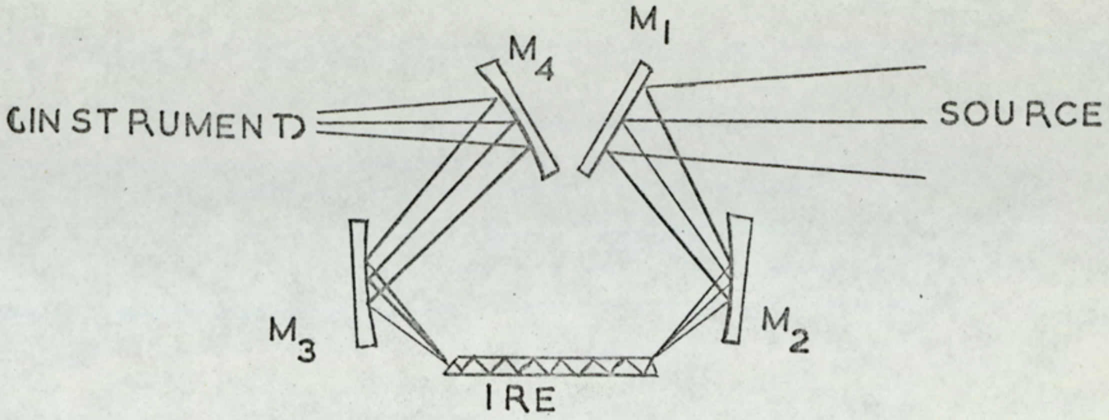
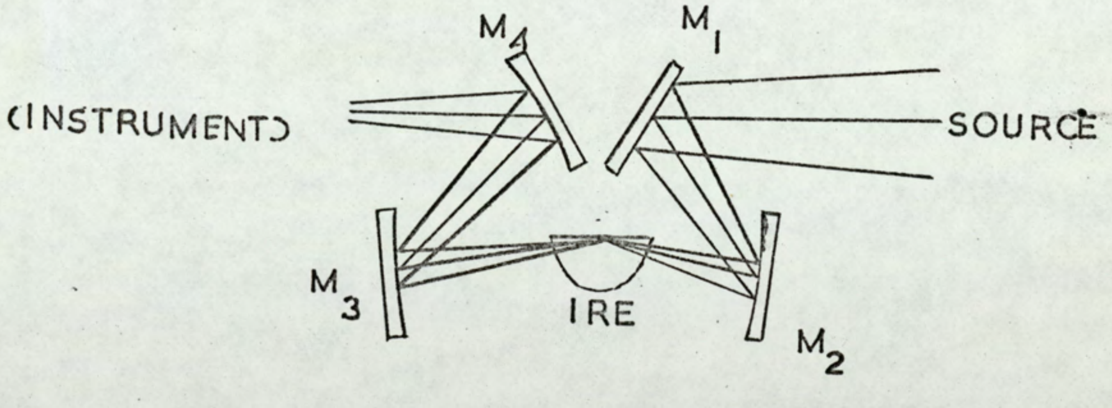


Figure 3-4

APPARATUS FOR DETERMINATION OF DECREMENT & TORSIONAL PERIOD OF BRAIDS

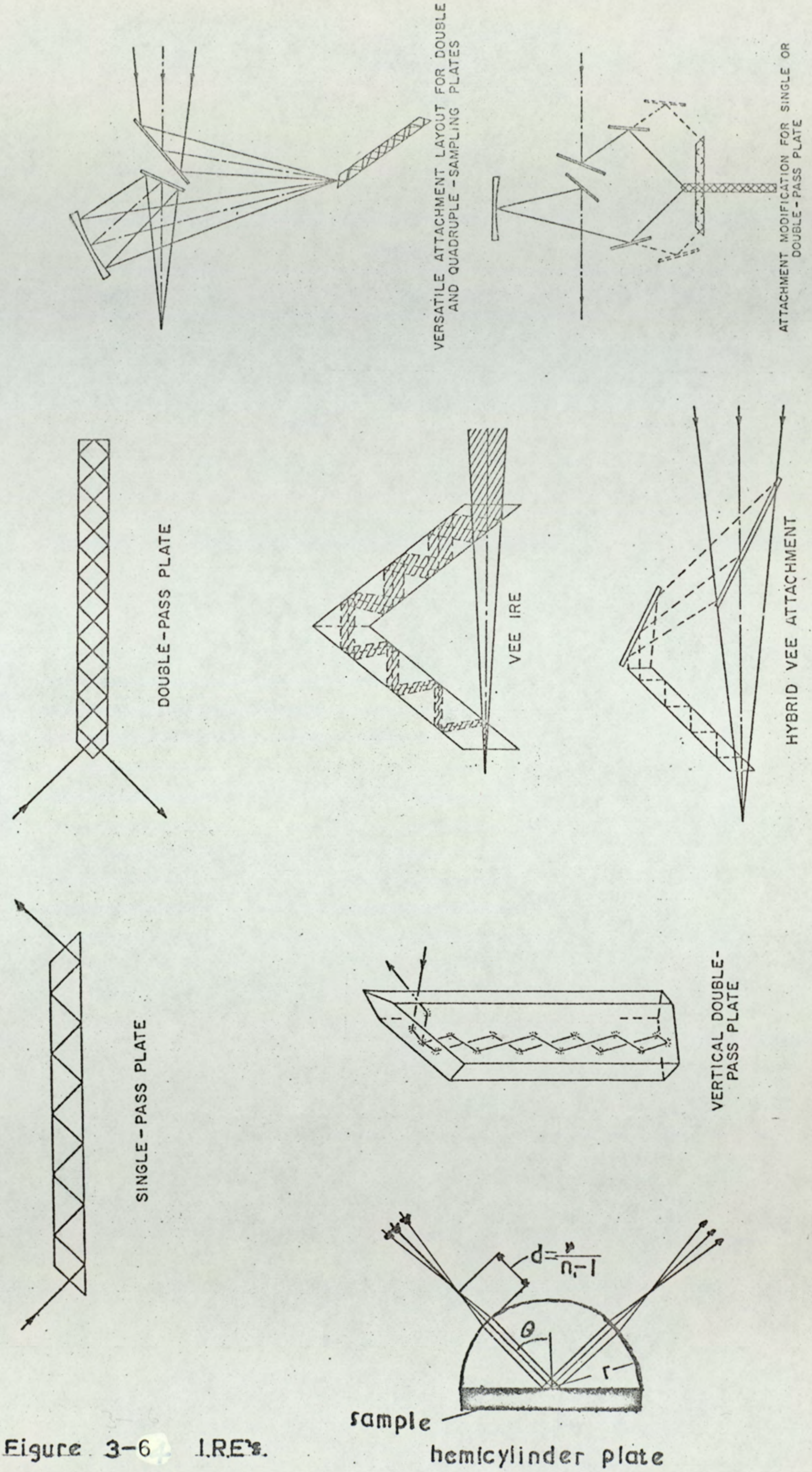


Model TR-25



Model TR-9

Figure 3-5 ATR OPTICAL BENCHES



SINGLE-PASS PLATE

DOUBLE-PASS PLATE

VERSATILE ATTACHMENT LAYOUT FOR DOUBLE AND QUADRUPLE-SAMPLING PLATES

ATTACHMENT MODIFICATION FOR SINGLE OR DOUBLE-PASS PLATE

VEE IRE

HYBRID VEE ATTACHMENT

VERTICAL DOUBLE-PASS PLATE

hemicylinder plate

Figure 3-6 I.R.E's.

CHAPTER 4

Chemical Changes on Irradiation

Irradiation of both the amine and the anhydride cured systems, in an inert or an oxidising atmosphere, resulted in the evolution of low molecular weight volatile compounds and chemical changes in the polymer matrix which gave rise to colour formation.

Infrared transmission spectroscopy failed to detect changes in the chemical structure of cured epoxide films greater than 20 microns in thickness. The use of films less than 20 microns in thickness, prepared by pressing between sodium chloride windows (1), did show the formation of a band in the carbonyl stretching frequency region, on irradiation of the amine cured materials. No changes were observed with the anhydride systems. However, because of the colour formation during degradation the transmission was not constant, and it finally decreased to less than 10% when the bands were almost completely lost.

Cured films of varying thickness (10 - 50 microns) were prepared from all three monomers ('828', '826' and '816') using the pressure technique. The amine samples were visually colourless, whilst slight yellowing was observed with the anhydride cured samples. All of the films were stored between flat glass surfaces in a vacuum desiccator for one week prior to use. Samples for irradiation in air or oxygen were allowed to equilibrate in air for one day prior to use. Preliminary experiments showed little spectral differences in samples irradiated in air and oxygen, consequently irradiation studies in oxygen were discontinued.

In order to investigate the effect of light penetration and degradation by reflected light, film samples were mounted before polished aluminium reflector plates and plate glass, backed with black photographic paper. The results from samples degraded by incident and reflected light allowed the efficiency of the reflector to be evaluated - little change in the efficiency of the reflector was observed for the first twenty four hours irradiation, thereafter the percentage reflection decreased.

The ATR spectra of the commercial amine and anhydride cured polymers, at a 39° angle of incidence on the KRS - 5 one reflection hemicylinder crystal, are shown (Figure 4 - 1 and 4 - 2 respectively).

A comparison of the equivalent transmission infrared curves for these materials showed a shift of all bands to slightly longer wavelengths. Otherwise the ATR spectra obtained were identical with their transmission counterparts. The band assignments, shown (Table 4 - 1 and 4 - 2) for the amine and anhydride cured materials, were similar to those used for the transmission work.

TABLE 4 - 1

Infrared Band Assignments of Amine Cured '828' Monomer
(Reflectance Spectroscopy)

Frequency cm^{-1}	Allocation	Reference
3320	O - H stretching (H - bonded)	2
3010	C - H stretching of aromatic nucleus	3
2950		
2920	C - H stretching of CH_2 and CH_3	3
2850		
1880	1, 4-disubstituted aromatic nucleus	3
1740		
1600		
1575	C = C stretching of aromatic nucleus	3
1500		
1450	C = C of aromatic nucleus	3
1410		
1380	CH_3 bending of gem dimethyl	3, 4
1360		
1285	Ether?	5
1220	phenyl - O stretching and epoxide	4, 6
1175	CH_3 isopropyl and epoxide	3
1100	phenyl - O (ether)	3
1080	secondary hydroxyl	3
1020	aliphatic C - O stretching	3
1005	1, 4-disubstituted aromatic nucleus	3, 5
920	oxirane ring	6
870		
820	out of plane bending of two adjacent hydrogens on p-disubstituted aromatic nucleus	3
800		
760		
735		
725		
550	oxirane ring (C - O - C bending)	7

TABLE 4 - 2

Infrared Band Assignment of Anhydride Cured '828' Monomer
(Reflectance Spectroscopy)

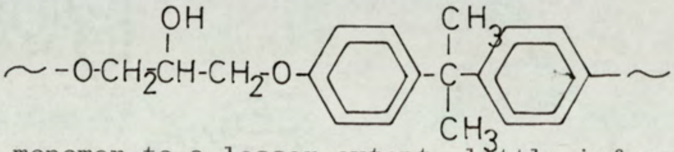
Frequency cm^{-1}	Allocation	Reference
3480	O - H stretching (H - bonded)	2
3010	O - H stretching of aromatic nucleus	3
2950		
2920	C - H stretching of CH_2 and CH_3	3
2850		
1880	1, 4 -disubstituted aromatic nucleus	3
1740		
1860	Residual HHPA	1
1790		
1720	carboxyl group (ester)	1
1640	carboxyl group acid	1
1600		
1580	C = C stretching of aromatic nucleus	3
1500		
1440	C = C of aromatic nucleus	3
1410		
1380	CH_3 bending of gem dimethyl	3, 4
1360		
1330	asym stretching ester C - O - C	8
1290		
1220		
1175	ester C - O stretching modes	1
1155		
1120		
1100	phenyl - O - ether	2
1070	sym stretching C - O - C	8
1020	aliphatic C - O stretching	2
1005	1, 4-disubstituted aromatic nucleus	2, 4

Table 4 - 2 Continued

Frequency cm^{-1}	Allocation	Reference
910 860	oxirane ring and anhydride groups	5
820	out of plane bending of two adjacent hydrogens on p-disubstituted aromatic nucleus	3
800		
760		
725		
720		
550	C - O - C bending oxirane ring	6

4 - 1 Spectral Change on Curing of Epoxide Resins

Few differences were observed between the spectra of the monomers and their cured polymers. This was due to the overlap of the absorption bands in the uncured monomer and in the curing agent with the existing bands, and with the new bands formed during the curing process. On curing the epoxide absorption band (10.93 microns) progressively disappeared, and a hydroxyl band appeared at 2.85 - 3.3 microns. This latter band obscured the N - H stretching mode of the amine curing agent. Since hydroxyl groups were present in the commercial '828' monomer as



and in the '826' monomer to a lesser extent, little information could be deduced concerning the rate of the curing reaction from the increase in the hydroxyl absorption. The disappearance of the primary amine absorption, at 7.72 and 7.81 microns, was obscured by the ether band of the monomer. Similar complications were found with the anhydride curing agent, though the anhydride carbonyl band at 5.59, and 5.38 microns could be distinguished from the ester carbonyl 5.81 microns. (The methylene bands of the anhydride are effectively masked by those of the monomer at 3.39 - 3.31 microns).

Similarities were observed between the infrared pattern of the two systems studied, and between all cured epoxide resins based on a common monomer (2), and it was difficult to distinguish, by conventional chemical techniques, the difference between cured systems, although some progress has been made using pyrolytic techniques (9). The complexities arise from the complicated spectrum of the monomer, most of which are carried over to the cured polymer. No band assignment can be made for the vibrations of the curing agents. Also, no definite assignment has been made of all the epoxide resin monomer bands (4).

Common to the curing of all epoxide resins is the decrease in intensity with increasing cure of the epoxide bands, 10.31, 10.93, 11.56, and 12.40 microns. The band occurring at 8.0 microns (due to epoxide and ether) appeared to be unchanged during the curing process. This was due to slight epoxide absorption at this wavelength. Investigation of the cure rate of these materials, by following the disappearance of the epoxide band, has been reported by Dannenberg (10) and others (6, 11).

4 - 2 A T R Studies

The A T R infrared spectra of the cured materials, using the KRS - 5 trapezoid crystal at two angles of incidence, are shown (Figure 4 - 3 and 4 - 4) for the amine and anhydride systems respectively. The loss in spectral definition and the shifts in band maxima can in part be ascribed to the change in the angle of incidence for values greater than 39°.

4 - 2. 1 Qualitative Spectral Changes

The change in the A T R infrared spectra for the amine and anhydride cured polymers, on irradiation with ultraviolet light (wavelength greater than 280 microns) in an oxygen atmosphere, is shown (Figures 4 - 5, and 4 - 6 respectively). The major absorption band changes are listed (Table 4 - 3 and 4 - 4).

TABLE 4 - 3

Infrared Absorption Band Changes on Ultra-Violet Irradiation

Amine Cured Polymers

Absorption Band	Observations	Duration of Irradiation (minutes)
hydroxyl	decrease, increase	120
isopropylidene	decrease	140
1, 4-disubstituted aromatic nucleus	decrease	long period
5.81 6.06	ingrowth of new bands	350 80
ether	decrease	long period
aromatic - CH -	decrease	Long period
residual epoxide	decrease	40

TABLE 4 - 4

Infrared Absorption Band Changes on Ultraviolet Irradiation of HHPA Anhydride Cured Polymers

Absorption Band	Observations	Duration of Irradiation (minutes)
hydroxyl	decrease, increase	200
isopropylidene	decrease	580
ester carbonyl	decrease, increase decrease	Long period
residual anhydride	decrease	130
1, 4-disubstituted aromatic	decrease	Long period
ether	decrease	Long period
aromatic - CH -	decrease	Long period
residual epoxide	decrease	150

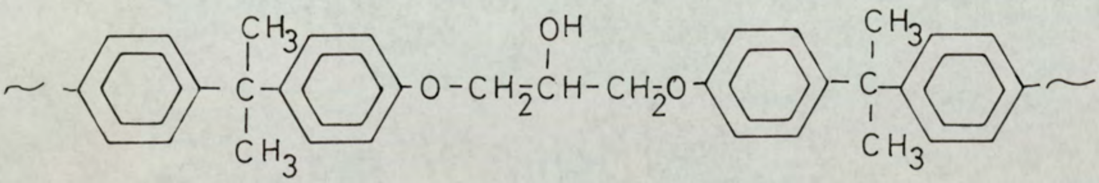
All systems, amine and anhydride cured, commercial and purified monomers, showed shifts in the absorption bands to longer wavelengths and a gradual broadening of all peaks. The wavelength shifts were most noticeable with the hydroxyl bands, being greater in the amine cured systems than in the anhydride systems. A sharpening of the hydroxyl band in the amine cured system was also noted. The band shifts and broadening can be explained in part by a dispersion effect on a very thin film. The thin film, in this case, is thought to be a new surface layer formed as a result of the photo-oxidation of the original polymer. The reflectivity of an interface of two materials for normal incidence can be expressed in terms of the simple equation:-

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

where n_2 and n_1 are the refractive indices of the sample and the A T R crystal respectively. Thus a change in the value of n_2 will lead to a different value of the reflectivity, R. The change in the value of n_2 for the polymers under study is due to colour formation (and associated changes) on irradiation. The effect of the refractive index change and the subsequent change in the depth of penetration of the light into the sample surface is considered in a later section.

Irradiation with short wavelength light caused similar effects to those already described. Only the rates of change of the band intensities differed. In particular the epoxide group in all systems is affected this way. This result was in accordance with the work of Doyle (12) and others (13, 14) on the ring opening of the epoxide groups of low molecular weight compounds on irradiation with short wavelength ultraviolet light. The anhydride cured resins showed a decrease in the ester carbonyl band, which was anticipated because of the absorption of the curing agent itself in the short wavelength region.

The degradation of the amine cured systems resulted in the appearance of two new absorption bands at 5.81 and 6.06 microns. A similar result was reported by Hearst for a bisphenol - A epoxide resin cured with diethylene triamine, in his study of pigmented and unpigmented epoxide resins exposed to ultraviolet light from mercury and xenon arcs (15). In his study two new peaks were observed at 5.82 and 6.02 microns. The difference in the band positions reported in this study can be partly accounted for in terms of the different angle of incidence used (45°). Also, since Hearst's amine curing agent (DETA) differs from the TETA used here only by the secondary amine and methylene content, it is reasonable to assume that his new bands resulted from similar reactions to those described below. Hearst also reported the formation of new bands at the same wavelength from the ultraviolet irradiation of a polyamide cured bisphenol-A epoxide resin. It is likely that the new bands in ultraviolet degradation studies are derived from the monomer unit of the resins.

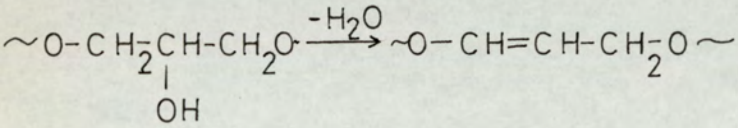


The bands located at 5.81 and 6.06 microns are located in the infrared finger print region normally associated with the carbonyl function.

The groups which absorb in this region and which are consistent with a degradation scheme initiated at C - N, isopropylidene or ether linkage are ketone (dialkyl, singly or doubly conjugated) 5.8 - 6.2 microns, aliphatic aldehyde 5.77, aromatic aldehyde 5.85, aliphatic acid 5.68 - 5.85, ester 5.76 - 5.82, aromatic acid 5.82 - 5.94, oxime 6.0 or vinyl compounds. The presence of the latter can be discounted in the photo-oxidised systems due to the known instability of vinyl compounds to ultra-violet radiation, especially over long periods of irradiation with short wavelength light (16). Since scission of the C - N bond was thought unlikely from the results of pressure measurements, the results obtained by Hearst (15) and bond energy consideration, the presence of the oxime is unlikely. Irradiation with a black lamp - fluorescent sunlamp combination through the OY filter, which transmitted the full intensity of the lamp from 360 nm, showed only differences in intensity of the 5.81 and 6.06 bands due to the increased light intensity and eliminated the possibility of scission of the C - N bond. The confirming band for carboxylic acids (broad diffuse band at 3 - 4 microns) might be obscured initially by the hydroxyl band of the cured system, but if it was present it would increase proportionally with its major band. However, because of variation in the absorption due to initial hydroxyl present, the presence of carboxylic acids cannot be ruled out. Since no confirming ester bands at 9.52 - 7.69 microns were found, the presence of the ester carbonyl may be discounted. Because of the complex nature of the epoxide resin spectra the definite presence or absence of specific confirmatory bands cannot be stated.

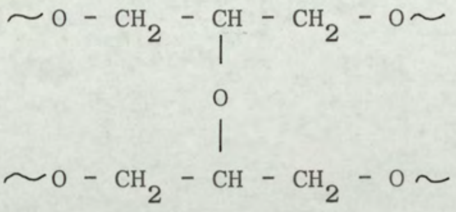
On the basis of the exact intensities the most likely assignments are conjugated ketone for the 6.06 microns, and ketone, aldehyde or aliphatic acid (17) and possibly vinyl groups on irradiation in inert atmosphere for the 5.81 micron band. The assignment of the 6.06 micron band to conjugated ketone is in agreement with work on the weathering of amine cured high molecular weight epoxide resins based on epikote 1004 (18).

In air and vacuum irradiation the intensity of the hydroxyl absorption band decreased initially. Further irradiation caused an increase and a further decrease in intensity in the air and vacuum systems respectively. Examination of the volatile low molecular weight degradation products from the initial irradiation (Table 4 - 5 and 4 - 6) showed the presence of quantities of water. On the basis of this, and the results of the photochemical degradation of phenoxy resins by Kelleher (19) the following reaction may have occurred in the aliphatic section



$$\sim O-CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2O \xrightarrow{-H_2O} \sim O-CH=CH-CH_2-O\sim$$

The ether bond may have been unaffected by the radiation used since little change in band intensity was observed even after long irradiation periods. However the high intensity of the ether band in glycidyl ethers may have masked changes which occurred. Ether bond scission with subsequent recombination of radicals may have occurred. New ether bonds may have been formed by crosslinking reactions at the aliphatic hydroxyl groups yielding structures of the type



$$\begin{array}{c} \sim O - CH_2 - CH - CH_2 - O\sim \\ | \\ O \\ | \\ \sim O - CH_2 - CH - CH_2 - O\sim \end{array}$$

This could also explain the presence of water in the volatile degradation products. Photochemical dehydration reactions of this type have been observed with simple alcohols which yielded vinyl compounds (20). The shifts of the ether band to longer wavelength may have been caused by the presence of these new bonds. Evidence of crosslinking reactions was found from the modulus changes that occurred on irradiation of both amine and anhydride cured systems. The loss of water and the crosslinking reactions were common to both air and vacuum irradiated polymers since the physical and chemical changes occurred to a similar extent in both systems.

TABLE 4-5

Volatile Degradation Products, Amine System

Compound	% by Volume				Quantum^{x} Yield x10^{6}
	A1	A2	VI	VII	
Hydrogen	0.08	0.13	2.14	7.33	2.05
Methane	0.02	0.03	1.92	6.20	1.75
Ethane	0.16	0.23	2.11	3.21	1.93
Propane	0.01	0.01	t	0.01	-
C-3 hydrocarbon					
Acetylene	t	0.01	0.01	t	-
Ethylene	t	0.01	t	-	-
C-4,C15 hydrocarbon	t	-	t	0.10	-
Carbon Monoxide	6.00	1.01	68.20	73.20	62.1
Carbon Dioxide	33.00	39.55	6.00	4.91	5.49
Alcohols (C-3,C-4)	t	0.16	t	t	-
Propionaldehyde	t	t	-	t	-
Acetaldhyde	0.14	0.32	t	-	-
Formaldehyde	0.11	0.73	t	t	-
Acrolein	0.01	t	t	0.04	
Acetic Acid	0.43	0.67	0.01	t	-
Formic Acid	0.37	0.94	t	0.02	-
Acetone	0.43	0.61	t	-	-
Chlorides	0.01	t	t	0.01	-
Phenols	t	t	t	0.14	-
Aromatics	t	t	t	t	-
Ethylene Diamine	t	0.01	t	0.06	-
Diethyl Amine					
Amines	t	0.12	t	0.30	-
NO_2 (?)	0.04	0.10	t	-	-

x Quantum yields for 500 minutes irradiation in vacuum

A1 - air irradiation, 500 minutes
A2 - " " 5,000 "
VI - vacuum " 500 "
VII - " " 5,000 "
t - trace (less than 0.01%)

TABLE 4-6

Volatile Degradation Products, Anhydride Systems

Compound	% by Volume				Quantum^{x} Yield x10^{7}
	A1	A2	VI	VII	
Hydrogen	0.33	0.49	6.22	7.94	7.27
Methane	0.01	t	2.14	6.30	2.87
Ethane	t	t	t	–	–
Propane	t	0.03	t	1.19	–
C-3 hydrocarbons					
Acetylene	–	t	0.01	–	–
Ethylene	–	t	t	t	–
C-4,C-5 hydrocarbons	t	t	0.07	0.11	–
Hexatriene	t	–	t	t	–
Cyclohexane	t	–	t	t	–
Carbon Monoxide	0.43	0.40	72.00	83.50	97.2
Carbon Dioxide	64.10	84.00	3.10	4.33	4.19
Alcohols (C3, C4)	t	–	–	t	–
Propionaldehyde	t	t	t	–	–
C - 6 Aldehyde					
Acetaldehyde	t	0.31	t	–	–
Formaldehyde	0.71	0.90	t	t	–
Acrolein	t	t	0.01	0.06	–
Acetic Acid	1.11	1.40	t	–	–
Formic Acid	2.40	3.00	t	t	–
Acetone	0.07	0.07	–	–	–
Chlorides	0.01	t	t	t	–
Phenols	0.10	0.11	0.10	0.10	–
Aromatics	0.10	t	t	t	–

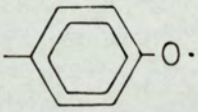
x Quantum yields for 500 minutes irradiation in vacuum.

A1 - air irradiation 500 minutes irradiatic
A2 - " " 5,000 " "
VI - vacuum " 500 " "
VII - " " 5,000 " "

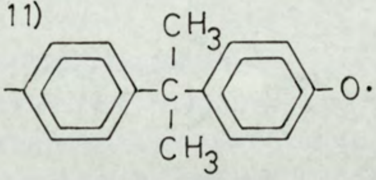
The subsequent increase on air irradiation in the hydroxyl absorption may be due to hydroperoxides and other species (carboxylic acids, phenols etc.). Alternatively direct ring opening of the residual epoxide groups could have caused the band increase. Examination of the rate of destruction of epoxide groups by near infrared and ATR spectroscopy (Figure 4 - 7) showed that, in both the surface layers and the bulk of the polymer, the ring opening reactions did not lead to hydroxyl formation and the removal of the epoxide groups was almost complete during the period of hydroxyl decrease. The difference in the rate of disappearance of epoxide groups during air and vacuum irradiation indicated that no direct ring opening occurred with the radiation used. This was in agreement with photodegradation studies on simple epoxide molecules (12, 13, 14)

An E S R investigation of the degradation process detected only one type of radical (symmetrical absorption g = 2.006, line width 9 Gauss) during vacuum irradiation of both amine and anhydride systems at room temperature. The signal intensity was weak and no hyperfine splitting was observed. These facts, together with the small line width, eliminated the presence of aliphatic radicals RO· and R·. Radicals of the type (i) and (ii)

(i)

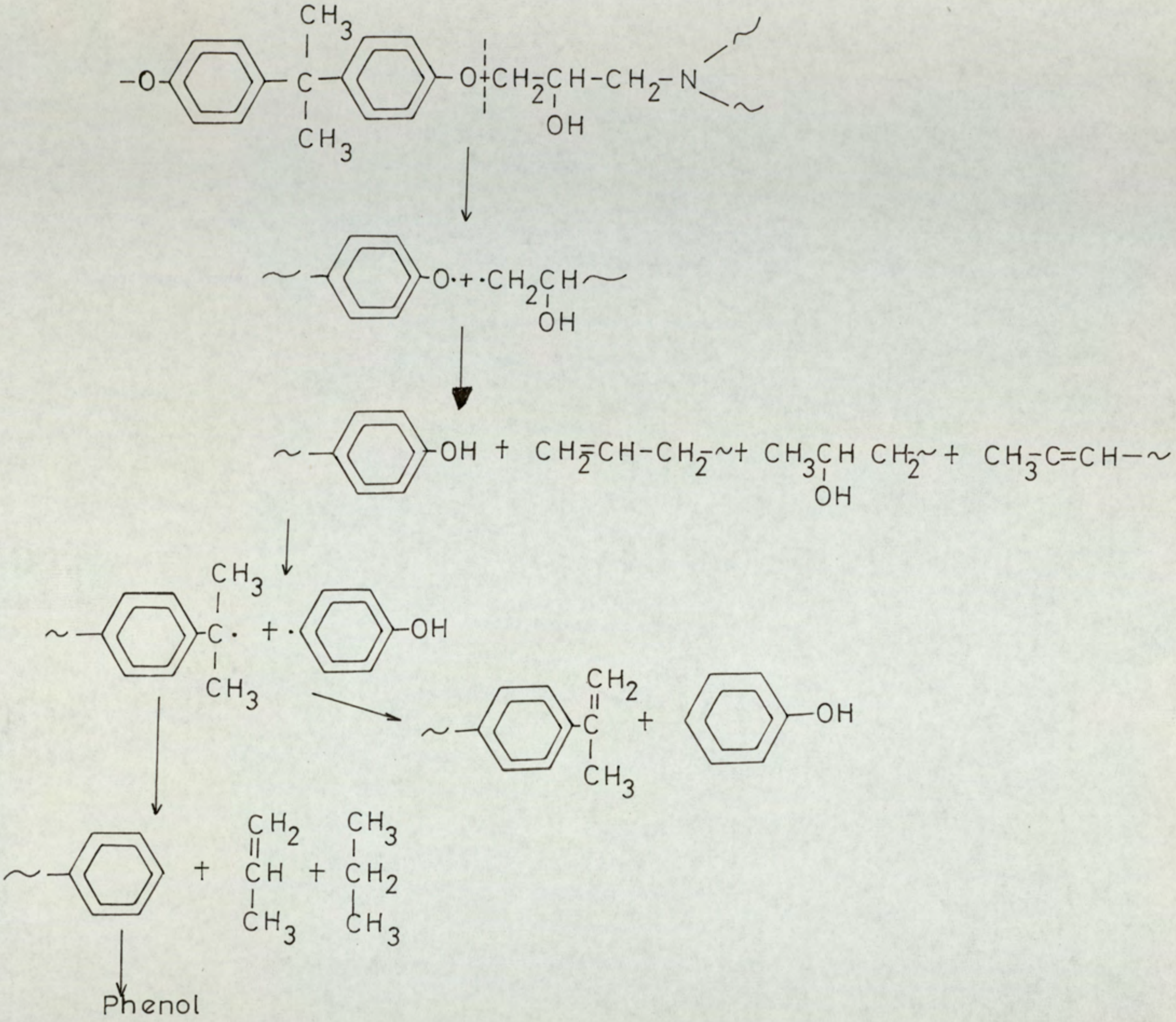


(ii)

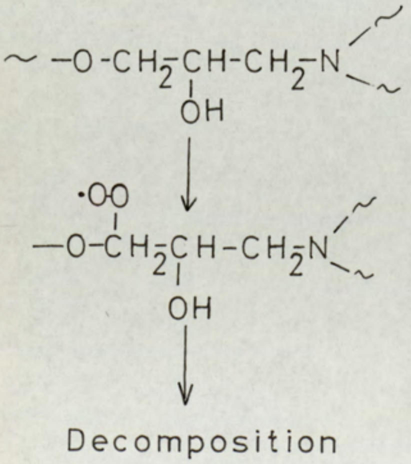


would give the observed spectra, since ether and isopropylidene groups were present in both the TETA and HHPA cured polymers. Type (ii) radicals are more likely to occur than type (i), since no change was observe in the isopropylidene absorption bands during the irradiation periods of one and three hours required to detect a signal in the amine and anhydride systems respectively.

Scission at the ether bond, independent of the curing agent, would explain the presence of these radicals. Examination of the volatile compounds evolved from irradiation of both amine and anhydride cured resins (Tables 4 -5 and 4 - 6) showed the presence of phenols, which could have been derived from radical type (ii). The initial degradation of the vacuum irradiated systems could be represented as follows

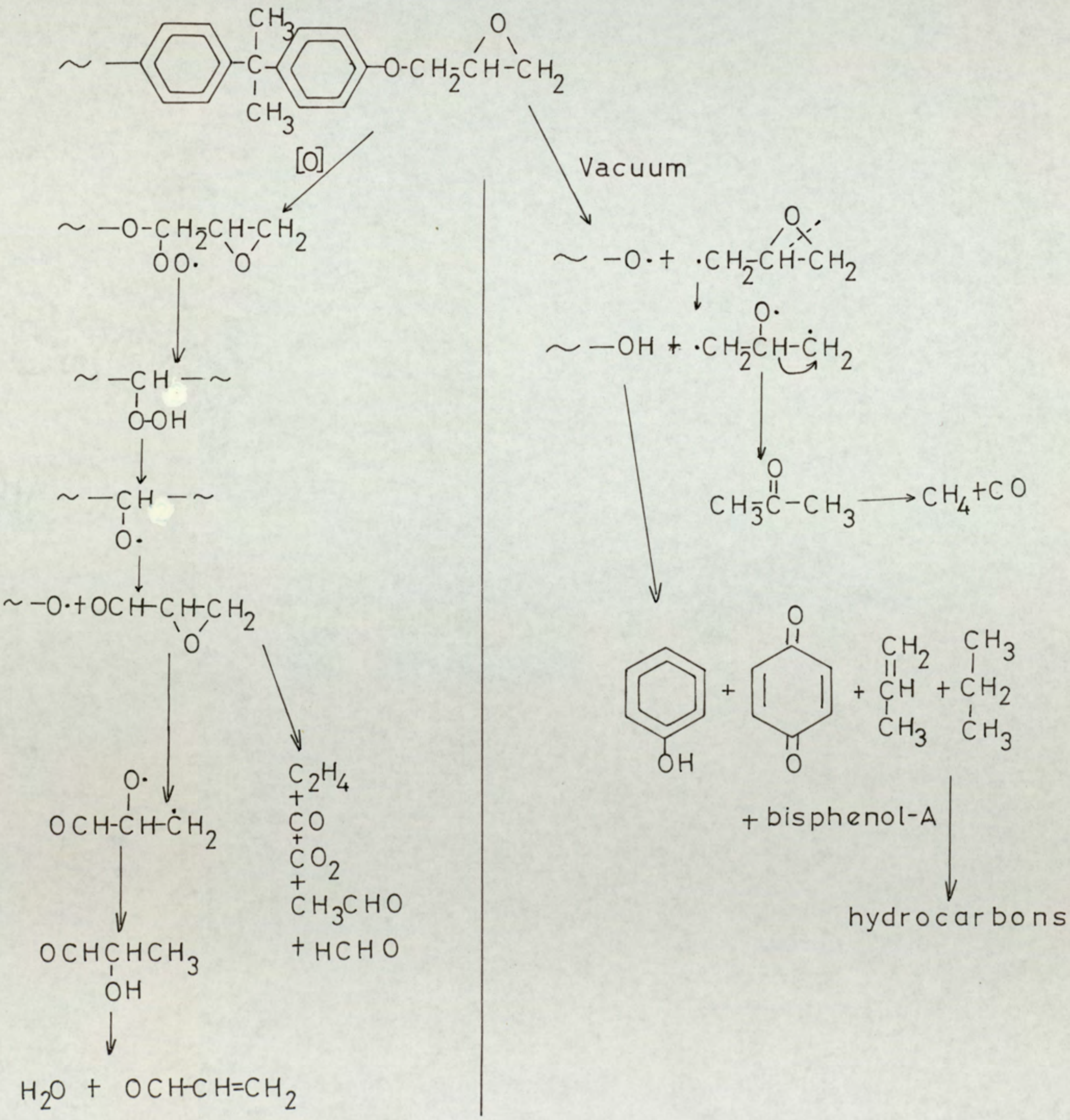


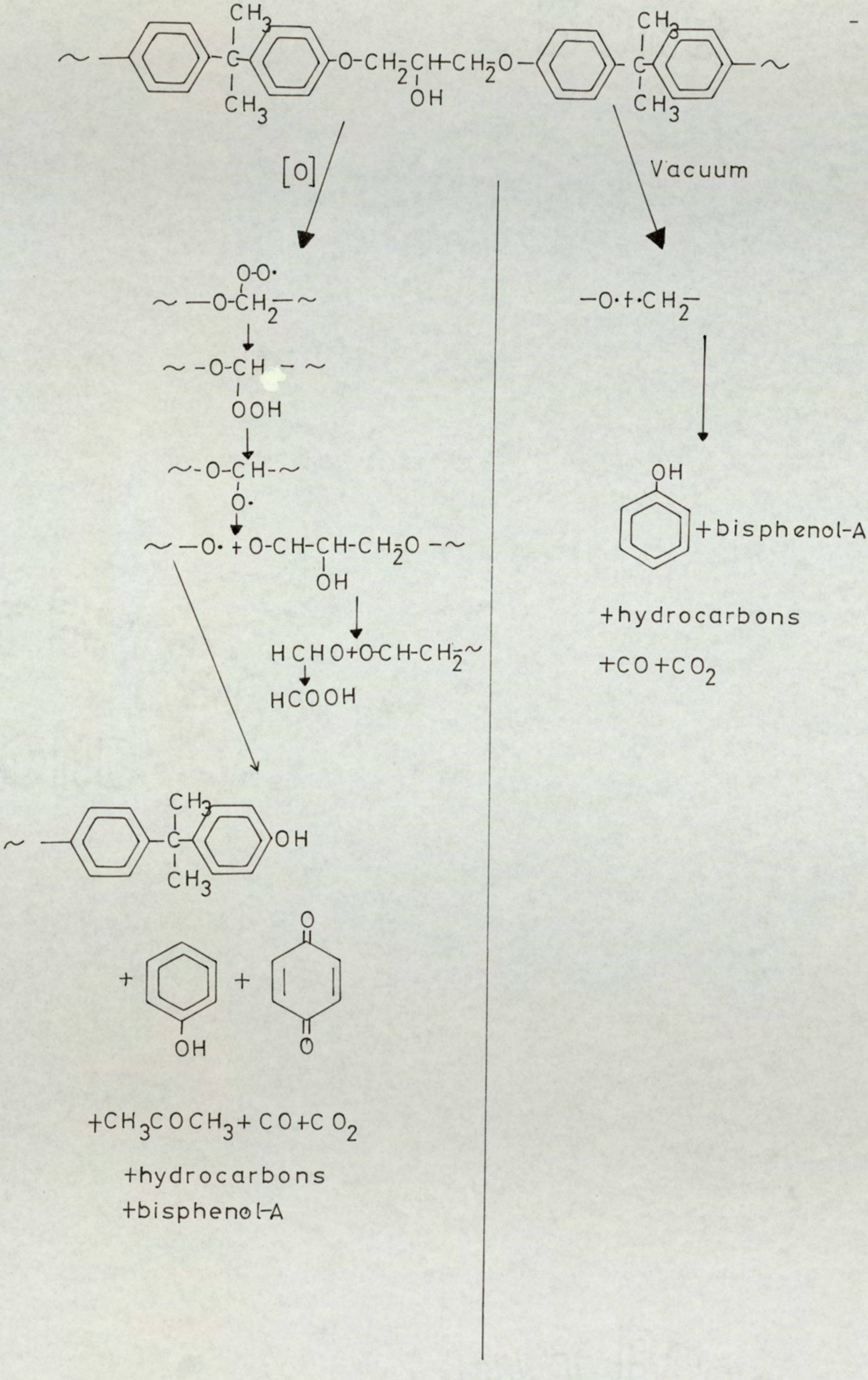
In air



Thus degradation is the result of direct homolysis of the carbon to oxygen bond. Bond energy considerations show that this is feasible with radiation of wavelengths up to 330 nm; from the types of aliphatic compounds identified in the volatile degradation products the following scheme is proposed for the aliphatic section of the molecule during photodegradation and photo-oxidation.

Unreacted chain ends



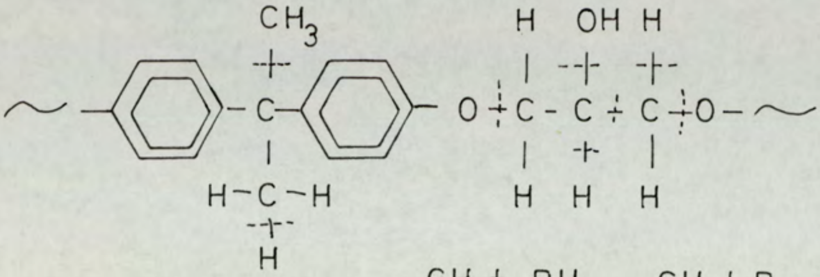

[O]
Vacuum
O-CH₂-CH-CH₂-O
OH
CH₃
O-O·
—O-CH₂—
—O-CH—
OOH
—O-CH—
O·
—O· + O-CH-CH-CH₂O —
HCHO+OCH-CH₂—
HCOOH
OH
+CH₃COCH₃+CO+CO₂
+hydrocarbons
+bisphenol-A
—O·+·CH₂—
+bisphenol-A
+hydrocarbons
+CO+CO₂

The presence of acidic compounds in the volatile degradation products together with the formation of quinones during vacuum irradiation is indicative of the presence of oxygen in the system. This oxygen may have been trapped in the polymer matrix, or on the walls of the evacuated reaction chamber. The decrease in the hydroxyl content after long irradiation periods could then be explained as being the result of depletion of the oxygen supply. Alternatively the oxygen may be attributed to peroxides on the polymer chain because of degradation of the polymer matrix at elevated temperatures namely: the high temperature cure of the HHPA system, and the large curing exotherm of the amine systems. Curing of the polymers in nitrogen and extensive degassing of the vessels did not prevent the formation of the oxygenated species. The peroxides and hydro-peroxides thus formed would undergo rapid decomposition on exposure to ultraviolet light, and the degradation could proceed by generation of free radicals. It is possible that trace amounts of oxygen in the nitrogen could have caused peroxide formation. However the use of helium, as the curing atmosphere, did not alter the type of degradation products obtained.

In both air and vacuum irradiated systems the hydroxyl concentration remained constant, because of the formation of the phenolic compounds. Further evidence of changes in the aliphatic monomer section was found from the shifts of the hydroxyl absorption band to longer wavelengths. This can be interpreted as a change from long to short range hydrogen bond, and molecular relaxations must have occurred as the environment and nature of the hydroxyl groups changed, giving rise to the surface crazing found in the irradiated epoxide systems. Because of the sensitivity of the techniques used no correlation was found between the time up to initial crack development and shifts in the absorptions.

The large quantities of methane, ethane and hydrogen found in the degradation products in both air and vacuum irradiation can be explained in terms of the random bond scission at all bonds except the aromatic C - C and C - H bonds.

i.e.



$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot$$

$$CH_3\cdot + RCH_3\cdot \longrightarrow C_2H_6 + R\cdot$$

The expected decrease in intensity of the ether band because of the loss of low molecular weight species was not observed. This may be explained by the formation of new ether bonds, and by a loss of film thickness as evidenced by the decrease in the 1, 4 disubstituted aromatic band on irradiation (21). Since very small quantities of aromatic volatile degradation products were found relative to the quantity of aliphatic material, even in the vacuum systems a considerable quantity of the former must remain in the degraded polymer. Possibly a high degree of radical recombination involving aromatic compounds occurred.

No new bands were observed with the anhydride cured materials even after long irradiation periods (100,000 minutes). A similar result was found during thermal ageing of similar systems (21). Small changes in the intensity of some bands occurred together with a gradual broadening of all bands, which was evidenced by the general shift to longer wavelengths. The increase in intensity of the ester carbonyl band was not associated with an increase in the degree of cure, since equivalent changes were not observed for the residual epoxide content. It is probable that the original intensity of the ester band masked subsequent ingrowth of other types of carbon bands, which were observed with the amine cured materials. No regular change was observed with the hydroxyl bands, and as in the case of the amine systems hydroperoxides may have been produced and decomposed, thus giving rise to the fluctuations in the band intensity. A decrease in the isopropylidene, residual anhydride, acid and epoxide occurred at equivalent rates in both oxidising and inert atmospheres.

An increase in the degree of cure may have been associated with the disappearance of the residual anhydride and epoxide, and since cure in the solid state is diffusion controlled, bond scission must have occurred on irradiation increasing the mobility of the reactive groups.

The decrease in the ether and aromatic bands as in the amine systems was attributed to bond scission and loss of film thickness.

4 - 3 Chemical Analysis of Irradiated Polymers

The results of the wet chemical analysis, by the swollen particle technique (2), of the HHPA cured polymer on irradiation in air and vacuum are shown (Figure 4 - 8 and 4 - 9). Since the ester carbonyl could have been the initiator of degradation in these materials, the effect of the degree of cure in terms of the mono and diester content was investigated. The results of irradiation of the HHPA systems with varying mono and diester content are shown (Figure 4 - 10).

The ATR technique showed a decrease in the isopropylidene band after long irradiation periods. Chemical analysis showed that a decrease occurred also in the free epoxide anhydride and ester content on irradiation. Since no increase occurred in the ester content with decrease of epoxide content, it can be assumed that degradation occurred as a result of bond scission in the aliphatic portion of the epoxide monomer, as outlined for the amine cured systems. This was confirmed by examination of the volatile compounds evolved during degradation (Table 4 - 6). The decrease in the anhydride curing agent may have been the result of ring opening by active hydrogens from the degradation of the monomer, and to some extent by breakdown of the cyclohexane ring. This would explain the large volumes of carbon monoxide and dioxide found in the volatiles, in comparison to the amine cured systems. Also since the rates of epoxide scission were similar for both the TETA and HHPA cured polymers, only unreacted chain ends were degraded initially in the HHPA systems.

Consideration of the ester content showed that the rate of change was influenced by the initial ratio of diester to monoester (Figure 4 - 10). The rate of decrease was greatest when the ratio was least. Low diester content resulted in an incomplete cure and therefore a high acid and hydroxyl content. The effect of variations in the mono and diester contents was also seen from the evolution of carbon dioxide from air irradiated systems (Table 4 - 7).

TABLE 4 - 7

Evolution of Carbon Dioxide from HHPA Systems

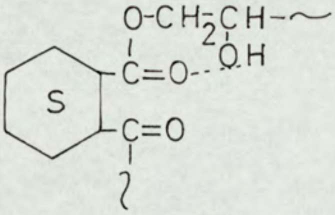
Diester/Monoester Ratio	Irradiation Time	% CO_2 by Volume
2.25	100 minutes	60.00
	500 "	64.10
1.10	100 "	72.50
	500 "	78.00
0.84	100 "	80.15
	500 "	92.66

The effect was greatest for systems of low diester content. Thus the instability of the cure link in these materials was associated with the presence of the acid groups and may have been physical or chemical in nature.

The ester and acid carboxyl groups should not have been affected by the radiation used, due to the presence of the cyclohexane ring. However, degradation would have been expected at the monomer section of the polymer as in the amine cured systems. Comparison of the volatile degradation products from the anhydride systems (Tables 4 - 5 and 4 - 6) with those from the amine systems showed that degradation occurred initially to some extent in both systems, as evidenced by the E S R results. This was attributed to the unreacted chain ends of the monomers. The slightly longer irradiation times required with the HHPA materials for equivalence with the TETA systems may be due to differences in crosslink density or difference in the ultraviolet transmitting powers of the materials.

If the latter was correct the HHPA materials should be colourless, while the TETA materials should be coloured. The reverse is in fact true of these cured resins. Therefore the curing agents themselves must play an important part in the ultraviolet susceptibility of epoxide resins.

By analogy with the work of Parker, (22) who observed shifts in the $n \longrightarrow \pi$ and π ——— π^* absorption bands to longer wavelengths by polar solvents in solution, it is possible that a similar physical interaction occurred between the curing agent in the polymer and some neighbouring groups. The effect, if it occurred, would be magnified by the rigid, three-dimensional nature of the polymer matrix. With anhydride cured resins this would be a hydrogen bonding interaction of the carbonyl oxygen and the hydroxyl group,



causing a greater separation in the n , π and π^* energy levels. This does not explain the greater stability of the isopropylidene group in the anhydride over that in the amine systems. However, since the proposed interaction affects the aliphatic portion of the resin it is likely that the benzene nucleus, which causes bathochromic effects, would be affected to some extent via the ether linkage. Possible evidence for this or other solid interaction was found in polyesters by Hirt (23). Consideration of the curing agents studied by Lee and Watson (24) showed that colour formation occurred when interaction was possible e.g. diethanolamine gave clear castings while tert-butylethanolamine cured yellow.

4 - 4 Validity of the ATR Technique for Quantitative Studies

It was expected that during the oxidation or curing of a polymer the refractive index of the sample would increase, and that with appropriate angle and crystal material the depth of penetration would increase with the degree of oxidation. The combination of difference in depth of penetration of various wavelengths throughout the spectrum and the variation in depth of penetration, as refractive index of the sample changes during curing or oxidation, might preclude the possibility of quantitively interpretating surface-layer changes from ATR spectra. The conditions for validity are that the sample composition should not be significantly different for thickness of 1 - 10 microns and that only a small variation in the refractive index occurred with the chemical changes being studied (25). The percentage changes in refractive index after 1,000 hours irradiation are shown (Table 4 - 7) for the 6.06 micron band.

TABLE 4 - 8

Percentage Change in Refractive Index on Irradiation *

Polymer	% Change in Air	% Change in Vacuum
'828'/TETA	30	36
'826'/TETA	27	34
'816'/TETA	27	30

A maximum variation of the refractive index of 30 % and 36 % was found for the amine systems in air and vacuum. This variation appeared to be acceptable for the chemical changes under study, since little difference was observed in the curves obtained when the three refractive indices of the surface layers were used.

4 - 5 Kinetics of Degradation from ATR Data

The kinetics of the degradation reactions were investigated by means of the normalised optical density technique, which describes the change in the depth of penetration of the light into the surface of the degraded polymer, by the change in infrared band intensity. The effective thickness d_e, defined as the thickness required to give the same absorption for transmission at normal incidence (26, 27, 28), is given by the expression of Harrick and du Pré (26) for reflection from a uniformly absorbing infinite substrate of refractive index n_3

---

* The large values indicated colouration & density increase. The crack formation did not agree with the density changes, indicating an error in the values which may have been due to the experimental technique or the method of data treatment used.

$$d_e/\lambda_o \quad = \quad n_{31}\, \mathrm{Cos}\theta /\ n_1\, (1 - n_{31}^2)\, (\mathrm{Sin}^2\theta\ -\ n_{31}^2)^{\frac{1}{2}}$$

for perpendicular polarised light 1a

$$d_e/\lambda_o \quad = \quad \frac{n_{31}\ \mathrm{Cos}\theta\ (\ 2\ \mathrm{Sin}^2\theta\ -\ n_{31}^2\ )}{n_1\ (1 - n_{31}^2)\ (1 + n_{31}^2)\ (\mathrm{Sin}^2\theta\ -\ n_{31}^2)\ (\mathrm{Sin}^2\theta\ -\ n_{31}^2)^{\frac{1}{2}}}$$

for parallel polarised light 1b

θ angle of incidence

n_1 refractive index of the ATR crystal

λ_o incident wavelength in vacuum

These equations are reduced, when a very thin absorbing surface layer (thickness d, refractive index n_2) on an infinite substrate is used, to;

$$d_e/d \ = \ 4\ n_{21}\ \mathrm{Cos}\theta /\ (1 - n_{31}^2)$$

for perpendicular polarised light 2a

$$d_e/d \ = \ \frac{4\ n_{21}\ \ \mathrm{Cos}\ \theta\ (1 - n_{32}^4)\ (\mathrm{Sin}^2\theta\ -\ n_{31}^2\ )}{(1 - n_{31}^2\ )\ \ (1 + n_{31}^2\ )\ (\mathrm{Sin}^2\theta - n_{31}^2\ )}$$

for parallel polarised light 2b

Values of d_e calculated from these expressions are given (Table 4 - 9). The d_e values increase with increasing depth of penetration of the reflected beam (26).

TABLE 4 - 9

Calculated Effective Thickness

				Infinite Substrate		Thin surface film	
				d_e/λ_0	d_e/λ_0	d_e/d	d_e/d
Reflection Element	n_{31}	θ	N	perpendicular	parallel	perpendicular	parallel
KRS - 5	0.635	39°	1	0.331	0.166	3.13	7.88
	0.625	45°	1	0.291	0.149	2.81	5.74
	0.625	51°	1	0.178	0.068	2.53	4.63

$n_{31} = n_3/n_1$ where $n_3 = 1.5$ and $n_1 = 2.4$

θ - angle of incidence

N - number of reflections for the KRS - 5 crystal (hemicylinder N = 1)

n_2 - refractive index of the thin film taken as 1.7

λ_0 - Wavelength of light in the denser medium

The beam penetration is seen to decrease in the sequence KRS - 5, 30°, greater than KRS - 5, 45°, greater than KRS - 5, 60°. The epoxide resins may be regarded as being infinitely thick (up to $\lambda_0 = 10$ microns) for all reflection conditions used in the experiments (incidence angle between 30° and 60°). The experimentally observed ATR band intensity for a particular reflection crystal and substrate depends on the sample area, the degree of contact of the sample with the crystal, the number of reflections from the interface and the effective thickness. Consequently it is difficult to make absolute quantitative comparison of the ATR intensity of a given infrared absorption, either from differently treated films, or for the same film under different reflection conditions. The problem can be overcome, in part, by using an absorption band as an internal standard. Ideally the band chosen as standard should not be affected by changes in the long and short range order or by extensive reaction. Nearly all bands of the epoxide resins studied were observed to change on exposure to long or short wavelength radiation.

However, the ether and benzene bands, 8.26 and 6.25 microns respectively, change very slowly over long irradiation periods and were thus suitable for use as internal standards. Since the benzene band was close to the carbonyl region, the ether band was chosen as the internal standard in this work. The validity of this normalisation procedure in the application of the ATR technique to polymer degradation has been reported by Carlson and Wiles (29). As a simplification only perpendicularly polarised radiation was used in the study, though it was found that theoretical separation of perpendicular and parallel components could be achieved from measurements with unpolarised radiation.

4 - 6 Degradation of Amine Cured Polymers

The ingrowth of the carbonyl bands in the amine cured polymer (thickness 50 microns) irradiated on a non reflecting surface is shown (Figure 4 - 11).

The variation in the normalised optical density value of the 6.06 micron band, as a function of the exposure time, is shown (Figure 4 - 12 and 4 - 13). A uniform distribution of absorbers across the thickness of the film gave rise to a set of normalised optical density values which were independent of the depth of penetration of the light beam. The normalised absorption curves indicated that there was extensive photo-oxidation very close to the film surface (small penetration depth). Little oxidation of the bulk of the sample had occurred as shown by the development of the 6.06 micron band by the transmission infrared technique, and also by the results of ATR examination of the film surface not exposed to incident radiation for relatively thick films, 50 - 100 microns. This was due to the preferential absorption at the surface incident to the radiation. Thus for thick films photo-oxidation progressed in from the film surface exposed to incident light, whereas for thin films (20 microns), the ATR examination of the exposed and unexposed surface during irradiation showed that the degradation occurred at both surfaces, with a decrease in the extent of degradation at the unexposed surface with increasing degree of irradiation.

This was due to increased light absorption by the exposed film surface. Examination of films irradiated under reflecting conditions showed that ingrowth of degradation occurred at approximately equal rates on both sides of the film.

The depth of penetration (dp) of the light into the sample, defined as the distance measured into the sample, normal to the interface, required for the electric field amplitude to fall to a value of 1/e of its value at the interface, is given by the expression of Harrick and du Pré (26).

$$d_p = \lambda_o / (2\pi \mathrm{Sin}\Theta - n_{21}^2)$$

$n_{2\,1}$ - ratio of the refractive index in the sample to that in the crystal.

Θ - angle of incidence

λ_o - wavelength in the denser medium

The dp values for the three angles used are shown (Table 4 - 10)

TABLE 4 - 10

ATR Conditions and Depths of Penetration

ATR Crystal	$n_{2\,1}$		N^*	dp $/\lambda_o$
KRS - S	0.625	39^o	1	0.502
Hemicylinder				
	0.625	45^o	1	0.441
	0.625	51^o	1	0.331

N^* - Number of reflections in the crystal

In these calculations the value of N_2, the refractive index of the polymer, was assumed to be constant. However from the observed colour changes on irradiation a refractive index change was known to occur.

Therefore the refractive index at the irradiation periods where colour change occurred had to be used. These were calculated from the expressions of Fahrenfort (27) and Fluornoy (28). In ATR infrared studies on the photo-oxidation of polypropylene (29) the refractive index of the material was assumed to be constant over a 200 hours irradiation period. This assumption was valid for this study since only a small variation in refractive index occurred.

The change in the normalised optical density values of the infrared bands of interest are shown (Figure 4 - 14 to 4 - 23). Using the equations of Carlsson and Wiles (29) and taking into account the refractive index changes in the polymers, the variation in the normalised optical density with dp can be represented by Figures 4 - 24 to 4 - 26 for the 5.81 and 6.06 micron bands.

No quantitative interrelation was found between the rates of new band formation and destruction of old absorption bands such as hydroxyl and isopropylidene. The decrease in the latter paralleled the rate of new band formation, but atdifferent rates.

The general broadening of the major bands, by equivalent amounts, was associated with the loss of film thickness, as indicated by the change in the 1,4 disubstituted aromatic absorption band (Figure 4 - 27), by the evolution of volatile degradation products. The effect was greater in vacuum irradiated samples than in air. This was due to the pressure gradient between the inside and the outside of the polymer films in the evacuated systems. A further indication of the loss of thickness and change in surface morphology was seen from the surface crazing, which again was greater during the vacuum irradiation. This may have been due to a predominance of chain scission reactions, while crosslinking reactions involving oxygen atoms would have occurred during air irradiation. The crosslinking and chain scission reaction can be used to explain the differences in the rates of new infrared band formation in both air and vacuum systems. In particular the 6.06 micron band showed a number of rate changes, and this may have been due to crosslinking reactions at the polymer surface, while a diffusion process occurred.

Because of the predominance of the scission reactions in vacuum systems the diffusion would be expected to proceed at a faster rate, if the absorption band (6.06 microns) was related to the same species in both air and vacuum irradiated systems. The initial rapid ingrowth of the band can be attributed to reactions in the uppermost layers of the polymer, where diffusion controlled reactions would not occur to any great extent in either air or vacuum systems.

4 - 7 Effect of Monomer Purity on Degradation

In all cases increased purity of the monomer resulted in a decrease in the rate of the degradation process as evidenced by the ingrowth of infrared bands. However, degradation did occur even in the '816' systems. Therefore the initiation of the polymer was not due to the presence of resin impurities but to some chromophoric group present in the polymers. The impurities may have accelerated the degradation processes.

In terms of the quinone band (5.81 microns) the presence of 1,2 or 1,3 disubstituted aromatic structures would lower the quinone concentration. However, it is unlikely that the overall differences between the three systems can be accounted for by this alone, since the impurities are present in small concentrations. The other main impurity, chlorine structures, should not themselves affect the rate of quinone formation since the chlorine was associated with the aliphatic chain. The C - Cl band, being photochemically weak, would be expected to undergo homolysis during the early stages of degradation giving rise to aliphatic chlorides and hydrochloric acid as indicated by the volatile degradation products identified. These products may have catalysed reactions such as the polymerisation of quinone (30). However, since in air irradiated systems other acids were formed in larger quantities, it is unlikely that the small quantities of chloride would have contributed to the differences observed between the monomers.

4 - 8 Product Concentration Profiles

To elucidate fully the mechanism of photochemical reactions it is necessary to know the quantum yields for product formation, disappearance of reactants, and also the variation in quantum yields with light intensity and wavelength of irradiation. Also, since it has been established that surface reactions occur during the photo- and photo-oxidative degradation of epoxide resins, a knowledge of product concentration profiles should aid in an investigation of the role of oxygen at the surface and in the bulk of the polymer.

For bulk materials the absorbance at a particular wavelength which results from a single attenuated reflection from the interface between an absorbing film and an ATR crystal is proportional to the concentration of the absorber, and the electric field amplitude E_z at a penetration z into the film, and is given by the expression (26)

$$\text{Optical density} = \varepsilon [C] E_o^2 \int_0^\infty e^{-yz} dz \qquad 3.$$

ε - molar extinction coefficient of the absorber
$[C]$- concentration of absorber at the interface
E_o^2- electric field amplitude at the interface
z- depth penetration of radiation into sample
y- experimental constant

and is usually expressed in the form:

$$O.D. = \varepsilon [C] d_e \qquad 4.$$

d_e - the effective thickness (equations 1 and 2, section 4 - 5)

for limiting concentrations viz (i) a bulk material of uniformly absorbing substrate, where $[C]$ is constant and (ii) a thin layer of absorber on a thick transparent substrate, where both $[C]$ and ε are constant across the thickness of the absorber, equation 3 can be solved by substituting the appropriate values of d_e from equations 1 and 2. If the refractive indices of the thin layer and bulk substrate are assumed to be equal ($n_2 = n_3$) the expression reduces to:

(i) Bulk Materials

Optical Density (O.D.) $= \lambda_0 n_{21} \, \varepsilon \, [C]_0 E_0^2 / 4\pi n_1 \mathrm{Cos}\,\theta \, (\mathrm{Sin}^2\theta - n_{21}^2)^{1/2} \qquad 5.$

where Eo for perpendicular polarisation $= \dfrac{2\,\mathrm{Cos}\,\theta}{(1 - n_{21}^2)^{1/2}}$

(ii) Thin Layer

$$\mathrm{O.D.} = n_{21} \varepsilon [C]_0 E_0^2 d \Big/ \mathrm{Cos}\,\theta \qquad 6.$$

where d is the thickness of the absorbing layer

Similar equations can be constructed for the case of different refractive index of the thin layer and bulk material.

(i) Bulk Materials

$$\mathrm{O.D} = \lambda_0 n_{31} \varepsilon [C]_0 E_1^2 \Big/ 4\pi n_1 \mathrm{Cos}\,\theta \, (\mathrm{Sin}^2\theta - n_{31}^2)^{1/2} \qquad 7.$$

where E_1^2 is the electric field amplitude at the interface

$E_0^2 = E_1^2$ if $n_2 = n_3$

$E^2 = 4\,\mathrm{Cos}\,\theta \Big/ (1 - n_{31}^2)$

(ii) Thin Layer

$$\mathrm{O.D.} = n_{21} \varepsilon [C]_0 E_1^2 d \Big/ \mathrm{Cos}\,\theta \qquad 8.$$

The optical density for the 5.81 and 6.06 micron infrared bands is given by the thin layer (ii) equations 6 and 8, while the optical density of the internal standard is obtained for equations 5 and 7, the case of an infinite substrate.

For a thin infrared absorbing layer of oxidised polymer on an infinite substrate (unde-graded polymer), the experimental parameter, the normalised change in optical density value of the band ingrowth is given by:

$$\Delta OD_A / OD_S = Kd\,[C]_A n_1 (\sin^2\theta - n_{21}^2)^{1/2} \qquad 9.$$

$$\text{for } n_2 = n_3$$

$$K = 4\pi\varepsilon_A / \lambda_o \varepsilon_S [C]_S$$

ε_A & ε_S - the extinction coefficients of bands A and S respectively

ΔOD_A - the change in optical density of band A

OD_S - optical density of internal standard band

and by $$\Delta OD_A / OD_S = K'[C]_A n_{23} (\sin^2\theta - n_{31}^2)^{1/2} \qquad 10.$$

$$\text{for } n_2 \neq n_3$$

where $K' = 4\pi\varepsilon_A n_1 / \lambda_o \varepsilon_S [C]_S$

$K' = n_1 K$

Expressions 5, 6, 7 and 8 are polarisation dependant, as seen from reference to expressions 1 and 2 from which they are derived. However, expression 9 is little affected by relatively large changes in the polarisation rate of the infrared beam at the wavelength in question. This is to be expected since $n_2 = n_3$ and the sample is assumed to be isotropic. Equation 10 on the other hand is polarisation dependant because of the anisotropy induced by oxidative degradation and is evidenced by the observed change in refractive index during irradiation. It is surprising that expression 9 is almost independent of the polarisation, since the cured polymer is itself anisotropic before irradiation due to the random build-up of the 3-dimensional structure. However, this expression has been shown to hold for corona modified polypropylene surfaces (29). The numerical value of K and K' can be calculated from a knowledge of extinction coefficient, band wavelength and original refractive index.

An alternative data treatment (32) involves the explicit solution of expression 3 for $[C]_Z$, the absorber concentration at various distances from the interfaces for the boundary conditions $[C]_z = [C]_o$ at Z = 0 and $[C]_z \longrightarrow 0$ as $Z \longrightarrow$ infinity.

Wilson (31), from his work on diffusion effects in the photochemistry of solid films, predicted an exponential dependence of product concentration on depth of penetration for polymer gas reactions. The function

$$[C]_Z = [C]_o e^{xZ} \qquad 11.$$

$$x = \text{constant}$$

fulfils these conditions.

Substitution in expression 3 and integrating leads to

$$O.D. = E[C]_o \, n_{21} E_o^2 / \cos\theta (x + 2y) \qquad 12.$$

The normalised O.D. value is thus derived for expression 12 for the new band, and for expression 5 or 7 for the internal standard

i.e. for $n_2 = n_3$

$$\triangle OD_A / OD_S = (2y[C]_o / (2y + X)) \,.\, (\lambda_o E)_A / ([C]_o \lambda_o E)_S \qquad 13$$

$$y = (2\pi n_1 (\sin^2\theta - n_{21}^2)^{1/2}) / \lambda_o$$

& $n_2 \neq n_3$

$$\triangle OD_A / OD_S = (2y'[C]_o / (2y' + x))_A \,.\, (E \lambda_o)_A / ([C] \lambda_o E)_S \qquad 14$$

$$y' = (2\pi n_1 (\sin^2\theta - n_{31}^2)^{1/2}) / \lambda_o$$

The three methods used to determine the variation in the concentration of absorbing species during irradiation were

1. Method of Harrick (26) and Fluornoy (28) using the normalised optical density curves.
2. Plots of optical density versus $n_1 (\sin^2\theta - n_{21}^2)^{\frac{1}{2}}$ or $n_{23} (\sin^2\theta - n_{31}^2)^{\frac{1}{2}}$
3. Explicit solution of the Harrick Equation (26)

The results from methods 1 and 2 are shown in Table 4 - 11 and those from method 3 in graphical form are shown (Figures 4 - 28 and 4 - 29) for the 5.81 and 6.06 micron bands respectively. Excellent agreement was found from the results of the three methods.

Extensive photo-oxidative degradation had occurred to depths at least as great as the smallest depths of penetration employed (approximately 500 microns from the surface) in all of the samples examined, even after 80 minutes irradiation. Prolonged exposure to the radiation in oxygen or vacuum resulted in the progressive ingress of the degradation into the polymer. Also both of the absorption bands (5.81 and 6.06) were found to be distributed uniformly across the degraded layers. From the results obtained by Fluornoy's method (Table 4 - 12) the anisotropy present from the random build-up of the three-dimensional structure had completely disappeared at 1,000 minutes irradiation. This must have been due to regularity of array of the absorbers, or to diffusion of the absorbers through the polymer. Since the amount of light transmission decreased with increased degradation, the reactions in the presence of air must have been dependent on the permeation of oxygen into the structure. The change in the relative volumes of volatile degradation products (Table 4 - 5) at different periods of irradiation indicated that most of the aliphatic section of the polymers in the upper surface layers was lost after the initial irradiation period, thereafter only small molecules such as oxides of carbon, hydrogen and low molecular weight hydrocarbons, were present together with the aromatic compounds. The low molecular weight species may have been produced by degradation of higher molecular weight compounds, trapped in the degraded surface layers, or diffusing under a concentration gradient from the interior of the films.

In all of the results, the distribution of the absorbers (Figures 4 - 28 and 4 - 29) was exponential as predicted from the results of Wilson (31). Therefore the three cases, inward diffusion of oxygen, outward diffusion of products, and surface removal of products, were applicable to the system.

TABLE 4 - 11

Absorber Concentration[*] Variation on Air and Vacuum Irradiation

Irradiation Time (minutes)	5.81 micron band				6.06 micron band			
	A1	A2	V1	V2	A1	A2	V1	V2
80	-	-	-	-	0.256	0.2	-	-
					0.238	0.2		
					0.190	0.13		
480	-	-	-	-	-	-	24	20
							-	20
							-	13
1,000	132	100	730	680	-	40	-	-
	140	100	-	700		31		
		100	-	500		20		
33,000	-	-	-	8000	-	-	-	-
				9000				
				4000				
50,000	53000	5000	-	-	-	60	-	-
	-	-				50		
	-	-				25		

[*] Values expressed as Molar quantities

A1 - estimated values from equation 10 for systems ('828'
('826'
('816'

A2 - extrapolated values for d_p = 500 microns for systems ('828'
('826'
('816'

V1 - estimated values from equation 10 for systems 828, 826, 816 on vacuum irradiation

V2 - extrapolated values for d_p = 500 microns for systems 828, 826 and 816 on vacuum irradiation

TABLE 4 - 12

Absorber Concentration* in Amine System (TETA/828)

6.06 micron band

Irradiation Time (minutes)	Cx	Cy	Cz
80	0.281	0.320	3.211
1000	40.300	41.000	47.000
30.000	69.200	69.500	70.322

* Values expressed in molar quantities

Cx - concentration in x direction

Cy - " " y " plane of film surface

Cz - " " z " perpendicular to film surface

The outward diffusion and surface removal of products would explain the results for the vacuum irradiated polymers. The inward diffusion of oxygen probably occurred during photo-oxidative degradation, since destruction of the surface non incident to the radiation was found to occur.

Outward diffusion of products and their surface removal probably occurred in a different manner in photo and photo-oxidised systems because of the different environments, matrix density and type of products formed.

4 - 9 Quantum Yields for the Degradation Process

The quantum yields determined by the graphical method of Carlsson (32) for the formation of new infrared bands is shown in Table (4 - 13). Polychromatic radiation was used in the quantum yield determinations and this introduced an error because of the wavelength effects in the degradation process.

The small quantum yields indicated that degradation was not propagated by chain reactions, but by random bond scission at the ether, isopropylidene and residual epoxide groups. The degradation may have been accompanied by deactivation processes (e.g. quenching). Also, since the yields were higher for vacuum than air irradiation, the rate of bond scission was greater in the former, and deeper colour formation resulted. A very small difference was found for the 6.06 micron ketone band and was attributed to the presence of oxygen in the system. As expected the quantum yields for product formation decreased with increase of purity of the monomer used.

Chemical analysis of the degraded HHPA cured polymers also showed small quantum yields (Table 4 - 14) indicating again that a random bond scission process occurred during the degradation process.

TABLE 4 - 13

Quantum Yield of Photo-and Photo-Oxidative Reactions

Polymer System	Irradiation Period (minutes)	Quantum Yield			
		5.81 micron		6.06 micron	
		Photo-Degradation	Photo-Oxidative Degradation	Photo-Degradation	Photo-Oxidative Degradation
‘828’/T	0-1000	0.034	0.00242	0.0026	0.00254
‘826’/T	0-1000	0.033	0.00234	0.00194	0.00159
‘816’/T	0-1000	0.010	0.00197	0.0014	0.00080

The quantum yields for product formation of the extracted material are shown (Tables 4 - 15 and 4 - 16). The aliphatic compounds had smaller values than the aromatic. This may have been the result of degradation of the former to produce further low molecular weight compounds which volatilised.

The values obtained were in all cases less than one, indicating a random bond scission degradation process. A considerable difference existed between the values obtained from quantification of the products and the infrared method of Carlsson and Wiles (32). This may have been due to the long irradiation periods used in the latter determination, further reaction of the degradation products may have changed the concentration of the species.

The primary process was the degradation of one monomer molecule into a number of fragments, some of which recombined giving the original molecule or new bonds by recombination with other species. With epoxide monomers scission at the ether bond was the primary process. Further reaction occurred in the bisphenol-A unit which gave rise to a number of aromatic compounds. Therefore, it was not possible to estimate primary quantum yields for the process. These quantum yields reported refer to the overall degradation reaction of primary and secondary reactions.

The low quantum yields for all products indicated that no chain reactions occurred during degradation, i.e. removal of the light source caused cessation of the degradation process. All of the decomposition products had undergone deactivation after light absorption, and in the case of the aromatic compounds only a small fraction of the molecules were further reacted. The aliphatic portion of the original molecule underwent reactions to form fragments in both oxidative and non-oxidative reactions, as indicated by the higher quantum yields. The non-oxidative process showed higher quantum yields over the oxidative process because a larger number of bonds were broken, or less deactivation occurred. The deactivation may have occurred by emission of fluorescent radiation, or by transfer of excess energy to a molecule of monomer or other accepter species. In the solid state the molecules were restricted in their movement, and collisions would occur in localised positions, until such a time as the molecules could diffuse out through the matrix. Therefore deactivation would be dependent on the rate of diffusion and would be extensive.

4 - 10 Colour Formation on Irradiation

It was not surprising that epoxide resins degrade on exposure to ultraviolet light, since both the monomer and cured polymer absorbed strongly up to 300 nm (Figure 4 - 30). As with other polymers (33) the degradation was associated with a decrease in the light transmission and with colour formation. The latter has been reported by a number of authors for epoxide resins cured with amines and acid anhydrides (24, 34).

Colour formation (yellowing) is essentially the difference between absorption at 400 and 700 nm wavelength. However, since the ultraviolet region is more sensitive to colour change than the visible, the 350 nm region was used as the index of change. The rate of colour formation as evidenced by the decrease in the transmission ultraviolet/ visible spectrum at this wavelength, as a function of the irradiation time, is shown (Figure 4 - 31 and 4 - 32) for the amine and anhydride cured materials respectively.

TABLE 4 - 14

Quantum Yields for Functional Group Changes in HHPA/'828' System

Functional Group	Quantum Yield
Epoxide	0.0004
Monoestor	0.006
Diester	0.0010

Quantum expressed for 500 minutes irradiation

TABLE 4 - 15

Product Quantum Yields, Amine System, Vacuum Irradiation

Compound	Quantum Yield
Acetaldehyde	0.072
Propyl Alcohol	0.0068
Phenol	0.0077
α - Methyl Styrene	0.0004

Irradiation Time 50,000 minutes

TABLE 4 - 16

Product Quantum Yields, Anhydride System

Compound	Quantum Yield
Acetaldehyde	0.0081
Propyl Alcohols	0.0066
Phenol	0.0081
α - Methyl Styrene	0.0001

Irradiation Time 50,000 minutes

The same general pattern was observed with all of the systems studied, a rapid decrease in transmission followed by a slight levelling off, which then decreased slowly to less than 10 % transmission in the amine systems. The initial colour change, from colourless to yellow for the amine, and from faint yellow to more definite yellow for the anhydride cured materials, was associated with the initial rapid decrease in transmission. In the amine cured materials the second slow stage was associated with a gradual 'browning' of the resins, at which time microcrack formation reached a maximum value. With the anhydride cured materials the browning was associated with the levelling off of the curve and gradual transmission decrease. The final colour observed was lighter with the anhydride cured resins, and at equivalent periods of irradiation these systems showed smaller changes in the transmission values than the amine films.

A resistance to colour formation was observed from the results with the '826' monomer materials which were ascribed to its increased purity over the commercial '828' material. The variation in the composition of the systems produced little effect on the rates of the colour formation. This was to be expected since the curing agents themselves absorbed in the short wavelength region.

Interpretation of the colour formation for the anhydride cured materials in terms of the structural changes, using ATR infrared spectroscopy, was not possible because of the small spectral changes observed. Also chemical analysis of these systems (35) showed no correlation with the colour formation. No correlation existed between the ESR data and colour formation in either type of polymer. This was probably due to the irradiation time necessary to build-up a detectable quantity of radicals.

A considerable difference in the rate of absorber development existed between the transmission ultraviolet/visible and ATR techniques. This was due to the intrinsic difference in the mode of operation of the techniques (transmission versus reflectance).

No relationship was found to exist between the 5.81 micron species and the rate of colour formation.

The changes in the ultraviolet transmission characteristics of all irradiated epoxide resins (24) followed the same general pattern, which again suggested that the common monomer unit was responsible for colour formation. The rate of colour formation was dependent on the type of curing agent used (24). Comparison with the results of Tahara (36) on the UV irradiation of polycarbonate, and of Kelleher (19) with similar polymers gave further evidence for colour formation by scission of the isopropylidene bonds.

Since the rate of transmission of light at 350 nm was faster for the pure 816 monomer than either the commercial monomer '828' or the purified '826' monomer, the initiation of the degradation reactions was not caused by impurities as found in similar studies on polyesters (37). The results obtained (Figure 4 - 31) indicated that the reactions leading to the change in light transmission characteristics were inhibited by the impurities, or by reactions influenced by them. The diference in the behavior of the '828' and '826' systems, both of which contained impurities, can be ascribed to the distribution and accessibility of the impurities to reactive sites in the systems.

Consideration of the monomer section of the polymer showed a number of possible initiation centres e.g. $\pi \longrightarrow \pi^*$ forbidden transition of the benzene nucleus at 258 - 273 nm or $n \longrightarrow \sigma^*$ transition involving promotion of a non bonding electron of the oxygen to an anti-bonding σ^* orbital in alcohols and ethers. Since the light source emitted radiation at wavelengths longer than that required for the above processes other factors must have been involved e.g. physical interactions between atoms. The most likely was hydrogen bonding between the hydroxyl group and the curing agent. This could have caused scission of the three bonds above with the resultant degradation of the resins (No experimental evidence has been presented for such interactions in other polymers). The curing agents themselves have been completely ignored as initiation centres because of their light absorption characteristics.

4 - 11 Soxhlet Extraction of Degraded Surfaces

The results of six day soxhlet extraction of the irradiated amine and anhydride cured polymers is shown (Table 4 - 17). The values quoted are relative to those from non-irradiated samples of the polymers.

The expected result of an increased yield of extractable material with increased time of irradiation was obtained. Also the yields from vacuum irradiated polymers were greater than those from air irradiation, which agreed with the ATR results of a predominance of crosslinking reactions on photo-oxidative degradation, and of chain scission on photo-degradation.

No overall difference was observed with the yields from '828' and '826' systems, which indicated that the overall rate of product formation was the same, or more likely that the surface density of the surfaces was the same order of magnitude for both monomers. The small difference observed for the film side, incident to the radiation, may have been caused by a decrease in the total light transmission through the film, since a 'black body' absorber was always used in conjunction with these samples.

It was interesting to note that a difference in product yields was obtained from irradiation of films on reflecting and non reflecting surfaces, which further substantiated the ATR results on the amine systems. As expected, the difference decreased with increasing degree of irradiation, because, as the degraded layer built-up on the front surface of the film, the light intensity decreased at the film side exposed to reflected light because of light absorption by the coloured film.

Variation in sample thickness showed an increase in the yield of extractables in the range from 20 to 100 microns with the amine cured films, for irradiation periods up to 36,000 minutes. This can probably be ascribed to an increase in the depth of penetration of the ultraviolet light because of degradation of the oxidised surface due to diffusion and volatilisation. The effect was not as apparent with vacuum irradiated films because of the less dense surface formed on degradation, little crosslinking would be expected under the vacuum conditions.

With the anhydride cured polymers little difference in yields occurred with films greater than 60 microns in thickness. As seen in table 4 - 17 a decrease in the yields occurred with the 100 µ thick films at 24,000 to 54,000 minutes exposure in air or vacuum. This again may have been due to volatilisation of degraded products as low molecular weight compounds. Alternatively, the difference in behaviour between the two types of curing agents might be ascribed to greater degradation of the HHPA curing agent and to greater surface density changes.

Extraction of irradiated polymers after periods of dark storage showed no difference in the final product yields, which indicated that the dark reactions, if present, were of physical rather than a chemical nature. Some difference should have been observed in the case of the amine cured films since diffusion and volatilisation were found by the ATR technique. However, the extraction procedure may have been too severe on the surfaces, and the volatiles themselves may have been passed into the atmosphere during the experiments.

The extracted material in all systems was light brown in colour. The colour was initially thought to be due to degradation of the new surface layer because of the thermal treatment during extraction. However, no variation in colour was observed for different extraction temperatures or different degrees of extraction. Product separation of the material was performed by TLC (Silica Gel, n - hexane/IPA solvent mixture 2:1) using GLC, (Porapak, Silicone, fluorinated Silicone columns) transmission infrared spectroscopy and mass spectrometry as the principal identification methods for the products separated. Product identification was aided by functional group tests for such materials as aromatics, acids and adehydes. The products identified are shown in Tables 4 - 18 and 4 - 19 for the air and vacuum irradiated '828' polymers respectively. Similar product distributions were obtained with the '826' materials.

The products identified confirmed the degradation scheme proposed earlier for the monomer units. Liebig and Laissaigne tests showed the presence of low molecular weight nitrogen containing products in the materials extracted from the irradiated TETA systems. This indicated that degradation occurred at the cure link or within the curing agent itself. Only one compound, diethylamine, was positively identified as a photodegradation product.

TABLE 4 - 17

Percentage Yield of Ultraviolet Degraded Material after 6 Days Soxhlet Extraction

Polymer System	Time of Irradiation (minutes)	Yield % (by weight)	
		Photo-Oxidation	Photo Degradation
TETA/'828'	80 (reflecting)	0.18	0.24
	(non reflecting)	0.15	0.23
TETA/'826'	80 (reflecting)	0.18	0.24
	(non reflecting)	0.16	0.23
TETA/'826'	1000 (reflecting)	0.79	0.92
	6000	1.21	1.53
	10,000	1.20	1.71
	36,000	2.43	2.98
	54,000	2.50	3.14
HHPA/'828'	500	0.12	0.22
HHPA/'826'	6000	0.46	0.52
	10,000	1.22	1.78
	24,000	1.20	1.80
	50,000	2.96	3.09
	54,000	3.00	3.91
TETA/'826'	80	0.18	0.24
	(Dark storage 14 days)		
	6000	1.22	1.53
	(Dark storage 30 days)		
	(Dark storage 50 days)		
	36,000	2.42	2.98
	(Dark storage 60 days)		

TABLE 4 - 17 (Continued)

Polymer System		Time of Irradiation	Yield % (by weight)	
			Photo-Oxidation	Photo Degradation
HHPA/'826'		10,000	1.22	1.78
		(Dark storage 10 days)		
		24,000	1.20	1.80
		(Dark storage 50 days)		
		50,000	2,98	3,10
		(Dark storage 50 days)		
TETA/'826'	20	80 (reflecting)	0.18	0.24
		80 (non reflecting)	0.15	0.23
	50	80 (reflecting)	0.20	0.24
		80 (non reflecting)	0.15	0.24
	100	80 (reflecting)	0.20	0.24
		80 (non reflecting)	0.16	0.24
TETA/'826'	20	1,000 (reflecting)	0.79	0.92
	50	1,000 (reflecting)	0.86	0.99
	100	1,000 (reflecting)	0.86	0.99
TETA/'826'	20	36,000 (reflecting)	2.42	2.98
	50	36,000 (reflecting)	2.42	2.98
	100	36,000 (reflecting)	2.43	2.99
HHPA/'826'	20	500	0.12	0.22
	60	500	0.14	0.26
	100	500	0.14	0.26
HHPA/'826'	20	24,000	1.20	1.80
	60	24,000	1.73	1.91
	100	24,000	1.71	1.90
HHPA/'826'	20	54,000	3.0	3.91
	60	54,000	3.0	3.90
	100	54,000	3.0	3.90

TABLE 4 - 18

Product Identification of Extracted Materials - Air Irradiation

Product	Polymer System					
	TETA/828			HHPA/828		
	% by volume of Total Yield					
	Irradiation Time (minutes)			Irradiation Time (minutes)		
	80	6,000	10,000	500	6,000	24,000
Acetaldehyde	1.7	1.2		0.6	2.1	-
Acetic Acid	5.2	3.7	1.9	1.2	1.1	1.4
Bisphenol-A	4.4	3.1	2.4	5.1	4.9	3.7
Formaldehyde	1.5	1.2	2.1	0.9	2.0	1.1
Formic Acid	3.2	2.8	-	2.7	1.7	1.1
Hydrochloric Acid	trace	-	-	trace	-	-
Propionaldehyde	0.6	1.2	1.1	0.3	1.4	1.7
Quinone	17.2	8.1	12.7	10.1	10.0	11.1
Propyl Alcohol	18.0	8.2	9.4	16.4	9.8	9.9
Diacid of HHPA	-	-	-	1.2	1.2	1.3
Diethyamine	0.8	0.3	0.4	-	-	-
∝ -methyl styrene	0.2	-	-	0.2	-	-
p-isopropyl phenol	4.4	2.4	2.0	11.2	0.9	trace
p-isopropenyl phenol	0.3	6.6	5.7	6.1	1.2	0.6
Water	trace	trace	-	1.0	1.0	0.7
Molecular Weight 440	20.0	30.0	-	-	-	-
" " 460	-	-	-	12.0	26.0	-
" " 470	-	-	40.0	-	-	-
" " 510	-	-	-	-	-	34.0
Unidentified	14.9	19.1	24.4	27.6	37.5	34.1

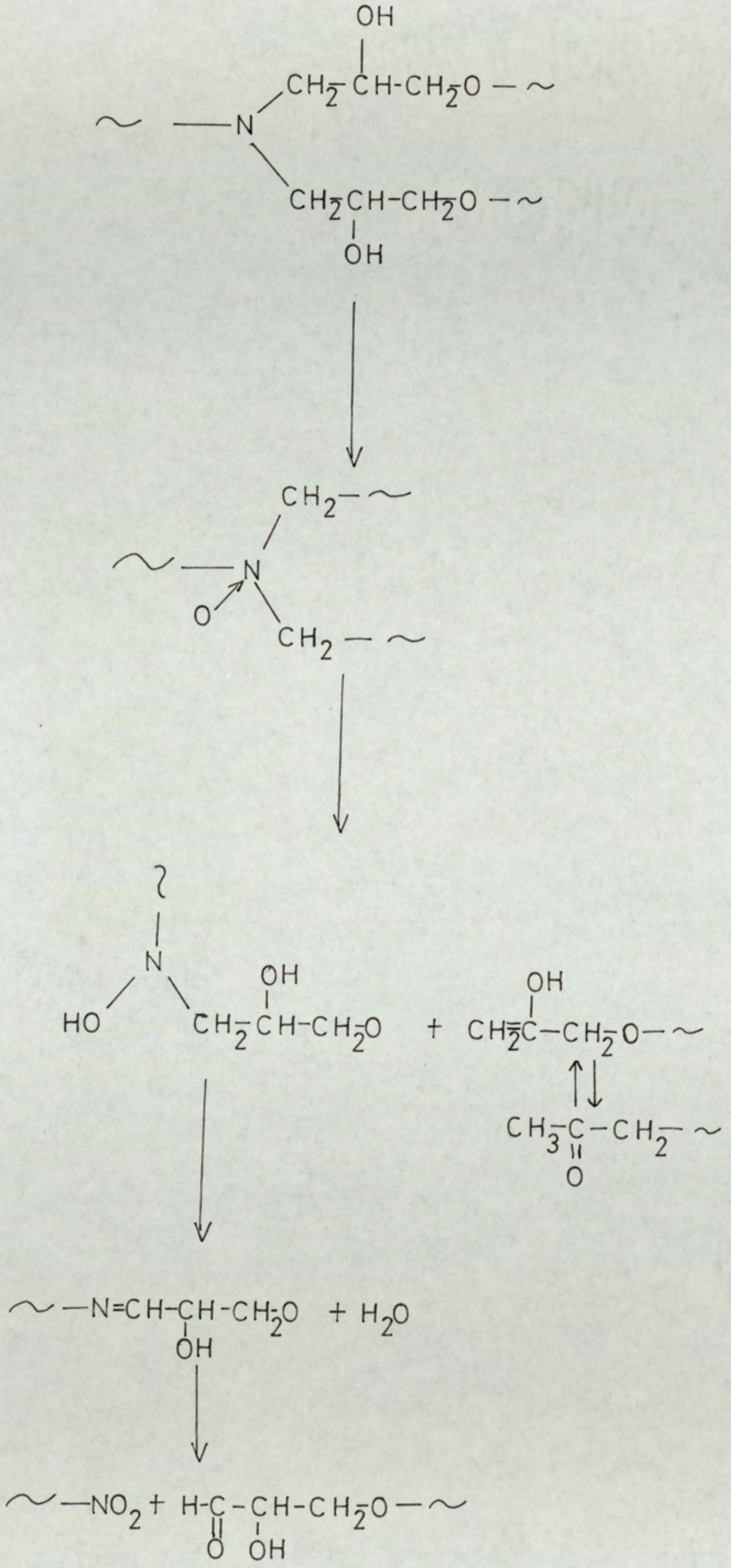
TABLE 4 - 19

Product Identification of Extracted Material - Vacuum Irradiation

Product	Polymer System					
	% by volume of total yield of extracted materials					
	TETA/828			HHPA/828		
	Irradiation Time (mins)			Irradiation Time (mins)		
	80	6.000	10.000	500	6.000	24.000
Acetalhehyde	0.7	2.0	0.4	-	1.9	2.0
Acetic Acid	1.2	-	-	-	0.7	-
Formaldehyde	0.2	-	-	0.8	-	-
Formic Acid	0.9	1.0	-	-	1.7	0.6
Hydrochloric Acid	Trace	Trace	-	Trace	-	-
Quinone	4.6	2.1	-	1.4	2.9	1.3
Propyl Alcohol	2.1	3.6	1.4	0.6	1.9	2.7
Phenol	66.9	60.9	53.0	75.9	64.4	57.7
Diacid of HHPA	-	-	-	3.7	1.4	0.2
Diethylamine	1.8	0.7	-	-	-	-
α -Methyl Styrene	-	10.4	16.8	0.6	1.7	6.2
α -Methyl Styrene dimer	-	0.1	-	0.1	0.3	-
Water	-	-	-	0.6	-	-
Propionaldehyde	-	0.7	-	-	-	-
p-isopropyl phenol	0.4	0.4	0.4	1.4	1.5	1.0
p-isopropenyl phenol	0.6	0.8	0.7	0.3	0.8	0.7
Molecular Weight 440	3.7	-	-	-	-	-
Molecular Weight 460	-	3.8	-	-	10.7	-
Molecular Weight 505	-	-	-	-	-	11.9
Unidentified	17.9	14.2	27.2	14.6	10.1	21.7

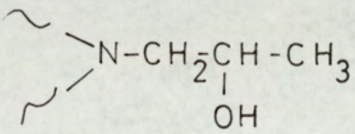
The degradation scheme for the amine cured system, based on the infrared data and the volatile degradation products, did not take into account the effect of the curing agent. The curing agent, TETA, contained primary and secondary amine groups which reacted with the epoxide groups during the curing process. The relative reactivity of the amine groups was determined by their accessibility to the reactive epoxide end groups. Prior to gelation the mobility of the reactive centres also determined the degree of cure. After gelation a number of amine groups remained unreacted. The terminal primary amine group was most likely to form secondary and tertiary amines. The reactivity of the secondary amine group in the original TETA molecule would be determined by the degree of reactivity of the terminal amine group because of steric conditions. A number of the centrally located secondary amine groups would remain unreacted in the cured polymer.

Little work has been presented in the literature on photo-and photo-oxidative degradation of amines (20) and only short wavelength radiation studies have been reported. The energetic short wavelength radiation caused scission of the carbon to nitrogen bond. It is possible that the photochemical and thermal degradation reactions may proceed through similar pathways. However, there is no experimental evidence to date to support this assumption. Activation of the amine group may have occurred similar to that suggested for the HHPA cured resins i.e. by hydrogen bonding between the nitrogen atoms and the hydroxyl groups. The initial degradation of the cured polymer was assumed to have occurred at the ether bond, with subsequent carbonyl formation (5.8 micron band), and further hydrogen bonding between the carbonyl and the amine groups would have occurred, resulting in destabilisation of the C - N bond. Degradation of this bond in the presence of air could have proceeded by reactions similar to the "Cope Degradation" as postulated by Conley (1) for the thermal degradation of an amine cured epoxide resin.

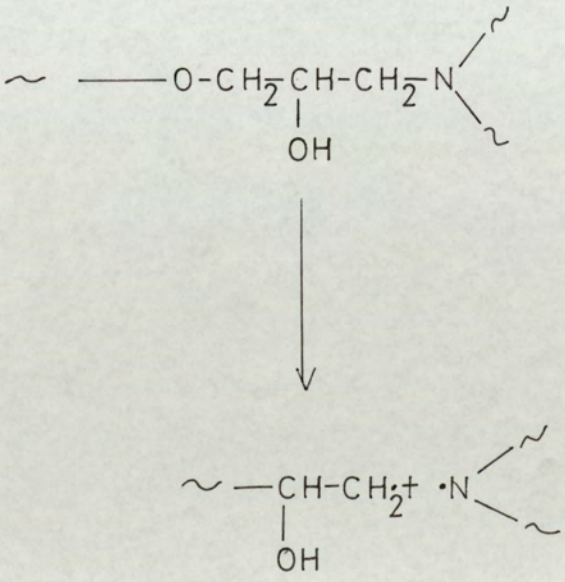

OH
CH2-CH-CH2O — ~
~ — N
CH2-CH-CH2O — ~
OH
CH2 — ~
~ — N
O
CH2 — ~
N
HO
OH
CH2-CH-CH2O
+
OH
CH2=C—CH2O— ~
CH3-C-CH2— ~
O
~ —N=CH-CH-CH2O + H2O
OH
~ —NO2 + H-C-CH-CH2O— ~
O OH

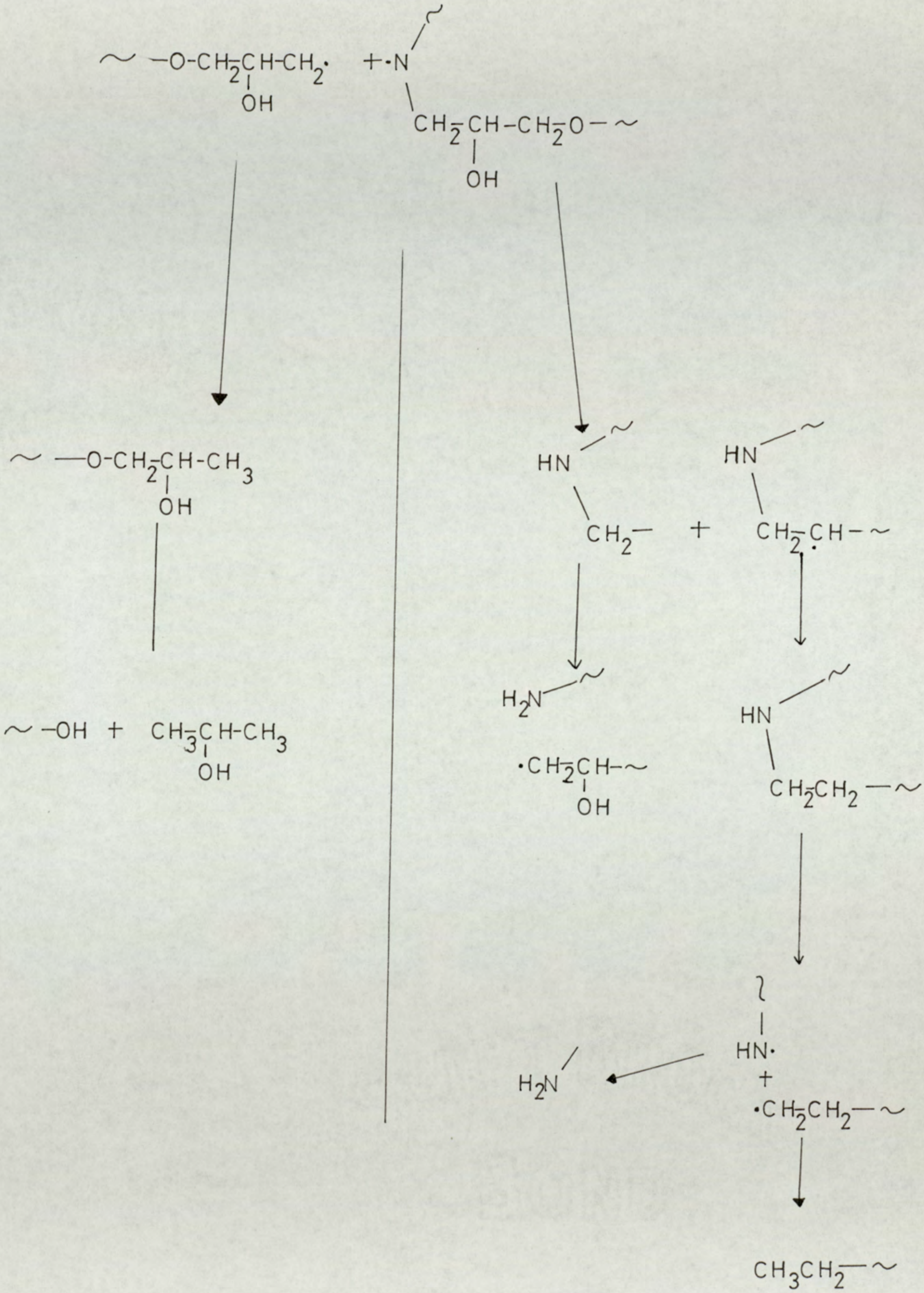
The glyoxal could undergo quinone formation (30). Since the 6.0 micron quinone band was detected at earlier irradiation times than the 5.8 micron aliphatic band, it is unlikely that such a degradation process occurred before the ether and isopropylidene bond scission.

In the photodegradation of the TETA cured resins the initial C - N bond activation would be different from that of the photo-oxidative degradation. Direct homolysis of the ether and isopropylidene bonds leads to the formation of the species.

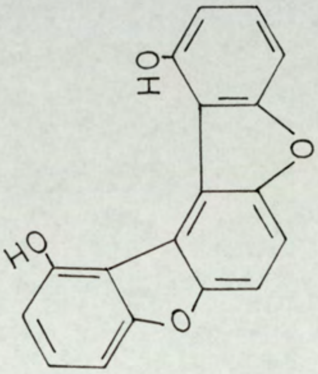


The size of the aliphatic chain containing the hydroxyl group is small and unrestrained and would contribute to the hydrogen bonding already present. Hydrogen bonding would also exist between carbonyl containing degradation products and hydroxyl groups in the resin structure. The outward movements of low molecular weight degradation products were restricted by the polymer matrix. Therefore activation of the tertiary amine could have occurred by hydrogen bonding with resultant homolysis of the C - N bond

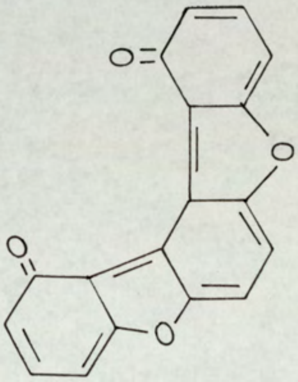



~ —O-CH₂-CH-CH₂·
OH
+ ·N
~
CH₂-CH-CH₂-O— ~
OH
~ —O-CH₂-CH-CH₃
OH
~ —OH + CH₃-CH-CH₃
OH
HN
~
CH₂—
+
HN
~
CH₂-CH- ~
H₂N
~
·CH₂-CH- ~
OH
HN
~
CH₂-CH₂ — ~
~
HN·
+
·CH₂CH₂— ~
H₂N
CH₃CH₂— ~

The high molecular weight materials were examined for functional group content by chemical analysis and by infrared spectroscopy. In all cases carbonyl containing compounds were found, which were highly aromatic and contained hydroxyl groups. The work of Erdtman (30) showed that quinones were polymerisable in the presence of acids, and the one compound identified had a structure as



molecular wt.~300



quinone form

Such compounds or similar ones may have been present in the degraded mixtures. In such compounds the resonance paths for colour formation to quinone structure are not destroyed. The extent of their formation may not be great. The structure did account for the strong ether band in the infrared spectra of the high molecular weight materials, which were the same regardless of the starting polymer.

The yellow colour formation in both the TETA and the HHPA polymers air irradiated was attributed to the presence of quinone (30) and the final colour to the complex of quinone/hydroquinone. In vacuum irradiated systems some quinone was formed from impurities (i.e. air) in the starting systems. However, the extent of formation of the 6.06 micron band was not related to the amount of quinone formed. The other assignment of this band (vinyl) can be attributed to α-methyl styrene and similar compounds. α - Methyl styrene is known to be photochemically reactive (33), and the final colour can possibly be attributed to it.

4 - 12 Diffusion Effects on Irradiation

The existence of various controlled photo-degradation reactions, dependent on the rate of diffusion of oxygen into the polymer due to depletion of the oxygen supply in the films, was investigated by irradiation of layers of polymer film (Table 4 - 20). This method was used initially by Carlsson and Wiles (38) in their photo-degradation studies on polypropylene. Evidence of diffusion of degradation products from the bulk of the polymer, under a pressure gradient, was shown by the existence of 'dark' reactions.

The variation in the normalised optical density values with dp for the ingrowth of the 5.81 and 6.01 micron bands, for up to 1,000 minutes irradiation in air of the 828 polymer system for each surface of all films (Table 4 - 20), are shown (Figures 4 - 33 to 4 - 42). The curves (1, 2 and 3) in each figure refer to the 5.81 micron (Figures 4 - 33 to 4 - 42) and 6.06 micron (Figures 4 - 43 to 4 - 52) band intensity variation with depth of penetration of the light into the sample surface of films referred to in Table 4 - 20 at three irradiation periods viz 80 minutes (Curve 1), 400 minutes (Curve 2) and 1000 minutes (Curve 3) air irradiation and 100 minutes (Curve 1), 300 minutes (Curve 2) and 1000 minutes (Curve 3) vacuum irradiation.

Figures	Curve	Sample
33 and 38	1	Front of film 1 (10 microns, Sample 1 Table 4 - 20)
34 and 39	1	" " " 2 (20 " " ")
35 and 40	1	" " " 3 (20 " " ")
36 and 41	1	" " " 4 (20 " " ")
37 and 42	1	" " " 5 (50 " " ")

During the first irradiation period (0 - 80 minutes) the rate of oxidation of each surface was constant for samples 1, 2 and 3, except for the vacuum closure surface of each film, which implied that there was sufficient supply of oxygen necessary for the oxidation reactions to proceed, even though the oxygen concentration at the film surfaces decreased progressively across the layers of film away from the light source.

This latter assumption was valid if the vacuum evacuation affected all of the films (dependent on the permeability of the polymer film).

TABLE 4 - 20

Amine Cured Film Sandwich Construction

Sample	Film Thickness (microns)	Total Number of films
1	10 20 20 20 50	5
2	10 20 20 20	4
3	10 20 20	3
4	50 50	2

The dissolved oxygen would be depleted rapidly during oxidative degradation and the replenishment of further oxygen would be slow, since the reported oxygen permeability of epoxide films was small (0.0049 - $0.16X^{-11}$ c.c. $cm/cm^2/torr$) (2). Due to this small value for oxygen permeability, the oxygen content between pairs of film may have been the same, accounting for the constant rate of degradation of the surfaces of the polymers. Further irradiation caused a decrease in degradation at the surfaces incident to the ultraviolet radiation. As a result of this and the low permeability of the films the preferential surface photo-oxidation was thought to be due to the depletion of the oxygen supply available to each film surface. From the work of Krapivin (39), on pulsed laser degradation of epoxide films, morphological changes and associated crack formation occurred, which resulted in a density increase at the polymer surface. The permeability of the materials therefore was expected to have decreased further on irradiation and in this way degradation products would be encapsulated in the material. Presumably a pressure gradient existed between the inside and outside of the films which eventually resulted in the diffusion of degradation products. The results from sample 4, the two 50 micron films, showed no comparison with the other films. This was attributed to the availability of oxygen within the film (which is less than in a composite of 10 + 20 + 20 micron films) and the decreased light transmission by the thicker film.

The initiation of photo-oxidation of many polymers has been attributed to the presence of impurities from the preparation or conversion operations, which introduced chromophores (38). The decrease in the rate of colour formation on ultraviolet irradiation of samples of increased purity with epoxide resins indicated that these polymers were affected in a similar manner. However, if this were so, the initial distribution of degradation products should have been concentrated in particular areas or showed unequal distribution over a particular surface. All of the samples examined by the ATR technique showed uniform distribution of the ultraviolet absorbing species. Also, the distribution throughout the oxidised layer has been found to be the same within the limits of experimental accuracy. Since the content of all impurities in the monomer '828' amounted to 2 - 3% (3), the effect of concentration gradient should have been seen (35). A uniform distribution of ultraviolet absorbing species in the cured polymer suggested that some group in the monomer or curing agent molecule was responsible for the uniform degradation pattern. Attempts were made to cause surface skin effects, by the quenching of heated polymer melts after gelation to magnify any impurity effects. However, due to the irregular surface patterns obtained, the technique was discontinued. Similar studies on polypropylene (40) showed that normal quenching procedures caused no enhancement of the photo-oxidation process. Conley's work (1) on the thermal degradation (30 minutes at 270 ^{o}C) was known to produce carbonyl and other bands in the 5.81 and 6.06 micron regions. This thermal treatment was attempted in order to magnify the concentration of chromophoric groups. However, the thermal degradation in all cases resulted in a fairly even distribution of oxidised species.

The ATR examination of similar film layers during irradiation in vacuum demonstrated the filtering effect of top layers during the degradation process (Figures 4 - 43 to 4 - 54). Since oxygen solubility was expected to be high in these materials, dissolved oxygen may have been responsible for the conjugated carbonyl band at 6.06. This band eventually decreased in intensity after long irradiation periods by reaction of the ketone or by diffusion. Also, further irradiation of the films caused a diminishing of colour formation , which decreased with distance from the source.

The decrease in intensity of the 6.06 micron band could account for the deeper colour in vacuum irradiated samples.

Examination of the dp curves for sets of films, comprising of a total thickness of 50 microns (Figure 4 - 53 and 4 - 54), showed that the extent of oxidative degradation at the inner surface of the third film in sample 1 (Figure 4 - 45) was less than at the corresponding surface of the first film in sample 4 (Figure 4 - 46). This was due to the efficiency of the oxygen removal by the vacuum system, which was greater for the 50 micron than 50 + 20 micron composite films. The possibility of the oxygen content at the film interface as a cause was eliminated, by the extent of degradation at the front surfaces of the vacuum film seals in sample 2 and 3 being almost the same. The protective effect of a 20 micron thick polymer film was seen from the results of the photo-oxidative degradation in the second and third films of samples 2 and 3, the degradation being greater in the latter system, as was expected.

The results of the vacuum irradiation of a 50 micron film and a composite of three films (10 + 20 + 20 micron), which was degassed for one week prior to irradiation, are shown in terms of dp curves (Figure 4 - 53 and 4 - 54) for the ingrowth of the 5.81 micron band. The extensive degassing did not remove all of the oxygen and low molecular weight fragments from the materials, as ingrowth of the 6.06 micron band was still observed on irradiation. However, the stability of the pressure head, (10^{-6} torr) in the vacuum apparatus, was fairly constant after this evacuation time. Greater degradation occurred in the composite of three films than in the single 50 micron film. The degassing process removed much of the oxygen from the surface layers of the films, and the degradation would have proceeded with equal speed in both the composite and the single thick film. This discrepancy was attributed to the rate of movement of degradation products through the materials. This was evidenced by an increased rate of volatilisation from the composite film.

Comparison of the evacuated side of the film surface showed that, in sample 2 and 3, more extensive photo-oxidation (6.06 micron band) had occurred in sample 3, because of the reduced thickness and greater oxygen permeability of the latter's composite structure. However, this was not the case for the inner film surface of the 10 micron thick films in samples 1, 2 and 3.

The rate of photo-oxidative degradation was in the order $3 \sim 2 > 1$. The explanation must lie in the rate of ultraviolet light absorption, the oxygen permeability of the extra 20 micron film or the thickness of the film exposed to the incident light.

The results of the vacuum irradiation of degassed films showed that ingrowth of the 6.06 micron band always occurred to some extent. This has been attributed to dissolved oxygen in the polymer matrix. Investigation of the extent of ingrowth of this band during 'dark' periods showed (Figure 4 - 55) that almost all of the ingrowth occurred during the first 100 minutes irradiation, and the subsequent ingrowth was caused by diffusion of the oxidised species to the upper surface layers of the films. The observed decrease in the intensity of the band after long irradiation periods was due to reaction or volatilisation of the species.

4 - 13 Dark Reactions

The initial evidence for the presence of 'dark' reactions in the amine cured materials was found by ATR examination of irradiated samples stored for long periods (up to 3 months). It was assumed that these reactions occurred as a result of the presence of long lived free radicals trapped in the polymer matrix or from the diffusion of degradation products under a pressure gradient which may have been accompanied by inward diffusion of oxygen.

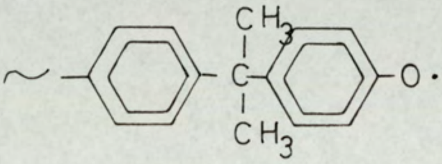
A series of films (25 micron thick) were irradiated in air and in vacuum with long wavelength light, then stored in air and in vacuum for up to 3 months, during which time the films were subjected to ATR examination for changes in the 5.81 and 6.06 micron bands. Ultraviolet/visible spectroscopy was also carried out to determine the extent of colour formation by analogy to that shown by ultraviolet irradiated polyesters which obey the Hunter - Driffield law of photographic materials (41). The results in the form of normalised optical density curves for the 5.81 and 6.06 micron bands respectively are shown (Figure 4 - 55 and 4 - 56 respectively).

Long lived free radicals in air irradiated samples were ruled out from the ESR results. The presence of 'dark' reactions was due to the competitive effects of outward diffusion of degradation products which from the results of air irradiated samples was due to a pressure gradient inside the film surface. The rate of diffusion was dependent on the degree of irradiation of the sample and can be interpreted in terms of the morphological changes at the sample surface. No change in colour, as evidenced by ultraviolet/visible spectroscopy, of the air irradiated samples occurred even after three months 'dark' storage. Greater changes occurred in the observed 'dark' reactions for the 5.81 micron band. This may have been due to the size of the compound responsible for this absorption which was smaller than the aromatic ketone (6.06 micron band). Alternatively preferential chemical reactions of the latter to form a highly crosslinked surface could have explained the results. Photo and photo-oxidative reactions were likely since some of the material would have been trapped in the three-dimensional structure.

The results confirmed the earlier findings concerning the accuracy of the reflectance technique over the normal transmission method. The initial degradation was uniform thoughout the sample and in the case of oxidative degradation it was dependent on the rate of diffusion of oxygen into the polymer from both the surfaces incident and non incident to the radiation. A gradual build-up of degradation products throughout the sample occurred. The light transmission of the sample decreased with irradiation time and a protective surface layer of degraded polymer was formed. The extent of the surface layer varied with the irradiation atmosphere used.

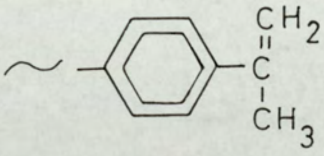
Subsequent 'dark' storage, in air or vacuum, of photo and photo-oxidatively degraded samples influenced the rate of band ingrowth (Figure 4 - 55 and 4 - 56). The results were interpreted in terms of the competitive nature of crosslinking and chain scission reactions. Constant evacuation of air irradiated samples caused an acceleration of the normal diffusion controlled process as seen in the results for 5.81 and 6.06 micron band ingrowth. Due to the crosslinking and volatilisation processes at the surface, the final value of the 5.81 micron band intensity was less than that observed in the normal diffusion process (air storage of air irradiated materials). Vacuum storage of vacuum irradiated polymers also showed different morphological changes at different irradiation periods.

In this case chain scission reactions are expected to predominate, although crosslinking reactions cannot be ruled out since the cured resins contain hydroxyl groups. Air storage of vacuum irradiated polymers showed greater morphological changes than vacuum storage of similar materials. This can be interpreted as chemical reactions of degradation products with each other or with oxygen. Alternatively it may have been due to the presence of long lived free radicals (not confirmed by ESR work) of the type



which reacted further by scission of the isopropylidene bond to produce the quinone species.

Some evidence of this phenomenon was seen in the ingrowth of the 6.06 micron species though the evidence was not conclusive. The 5.81 micron band in photo-degradation reactions may have been due to unsaturation of the type



and would be expected to remain constant in both air and vacuum storage. The small difference observed may have been due to other types of unsaturation which reacted with oxygen.

No 'dark' reactions, as exemplified by the ATR technique, were found for the anhydride cured materials. On removal of the light source the functional group content of the material was found to remain constant even on storage in diffuse sunlight. However, this does not mean that physical changes such as diffusion did not occur. The colour lightening effect observed with vacuum irradiated amine films was also observed with the anhydride cured polymer, and due to this fact and the similarities in evolution of volatiles for all systems it is assumed that diffusion of degradation products did occur during and after irradiation.

Also, since similarities were observed between thermal degradation studies on amine and anhydride cured epoxide resins, it was thought that the photo-and photo-oxidative degradations were accompanied by crosslinking and chain scission reactions in both materials. Chemical analysis of the anhydride cured films during air and vacuum irradiation showed on 'dark' storage slight variation in the ester content.

REFERENCES

1. Conley, R.T., RETEC, SPE 10, 118, 1964
2. "Epoxy Resins" by Lee, H., Nevill, K., Chapter 4
   McGraw Hill Ltd., New York, 1967
3. Patterson-Jones, C., et al, Report CoA Note Mat. No. 10
   The College of Aeronautics, Cranfield 1967
4. Serboli, G., Kunststoffe Plastics 3, 106, 1966
5. Keenan, M.A., Smith, D.A., J. Appl. Polym. Sci. 11, 1009, 1967
6. Dannenberg, H., SPE Trans. Jan. 78, 1963
7. "Infrared Analysis of Polymers" by Hummel, D.O., 1, part 2
   John Wiley and Sons, Inc. New York 1969
8. "Infrared Absorption Spectroscopy" by Nakanishi, K.,
   Holden-Day, Inc. San Francisco 1964
9. Sugita, T., J. Polym. Sci. Part C No. 23, 765, 1968
10. Dannenberg, H., Harp, W., Anal. Chem. 28, 86, 1956
11. Lee, S. M., et al Modern Plastics, 41, 150, 1963
12. Cetanoic, R.J., Doyle, L.C., Can. J. Chem. 35, 605, 1957
13. Gomer, R., Noyes, W.A., J.A.C.S. 72, 101, 1950
14. Gritter, R.J., et al J. Org. Chem. 29, 1965, 1964
15. Hearst, P.J., U.S. NCEL Tech. Note N- 685
16. Oster, G., Yang, N.L., Chem. Rev. 68 (2), 125, 1958
17 "Infrared Spectra of Complex Molecules" by Bellamy, L.J.,
   Methuen Limited, London, 1964
18. Smith, D.G., Private Communication, 1968
19. Kelleher, P.J., et al J. Appl. Polym. Sci. 13, 9, 1969
20. "Photochemistry" by Clavert, J., Pitts, J., p428
   J. Wiley & Sons, New York 1967
21. Dante, M.F., Conley, R.T., A.C.S. Symposium, 135, Sept. 1964
22. "Photoluminescence of Solutions" by Parker, C.A., p373
   Elsevier, Amsterdam 1968
23. Hirt, R.C., et al ACS Symposium, 314, 1961
24. Lee, H., Watson, R.T., 20th ANTEC of SPE 21 (1) 1964
25. "Treatise on Coatings" 2nd ed., Meyers, R. R., p484
   Marcel Dekker, New York, 1964
26. "Internal Reflectance Spectroscopy" by Harrick, N.J., p67
   Interscience, N.Y., 1967
27. Fahrenfort, J., Spec Acta, 18, 1103, 1962
28. Fluornoy, P.A., et al Spec. Acta, 22, 5, 1966

29. Carlsson, D.J., Wiles, D.M., Can. J. Chem. 48, 2397, 1970

30. "Advanced Organic Chemistry" by Fieser, L.F., Fieser, M., p846
Reinhold, New York, 1961

31, Wilson, I.E., J. Chem. Phys. 22, (2), 334, 1954

32. Carlsson, D.J., Wiles, D.M., Polymer Letters 8, 419, 1970

33. Fox, R.B., et al U.S. N R L Rept., 6284, 1965

34. Nelson, I., U.S. Army Prosthetics R.L., Rept. 5814, 1958

35. Fisch, W., Hofmann, W., Plast. Technol 28, Aug., 1961

36. Tahara, S., Chem. High Polymers (Japan) 25, (253) 303, 1966

37. Hirt, R.C., et al 15th Ann. Tech. Mang. Conf. SPI Feb., 1960

38. Carlsson, D.J., Wiles, D.M., Macromolecules 2 No. 6, 587, 1969

39. Krapivin, L.L., et al Med. Pom. No. 3, 460, 1969

40. Carlsson, D.J., Wiles, D.M., to be published 1971

41. Hirt, R.C., Schmitt, R.E., 14th Ann. Meeting Reinforced Plast.
Div of SPI, 12A

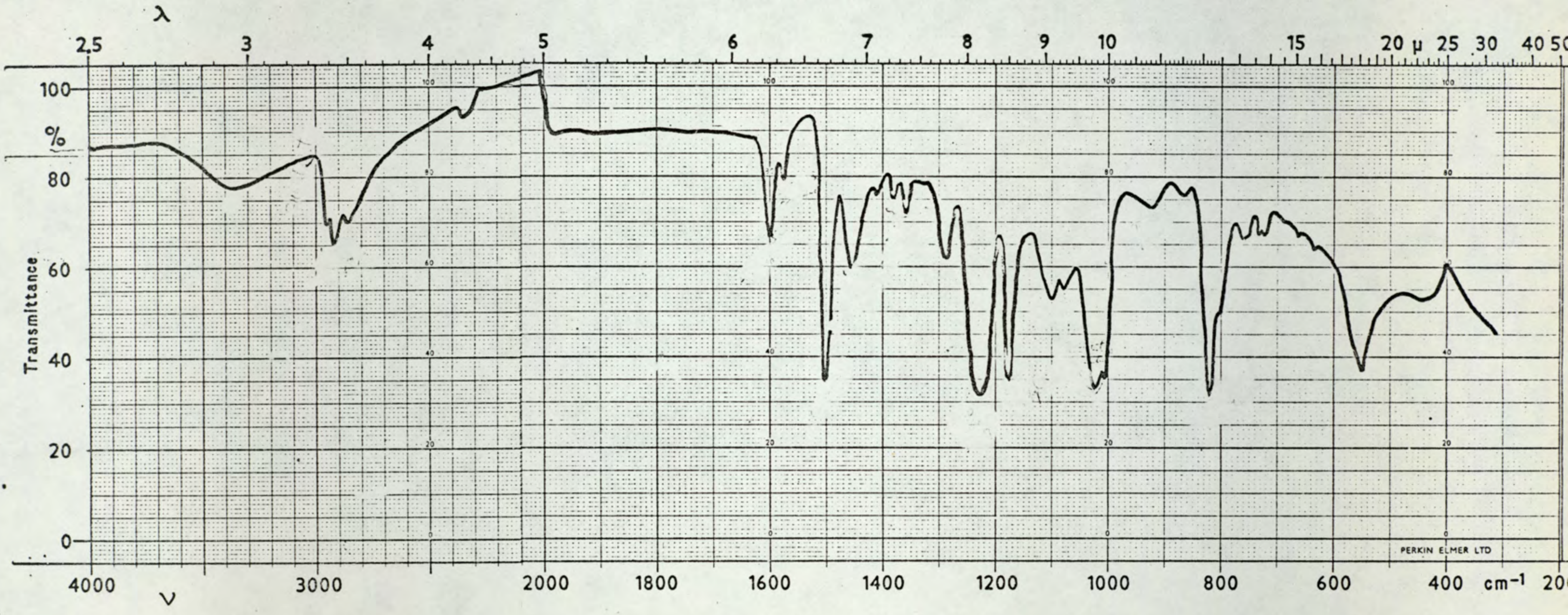


FIGURE 4-1 , ATR SPECTRUM of TETA/828, 0 005mm., $\alpha=39°$.

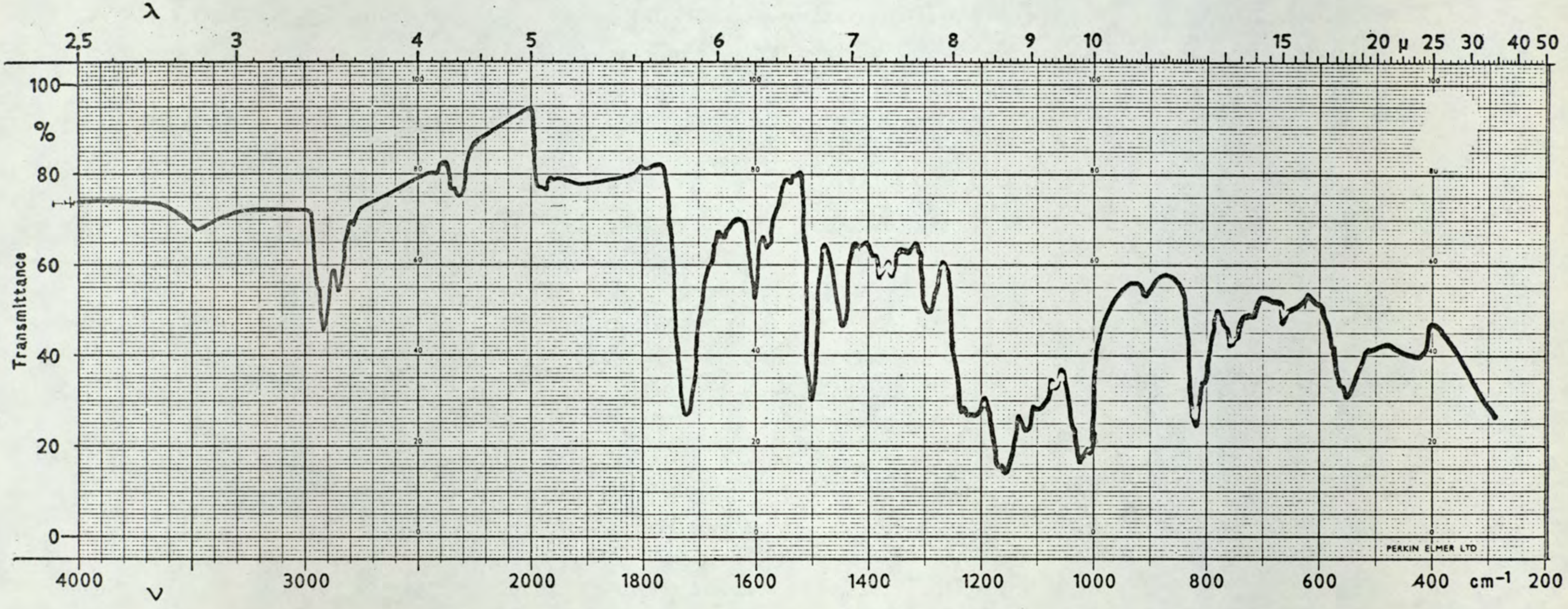


FIGURE 4-2. ATR SPECTRUM of HHPA/828, $\alpha = 39°$.

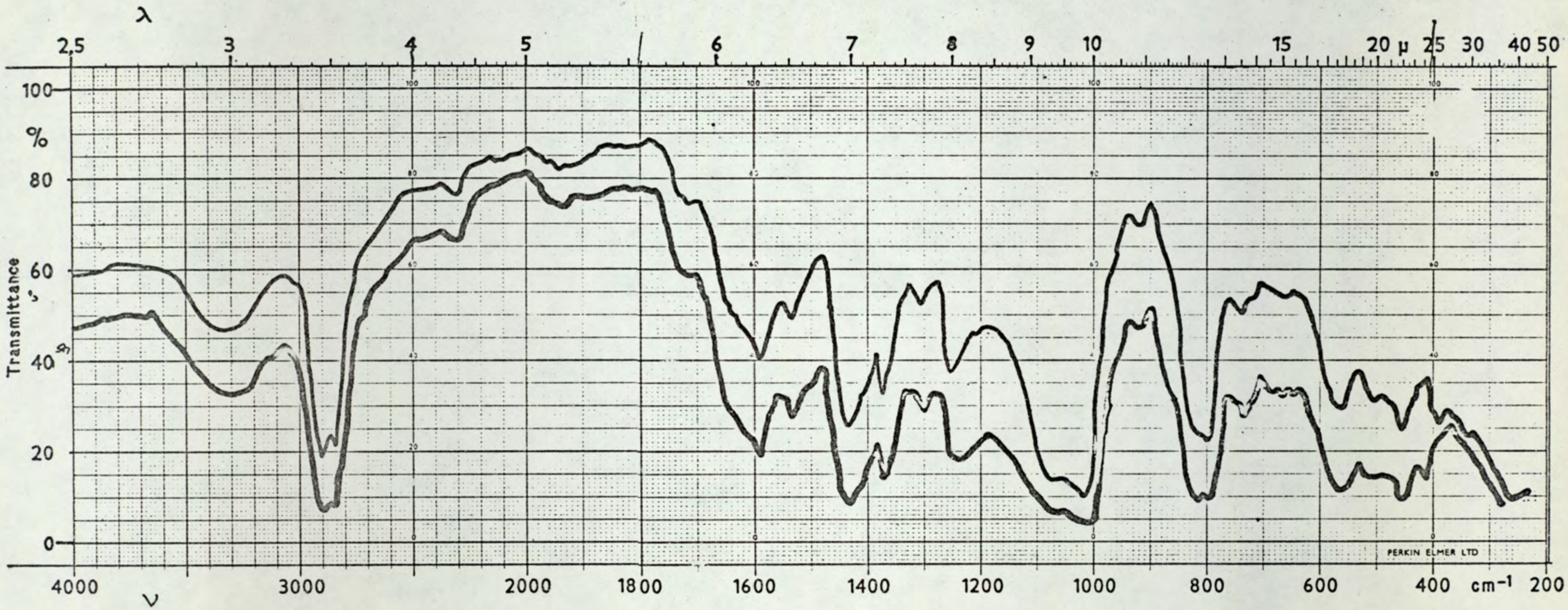


FIGURE 4-3 . <u>ATR SPECTRUM .</u> TETA/828, $\alpha = 45^\circ$, $\alpha = 60^\circ$, 0·005mm.

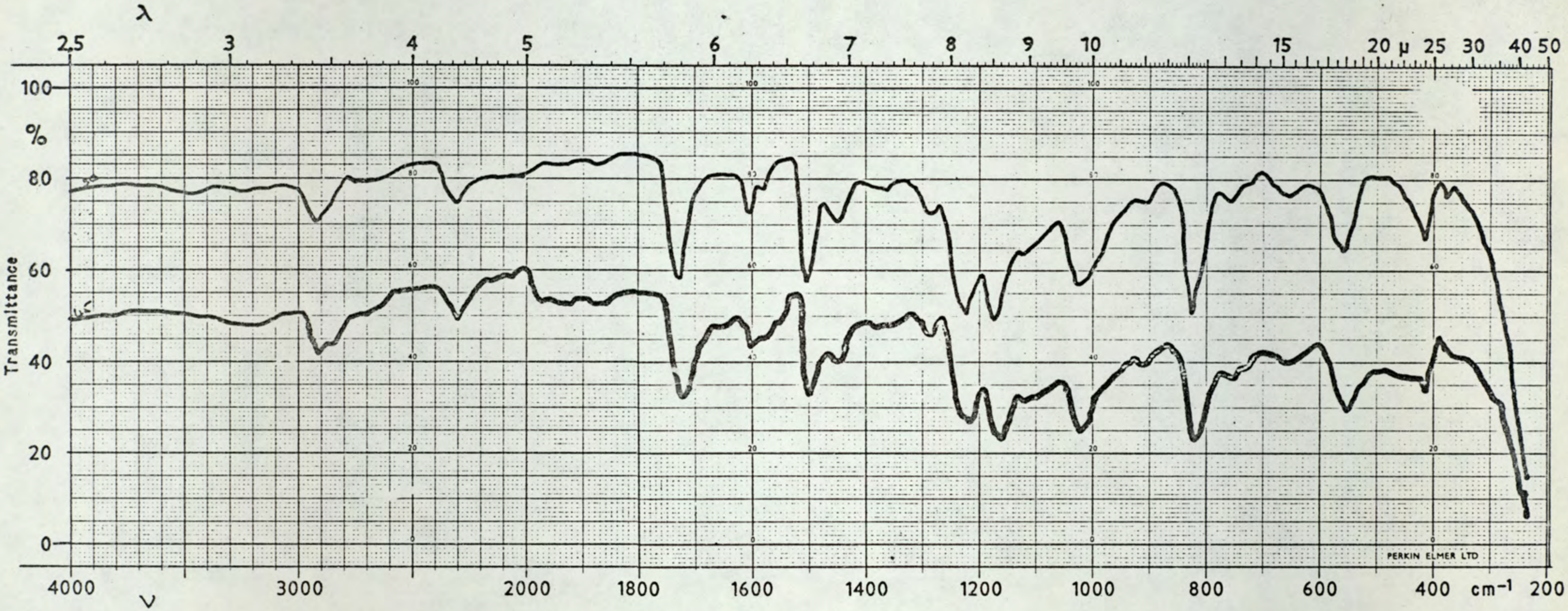


FIGURE 4·4 ATR SPECTRUM of HHPA/828 0005mm., $\alpha = 45°$.
$\alpha = 50°$

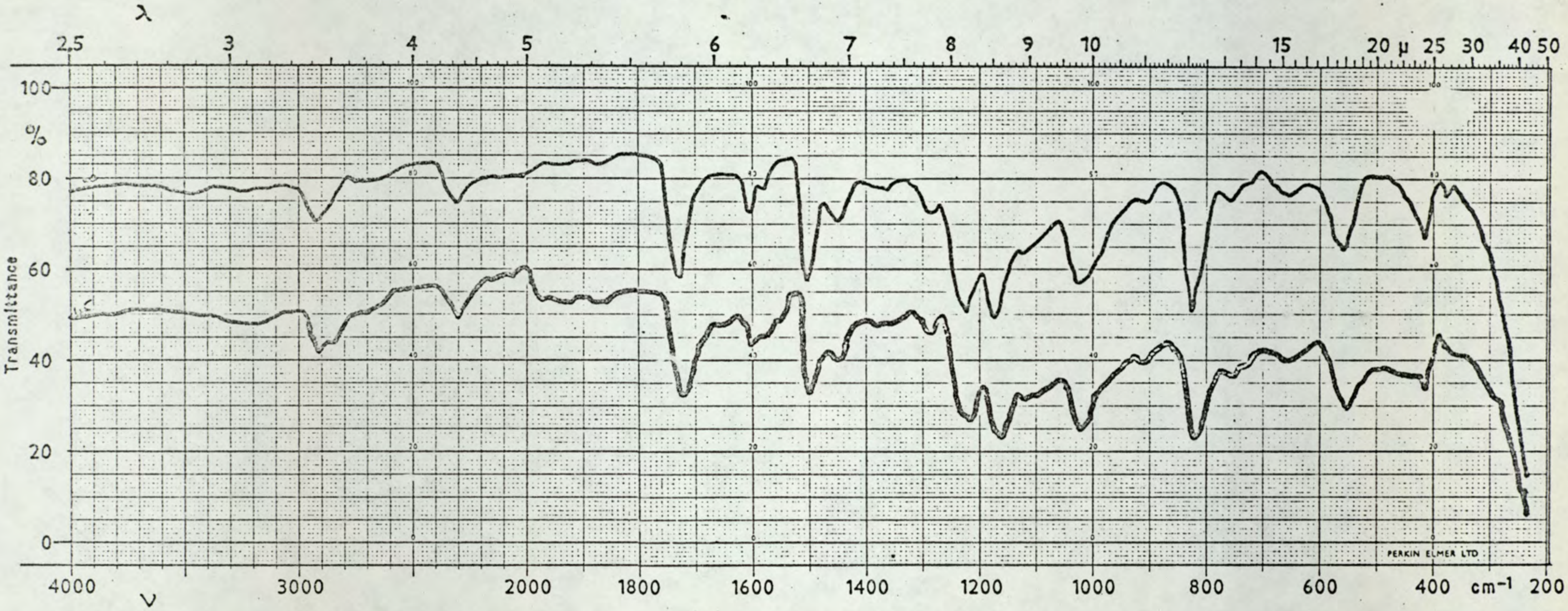


FIGURE 4-5 ATR SPECTRUM of HHPA/828, 0.005mm., $\alpha = 39^\circ$,
(irradiated with light of $\lambda > 280$nm.)

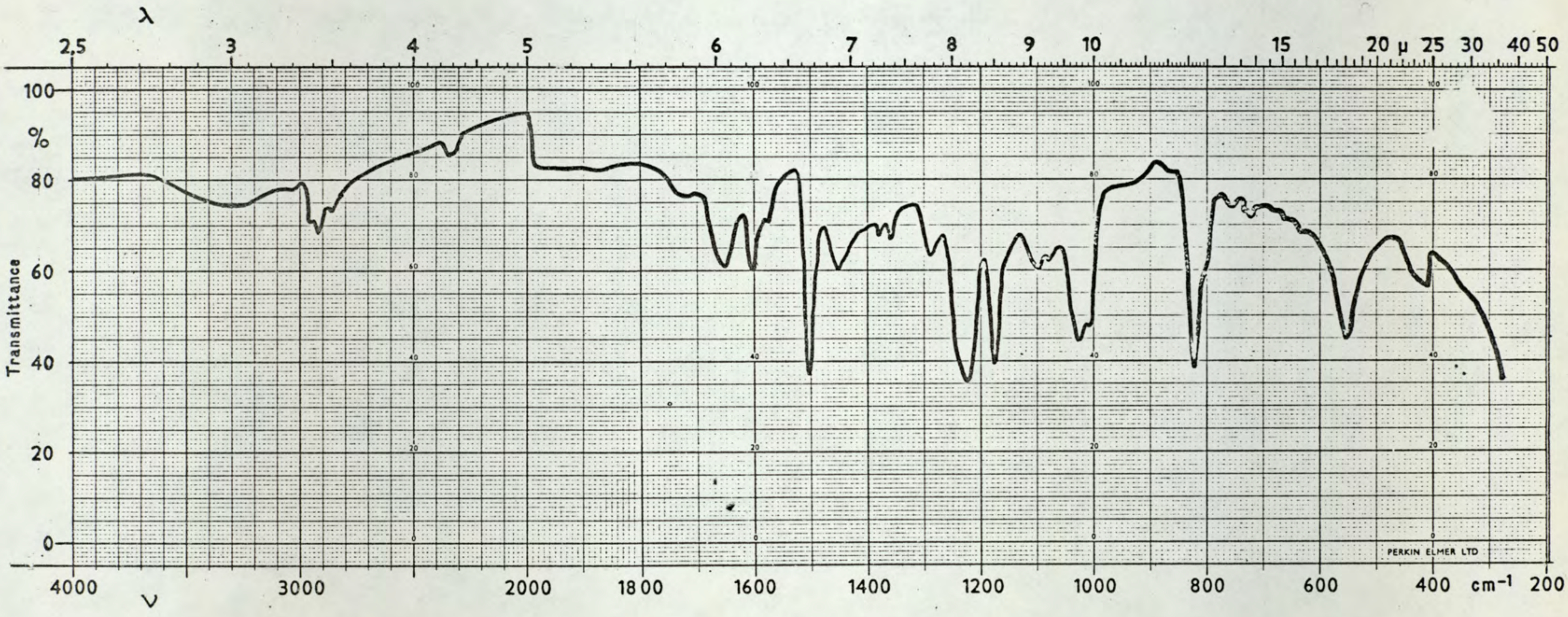


FIGURE 4-6 ATR SPECTRUM of TETA/828, 0·005 mm. $\alpha = 39^\circ$, (irradiated with light of $\lambda > 280$ nm.)

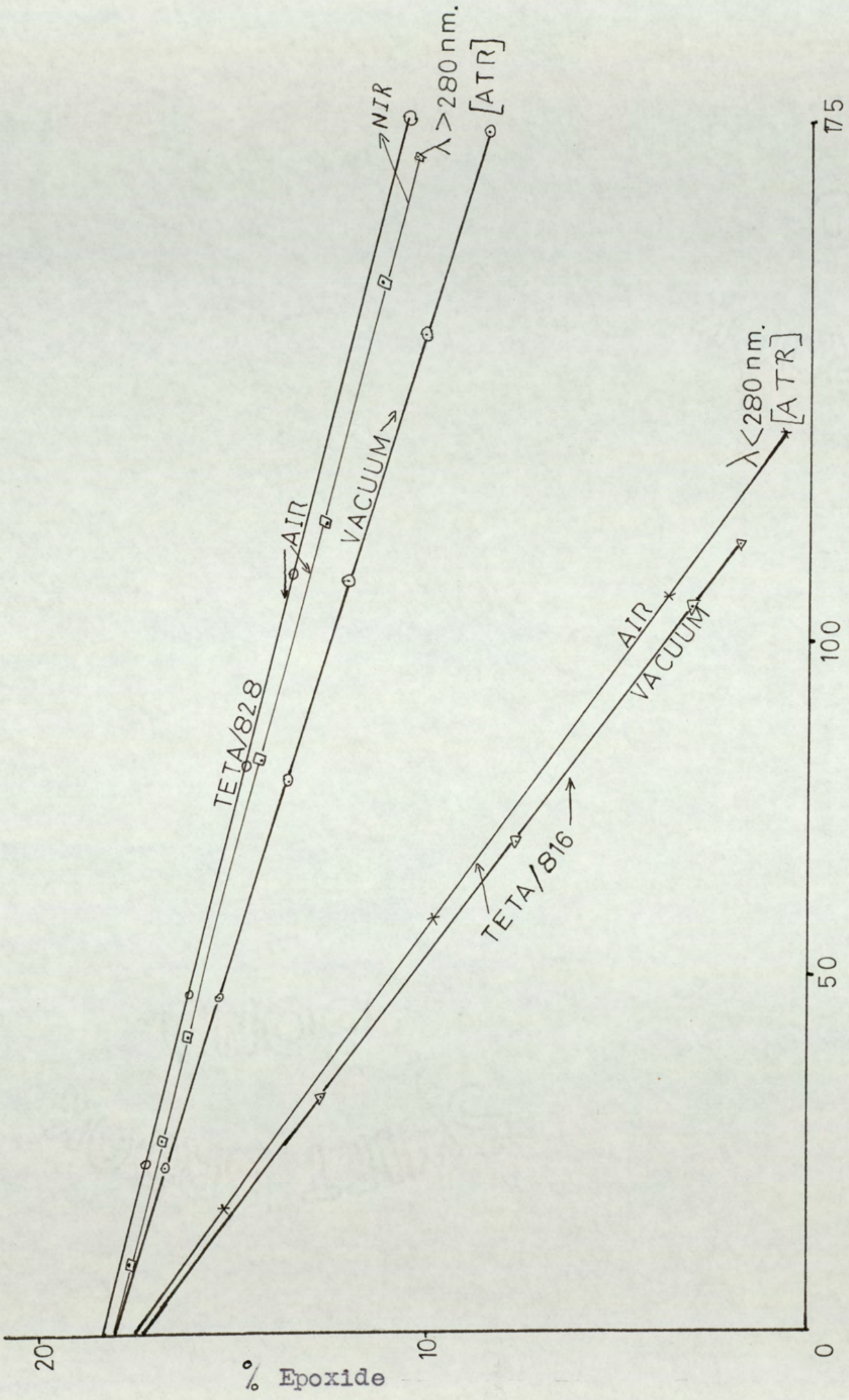


FIGURE 4-7 Comparison of methods of analysis

(epoxide content)
(NIR is the near IR technique of Dannenberg)

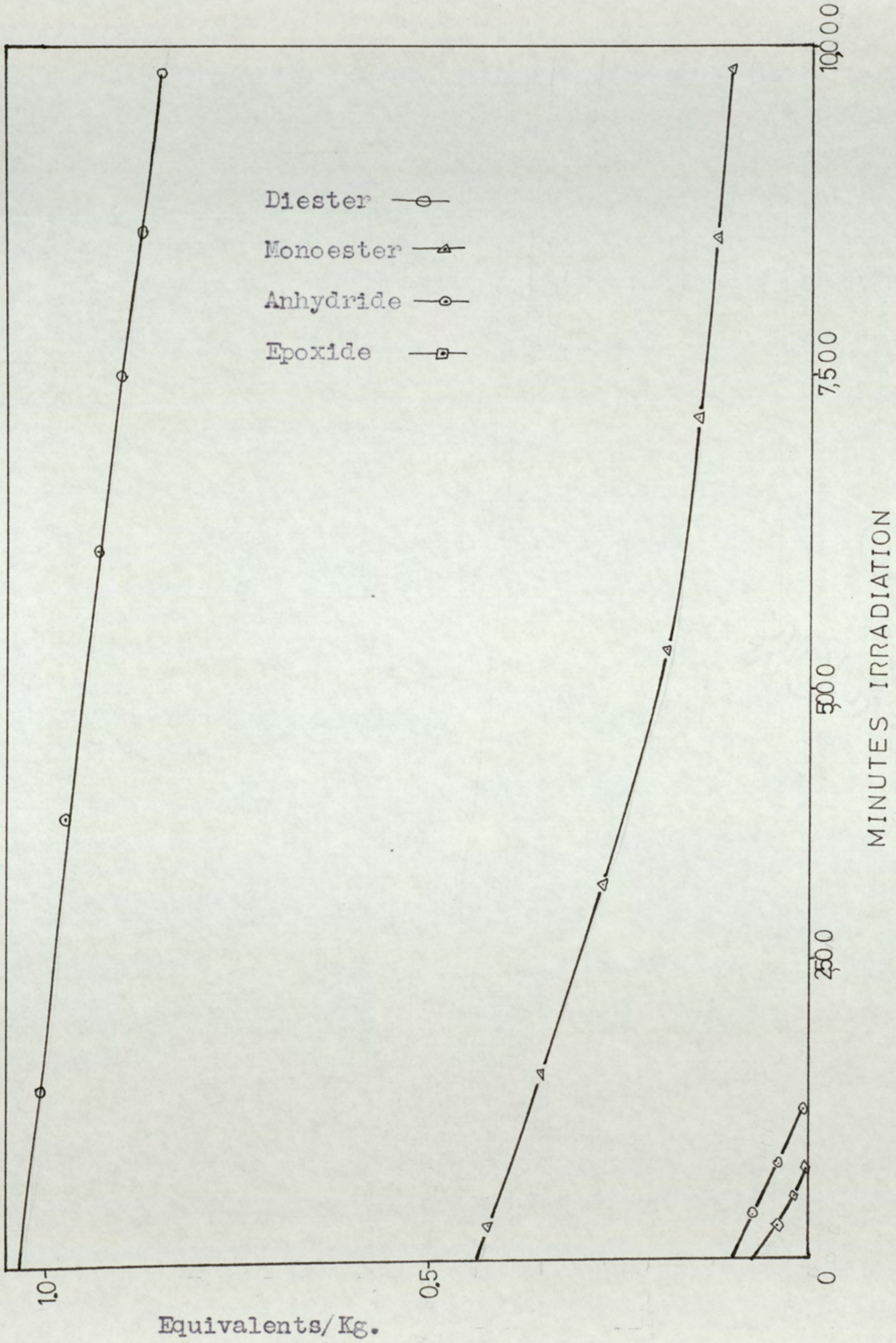


FIGURE 4-85 <u>Functional Group Changes on Irradiation.</u>

(anhydride system)

(AIR IRRADIATION)

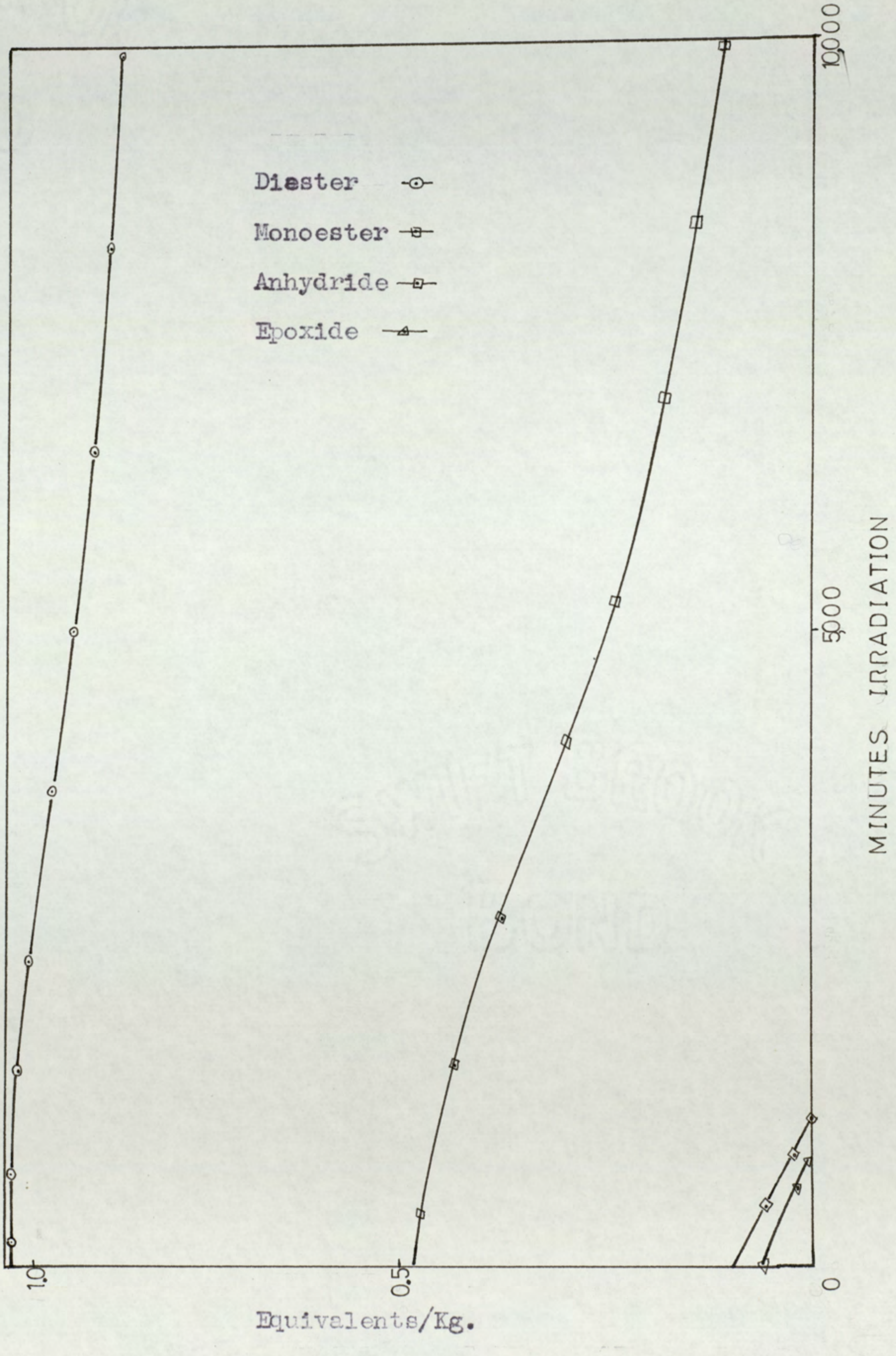


FIGURE 4-9 Functional Group Changes on Irradiation.

(vacuum irradiation)

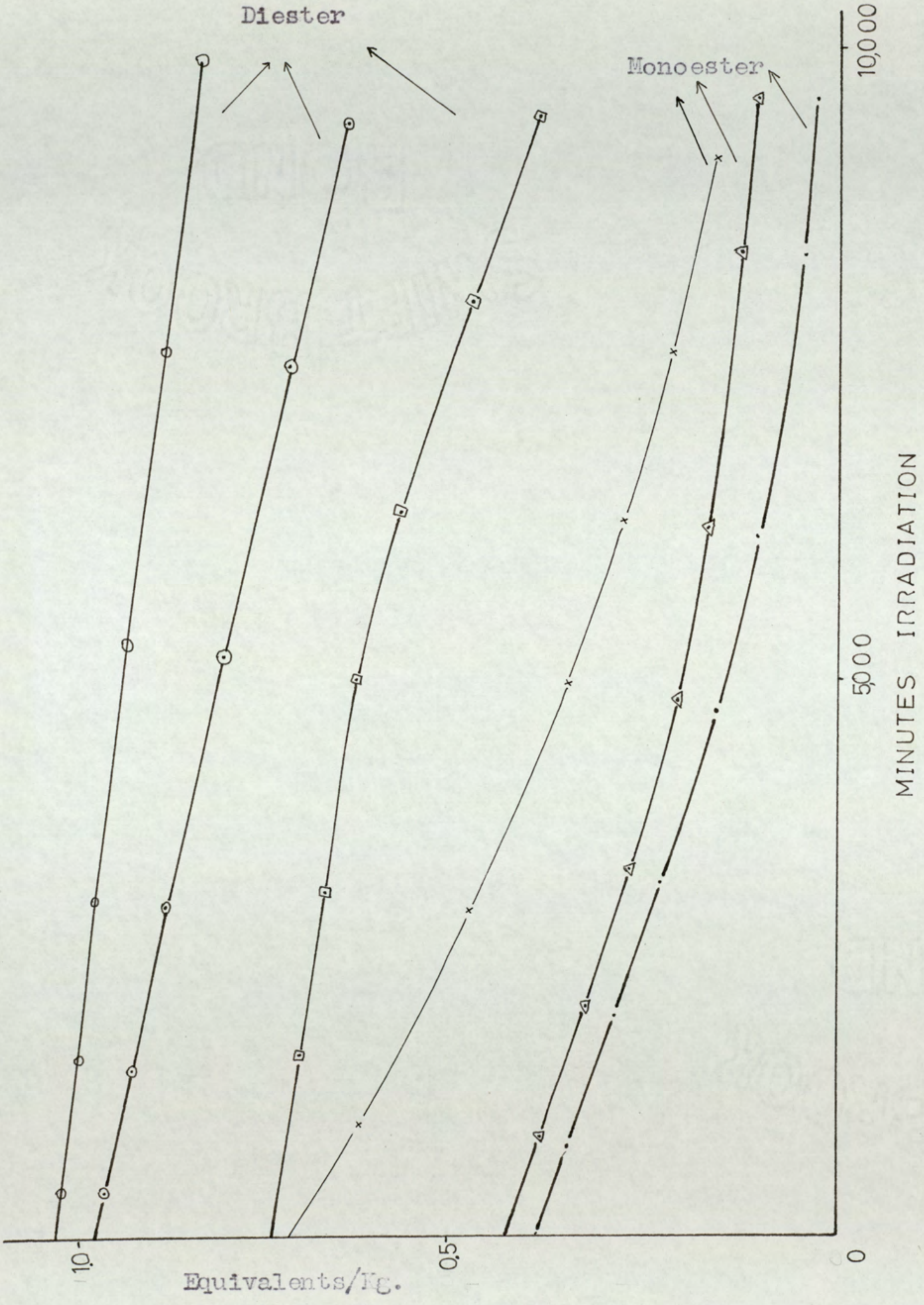


FIGURE 4-10 EFFECT of DEGREE of CURE on DEGRADATION.

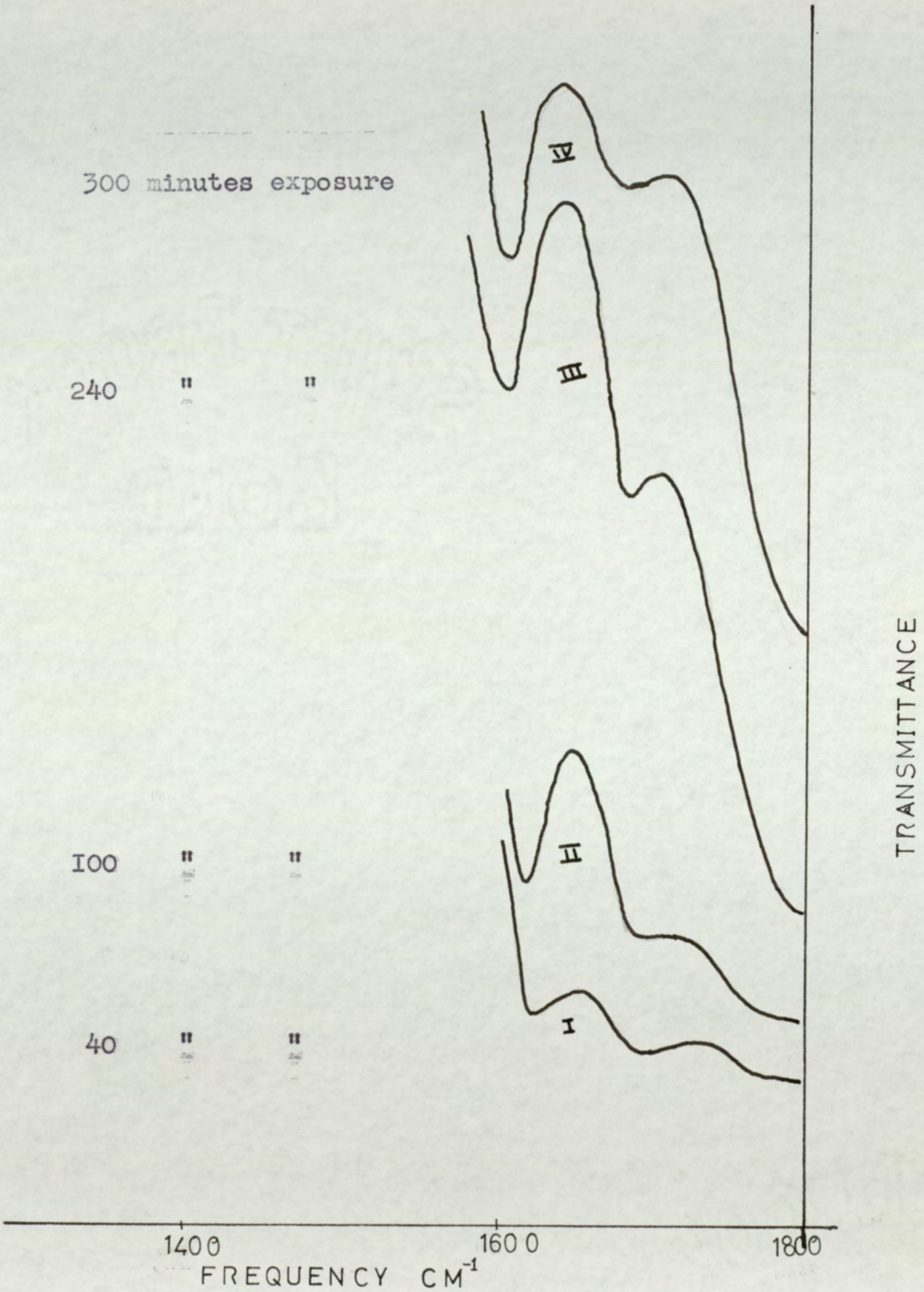


FIGURE 4-11 GROWTH of NEW INFRARED BANDS,

for TETA /SYSTEMS., onEXPOSURE
to ULTRAVIOLET LIGHT(> 280nm)

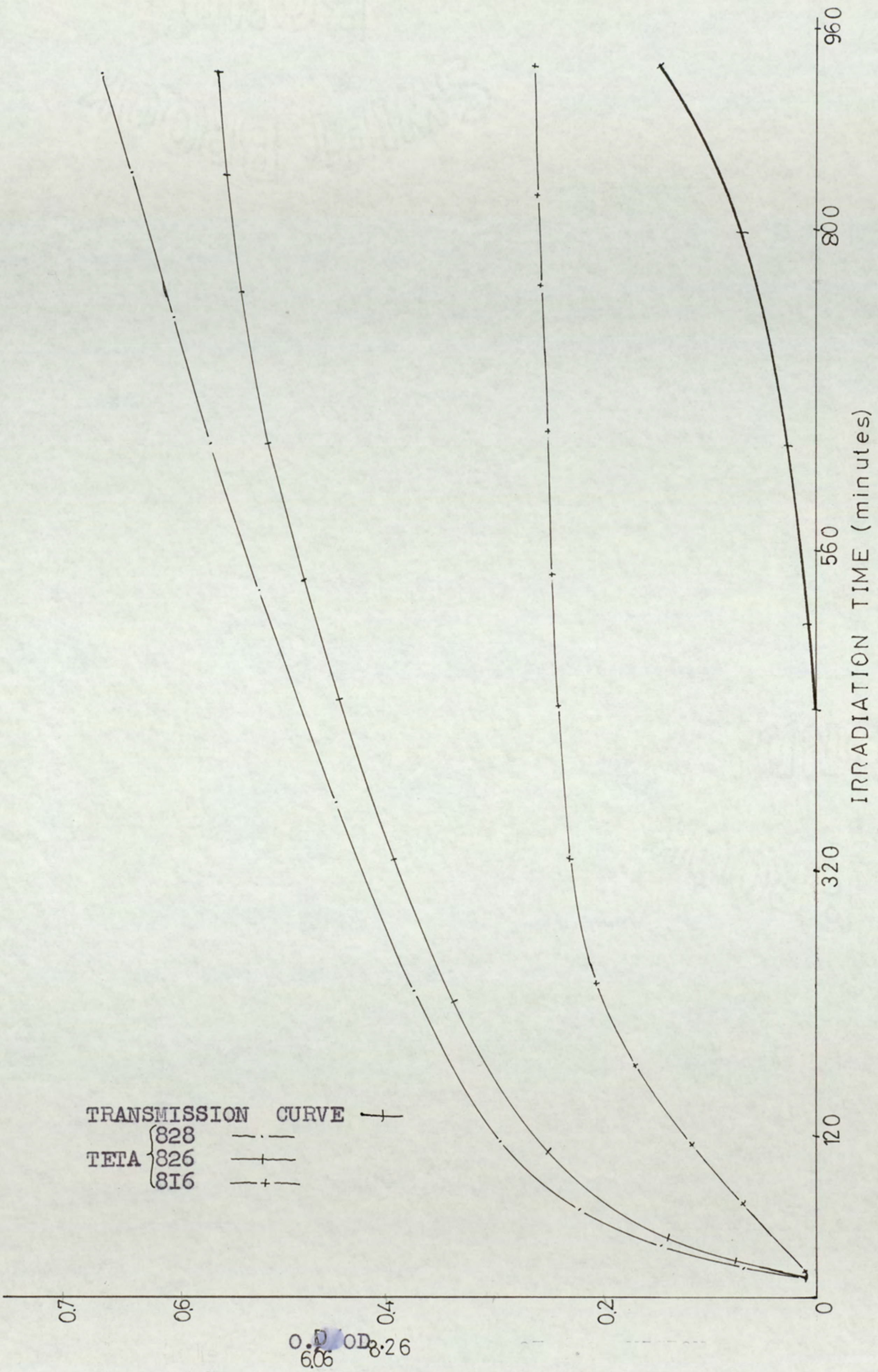
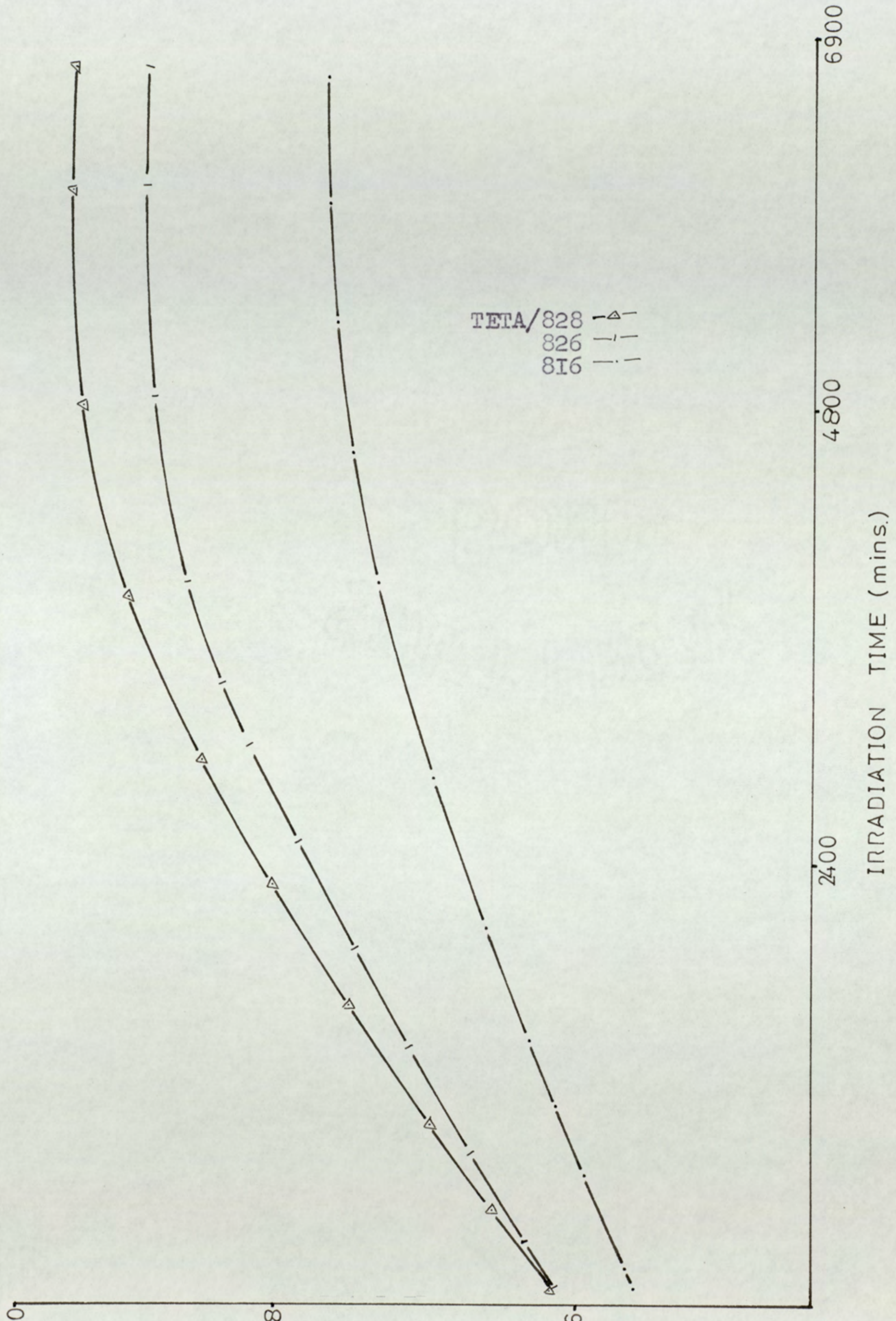


FIGURE 4-12 NORMALISED INGROWTH of 6.06 micron BAND.
(photo-oxidation)



GIGURE 4-13 NORMALISED INGROWTH of 6.06 micron band.

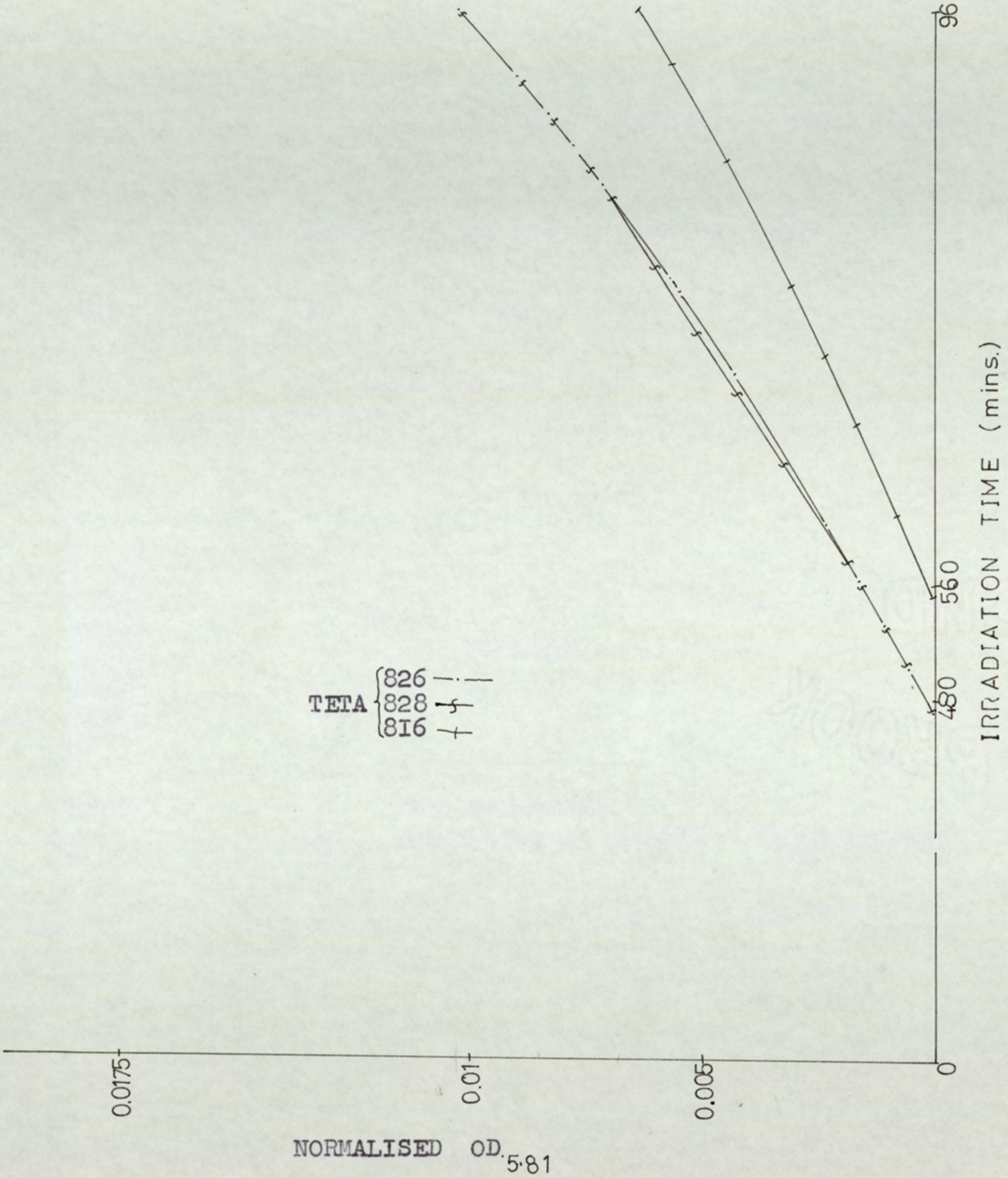


FIGURE 4-14 NORMALISED INGROWTH of 5.8I micron BAND.

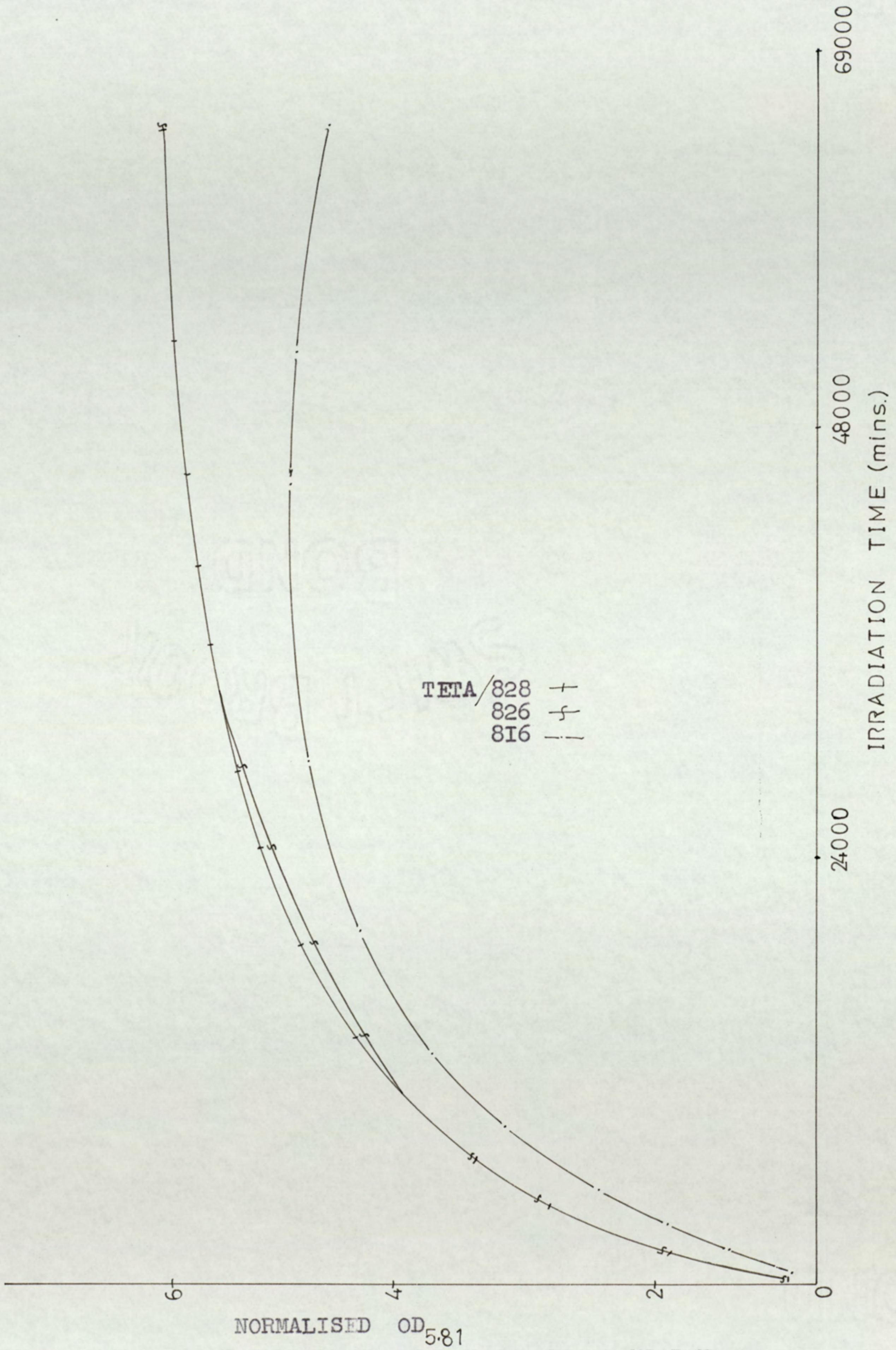


FIGURE 4-15 NORMALISED INGROWTH of 5.81micron BAND.

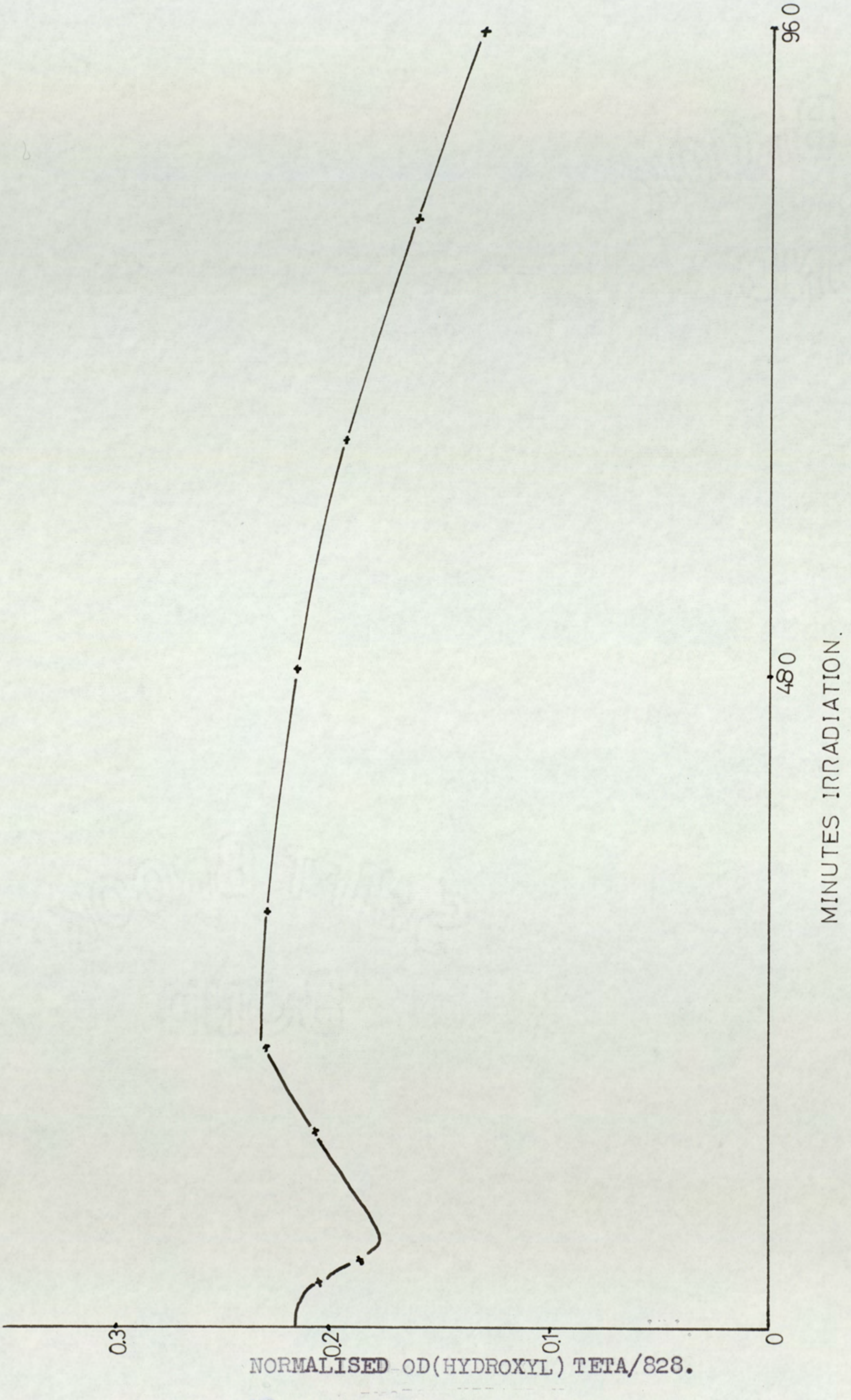
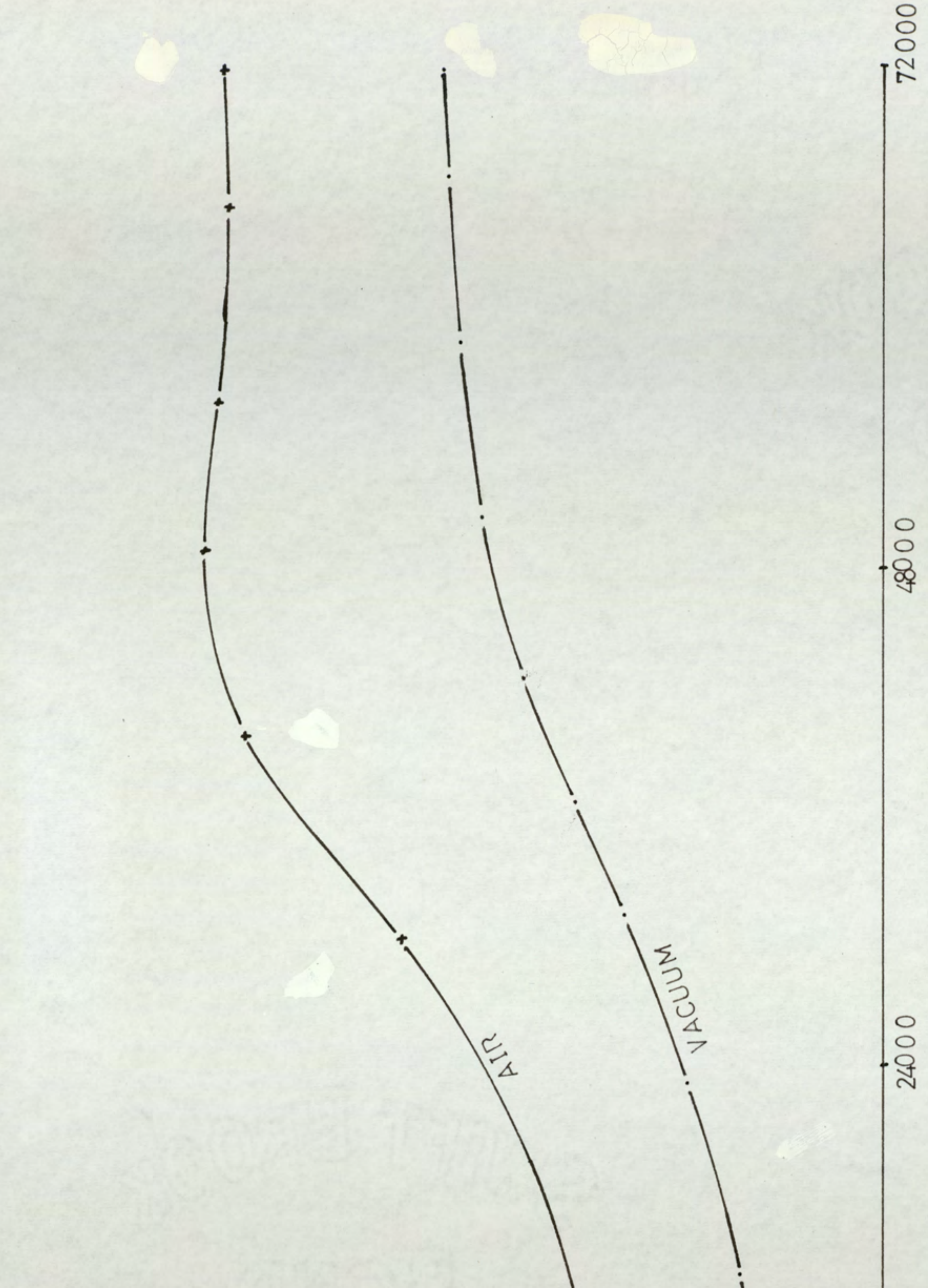


FIGURE 4-16 CHANGE in HYDROXYL ABSORPTION.
(photo-oxidation)



NORMALISED HYDROXYL ABSORPTION (TETA/82[illegible])
(photo oxidation)

FIGURE 4-17 CHANGE in HYDROXYL ABSORPTION.

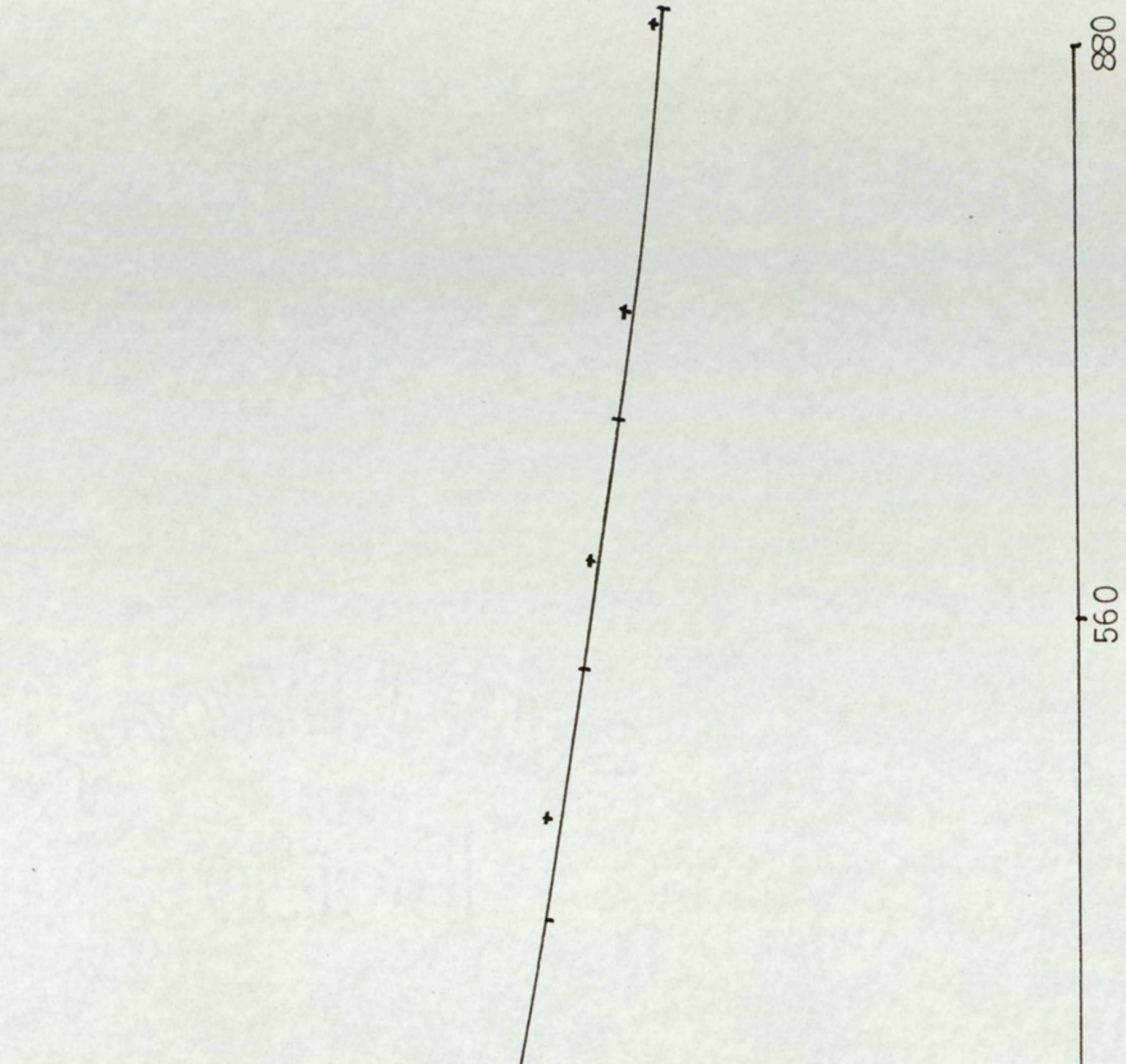


FIGURE 4-18 VARIATION in ISOPROPYLIDENE ABSORPTION.

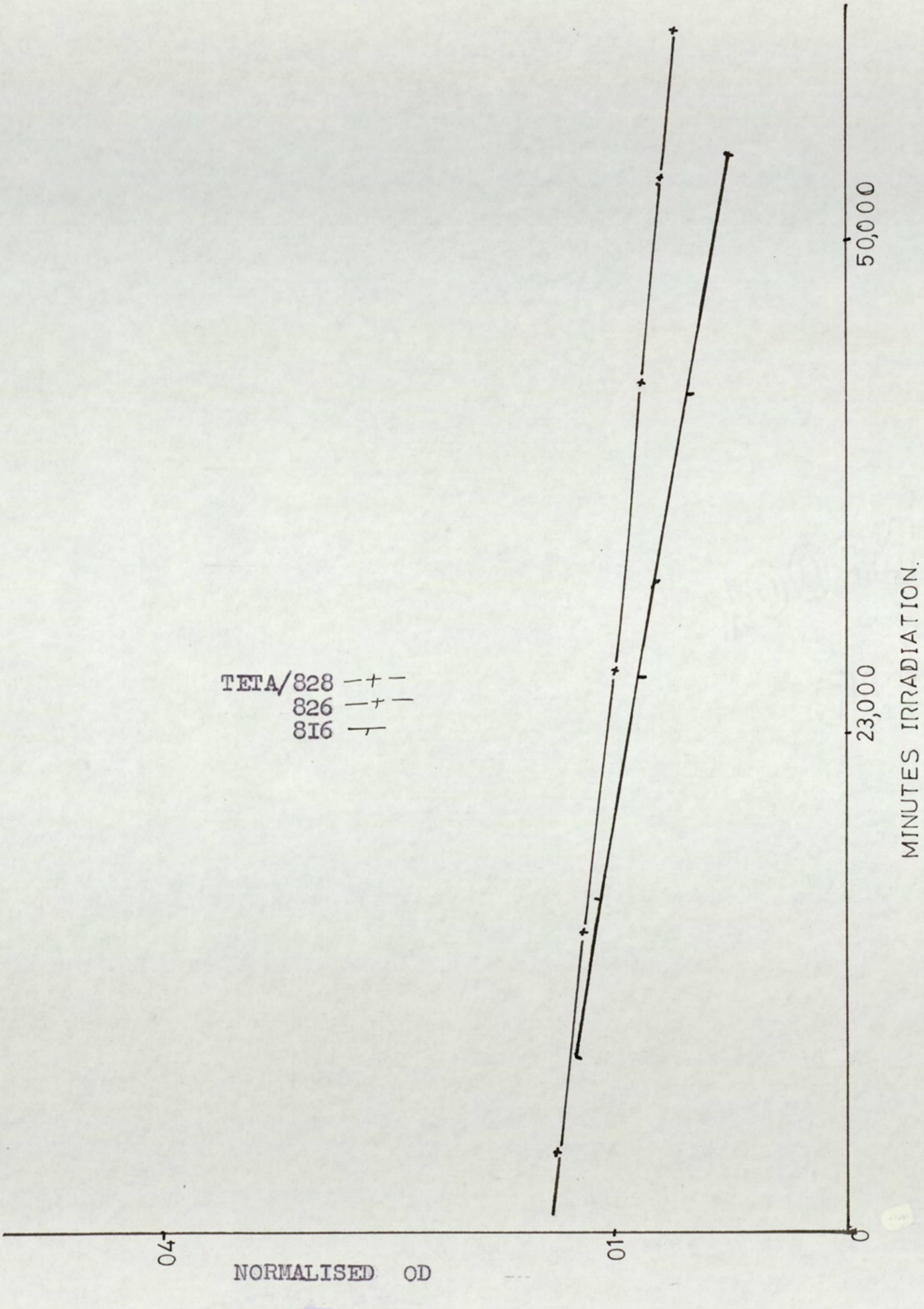


FIGURE 4-19 VARIATION in ISOPROPYLIDENE ABSORPTION.

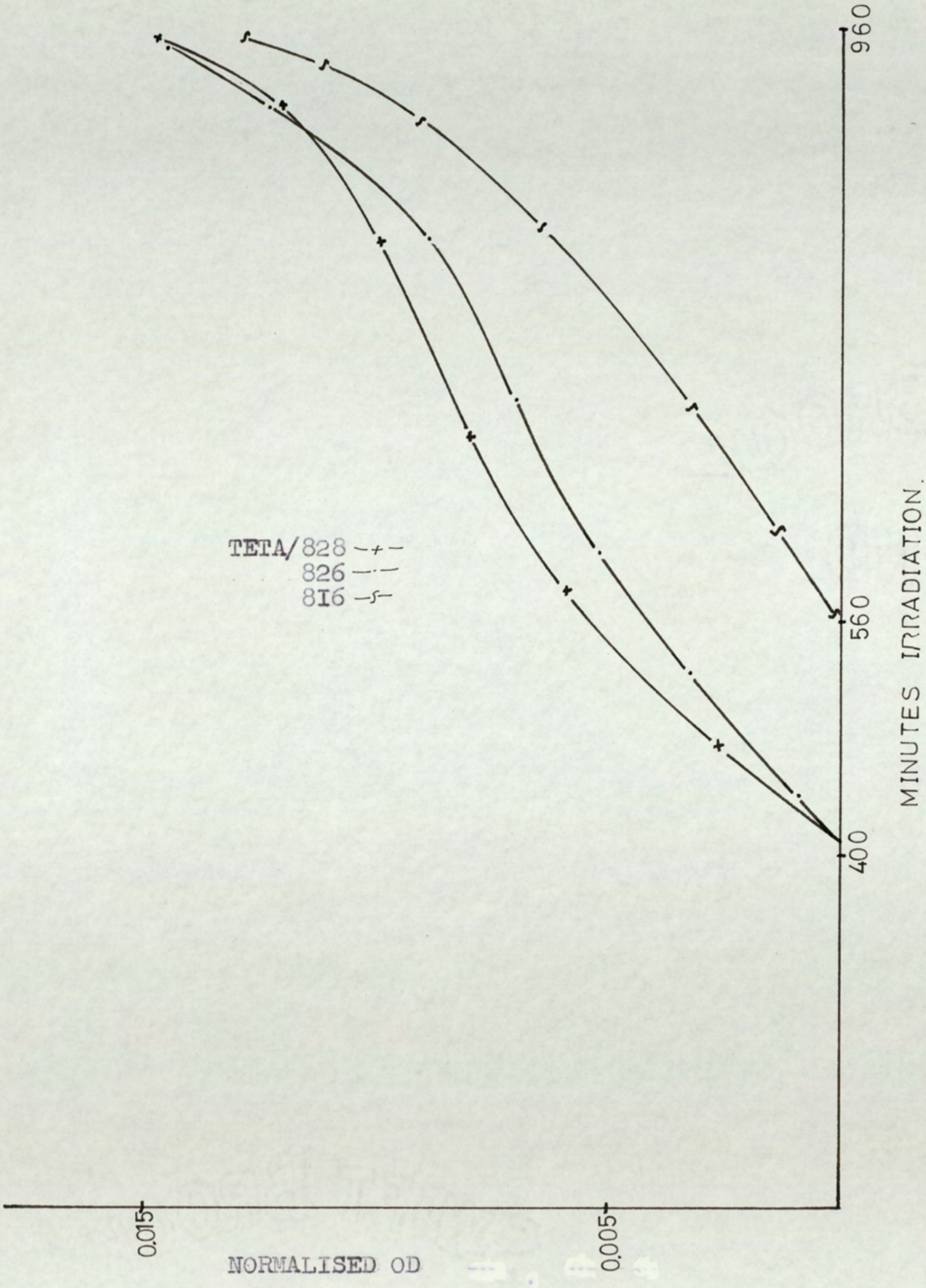


FIGURE 4-20 VARIATION in 5.81micron ABSORPTION BAND.

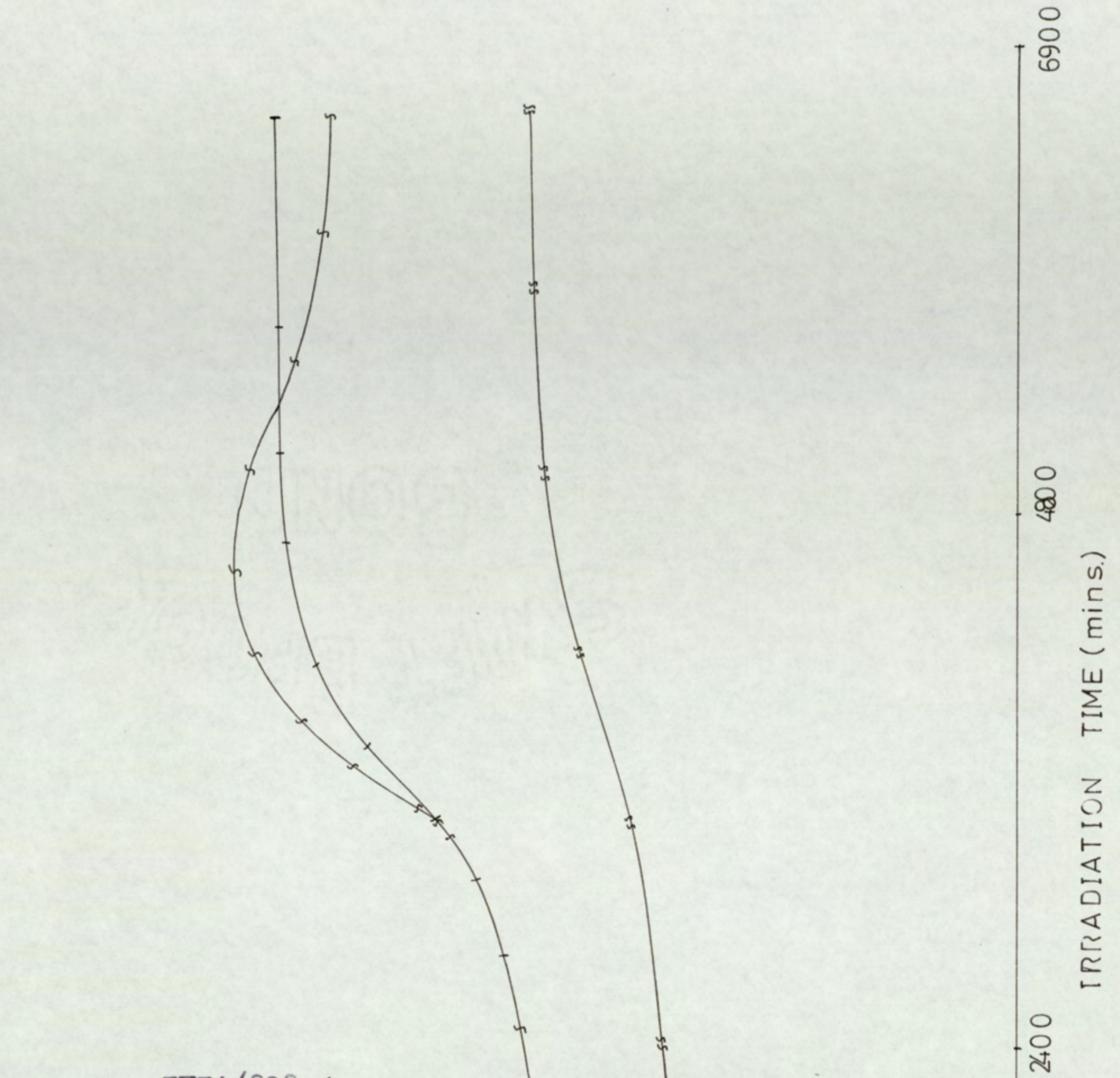


FIGURE 4-21 VARIATION in 5.8I micron ABSORPTION BAND.

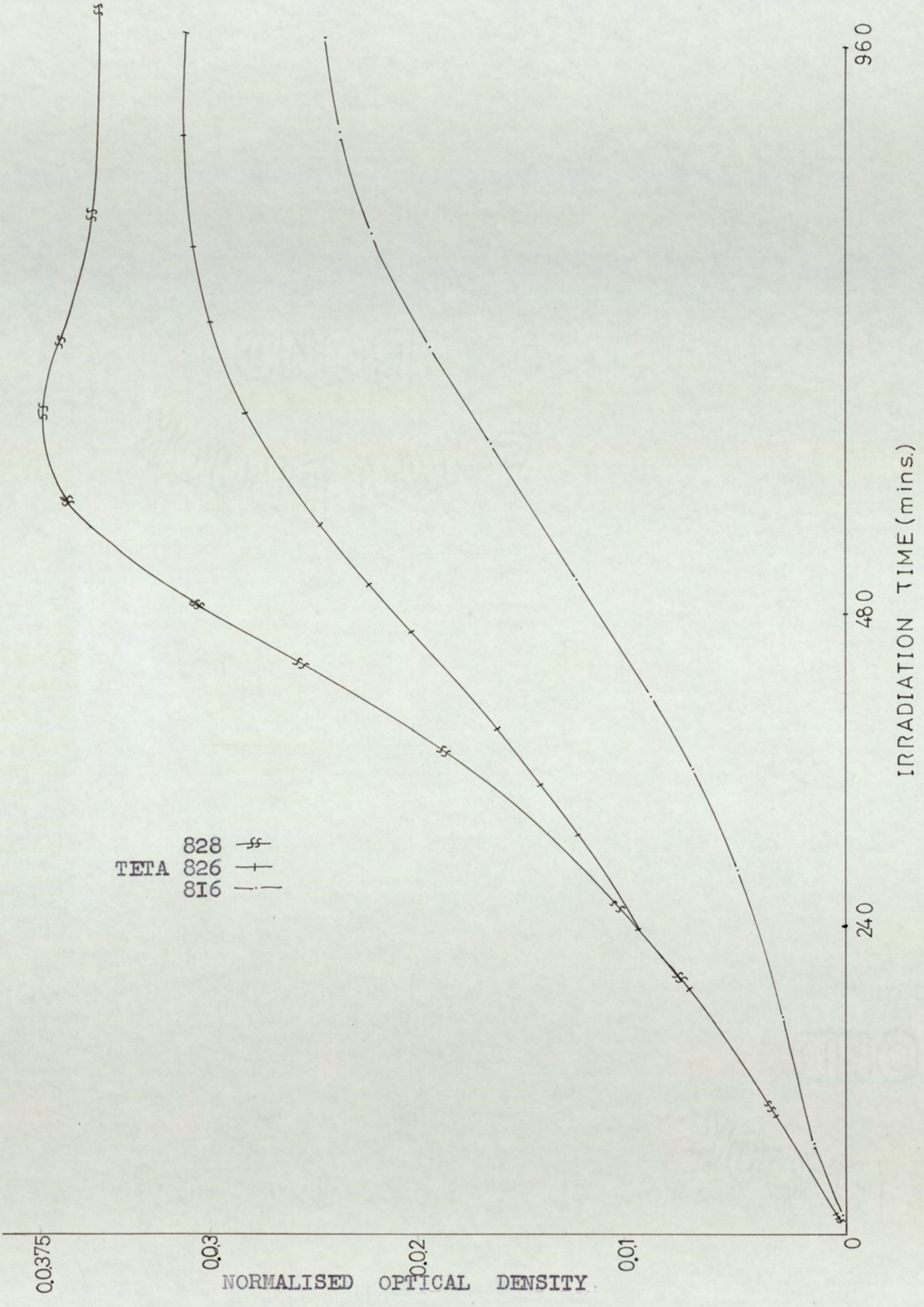


FIGURE 4-22 INGROWTH of 6.06 micron ABSORPTION BAND.

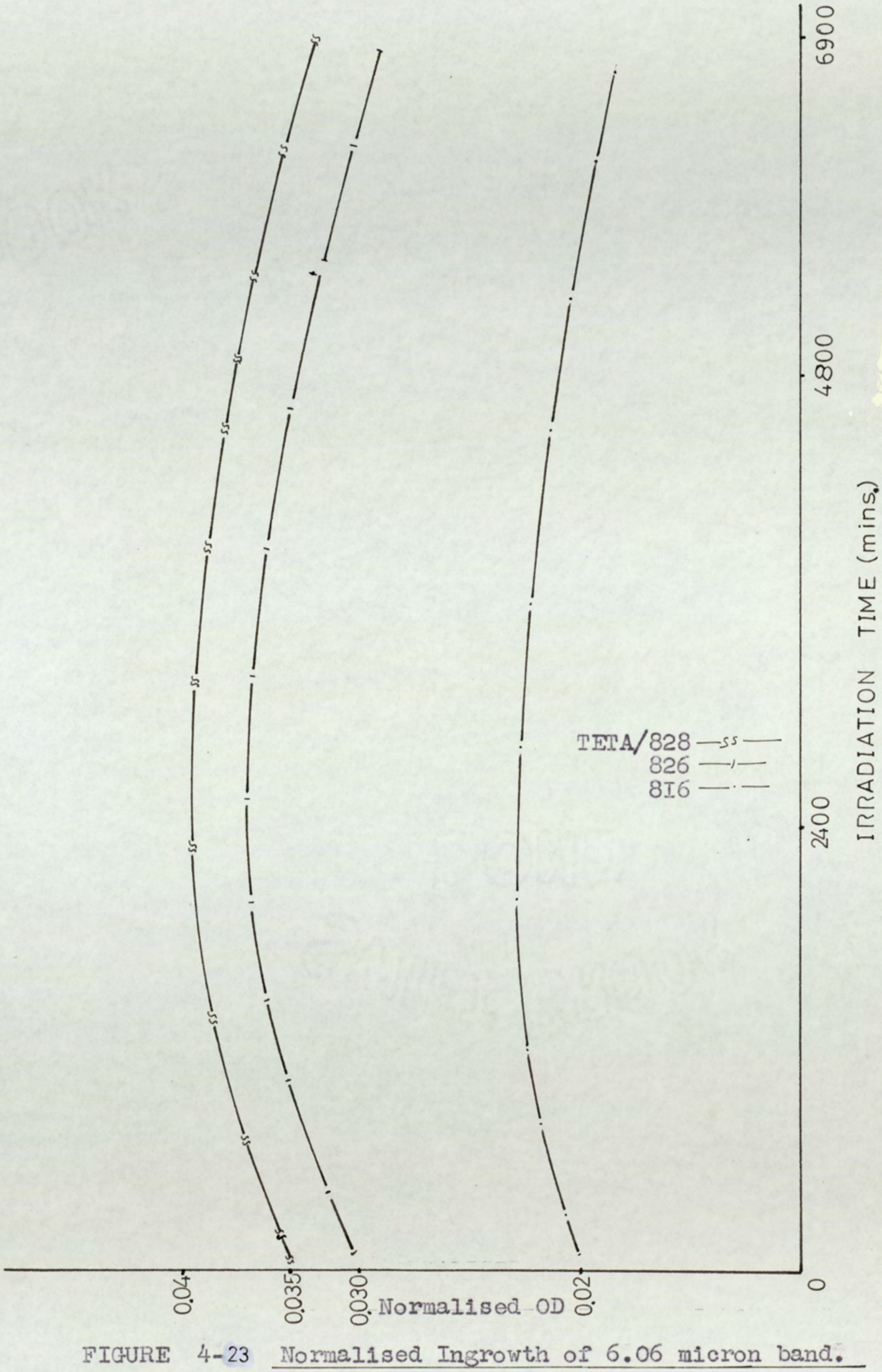


FIGURE 4-23 Normalised Ingrowth of 6.06 micron band.

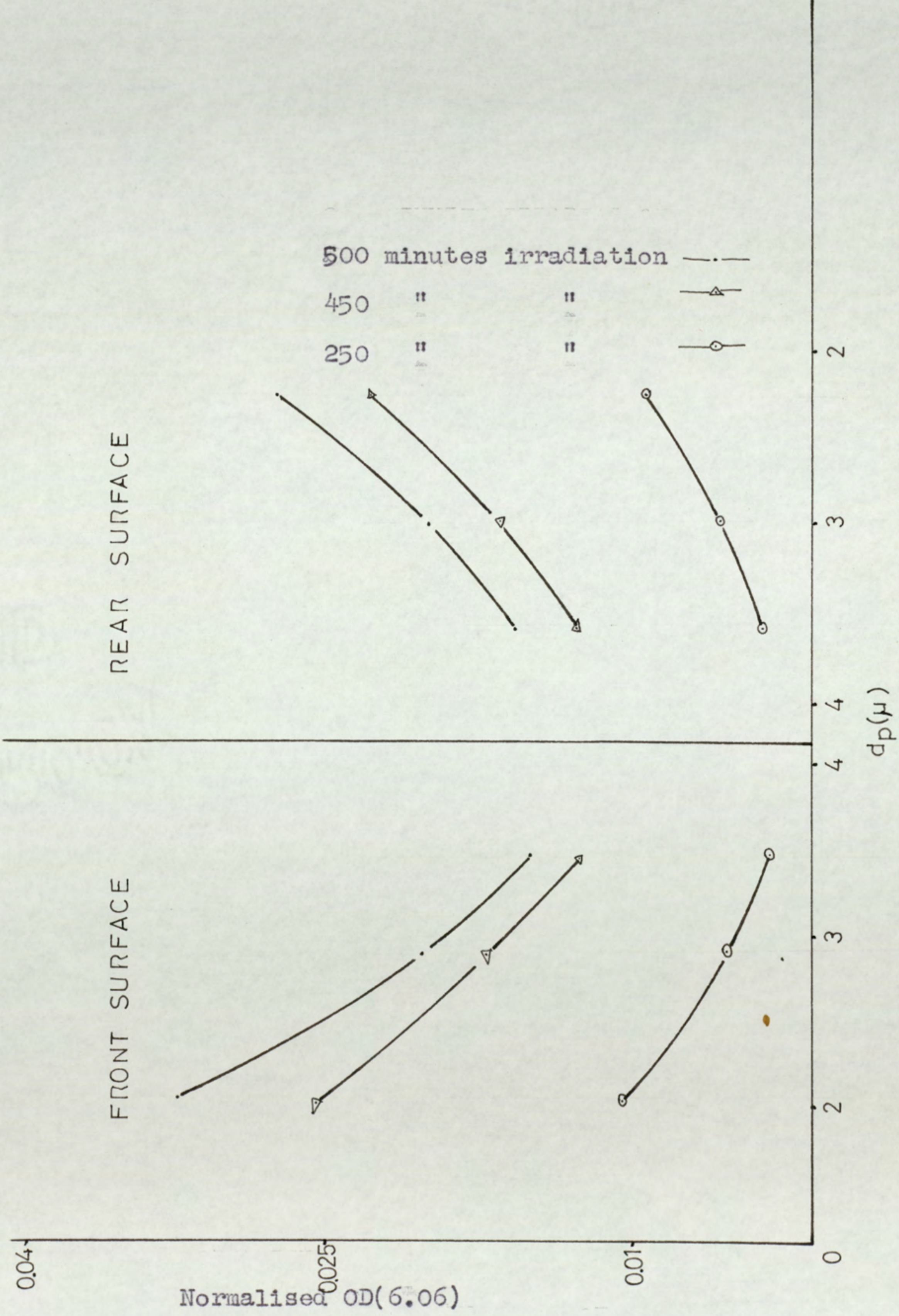


FIGURE 4-24 VARIATION in DEPTH of PENETRATION.

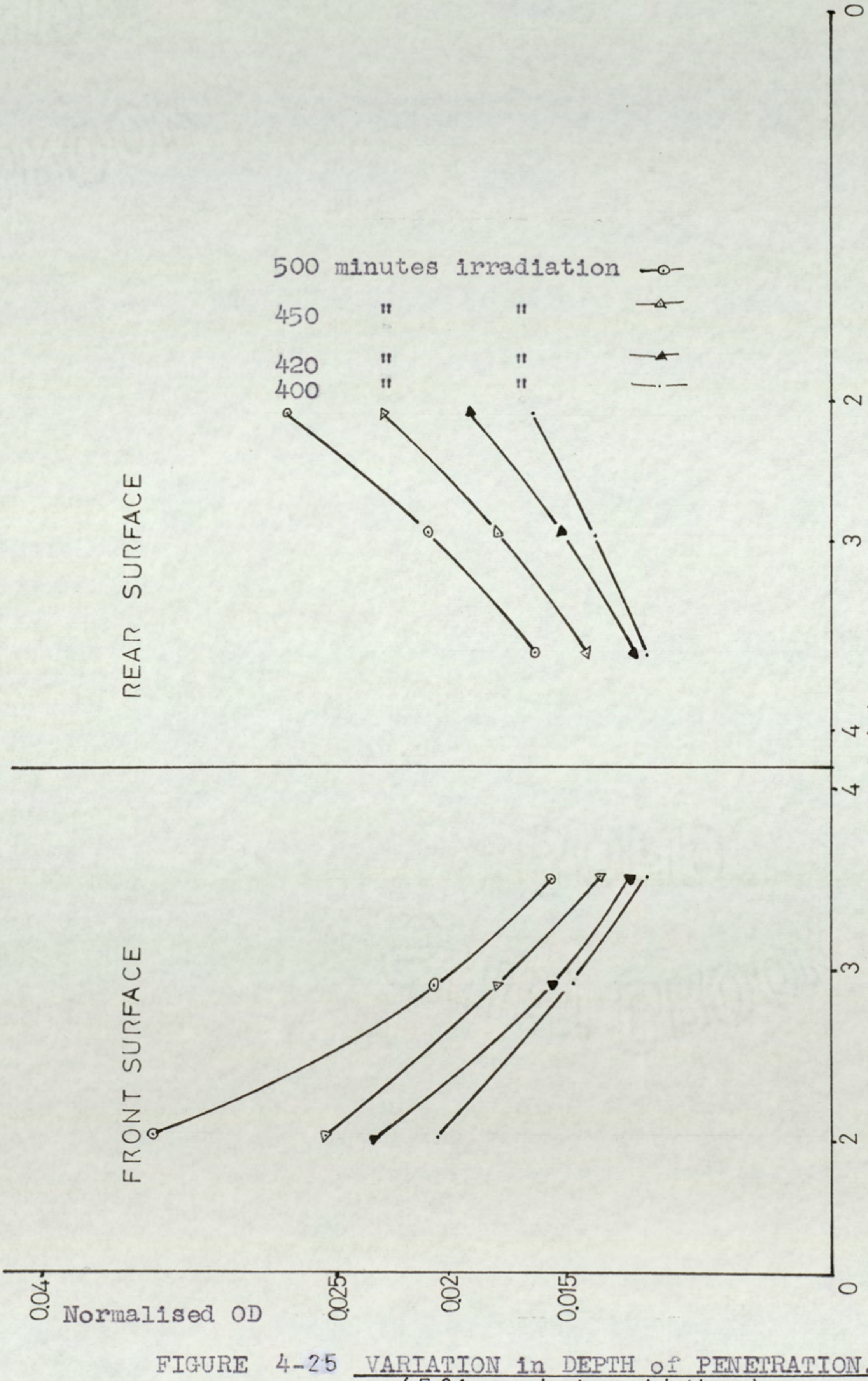


FIGURE 4-25 VARIATION in DEPTH of PENETRATION.
(5.81μ, photo-oxidation)

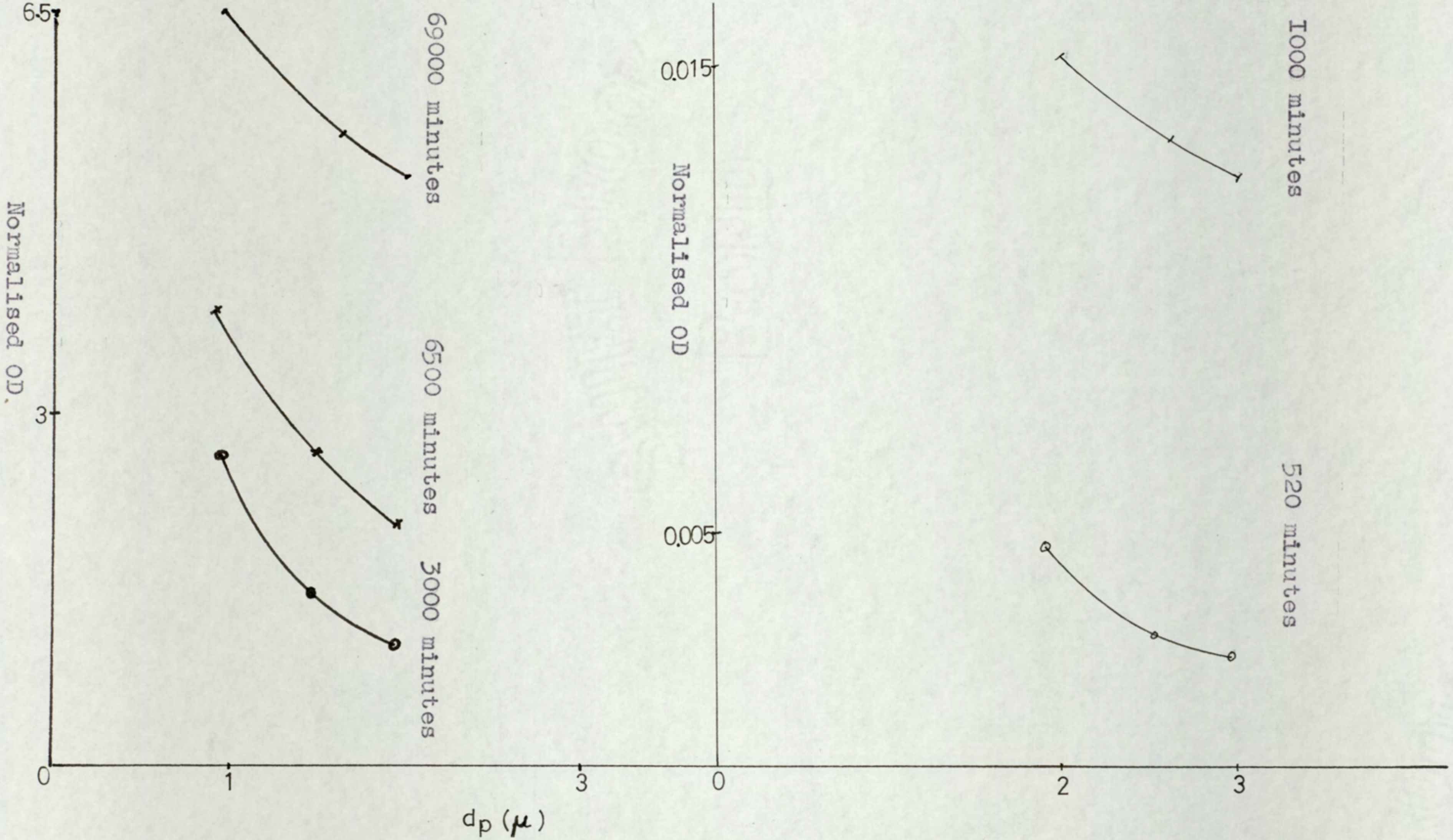


FIGURE 4-26 FIGURE 4-26

VARIATION in d_p on IRRADIATION (5.81μ, photo-oxidation)

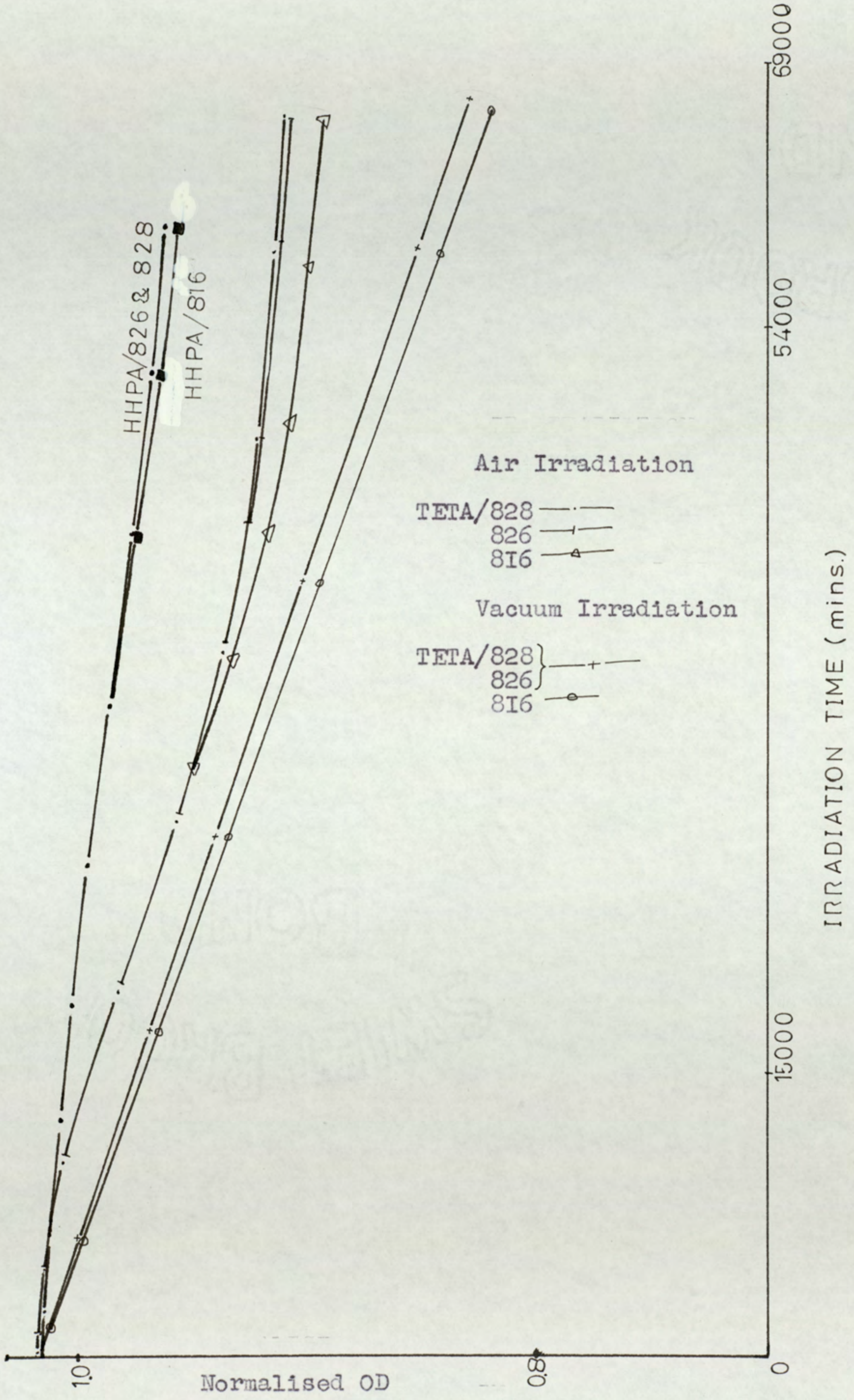


FIGURE 4-27 VARIATION in SUBSTITUTED AROMATIC ABSORPTION BAND.

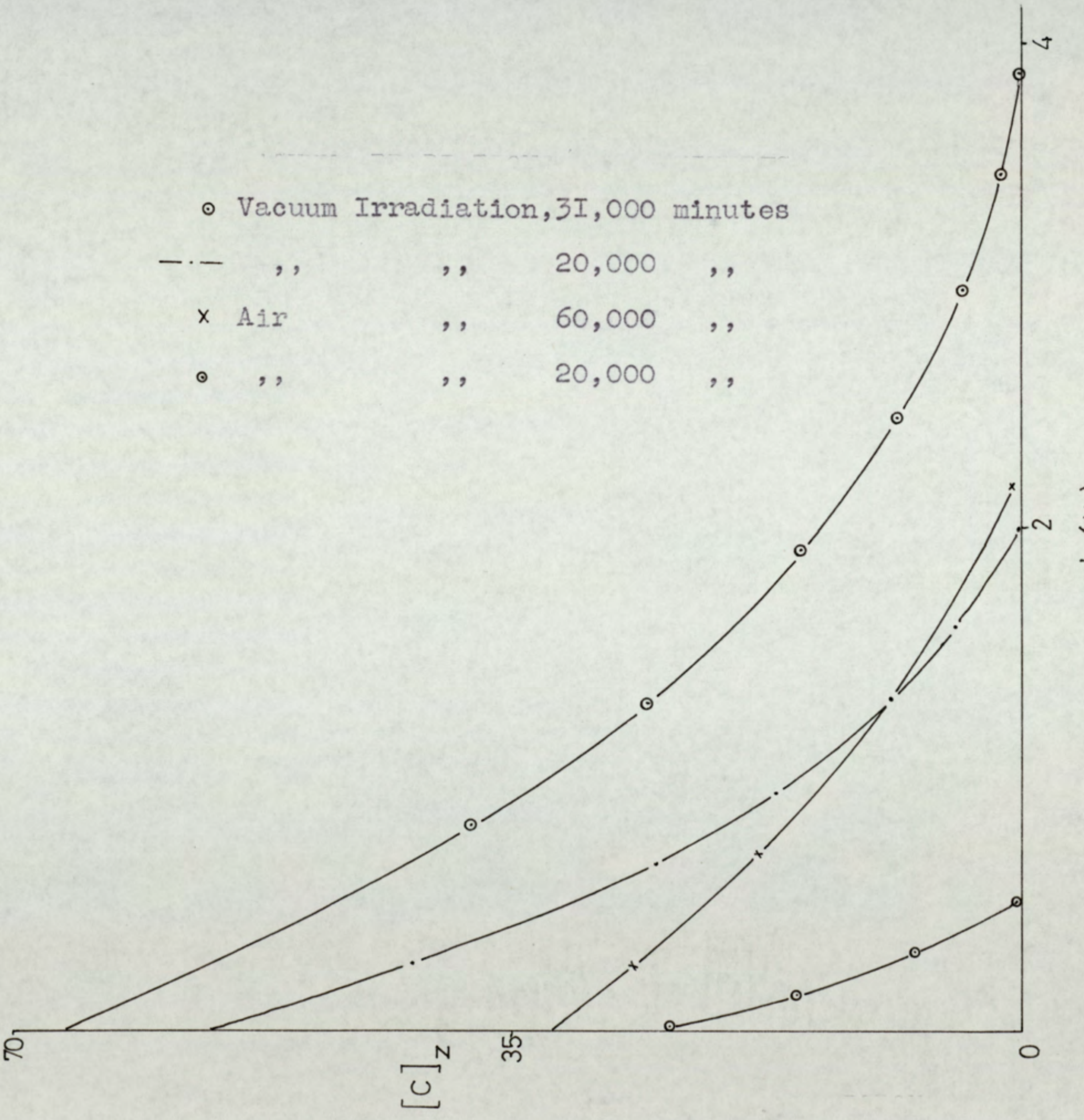
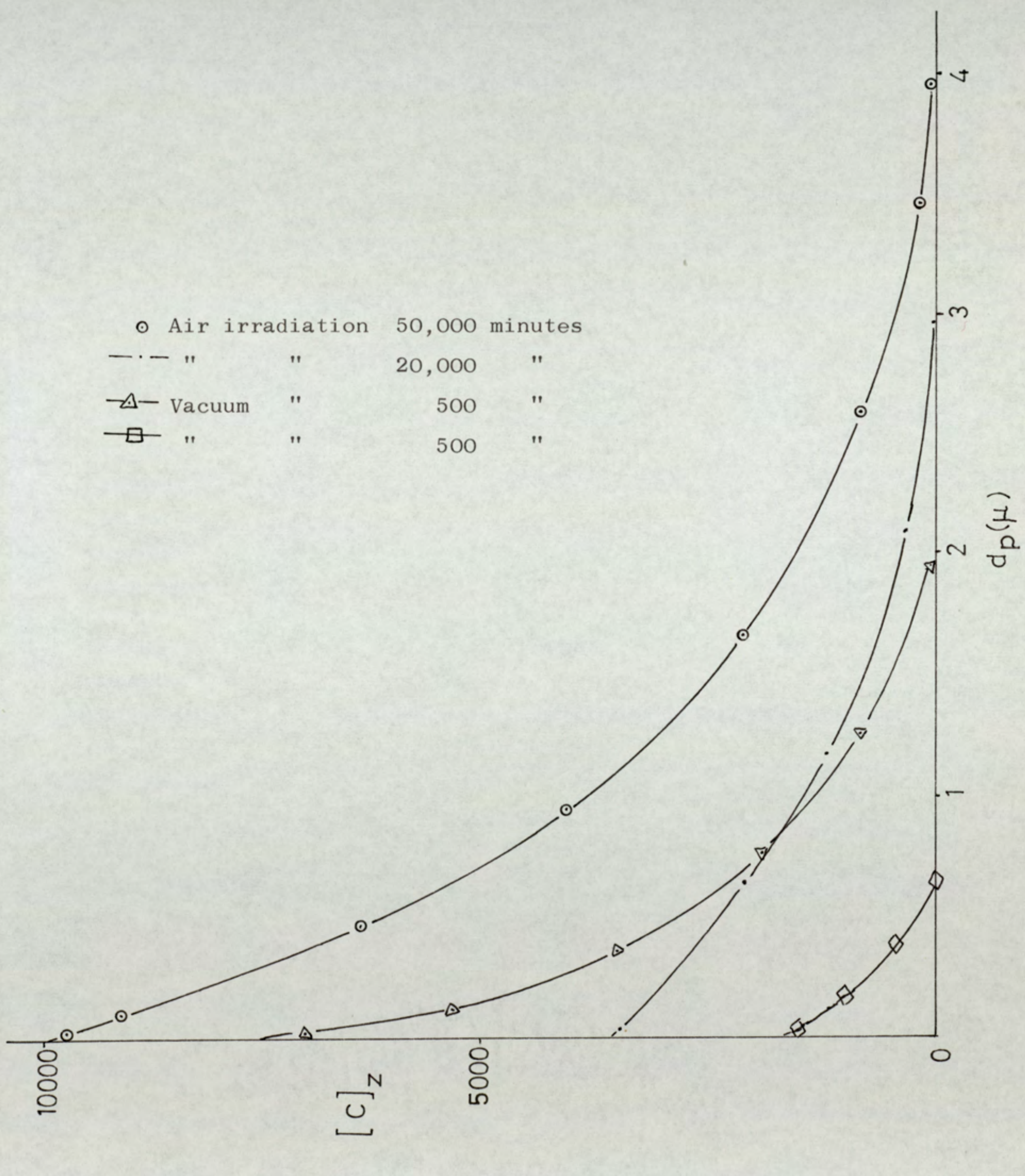


FIGURE 4-28 <u>ABSORBER CONCENTRATION ,5.8I micron BAND.</u>

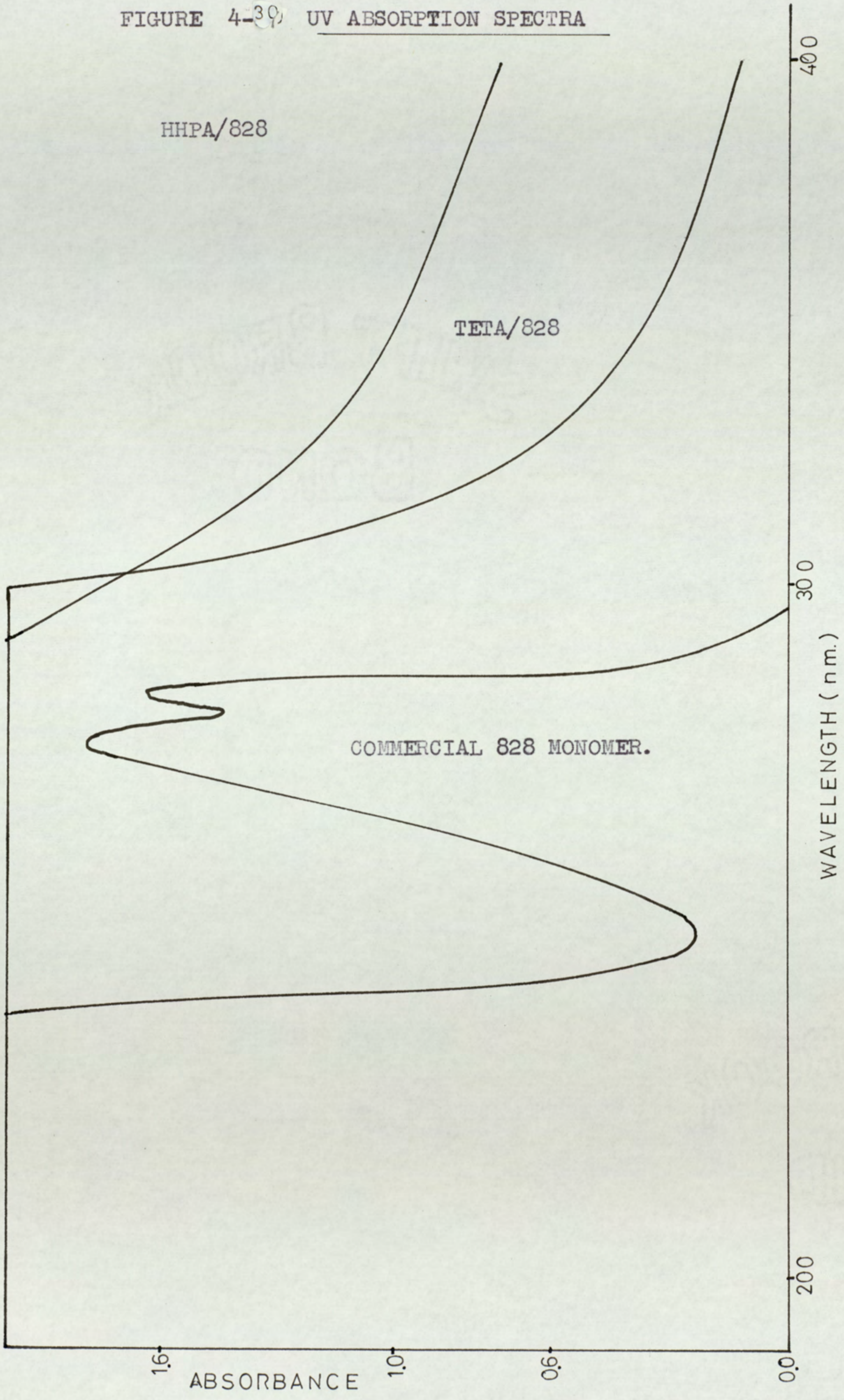
($[C]_z$ is the concentration of absorber and d_p the depth of light penetration)



FIGURES 4 - 29 Absorber Concentration, 6.06 micron band.

($[C]_z$ is the absorber concentration and d_p is the depth of penetration of the light beam)

FIGURE 4-30 UV ABSORPTION SPECTRA



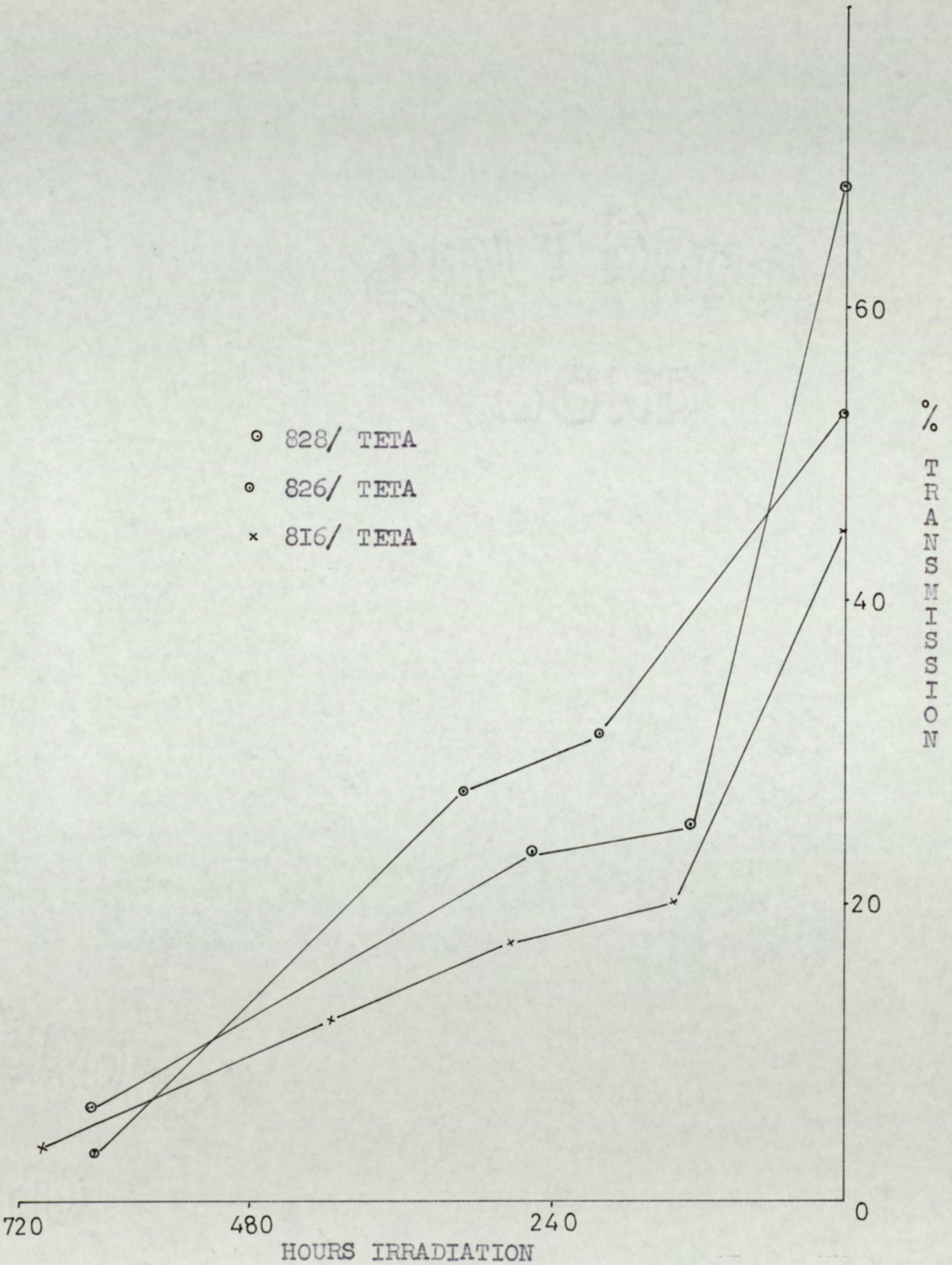


FIGURE 4-31 CHANGE in LIGHT TRANSMISSION at 350 nm on IRRADIATION.

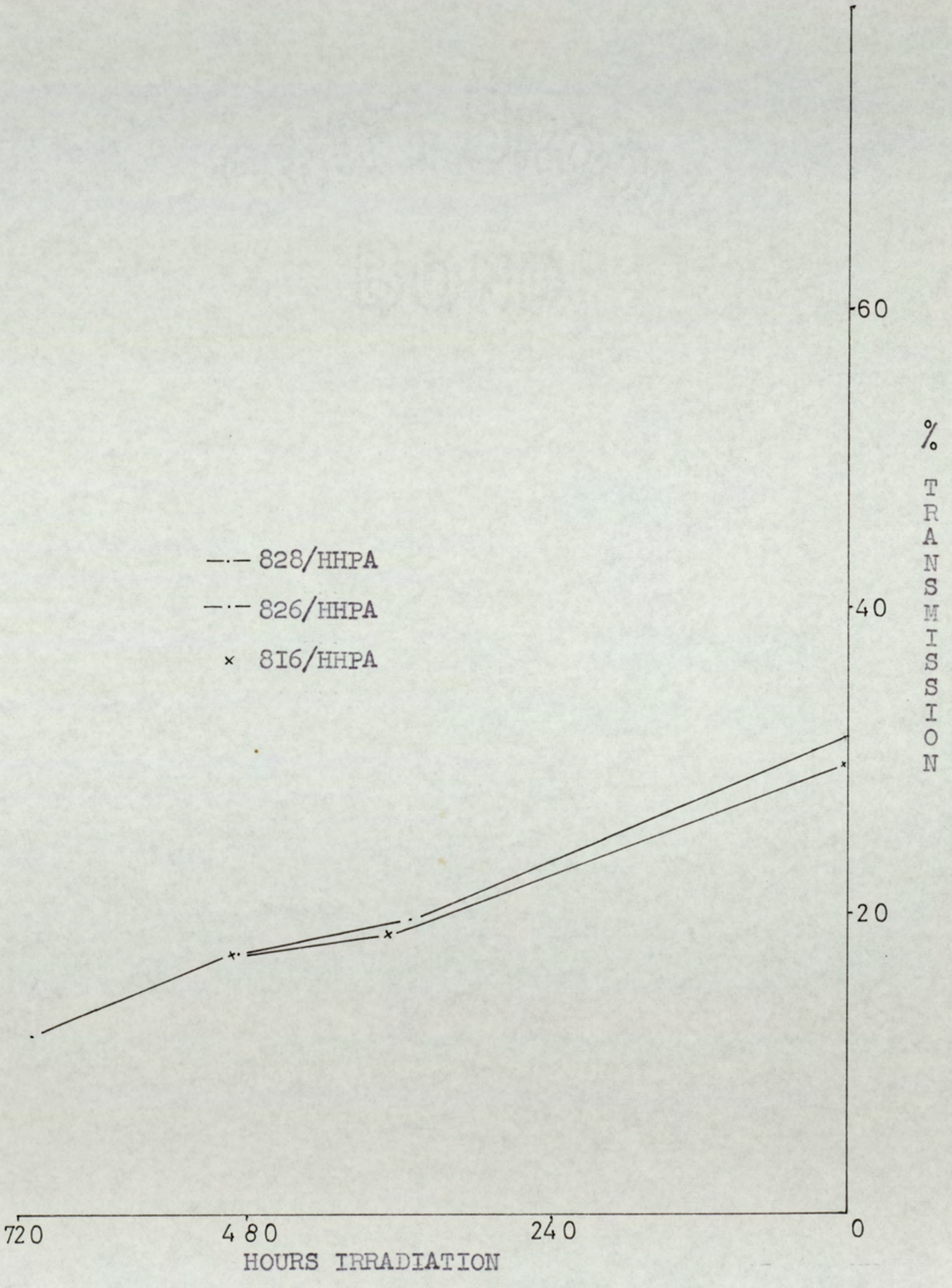


FIGURE 4-32 CHANGE in LIGHT TRANSMISSION at 350 nm on IRRADIATION.

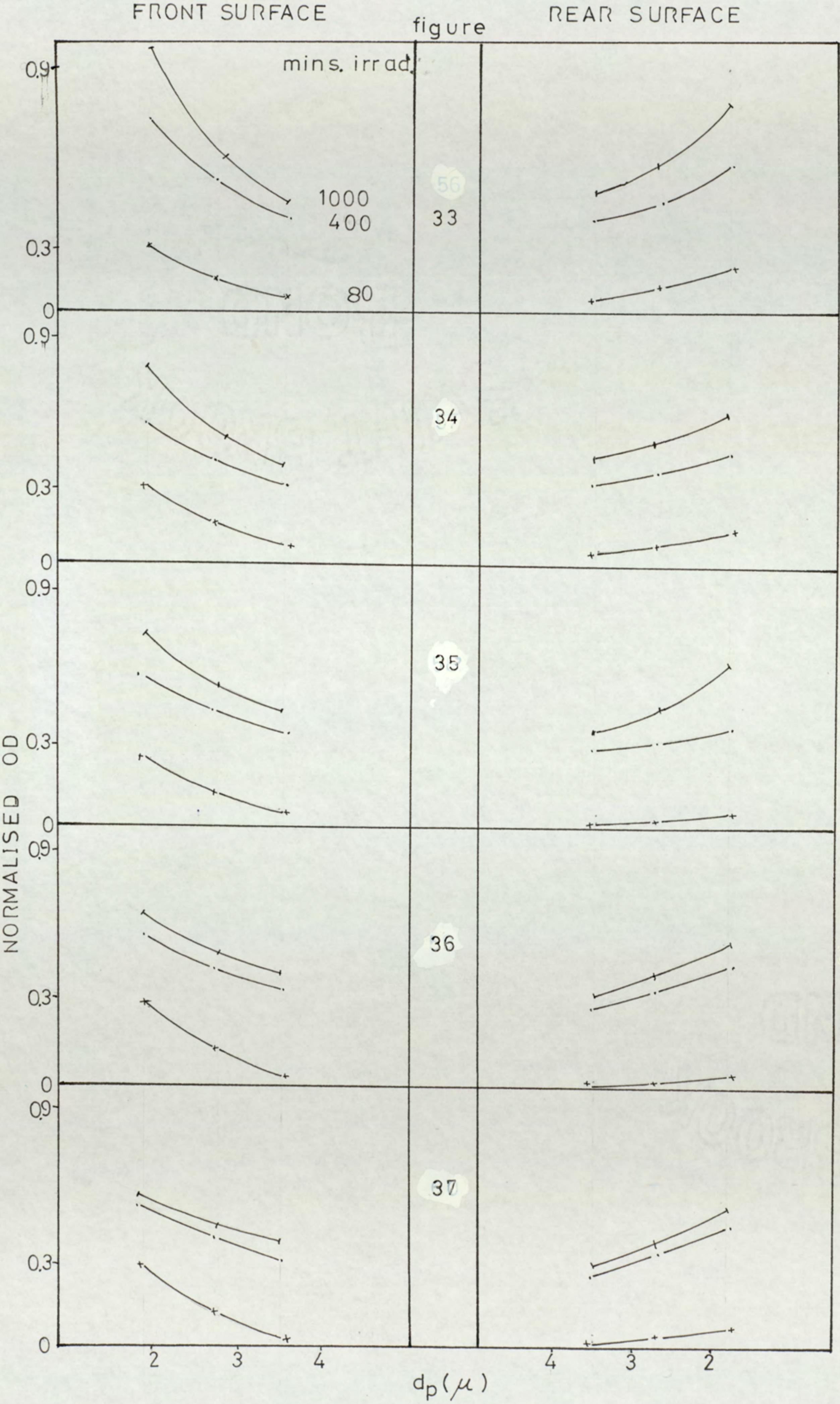


FIGURE 4–33 TO 4–37 PHOTOXIDATION OF FILM SANDWICH (5.81)

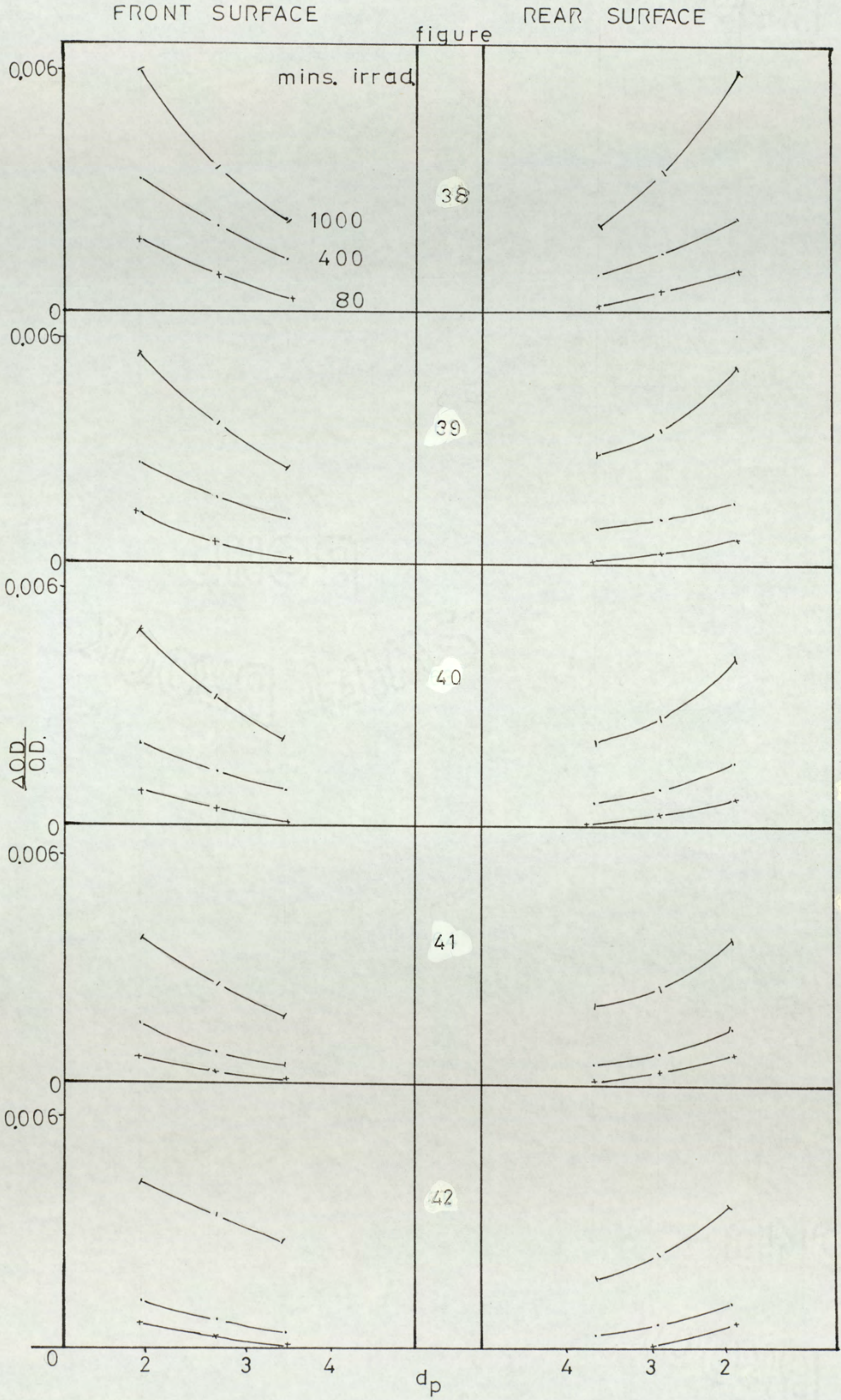


FIGURE 4-38 TO 4-42. PHOTOXIDATION OF FILM SANDWICH (6.06μ)

FIGURE 4-43 to 4-47 SANDWICH EFFECTS (5.8I micron)

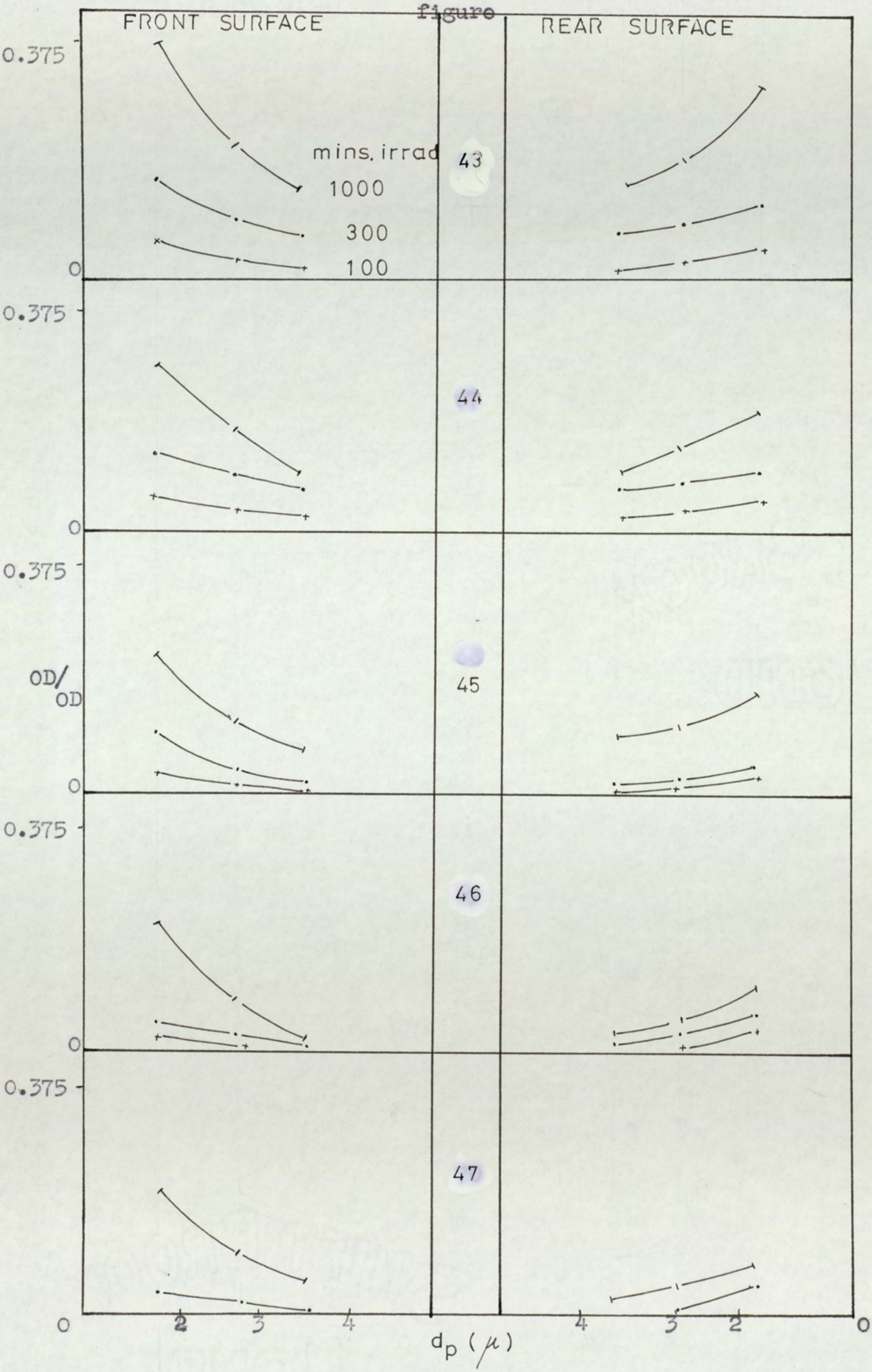
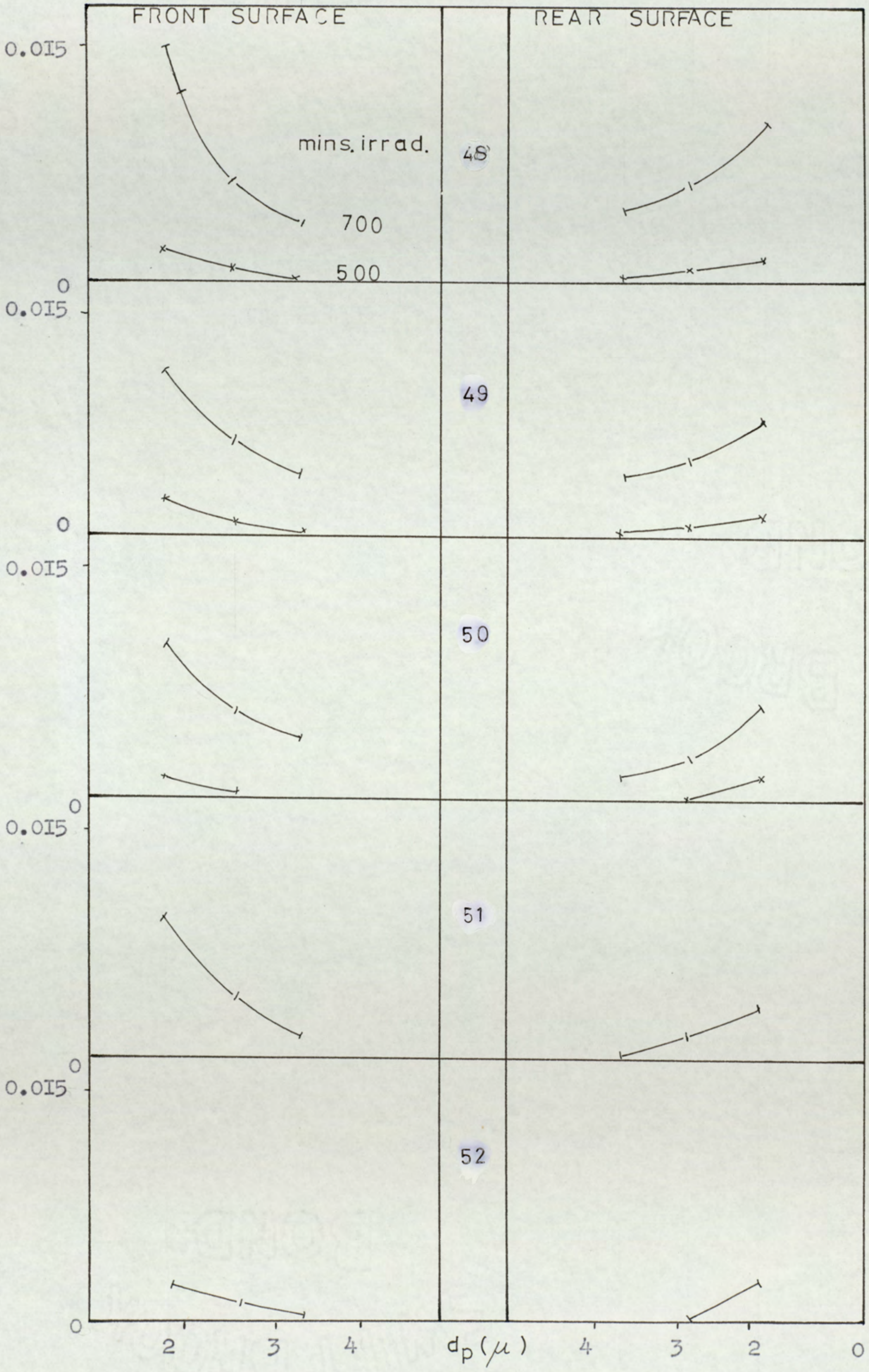


FIGURE 4-48 to 4-52 SANDWICH EFFECTS (6.06 micron)
figure



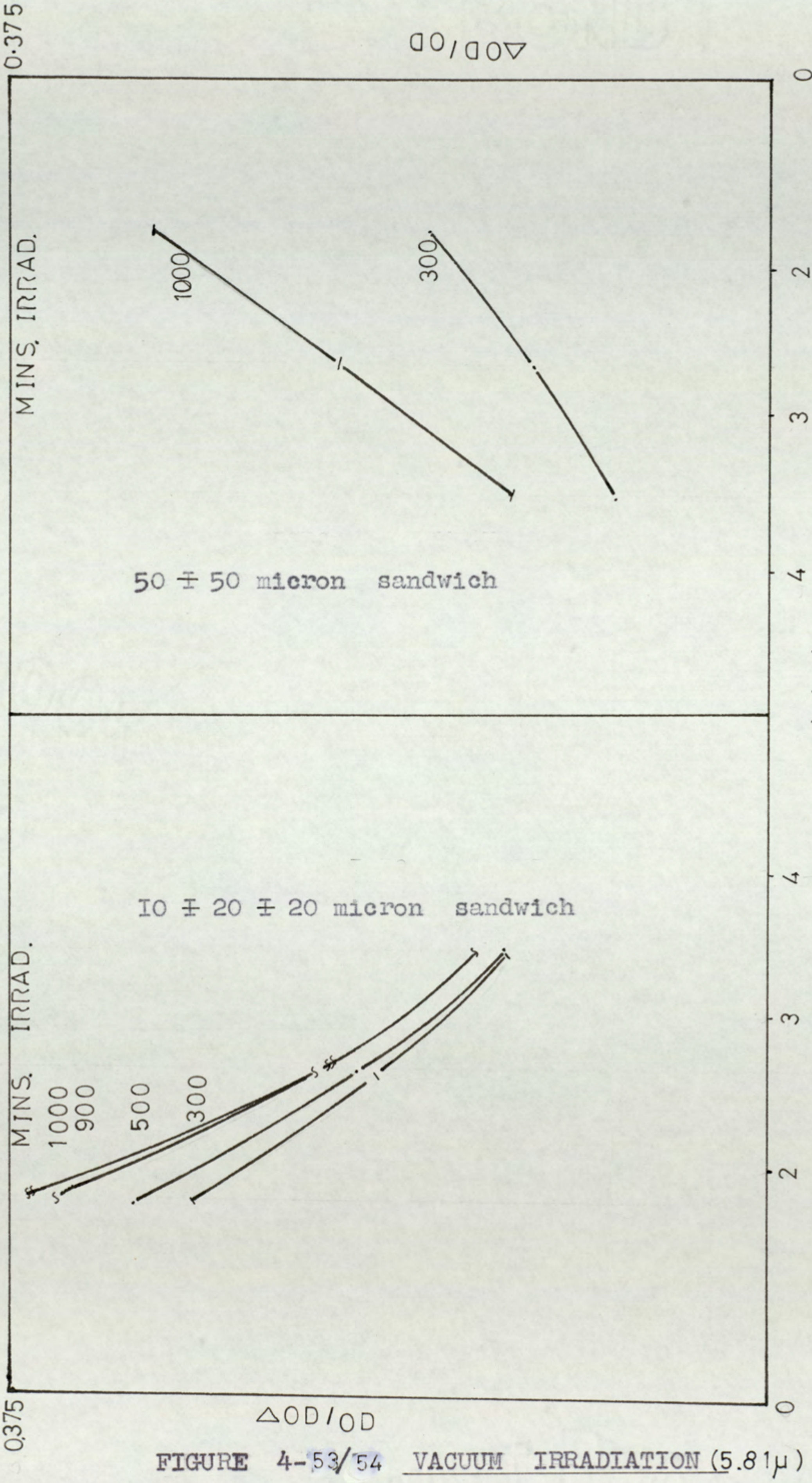


FIGURE 4-53/54 VACUUM IRRADIATION (5.81μ)

(Composites)

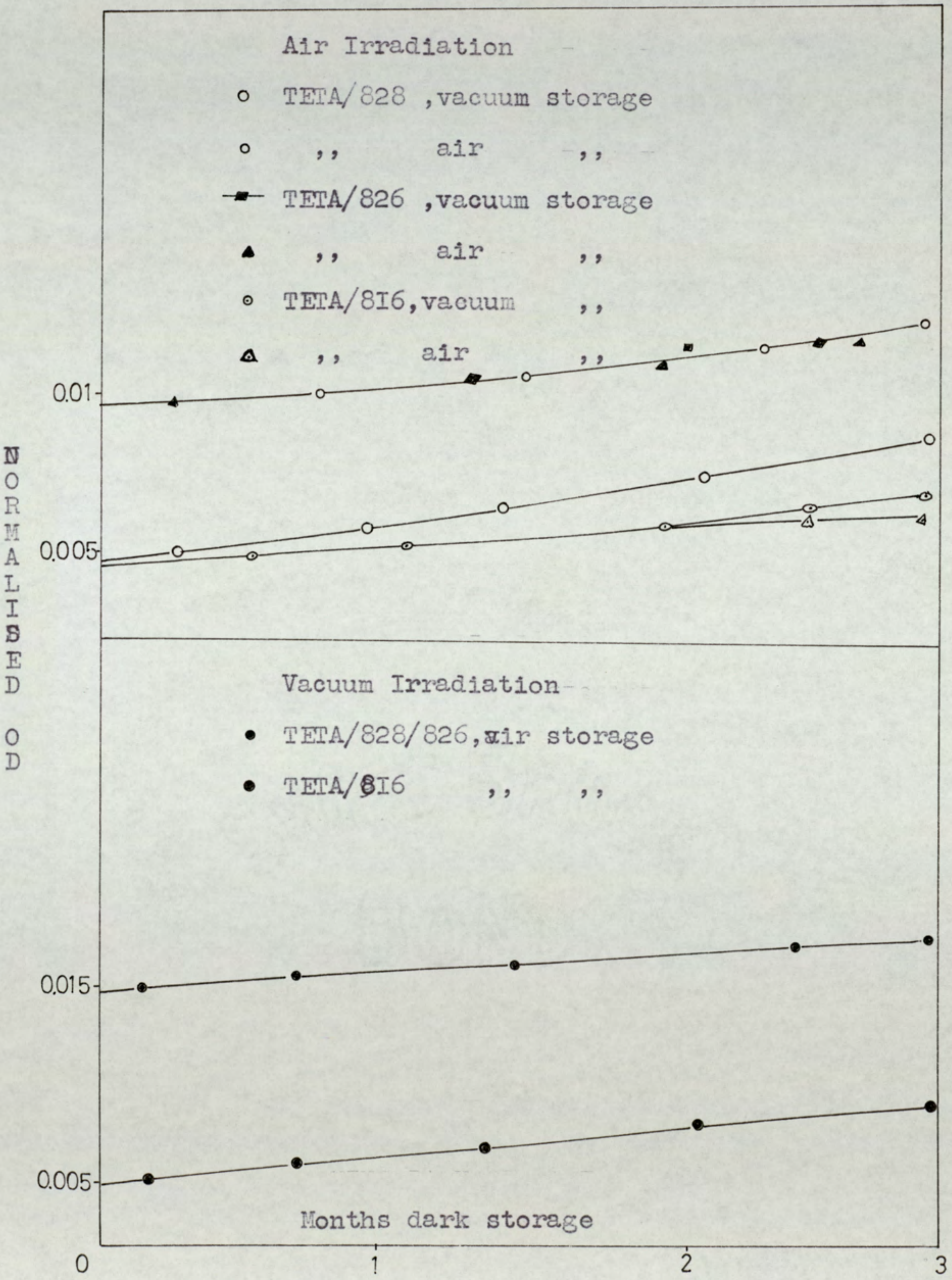


FIGURE 4-55 EFFECT of DARK STORAGE on INGROWTH of 5.81u BAND.

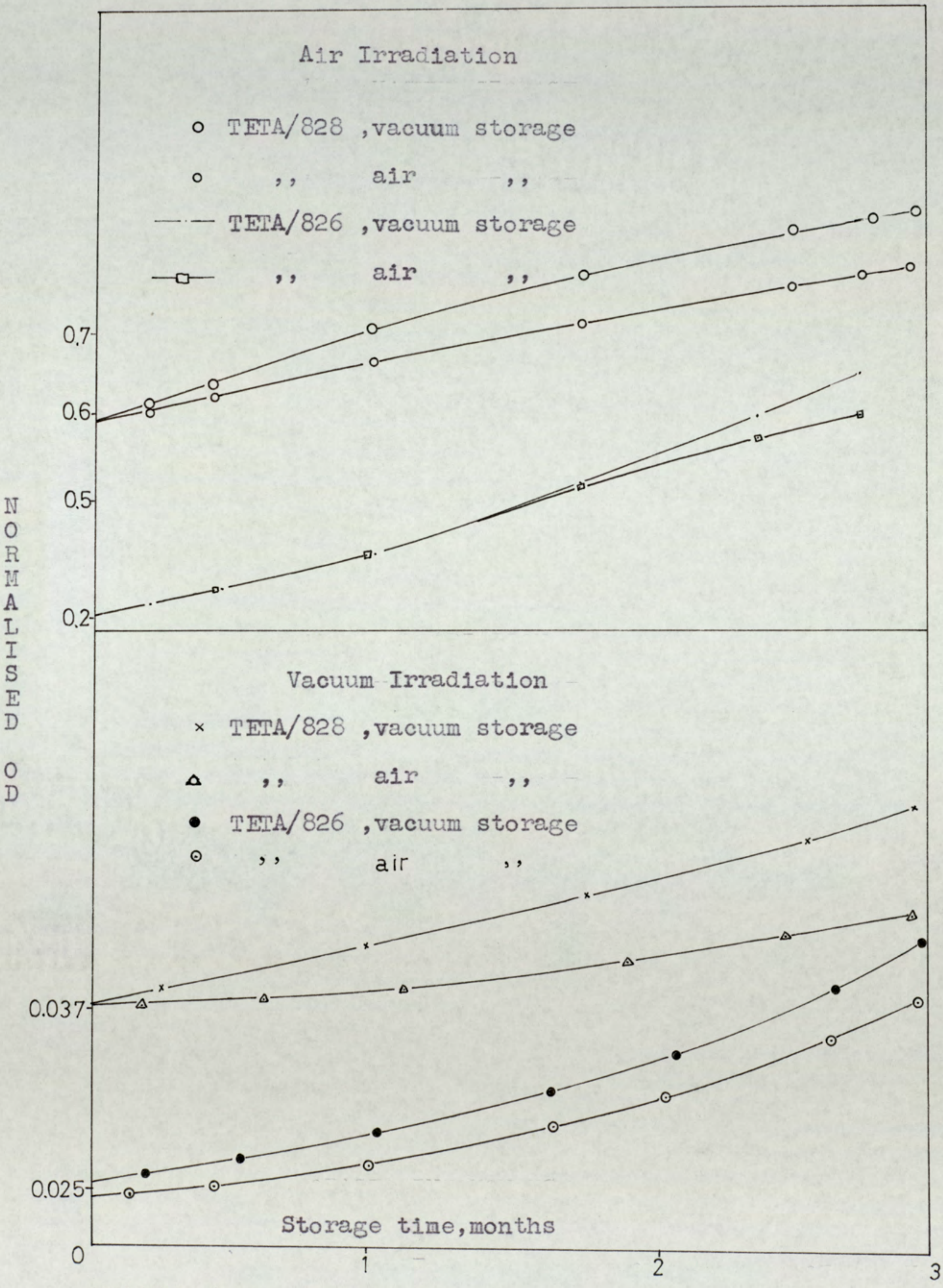


FIGURE 4-56 EFFECT of DARK STORAGE on INGROWTH of 6.06μ BAND.

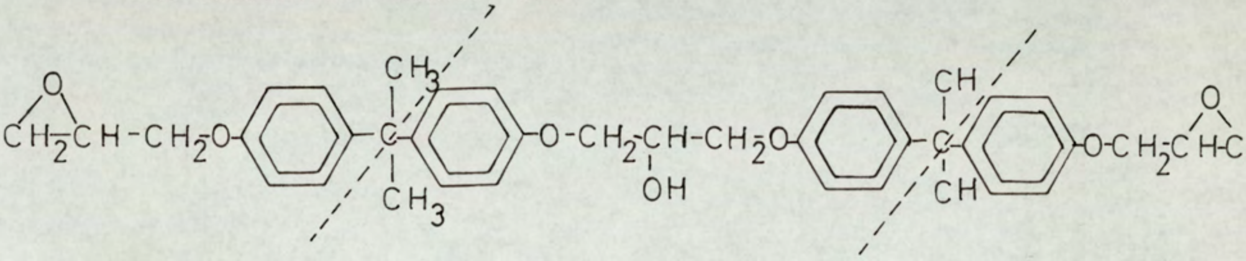
C H A P T E R   5

MODEL COMPOUND STUDIES

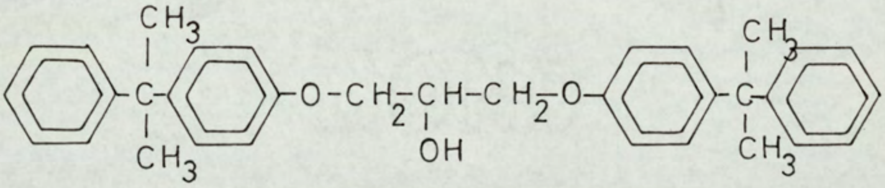
Introduction

The model compounds studied included curing agents, possible degradation products, units representing the epoxide monomer and compounds which contained "cure" links found in amine and anhydride cured resin systems.

The commercial monomer '828'

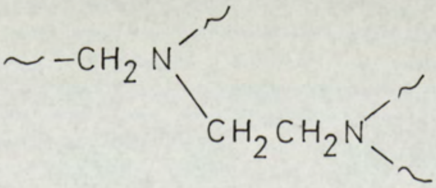


represented two compounds, two molecules of tolyl glycidyl ether and one of tolyl glyceryl ether. The unit representing the bisphenol-A monomer section was



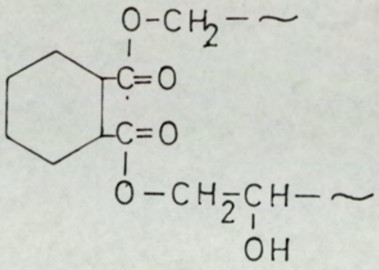
the glyceryl ether of diphenyl propane. Bisphenol-A was used to study the absorption of light by the benzene rings. Phenyl glycidyl ether which was available commercially was used as the unit representing unreacted chain ends in the cured system. The complete list of simple model compounds studied is shown (Table 5 - 1). Although these compounds were representative of the monomer no structural correlation existed with the cured resins. It was therefore necessary to investigate model compounds representing the cure links formed from the reactions of the curing agents TETA and HHPA. Bonds of the type

(1)

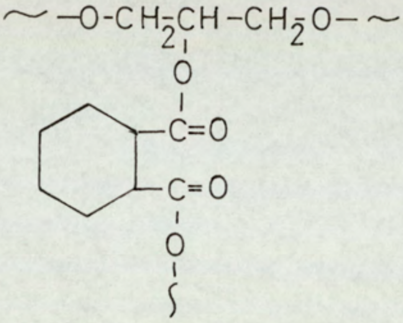


existed in the amine systems

(2)



(3)



in the anhydride materials

These compounds were reaction products of the epoxide group with the amine in (1) or with the anhydride in (2) and of the hydroxyl and anhydride in (3). Phenyl glycidyl ether was used as the epoxide containing molecule and it was reacted with TETA, ethylene diamine and di-ethyl amine.

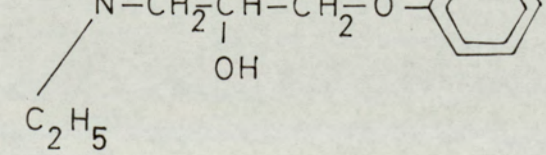
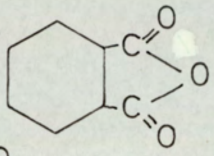
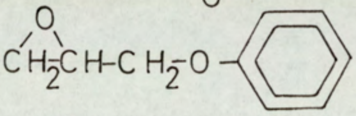
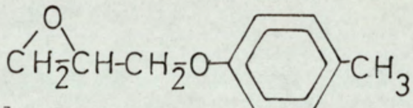
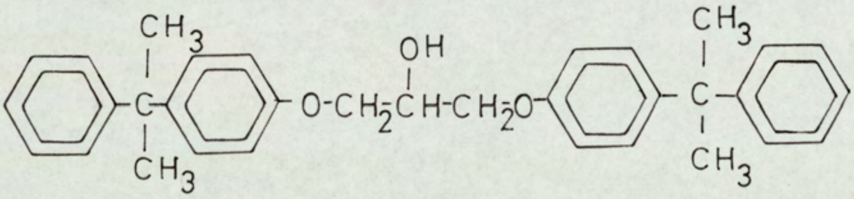
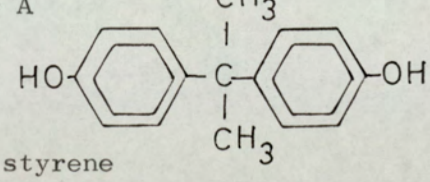
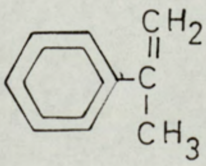


TABLE 5-1

Simple Model Compounds

No.	Compound	
1	triethylene tetramine	$NH_2-(-CH_2-)_2-NH-(-CH_2-)_2-NH-(-CH_2-)_2-NH_2$
2	hexahydrophthalic anhydride	
3	phenyl glycidyl ether	
4	tolyl glycidyl ether	
5	glyceryl ether of diphenyl propane	
6	monomer '826'	
7	monomer '828'	
8	bisphenol - A	
9	α - methyl styrene	

The di-ethylamine adduct represented the secondary nitrogen groups of TETA. Phenyl glycidyl ether and the glyceryl ether of diphenyl propane were reacted with HHPA and with cyclohexane carboxylic acid to form terminal and central ester bonds. The acid was used to prevent any gel formation and to allow chemical analysis by conventional techniques. The compounds studied are shown in Table 5 - 2.

The degradation of the materials resulted in the evolution of low molecular weight compounds and chemical changes in the bulk of the materials. The constituents of the liquid or solid phase were separated by TLC (acid washed silica stationary phase and carriers of benzene/ethyl acetate or ether/acetone/chloroform). GLC (Porapak-S and silica columns) was used for identification purposes using the internal standard technique. Since degradation reactions were known to result in chain scission and/or crosslinking (1) it was necessary to investigate molecular weight changes (by viscometry and mass spectrometry) during the irradiation. Mass spectrometry proved of little use with the complex high molecular weight materials because of the number of possible splitting patterns that resulted during the electron bombardment. Viscometry (Ubblode Viscometer) proved of greater use in the investigation of molecular weight changes. In some compounds irradiation resulted in gel formation. The gel was separated by gravity filtration and investigated by the viscometric technique and by infrared spectroscopy.

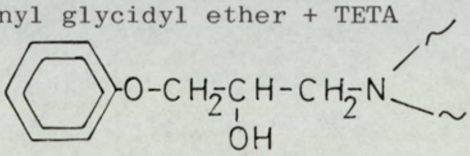
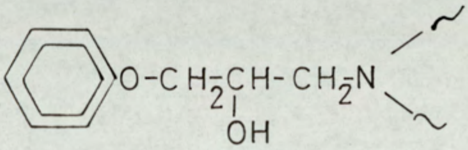
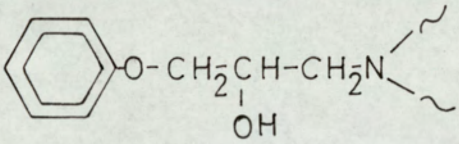
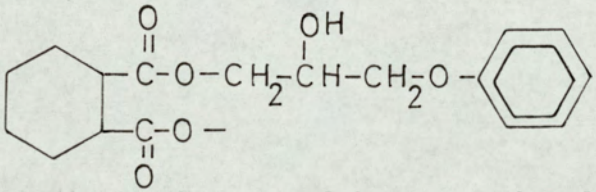
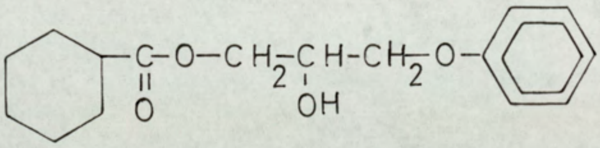
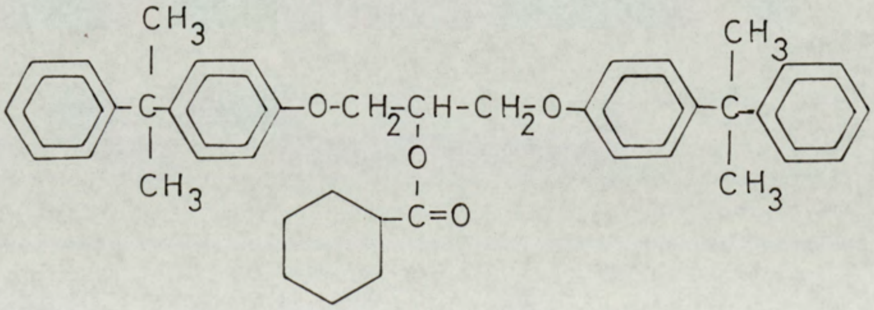
Transmission infrared spectroscopy was attempted to follow functional group changes during irradiation. However, because of the poor quality of the results the technique was discontinued. Some useful results were obtained,by this technique, in particular the detection of the ingrowth of new bands with a number of compounds.

The volatile degradation products were collected and identified. Quantification, however, proved difficult because of the type of material used and because of the number of products obtained.

The solid samples were prepared as thin films on the walls of the glass vessels (compounds 5 to 8) and by solvent casting (compounds 10 to 15). Vessels containing finely divided solid powder 2 cm in depth were used. The low viscosity liquid compounds (numbers 3, 4 and 9) were applied as thin films (up to 1 mm thickness) on quartz plates which were then placed in a horizontal position inside glass vessels.

TABLE 5 - 2

Cured Model Compounds

No.	Compound
10	phenyl glycidyl ether + TETA 
11	phenyl glycidyl ether + ethylene diamine 
12	phenyl glycidyl ether + diethyl amine 
13	phenyl glycidyl ether + HHPA 
14	phenyl glycidyl ether + cyclohexane carboxylic acid 
15	glyceryl ether of diphenyl propane + ropane + cyclohexane - carboxylic acid 

Bulk liquid samples (5 cm. depth) were also used for irradiation over long periods where concentration build-up of degradation products was expected to occur.

5 - 1 Physical Changes

Irradiation in oxygen or helium atmospheres resulted in colour formation in all compounds, save numbers 1, 2 and 9. Viscosity changes occurred in all compounds except the curing agents (Figure 5 - 1 to 5 - 4). In some compounds (5 to 7 and 11 to 15) gel formation occurred on irradiation (Figure 5 - 5 to 5 - 7).

Irradiation of the curing agents with the mercury arc caused no chemical changes in the bulk of the materials as evidenced by spectroscopic and chemical means. However, volatiles were evolved from both systems after 60,000 minutes irradiation. Thus although both of the materials did not absorb in the ultraviolet region at wavelengths greater than 250 nm, they were both subject to chemical degradation. This may have been due to impurities in the materials. Some hydrolysis of the HHPA by atmospheric moisture was found during photo-oxidative degradation in air. In oxygen filled, sealed vessels the hydrolysis was prevented and the time for detection of volatile degradation products was extended up to 100,000 minutes. The result was interpreted as being due to light absorption by the diacid formed. In the TETA, purification by distillation reduced the extent of the degradation, and the degradation was thought to have been caused by the impurities present in the commercial material. These results showed that the curing agents themselves were not the source of the degradation in the incompletely cured resins since very long irradiation times were required to cause the changes observed. The decrease in the free anhydride content of HHPA cured resins was not due to direct absorption of light by the anhydride, but to ring opening of the anhydride by active hydrogens and subsequent degradation or chemical reaction of the diacid.

α - Methyl styrene was sensitive to the radiation used as evidenced by the evolution of volatiles and the changes in the infrared spectrum of the material. Dimerisation occurred in oxygen and helium irradiation together with degradation of the monomer. Reproducibility of the results for this material was poor and confirmed the earlier work of Fox (2).

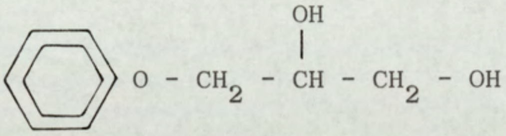
The colour formation with the simple models was seen by the shifts in the ultraviolet/visible spectral shifts (Table 5 - 3) and was found to be dependent on the purity of the materials used. This was reported by Lee and Watson (3).

TABLE 5 - 3

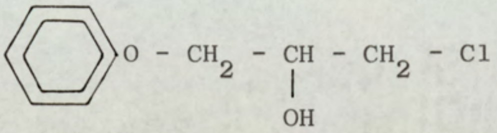
Wavelength Shift on Irradiation in Oxygen

Compound	Irradiation Time (minutes)	Maximum Wavelength (nm)	
Phenyl Glycidyl Ether	0	206.5	250
	60	216	278
	80	214	273
'828'	0	210	278
	60	218	278
	80	218	279
Glyceryl Ether of Diphenyl Propane	0	210	292
	60	218	292
	80	218	292

Structures such as



and



were known to be present in compounds 3, 4 6 and 7. The presence of the chlorine containing compounds undoubtedly contributed to the degradation in the systems. Purification of phenyl glycidyl ether did not prevent degradation as seen by the volatile degradation products (Table 5 - 4).

TABLE 5 - 4

Volatile Degradation Products from Phenyl and Tolyl Glycidyl Ether

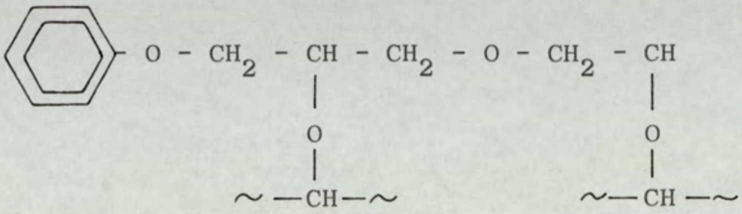
500 minutes Irradiation

Compound	Percentage by Volume			
	PhGE/O_2	PhGE/He	TGE/O_2	TGE/He
hydrogen	0.4	0.1	0.3	t
methane	t	0.2	0.2	0.2
ethane	t	0.2	t	t
propane	t	0.1	t	t
acetylene	t	0.1	t	0.1
ethylene	t	t	t	0.2
propylene	t	0.1	t	t
carbon monoxide	3.1	92.4	5.8	90.0
carbon dioxide	88.4	6.2	88.0	5.7
alcohols (C-3)	t	-	t	-
acetaldehyde	0.1	t	0.2	t
formaldehyde	0.1	0.1	0.1	t
acetic acid	0.2	t	t	-
formic acid	0.1	-	0.2	-
acrolein	t	-	t	-
chlorides	t	t	t	t
acetone	t	t	-	t
water	6.6	t	4.4	3.3
aromatics	t	t	t	t
unidentified	t	-	-	-

PhGE/O_2	phenyl glycidyl ether irradiated in oxidising atmosphere
PhGE/He	" " " " " helium "
TGE/O_2	totyl glycidyl ether irradiated in oxidising atmosphere
TGE/He	" " " " " helium "

t trace (less than 0.01 % by volume)

The large quantities of water evolved indicated some reaction of the hydroxyl group, either elimination of water from a molecule or condensation of two molecules of this type to form a new ether bond. However, no evidence was found for structures such as



No interrelation was found between changes in the ultraviolet/visible absorption spectra and the structural changes in the compounds seen by infrared spectroscopy. The degree of colouration was in the order

$$3 \sim 4 < 5 \lll 6 \sim 7 < 8$$

Secondary colour development (browning) was observed with compounds which contained the bisphenol-A group.

The cured model compounds (numbers 10 - 15) developed colour during their preparation. In particular the simple amine compounds were highly coloured (dark brown viscous liquids) and degradation by direct light absorption may have occurred on exposure to the radiation.

The change in the intrinsic viscosity of compounds 3 to 8 and 10 to 15 are shown for photo-and photo-oxidative degradation (Figures 5 - 1 to 5 - 4). Gel formation on irradiation is shown (Figures 5 - 5 to 5 - 7). In all systems the viscosity decreased to a constant value which was greater for photo-oxidative degradation. As expected little difference in behaviour was found for structurally similar materials e.g. compounds 6 and 7. The viscosity changes and gel formation were indicative of extensive molecular weight changes in the compounds. The results of the mass spectrometry determination of molecular weight are shown (Table 5 - 5). Little useful interpretation could be made of the results because of their poor reproducibility, which was undoubtedly due to the large number of splitting patterns which occurred on electron bombardment. The results showed that a reduction in molecular weight occurred during irradiation in inert atmosphere because of chain scission reactions in the compounds, while crosslinking reactions during photo-oxidation caused an increase in molecular weight.

TABLE 5 - 5

Molecular Weight Changes on Irradiation

Compound	Irradiation Time (minutes)	Molecular Weight	
		Oxygen	Helium
Phenyl Glycidyl Ether	0	150	150
	300	176	136
	3000	148	119
Tolyl Glycidyl Ether	0	169	169
	300	184	139
	3000	132	127
Monomer '828'	0	367	367
	300	476	530
	3000	387	356
Monomer '826'	0	294	294
	300	182	291
	3000	157	139

5 - 2 Chemical Changes on Irradiation

The chemical changes on photo and photo-oxidative degradation were investigated by transmission infrared spectroscopy and by wet chemical analysis (3).

5 - 2. 1 Spectroscopic Changes

Ingrowth of at least one new infrared band was found with all of the ethers studied. The results are shown in Table 5 - 6 for photo-oxidative degradation. The band assignments were the same as those used with the cured polymers. The rate of band ingrowth is shown for all of the compounds (Figures 5 - 8 to 5 - 13). The band at 6.1 microns was observed in all inert gas irradiated systems during the initial irradiation period, but decreased or disappeared after long irradiation periods.

Infrared spectra of all of the compounds were complex and many of the structural changes which occurred on irradiation were masked by strongly absorbing species in the undegraded materials.

TABLE 5 - 6

Spectroscopic Changes on Irradiation in Oxygen

Compound	Spectral Changes
3, 4	Reduction in epoxide band, ingrowth of hydroxyl band and band at 5.9 μ
5	Variation in hydroxyl and isopropylidene bands, ingrowth of two new bands at 5.9 μ and 6.1 μ, reduction in 1, 4,-disubstituted band
6, 7	Reduction in epoxide, isopropylidene and 1, 4,-disubstituted aromatic bands, variation in hydroxyl band, ingrowth of two new bands at 5.9 and 6.1 μ
8	ingrowth of new band at 6.1 μ
9	ingrowth of new band at 6.1 μ
10, 11 and 12	variation in hydroxyl band, ingrowth of new band at 5.9 μ
13, 14	ingrowth of new band at 5.9 μ
15	ingrowth of two new bands 5.9 and 6.1 μ Loss of ester band

5 - 2. 2 Functional Group Changes

The compounds were analysed for changes in the hydroxyl, epoxide and ester group contents during irradiation. The results are shown (Figure 5 - 14 to 5 - 19).

5 - 3 Identification of Degradation Products

The volatile degradation products for the model systems are shown (Table 5 - 6 to 5 - 9). The product analysis (solid and liquid phases) are shown (Table 5 - 10 to 5 - 15). In many of the systems the analysis was incomplete, because of difficulties with the identification of a large number of compounds and/or the small quantities present. Attempts to quantify the data were unsuccessful because of poor reproducibility of results.

Discussion of results

The decrease in intrinsic viscosity together with the type of compounds formed were indicative of a random bond scission degradation process. The greater decrease in viscosity during photo-degradation showed that bond scission occurred to a greater extent than during the photo-oxidative processes. The rate of change of viscosity was greater during photo-degradations for all of the compounds. This can be interpreted as crosslinking during photo-oxidative degradation and bond scission occurring during inert gas irradiations.

The presence of crosslinking reactions was shown by gel formation and occurred in all compounds save bisphenol-A which contained aliphatic hydroxyl groups in the undegraded state. Gel formation in both photo- and photo-oxidative degradation indicated that the phenomenon was the result of reactions of species present in the backbone of the compounds or from radicals derived from them, rather than from peroxide radicals. Oxygen present in the helium filled reaction vessels may have contributed to the initial gel formation. This oxygen would have been consumed in the formation of peroxy radicals during early stages of gel formation. Since the extent of gel formation was greater in photo-oxidised compounds oxygen may have contributed to the process. Gel formation did not occur in phenyl or tolyl glycidyl ether, though ring opening of the epoxide group would have been expected to produce compounds such as

TABLE 5 - 6

Volatile Degradation Products from Monomers '826' and '828'*

Compound	% by Volume			
	'826'		'828'	
	Oxygen	Helium	Oxygen	Helium
Hydrogen	0.39	6.94	0.52	7.50
Methane	0.55	8.37	0.67	9.0
Ethane	0.04	5.36	0.01	6.41
C-3/C-4 hydrocarbons	-	0.88	-	-
Ethylene	0.01	0.77	0.01	0.63
Acetylene	0.07	0.09	0.01	0.18
Acetone	0.03	-	0.04	-
Acetaldehyde	0.69	-	0.57	-
Formaldehyde	0.06	-	0.04	-
Propionaldehyde	t	-	t	-
Acetic Acid	t	-	t	-
Formic Acid	t	-	-	t
Carbon Monoxide	8.12	69.45	7.88	66.75
Carbon Dioxide	89.88	7.26	89.92	7.88
Acrolein	0.02	-	0.03	-
Water	0.01	-	0.03	0.58
Chlorides	t	t	-	0.04
Benzene	-	-	-	t
p-Cresol	t	-	t	-
Phenols	0.10	0.86	0.23	0.99
Propanol	0.03	t	0.03	t
α - Methyl Styrene	-	t	-	0.02

* 500 minutes irradiation

t - trace, less than 0.01 %

TABLE 5 - 7

Volatile Degradation Products from models 5 and 8*

	% by Volume			
	Bisphenol-A		GE DPP (5)	
	Oxygen	Helium	Oxygen	Helium
Hydrogen	0.37	1.12	1.73	10.22
Methane	t	0.01	0.67	10.69
Water	t	t	0.93	0.44
Acetylene	-	0.11	-	0.46
Ethylene	-	0.10	0.35	0.67
Ethane	-	t	0.87	4.01
Acrolein	-	-	0.07	-
C-3/C-4 hydrocarbon	-	0.77	-	1.00
Acetone	3.49	2.00	2.92	0.78
Acetaldehyde	t	t	0.08	-
Formaldehyde	t	-	0.01	t
Acetic Acid	0.11	-	-	-
Formic Acid	0.43	-	-	-
Carbon Monoxide	t	84.53	2.91	66.94
Carbon Dioxide	93.33	9.30	89.12	3.55
Benzene	-	-	-	t
Phenols	2.11	0.84	0.08	0.04
α-Methyl Styrene	-	t	-	t
C-3 Alcohols	0.30	1.22	0.26	0.14

* 300 minutes irradiation

t - trace

TABLE 5-8

Volatile Degradation Products from Amine Cured Models*

Compound	% by Volume					
	10		11		12	
	Oxygen	Helium	Oxygen	Helium	Oxygen	Helium
Hydrogen	0.78	0.91	0.22	4.11	0.33	3.70
Methane	t	0.20	t	6.20	t	3.10
Ethane	t	0.20	t	0.90	t	0.70
Propane	t	0.10	t	0.40	t	0.30
Acet-ylene	t	t	t	0.01	t	0.01
Ethylene	t	t	t	t	t	0.01
C-3 Hydrocarbon	0.10	0.15	t	0.18	t	0.11
C-3 Alcohol	-	t	t	t	t	t
C-6 Glycol	-	-	t	0.01	-	-
Carbon Monoxide	3.36	82.01	2.77	76.44	1.20	70.32
Carbon Dioxide	80.70	5.10	88.50	2.00	84.70	4.11
Acetaldehyde	t	t	t	t	0.01	t
Formaldehyde	t	-	0.04	-	0.03	-
Acetic Acid	0.10	-	0.04	t	0.01	-
Formic Acid	0.10	t	0.01	t	0.04	-
Acrolein	t	t	-	t	-	-
Acetone	t	t	t	0.03	t	0.03
Water	4.77	3.20	3.73	3.46	5.12	3.20
Aromatics	t	t	t	t	t	t
Ethylene diamine	-	0.01	-	-	-	-
Ethyl amine	-	-	-	-	-	t
Dimethyl Hydroxylamine	-	-	-	0.04	-	-
Unidentified	10.07	8.1	4.67	6.25	8.54	14.40

* 100 minutes irradiation

t - trace, less than 0.01 %

TABLE 5 - 9

Volatile Degradation Products from Models 13, 14, 15*

Compound	% by Volume					
	13		14		15	
	Oxygen	Helium	Oxygen	Helium	Oxygen	Helium
Hydrogen	0.01	0.04	0.01	t	2.0	7.63
Methane	-	t	t	0.01	-	8.92
Water	4.11	t	t	t	0.91	0.72
Acetylene	-	t	-	t	-	0.44
Ethylene	-	t	-	t	-	0.71
Ethene	-	-	t	t	t	t
Acrolein	-	t	-	-	-	-
C-3 Hydrocarbon	-	t	-	0.03	t	0.60
C-6 Hydrocarbon	-	0.01	-	t	-	0.10
Acetone	t	t	t	t	t	t
Acetaldehyde	0.20	0.01	0.10	-	0.01	t
Formaldehyde	0.04	-	0.10	-	0.01	-
Acetic Acid	0.01	t	0.01	t	0.01	-
Formic Acid	t	-	0.02	t	t	-
Carbon Monoxide	2.60	80.00	3.90	86.70	2.97	70.06
Carbon Dioxide	90.17	6.90	91.40	5.00	90.20	5.11
Benzene	t	t	t	t	-	t
Phenols	t	t	0.01	t	t	-
C-3 Alcohols	t	-	t	-	0.40	0.10
Cyclohexane	t	t	-	t	t	t
Unidentified	2.84	13.02	4.44	8.23	3.49	5.60

* 100 minutes irradiation

t - trace

TABLE 5 - 10

Product Identification from Photo-and Photo-Oxidative Degradation of Phenyl and Tolyl glycidyl Ether

Product	Compound			
	Phenyl Glycidyl Ether		Tolyl Glycidyl Ether	
	Oxygen	Helium	Oxygen	Helium
Phenol	+	+	-	-
p -Cresol	-	-	+	+
p -Hydroxy-benzaldehyde	-	-	+	+
p -Hydroxybenzoic acid	-	-	+	-
Acrolein	+	-	+	-
Acetone	-	+	-	+
Acetaldehyde	+	-	+	-
Acetic Acid	+	-	+	-
Formaldehyde	+	-	+	-
Formic Acid	+	-	+	-
Unidentified	+	+	+	-

\+ Present

\- Absent

TABLE 5 - 11

Product Identification for Photo-and Photo-Oxidative Degradation of Bisphenol-A and Glyceryl Ether of Diphenyl Propane

Product	Compound			
	Bisphenol-A		Glyceryl Ether	
	Oxygen	Helium	Oxygen	Helium
Phenol	(l)	(l)	+	+
p-Isopropyl Phenol	+	+	-	-
p-Isopropenyl Phenol	-	+	-	+
Quinone	(s)	+	+	-
Hydroquinone	+	-	-	+
Acetone	+	-	-	+
Acetaldehyde	+	+	+	+
Formaldehyde	+	+	+	+
Propanol	-	-	-	+
α-Methyl Styrene	-	-	-	+
Gel	-	-	+	+
p-Isopropylbenzene	-	-	-	+
Acetic Acid	-	-	+	-
Formic Acid	-	-	+	-
Benzene	-	-	+	-

l	large quantity
s	small quantity
+	present
-	absent

TABLE 5 - 12

Product Identification for Photo-and Photo-Oxidative Degradation of Compounds 6 and 7

Product	Compounds 6 and 7	
	Photo-Degradation	Photo-Oxidative Degradatio
acetaldehyde	+ (s)	+ (s)
acetic acid	-	+ (s)
acrolein	+ (s)	+ (s)
acetone	+ (s)	+ (l)
formaldehyde	+ (s)	+ (s)
formic acid	+ (s)	+ (s)
propionaldehyde	+ (s)	+ (s)
water	+ (s)	+ (s)
phenol	+ (l)	+ (l)
bisphenol-A	+ (s)	+ (s)
p-isopropyl phenol	+ (s)	-
p-isopropenyl phenol	+ (s)	-
quinone	+ (s)	+ (l)
hydroquinone	+ (s)	-
unidentified	+ (s)	+ (s)
gel	+ (l)	+ (l)

s	small quantity
l	large quantity
+	Present
-	absent

TABLE 5 - 13

Product Identification for Photo-and Photo-Oxidative Degradation of Compounds 10, 11 and 12

Product	Compound					
	10		11		12	
	p.oxid.	Photo	P.oxid.	Photo	P.oxid.	Photo
Phenol	+	+	+	+	+	+
Propanol	−	+	−	+	−	+
Formaldehyde	+	+	+	−	+	−
Formic Acid	+	−	+	−	+	−
Water	+	+	+	+	+	+
Gel	+	+	+	+	+	+
Ethylene diamine	−	+	−	+	−	−
Unsaturated amine	−	+	−	−	−	+
Aldehyde	+	−	−	−	+	+
Unsaturated ether	+	−	−	−	+	+
Oxime	−	−	+	−	+	+
Ethyl amine	−	−	−	−	−	+
Coloured nitrogen compounds	−	−	+	+	−	+
C - 6 glycol	−	−	−	+	−	+

P.oxid. - Photo-oxidative degradation

Photo - Photo-degradation

TABLE 5 - 14

Product Identification for Photo-and Photo-Oxidative Degradation of Compounds 13 and 14

Product	Compound			
	13		14	
	P.oxid.	Photo	P.oxid.	Photo
Phenol	+	+	+	+
Curing agent	+	+	+	+
Benzene	-	-	-	-
Cyclohexane	-	+ (t)	-	+ (t)
Propanol	-	+	-	+
Acetone	-	-	-	+ (t)
Gel	+	+	+	+
Water	+	+	+	+
Unidentified	+	+	+ (1)	+ (1)
C-6 unsaturated ether	+	-	+	-
Aldehyde	+	-	+	-
C-3 aldehyde	-	-	-	-

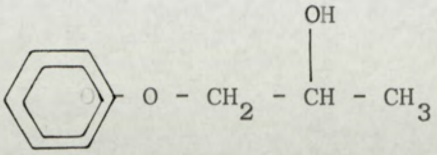
P.oxid. - Photo-oxidative degradation

Photo - Photo-degradation

TABLE 5 - 15

Product Identification for Photo-and Photo-Oxidative Degradation of Compound 15

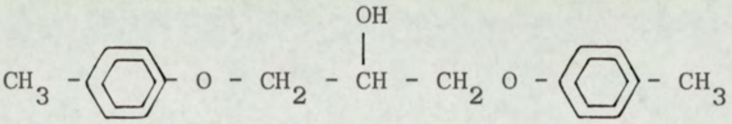
Product	Compound 15	
	Photo-Oxid,	Photo
p - cresol	-	-
Phenol	+	+
Quinone	+	-
p - isopropenylphenol	+	+
Acetone	+	-
Curing Agent	+	+
cyclohexane	+	+
Ether saturated	-	-
C - 6 alcohols	+	-
C - 8 alcohols	+	-
p - hydroxybenzaldehyde	-	-
acetaldehyde	+	-
Acetic acid	+	-
Unidentified	+	-



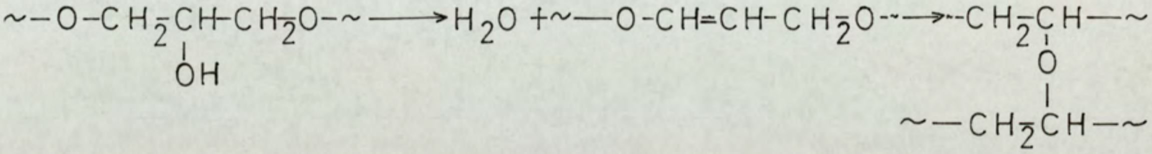
during photo-degradation.

However, no compounds of this type were found in the degradation products identified. The hydroxyl content of both of these compounds was due to formation of low molecular weight degradation products, which occurred at time intervals greater than the time of elimination of the epoxide groups.

Gel formation was found in compounds which contained aliphatic hydroxyl groups in the undegraded state. Also irradiation of tolyl glyceryl ether



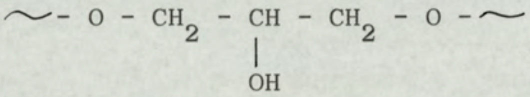
resulted in gel formation at an equivalent rate, but not to the same extent as that found with the glyceryl ether of diphenyl propane. Therefore the bisphenol-A portion of the latter was not responsible for the gel forming reactions. Gel formation in all cases was accompanied by the formation of water as a volatile degradation product, which increased in quantity with increase in gel formation. It therefore seemed likely that a condensation reaction occurred at the aliphatic hydroxyl group, as with simple alcohols (4)



$$\sim\!-O-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2O-\sim\;\longrightarrow H_2O+\sim\!-O-CH{=}CH-CH_2O-\sim\;\longrightarrow\begin{array}{c}-CH_2-CH-\sim\\ |\\ O\\ |\\ \sim-CH_2-CH-\sim\end{array}$$

Elimination of water in simple alcohols occurs with radiation of wavelength less than 200 nm. This rules out the possibility of such reactions with the radiation source used. However bathochromic shifts may have been induced by neighbouring groups such as ether or the aromatic ring. Further support for this water elimination was found by the isolation of an unsaturated ether compound in the degradation products of the gel forming model compounds. Acetylation of the hydroxyl group of compound 5 with acetyl chloride prevented gel formation on irradiation. This also indicated that the initiation of the gel forming reactions was not by peroxides.

Gesner and Kelleher (5) reported that gel formation occurred with phenoxy resins which were structurally similar to the model compounds. Studies (6) on polysulphone and polycarbonate showed no gel formation, which was further proof of reaction at the aliphatic hydroxyl group. Consideration of the simplest gel forming model compounds, glyceryl, ether of diphenyl propane and tolyl glyceryl ether, showed they contained a common structural unit.



$$\sim\!-O-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-O-\!\sim$$

The difference in the rate and extent of the gel formation in compound 5 must have been associated with the terminal substituents on the molecules. Since greater quantities of gel were formed under photo-oxidative conditions, oxygen obviously assisted the process. In photo-oxidative degradations the following recombinations are possible

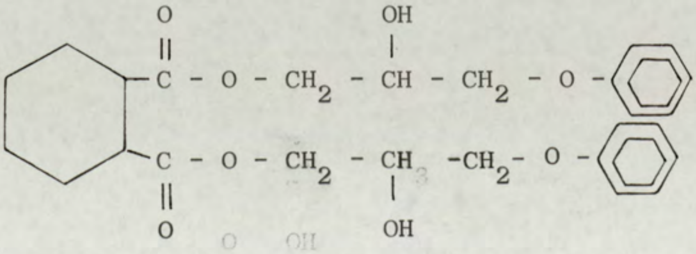
(i) ROO. + R. $\longrightarrow$ ROOR $\longrightarrow$ decomposition

(ii) RO. + R. $\longrightarrow$ ROR

In an inert atmosphere only the latter type of reaction can occur. The similarities in the rates of gel formation in photo-oxidative and photo-degradative processes can be explained by type (ii) reaction. The difference in the extent of gel formation can be explained by type (i) reaction or a combination of both reactions. Gel formation was observed with the commercial epoxide monomer '828' only after long irradiation periods (Figure 5 - 5). This was probably due to the small quantity of hydroxyl containing species in the material, and although gel formation did occur its presence was not detected due to the small quantities involved. Also because of the high viscosity of this model compound diffusion controlled reactions would be expected to occur, but to a lesser extent than in the solid state. The initial degradation, by analogy with the cured resins, would be expected to be uniform throughout the sample and decrease with the degree of colour formation. Therefore an inhibition of the gel forming process may have occurred with time.

The rates of viscosity change and gel formation differed in the simple and cured model compounds which contained structural units. No gel formation was observed with compound 10 which was similar to compounds 11 and 12. This can be ascribed to the solid nature of the compoundsas opposed to the viscous liquid state (compound 11 and 12) where the mobility necessary for the gel forming process was possible. This does not rule out the possibility that gel formation occurred to some degree in compound 10 as water was evolved as a degradation product. Gel formation was detected in the solid, compound 5, the glyceryl ether of diphenyl propane. The rate of gel formation was greater with the amine compounds than with compound 5. This may have been due to the carbon to nitrogen bond in the former or more likely to the bulky substituents in the glyceryl ether of diphenyl propane.

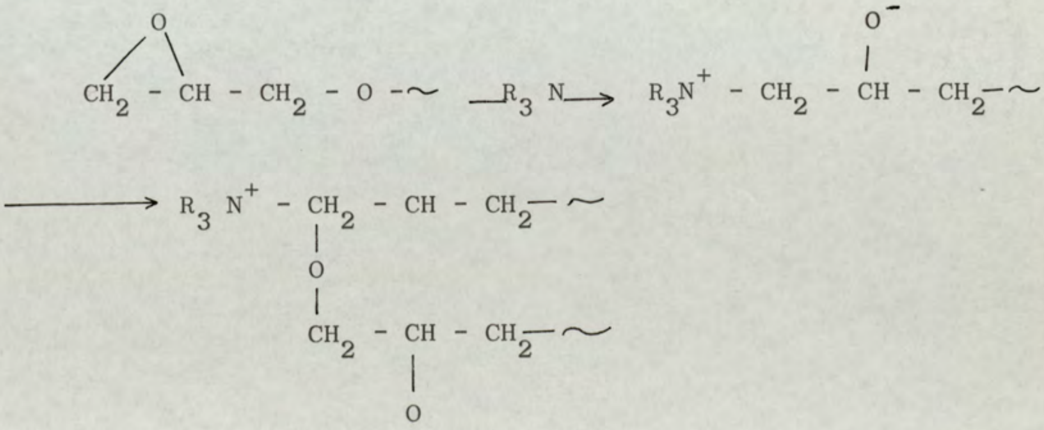
The rate of viscosity decrease was greater in the amine cured models (compounds 10, 11 and 12) than the monomer phenyl glycidyl ether. This could have been due to the presence of the amine groups or to rearrangements in the amines resulting in species which absorbed strongly in the visible spectrum. Similar rearrangements were not possible in the three-dimensional crosslinked resins. However after the initial bond scission reactions, rearrangements may have occurred accounting for the formation of colour forming species. This steric restriction in the solid state may have been responsible for the small quantity of high molecular weight material isolated from the degraded resins. The viscosity changes in the terminal ester compounds 13 and 14 occurred at faster rates than in phenyl glycidyl ether. This was attributed to a hydrogen bonding interaction, which was greatest in compound 14 and accounted for the greater viscosity change in this compound. Gel formation did not occur in compound 13 because of the steric restrictions on the molecule



Attempts to identify the gel by infrared spectroscopy and functional group tests failed. However, the results suggested that the predominant constituent was an aliphatic ether of molecular weight approximately 300. Pyrolysis GLC was attempted as a method of identification, however, due to the number and proportion of constituents in the gel little useful results were obtained, other than showing the aliphatic nature of the gel.

No gel formation occurred with the simple epoxide ethers (compounds 3 and 4). Photo-and photo-oxidative irradiation of tolyl glycidyl ether resulted in chain scission and crosslinking respectively. Phenyl glycidyl ether behaved in a different manner, irradiation in an oxidising atmosphere yielded a brown/grey crystalline material. No similar compound was found in the degraded amine or anhydride cured materials. Examination of the crystalline material by spectroscopic and chemical techniques showed that the compound was of molecular weight 600 to 900 and contained hydroxyl groups. No epoxide groups were found by either chemical analysis or infrared spectroscopy. Comparison with the work of Ada (7) and others (8, 9, 10) showed that polymerisation of phenyl glycidyl ether had occurred. The infrared pattern was similar to that of fraction three of the 700 to 800 molecular weight species isolated by Tanaka (8), from the catalysed polymerisation of phenyl glycidyl ether.

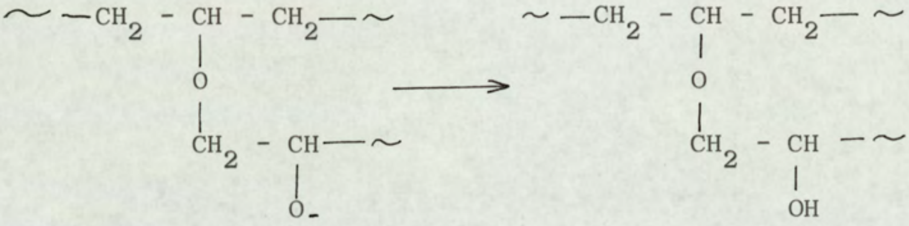
Normally polymerisation of epoxides is catalysed by metal hydroxides, tertiary amines and other species capable of causing ring opening of the epoxide group.



The initiation with the observed photo-oxidative polymerisation may have been caused by peroxides or the degradation products which resulted from ether bond scission.

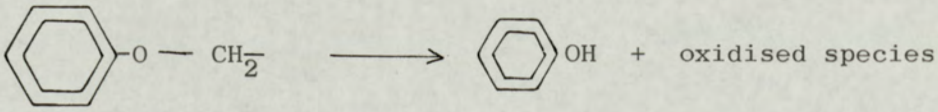
Examination of the degradation products from photo-and photo-oxidation (Table 5 - 4) showed a qualitative difference in the aliphatic compounds obtained. Since these products were thought to be the result of peroxide formation during photo-oxidative degradation and since polymerisation occurred after long exposures to the radiation, the oxidised degradation products probably controlled the polymerisation process. No high molecular weight material was found from the photo-degradation of phenyl glycidyl ether. Degradation of tolyl glycidyl ether did not yield crystalline high molecular weight products but resulted in formation of similar aliphatic compounds to those of phenyl glycidyl ether. However, the aromatic compounds differed in that highly acidic compounds were formed from tolyl glycidyl ether and the conditions necessary for polymerisation were not attained.

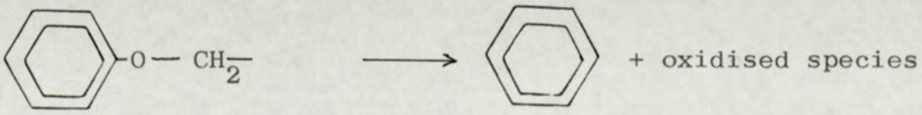
A high rate of chain termination occurred during the formation of polyphenyl glycidyl ether as evidenced by the formation of hydroxyl groups



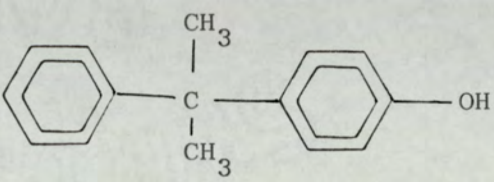
and the low degree of polymerisation (four to six for molecular weights of 600 to 900, based on the molecular weight of the original phenyl glycidyl ether of 150).

The product analysis (Table 5 - 4 to 5 - 15) indicated that the degradation of the model ethers occurred at the ether bond, as was also the case with the cured resins. The degradation resulted in the formation of phenolic compounds together with small quantities of benzene

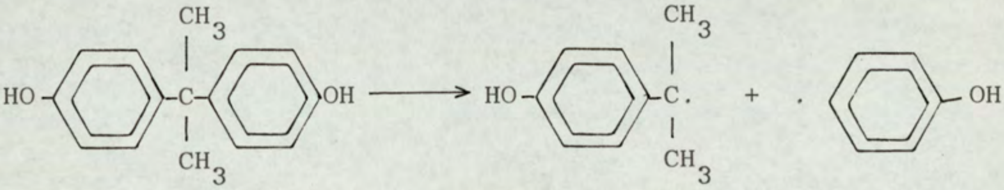




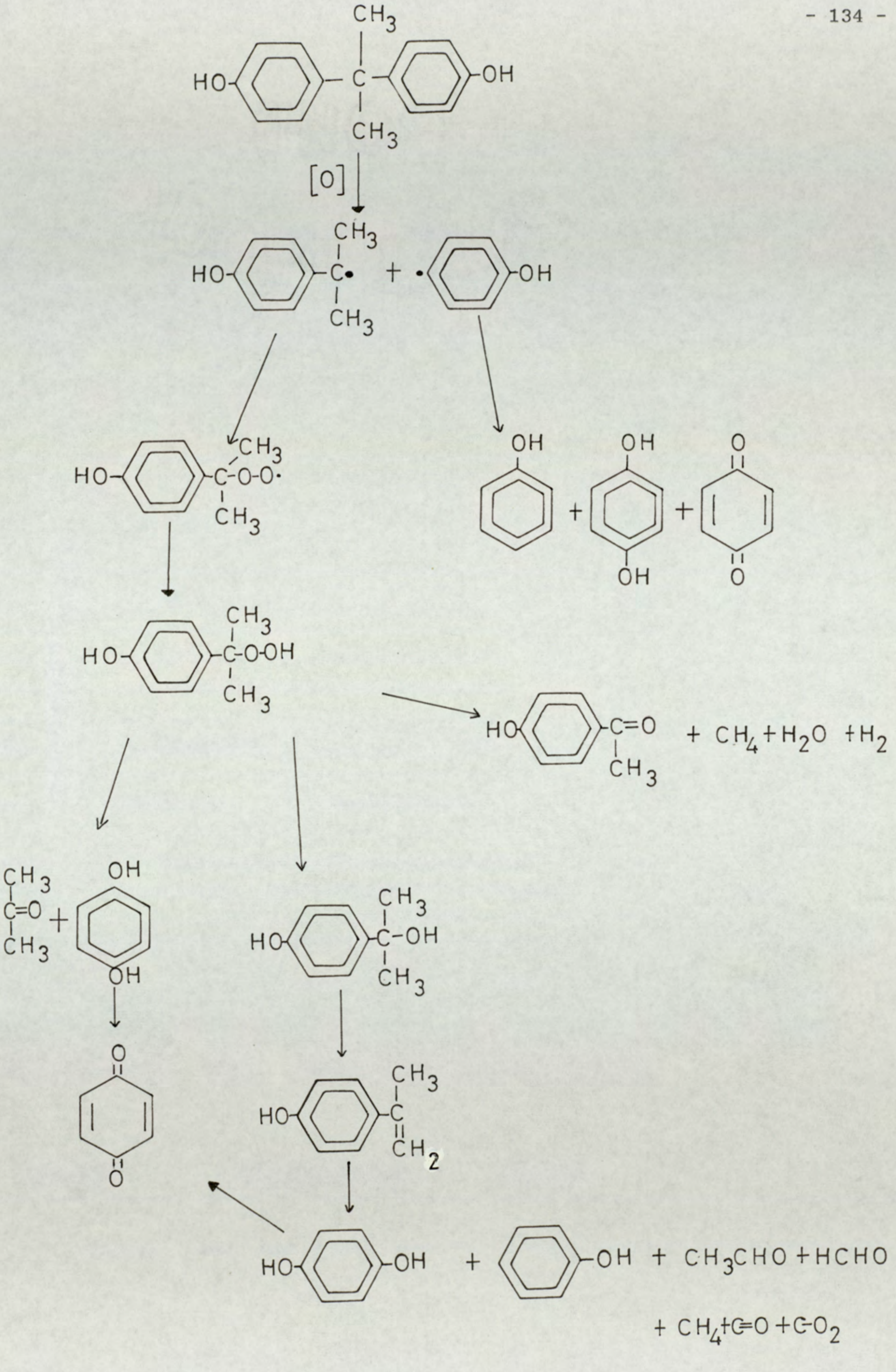
The quantity of bisphenol -A type material found in the photo-oxidative degradation products of compound 5 was very small. This may have been due to the unsymetrical nature of the primary product.

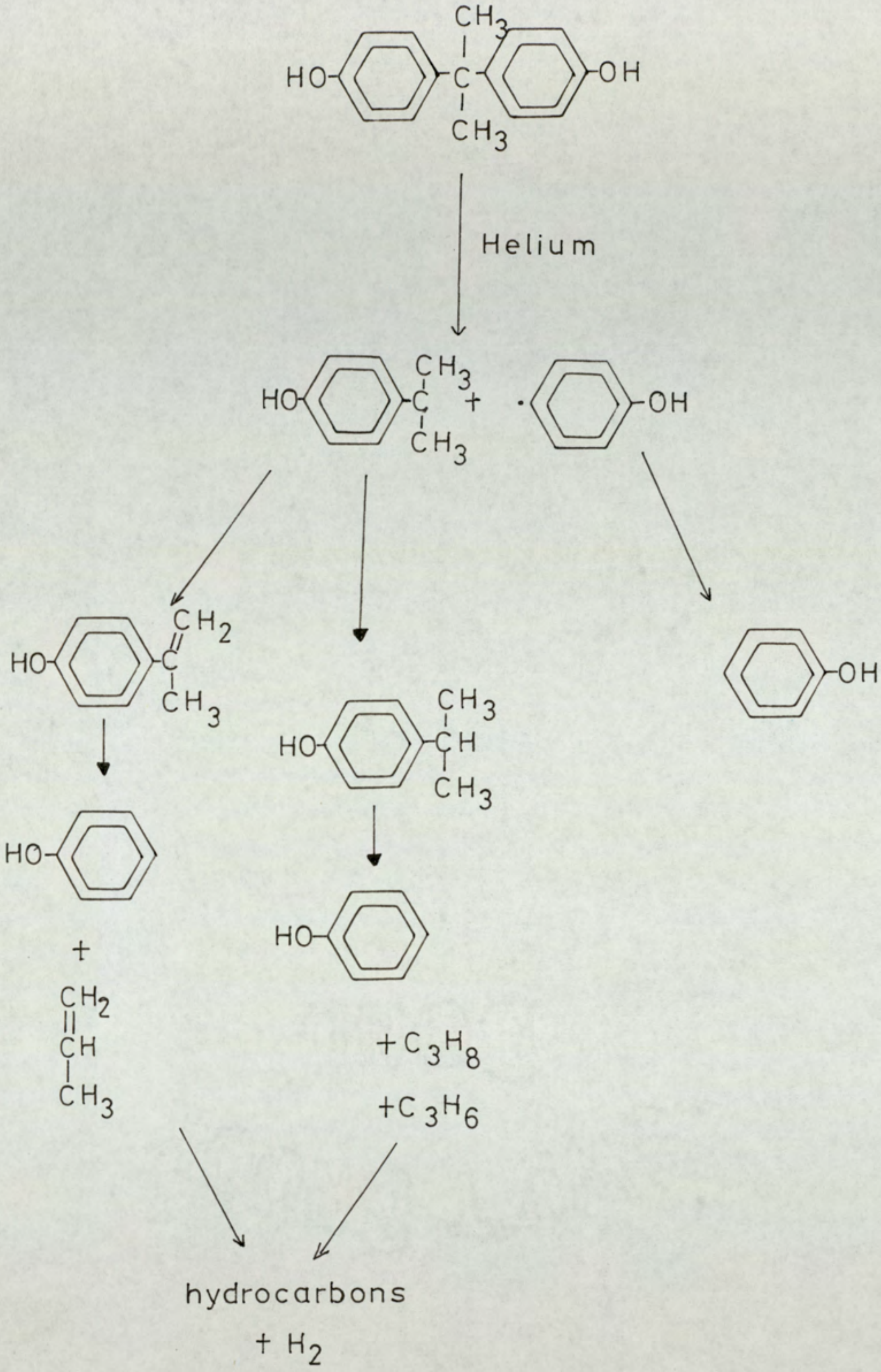


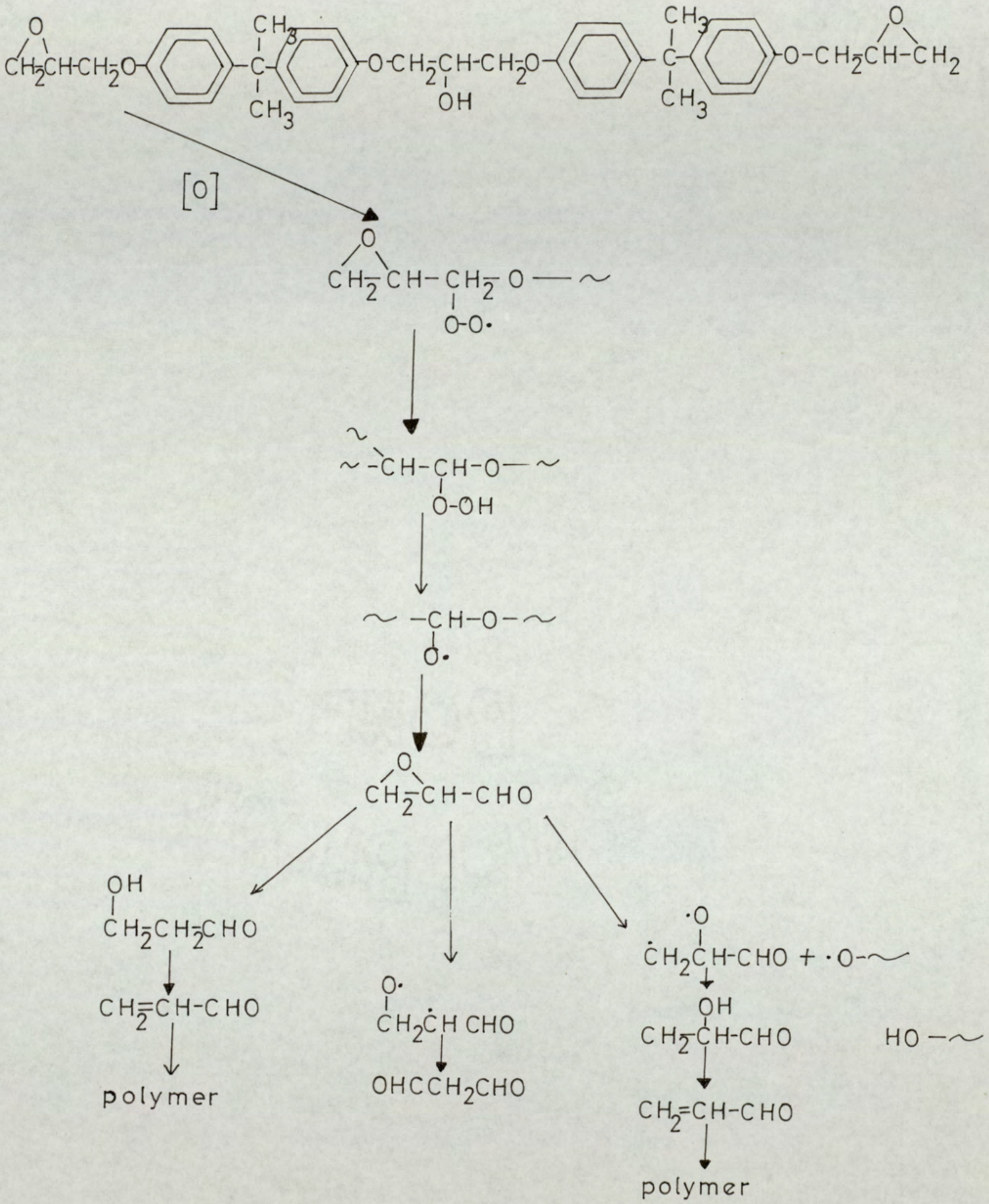
which underwent further degradation. Examination of the degradation products from bisphenol-A itself showed that, irrespective of atmosphere, scission occurred at the isopropylidene linkage.

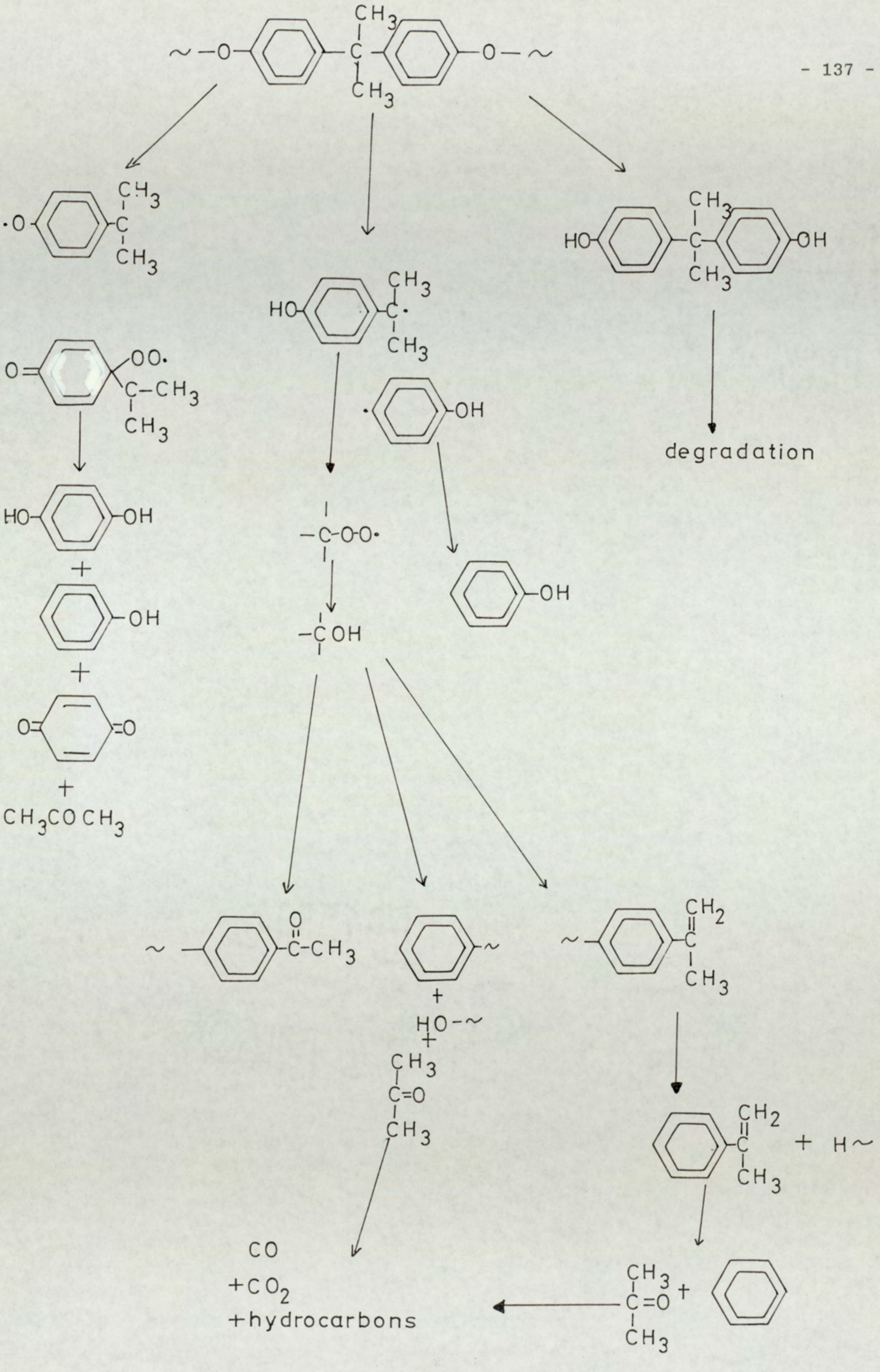


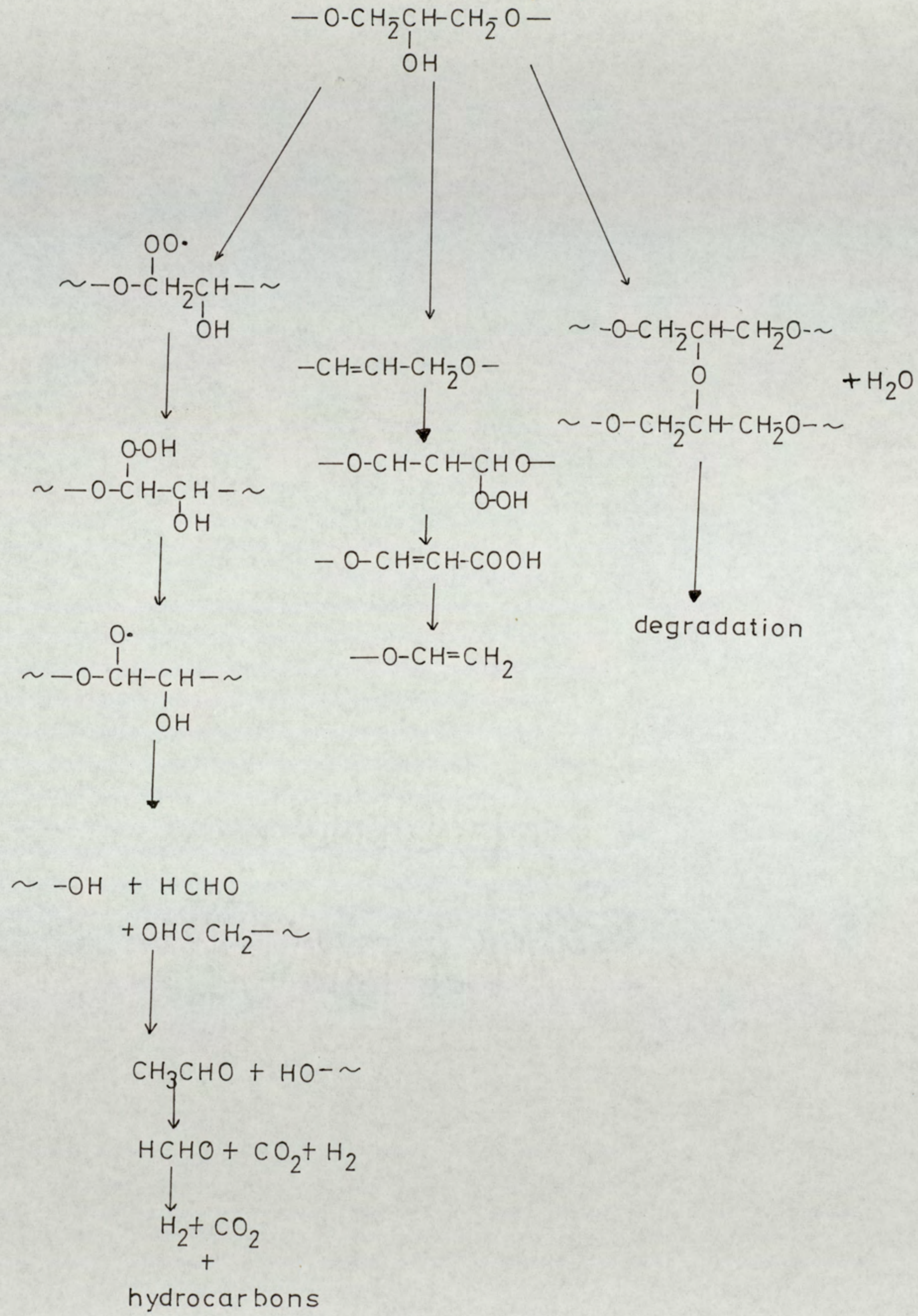
and that the time for the initial scission was the same under oxidative and non oxidative conditions. Therefore the initial breakdown resulted from direct absorption of radiation—probably by excitation of the benzene nucleus ($\pi \longrightarrow \pi^*$ forbidden transition) by the short wavelength region (280 nm) of the source. The absorption may have been the result of excitation by some other neighbouring group e.g. ether. After the initial reaction the irradiation atmosphere determined the type of degradation products formed. The degradation products can be explained by the scheme (page 134/135). Quinone formation was supported by the infrared band ingrowth at 6.1 microns. A similar band was found during the degradation of the TETA cured resins, and since bisphenol-A was identified as a degradation product of the systems it is likely that quinone formation occurred by the same degradation pathways. Quinone was also found in the degradation mixtures of other models which contained the bisphenol-A grouping, as was the 6.1 micron infrared band. Quinone was found in small quantities during the photo-degradation of the glycidyl ethers, and the infrared band observed was assigned to unsaturation in α-methyl styrene and similar compounds. The similarities between the degradation products from compounds 3 to 8 can be explained by the chemical structure of these materials. The overall degradation can be described in terms of the reactions in the '828' monomer. (page 136 to 141).

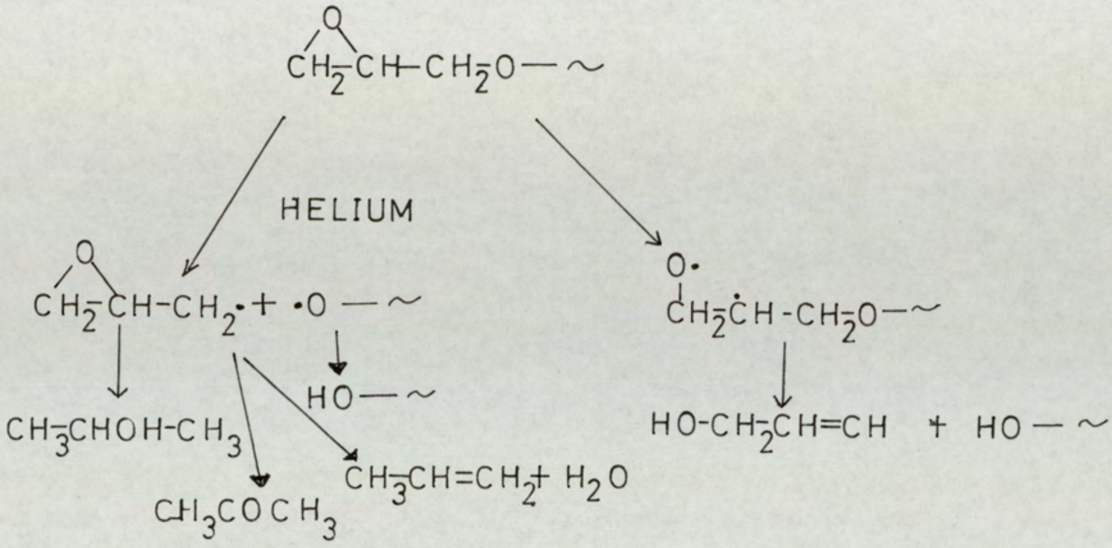

[O]

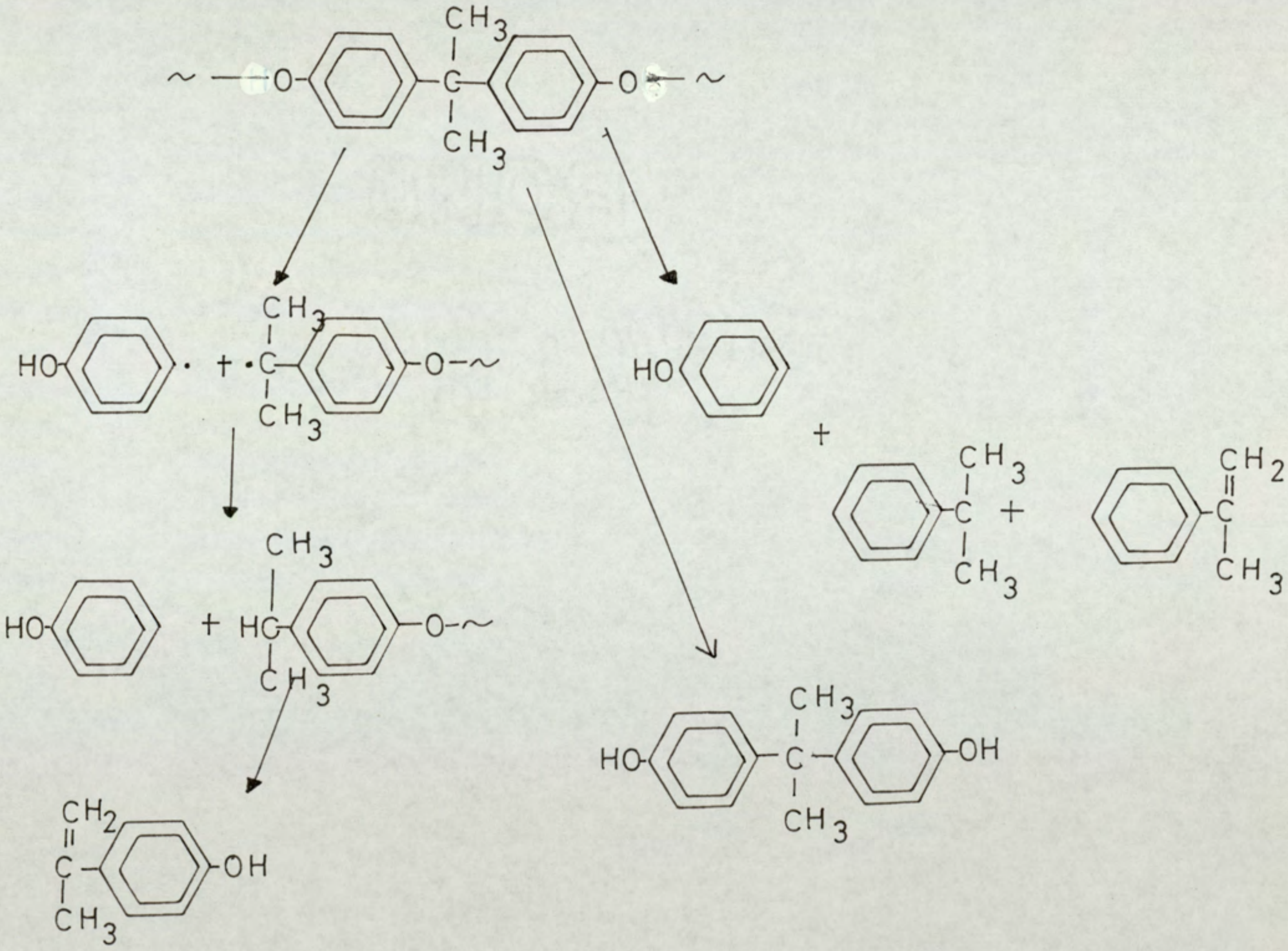

Helium
+
+ C_3H_8
+ C_3H_6
hydrocarbons
+ H_2

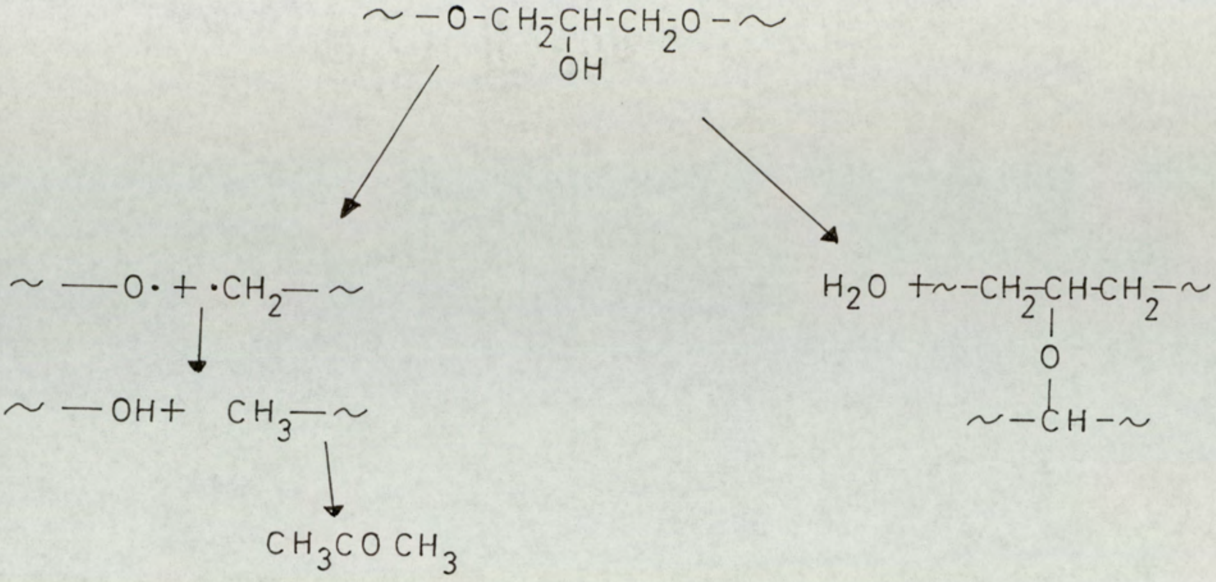


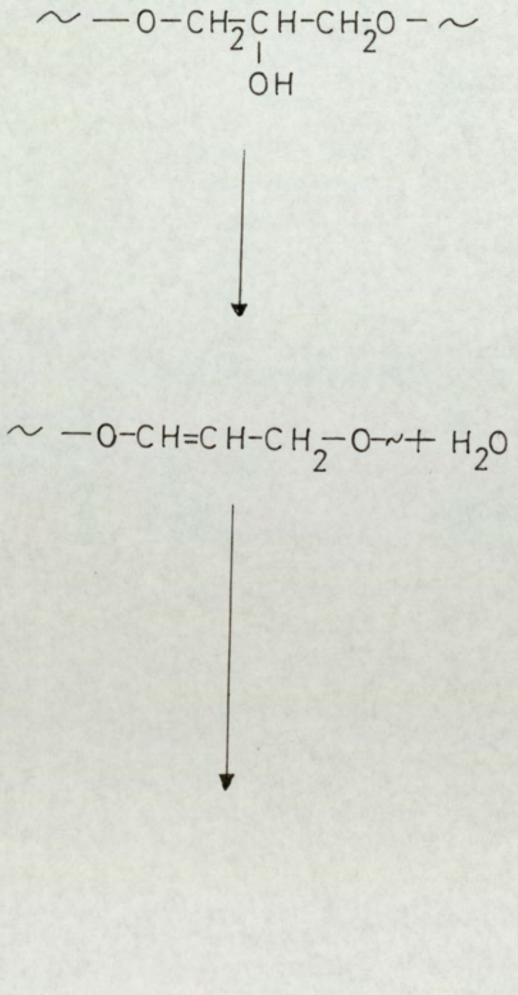

degradation
CO
+CO2
+hydrocarbons
CH3COCH3
HO-~
H~

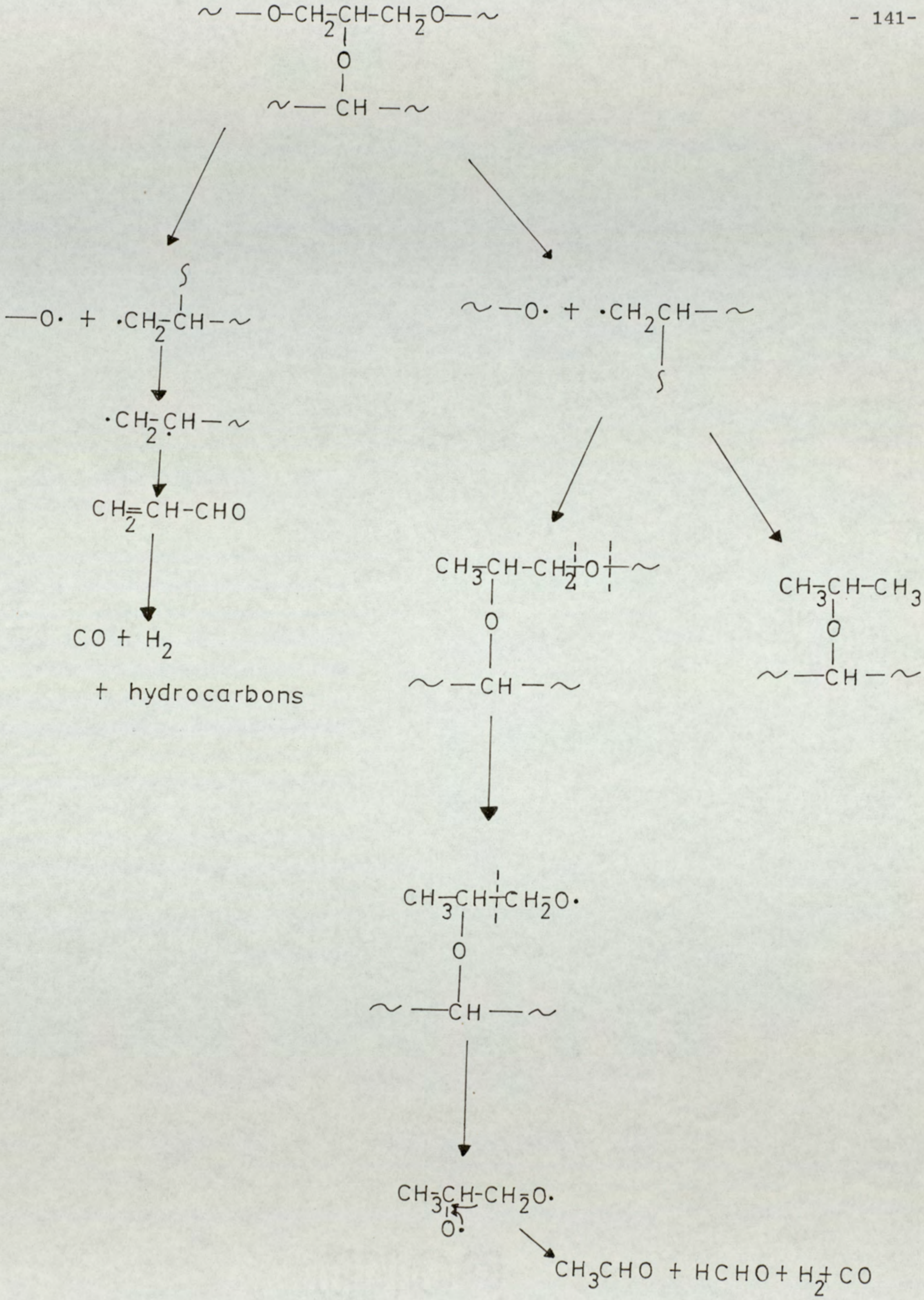

—O-CH2-CH-CH2-O—
OH
OO·
~—O-CH2-CH—~
OH
O-OH
~—O-CH-CH—~
OH
O·
~—O-CH-CH—~
OH
~ -OH + HCHO
+OHC CH2—~
CH3CHO + HO-~
HCHO + CO2 + H2
H2 + CO2
+
hydrocarbons
-CH=CH-CH2O-
—O-CH-CH-CHO—
O-OH
—O-CH=CH-COOH
—O-CH=CH2
~ -O-CH2-CH-CH2O-~
O
~ -O-CH2-CH-CH2O-~
+ H2O
degradation


HELIUM




~ –O-CH₂-CH-CH₂O-~
OH
~ —O· + ·CH₂—~
~ —OH+ CH₃—~
CH₃CO CH₃
H₂O +~-CH₂-CH-CH₂-~
O
~-CH-~


~ —O-CH₂-CH-CH₂O-~
OH
~ —O-CH=CH-CH₂-O~+ H₂O


~ —O-CH2-CH-CH2-O— ~
O
~— CH —~
—O· + ·CH2-CH-~
·CH2-CH·—~
CH2=CH-CHO
CO + H2
+ hydrocarbons
~—O· + ·CH2CH—~
CH3-CH-CH2-O—~
O
~—CH—~
CH3-CH-CH3
O
~—CH—~
CH3-CH-CH2O·
O
~—CH—~
CH3-CH-CH2O·
O·
CH3CHO + HCHO + H2 + CO

Little evidence for recombination reactions was obtained from the products identified. Ultraviolet degradation studies on simple cyclic ethers did show recombination reactions (compounds 11 and 12). Short wavelength radiation was used and direct epoxide ring opening occurred yielding a high concentration of reactive radicals. However, the gel formation may be ascribed to crosslinking or recombination reactions, or both. Also the molecular weight changes during irradiation were indicative of recombination reactions. In studies on the phenoxy resin (5) evidence of recombination of radicals was found by the gel formation, the gel being more oxygenated than the original polymer.

Irradiation of the cured model compounds showed that the degradation reactions occurred in a manner similar to that found with the reactants. In the case of the amine/phenyl glycidyl ether systems the product distributions were similar to those found with phenyl glycidyl ether itself. This was expected since an excess of the latter was used in these reactions. No crystalline products were obtained despite the presence of tertiary amine groups which would have been expected to function as polymerisation catalysts for the residual unreacted epoxide groups. Amine degradation products were found with all of the amine/ether adducts which indicated that the amine curing agent TETA in the cured resins underwent degradation itself. However there is no experimental evidence that long wavelength radiation affects the carbon to nitrogen bond in the simple amines (4).

Consideration of the original colour of the amine cured systems showed that the depth of colour was of the order:

diethyl amine > ethylene diamine > TETA

Thus the colour was in the order of ease of complete reactivity of the amine groups. Reaction of TETA with phenyl glycidyl ether yielded a thermoplastic material which contained unreacted amine groups. The latter were probably the secondary groups in the central portion of the TETA molecule. With the simple amines the primary amine groups is twice as reactive as the secondary group, thus ethylene diamine would react faster than diethyl amine. The final degree of reactivity would be determined by the ease of access of the epoxide group to the molecule.

The mobility of the amine adducts was in the order:

diethyl amine > ethylene diamine > TETA

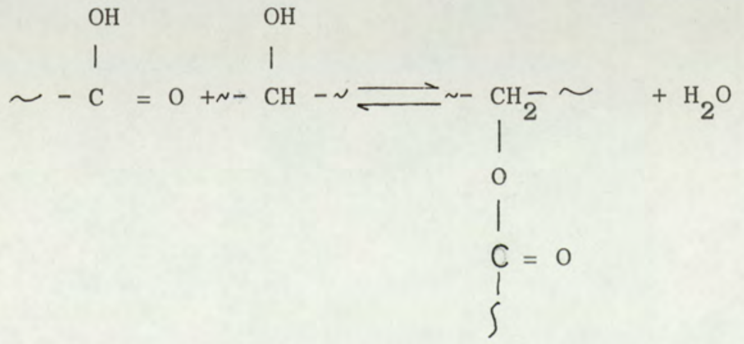
The extent of physical interactions such as hydrogen bonding or cyclisation would be expected to be greatest with the diethyl amine system and resultant colour formation would be greatest with this compound. The degree of colour formation was of the order:

diethyl amine > ethylene diamine > TETA

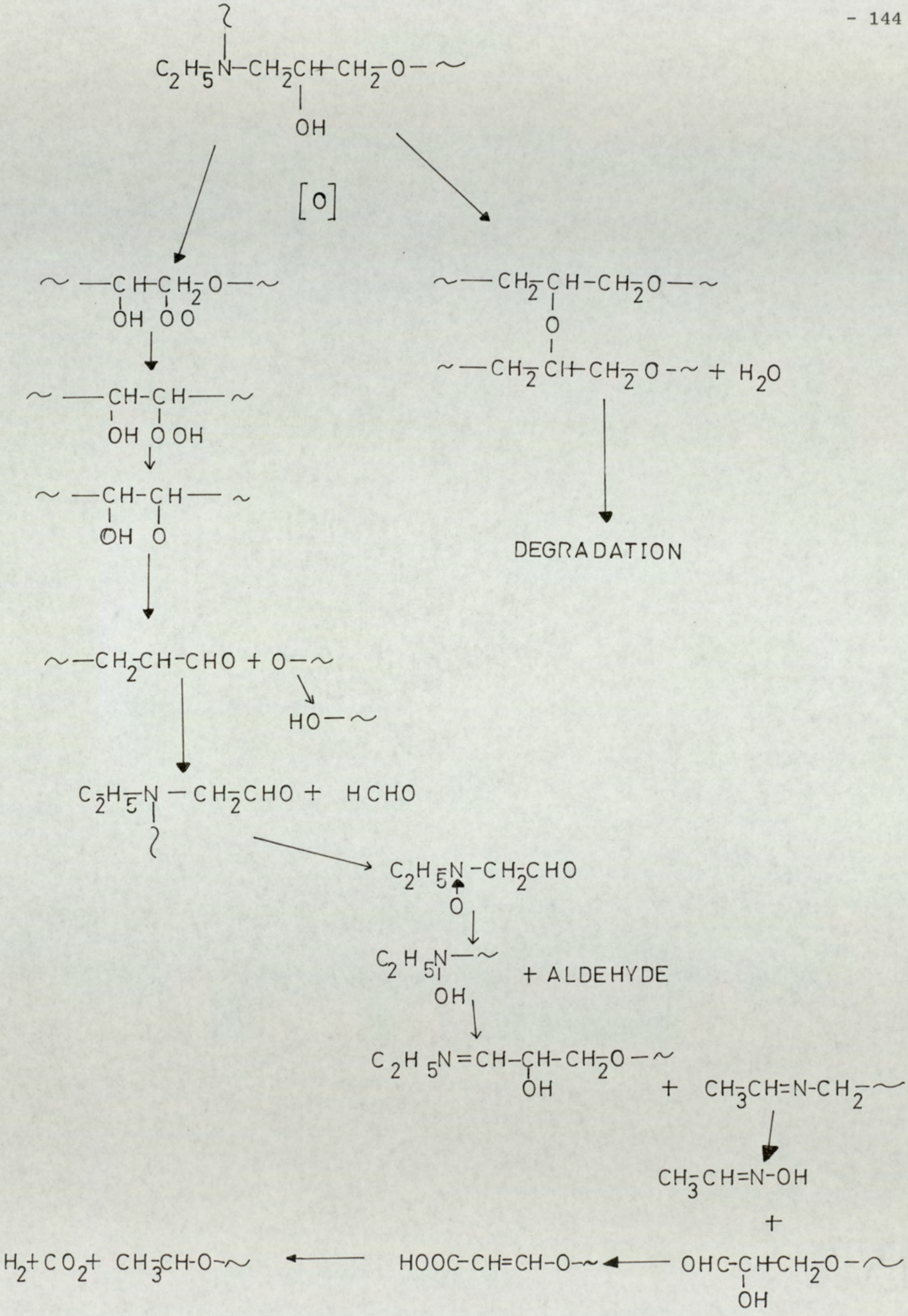
The types of degradation products identified indicated that the photo-degradation process was similar to the thermal degradation of amino alcohols, especially in the case of the tertiary amine group. Possible degradation schemes involving these amines are outlined (page 142 - 149).

Comparison of the amine cured resins with the simple and amine cured models showed that the epoxide monomer backbone and the curing agent were degraded by ultraviolet light. The curing agents did not absorb the radiation used (4), and therefore the degradation was initiated by the absorption of light by chromophores in the monomer itself. Transmission infrared spectroscopy showed the ingrowth of new infrared bands in all of the compounds studied, which corresponded to the new bands formed during degradation of the TETA cured resins. Those compounds which contained the complete structural unit, '826', '828', glyceryl ether of diphenyl propane and their reaction products, showed ingrowth of two new bands, which from the results with phenyl and tolyl glycidyl ether can be assigned to aromatic ketone (6.1 micron) and aliphatic carbonyl or unsaturation (5.9 micron). No correlation of band ingrowth with colour formation on irradiation was found with the model systems.

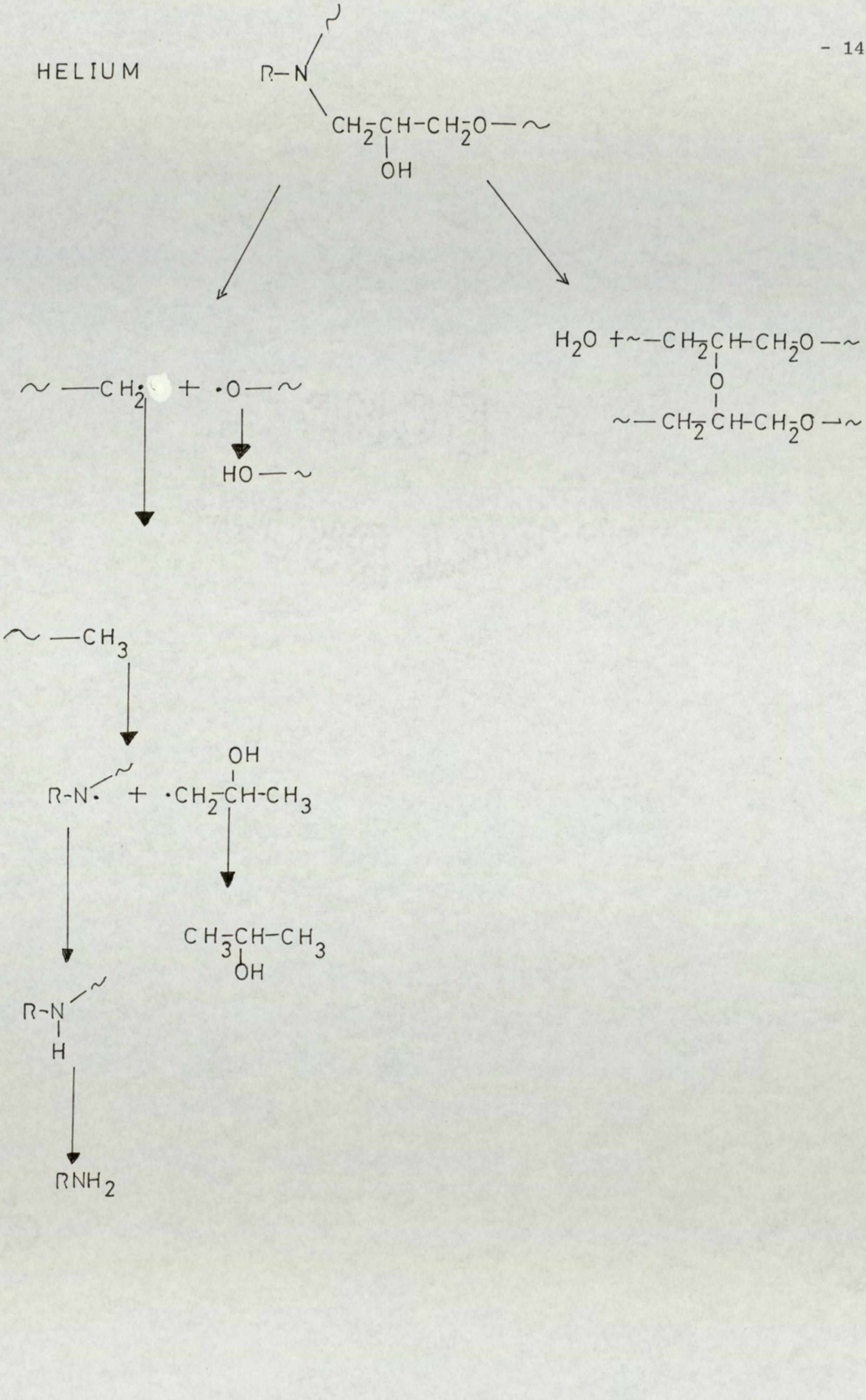
The model ester compounds represented both terminal and central aliphatic ester bonds. The latter are not formed during the normal epoxide/HHPA curing reaction unless the equilibrium of the reaction is upset by the use of excess glyceryl ether.



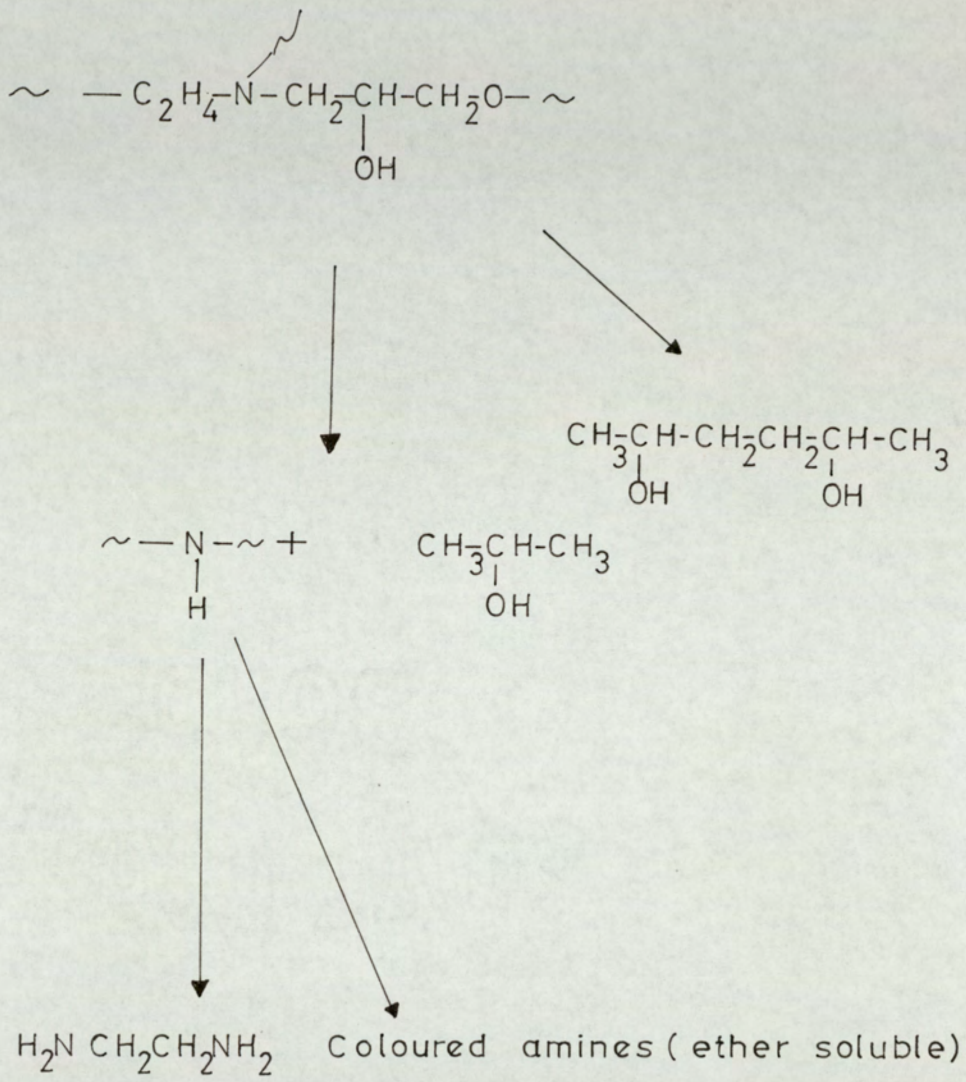
$$\sim - \overset{\overset{\text{OH}}{|}}{\text{C}} = \text{O} + \sim - \overset{\overset{\text{OH}}{|}}{\text{CH}} - \sim \rightleftharpoons \sim - \underset{\underset{\underset{\underset{\wr}{|}}{\text{C}=\text{O}}}{\underset{|}{\text{O}}}}{\underset{|}{\text{CH}_2}} - \sim \quad + \text{H}_2\text{O}$$

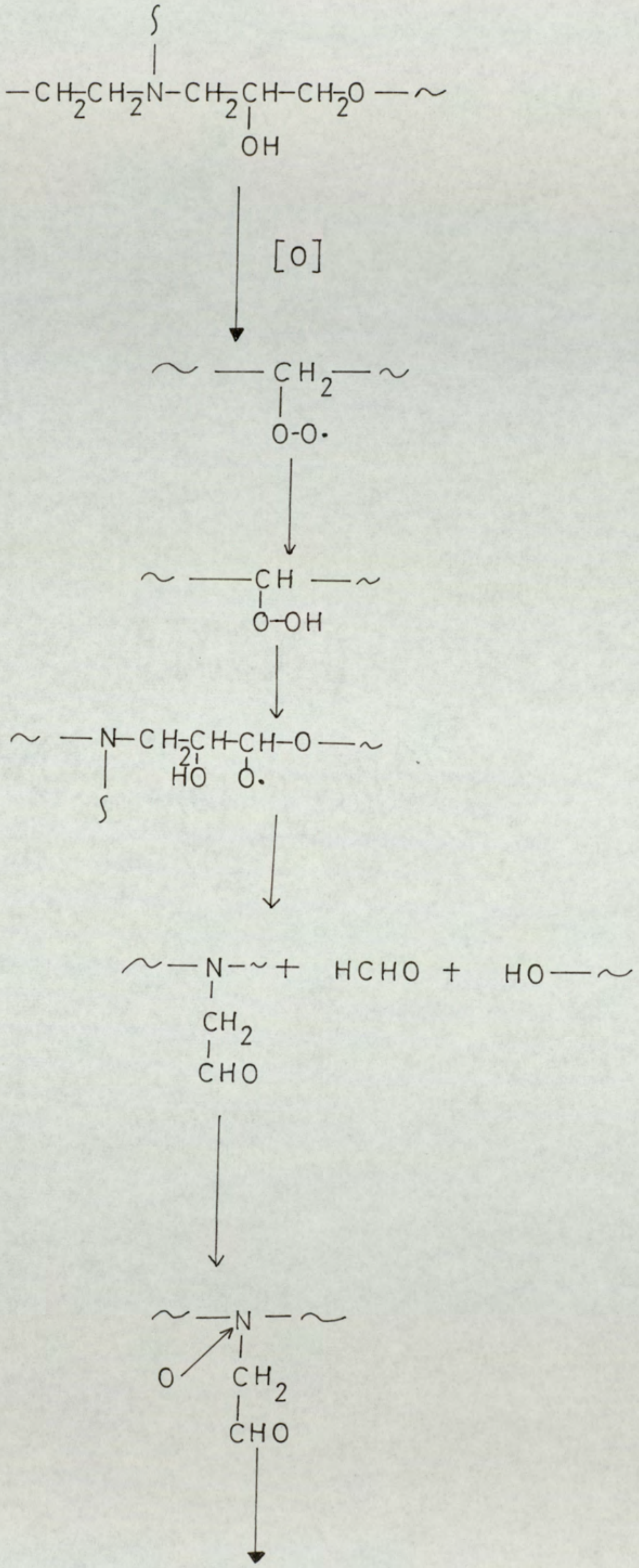

[O]
DEGRADATION
+ ALDEHYDE
+ H2O

HELIUM



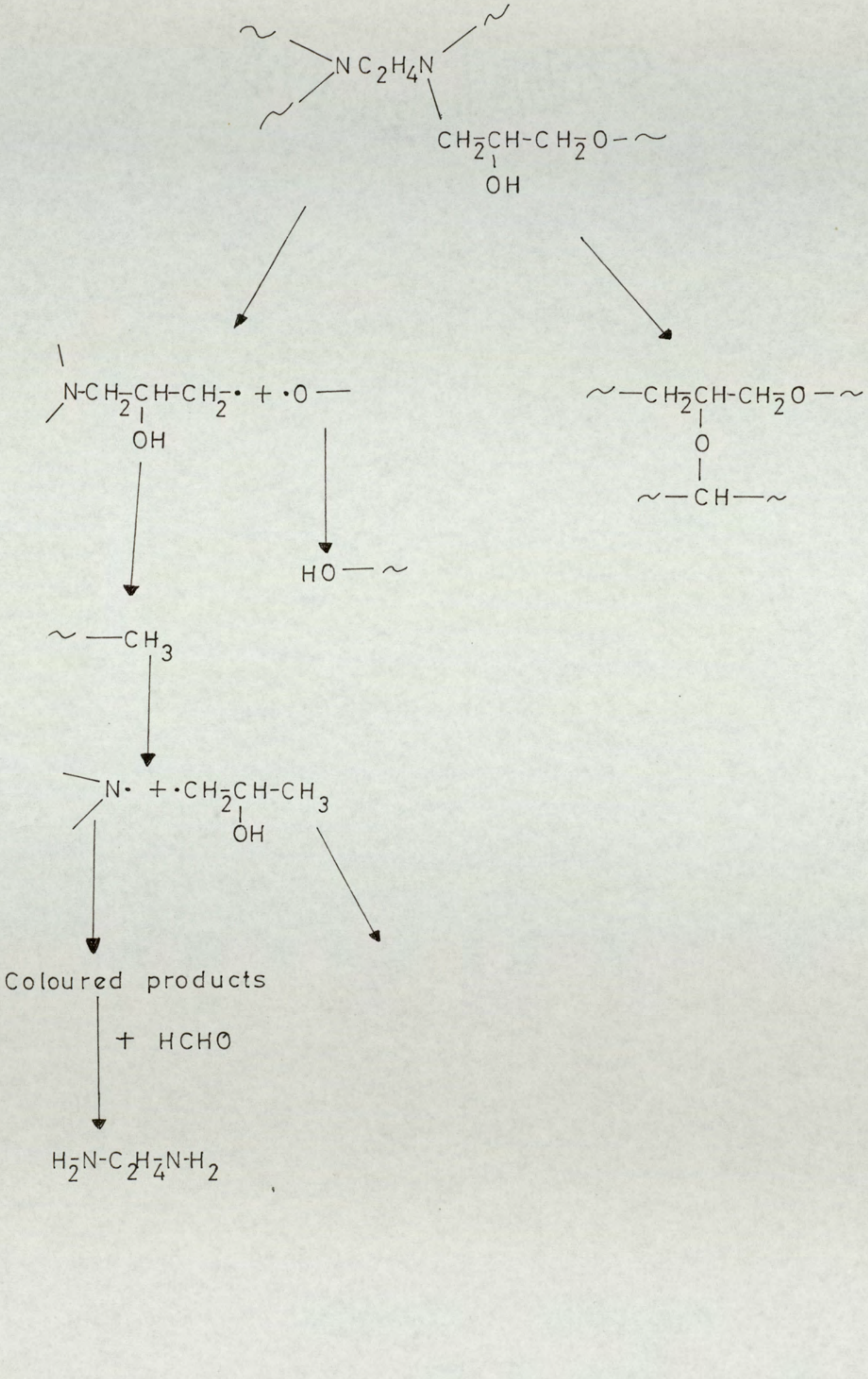
HELIUM

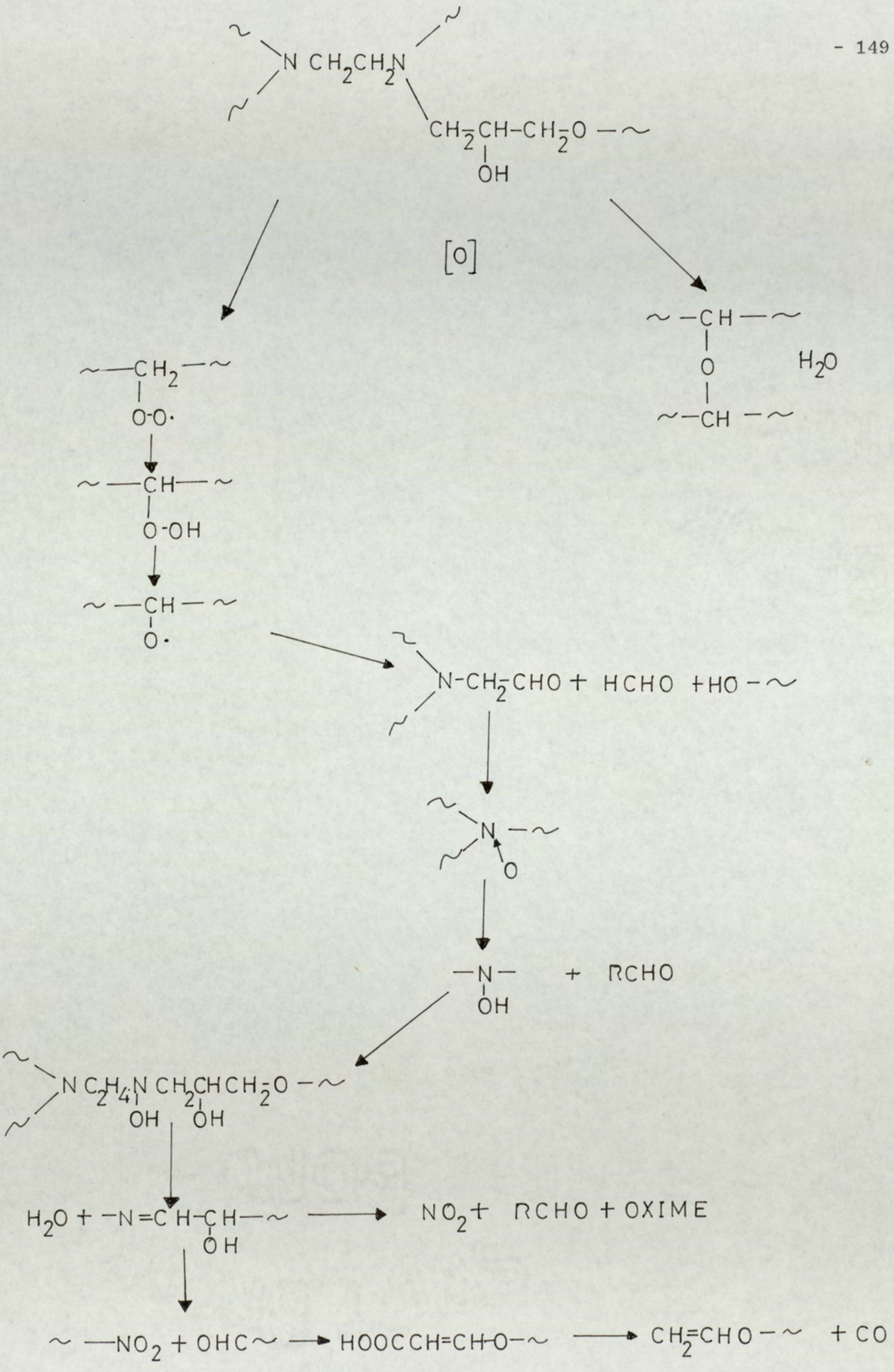

~ —C2H4-N-CH2-CH-CH2O- ~
OH
CH3-CH-CH2-CH2-CH-CH3
OH OH
~—N-~ +
H
CH3-CH-CH3
OH
H2N CH2CH2NH2
Coloured amines (ether soluble)



Coloured nitrogenous products (oximes)
(N,N-dimethyl hydroxylamine)

HELIUM


NC2H4N
CH2-CH-CH2-O-~
OH
N-CH2-CH-CH2• + •O—
OH
~—CH2-CH-CH2O—~
O
~—CH—~
HO—~
~—CH3
N• + •CH2-CH-CH3
OH
Coloured products
+ HCHO
H2N-C2H4-NH2


N CH2CH2N
CH2-CH-CH2O —
OH
[O]
—CH—
O
—CH —
H2O
—CH2—
O-O·
—CH—
O-OH
—CH —
O·
N-CH2CHO + HCHO + HO —
N —
O
—N—
OH
+ RCHO
N C2H4 N CH2CHCH2O —
OH OH
H2O + —N=CH—CH—
OH
NO2 + RCHO + OXIME
—NO2 + OHC
HOOCCH=CH-O—
CH2=CHO —
+ CO

The ingrowth of the 5.9 micron infrared band occurred at a faster rate with the terminal ester compounds. This disagreed with the postulated hydrogen bond interaction of hydroxyl and carbonyl groups. The degradation of compounds 13 and 14 can be represented as shown (page 151 to 153).

The faster degradation of the ester bond in compound 15 to compounds 13 and 14 can be explained in terms of the excess glyceryl ether used in the preparation of 15. The excess ether which contained aliphatic hydroxyl groups would, from the earlier results, be expected to crosslink with subsequent evolution of water. The equilibrium of the ester forming reaction

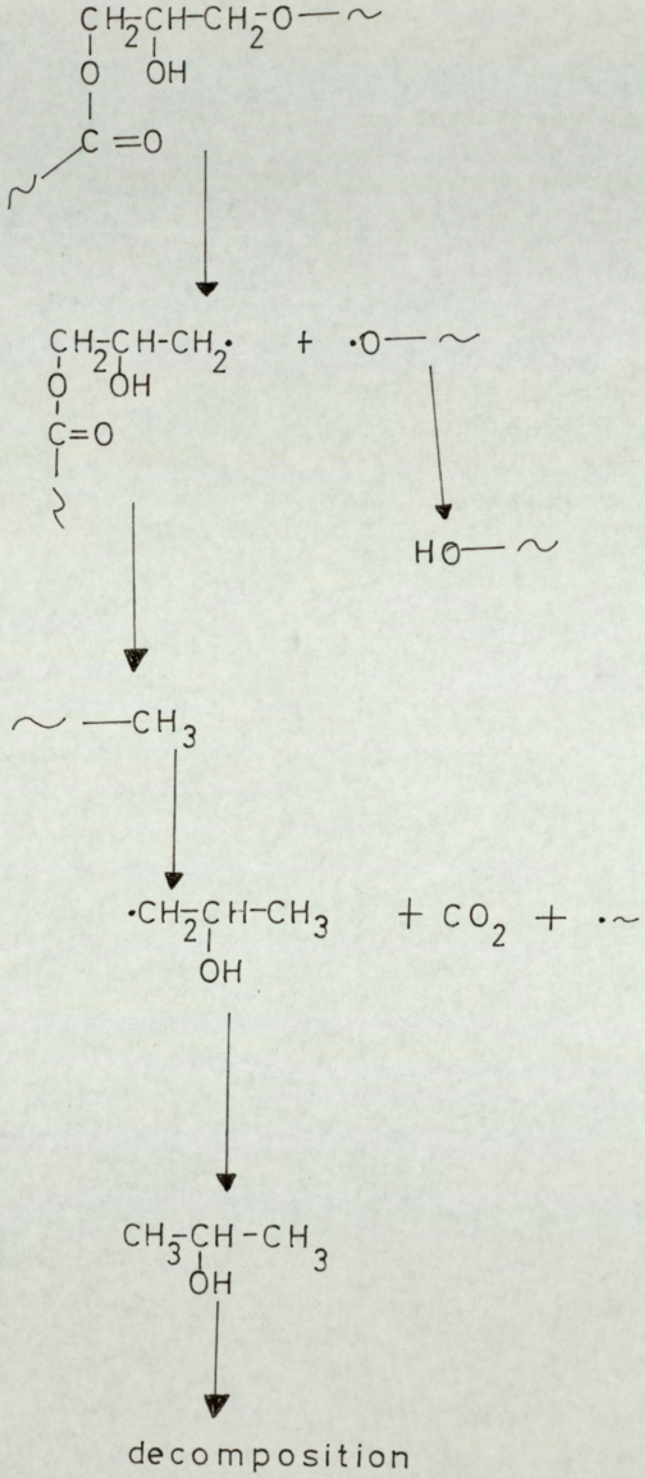
$$\mathrm{ROH + RCOOH \rightleftharpoons RCOOR + H_2O}$$

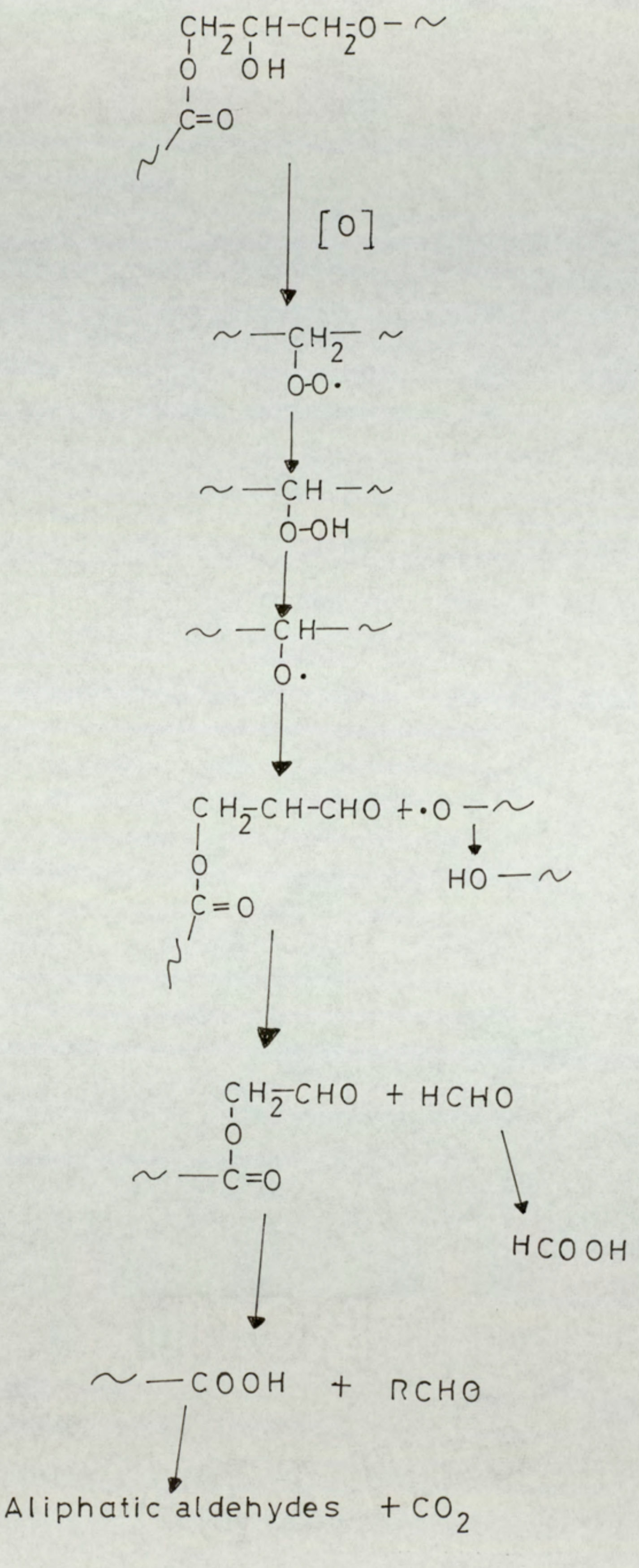
would then be shifted to the left and further degradation of the alcohol would occur. Some hydrogen bonding interactions would also have occurred between the ester carbonyl group and the unreacted glyceryl ether and this may have contributed to the degradation process.

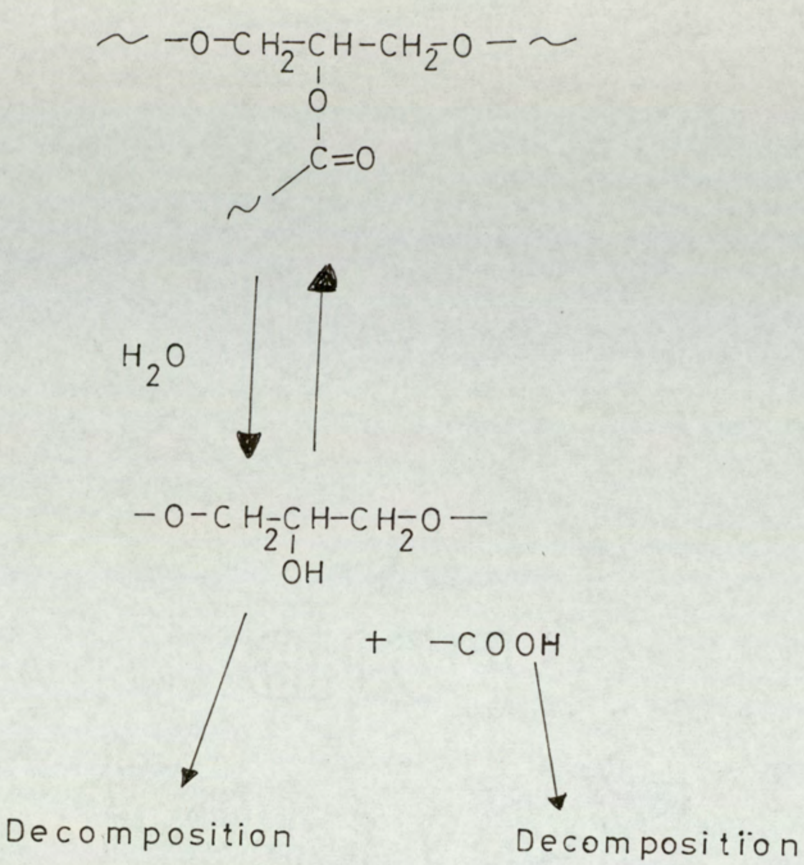
The ingrowth of new infrared bands was halted by removal of the light source. No 'dark' reactions were observed in any of the model systems studied, except for phenyl glycidyl ether which crystallised on dark storage to yield polyphenyl glycidyl ether together with degradation products. The absence of 'dark' reactions may have been due to the insensitivity of the transmission infrared technique used. The translucent or transparent solid systems would have been expected by analogy with the cured resin to show diffusion of low molecular weight species after removal of the radiation source. The highly coloured nature of the solids, however, may have confined the degradation reactions to the solid surface by a screening effect.

Little quantitative information was obtained from the results with model compounds which could be correlated with the degradation of the cured three-dimensional polymers. The extent of degradation for the simple models was greater than for their 'cured' counterparts because of the physical interaction between the reactants in the cured state. Also since the simple models were liquids, diffusion of oxygen into and/or degradation products out of the matrix could occur with greater ease than in the solid state.

HELIUM


CH₂-CH-CH₂-O—~
OH
C=O
+ ·O—~
HO—~
~—CH₃
·CH₂-CH-CH₃ + CO₂ + ·~
CH₃-CH-CH₃
OH
decomposition


CH2-CH-CH2O-~
O OH
C=O
[O]
~-CH2-~
O-O·
~-CH-~
O-OH
~-CH-~
O·
CH2-CH-CHO +·O-~
O
C=O
HO-~
CH2-CHO + HCHO
O
~-C=O
HCOOH
~-COOH + RCHO
Aliphatic aldehydes + CO2


~ –O–CH$_2$–CH–CH$_2$–O – ~
O
C=O
~
H$_2$O
–O–CH$_2$–CH–CH$_2$–O –
OH
+ –COOH
Decomposition
Decomposition

The extent and rate of ingrowth of the new infrared bands showed the susceptibility of the compounds to degradation and was greater for the simple models than for the cured systems. This can be attributed to the form and/or colour of the models. From the data on the ingrowth of the 5.91 micron band (Figure 5 - 8 to 5 - 11) it is evident that unreacted chain ends in the cured polymer exposed to incident radiation were more susceptible to degradation than the amine or ester cure links because of breakdown at the ether group. This was also seen to some extent by the rate of disappearance of epoxide groups in compounds 3 and 6 (Figure 5 - 15).

The rate of aliphatic carbonyl formation with the amine adducts was found to be

$$12 > 11 > 10$$

This was also the order of ease of complete reaction of the amine groups and of maximum mobility of molecules. Lee and Watson (13) suggested that the secondary amine groups acted as sites for degradation and colour formation. This was due to steric conditions after gelation during the curing process. During degradation the hydroxyl absorption band of all of the amine compounds shifted in the order

$$12 > 11 > 10$$

which indicated the effect of increased hydrogen bonding in the radiation resistance of the materials. Consideration of the extent of reaction of the three adducts showed that complete disappearance of epoxide groups had occurred with compounds 11 and 12 while some remained unreacted in the TETA adduct.

The use of excess phenyl glycidyl ether did not alter the quantity of unreacted epoxide groups. Also use of elevated temperature during the reaction did not aid the reaction very much and resulted in carbonyl formation because of degradation of the phenyl glycidyl ether. The use of excess curing agent would decrease the quantity of unreacted epoxide groups. However the secondary amine content of the system would be high and in accordance with the postulate of Lee and Watson (13) the stability would be decreased. Thus the secondary nitrogen content of the latter was high and since the material was solid only long range hydrogen bonds operated, while in the viscous liquids long and short range interactions were possible.

All of the model compounds studied were susceptible to the radiation used, in particular, the simple amine adducts of phenyl glycidyl ether, which were highly coloured, absorbed in the visible region of the spectrum and degraded more rapidly than the glycidyl ether itself. The terminal ester compounds increased in colour with the presence of acid groups and their stability was greater than phenyl glycidyl ether. The ester from the aliphatic hydroxyl and the acid curing agent were less stable than the terminal esters because of the formation of water which caused ester hydrolysis.

In the simple model compounds the phenyl glycidyl ether was found to degrade more rapidly than the hydroxyl containing compounds. This was seen in the increased rate of disappearance of the epoxide group in phenyl glycidyl ether to both of the monomers '826' and '828'. Thus unreacted chain ends in cured resins would be expected to act as degradation sites.

Compounds containing aliphatic hydroxyl groups in the undegraded state were found to form insoluble gels on ultraviolet irradiation with evolution of water. The effect was greatest in compounds consisting of small mobile molecules and least in compounds where steric restrictions prevented rearrangements. Gel formation could occur in the cured epoxide resins if molecular rearrangements were possible. Greater gel would be expected with TETA cured systems if complete reaction occurred, since bulky cyclohexane groups would not be present to separate the polymer chains.

The decrease in viscosity in all compounds was attributed to bond scission on ultraviolet irradiation. This was greater for inert gas irradiations which indicated a predominance of chain scission over recombination reactions. Increased gel formation occurred with photo-oxidised systems. This was attributed to the presence of oxygen which aided recombination of radicals.

Few comparisons could be made between the cured three-dimensional epoxide polymers and the cured and uncured simple model compounds because of the liquid on thermoplastic nature and/or colour of the latter.

REFERENCES

1. Thesis, Chapter 4
2. Fox, R.B., et al U.S., NRL - TR - 6284, 1965
3. "Epoxy Resins" by Potter, W.G., Butterworths, London, 1970
4. "Photochemistry" by Calvert, J.G., Pitts, J.N., Chapters 2 and 5, J. Wiley, New York, 1967
5. Kelleher, P.G., Gesner, B.D., J. Appl. Polym. Sci 13, 9, 1969
6. Kelleher, P.G., Gesner, B.B., J. Appl. Polym, Sci 13, 2183, 1969
7. Ada, R., et al Kogyo Kagaku Zasshi, 55, 673, 1952
8. Tanaka, Y., et al J. Polym. Sci., A-1, 4, 109, 1966
9. Kambara, S., et al Makromol. Chem. 63, 89, 1963
10. Takashashi, A., et al Makramol. Chem. 72, 92, 1964
11. Gomer, R., Noyes, W.A., J.A.C.S. 72, 101, 1950
12. Gritter, R.J., Sabatino, E.C., J. Org., Chem. 29, 1965, 1964
13. Lee, H., Watson, F.T., 20th ANTEC of SPE XXI, 1964

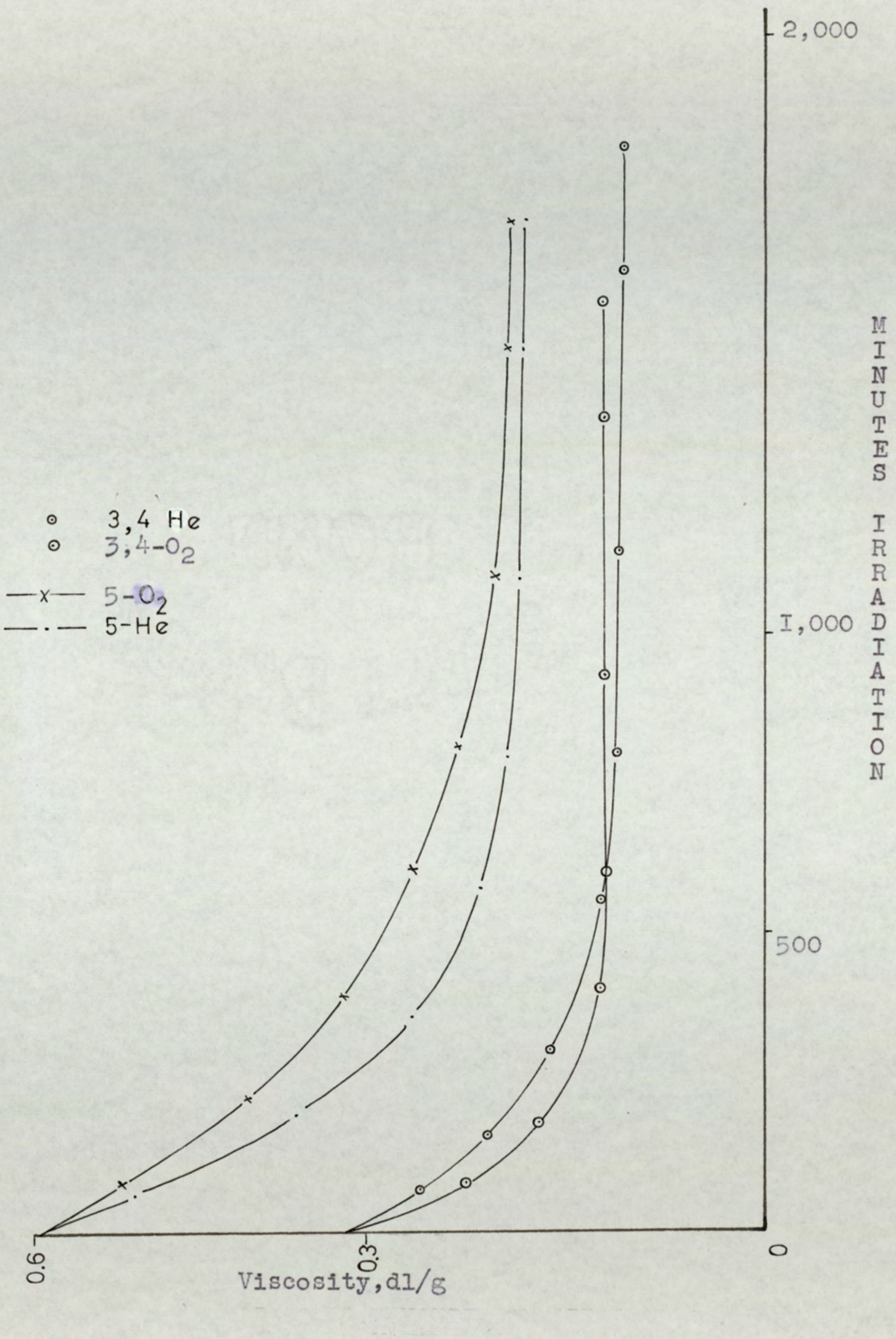


FIGURE 5-I Viscosity changes on irradiation. (models 3,4,5)

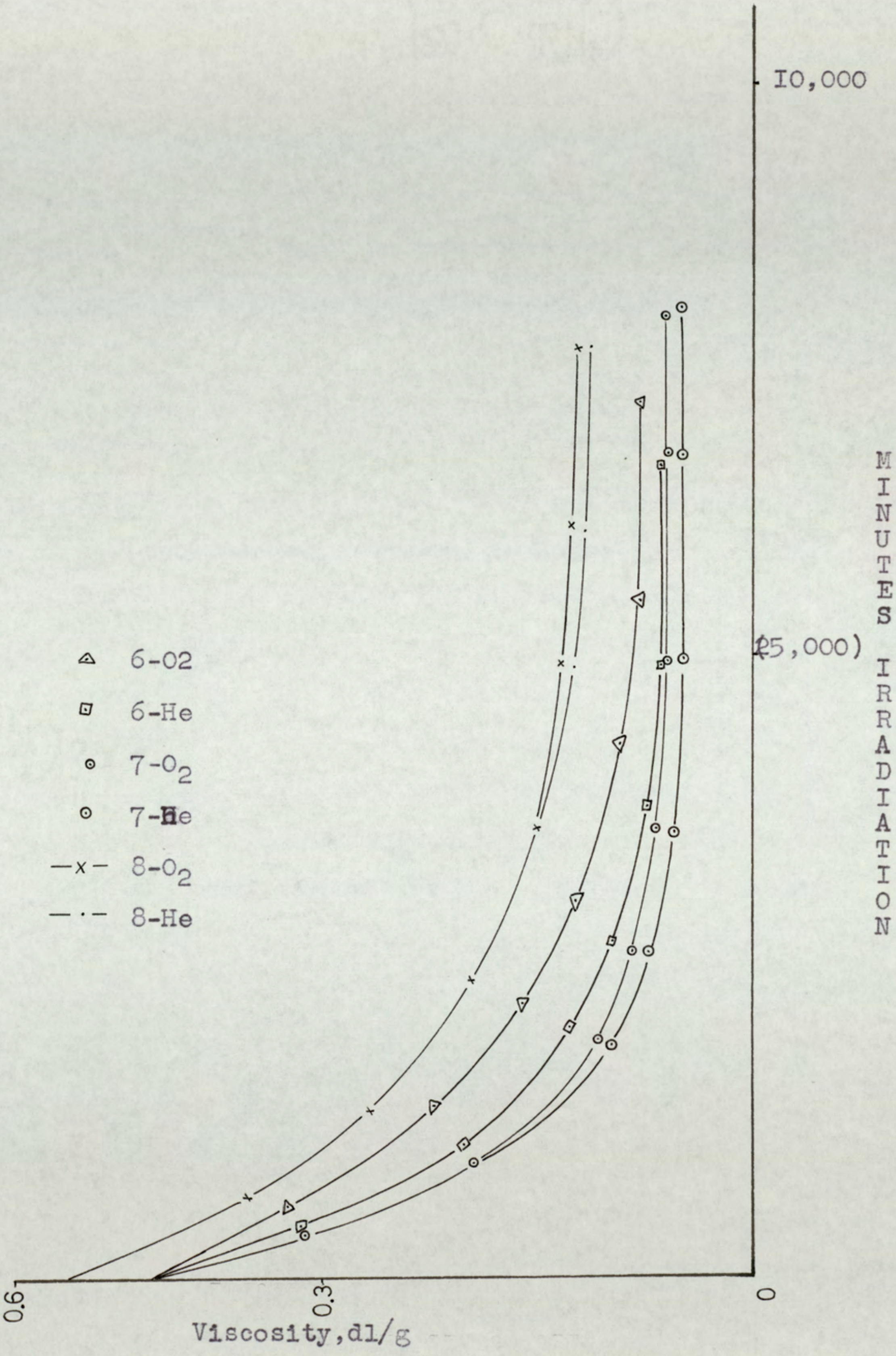


FIGURE 5-2 Viscosity changes on irradiation.

(models 6,7,8)

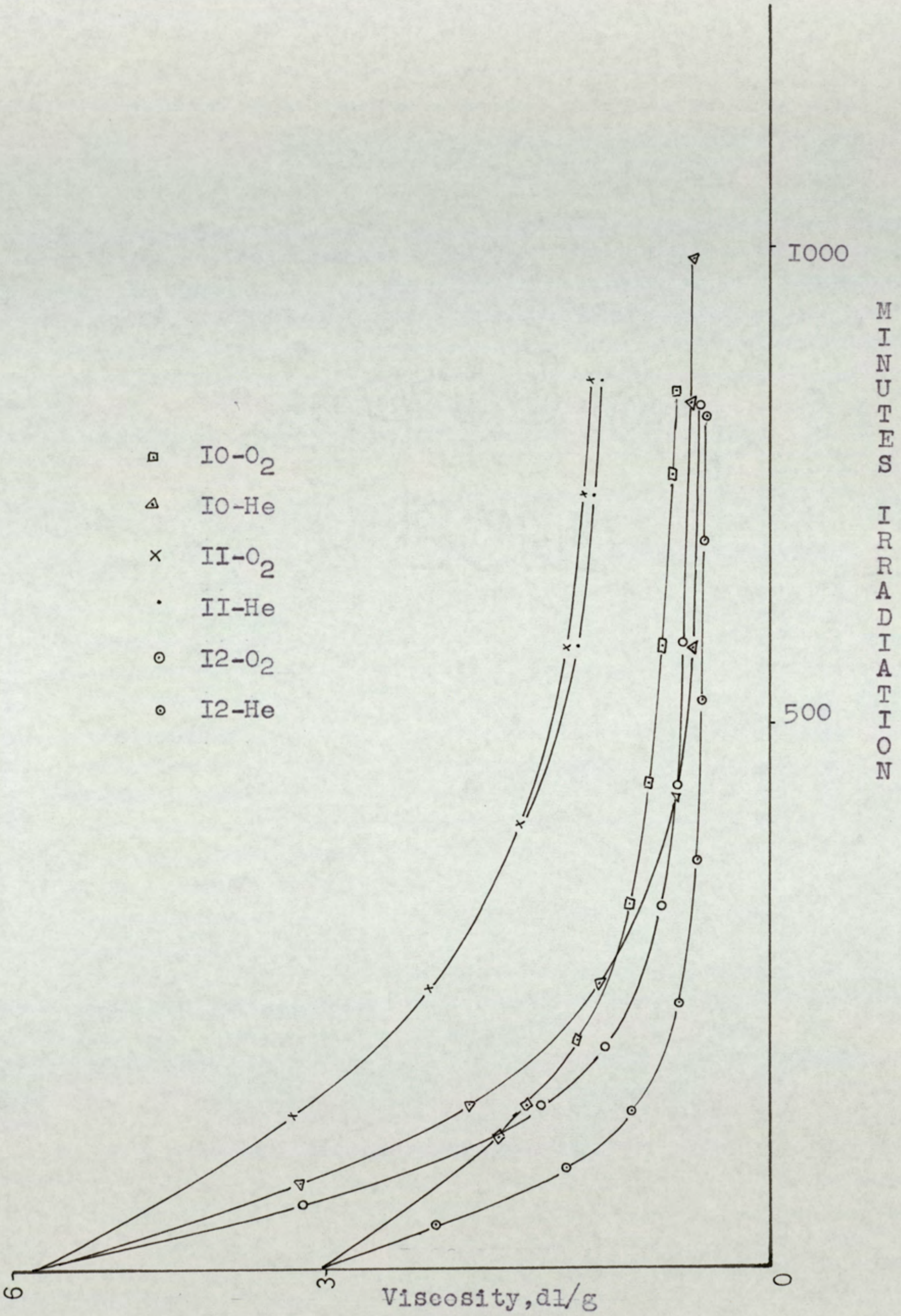


FIGURE 5-3 Viscosity changes on irradiation

(models IO, II, I2)

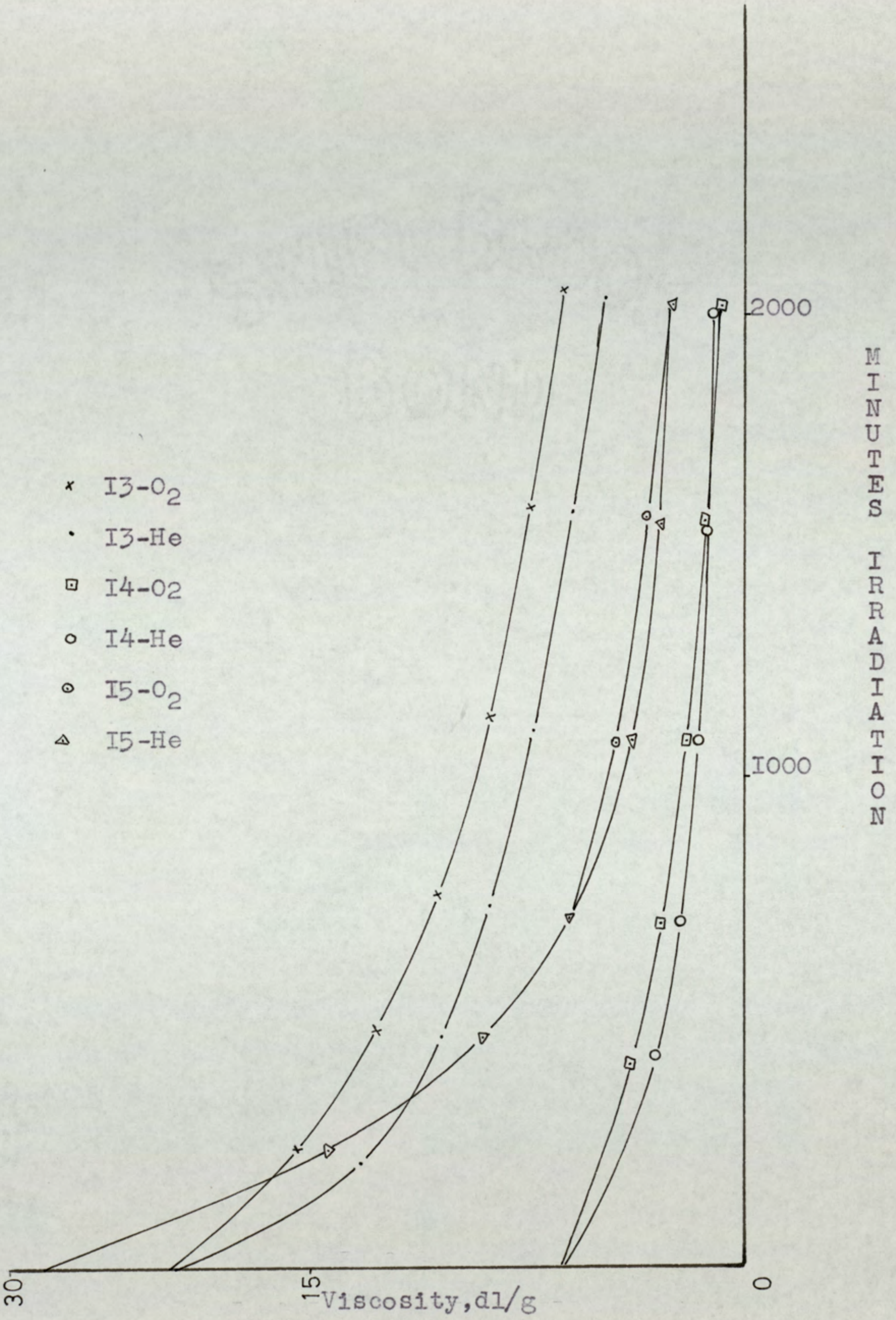


FIGURE 5-4 Viscosity changes on irradiation,

(models I3,I4,I5)

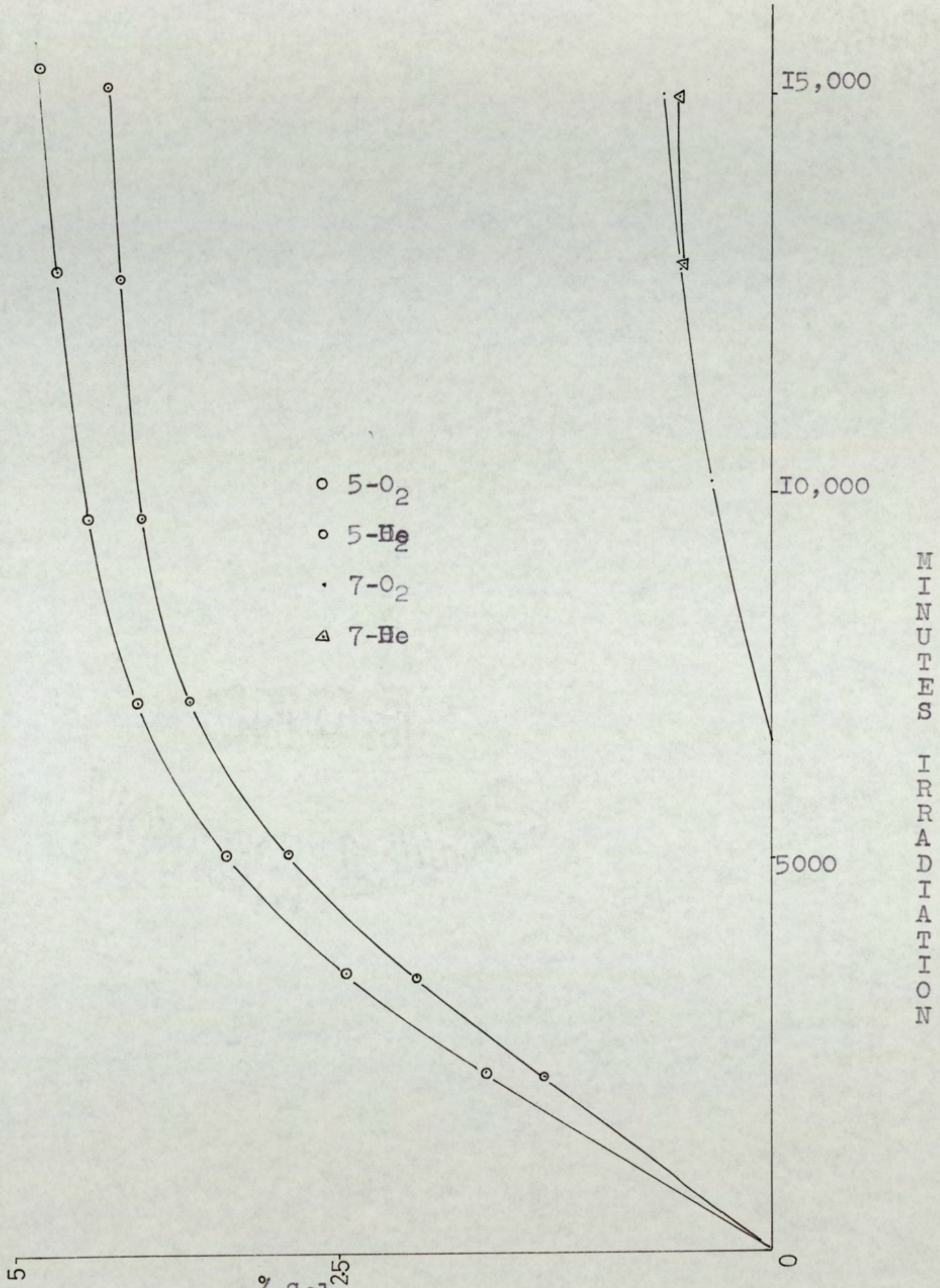


FIGURE 5-5 Gel formation on irradiation.

(models 7,5)

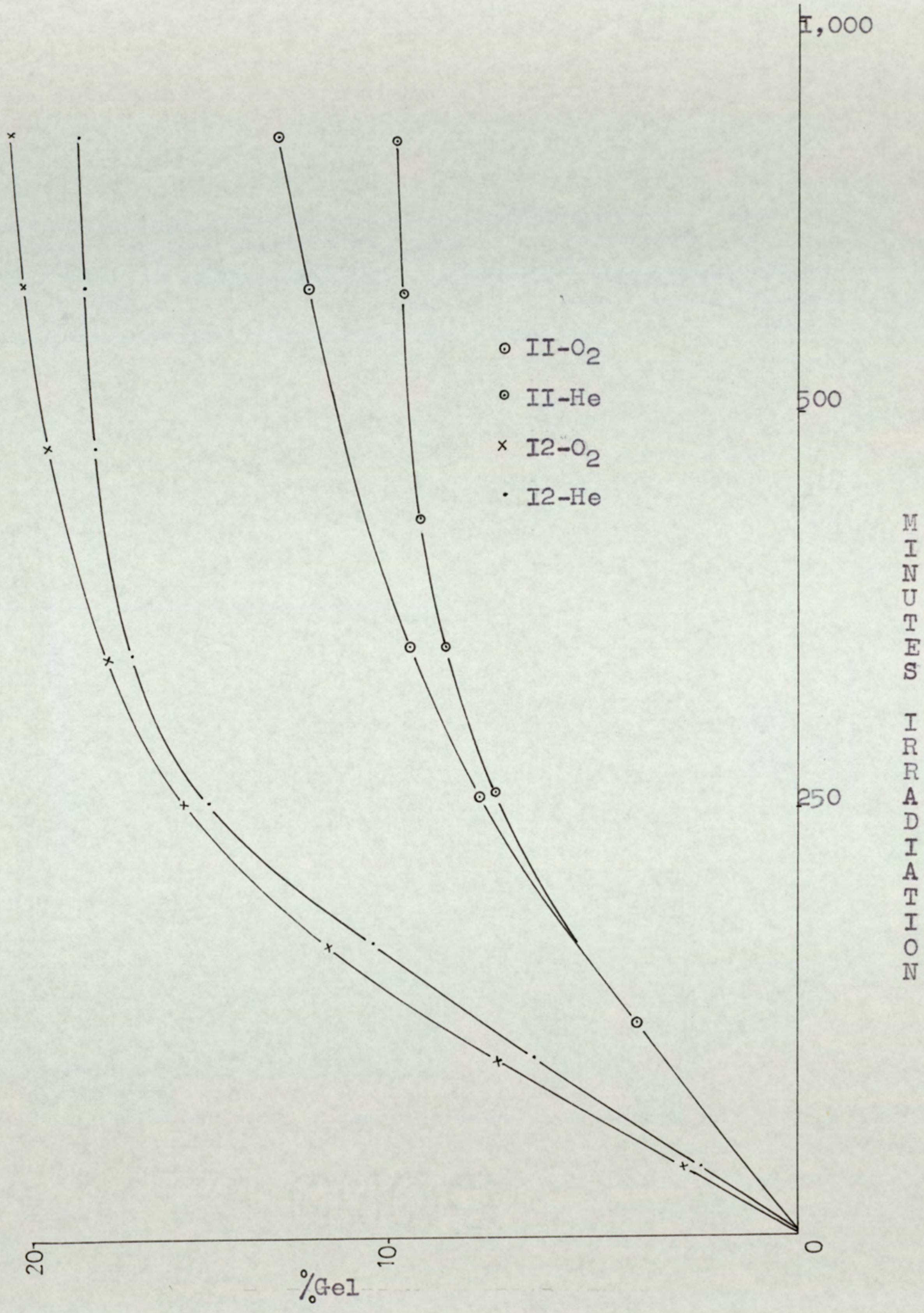


FIGURE 5-6 Gel formation on irradiation.

(models II,I2)

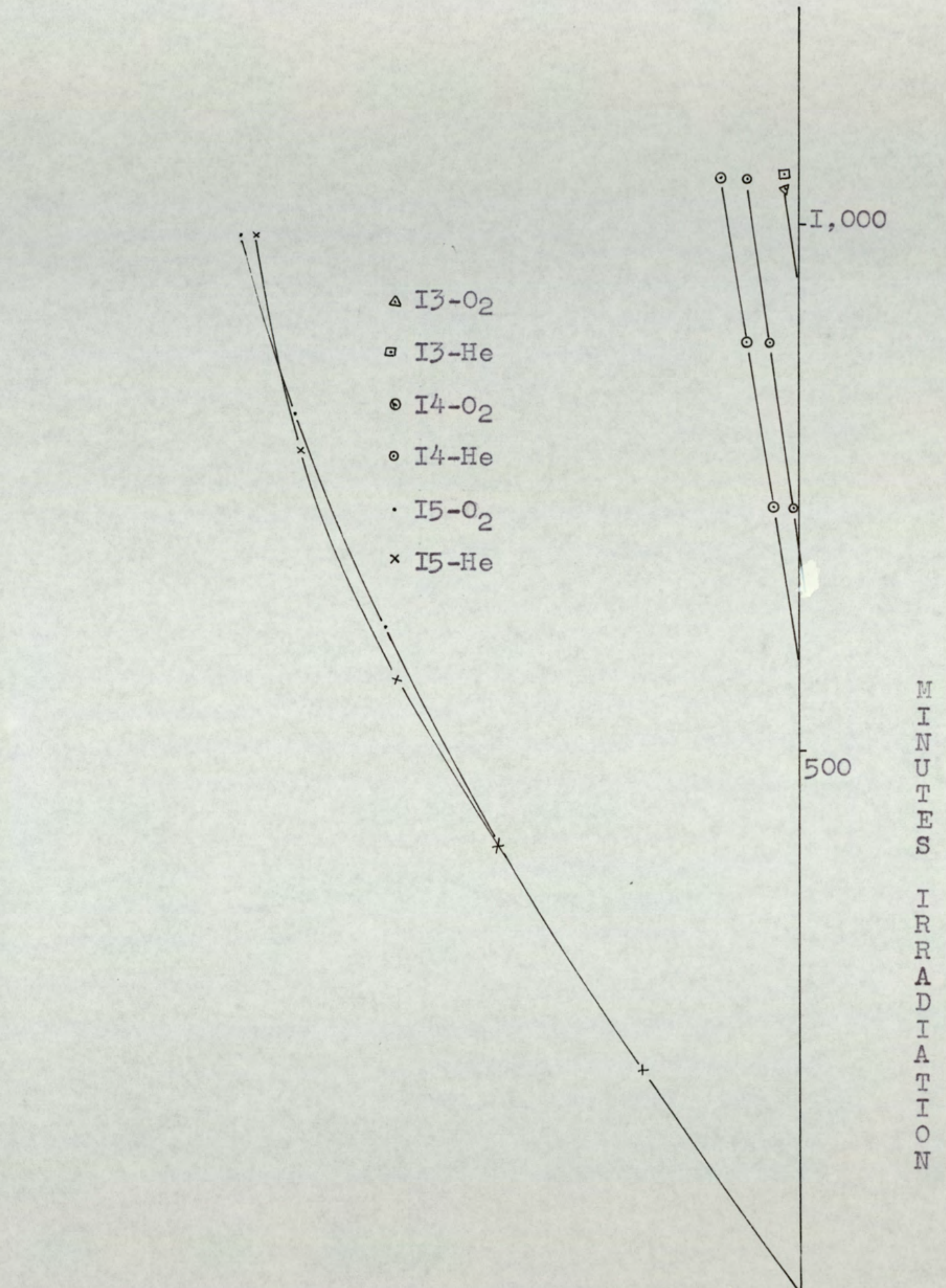


FIGURE 5-7 Gel formation on irradiation.

(models I3,I4,I5)

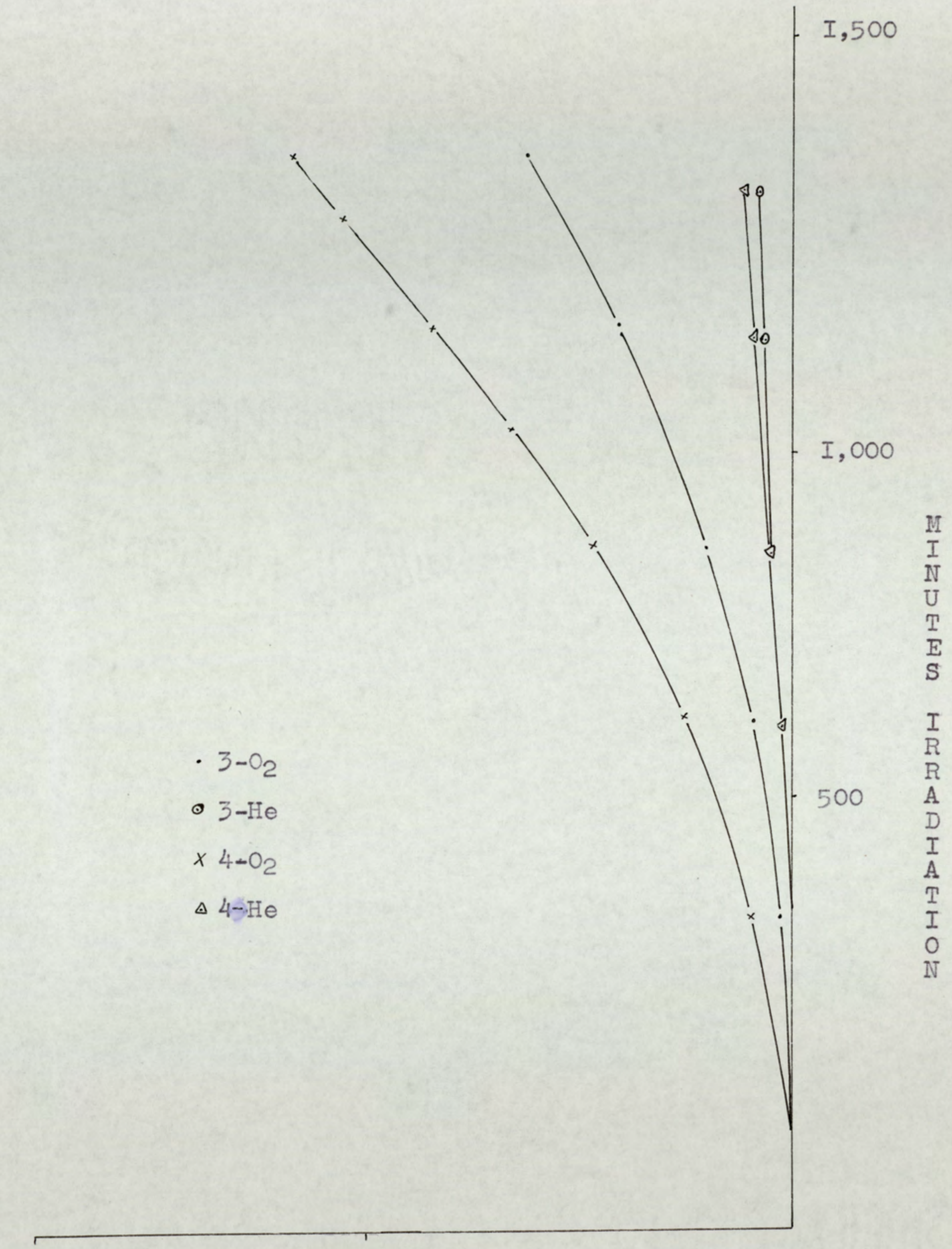


FIGURE 5-8 Ingrowth of 5.9μ IR Band.

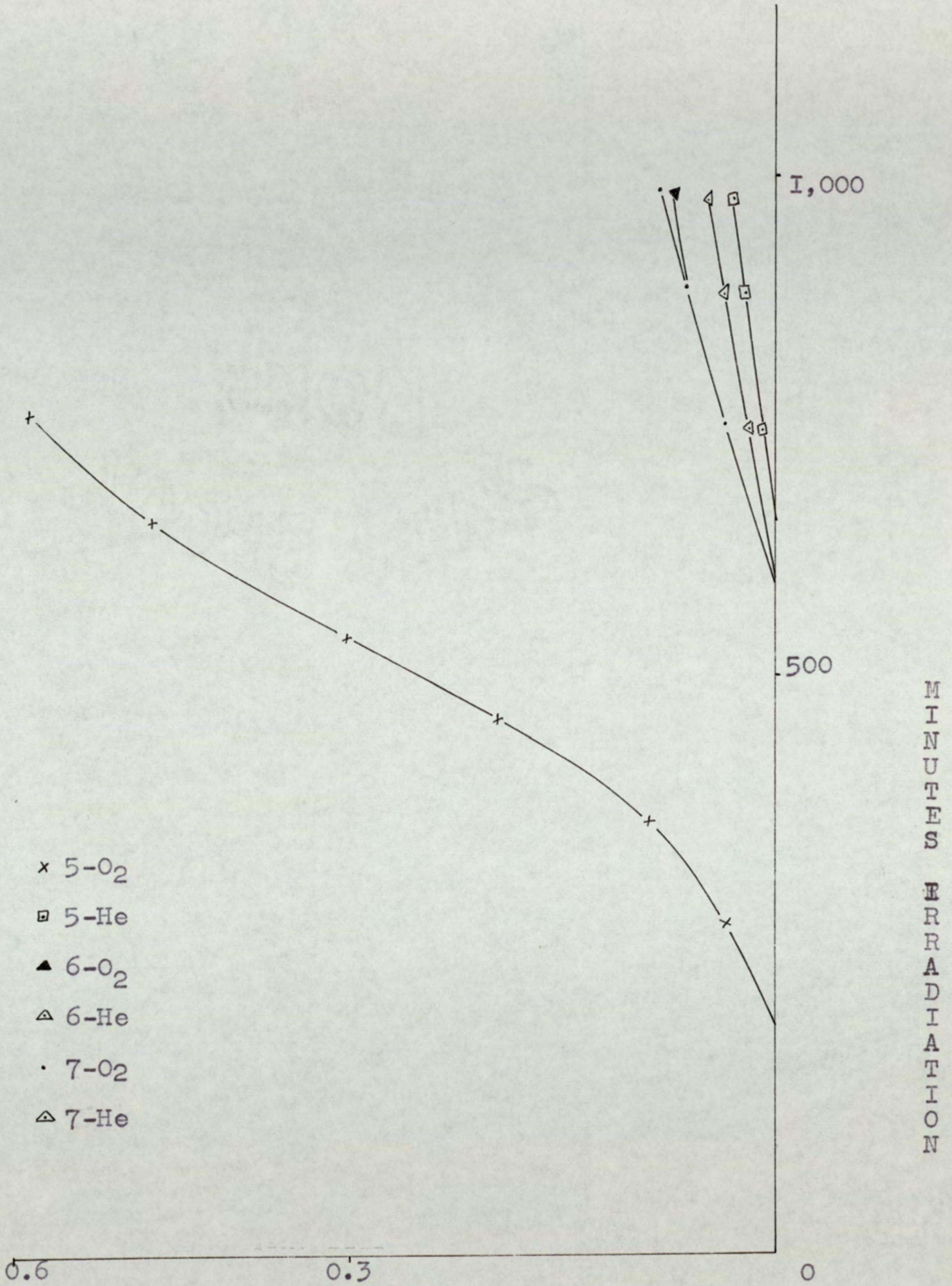


FIGURE 5-9 Ingrowth of 5.9 μ I R Band.

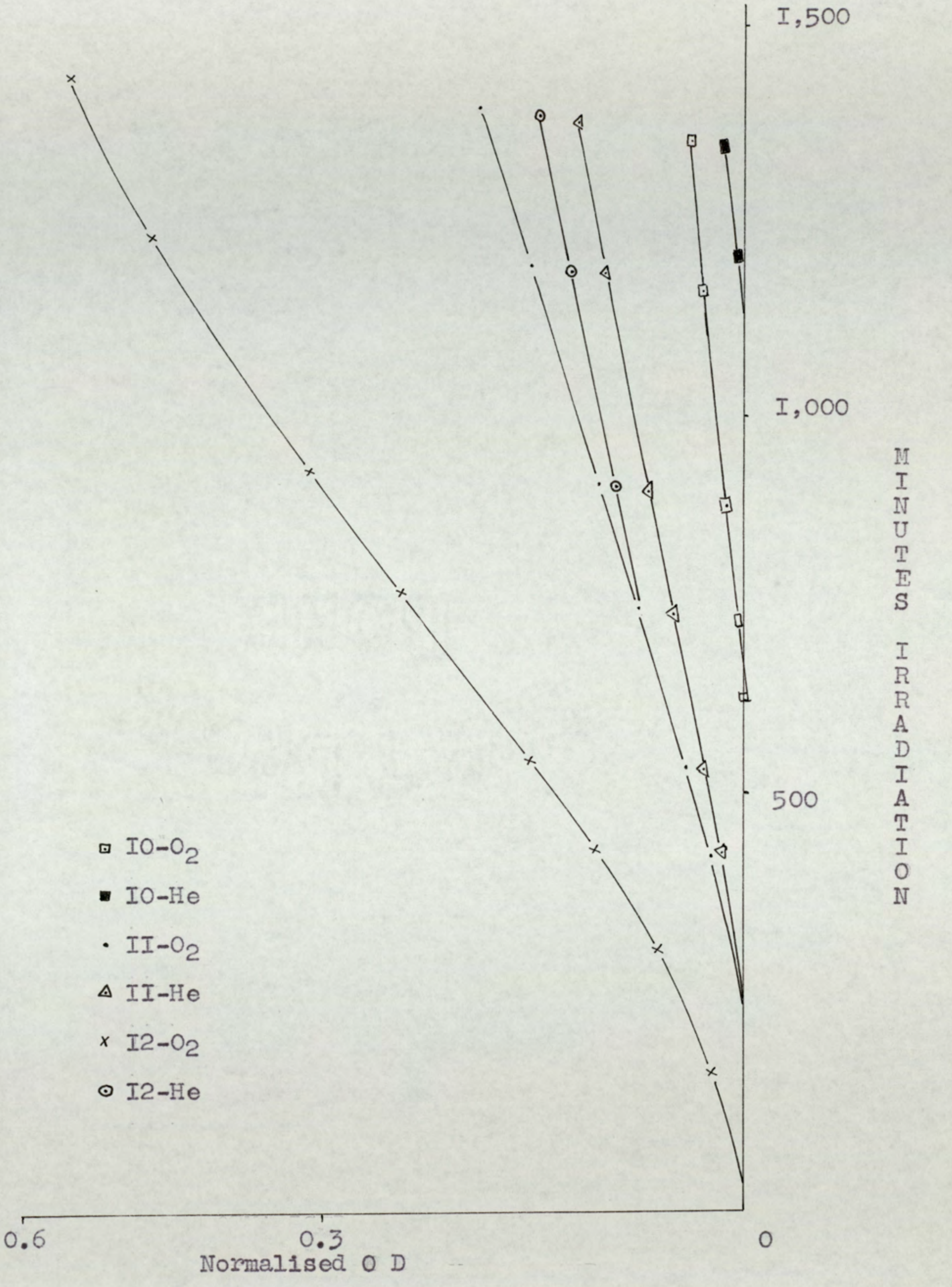


FIGURE 5-IO Ingrowth of 5.9 μ I R Band.

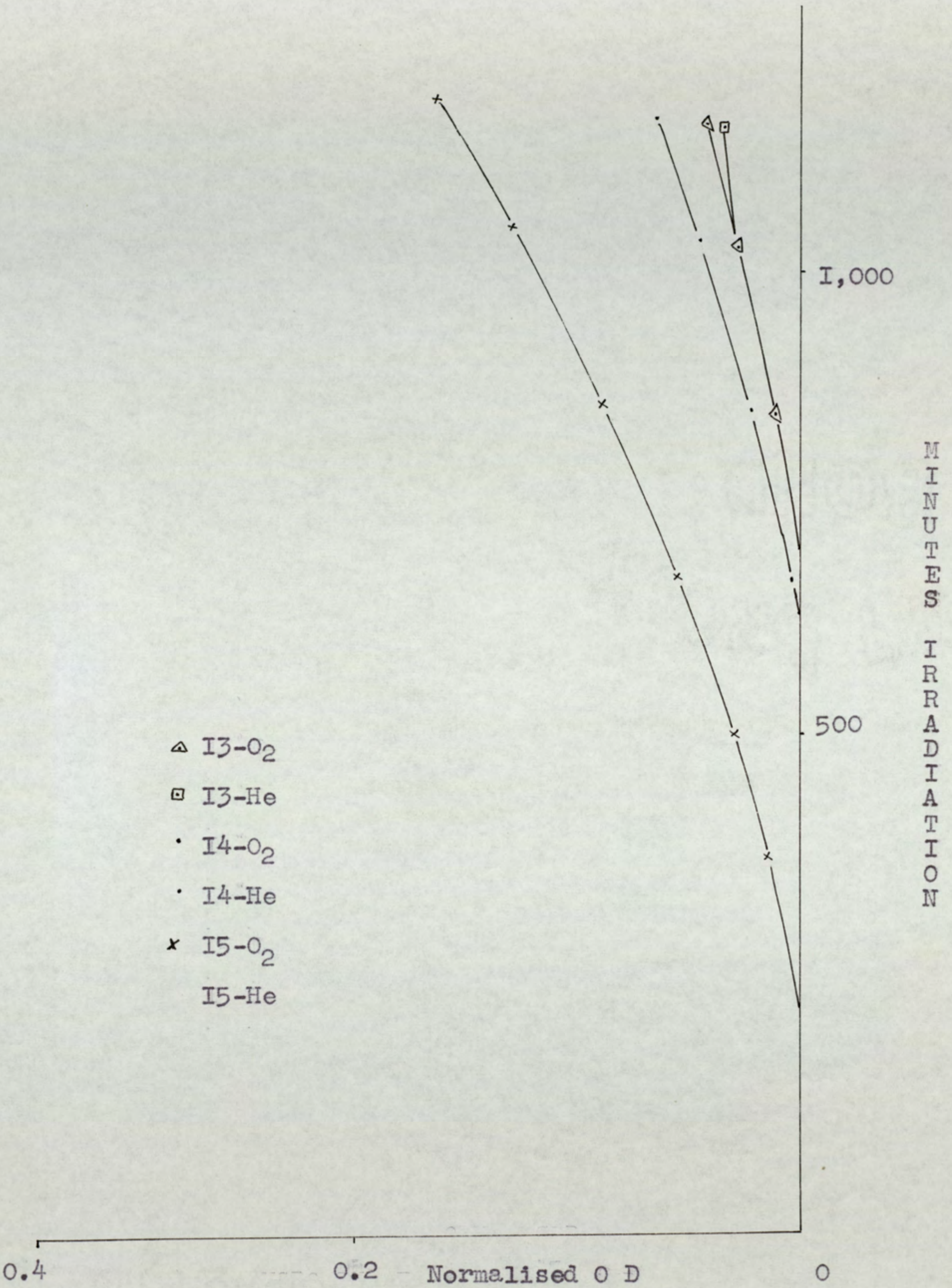


FIGURE 5-II Ingrowth of 5,9 μ I R Band.

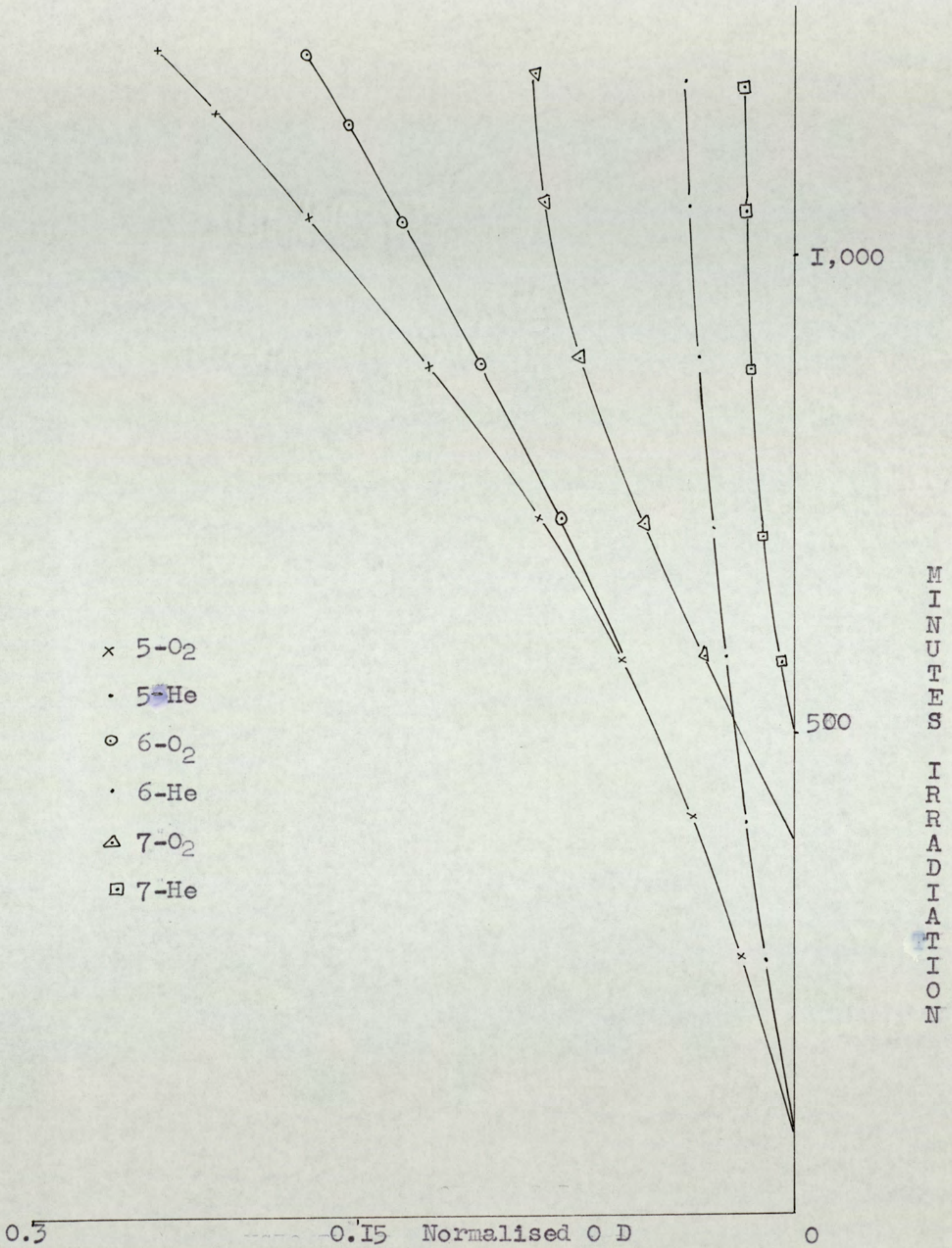


FIGURE 5-I2 Ingrowth of 6.0I μ I R Band.

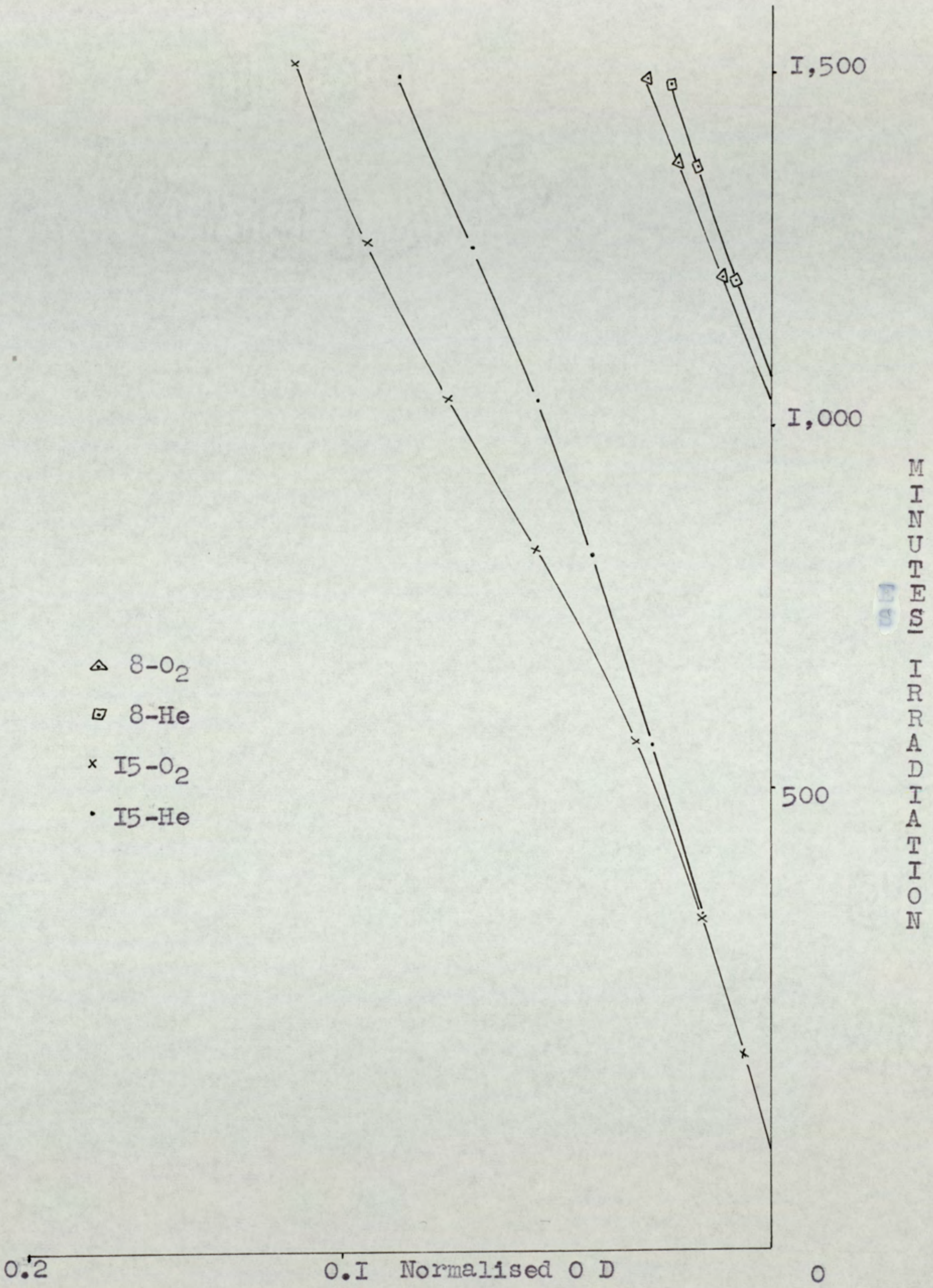


FIGURE 5-I3 Ingrowth of 6.0I μ I R Band.

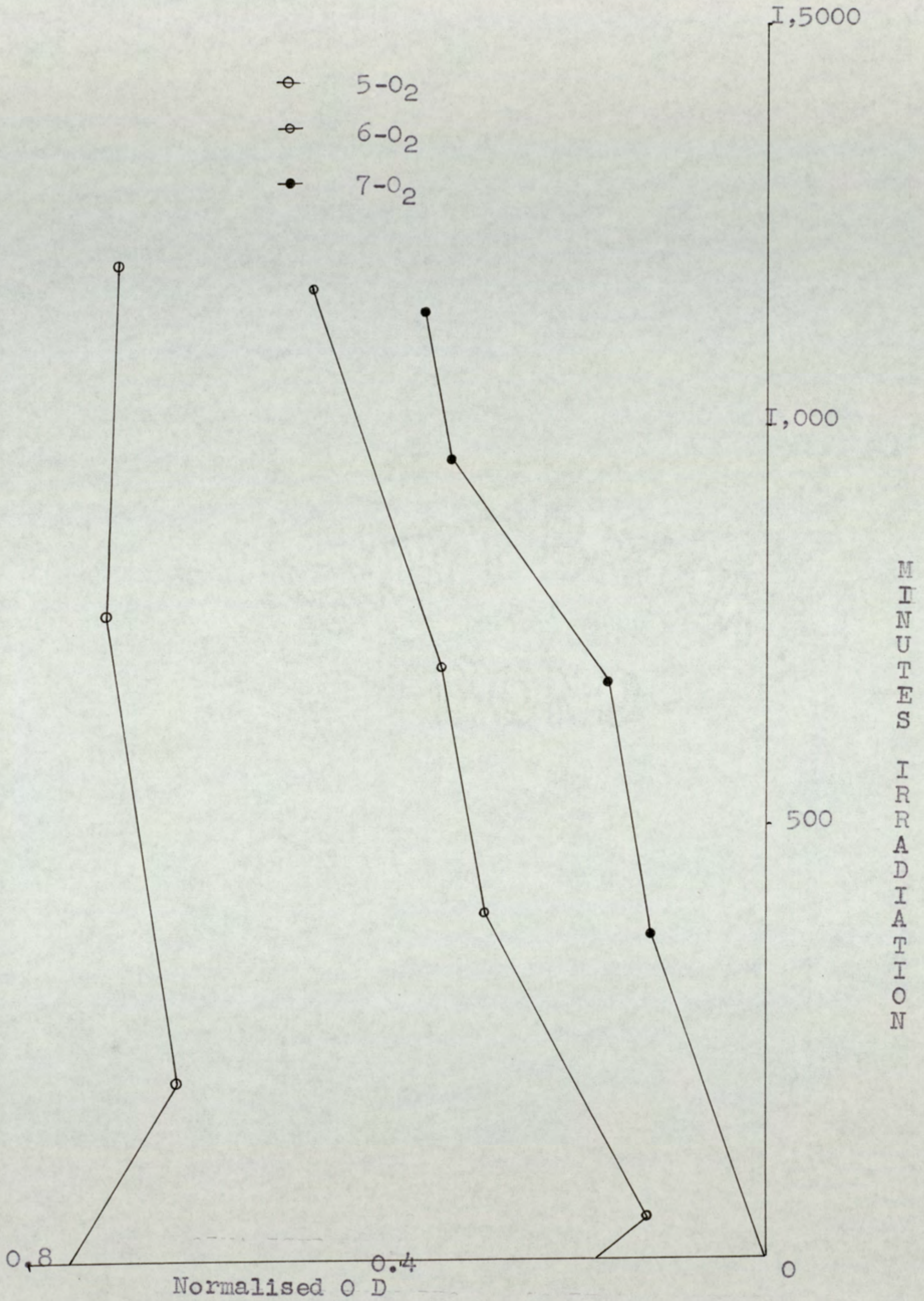


FIGURE 5-I4 Change in hydroxyl content on irradiation.

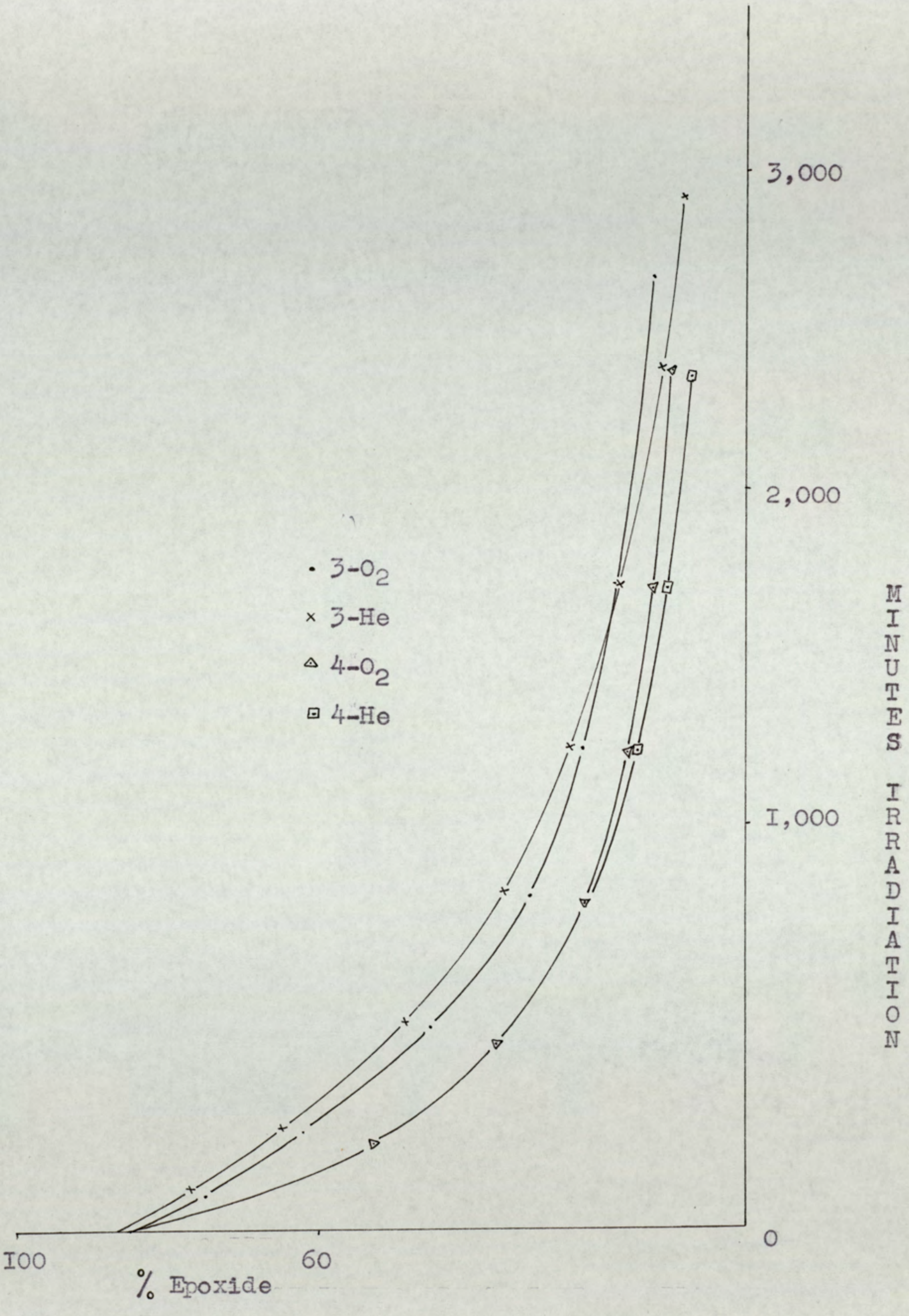


FIGURE 5-I5 Change in epoxide content on irradiation.

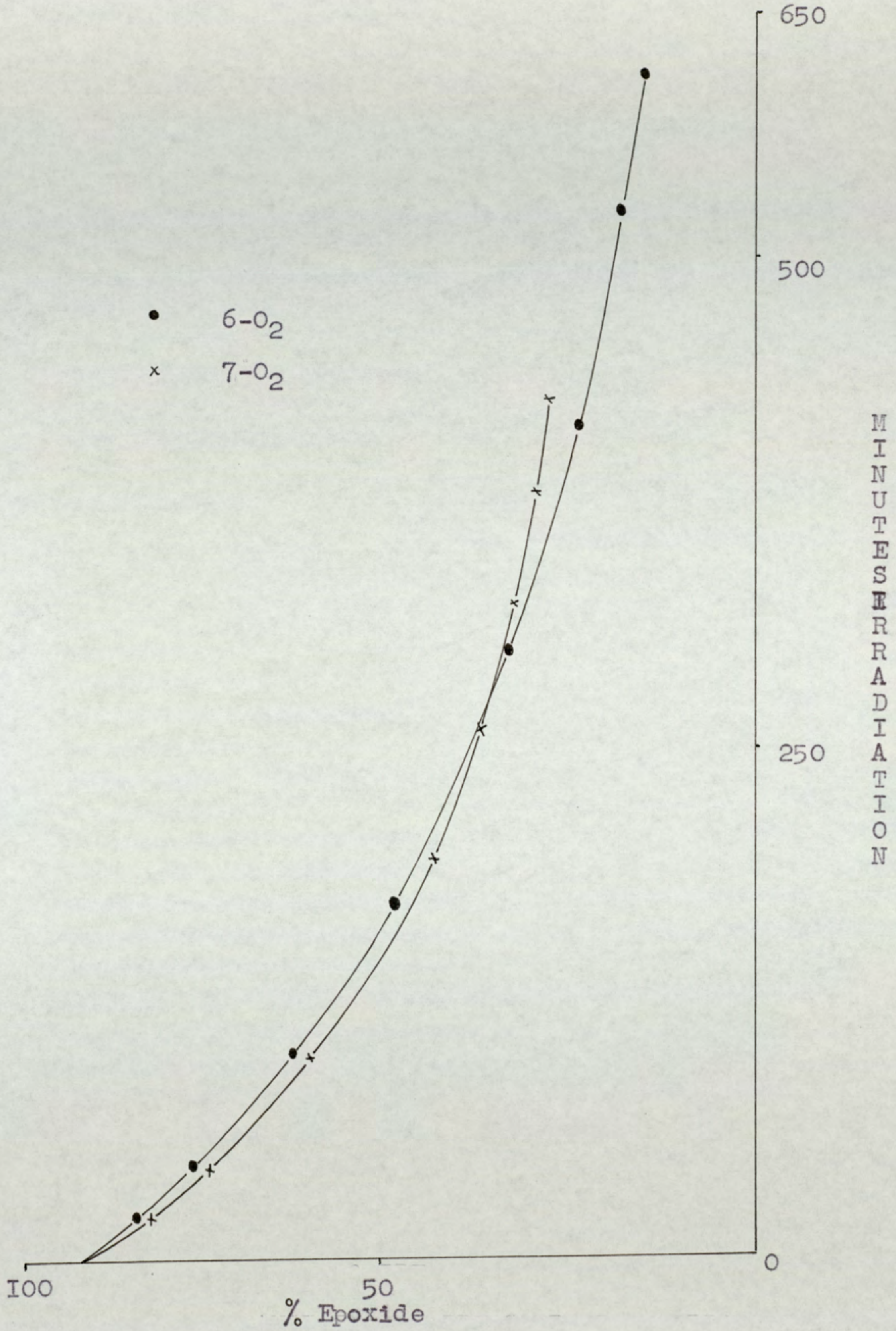


FIGURE 5-16 Change in epoxide content on irradiation.

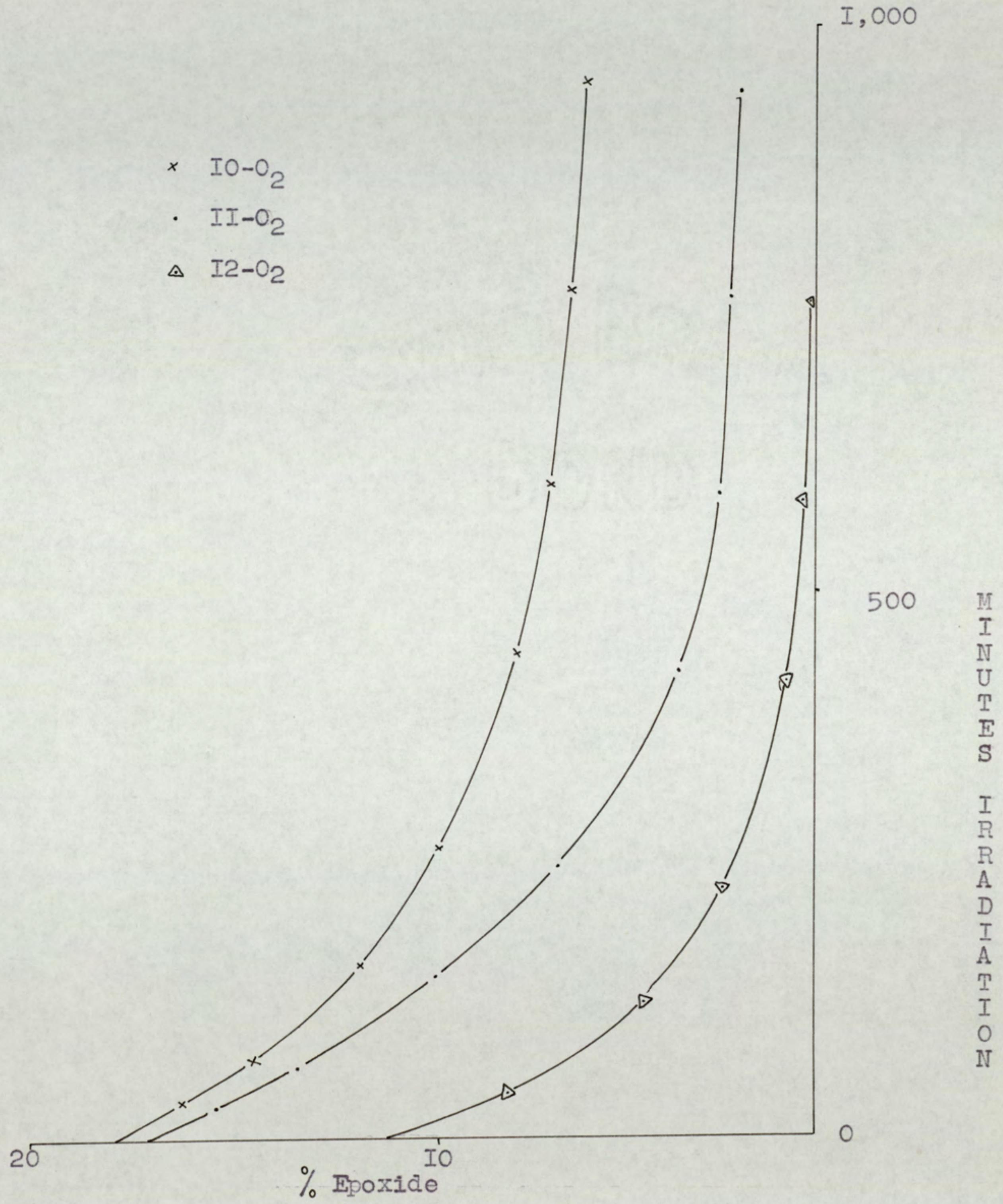


FIGURE 5-I7 Change in epoxide content on irradiation.

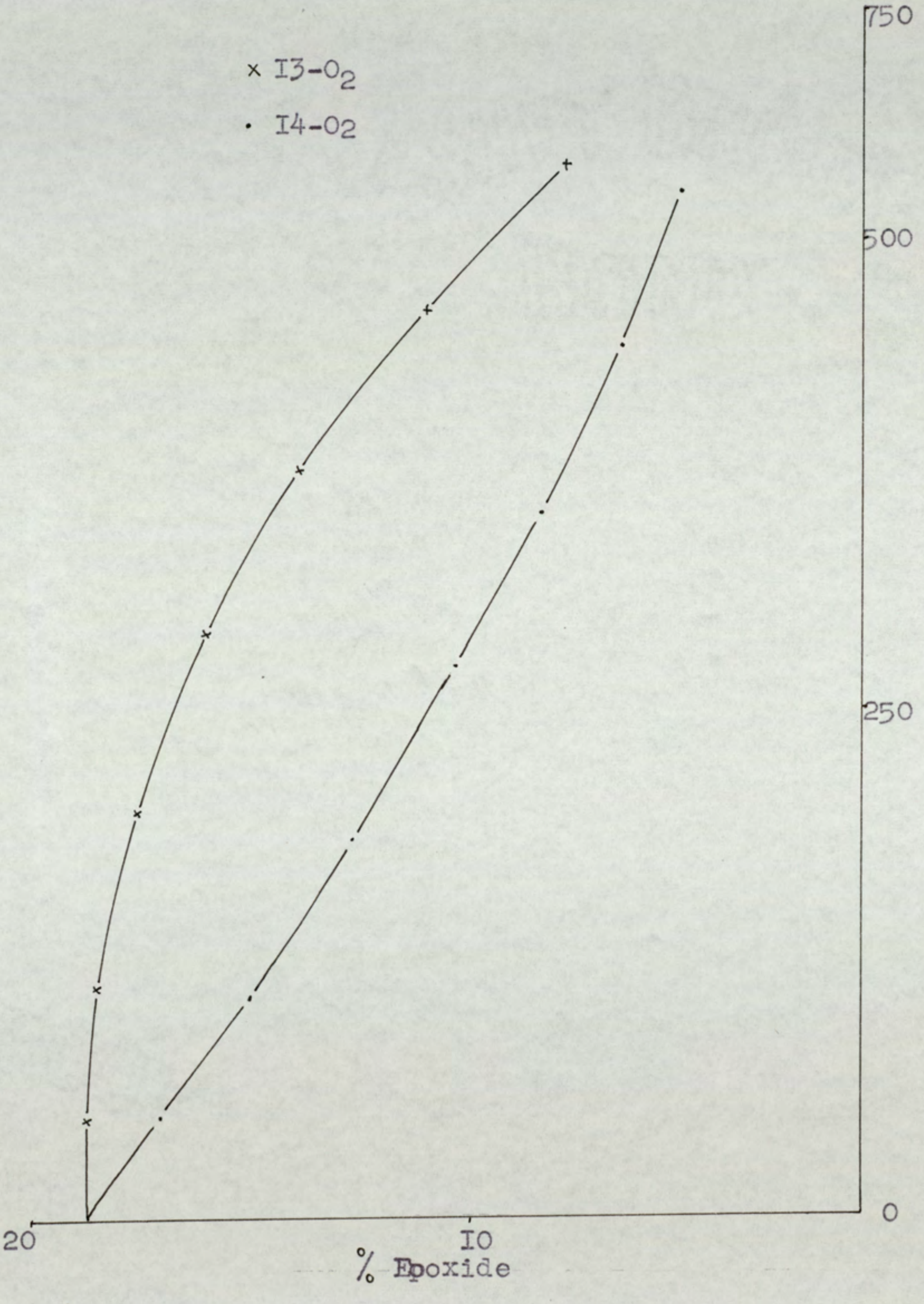


FIGURE 5-18 Change in epoxide content on irradiation.

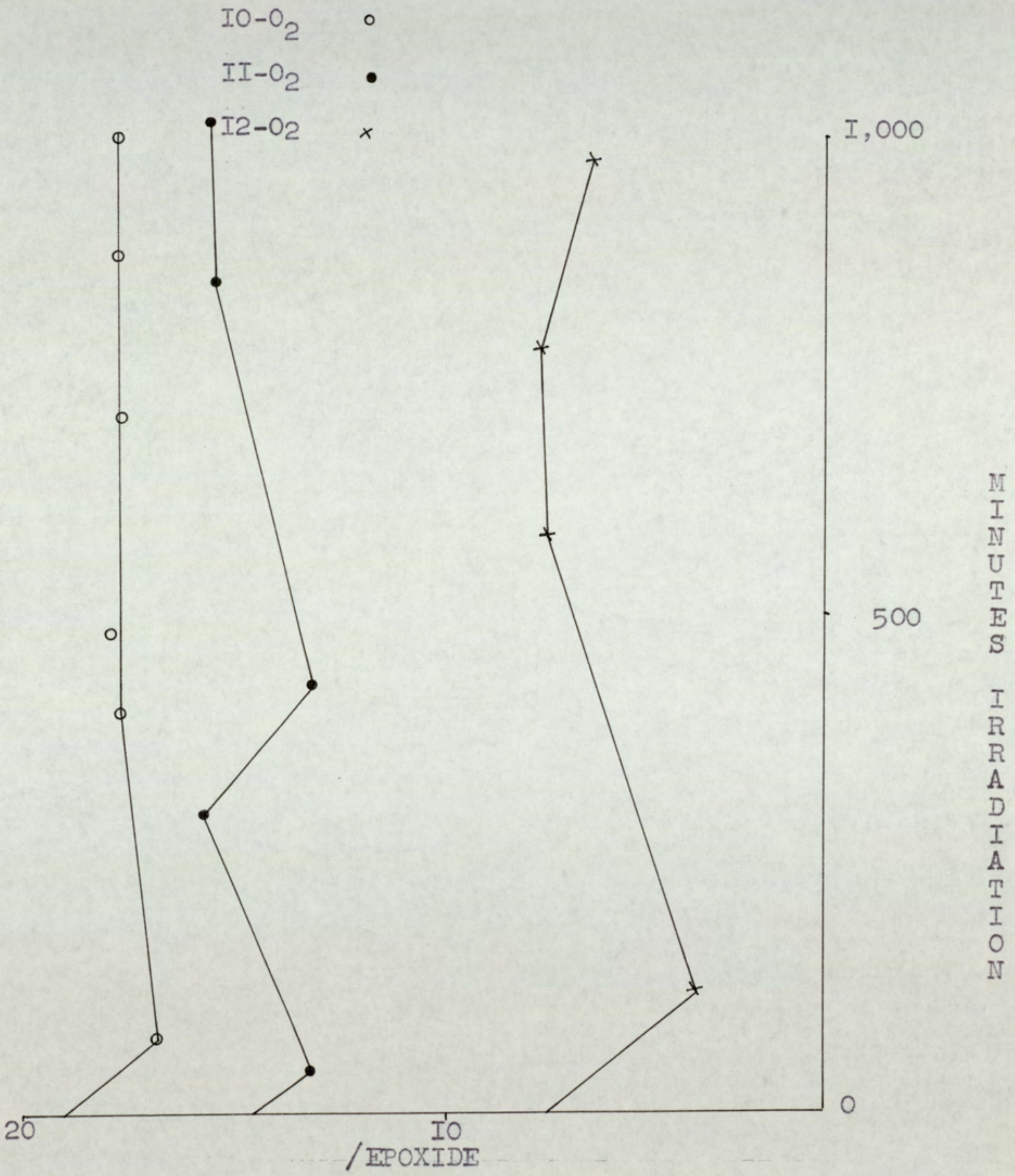


FIGURE 5-I9 Change in epoxide content on irradiation.

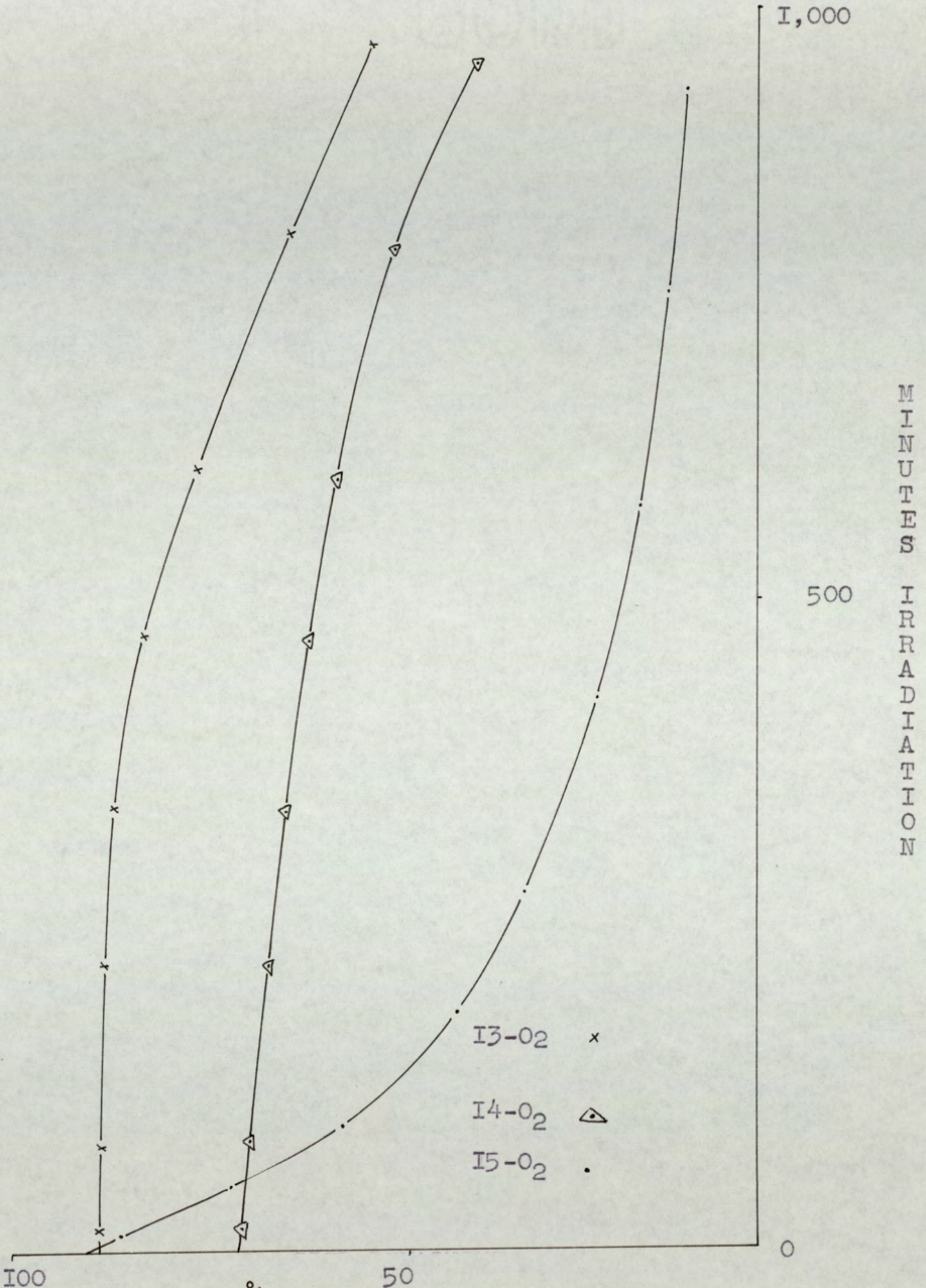


FIGURE 5-20 Change in ester content on irradiation.

CHAPTER 6

Mechanical Properties

The mechanical properties, modulus and decrement, were studied over the temperature range 100 °C to 200 °C. The apparatus and sample preparation technique used were described in Chapter 3. Irradiation of the polymer coated glass braids was performed in both oxidising and non oxidising conditions using pyrex, quartz and commercial glass filters. Difficulties were encountered because of water vapour condensation at low temperature and surface oxidation of the polymer at the high temperature. The latter was overcome by carrying out measurements in a helium atmosphere. The use of lagging and helium gas flow did not overcome the condensation problem encountered at low temperature. Because of this, some difficulties occurred with the interpretation of the low temperature data. Also, since the frequency of the pendulum used was fixed difficulties occurred in observing low temperature transitions from the modulus curves and decrement curves were used where possible.

The results are shown (Figures 6 - 1 to 6 - 3) for the modulus and decrement of the materials before irradiation. The usual methods of spectroscopy and chemical analysis (1) were used to characterise the monomers and the cured polymers.

Typical monomer analysis data is shown (Table 6 - 1)

TABLE 6 - 1

Composition of Epoxide Monomers

Material	Epoxide Equivalent	Hydroxyl Equivalent	Molecular Weight*
Monomer '828'	185	0.015	370
'826'	175	0.014	352
'816'	170	--	340

* by osmometry

Because of the difficulties encountered in the preparation of monomer '816' only a limited number of braids could be prepared and the measurements were performed at long irradiation intervals.

The analysis of the cured braid systems is shown (Table 6 - 2).

TABLE 6 - 2

Composition of Cured Systems

System	Epoxide equiv./1kg.	Hydroxyl equiv./1kg.	Monoester equiv./1kg.	Diester equiv./1kg.	Anhydride equiv./1kg
'828'/HHPA	0.0575	1.842	0.509	1.431	0.024
'826'/HHPA	0.0491	1.972	0.492	1.327	0.027
'816'/HHPA	0.0420	1.998	0.489	1.339	0.021
	equiv./litre	equiv./litre			
'828'/TETA	2.213	1.13			
'826'/TETA	1.984	1.12			
'816'/TETA	1.997	0.930			

6 - 1 Results

The results in terms of the modulus and decrement changes are shown (Figures 6 - 4 to 6 - 7) for photo-and photo-oxidative degradation. A number of mechanical relaxations were found to occur in the systems studied. The high temperature peak is termed the α relaxation (1) and corresponds to the glass transition of the polymer. The lower temperature transitions are labelled β and γ .

In oxidative degradation the γ peak increased in magnitude, shifted to lower temperature and then decreased in magnitude on further irradiation. During this time the α peak shifted to lower temperature and decreased in magnitude. A new peak called α' (2) appeared at a temperature higher than the Tg in both the TETA and HHPA cured polymers.

In helium, the γ peak again increased in magnitude and then decreased. A shift to lower temperature was then observed. The α peak shifted to lower temperature and decreased in magnitude.
No new α' peak was observed during the photo-degradation process.

6 - 2 Qualitative Interpretation of Results

Epoxy resins, like many polymers, show a number of molecular relaxations spread over a wide temperature range. The exact temperature positions of the relaxations depend on the isotropy of the samples. This was seen (Figures 6 - 2 and 6 - 3) by considering the positions of the transitions in the three systems comprising commercial and purified monomers. Studies by Pogany (2, 3, 4) on the viscoelastic properties of similar resin systems, confirmed the earlier work of May and Weir (5) who showed that the α relaxation in epoxide resins was associated with movement of the substituents on the central carbon bridge of the bisphenol-A portion of the cured structure, and also with the crosslink density of the material. In accordance with the work of Boyer (6), this high temperature relaxation is associated with the Tg. of the resin system. The measured Tg. values are shown (Table 6 - 3).

TABLE 6 - 3

* Glass Transition Temperatures

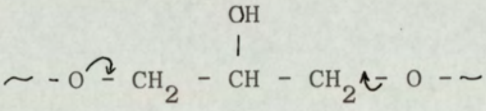
System	Tg (°C)
TETA/'828'	138
TETA/'826'	140
TETA/'816'	148
HHPA/'828'	135
HHPA/'826'	143
HHPA/'816'	152

* Determined by Tobolsky's Method (7)

The lower Tg. values observed with the impure monomer resins were thought to be due to the plasticising effect of the impurities (8), which occurred in the '828' material to a 3 - 4% level. The effect of the existing polymerised units in this system reduced the extent of crosslinking and were expected to contribute to the change in the Tg value over the purer '826' and '816' materials. The very small difference in the Tg observed with the '828' and '826' systems was due to impurities, whose Tg was close to that of the monomer and the plasticising effect was then reduced. This was seen in the results for the '816' systems.

The β transition observed in some systems was reported by Pogany (2) to be an artifact associated with the main relaxation and only occurred in undercured resins.

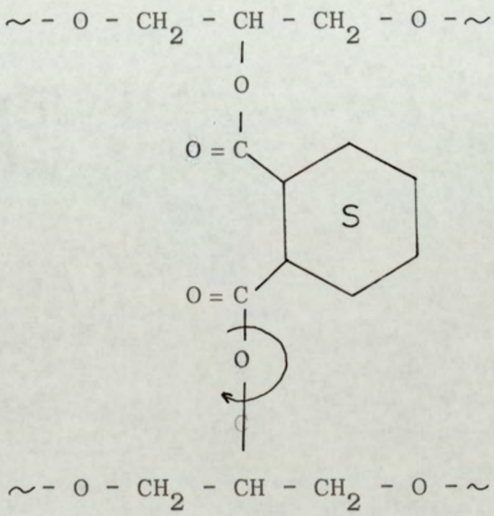
The low temperature or γ - transition in amine cured resins has been associated by other workers (9) with the movement of the hydroxyl portion of the cured structure. From bond angle considerations of the backbone structure (10) a crankshaft rotation of the group



$$\sim - O \curvearrowright - CH_2 - \overset{\overset{OH}{|}}{CH} - CH_2 \curvearrowleft - O - \sim$$

has been suggested to explain the transition. However movement of a complete unit such as the above is difficult to visualise in a cured resin. The relaxation may have been a combination of a number of molecular movements including the above. This transition has been shown to be associated with the degree of cure of amine systems. Pogany (3) found that the area under the peak was proportional to the degree of cure.

In the acid anhydride cured resins the low temperature transition has been assigned by Cuddily and Moacanin (10) to a rotation of the diester bridge:



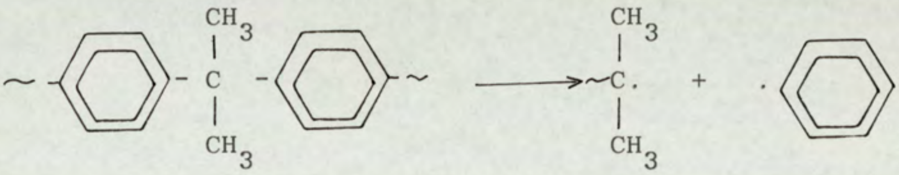
However, as with the assignment in the amine systems complete movement may not have been possible in cured resins.

The first observed effect, on photo-oxidative degradation of the amine systems, was an increase in the area of the low temperature γ relaxation. Since this movement was associated with the degree of cure of the resin, the increase was interpreted as being due to further reaction of residual epoxide groups. This may not have represented an actual cure crosslinking reaction, since from previous work it was known that chain scission at the ether bond also occurred, which produced alcoholic moieties by ring opening of the epoxide, or by ring opening and reaction with a neighbouring amine group. Direct photochemical ring opening of the epoxide group was ruled out from the type of radiation used. The subsequent shift to lower temperature and reduction in size were indicative of a freer rotation or movement of the group responsible for the relaxation. Possible explanations included loss of hydroxyl by formation of an ether bond or loss through scission of the ether bond by the usual peroxide formation. This would have resulted in a reduction in the number of crosslinks between chains.

During photo-degradation in a helium atmosphere, the initial increase in magnitude may have been associated with further curing. Further irradiation caused a reduction in the magnitude of the peak because of chain scission reactions which were found to occur by the ATR technique.

In the HHPA cured resins similar results were noted for the low temperature peak. It was difficult to find any increase in the peak intensity during the early irradiation in helium or oxygen, because of condensation and freezing of water vapour on the specimen surface. However the decrease in intensity and the shift in the peak maximum was again found during photo-oxidation. As with the amine systems a reaction in the aliphatic monomer section explained the observed facts. The magnitude of the shifts was of the same order in both the amine and the anhydride cured polymers. This may have been due to a common reaction viz. scission at the ether bond in the monomer. The rate of change, however, was greater with TETA cured resins as expected from their poor ultraviolet light stability. The results were borne out by the photo-degradation reactions.

The shifts and intensity changes for the γ relaxation were associated with similar changes at the main transition. However, a difference was found between photo-and photo-oxidative degradation. In the latter a new peak was formed at a temperature greater than the Tg of the system. A decrease in magnitude and a shift to lower temperatures also occurred in both oxidising and non oxidising atmospheres. No new peak was found during the photo- degradation reactions even after extended irradiation periods. The results were interpreted in terms of rupture of the monomer at the isopropylidene group



with subsequent reactions of the radicals formed. The product formation on photo-oxidation differed from that on photo-degradation in the quantity of oxidised aromatic compounds found. This applied to both amine and anhydride cured resins. This suggested that the new α' peak was due to the presence of the quinone or quinone/hydroquinone species, or some polymeric quinone compound. However ATR examination of the degraded braid/polymer amine systems in the infrared region showed that quinone formation occurred at earlier irradiation times. The first appearance of the α' peak corresponded to the initial decrease in the aliphatic carbonyl compounds. The sensitivity of the ATR technique was obviously greater than the TBA method used. Also, it is possible that the frequency of the pendulum, chosen for maximum response, may not have been of the correct order of magnitude for correlation of the two techniques. This was seen in the shapes of the decrement curves obtained, which were slightly askew.

Evidence for a surface degradation process was found by surface removal of the degraded material from the braids by abrasion with fine emery paper. The result, in terms of the logarithmic decrement curve of the main transition, is shown (Figure 6 - 8) for both the amine and the anhydride cured '826' monomer during both photo-and photo-oxidative degradation. The small discrepancies were found, by the ATR examination of the amine system, to be due to incomplete removal of the degraded surface or surface oxidation from the abrasion method used.

The discrepancy was greater for the helium irradiated samples and may have been due to long lived free radicals diffusing out to the polymer surface where reaction occurred with oxygen, resulting in carbonyl formation. Some evidence for the diffusion of oxygenated compounds from the amine system was found during the ATR examination. However due to the amount of damage by the coated braids to the soft KRS-5 trapezoid crystal, this work was discontinued. The surface removal by abrasion reduced the colour of all materials though not to the original colourless amine and faint yellow anhydride material. This we know to be due to the fairly uniform distribution of colour forming species throughout the bulk of the polymer and was shown in the case of the amine films in the form of ingrowth of carbonyl from both sides of the film surface.

6 - 3 Effect of Light Intensity and Wavelength

The effect of light intensity showed that no chemical reactions occurred on removal of the light source. Also, up to irradiation periods of 100 hours the extent of degradation was dependent on the light intensity, though in all cases the reaction occurred at the specimen surface. Presumably some of the newly formed degraded surface underwent further decomposition during long irradiation periods. This was not detected by the ATR technique.

The effect of irradiation wavelength (Figure 6 - 9) showed that the short wavelength region caused the major effect. In particular, the shifts of the α transition were most noticeably affected by this wavelength region. In both the amine and the anhydride systems the 365 nm band caused changes with the α and γ transitions, being greater for the latter in the amine systems.

The effect of the short wavelength radiation was again seen to cause excitation of the benzene nucleus, which resulted in scission of the isopropylidene group. This excitation could, from the TBA data, be interpreted as causing the ether bond scission during inert gas irradiation, since both the α and γ transitions were equally affected. Elimination of the 365 nm band caused little effect in either system during photo-degradation. The photo-oxidative degradation reactions were affected by the 365 nm band, in particular the movement of the low temperature transition.

Removal of the 280 - 330 nm radiation prevented formation of the α' peak on oxidative degradation with both the amine and anhydride materials. This indicated that the benzene excitation together with the resultant quinone formation, during degradation of the bisphenol-A portion, was caused by the short wavelength radiation. No synergism was observed in the anhydride cured polymer between the 280 - 330 and 365 nm radiation.

6 - 4 Effect of Post Cure on Tg during Photo-Oxidative Degradation

The post curing schedules used are shown (Table 6 - 4)

TABLE 6 - 4

Post Cure Schedules and Temperatures

System	Post Cure
'826'/TETA	4 hours at 100 °C
'826'/HHPA	8 hours at 150 °C

The results are shown (Figure 6 - 10). It was found by the ATR technique that high temperature post cure of TETA cured resins resulted in degradation of the resin with carbonyl (aliphatic and aromatic) formation. Thus colour centres were introduced into the system before irradiation, These chromophoric groups then absorbed radiation and caused further rapid colour formation. The result by the TBA technique was seen in the formation of the α' transition at earlier irradiation times, together with greater shift of the α peak to lower temperatures. Therefore the brittleness of the material was well characterised after short ultraviolet light exposures. A similar result was observed with the anhydride cured polymer though at longer irradiation times. Also, the growth rate of the α'- transition in the latter system was slower than in the amine system, probably because of the lack of reaction of the HHPA acid, known to be little affected by long wavelength radiation, while the amine, TETA, from the model compound studies did undergo some degradation.

6 - 5 Effect of Monomer Purity on Photo-Oxidation

Initially the effect of monomer purity was investigated by the addition of epichlorohydrin to the resin curing agent mixtures. However, the presence of the small chain in the cured system caused noticeable plasticisation, as evidenced by the lower Tg. Because of this fact the three monomer systems were investigated in terms of the relative shifts and changes in the α and γ relaxations. The results are shown (Figures 6 - 11 and 6 - 12) for the amine and anhydride cured materials respectively. Little difference in the extent of change of the transitions was seen for the '828' and '826' systems. The slight differences were due to the increased purity of the '826' monomer and its greater degree of crosslinking over the '828' systems. The data for the pure '816' systems showed that the rate of degradation of the aliphatic section of the monomer was slower than in either of the other systems. The same overall effect was found regardless of the type of curing agent used. The results for the α transition also showed that the rate of degradation was slower than for the other systems, in terms of time, rate of formation of the α'peak and the shift of the α transition to lower temperature.

6 - 6 Quantitative Interpretation of Data

The rubber modulus for the compounds studied, measured at 200 °C, is shown (Table 6 - 5).

TABLE 6 - 5

Values of the Rubber Modulus at 200 °C

System	Quanta x 10^{-20} 280 nm	Gr dynes/cm^2 x 10^{-9}	Post cured Gr dynes/cm^2 x 10^{-9}
'828'/HHPA	0	2.0	5.9
	18	6.6	-
	2241	8.2	5.94
surface removed		2.7	2.3
'826'/HHPA	0	3.0	7.2
	15	7.6	-
	2384	8.5	7.6
surface removed		3.1	2.9

TABLE 6 - 5 (Continued)

System	Quanta x 10^{-20} 280 nm	Gr dynes/cm^2 x 10^{-9}	Post cured Gr dynes/cm^2 x 10^{-9}
'816'/HHPA	0	5.8	8.7
	40	9.2	-
	5520	11.1	8.7
surface removed		6.1	5.9
'828'/TETA	0	0.04	0.28
	26	0.23	-
	3100	3.2	2.83
surface removed		0.1	0.53
'826'/TETA	0	0.1	0.52
	20	0.41	-
	2980	6.9	5.24
surface removed		0.17	0.101
'816'/TETA	0	0.64	0.984
	75	1.08	-
	4700	1.81	0.984
surface removed		1.92	0.652

The effect of monomer purity was reflected in the higher values of the rubber modulus, Gr, in the undegraded resins. Similar results were reported by Pogany (11) using different curing agents.

The value of the rubber modulus can be calculated from the theory of rubber elasticity by the equation (12).

$$Gr = N K T = d R T/Mc \qquad (6 - 1)$$

Gr - shear modulus
N - number of chains per unit volume
K - Boltzmann constant
T - absolute temperature
d - density
R - gas constant
Mc - molecular weight between cross links

This relationship holds if there is Gaussian distribution of chain segments between cross links. The epoxide resin contains twelve links. Therefore quantitative application of the equation is subject to errors. Tobolsky modified equation (6 - 1) by introducing a front factor

$$Gr = \tau Z c K T \qquad (6 - 2)$$

Z - number of network chains per crosslinking molecule

c - number of crosslinking molecules per ml

τ - front factor

The latter can be obtained from the expression

$$\tau = \bar{R}i^2 / \bar{R}_f^2 \qquad (6 - 3)$$

$\bar{R}i^2$ - mean square distance between network junctions

$\bar{R}_f^2$ - mean square end to end length of the network chain considered as a chain in free space.

For an epoxide resin (Shell "826") cured with TETA the value of Gr was given by Katz and Tobolsky (13) as 1.78 by measurement and 1.32 by calculation.

The value of Mc for a fully cured resin was the molecular weight of the monomer as shown in Table 6 - 1. This ignored the methylene sequences in TETA and also assumed that each nitrogen atom was a single point of crosslinking. The value of Gr calculated from equation (6 - 2) should have been 1.0×10^8 dynes/cm^2. The measured value (Table 6 - 5) was 0.4×10^8 dynes/cm^2 i.e. 2.5 times less, which was in good agreement with the value of Katz and Tobolsky 1.78×10^8 dynes/cm^2 despite the type of equipment used for the measurement. The value for the '826' monomer system was that predicted by theory for a pure epoxide monomer and can be assumed to be slightly inaccurate, as can the value for the '816' system.

The validity of the rubber elasticity theory has been tested (11) for the amine cured epoxide resins using network models and a series of approximations.

Irradiation in oxygen resulted in an increase in Gr measured at 200 °C (Table 6 - 5). This increase in Gr above the Tg was indicative of crosslinking (12).

Irradiation in helium showed a decrease in Gr and was indicative of chain scission reactions. It is probable that both chain scission and crosslinking reactions occurred in both irradiation studies, with a predominance of the former in inert gas irradiations and of the latter in oxidative atmospheres.

There is no satisfactory theory relating Tg to crosslink density. Empirical relationships were proposed by Ueberreiter and Kanig (14). They noted that Tg increased with crosslink density and related this to a reduction in the specific volume. Pogany, using the data on the phenoxy resin as a standard, established a relationship for Tg and Mc in epoxide resins (11). He found that Mc had to fall below a critical value to increase Tg. A similar result was established by Heinze for rubber (15). For epoxide resins the critical Mc value was 400. Therefore since a reduction in Tg occurred on irradiation in oxygen and helium the Mc value would have been expected to increase if the cross link density remained constant. Murayama and Bell (16) suggested the use of the equation

$$Mc = \frac{3.9 \times 10^4}{Tg - Tg_o}$$

Tg_o - transition temperature of uncrosslinked polymer

An example of such an uncrosslinked polymer was phenoxy resin with Tg = 100 °C (11). Using this value the initial calculated Mc for the undegraded '828'/TETA system was approximately 10^3, which was considerably different from the initial value of 370. However, from the shift in the Tg of the amine system the value of Mc decreased by 50 % as was expected by the proposed monomer breakdown.

The slopes of the modulus curves for both the amine and the anhydride systems changed on irradiation. Kwei,(17) investigating the change in the slope of the modulus curve for a series of amine cured epoxide resins, found that a relationship existed between the slope and the number of methylene groups between points of crosslinking. A similar relationship was expected during degradation of the resins, if the bond scission occurred in the TETA curing agent. Using the Kwei equations

$$\log G^1/G^1_2 \Big/ \log^1/G^1_2 = \tfrac{1}{2}\left[1 + (e\ r\ f)h\ \left(\frac{1}{T} - \frac{1}{T_o}\right)\right]$$

T - absolute temperature (^oK)

T_o - temperature at which $G^1 = (G^1_1 . G_2)^{\frac{1}{2}}$

G^1_1 and G^1_2 - the upper and lower plateau of the dynamic shear modulus

h - parameter representing the steepness of frequency dispersion

(e r f) - error function, which was derived from equation for the relaxation modulus by Tobolsky (18) by substitution of temperature change for frequency change.

A graph of the left hand side of equation (6 - 5) should have yielded, on normal probability paper, a straight line from the slope of which 'h' could be calculated.

Graphs of the experimental data for the TETA/'828' polymer are shown (Figure 6 - 13). The data above and below the Tg was represented by parameters h_r and h_g respectively. The values obtained are shown (Table 6 - 6).

TABLE 6 - 6

Parameters for Amine Cured Resins

System	Irradiation Time (minutes)	$h_r \times 10^{-3}$	$h_g \times 10^{-3}$
'828'/TETA	0	8.14	3.47
	30.000	8.11	3.70
	60.000	8.13	-
'826'/TETA	0	8.17	3.44
	30.000	8.17	3.73
	60.000	8.10	3.91

The h_g values, before irradiation, were of the same order of magnitude as found for the '828' monomer cured with ethylene diamine and diethylene triamine (17). These curing agents had the same number of methylene units between the crosslink junctions. Kwei suggested that h_g was related to the methylene sequence and therefore to the steepness of the dispersion curves. This indicated that no scission had occurred in the curing agent during irradiation. This was valid for the initial irradiation periods.

The other parameter, h_r, according to Kwei may have been associated with the motion involving the trifunctional nitrogen junction. A correlation occurred between the above data for an undegraded polymer and the value of h_r for a diethylenetriamine cured systems. This was probably due to the primary and secondary amine groups present in diethylenetriamine and TETA. The increase in the value was assigned to increased motion of the degraded chain ends from scission at the ether or other bond. This scission resulted in the formation of low molecular weight amines of high mobility.

The modulus and decrement changes reported on ultraviolet irradiation confirmed some of the earlier results of Pierce (19), who reported on the mechanical properties of epoxide paint films on timber substrates. The result for the low temperature relaxation was very different. Pierce reported a shift of this peak to higher temperatures, as seen by the modulus and decrement curves. This may have been due to the substrate used by Pierce or to the presence of ice and water at the surface of the coated braids during the measurements. However the general increase in Gr confirmed the higher α' relaxation.

Comparison with the effects of high energy radiation on cured epoxide resins showed some similarities with ultraviolet light degradation. The γ transition was observed to decrease and shift to lower temperature, while the major relaxation, α, shifted by 50^{o} to lower temperatures (20, 21, 22). The changes were interpreted as being caused by direct bond scission in the portions of the molecular chain between the phenyl groups of the monomer and the benzene ring of the curing agent used. The similarity to the ultraviolet irradiation effects was due to similar degradation reactions, which occurred by direct scission due to high energy radiation in one case and absorption of light in the other.

REFERENCES

1. Boyer, R.F., J. Polym. Sci. C 14, 3, 1966
2. Pogany, G.A., Br. Polym. J. 1, 177, 1969
3. Pogany, G.A., Eu. Polym. J., 6, 343, 1970
4. Pogany, G.A., Polymer 11, 66, 1970
5. May, C.A., Weir, F.E., SPE Trans. 207, July 1962
6. Boyer, R.F., Rubber Chem. Tech. 36, 1303, 1963
7. Tobolsky, A.V., et al J. Polym. Sci. 62, 171, 1962
8. "Mechanical Properties of Polymers" by Neilson, L.E., Reinhold, New York, 1967
9. Nowak, R., Steinbacker, E., Kunstoffe, 48, 558, 1958
10. Cuddily, E.F., Moacanin, J., ACS Symposium 449, 1968
11. "Viscoelastic Properties of Epoxide Resins" by Pogany, G.thesis, 1967
12. "The Physis of Rubber Elasticity" by Treolar, L.R.G., Clarendon Press, Oxford, 1967
13. Katz, D., Tobolsky, A.V., Polymer 4, 417, 1963
14. Ueberriter, K., Kanig, G., J. Chem. Phys. 18, 399, 1950
15. Heinze, H.D., at al Rubber Chem. Tech. 35, 776, 1962
16. Murayama, T., Bell, J.P., J. Polym. Sci., A-2, 8, 437, 1970
17. Kwei, T.K., J. Polym. Sci. A-2, 4, 943, 1966
18. "Properties and Structure of Polymers" by Tobolsky, A.V., p177 John Wiley, New York 1960
19. Pierce, P.E., et al, J. Paint. Technol., 38, 588, 1966
20. Kline, D.E., J. Polym. Sci., XLVII, 237, 1960
21. Kline, D.E., Saver, J.A., SPE Trans., 21, January 1962
22. Kline, D.E., Saxton, J.H., J. Opt. Soc. Am. 50, 11, 1103, 1960

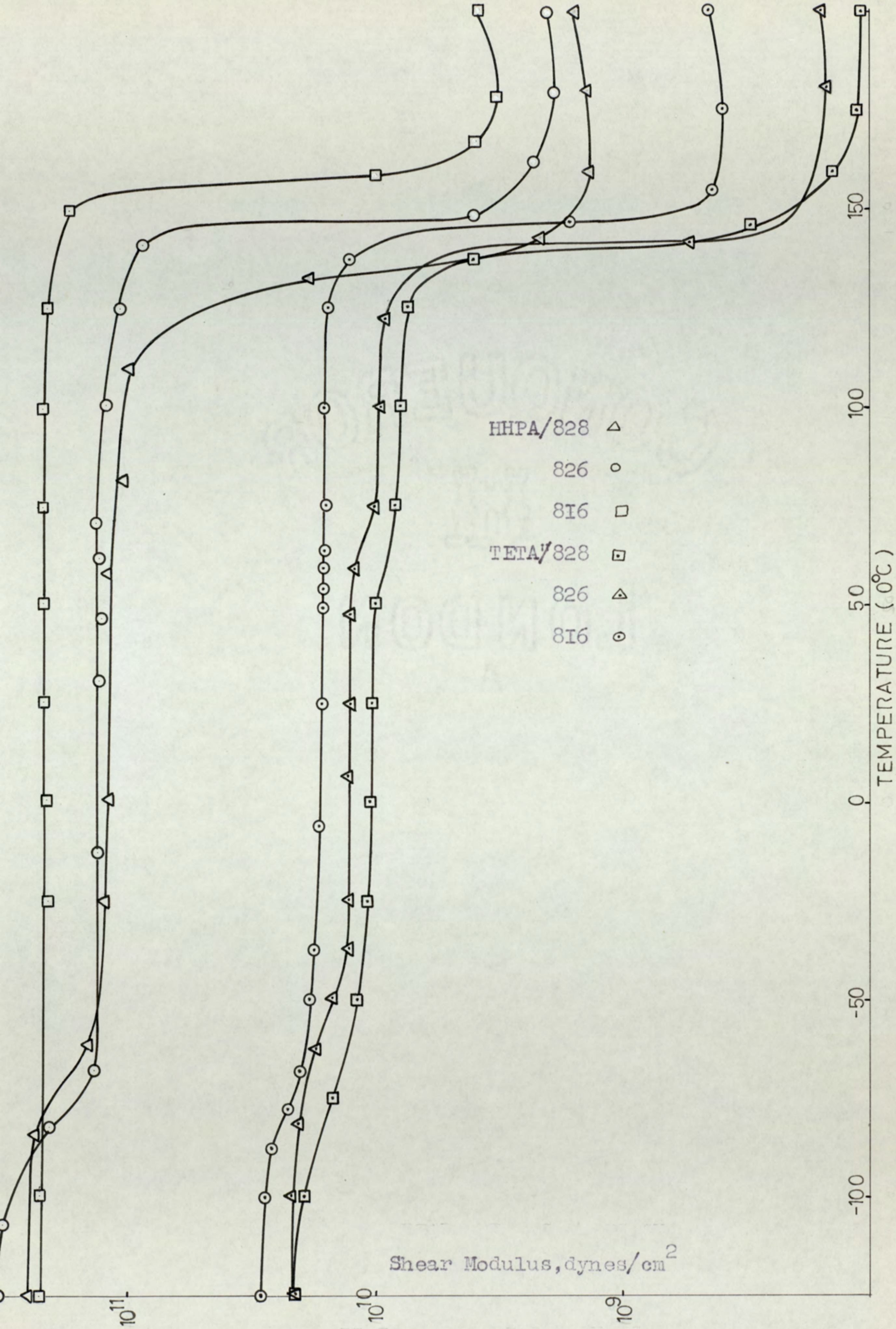


FIGURE 6-I Variation in Shear Modulus.

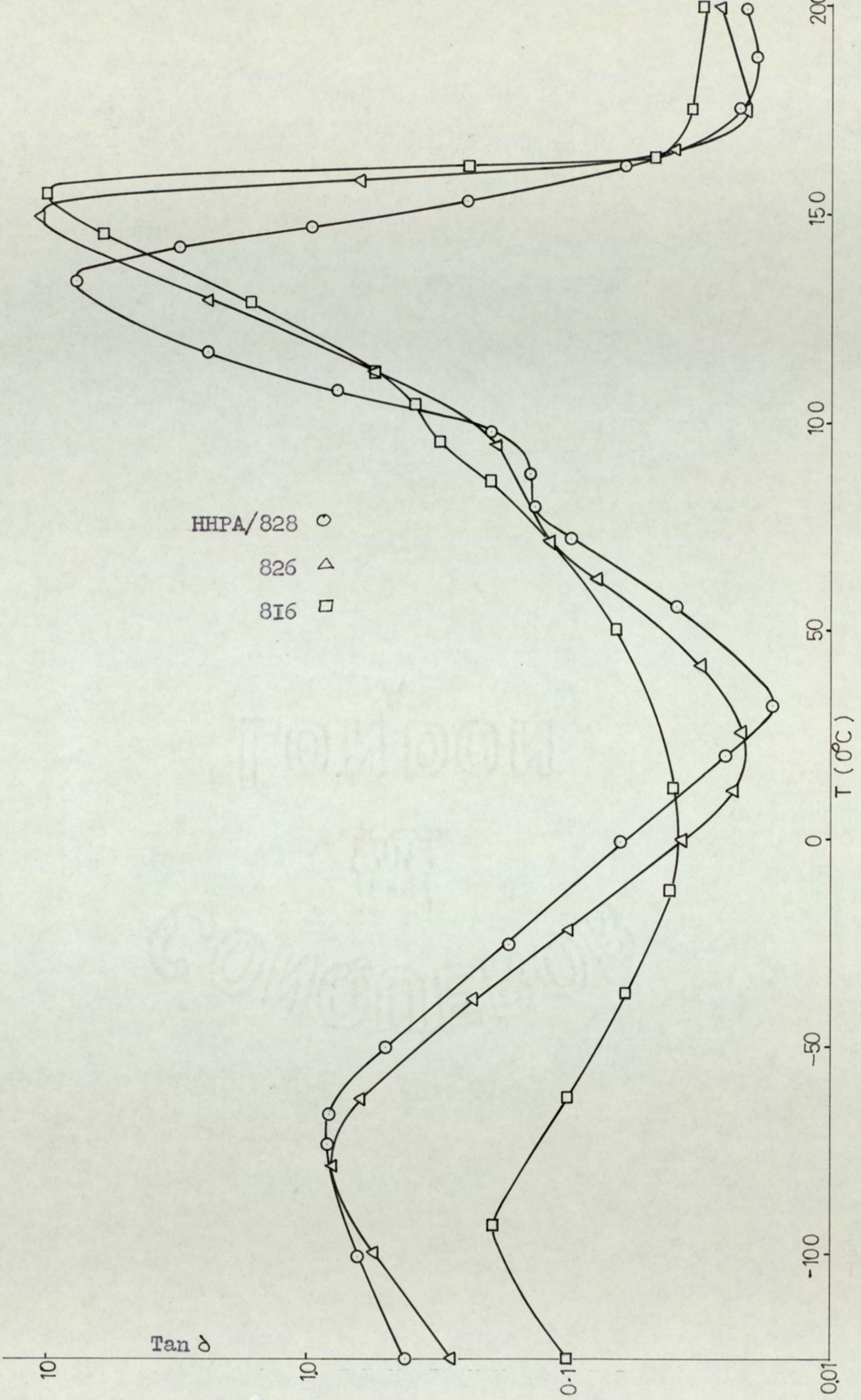


FIGURE 6-2 Decrement Curve, Anhydride Cured Resin.

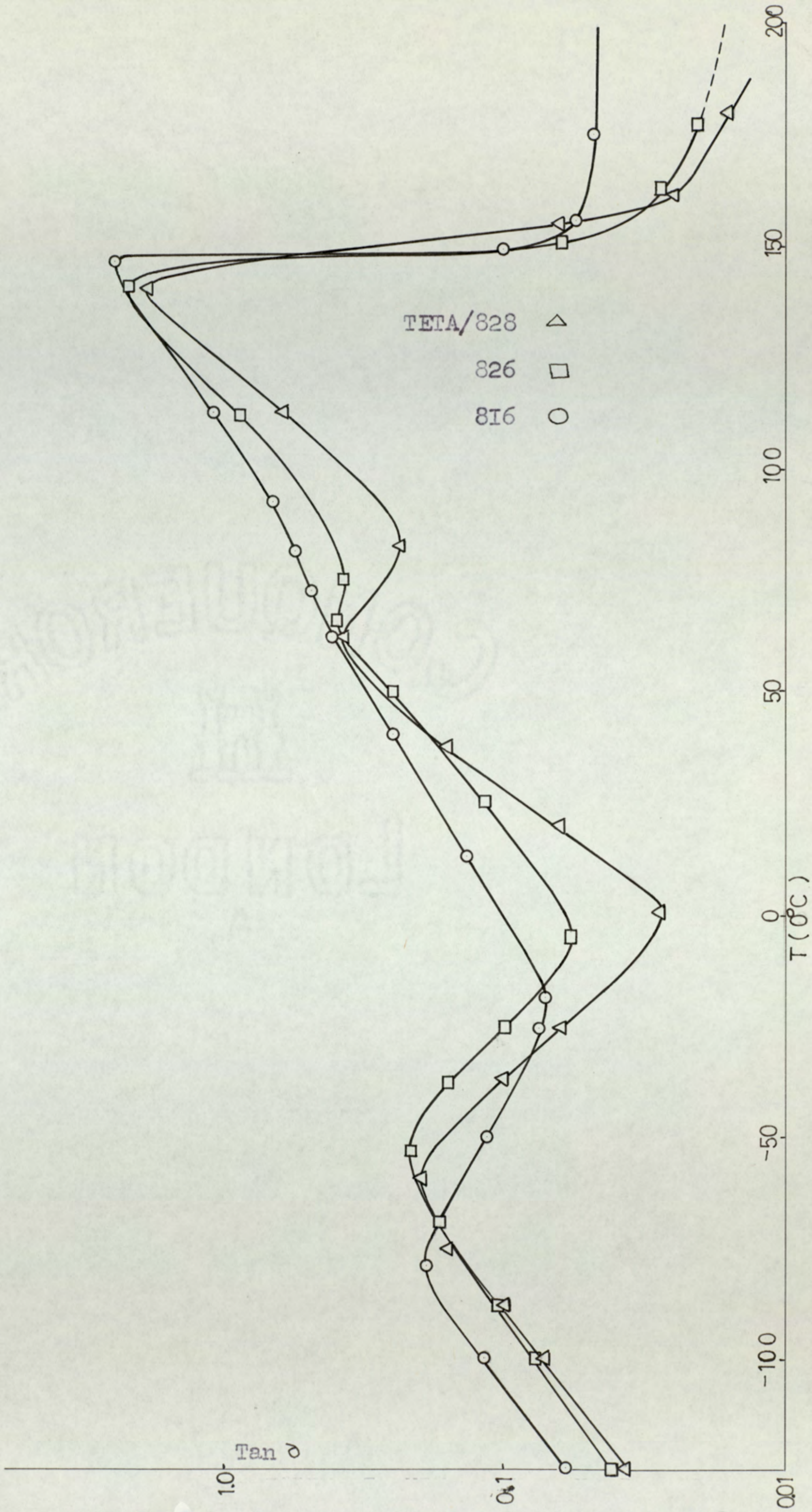


FIGURE 6-3 Decrement Curve, Amine Cured Resin.

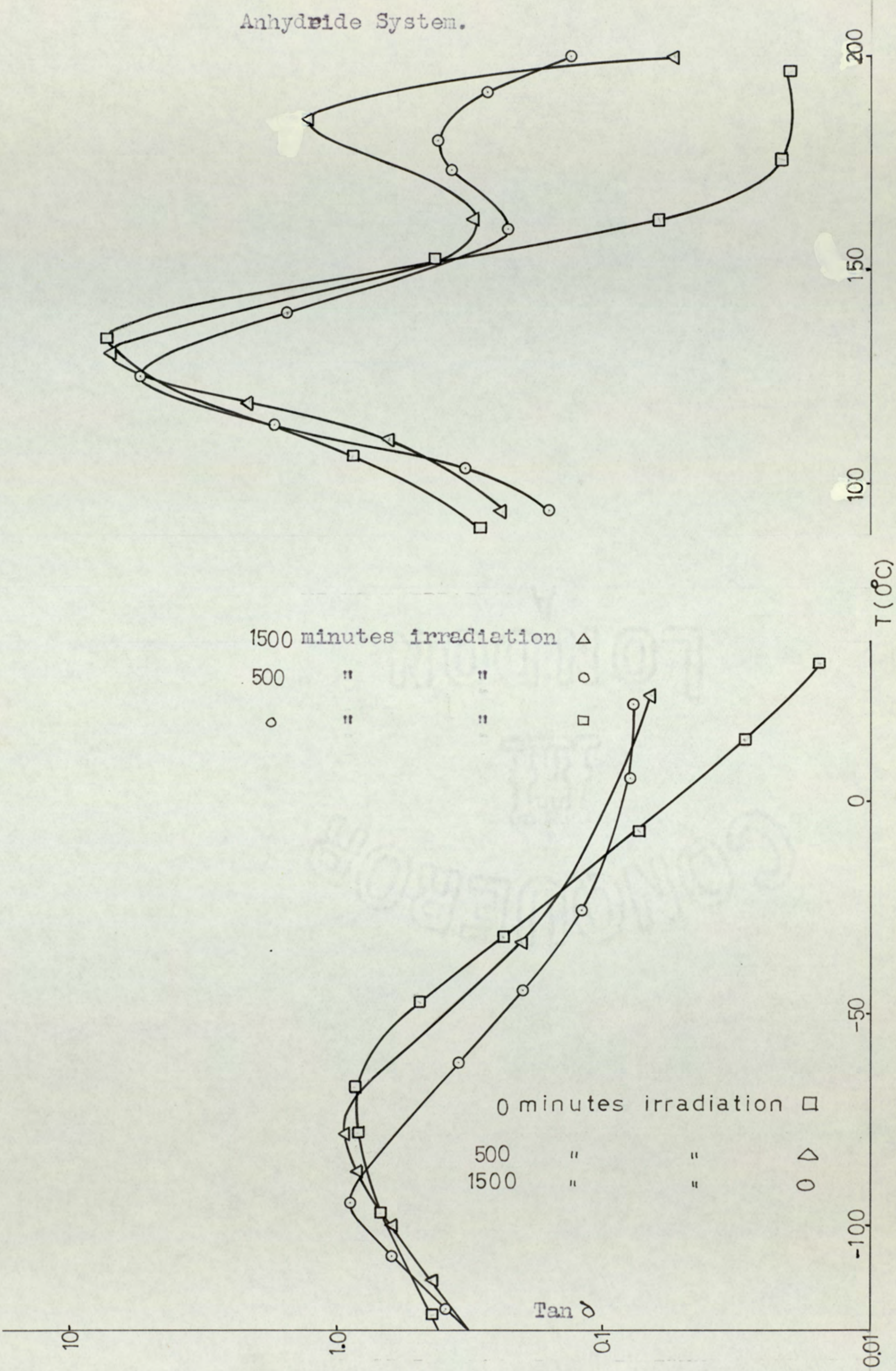


FIGURE 6-4 Change in Mechanical Spectrum on Irradiation.

(oxygen)

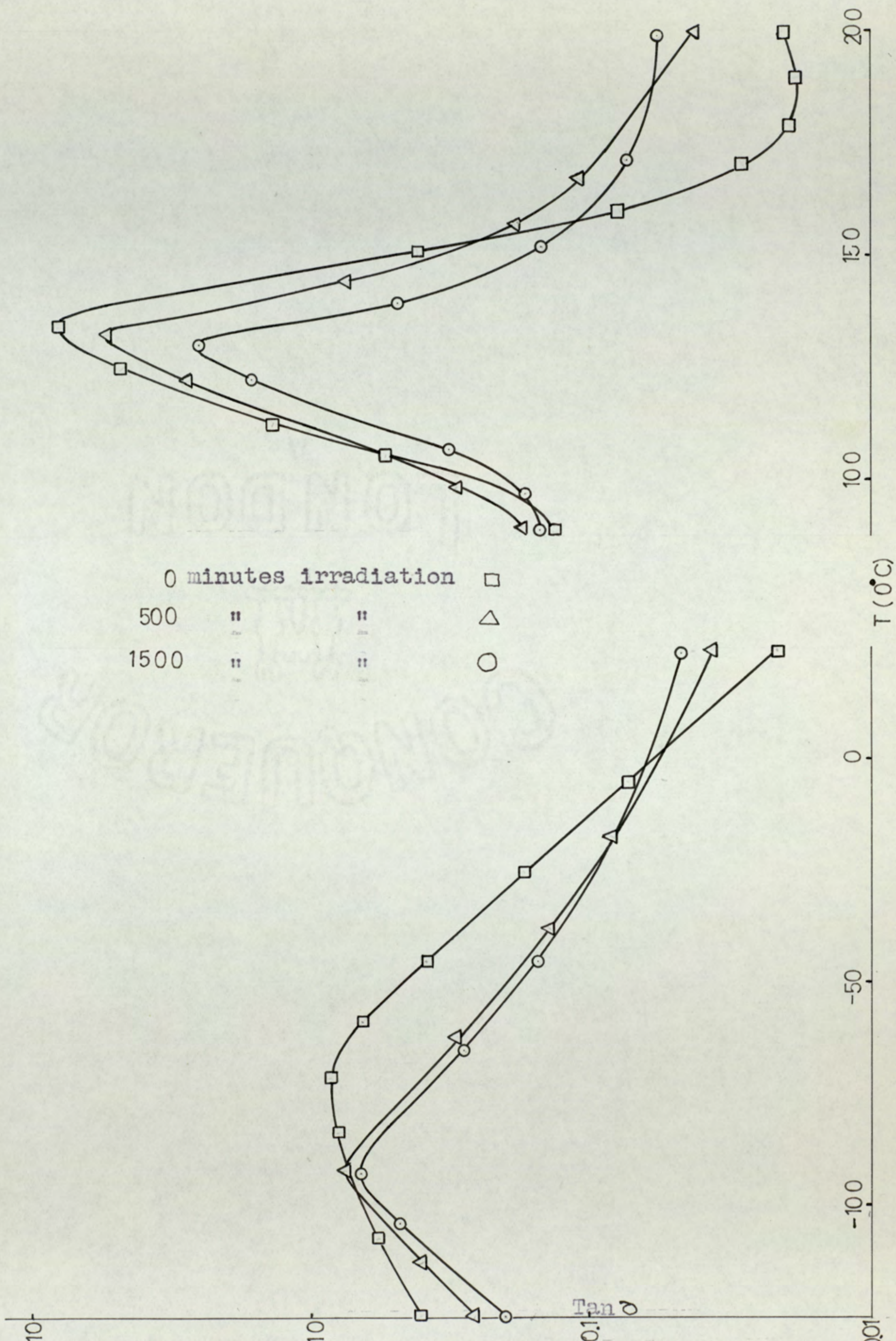


FIGURE 6-5 Change in Mechanical Spectrum on Irradiation(helium)
Anhydride system.

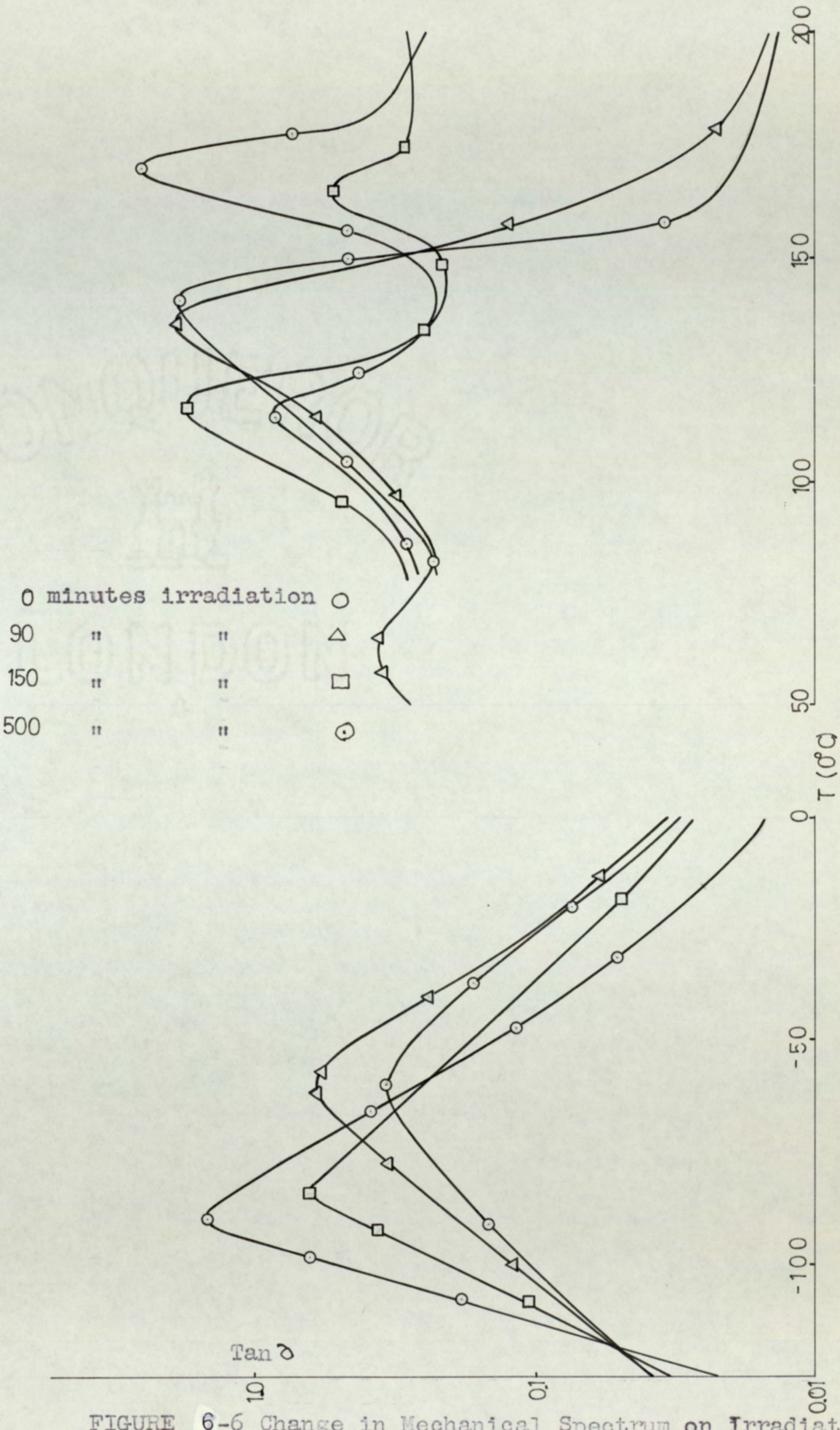


FIGURE 6-6 Change in Mechanical Spectrum on Irradiation.
(amine system, oxygen atmosphere)

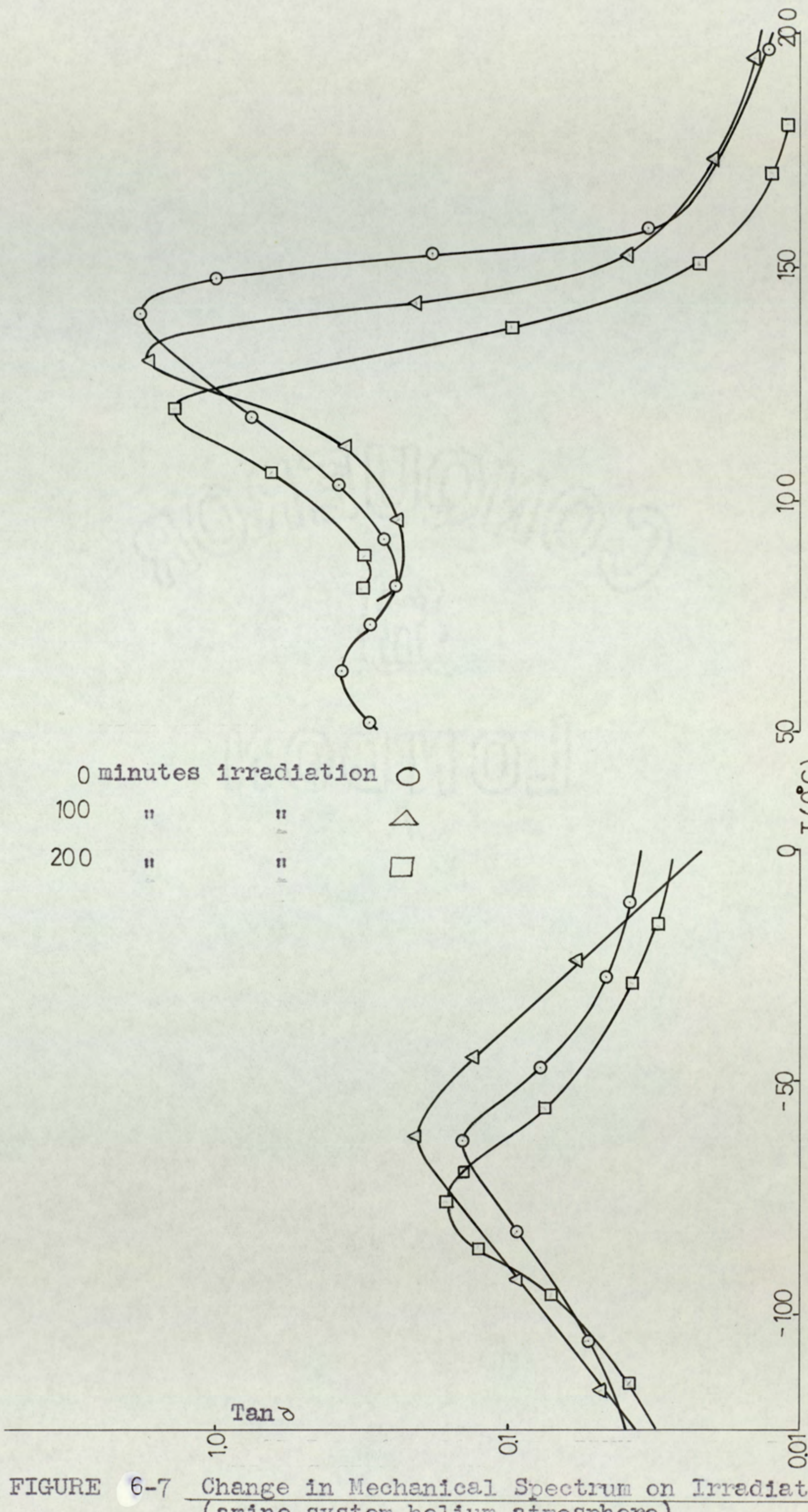


FIGURE 6-7 Change in Mechanical Spectrum on Irradiation.
(amine system,helium atmosphere)

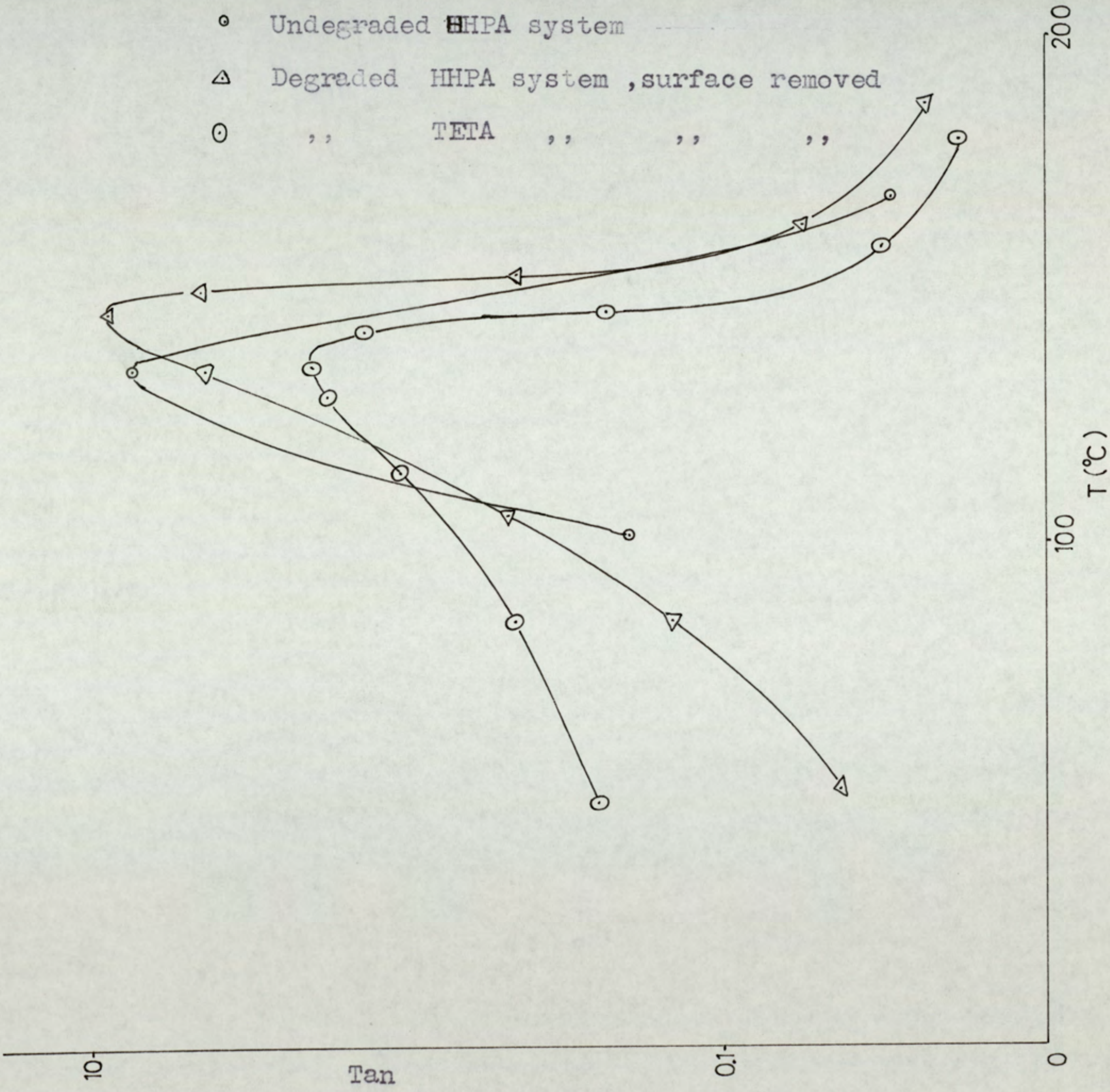


FIGURE 6-8 EFFECT of REMOVAL of DEGRADED SURFACE.

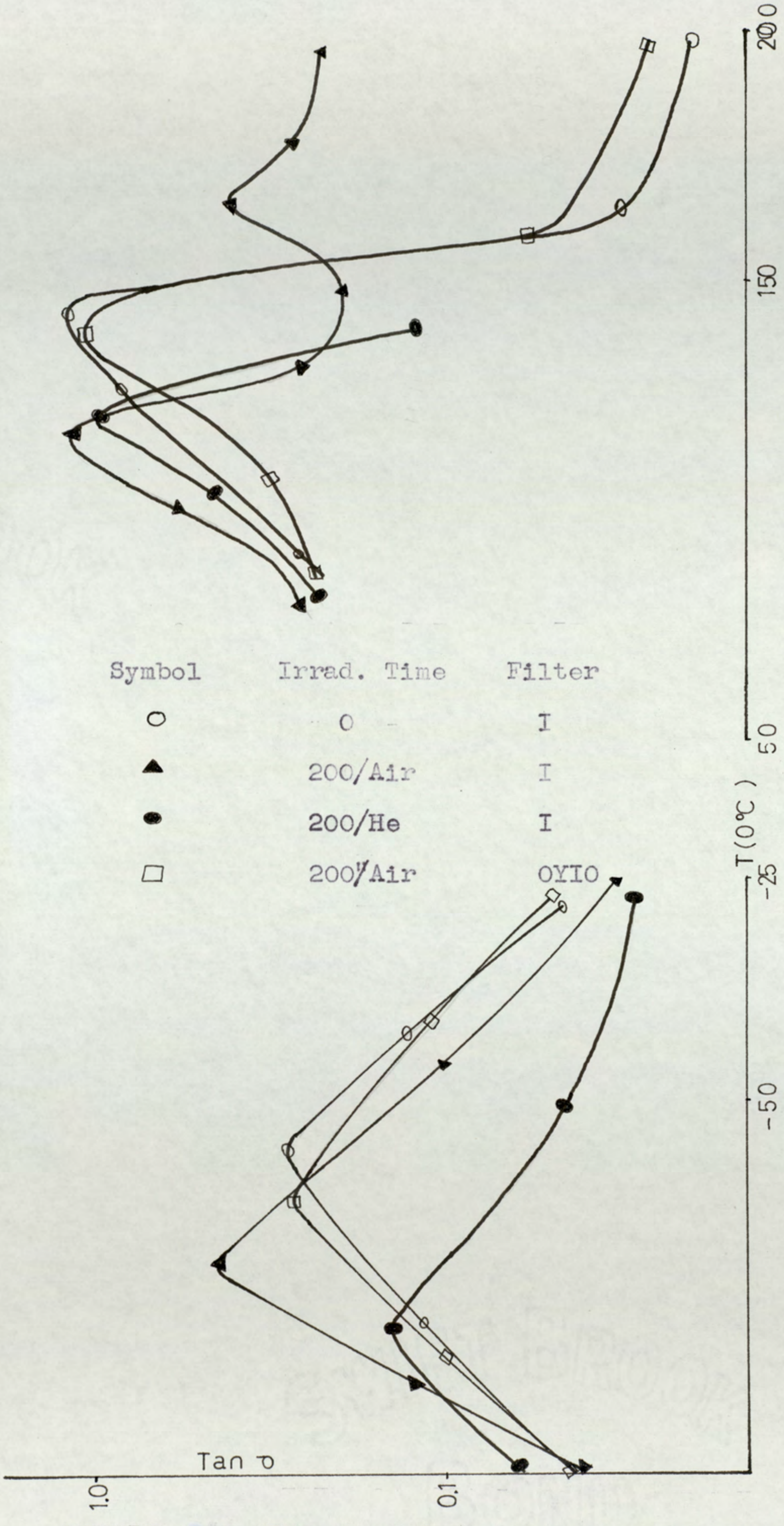


FIGURE 6-9 **Effect of Irradiation Wavelength on Degradation**

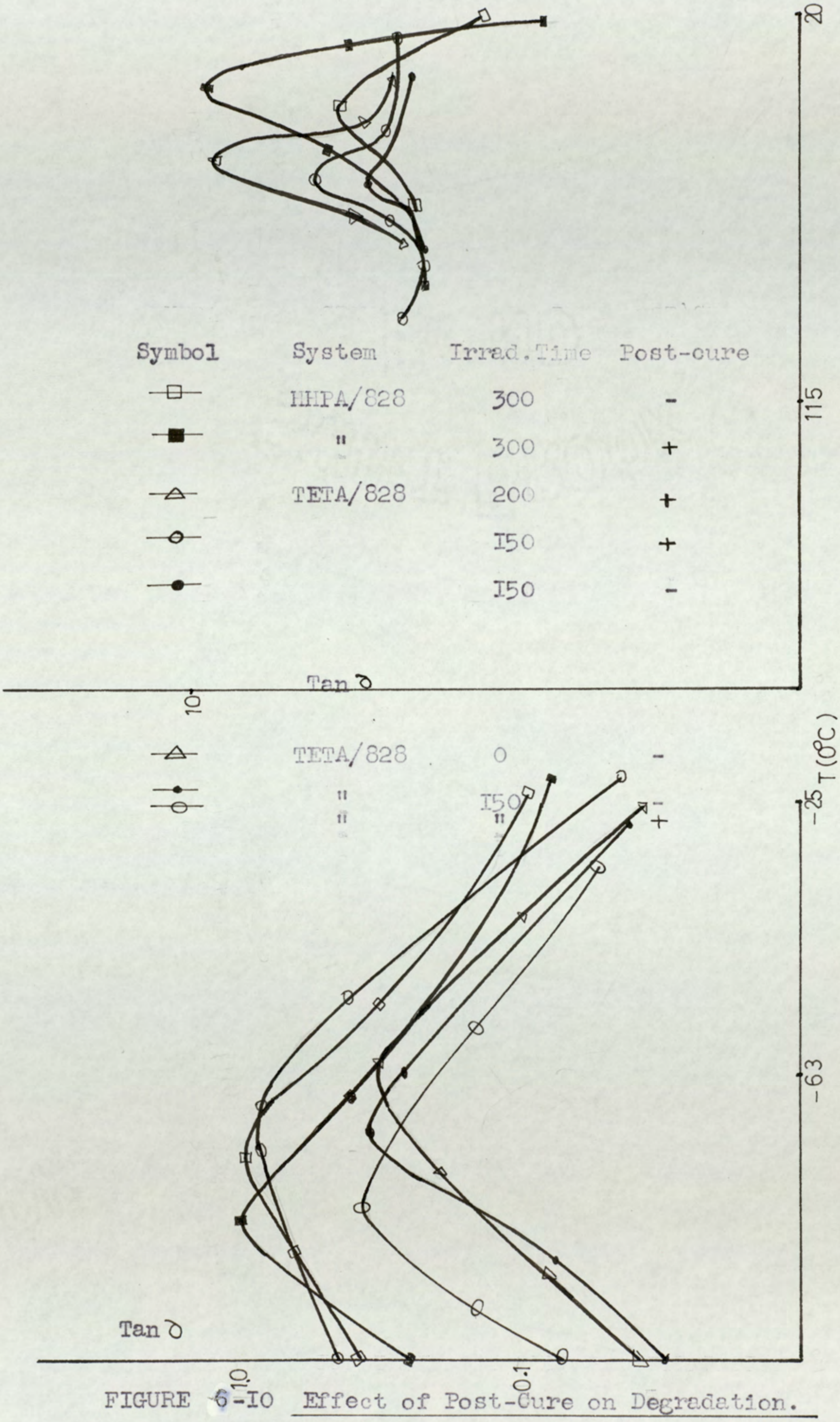


FIGURE 6-I0 Effect of Post-Cure on Degradation.

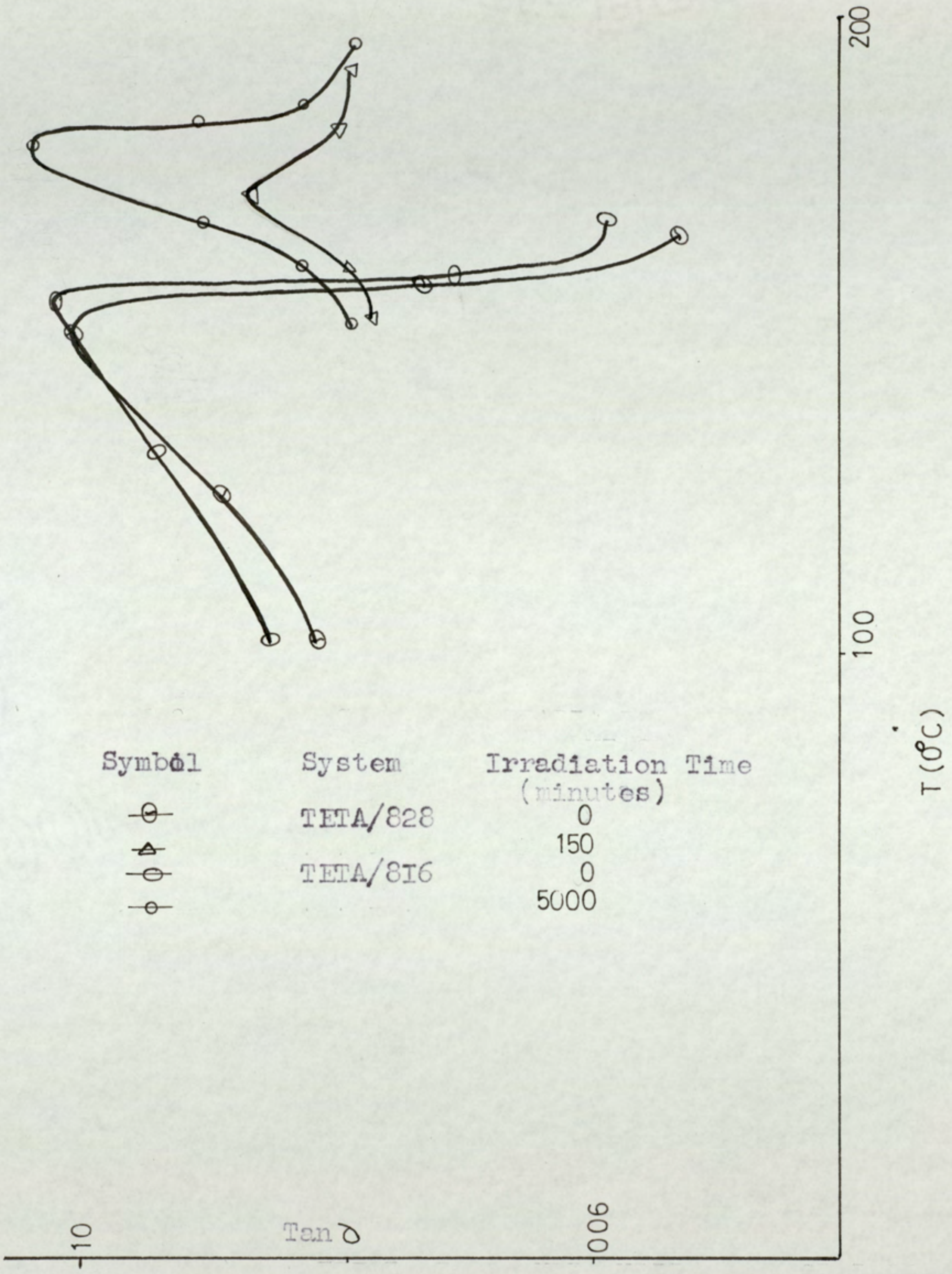


FIGURE 6-II Effect of Monomer Purity on Degradation.
(Irradiation in Oxygen, Amine System)

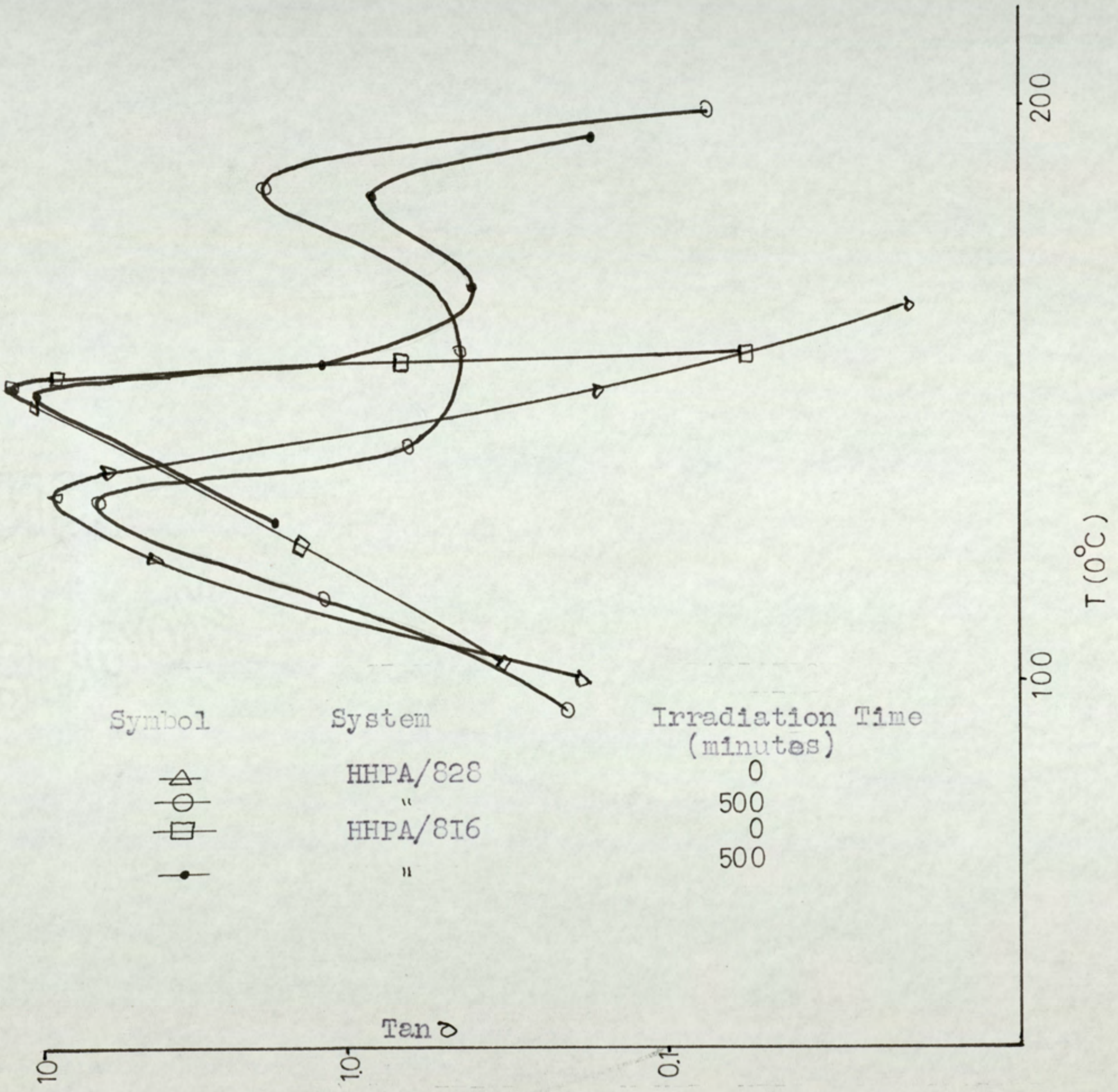


FIGURE 6-12 Effect of Monomer Purity on Degradation.

(Irradiation in Oxygen, Anhydride System)

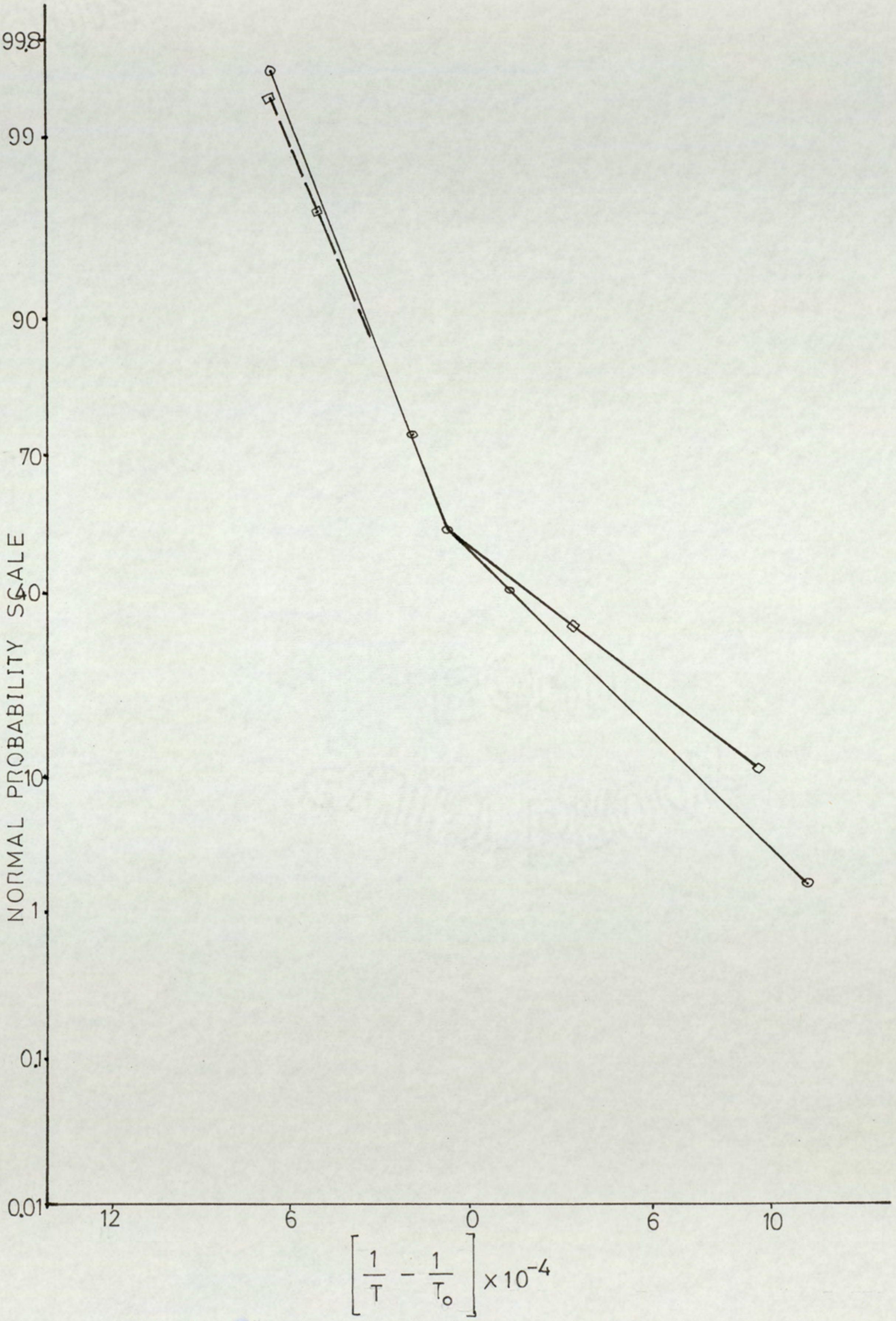


FIGURE 6-13 Normal Probability Graph (TETA/828 system)

CHAPTER 7

The Stabilisation of Epoxide Resins

Introduction

This chapter is concerned with the stabilisation of the two epoxide monomers, TETA/'828' and HHPA/'828', to ultraviolet radiation normally encountered during exposure to the environment.

The choice of stabiliser was based on the results obtained for the cured systems, the model compounds studied in this work and from published work (1- 7). In most cases the compounds were used 'as supplied' by the manufacturers. Where the ultraviolet/visible spectrum showed deviations from published data, the material was purified by recrystalisation or distillation until the quoted specifications were obtained (8 - 10). A number of the stabilisers used were registered trade names and their exact chemical nature was unknown. These are quoted as mixtures in the results. Only the direct action of the stabilisers was investigated. No attempts were made to investigate the influence of the conversion or reaction products of the additives, some of which were known to be degradable under the conditions of irradiation used (11 - 14). The methods of evaluation of the stabiliser action were by the techniques established for the cured resin systems and included ATR spectroscopy, TBA and the change in the light transmittance of the polymers.

7 - 1 Choice of Stabiliser

The normal methods of stabilisation of polymers to ultraviolet light (8, 14, 16, 17) are th incorporation of antioxidants which terminate chain reactions, or incorporation of ultraviolet absorbers which absorb and/or dissipate the energy absorbed by the polymer. The latter can be judged to some extent from the light absorption characteristics of the stabilisers. The results of the irradiation of the cured polymers and model compounds showed low quantum yields for product formation. Also the radicals initiating chain reactions were short lived. This was borne out by the absence of chemical "dark" reactions on the removal of the light source.

The other possibility is that chain reactions were not involved in the degradation process. This is unlikely since free radicals were detected by the ESR technique. Because of this, the feasibility of stopping the degradation after the initiation process was possible by the incorporation of small quantities of antioxidants.
The stabilisation of epoxide resins by ultraviolet absorbers was reported by a number of authors (1 - 7). Limited success was obtained in all cases. However, the efficiency of the additives was low in most cases since colour development was not prevented. Lee and Watson concluded from their exhaustive study that commercial ultraviolet stabilisers available up to 1964 were ineffective in preventing colour formation.

A number of variables affect the choice of stabiliser. These include:
(a) mutual solubility of additive in the polymer
(b) volatility of additive from the surface of the polymer
(c) diffusibility of additive through the polymer
(d) protective effect of additive, in terms of its absorption spectrum
(e) thickness and surface area of the polymer film
(f) compatibility of additive with the polymer
and (g) reaction products from degradation of the stabiliser

The mutual solubility of the additive can be thought of in terms of simple organic compounds. Thus polar substituents would be expected to be soluble in the resin monomer. The compatibility of the additive with the polymer was found to be an important restriction on the type of stabiliser used, in particular where direct incorporation of the additive into the mixture of monomer and curing agent was attempted. Additive volatility has been investigated by a number of authors (17 - 21). These authors worked with thermoplastic polymers where diffusion effects were high. However, they did show that physical interactions between additive and polymer determined to some extent the rate of volatilisation e.g. thiodipropionate compounds were less volatile than phenols because of the increased molecular interaction between the two ester groups. Also, the volatility was found to be temperature and pressure dependent and would be expected to be of importance during the pre gel stage in the high temperature cured epoxides.

The anhydride system would therefore be affected to a greater extent than the amine. Sanin (21) reported that, above the decomposition temperature, degradation of the stabiliser rather than volatility was more important. Increase in the length of hydrocarbon or other aliphatic chain decreased the volatility of the additive. However, other modifications of the stabiliser molecule were dependent on the chemical composition of the stabiliser. This was found to be important with phenolic compounds.

The diffusibility of additives through cured epoxide resins was dependent to a very large extent on the size of the additive molecules. Therefore the large stabiliser molecules would not be expected to be able to diffuse through the bulk to the surface of the films. Also since surface density effects have been shown to occur during degradation which resulted in increased crosslinking in the upper surface layer of the polymer film, diffusion of additives if occurring would be drastically reduced in speed. This was demonstrated by heating samples of the TETA/'828' films which contained stabilisers at the 5 % level at 50 °C for one week. The results in terms of the ingrowth of carbonyl (5.8 to 6.0 micron) bands is shown (Figure 7 - 1). It was obvious from the results of the unstabilised films that some thermal degradation of the films occurred during the heat ageing process. Diffusion of carbonyl additives under a temperature gradient was minimal. Since this was true of the small molecules investigated, the effect of diffusion of the additive to the surface of the polymer can be ignored with the range of additives used in these studies.

The protective effect of ultraviolet absorbers in terms of their wavelength maxima has been reported (16). In general those stabilisers with high absorption peaks in the 300 - 400 nm range gave the best results. However a number of other factors must also be taken into account in particular the method by which dissipation of absorbed energy is achieved. Some ultraviolet absorbing compounds fluoresce in the ultraviolet region and generally promote photo-oxidation because of the slow release of energy by excited electrons prior to fluorescence. In both fluorescence and phosphorescence incident light is converted into longer wavelength radiation of lower energy and this might reduce the harmful effects of the radiation if it occurred at a sufficiently high rate.

The wavelength maximum values of the ultraviolet absorbers used is shown (Table 7 - 1). Some antioxidants absorb ultraviolet light, but these are known to be poor photo-stabilisers. They may even initiate the ultraviolet degradation process by decomposing into free radicals (22, 23). The other main effects of the light absorbing properties of the ultraviolet absorber are its extinction coefficient, concentration and distribution. The energy and distribution of the sources used are also of importance. These have been discussed previously. Since the maximum wavelength of the stabilisers used covered the region of maximum degradation (270 - 320, 365 nm) in both polymers, some stabilisation would be expected with these compounds.

The effect of film thickness and surface area of polymers in terms of antioxidant efficiency has been investigated by Plant and Scott (17) for polypropylene. The conclusion was that the effect of antioxidant volatility rather than inherent antioxidant activity was the dominant factor in determining stabilising effectiveness. No similar study has been reported on thermosets. It can be assumed that the results will be similar to those obtained with thermoplastics but to a lesser extent, since volatility will be much lower in the cured, three-dimensional polymer. By analogy with the results on antioxidants the ultraviolet absorbers would be expected to be affected by stability to light and volatility. Other factors, such as concentration and distribution of absorbing species and the degradation products (type and concentration), would be expected to exert some effect. The effect of concentration and distribution of absorber together with the film thickness of the polymer are reported in this study.

7 - 2 Stabilisers Evaluated with Epoxide Resins

The stabilisers used together with the recommended concentration level are shown (Table 7 - 1 and 7 - 2).

To investigate the effect of the additives on the degree of cure of the polymer films the rate of disappearance of the epoxide group with time was measured for each system. The normal curing reaction temperatures of 100 °C for TETA, and 80 °C and 150 °C for HHPA were used during the studies. The rate constants for the reactions are given (Table 7 - 3).

TABLE 7 - 1

Stabilisers

No.	Trade and Chemical Name	Longest λ maxima (nm)	Concn. Level (phr)
1	Stanclere 55, organotin	-	1 - 5
2	Stanclere 70, organotin	-	1 - 5
3	Stanclere M 128, Ba/Cd salt	-	1 - 5
4	Stanclere 1200, Ba/Cd Laurate + additives	-	1 - 5
5	Phosclere P 98, phosphite	-	3 - 5
6	Mellite 4, di-butyl tin maleate	-	2 - 2.5
7	Mellite 12, di-butyl tin laurate	-	0.4 - 1
8	Mellite 29, di-butyl tin methyl maleate	-	3 - 5
9	Mellite 31, di-butyl tin bis (iso octyl)-thio glycollate	-	2 - 2.5
10	Mellite 39, di-butyl tin bis (lauryl mercaptan)	-	2 - 3
11	Mellite 101, Ba/Cd soap	-	1 - 1.25
12	Mellite 102, Ba/Cd soap	-	1 - 1.25
13	Irganox 1010, (3,5 di-tert-butyl-4 hydroxy phenyl) propionic ester of pentaerythritol	290	0.5 - 5
14	DLTDP, di lauryl thiodipropionate	-	0.5 - 5
15	zinc di-isopropyl di-thio phosphate	-	0.5 - 5
16	zinc di-butyl di-thio-carbamate	290	0.5 - 5
17	Tinuvin 320,	350	0.1 - 10
18	Tinuvin 326,	360	0.1 - 10
19	Tinuvin 327, triazole compounds	355	0.1 - 10
20	Tinuvin 328,	350	0.1 - 10
21	Tinuvin P	340	0.1 - 10
22	Irgastab 2002, nickel complex	-	0.1 - 10
23	Advastab 48, 2, 4 dihydroxy-benzophenone	323	0.1 - 10

TABLE 7 - 1 (Continued)

No.	Trade and Chemical Name	Longest maxima (nm)	Concn. Level (phr)
24	Cyasorb 9, 2-hydroxy-4-methoxy-4 methyl benzophenone	330	0.1 - 10
25	Cyasorb 24, 2, 2 di hydroxy-4 methoxy benzophenone	327	0.1 - 10
26	Cyasorb 207, 2-hydroxy-4 methoxy-2-carboxy benzophenone	320	0.1 - 10
27	Cyasorb 284, 2-hydroxy-4 methoxy-5-sulfo-benzophenone	290	0.1 - 10
28	Cyasorb 314, 2, 2-dihydroxy-4-octyloxy-benzophenone	355	0.1 - 10
29	Cyasorb, 531, 2-hydroxy-4-n-octoxy-benzophenone	330	0.1 - 10
30	Cyasorb 1376, 2-hydroxy-4-methoxy-benzophenone	326	0.1 - 10
31	Cyasorb 1988, metal complex	290	0.1 - 10
32	Cyasorb 2000 mixture	310	0.1 - 10

Obviously a reaction had occurred between the epoxide group of the monomer and the additive. The extent of the reaction depended to a large extent on the accessibility of the reactive group (such as hydroxyl) to the epoxide chain end (Table 7 - 4). In the absence of the curing agent complete reaction of the additive/epoxide occurred at the temperatures used. This was due in part to the increased mobility of the groups at higher temperatures, as seen by the extent of reaction at room temperature. However, the major effect was due to the large excess of monomer present in the system which contained 5 phr of additive. In the presence of the curing agent the rate of decrease of the epoxide group was increased by the additive. The increase was greater in the HHPA system in the presence of the nitrogen containing compounds because of the increased rate of ring opening of the anhydride. Thus an apparent increase in the degree of cure was obtained with all systems. The effect of the chain ends terminated by reaction with the additive was seen by the TBA technique, a shift of the Tg to lower temperatures occurred because of the plasticising effect of the diluent chain ends.

TABLE 7 - 2

Synergists

'828'/TETA

phr 0.5 + 1.5

Components

DLTDP + Tinuvin P
" + Tinuvin 320
" + Tinuvin 326
" + Tinuvin 327
" + Irganox 1010
" + Irgastab 2002
" + Stanclere 1200
" + Cyasorb 314
" + Cyasorb 531
" + Cyasorb 1376
" + Cyasorb 1988
" + Cyasorb 2000

'828'/HHPA

phr 0.5 + 1.5

Components

DLTDP + Cyasorb 24
" + " 207
" + " 284
" + " 314
" + " 531
" + " 1376
" + " 1988
" + " 2000
" + Stanclere 1200
" + " 70
" + " M128
" + Tinuvin P
" + " 320
" + " 326
" + " 327
" + Mellite 29
" + " 31

TABLE 7 - 3

RATE CONSTANTS FOR CURING REACTIONS

Additive No.	K_1 (TETA/828)	K_2 (HHPA/828)
0	1.33	0.23
1	2.01	0.71
5	1.54	0.47
6	1.44	0.48
13	1.40	0.18
14	1.71	0.28
15	1.62	0.28
16	1.77	0.27
17	1.36	0.40
18	1.90	0.28
19	1.90	0.28
20	1.33	0.23
21	3.05	1.81
24	1.33	0.23
25	2.30	0.30
26	1.33	0.23
27	1.83	0.27
28	2.31	0.72
29	1.33	0.23
30	1.34	0.25
31	1.44	0.23
32	1.38	0.27

Rates expressed as loss of epoxide group,

K_1, 0 to 15 minutes and K_2, 0 to 60 minutes.

TABLE 7 - 4

Extent of Curing Reaction*

Additive No.	TETA/'828'	HHPA/'828'
0	11.6	18.2
5	7.0	9.8
6	6.6	14.6
13	10.2	18.0
14	7.9	18.0
15	7.4	17.3
16	8.3	17.0
20	8.7	11.7
21	6.2	10.6
23	10.1	6.4
26	10.3	6.9
30	7.3	6.7

* Expressed as the % of the original epoxide content after a reaction time of three hours.

These shifts did not obey the usual equation for copolymers (24, 25). Since the curing agent was used in greater quantity than the additive it was expected that some unreacted additive would be present. This was seen (Figure 7 - 2) for the quantity of unreacted anhydride with and without additive at the completion of the reaction. Since both systems were cured under identical condition, in the same oven, at the same temperature and for the same time, any differences found were caused by the additive. The fact that only a slight difference in unreacted anhydride was found in both systems indicated that either the additive was involved only in the transition states of cure, or that the bulk of the additive reacted in a specific distribution of chain ends which were unreacted during the normal curing process. This was not the case with the amine system as evidenced by the hydroxyl content. A possible explanation for the observed difference between amine and anhydride systems may be due to reaction of the amine with the additive or to the difference in the quantities of the curing agents used, 10 - 12 phr for the amine and 85 - 90 phr for the anhydride.

This problem of the high rate of reactivity of the epoxide with the additive was overcome by the use of bulky substituents to protect the reactive group of the additive e.g. Irganox 1010 and some of the Tinuvin series.

The final colours of the cured films are shown (Table 7 - 5). Many of the stabilisers did yield coloured products. However, since with some systems unreacted stabiliser was present and presumably able to function normally, all systems were evaluated during the initial trials. In the use of epoxide resins for outdoor applications the colour of the resin is unimportant since fillers and pigments are also incorporated for aesthetic and financial reasons. Only those stabilisers which proved successful were used in the synergistic mixtures.

7 - 3 Results

The results of the evaluation of the separate antioxidants and ultraviolet absorbers are shown (Table 7 - 6) for the change in the ultraviolet/visible spectrum at 350 nm relative to that of the unstabilised control sample after 100 hours irradiation.

Only the slope of the initial decrease in transmission is shown (Table 7 - 6). The result of the ATR evaluation of some additives is shown (Table 7 - 7). The evaluation of the synergists in terms of the change in light transmission (Table 7 - 8) and relative modulus (Figure 7 - 3 and 7 - 4) is shown.

7 - 4 Discussion

Photo-oxidative stabilisation of polymers can be achieved by sensitisers which prevent light absorption, by deactivation of light excited sensitisers, by inhibition of the propagation of auto-oxidation, by the transfer of the chain propagating radicals into harmless radicals by antioxidants and by the prevention of the initiation of secondary auto-oxidation chains by hydroperoxides. The effectiveness of the latter is minimised by ionic decomposition by synergists or by suppression by metal deactivators. The actual stabilisation process has been discussed by a number of authors (8 - 16, 26 - 30).

The initial screening tests showed that direct incorporation of additives containing reactive groups such as hydroxyl resulted in chemical incorporation of the additive at the monomer chain ends. The resonance path for stabilisation by ultraviolet absorbers was thus destroyed, as was the ability of the other compounds to scavenge free radicals. Irrespective of additive concentration, the degradation reactions progressed in the polymers at rates equivalent to those in the unstabilised systems. The successful antioxidants were successful only in high concentration which indicated the presence of a large number of reactive centres in the degraded polymer or poor dispersion of additive. The latter possibility was eliminated by the results of well dispersed systems.

Different additives were affective in the two types of cured resins. All other things being equal this was indicative of either different degradation mechanisms occurring or different degradation products being formed which influenced the effectiveness of the stabilisers. Some overlap was found with the two types of polymer. The anhydride cured resin was more amenable to the stabilisers used. This may have been due to the degree of cure in the material since it was found that the extent of cure influenced the rate of degradation.

TABLE 7 - 5

Colour of Polymer Films with Additive (Cured)

Additive Number	TETA/828	HHPA/828
1	orange/red	light green
2	red	green
3	red	light green
4	colourless	orange
5	orange/red	light green
6	green	orange
7	white	green
8	red	light green
9	colourless	orange/red
10	white	orange/red
11	colourless	yellow/orange
12	white	dark brown
13	colourless	pale orange
14	colourless	colourless
15	green	green
16	yellow	yellow/orange
17	slight green tint	pale yellow
18	Green	pale yellow
19	colourless	pale yellow
20	light green	honey
21	green	honey
22	colourless	orange/red
23	orange	orange/red
24	orange	pale colourless
25	orange	pale green
26	orange	pale yellow
27	orange	pale yellow
28	orange	pale green
29	colourless	colourless
30	orange	colourless
31	colourless	colourless
32	orange	colourless

TABLE 7 - 6

Evaluation of Stabilisers

Additive No.	Change in the Rate of Light Transmission at 350 nm	
	TETA/828 x 10^4	HHPA/828 x 10^4
0	1.67	1.0
1	1.67	1.0
2	1.63	0.96
3	1.69	0.96
4	1.69	0.95
5	1.67	1.0
6	1.66	1.0
7	1.67	1.0
8	1.68	0.94
9	1.68	0.97
10	1.67	1.1
11	1.62	1.0
12	1.66	1.0
13	1.60	1.11
14	1.58	0.96
15	-	-
16	-	-
17	1.60	0.94
18	1.61	0.94
19	1.60	0.96
20	1.65	0.99
21	1.68	0.91
22	1.68	1.0
23	-	-
24	1.67	1.01
25	1.67	0.97
26	1.68	0.94
27	1.68	0.96
28	1.62	0.95
29	1.64	0.97
30	1.61	0.95
31	1.62	0.92
32	1.63	0.94

stabiliser concentration at upper limit see Table 7 - 1

TABLE 7-7

Effectiveness of Stabilisers by the ATR Method

Stabiliser	System (TETA/828)*		
	1	2	3
Tinuvin P	1.37	1.04	1.01
320	0.51	0.50	0.44
326	2.13	2.01	1.77
327	2.00	2.00	1.92
Irganox 1010	2.77	2.71	2.41

1. 0.5/1 phr
2. 0.5/2 phr
3. 0.5/5 phr

* Results expressed as the rate of formation of carbonyl band at 6.06 (x 10^3) microns, over the irradiation period 0 to 80 minutes. Control sample rate 2.78 x 10^{-3} per minute.

TABLE 7 - 8

EFFECTIVENESS OF SYNERGISTS

TETA/828		K	HHPA/828		K
DLTDP / Tinuvin P		1.51	DLTDP / Cyasorb	24	0.97
"	320	1.51	"	207	0.94
"	326	1.53	"	284	0.96
"	327	1.53	"	314	0.95
Irganox	1010	1.60	"	531	0.97
Irgastab	2002	1.68	"	1376	0.95
Stanclere	1200	1.69	"	1988	0.92
Cyasorb	314	1.62	"	2000	0.94
"	531	1.64	Stanclere	1200	0.95
"	1376	1.61	"	70	0.96
"	1988	1.62	"	MI28	0.96
"	2000	1.63	Tinuvin P		0.72
			"	320	0.72
			"	326	0.81
			"	327	0.81
			Mellite	29	0.95
			"	31	0.97

K values expressed as slope of change in light transmission curves.

The addition of quantities of Irganox 1010 to levels greater than that of monomer impurities should have suppressed the degradation by anti-oxidant activity at the initiation sites. However this was not so and the possibility of initiation of degradation solely by the monomer impurities can be ruled out. Further evidence of this was found from the results of coating the amine cured polymer with a film of polymer containing 15% Irganox 1010 (Figure 7 - 5).

The photochemical degradation of the polymer was almost completely eliminated with such a system. However the excellent physical properties of the epoxy resin were lost initially because of the plasticising action of the additive. Stabilisation by this method has been successfully demonstrated by Carlsson and Wiles (31).

The effectiveness of high concentration of benzophenone ultraviolet absorbers was also found to be dependent on the distribution of the stabiliser in the upper layers of the polymer film. The difficulty with such materials was the highly coloured nature of the film. Thus the method of evaluation, change in light transmission characteristics, did not give a conclusive result. The effectiveness in the TETA/'828' films was in the order of decreasing efficiency

$$314 > 531 > 2000 > 1988 > 1376 > 9 \sim 24 > 207 \sim 284$$

and the HHPA/'828'

$$314 \sim 531 > 2000 > 1988 > 1376 > 24 > 207 > 284 > 9$$

The effectiveness of these additives was not dependent on the reactivity of the hydroxyl group since in some cases no protection from reaction was available for the hydroxyl group. The low wavelength maxima of some of the additives indicated that a quenching mechanism was incorporated into the structure, in particular with 1376, 1988 and 2000. Therefore dissipation of absorbed energy was accomplished by a bimolecular process which was diffusion controlled. The size of the additive molecules and the low permeability of the resins suggested that good dispersion had occurred.

Consideration of the Tinuvin series of stabilisers which were successful, showed that the order of effectiveness was

$$p \sim 320 > 327 \sim 326 > 328$$

for both the amine and anhydride systems. The order of reactivity of the epoxide and hydroxyl groups was

$$328 > 320 > 327 \sim 326 > p$$

while the ultraviolet absorption maxima were in the order of increased effectiveness, except for Tinuvin 328. This anomaly may have been due to the amyl chain, which because of its size would have exerted a physical effect on movement of the additive during the reforming of the polymer surface on ultraviolet irradiation. A similar effect may have been responsible for the efficiency of Tinuvin P, though this compound had a lower wavelength maximum than the other successful triazoles and would absorb the short wavelength light emitted by the mercury source used.

In the amine films only one metal compound, Stanclere 1200, caused an improvement in the ultraviolet stability. The exact composition of this compound was unknown. However, since it is normally used as an anti-oxidant it is assumed that it has no ultraviolet absorbing properties. Its efficiency as a stabiliser was less than any of the other successful additives. In the anhydride cured polymers five metal compounds were effective. Their efficiency was in the order Mellite 31 > Mellite 29 ∼ Stanclere 70 ≫ Stanclere M128 ∼ Stanclere 1200. As with the amine system the efficiency was lower in all cases than with the other successful stabilisers. Increased concentration of these compounds up to the maximum values indicated in Table 7 - 1 caused some increase in their effectiveness.

Insurmountable difficulties were encountered in the incorporation of the DLTDP, dithiophosphates and dithiocarbamates. The DLTDP in polymer films was difficulty soluble and the resulting films were light green in colour. Stabilisation of the polymers to ultraviolet light was still found. However with the dithiocarbamate and dithiophosphate no stabilisation occurred and their use was discontinued.

The expected synergism (14 - 16) of DLTDP with phenolic compounds was found to occur with the Irganox 1010. The mechanism of the action for the Irganox 1010 can be explained by the presence of the two inhibitors, one of which terminates the oxidation chain and the other breaks down hydroperoxides. This synergistic process has not been found for thermal degradation of polymers (29). No synergistic action was observed with the benzophenone/DLTDP mixtures in either of the polymer films.

However with the benztriazoles,synergism was found to occur with each mixture investigated. The order of effectiveness was the same as that for the individual benztriazole absorbers. This type of synergism in polyethylene between DLTDP/substituted benzophenone has been reported by Newland and Tamblyn and their co-workers (15, 33 - 37) and improvements of the 3 - 4 fold order were reported. Scott (15) reported that the more efficient peroxide decomposers (e.g. zinc dialkyl-dithio-carbamates) have quite a high order of ultraviolet deactivating activity which was to be expected because of the suppression of the decomposition of hydroperoxides to chain initiating fragments. In this way the synergism between DLTDP and the benztriazoles can be explained by the anti-oxidant activity of the former (15) and the reduction of photo initiated products by the ultraviolet absorber to a level at which the anti-oxidant could render them inactive. Therefore since the degradation was not prevented completely, the result of the synergistic stabilisation was longer kinetic chains which gave 5 and 7 fold improvements in reducing the degradation of amine and anhydride cured epoxide resins.

REFERENCES

1. U.S. Pat. 3, 226, 358, 1960
2. U.S. Pat. 3, 113, 907, 1960
3. U.S. Pat. 3, 142, 687, 1962
4. Lee, H., Watson, R.T., 20th ANTEC, SPE paper 21, 1964
5. Nelson, J., TR 5814, U.S. Prosthetics RL, 1958
6. Hirt, R.C., Schmitt, R.G., A C S Symposium, 314, 1961
7. Hirt, R.C., Schmitt, R.G., J. Appl. Polym. Sci. 7, 1565, 1963
8. "Die Stabilisierung der Kunststoffe" by Voight, J., Springer Verlag, Berlin, 1966
9. Heller, H.J., Eu. Polym. J. Supplement 1969, p105
10. King, A., Plastics and Polymers 195 June 1968
11. "The Ageing and Stabilisation of Polymers" by Kuzminski, A.S., Elsevier, Amsterdam, 1971
12. Weiss, P., Pure Appl. Chem. 15, 587, 1958
13. Searle, W.Z., Hirt, R.C., SPE Trans., 32, Jan. 1962
14. "Ageing and Stabilisation of Polymers" by Neiman, M.B., Consultants Bureau, New York, 1965
15. "Atmospheric Oxidation and Antioxidants" by Scott, G., Elsevier, Amsterdam, 1965
16. "Stabilisation of Synthetic High Polymers" by Gordon G. Ya. Isreal Program for Scientific Translations, 1964
17. Plant, M.A., Scott, G., Eu. Polym. J. 7, 1173, 1964
18. Schmitt, R.G., Hirt, R.C., J. Polym. Sci., 35, 35, 1960
19. Newland, G.C., Solar Energy, 12, 65, 1968
20. "Stabilisierung und Alterung von Plastwerkstoffen", 1, by Tinneus K., Verlag Chemie GmbH, 1969
21. Sanin, P., et al, Soviet Plastics 1, 39, 1970

22. Field, J.F., J. Polym. Sci., 15, 51, 1955
23. Burgess, A.R., Chem. Ind., 78, 1952
24. "Mechanical Properties of Polymers" by Nielsen, L.E., Reinhold, New York, 1967
25. Wood, L.A., J. Polym. Sci. 28, 219, 1958
26. Winstein, H., J.A.C.S. 65, 2196, 1943
27. Fitton, S.L., et al Br. Polym. J., 2, 217, 1970
28. Ingold, K.U., NRC, TR - No. 6537, 1961
29. Levin, P.I., et al Russ. Chem. Rev. 39, (9), 799, 1970
30. Ershov, Yu. A., et al Russ. Chem. Rev. 38, (2), 147, 1969
31. Carlsson, D.J., Private Communication 1971
32. Schmitt, R.G., Hirt, R.C., J. Polym. Sci., 61, 361, 1962
33. Newland, G.C., SPE Trans. 1, 26, 1960
34. French Pat. 1, 249, 175
35. U.S. Pat. 2, 972, 597
36. U.S. Pat. 2, 975, 596
37. Kasha, M., Radiation Res. 20, 55, 1963

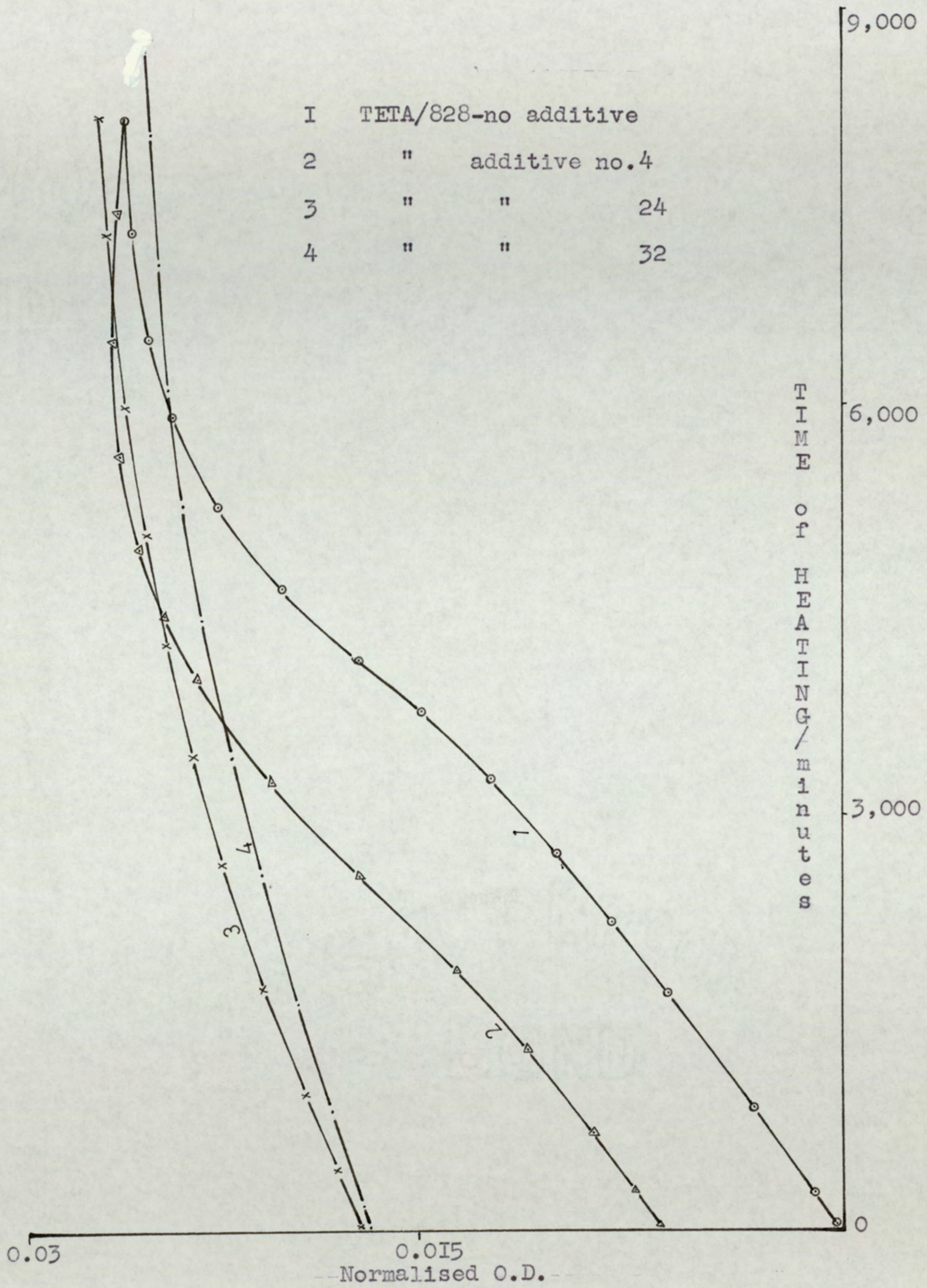


FIGURE 7-I Diffusibility of Additives -TETA/828

(additive concentration 5% ,heated at 50°C for I week)

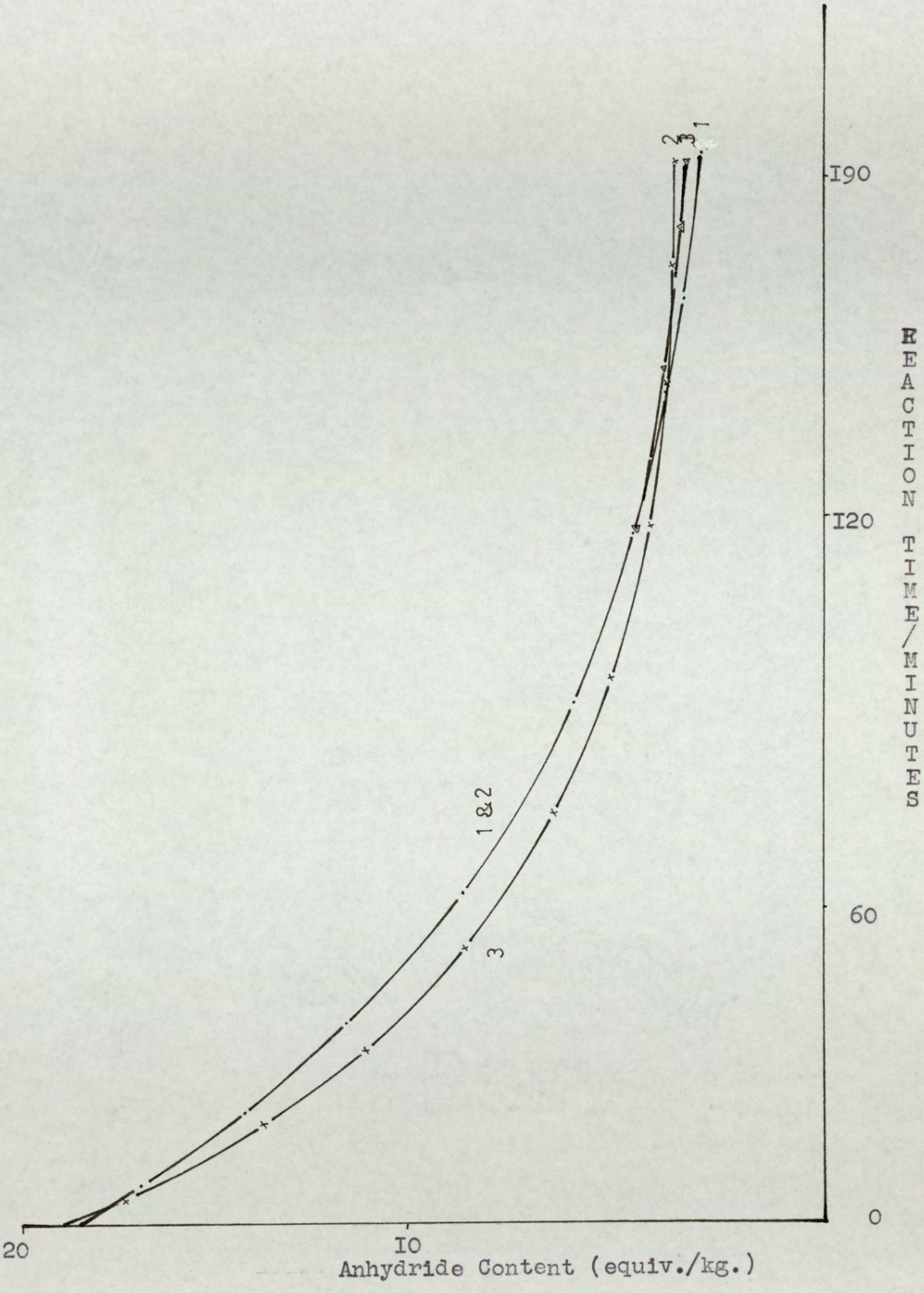


FIGURE 7-2 Effect of Additive on Extent of Cure. (HHPA/828)

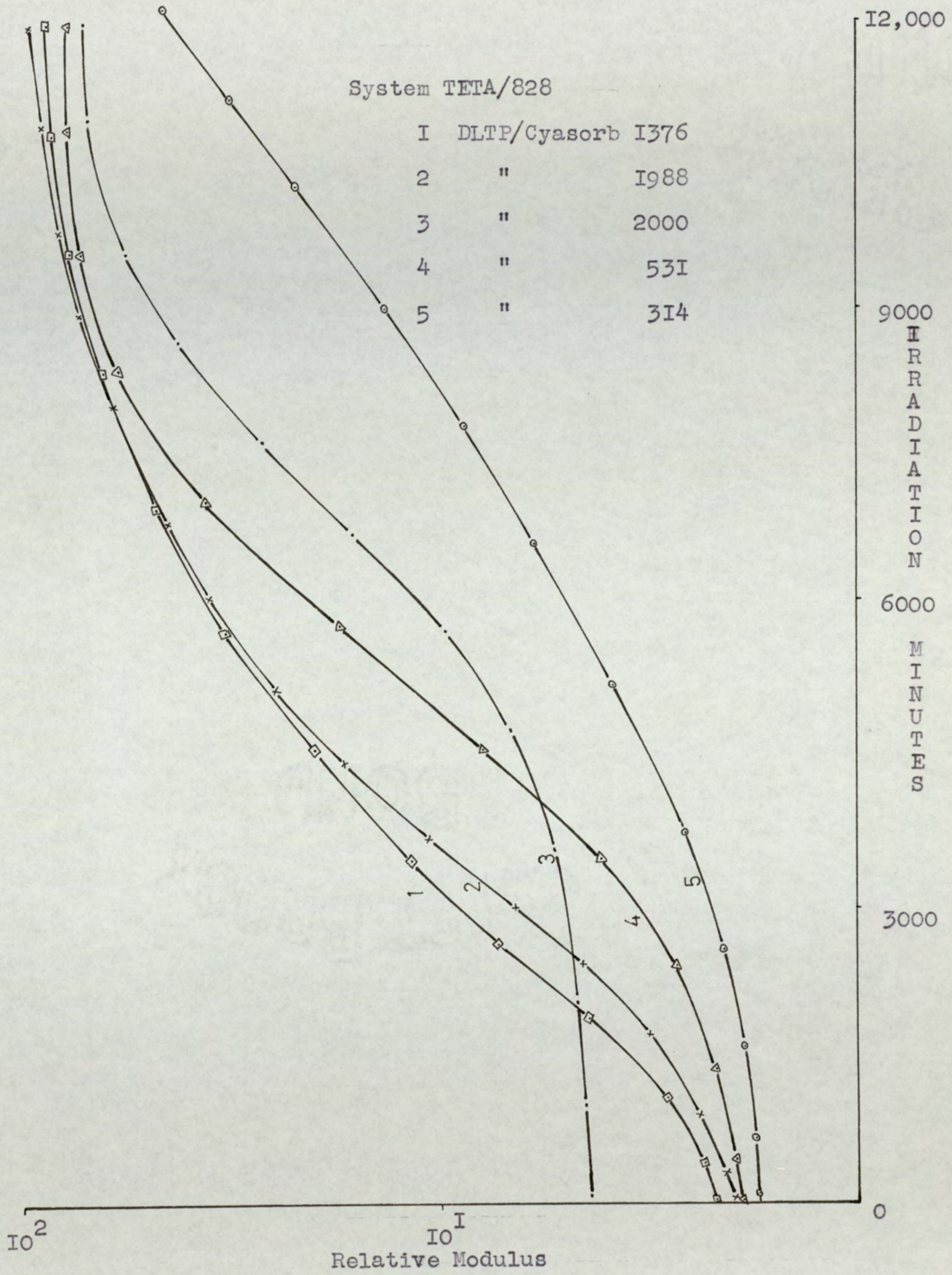


FIGURE 7-3 Change in Relative Modulus on Irradiation.

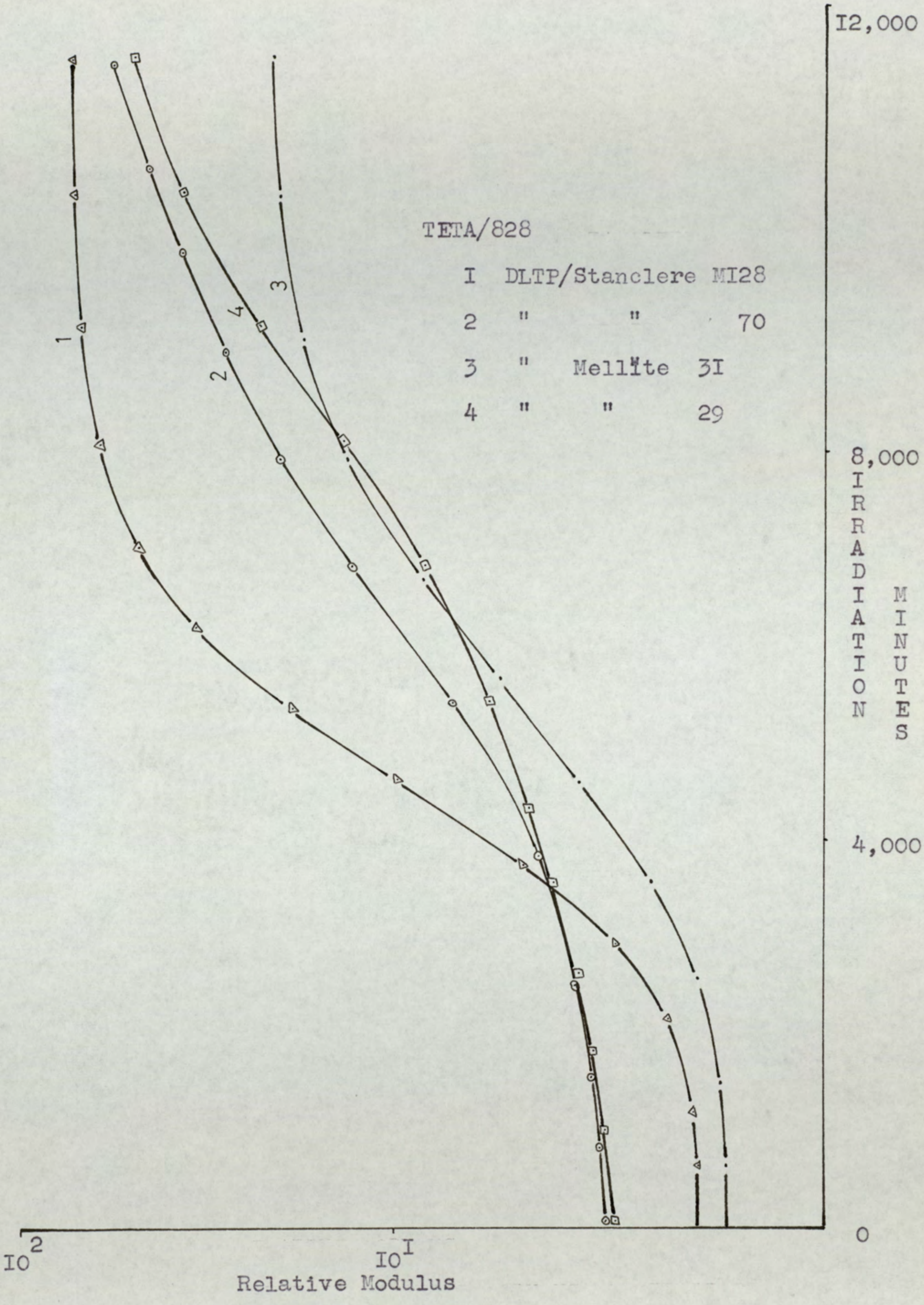


FIGURE 7-4 Change in Relative Modulus on Irradiation.

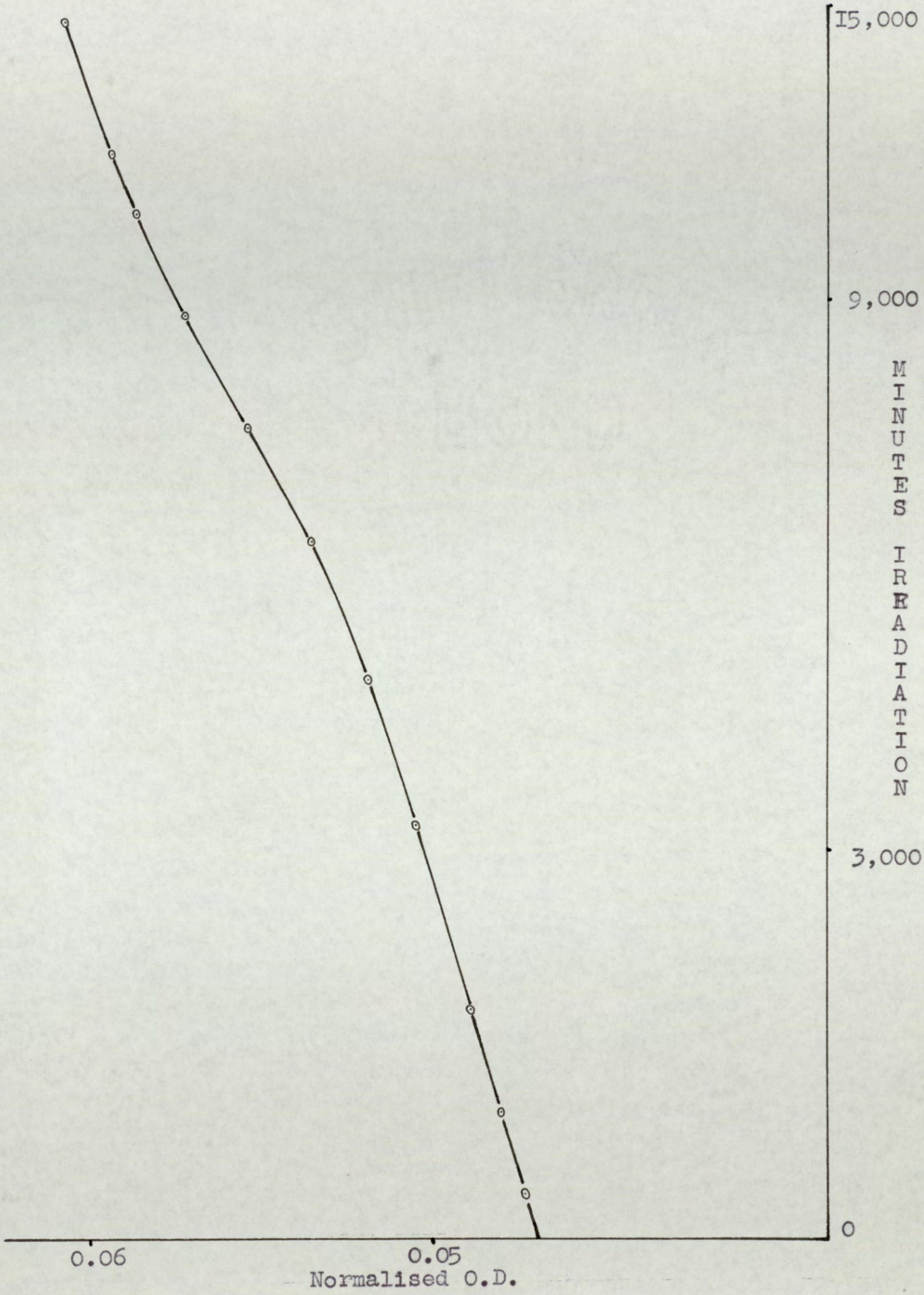


FIGURE 7-5 Effect of Surface Concentration of Stabiliser.

(TETA/828)

CHAPTER 8

Conclusions

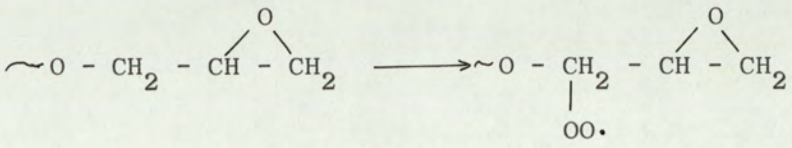
The degradation of the two cured epoxide resins by ultraviolet radiation of wavelength greater than 280 nm resulted in the evolution of volatiles and scission in the monomer backbone. Examination of a series of resins showed that regardless of monomer purity degradation occurred on exposure to the radiation. The rate of degradation was reduced by the increased purity in the resins. This indicated that some chromophore in the polymers absorbed radiation with resultant bond scission. The types of degradation products identified from both photo and photo-oxidative degradations indicated that a random bond scission of all bonds,except the aromatic carbon to carbon and carbon to hydrogen,occurred in the monomer backbone.

Since all of the epoxide monomers used absorbed in the ultraviolet spectral region up to 300 nm it was not surprising that the resins degraded. The unreacted curing agents used, TETA and HHPA, did not absorb above wavelengths greater than 250 nm. Therefore these compounds should not have been affected by the radiation used. Long exposures to the ultraviolet light did however indicate degradation of the curing agents. This can be attributed to the presence of impurities in both compounds. Also hydrolysis of the HHPA was observed during air irradiation. Studies on the reaction products of the curing agents with phenyl glycidyl ether showed that breakdown of the curing agents occurred at irradiation periods considerably less than was required to affect the curing agents alone. This was attributed to the initial degradation reactions in the resin monomer and to the morphology of the cured three-dimensional structures. The TBA data on the TETA cured resins indicated that the TETA was affected during the degradation process.

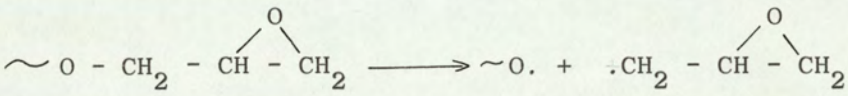
The HHPA cured resins were found to be more stable to the ultraviolet radiation than the TETA cured systems. No known chromophores were present in the cured structures which could initiate the degradation.

In many polymers photochemical reactions are known to be irradiated by impurities introduced during processing. Peroxides in particular cause degradation in polyethylene and polypropylene.

This was not the case with the epoxide resins studied. The use of a controlled atmosphere and curing conditions eliminated any possibility of peroxide formation during the preparative processes. Evolution of volatiles occurred at equivalent irradiation periods in both the TETA and HHPA cured resins. Also, during the early irradiation periods of both systems the distribution of the volatile degradation products was similar. The presence of unreacted chain ends could account for this phenomenon. The slight difference in the rate of evolution of volatiles can be attributed to the different absorption characteristics of the system. Degradation was postulated to occur by peroxide formation



during photo-oxidation, and by the direct absorption of light by the ether bond during photo-degradation.



The isopropylidene group may have affected the degradation process. Some evidence of this effect was found with studies of phenoxy, polysulphone and polycarbonate resins.

Interaction between the aliphatic hydroxyl group and the carboxyl group of the HHPA curing agent was postulated to account for the increased ultraviolet radiation resistance of the material. The interaction would be stronger after degradation of the unreacted chain ends. Similar interactions may have occurred in the amine cured systems between hydroxyl groups and the nitrogen atoms, but to a lesser extent than in the case of the HHPA materials. The presence of primary, secondary and tertiary nitrogen atoms would also be expected to affect the rate of degradation. Spectroscopic data showed a change from long to short range hydrogen bonding in the amine cured systems. As a result greater colour formation would be expected to occur in these systems. No direct correlation was found between the infrared data and the degree of colour formation in any of the systems.

Auxochromes including hydroxyl, ether and benzene present in the monomer may have contributed to the absorption of light by the materials. This however did not explain the initial yellow colour of the HHPA cured resins. The degree of colour formation in these resins decreased with increased monomer purity. Impurities such as the chlorine containing compounds would be expected to affect the degradation process but not the initial colour of the system. Samples of HHPA cured resins prepared in a 'dark' room showed similar colour formation to those prepared under standard laboratory conditions. This also indicated that some intrinsic property of the materials caused or contributed to the colour formation.

The extent of degradation was proportional to the light intensity for both types of polymer. No 'dark' chemical reactions occurred on removal of the radiation source. The TETA cured systems showed the presence of 'dark' reactions, which were found to be due to the diffusion of degradation products through the degraded matrix. No correlation in terms of diffusion rates was possible with the three epoxide monomers used. Varying degrees of cure in the system caused morphological differences in the polymers. The TBA data showed that crosslinking and chain scission reactions occurred during photo and photo-oxidative degradation. The predominance of either process was dependent on the irradiation atmosphere. Oxygen aided the crosslinking and inert atmosphere the chain scission process. The morphological effects were also seen in the differences in the rate of diffusion controlled processes at different irradiation times. The rates fluctuated over long irradiation periods and were attributed to volatilisation at the surface of the polymers indicating that further reaction of the primary degradation products occurred.

Exposure to ultraviolet light caused degradation throughout the bulk of the polymer during the early stages of reaction. This was seen by the results of TBA investigations on both types of polymer and by the ATR results on the TETA cured resins. The extent of degradation was found to be dependent on the rate of colour formation and on the rate of diffusion of oxygen into the polymer. The degradation process in air or inert atmosphere resulted in the formation of a degraded surface layer which consisted of a mixture of oxidised and non-oxidised products.

The oxidised species were found, by TBA and ATR, to consist of cross-linked material while the non-oxidised species were the result of chain scission reactions.

A uniform distribution of degradation products was found throughout the degraded surface layers, which indicated that reorientation of some species had occurred in the cured systems. The ATR data indicated that during oxidative degradation the nature of the colour forming species was a quinone, a quinone/hydroquinone complex or some polymeric quinone type compound. Irradiation in vacuum gave rise to products including a α- methyl styrene which may have contributed to the colour forming process.

The TBA results showed uniform degradation of both the amine and the anhydride systems. Removal of the degraded surface, by grinding, resulted in exposure of a new surface layer of polymer which was partially degraded. This new layer was coloured and degraded at a faster rate than the original polymer. Since morphological changes occurred during degradation the rate of diffusion of oxidised species would be expected to decrease during photo-oxidation. This was not the case with the aliphatic compounds. It is possible that some degradation products from the initial reactions were trapped in the polymer system and underwent further reactions at later irradiation periods.

Studies with model compounds showed that the primary reaction in photo and photo-oxidative processes occurred in the aliphatic section of the monomer unit with secondary reactions in the bisphenol-A section. Gel formation involving the hydroxyl group occurred in all model compounds. Steric conditions in the cured polymer would have prevented gel formation. After the initial degradation, gel formation may have have occurred in the cured resins because of the mobility of the degraded fragments. This could explain the high molecular weight species found in the degradation products of the cured resins. The secondary amine cure link in TETA cured resins was more susceptible to photo-oxidative attack in accordance with the postulated Cope Degradation. In the HHPA systems the ester link in the central aliphatic section was less stable than the terminal ester group because of ester hydrolysis. The degree of cure of the anhydride materials influenced the rate of degradation being greatest with the undercured resins.

Also although the anhydride systems were more resistant to ultraviolet radiation than the amine materials degradation as evidenced by the evolution of volatile products occurred at equivalent irradiation times. This has been attributed to the presence of unreacted chain ends in both types of resin. An anomaly existed between the model systems and the cured resins in their response to the radiation used. The deeper initial colour of the amine cured models was attributed to molecular rearrangements involving the nitrogen atoms. These gave rise to chromophores which absorbed in the ultraviolet and/or visible spectral regions. Such rearrangements would not occur in the three-dimensional resins. Molecular rearrangements also occurred in the ester model compounds due to interactions between adjacent groups. Similar rearrangements would be expected to occur during the degradation of the cured resins and may also have contributed to further degradation.

The low product quantum yields indicated that if chain reactions were involved in the degradation process frequent chain termination occurred. Therefore chain stopping antioxidants or free radical scavengers were not expected to influence the rate of degradation. The stabilisation of the resins was attempted with known antioxidants and ultraviolet absorbers.

Elimination of both the degradation and the colour forming reactions was not achieved with the resins studied. However stabilisation by deceleration of the destructive processes was accomplished to some extent. The mode of action of the antioxidants and ultraviolet light absorbers explained the success obtained with the compounds used in terms of the known variables e.g. diffusibility and volatility. The efficiency of the ultraviolet absorbers was found to be dependent on their distribution in the polymer matrix. During the initial irradiation period all of the additive functioned because of uniform degradation throughout the polymer. After the initial degradation only that quantity of additive in the upper surface layers functioned as a light absorber, because of the screening effect of the degraded surface layers of the polymer. Therefore the method of additive incorporation and dispersion determined to a large extent the efficiency of the stabiliser action.

Stabilisation of both polymers was attempted using mixtures of DLTP and ultraviolet light absorbers.

In both polymers successful stabilisation causing a decrease in the rate of degradation was achieved with DLTDP/benztriazole synergists.

Suggestions for Future Work

Since some success was achieved using synergistic mixtures for the stabilisation of the epoxide resins this method offers hope of further success. The range of possible synergists is limited only by the availability of materials. In particular the use of carbon black may prove successful. Also, Since stabilisation of these materials has been reported using peroxides possible success may be obtained with synergistic peroxide mixtures. Multi-component synergistic mixtures may also be successful.

Direct modification of the monomer backbone may also serve to stabilise epoxide reins. In particular with such curing agents as HHPA, PA and other anhydrides an increased physical interaction may be achieved with the groups in the aliphatic chain of the '828' monomer. Since degradation is known to be a surface phenomenon such compounds need only be applied as a gel coat. Alternatively substitutions in the 3 and 5 positions on the benzene rings to prevent peroxide formation in the aliphatic section of the monomer may be successful in stabilising these materials. In amine cured structures it may be possible to control the degradation process by the use of curing agents which degrade, producing amine antioxidants. However such work demands a change in the basic manufacture of monomers, raw materials and curing agents. In the immediate future increasing the light stability of epoxide resins will be best achieved by synergistic mixtures.