Citation: Prosser, J. L. (1992). The kinetics of reaction of epoxy powder coatings. (Unpublished Doctoral thesis, City, University of London)

THE KINETICS OF REACTION
OF
EPOXY POWDER COATINGS

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A THESIS SUBMITTED FOR
THE AWARD OF THE DEGREE
OF DOCTOR OF PHILOSOPHY

CITY UNIVERSITY
CHEMISTRY DEPARTMENT

JUNE 1992

ACKNOWLEDGEMENTS

I WISH TO EXPRESS MY
THANKS TO MY SUPERVISOR
PROFESSOR JOHN DONALDSON
FOR HIS HELP AND
ENCOURAGEMENT TO ME
TO UNDERTAKE THE WORK
DESCRIBED IN THIS THESIS
AND TO
Dr A J CHAUDHARY
MR N LESCURE
AND Dr P D GAITONDE
FOR PRACTICAL HELP
IN TRANSFORMING A
MANUSCRIPT
INTO A PRINTED THESIS

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ABSTRACT

The kinetics of reaction of a number of reactive epoxy powders (epoxy resins containing hardeners and, variously, pigments, a flow control agent, or no additives), using IR spectroscopy and thermal analysis, have been studied.

Spectroscopic methods involving absorbance and reflectance techniques were initially promising, but were then found to be unacceptable because of poor repeatability.

Dynamic thermal analysis showed that sample size was more important than particle size; an epoxy powder divided into two portions of different particle size gave the same heats of reaction, glass transition temperature and peak temperature according to sample mass; particle size had a negligible effect.

Pigmentation affected kinetics. TiO_2 and SiO_2 had a marked effect on exotherms, in that TiO_2 slightly retarded reaction and SiO_2 gave multiple exotherms; an adsorption/release mechanism of low molecular weight resin components on surface active pigments is postulated.

Variation in heating rate produced a significant break in the course of the reaction, the break occurring at a heating rate in the 10–15 degree per minute heating range; this was detected using a Kissinger analysis; the powder contained a dicyandiamide hardener and was tested in a Differential Scanning Calorimeter. Another powder, containing o-tolylbiguanide as hardener and tested in a Differential

Thermal Analyser had two distinct exotherms, the more pronounced the faster the heating rate; the phenomenon is attributed to sequential reaction of primary and secondary amines with a contribution from the change in viscosity dependence on the heating rate.

Comparison of oven and DSC dynamic heating studies showed that a DSC experiment was not sufficient to predict the results of an oven heating cyle with any accuracy; this was true for both convection and IR heating cycles.

A reactive epoxy powder at four constant temperatures gave a stepped conversion/time plot, the two steps being at the same degree of conversion for three temperatures; at the highest temperature, only one step was detected. A reactant exhaustion/renewal cycle similar to a Lotka-Volterra cycle is considered.

The importance of the dependence of viscosity changes (and hence molecular mobility) on heating rate is emphasised.

CHAPTER 1

POWDER COATINGS: A GENERAL REVIEW

INTRODUCTION

Powder coatings, that is coatings applied in powder form without the aid of solvent, are of growing commercial importance, for they have many advantages over solvent-thinned coatings. They also have limitations as to use.

The principal reason for their displacement of solvent-thinned coatings in many applications is undoubtedly the absence of toxic and inflammable solvents associated with the latter. Additionally, solvent-thinned films must be allowed space and time to flash off after application, and consideration has to be given to total sovent loss to the atmosphere. The nearly complete recovery and re-use of powder after spraying is also an advantage.

The limitations as to use mentioned, include the ever-present danger of explosion associated with the handling and transport of powders, so rigorous precautions must be taken to guard against this. Colour change is something of a problem. With solvent-thinned paints, to change from black to white merely requires either a second spray gun or a clean out/change-over of a single gun, to spray-apply the black paint; to spray black powder after white runs the risk of producing a grey finish, because overspray powder remains as such (solvent-thinned overspray hardens) and can re-charge and mix with the next coat, the particles of which are electrically charged.

COMPOSITION OF POWDER COATINGS

A powder coating comprises a base resin, which may be a thermoplastic one like nylon or polyethylene, or a thermosetting one such as epoxy, polyester or acrylic.

The thermosetting resins, especially epoxy-based ones, are of primary interest in this Thesis.

A second essential component is a curing agent, which serves to cross-link the base resin during a reaction promoted by heating. The commonest such agents are polyamines of various types, of which the earliest finding commercial application was dicyandiamide. More recently, substituted dicyandiamides have been introduced, for instance o-tolylbiguanide.

The principal cross-linking reaction is of cyanogen, primary amine and secondary amine groups with epoxy and hydroxyl groups.

Additional components can be pigments, for colour, and flow control and/or wetting agents to facilitate fusion of the powder granules into a continuous film and to promote wetting of the substrate to be coated.

The chemistry of the epoxy resin is important in obtaining good results. The principal properties of interest are molecular weight, epoxy molar mass and softening temperature range. Too high a molecular weight produces poor pigment dispersion and film flow-out, and although film properties are improved, adhesion can be adversely affected because poor flow reduces surface wetting. The best compromise appears to be an epoxy molar mass in the range 700-950 (this is the weight of resin containing one gram equivalent of epoxy group). At the lower end of this range, the very high flow associated with the resin may in fact cause premature particle-particle adhesion. This phenomenon can in any case occur under too high storage temperature conditions, which can also promote actual cure if the system is sensitive enough, so storage at less than 40° is recommended.

The temperature dependence of viscosity is another important property; common behaviour is a fall from a viscosity in the range 45-75 Stokes at 140° to below 10 Stokes at 180° (1).

Apart from the polyamines mentioned, there are other cross-linking agents with a minor usage, including imidazoles, acid anhydrides and BF_3-amine complexes.

Dicyandiamide, or 1-cyanoguanidine has the formula:

$$N{=}C.NH.C({=}NH).NH_2$$

and thus contains one cyanogen, one primary amine and two secondary amine groups for reaction with the epoxy and hydroxyl groups of the resin.

This curing agent gives excellent results when incorporated into the resin in amount 4.5 parts per hundred (phr), but requires a high temperature and long time for complete cure, e.g. 30 minutes at 180°, so nowadays a catalysed version is usually employed, giving a typical cure time of 10 minutes at 180°.

A second commonly used polyamine curing agent, used in the experiments described in this Thesis is o-tolylbiguanide, of formula:

$$o\text{-}CH_3.C_6H_4.NH.C(=NH).NH.C(=NH).NH_2$$

which contains one primary amine and four secondary amine groups. It produces mixtures with a lower useable cure temperature than uncatalysed dicyandiamide.

The "useable" cure temperature limitation should be noted. The amine/epoxy reaction will actually proceed at a much lower temperature. However, it is then so slow that it cannot be used in industrial practice. Many powder coatings will in fact cure slowly at room temperature, albeit in months, creating a storage problem.

Flow control agents, of which acrylics are probably the most common, reduce the viscosity of the reactant mixture at the relevant cure temperature and facilitate flow out. There is some reason to believe (see CHAPTER 6)that they have a small effect on cure kinetics.

Pigments can also be shown to have an effect on cure. Organic pigments certainly do; for example with basic hardeners like dicyandiamide, "plate-out" can occur, when the pigment exudes from the film.

Inorganic pigments can also be reactive, for example different grades of rutile titanium dioxide have an effect on gloss, levelling and cure time of a dicyandiamide-cured mixture. Probably the principal reason for this arises from the effect of the pigment on the melt viscosity of the film. Rutile TiO_2 pigments differ from one another in surface treatment, and this may produce differences in pigment wetting and perhaps in preferential adsorption of one component of the reactant mixture (2). An original contribution to this subject has been made by Foulger and Simpson (3), using dielectric analysis to follow cure. They showed that the presence of zinc - used commonly as a rutilisation catalyst, retards the onset of cross-linking, gelation and degree of cure.

It is rather interesting that increasing the loading of an extender pigment in a powder coating is not an effective means of securing a low gloss or matte finish - as would be the case with a solvent-thinned paint.

MANUFACTURE OF POWDER COATINGS

Basically, the powder components, themselves powders, are mixed as efficiently as possible. First of all, all the components are mixed together in a Z-blade mixer, which may be heated to ensure that the powders are dry. The uniformity of dispersion of the components is probably low at this stage, and a more effective mixing takes place next in a screw-type plastics extruder. The initial mixture is fed into the hopper of the extruder and traversed through the barrel by the screw, the barrel being heated; residence time in the mixer is usually a minute or so. The homogenised mass is then fed on to a travelling stainless steel band, which cools it. The solidified film is scraped away from the band and broken up - at this stage being called a kibble. The kibble is fed to a dry grinder, usually a coarse one followed by a fine grinder,when the powder assumes the final form and fineness. Sieving is used to separate out oversize and coarse particles, to give a powder with a maximum particle size of 100 µm.

Since the powder is being subjected to an elevated temperature, the question arises whether the mixture cures at all in the process. Dreher (5) has discussed this possibility. He showed that an epoxy/polyester powder mixture had initially a glass transition temperature of 334K, unreacted, and after five passes through an extruder, this had risen to 341K. For one pass, clearly the increase in Tg was negligible; however, his studies may have been on a relatively insensitive mixture.

APPLICATION OF POWDER COATINGS

Powder coatings are applied electrostatically, that is, an electric charge is impressed on the powder particles by a variety of means, and directed down a potential gradient to the article being coated, which is at earth potential. The impressment of the charge may be triboelectric or by use of an active charge generator.

Three types of applicator can be distinguished.

(1) Manually operated gun, impressing a charge from an electrode attached to the gun (externally or internally, using an external charging source), or impressing a charge by friction of the expelled powder in an air stream against a dielectric surface.

(2) Some form of automatic equipment as in 1, but enclosed in a tunnel through which the article passes on a

conveyor for continuous painting, the guns being programmed to coat articles of different shapes and sizes. The tunnel is so constructed as to contribute to the efficiency of powder deposition and recovery, for example by having a travelling floor that carries away overspray.

(3) A fluidised bed machine, fluidisation being by means of an air supply fed through a porous bed, the powder particles additionally carrying an electric charge by impressment. The article is traversed through on a conveyor and is at earth potential.

A detailed description of guns and other equipment is not appropriate in this Thesis, but the author has given such a description in another publication (6). However, some comment on the scientific aspects of powder deposition may be useful.

Guns usually have a charging electrode in the nozzle. Deposition efficiency depends on the effectiveness of charging of the powder. The charging electrode is commonly a wire projecting from the nozzle, but in one patented device the powder passes through a needle/ring electrode. However, because of the Faraday Cage effect,the more efficient the charge impressment, the poorer the penetration of the powder into recesses in the article, so in some guns, a compressed air jet is additionally employed to carry the powder forward. Triboelectric charging, being relatively inefficient, gives the best penetration characteristics. Overall, probably only 1% of the powder particles actually carry a charge in any system.

Once the powder has been deposited, the particles have to be fused in order to form a continuous film. Sometimes, the fusion is not complete, and vacuoles are formed; these are air voids in the body of the film, which may not be visible from the outside, but which necessarily detract from the protective value of the coating. The formation of vacuoles has been studied and reported by the author (7).

When the powder is deposited, it necessarily contains interstitial air voids, and it appears that in certain circumstances, the particles do not fully fuse and displace the air; complete displacement is a function of minimum viscosity attained by the melt and the surface tension of the resin.

Flow characteristics have been examined by microscopic examination of a small pile of powder on a temperature-variable base. As the temperature was raised, the following observations were made.

(1) A sharp fall in area on the attainment of a certain temperature. This was probably due to the reduction of viscosity to the point where cohesive forces are greater than those promoting spreading (surface tension and gravity), so the powder assumes a shape corresponding to a minimum internal energy, that is, a sphere.

(2) A rapid and large increase in area with rising temperature. This is a true wetting/spreading operation. Its speed is dependent on viscosity and surface tension and their change with temperature.

(3) An approach to a maximum wetted area. This is the culmination of Stage 2, where spreading energy is in equilibrium with surface tension and onset of gelation due to cross-linking.

In a further study, where viscosity changes during heating were measured, it was found that the viscosity of a normal epoxy powder fell to a minimum of 145 Stokes after 60 seconds at 185-195°, but then rapidly increased to above 1300 Stokes in 150 seconds.

Finally, it should be noted that the flow at minimum temperature above, where the powder assumes a hemispherical shape, occurs in the range 60-80° for all the epoxies studied, and this then is the melting range, and corresponds to the endotherm in thermal analysis.

The significance of these observations for work in this Thesis is, that it emphasises the importance that must be attached to viscosity changes when considering the mechanism of reaction of the epoxy powder. Most of the reaction must be diffusion controlled.

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CHAPTER 2

CHEMISTRY OF THE CURE OF EPOXY RESINS

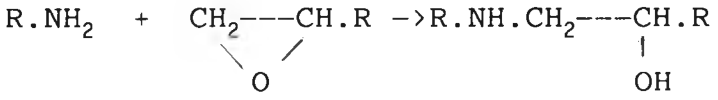
The reaction between amines and an epoxy compound is an example of step growth polymerisation, as distinct from free radical polymerisation. In the latter, as polymerisation proceeds and gelation occurs, the speed of reaction may actually increase, but in step growth polymerisation gelation is likely to substantially retard the reaction rate.

Epoxides react with a variety of other compounds besides amines, generally by opening the epoxy ring, but in this Chapter only the amine/epoxy reaction will be discussed. The basic reaction appears to be simple, but most contemporary authorities are agreed that it is in fact complex and not completely understood. Barton (1) has suggested that complex parallel or sequential reactions requiring more than one rate constant may be involved, and that the basic autocatalytic reaction may become diffusion controlled as the viscosity of the system increases. The complexity arises from the mixture of products resulting from reaction of even the simplest amine and an epoxy compound, especially an epoxy polymer.

The molecular structure of an epoxy resin is shown in Figure 2:1 as a molecular model, written as having two repeating units. The resin is made by reacting epichlorohydrin with the diglycidyl ether of bisphenol-A, and as shown the chain contains two terminal epoxy groups and two hydroxyl groups as the main reactive groups, although some authors have reported opening of the aromatic rings. It should be noted that if phenylglycidyl ether is reacted with epichlorohydrin, as is often done to prepare a model molecule to study the amine/epoxy reaction, then this does not contain a hydroxy group, and etherification (a feature of reaction with an epoxy resin) occurs only with a newly formed hydroxy group.

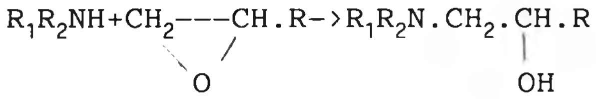
Excluding the possibility of aromatic ring fracture, the following reactions can occur in an amine/epoxy reaction, as reviewed by Lee and Neville (2):

(1) Reaction of a hydrogen of a primary amine (if present) to produce a secondary amine and an hydroxy group;



$$R.NH_2 \quad + \quad \underset{\diagdown\;O\;\diagup}{CH_2---CH}.R \rightarrow R.NH.CH_2---\underset{OH}{\underset{|}{CH}}.R$$

(2) Reaction of the remaining hydrogen of the formed secondary amine or of an added secondary amine with an epoxy group to produce a tertiary amine and an hydroxy group.



$$R_1R_2NH+\underset{\diagdown\;O\;\diagup}{CH_2---CH}.R \rightarrow R_1R_2N.CH_2.\underset{OH}{\underset{|}{CH}}.R$$

(3) Reaction of an epoxy group with an existing hydroxy group or with one freshly formed in (1) or (2) to produce an ether.

(4) The amine/hydroxy and amine/epoxy group reactions are catalysed by the tertiary amines formed in the amine/epoxy reactions and by the hydroxy groups. All these reactions may occur simultaneously or in some sequence, each reaction having its own rate constant and probability. It is likely that a primary amine reacts at least twice as fast as

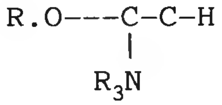
a secondary amine, and that the etherification reaction is not important except in the presence of a stoichiometric excess of epoxy, or at a higher temperature. Another factor limiting reaction is steric hindrance. When one amine hydrogen has reacted, inevitably the size of the now greatly enlarged secondary amine is such as to hinder further reaction to form a tertiary amine and probably to reduce the diffusion coefficient, so as to immobilise the molecule. Partial immobilisation must also result from gelation of the resin structure, even at a higher temperature, as polymerisation and cross-linking proceed. At any one stage in the reaction there must exist a mixture of all the products resulting from the reactions described above. The reactions and their products are now considered in more detail.

A primary amine has a functionality of two and a secondary amine is monofunctional, but functionality may be lost because, inter alia, of the direction of the reaction, the absence of co-reactant groups, steric hindrance or molecular immobility in general. System functionality may be reduced if one reactant is present in excess. Reactive sites may be blocked by steric factors, e.g. in a primary amine reaction, the formed tertiary amine may be too hindered to promote cure by a self-propagating mechanism, such that any epoxy in excess of stoichiometric will be reacted.

The structure of the amine is important, particularly the number of methylene groups present between the amine groups. Delmonte (3) stated that when the amine groups are close together in a diamine, the reaction of one primary nitrogen-hydrogen is rapid, but this leads to a secondary amine hydrogen being hindered, and it is then only effective as a catalyst. The importance of polymer structure has been confirmed by Allen and Huntly (4), and also in a detailed study by Horie, Hiura, Sawada, Mita and Kambe (5) who examined the reaction of ethylene diamine, triethylene diamine and hexamethylene diamine with an epoxy resin. A theoretical analysis first permitted these authors to isolate the rate constant for the first primary amine hydrogen reaction and use this in a DSC study. Their tabulated data show the rate constants at 70° for the ethylene, diethylene and triethylene compounds to be 1.90, 2.70 and 3.42×10^{-4} sec^{-1} respectively, that is, the rate constants increased as the number of methylene groups between the amine groups increased, or conversely, decreasing the interval separating the two amine groups had an adverse effect on reaction kinetics. The steric hindrance by the epoxy group attached to one end of a diamine affects the reactivity of the amine at the other end. Interestingly, the activation energies for the reactions of the three amines with the resin are the same, within the limits of experimental error, so that the differences in the values of the rate constants found are likely to be caused by differences in the pre-exponential factors.

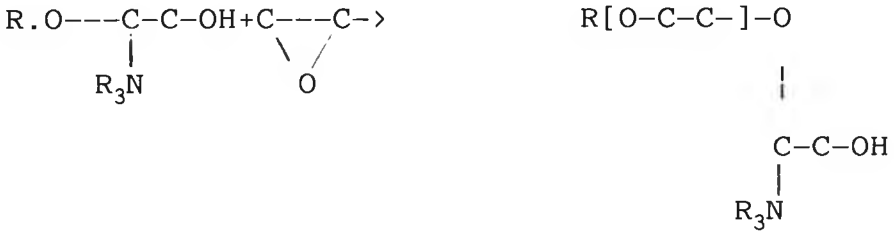
The secondary amines produced by the initial reaction of primary amines are themselves slow to react unless a proton donor is present, provided for example by the hydroxyls of the resin. The tertiary amines finally formed have a marked catalytic activity and this originates in the presence of non-bonding electron pairs on the nitrogen atom, that is, the amines are Lewis bases.

The process goes as follows: an activated complex is formed between the tertiary amine and the epoxy group, with a hydroxyl group providing hydrogen bonding for the epoxy oxygen;



$$\begin{array}{l} R.O{-}{-}{-}C{-}C{-}H \\ \qquad\quad | \\ \qquad R_3N \end{array}$$

Then additional epoxy groups could add to the complex without increasing the charge separation;



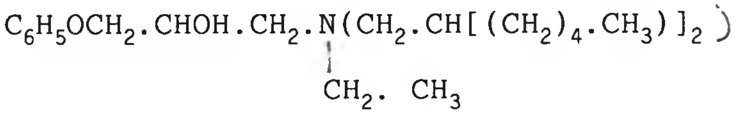
and chain termination then follows:

$$R.O{-}{-}{-}H{-}C{-}NR_3{-}{>}\ ({-}C{=}C{-})\ +\ R_3N\ +\ ROH$$

Lee and Neville state that the effectiveness of the tertiary amine is not dependent on its basicity, but only on steric factors, bulky side chains for example, and citing two examples of differing efectiveness, thus

$$C_6H_5.CH_2.N(CH_3)_2$$

is effective



$$\begin{array}{l} C_6H_5OCH_2.CHOH.CH_2.N(CH_2.CH[(CH_2)_4.CH_3)]_2) \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad CH_2.\ CH_3 \end{array}$$

is not effective. In the latter case, however, as well as a side chain, there are long chains attached to the nitrogen, and Schechter and Wynstra (6) point out that a longer chain alters the s,p electron balance on the nitrogen. However, what is important about the reaction scheme outlined above is, that the chain termination reaction produces both vinyl unsaturation and alcohol groups.

If the functionalities of the primary and secondary amine hydrogens are taken as 2 and 1 respectively, then the ideal rate constant ratio k_1/k_2 is 2, and the reality of this value has been discussed in numerous papers. Thus Dusek (7) who used HPLC and GPC to obtain quantitative separation of reactants and reaction products in an epoxy/amine mixture obtained a k_2/k_1 value of 0.4-0.6 for aliphatic amines and 0.1-0.3 for aromatic amines, that is, aromatic amines were not as reactive as aliphatic amines.

There is a spread of opinion on the value of the ratio and examining the different opinions provides interesting information on the cause of such differences.

Charlesworth (8) reports the k_1/k_2 value for simple aliphatic amines as 1.5-2, but when steric hindrance is present in the amine, reaction rates are reduced and k_1/k_2 becomes large. Rinde, Happe and Newey (9) reacted 2,5-dimethyl 2.5-hexanediamine with phenyl glycidyl ether and followed the reaction with NMR measurements. They found a k_1/k_2 ratio of 60:1. So large indeed was this ratio, and so hindered in reaction the formed secondary amine that a first reaction with the primary amine hydrogen effectively prevented reaction of the secondary amine hydrogen, at ambient temperatures at least, and the mixture could be left at this stage for a long period without further reaction occurring.

Schneider, Sprouse, Hagenauer and Gilham (10) confirmed the importance of steric hindrance imposing restrictions on ambient temperature reaction and the need to apply heat to complete the cure; during this latter stage, they identified polyetherification as dominating the reaction.

Another factor determining the k_1/k_2 value is the temperature, which two authors have discussed. Chen (11) reported the effect of temperature as increasing the ratio, but Wang and Gilham (12) found a different result in a study of the isothermal reaction of an epoxy/amine mixture. They reported a k_1/k_2 ratio change from 1:0.58 at 100° to 1:0.33 at 160° with a derived activation energy difference of 15.5 Kcal/mole. In this cure at least a 6.3:1 preponderance in the primary hydrogen rate constant had been reduced to 3.0:1 by a rise in temperature. This is again an indication of a significant difference in the reactivities of primary and secondary amine hydrogens which must have some effect on the cured epoxy structure.

Etherification, resulting from the reaction of a hydroxyl group with an epoxy group, is a reaction which occurs to different extents according to composition, and its possibility at some stage of the reaction is the theme of several papers. In general, it is considered to follow a nearly complete epoxy/amine reaction. Thus, Simon, Wisenrakkit and Gilham (13) using an aromatic diamine curing agent reported that etherification occurred only in a stoichiometric excess of epoxy. Pyun and Sung (14) examined the question in a study with a diaminodiphenylsulphone/1% diaminoazobenzene hardener/accelerator and measurement of reactant composition at selected stages with IR spectroscopy. They also reported the late appearance of ether groups and identified tertiary amine groups. Dusek (15) confirmed the importance of the epoxy:amine ratio in promoting etherification, as did also Riccardi, Adabbo and Williams (16) using aliphatic amines. Mijoric, Kim and Saby (17) showed that etherification was more significant for aromatic amines than for aliphatic, because of the lower basicity of the aromatic amines; this was confirmed by Simon(18) using the aromatic diamine trimethylene glycol di-p-aminobenzoate.

The hydroxy group involved in etherification has a second function, that of a catalyst for the amine/epoxy reaction. The nature of the alcohol is significant in this process with polyfunctional and substituted alcohols being effective (19), although the alcohols produced in the amine/epoxy reaction are particularly effective (20).

THE REACTION WITH COMPLEX AMINES

At this point it has to be emphasised that all the discussion so far has dealt with the reaction of an epoxy with relatively simple amines, such as m-phenylenediamine and hexamethylene diamine. However, in this Thesis two relatively complex amines are used as cross-linking agents, namely dicyandiamide and o-tolylbiguanide, and it is of particular importance to establish how they differ, if at all, in reaction from simple amines. Dicyandiamide is a tetrafunctional nitrogen compound containing a cyano group (not discussed in any of the papers reported so far) and with a minimum separation between the aliphatic amine groups (shown to be important earlier); o-tolylbiguanide is a mixed aromatic/aliphatic amine, also with minimum intervals between the amine groups. The literature deals with dicyandiamide fairly extensively, but a study of the chemistry of reaction with o-tolylbiguanide has not previously been reported. Levine (21) accepts the tetrafunctional nature of dicyandiamide, all of the nitrogen groups participating in the reaction, and producing guanylureas as an end product. Hodd (22) however is of the opinion that dicyandiamide is only trifunctional and the end products are cyanoguanidines. Gilbert (23) has made a detailed study of the reaction, using as a model a monofunctional epoxy and dicyandiamide. The initial reaction was established as the formation of an N-alkyldicyandiamide via a simple epoxy/amine addition. This reaction was followed by cyclisation by intramolecular nucleophilic substitution of hydroxyl at the imido functionality, leading to the elimination of alkylamines. The 2-cyanoimidooxazolidines formed by this reaction are effectively difunctional and act as chain extenders. Tertiary amines formed by further reaction of alkylamines with epoxy then act as trifunctional cross-linking agents. In the polyfunctional epoxy resin etherification can also occur (24).

A detailed study using the polyfunctional epoxy resin has been reported by Saunders, Levy and Serino (25), who showed that the exact reaction path depended on the stoichiometry, catalyst and cure temperature. At 160° in the presence of 1% benzyldimethylamine, the epoxy/amine and epoxy/epoxy reactions compete, and in the early stages lower dicyandiamide concentrations favour homopolymerisation to a degree of polymerisation of 2-3. Amino alcohols formed by the epoxy/amine reaction are a source of protons for homopolymerisation, but fully reacted amino groups are then present, especially at low diamide concentrations, indicating that the reaction of secondary amine hydrogens is not suppressed.

In a simultaneous spectroscopic study, a reduction in the intensity of the 2180 cm^{-1} absorption was observed, indicating a fall in the cyano group; but absorption at 1740 cm^{-1} increased, indicating the formation of an amide. Other IR changes, representing structural development, covered 1680 -1560 cm^{-1} (imino), 1120 cm^{-1} (ether) and 1740 cm^{-1} (carbonyl). These and other changes involved the formation of cyclic N,N'-substituted ureas.

The early reaction of dicyandiamide and epoxy has been described by Jackson (26) as follows. The epoxy ring is first opened by the accelerator, not by the dicyandiamide with the formation of a zwitterion, which then abstracts a proton from the dicyandiamide to form an anion, and this is the effective further cross-linking agent.

THERMAL ANALYSIS IN THE STUDY OF THE CHEMISTRY OF CURE OF EPOXY RESINS

Thermal analysis is the measurement of the thermal energy changes which occur in compounds when they are heated. The subject is treated in more detail in Chapter 4, preparatory to its use in the experimental work for this Thesis, so it suffices to say that the heat content changes measured include second order transitions, melting points, chemical reactions (exotherms) and thermal degradation. Of these, only heats of reaction (exotherms) will be considered in this section. The changes that can be readily detected have been summarised by Franian (27) as indicating the following sequence on heating a heat-curing resin:

Tg->Melting->Partial Cure->Gelation->Total Cure

He also stated that the heat of reaction ΔH between the onset of cure and the peak temperature represents the partial cure stage, beyond which reaction is diffusion controlled, and in the light of later discussion also represents the point at which the chemistry of the reaction can change.

If we write, $\alpha(\text{gel}) = \Delta H_1/\Delta H_T$

where ΔH_1 is the partial cure heat and ΔH_T is the total heat of reaction, then gelation is usually found to occur at a degree of reaction of about 0.6-0.7.

The reactions actually occurring before and after gelation are complex; that they are so is indicated by the dependence of the kinetic parameters on the heating rate (28), confirmed by the experimental data obtained in the present work and described in Chapter 8, where a Kissinger analysis (29) clearly indicates a break in kinetics in the 10-15 degree per minute heating rate range. It is likely that several parallel and competing reactions are in action at any one time.

One criterion for the identification of a reaction is the energy of activation, E, which may be obtained from;

$$\ln k = \ln A - E/RT$$

by plotting the rate constant, k, against the reciprocal of the temperature, usually from a series of experiments at different heating rates; A is the pre-exponential factor and is itself useful for this purpose.

Acitelli, Prime and Sacher (30) have reported on activation energies for a variety of epoxy/hardener systems, measured by DSC, and conclude that the values are closely similar irrespective of whether the amine is monomeric or polymeric, and that the reactions are diffusion controlled. This is perhaps an exaggeration because their data may only mean that the activation energies are the same for the two parts of Franian's scheme, above. However, confirmation of the uniformity of activation energies has been provided by Horie, Hiura, Sawada and Kamba (31) for monomeric amines and by Gough and Smith (32) for polymeric amines, whilst Hollander and Kalinin (33) have provided data also on activation energies for self-diffusion in polymers, and these again are not dissimilar from values for the epoxy/amine reaction.

In the opinion of the Author, there is a dilemma to be resolved here. Acitelli et al use experimental data to conclude that all the possible reactions proceed with the same activation energies; in particular, they used m-phenylenediamine as a hardener and inferred from the experimental results that they are consistent with equality of energy of reaction between primary and secondary amine hydrogens, although accepting a possible 2:1 variation in rate constants - easily accomodated into a quantitative equal reaction probability in view of experimental error and overall reaction complexity.

In Chapter 8 of this Thesis, a treatment of multiple exotherms carried out in the present work is described. It leads to a k_1/k_2 ratio of 26.8:1 for a (hypothetical) predominantly primary:predominantly secondary amine sequential reaction; this may seem unacceptably high, but it is lower than the 60:1 ratio found by Rinde, Hoppe and Newey (9) (earlier discussed) using the relatively simple hardener hexamethylenediamine.

Duffy, Hui and Hartmann (34) also reported the existence of multiple exotherms, using 2,5-dimethyl-2,5-hexanediamine and quoted a ratio of 9:1.

An interesting effect observed in thermal analysis is that of the addition of a surfactant to an epoxy/amine reacting mixture. Hagenauer and Dunn (35) noted an acceleration in the rate of cure with dicyandiamide hardener, and this they attributed to a more effective solubilisation of the amine. Sacher (36) confirmed the solubilisation effect with a 1.2% addition of a chemically unidentified surfactant and provided interesting experimental data. He found that the pre-exponential factor and the activation energy were both decreased, from 3,85x10^9 to 1.46x10^7 for A and from 24.1 to 19.3 Kcal/mole for E, and the glass transition temperature was substantially reduced, from 73.7° to 48.9°; altogether a very significant effect from the addition of a small amount of surfactant.

In Chapters 4 and 6 of this Thesis, reference is made to the effect of addition of 1% of an acrylic flow control agent to an epoxy/o-tolylbiguanide mixture. A flow control agent is not quite the same as a surfactant, nevertheless, there is a similarity in that both promote the inter-diffusion of components of the reacting mixture. The two relevant systems examined are identified as R161 (reference) and R162 (contains the agent). The most obvious difference is that the heat of reaction is 7.2% lower for R162 than for R161; the shapes of the exotherms are different, as if surprisingly, the start of the reaction was delayed by the inclusion of the flow control agent, as indeed appears to be the case on incorporating a pigment. However, it would seem that the effects observed, on addition of a surfactant, and to a certain extent of the flow control agent, reflect some influence on the chemistry of the epoxy/amine reaction.

MULTIPLE EXOTHERM PEAKS

The question of the occurrence of multiple exotherm peaks is one of the most interesting observations in the literature.

In the paper by Acitelli et al (30) already noted, a dynamic DSC trace shows a diffuse two-peak exotherm which is resolved into three distinct ones at three increasing temperatures. In addition, at a reaction temperature of 110°, a DC conductivity trace showed three points of inflection as cure proceeded. These peaks were identified by Acitelli et al as representing the following reaction steps;

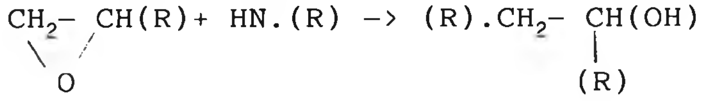
(1) Epoxide/hardener reaction;

(2) Ester formation at the expense of amide;

(3) Loss of amide.

These conclusions are drawn from a simultaneous IR study. The reactive stages can be formulated as follows:

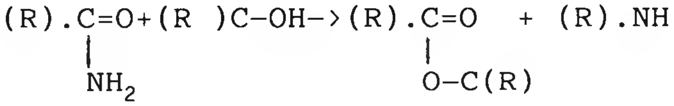
(1)



$$\underset{\backslash\ O\ /}{CH_2-\ CH}(R)+\ HN.(R)\ \rightarrow\ (R).CH_2-\ \underset{\underset{(R)}{|}}{CH}(OH)$$

At higher temperatures:

(2)



$$(R).\underset{\underset{NH_2}{|}}{C}{=}O+(R\ )C-OH\rightarrow(R).\underset{\underset{O-C(R)}{|}}{C}{=}O\ +\ (R).NH$$

Then at higher temperatures again:

(3) (R).CN(R) + (R).C–OH -> ?

The bracketted R's merely express the rest of the molecule. The sequence must be as written, because the second reaction uses an alcohol group formed in the first reaction. The reaction scheme is not complete because no further reaction occurs on heating either reactant separately with added alcohol. It is possible that in the actual epoxy/amine mixture, progress depends on the presence of a tertiary amine as a catalyst from the first reaction.

Several other papers describe multiple exotherms. Thus, Prime and Sacher (37) reported two diffuse exotherms in an epoxide resin/polyamide system, which they further resolved into three distinct ones, similar to those found by Acitelli et al, and additionally two marked points of inflection on a DC conductivity trace. Their further analysis of the chemistry of the reaction is similar to that given by Acitelli.

Barton (38) employing a rather exotic mixture, made the interesting observation that the number of exotherms appearing depends on the ratio of constituents. Thus, at a ratio of 100/30/1 and 100/10/1 for resin/hardener/accelerator two peaks appear, but at a ratio of 100/30/0, that is elimination of accelerator, only one peak is detectable. Barton does not attempt to make a detailed analysis of the DSC curves in terms of reaction chemistry, remarking only that multiple scan exotherms are indicative of a complex cure mechanism.

Another paper by Barton, in conjunction with Greenfield (39), again shows multiple peaks, this time the hardener is dicyandiamide. Two major peaks were detected at 185° and 192°; if Diuron was added, the effect was to shift the cure reaction to a lower temperature region with a large peak at 159°, followed by one at 257°. A further effect of diuron is to lower both the overall heat of reaction and the apparent activation energy relative to those for resins containing dicyandiamide alone.

CONCLUSION

It is not possible, to give, unequivocally, a reaction scheme for the epoxy/amine reaction that would satisfy all the observations of analytical studies, spectroscopic and thermal, especially since quite small variations in composition or in the nature of one constituent can leave a large uncertainty - as witness the thermal analysis results just considered and the effect of component ratio changes, or the addition of surfactants, or the ambiguity as to the value of k_1/k_2 for primary and secondary amines and its probable dependence on the nature of the resin and amine, and the temperature. The outline is simple enough: amine reacts with epoxy to open the ring, to form a secondary amine and an alcohol. The secondary amine is only further reactive if a hydrogen donor is present or is nascent. Tertiary amines formed act as a catalyst, especially for ether formation from epoxy and hydroxyl, and have other functions. Any attempt to describe the situation in greater detail does not at present lead to a satisfactory treatment of the chemistry.

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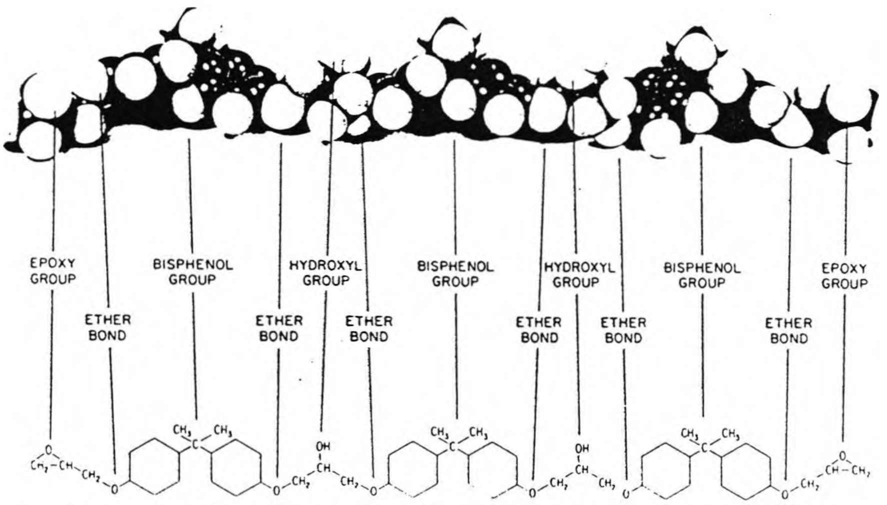


Atom model of widely used solid epoxy resin, diglycidyl ether of bisphenol A, degree of polymerization of 2 (DGEBA, $n = 2$). Approximate magnification: 100 million times. (*The Epoxylite Corporation.*)

FIGURE 2:1 EPOXIDE RESIN MOLECULE MODEL

CHAPTER 3

COMPOSITION OF POWDER COATINGS USED IN THE PRESENT THESIS

The powder coatings used were obtained partly from commercial sources, partly made on semi-plant scale equipment and partly made in the laboratory. Commercial preparation is valuable because one is testing material that would be acknowledged to be representative of industrial use, and which could not be dismissed as laboratory curiosities. Semi-plant scale production of powder coatings has to be resorted to when a series, such as R161-164, is not in actual production and variation of formulation in the series can be used to study the effects of the changes made. If a powder is required quickly, the simplest method is to prepare it in the laboratory from the constituents; at least one can be sure that the formulation is exact and the powder fresh. As will be seen later, there is some suspicion that commercial preparation may actually reduce the reactivity of the powder.

All the powders used were based on epoxy resins, with a hardener and, in some formulations a flow control agent, and in others, pigments.

In R160, the epoxy resin is Epikote 1055, and the hardener catalysed dicyandiamide; in R161-165, the resin is Epikote 3003 and the hardener o-tolylbiguanide. The number average molecular weight of 3003 is slightly lower than that of 1055.

The nomenclature used to identify the powders is the following: each number identifies a powder in formulation and preparation. Thus, R161 and R165 have the same formulations, but they are differently numbered because R165 was made in the laboratory; they may differ slightly in properties because they were prepared differently; passage through a hot plastics extruder may have reduced the latent heat of reaction of R161.

Formulation R160 was supplied as a ready-for-use powder and was stored after receipt as described below.

Formulations R161-164 were supplied as "kibble", that is, coarsely broken up film from the stainless steel cooling band after extrusion of the hot melt. These were stored in stoppered plastic bins and placed in a refrigerator at -5°, When required for analysis, a sufficient supply was reduced to a powder in a laboratory propeller-type coffee mill, in 3x5 second runs, this procedure minimises heating and produces a powder of about 50 µm mean particle size. The powder was stored in a desiccator over fresh silica gel.

The known specifications of the epoxy resins are given in Table 3:1, and the formulations of the powder coatings in Table 3:2.

R160, a commercial product, was pigmented with titanium dioxide and was used as a standard for many experiments, because, as a currently manufactured product, fresh supplies could be readily obtained when required.

R163 and 164 were also pigmented, but differently, and were used to establish whether pigmentation had an effect on cure; the reference was R161, not pigmented. R162 was similar to R161 but contained a flow control agent to check whether the presence of this additive affected cure.

An effect on cure from pigmentation was thought possible because of the known ability of finely divided powders to adsorb components of the binder on their surface, and this might affect cure rates.

Since powder coatings change their properties on storage, at a rate determined by temperature and ambient humidity, testing such a material after a period of storage does not always yield the same result as fresh material. It is important to have a fresh sample always available. To ensure this, one powder was made up as a copy - in formulation, of R161, by mixing together resin 3003 after fine milling and addition of o-tolylbiguanidine and milling; the milling was performed in the laboratory coffee mill as described above. The new powder was designated R165.

It should be emphasised that R165 was not expected to mirror the properties of R161 exactly. The "copy" was in formulation only. The difference in thermal properties, if any existed, would arise from the method of preparation only. In R161, all the ingredients had been melted together and mixed in the molten state in the extrusion machine; in R165, the ingredients had been mixed without melting.

A possible consequence is, that in R161, the resin and hardener were intimately dispered one in the other in molecular form; in R165, the dispersion would be likely to be much coarser. One could expect differences, perhaps, in melting points if hardener and resin form eutectic mixtures, as seems at least probable, and in the shape of the exotherm.

In fact, in several runs comparing R161 and R165, no difference in shape of the exotherms, at a heating rate of 10DPM was detected, but the melting points did differ - about 69° (peak) for R161 and 80° (peak) for R165. Consequently, R165 was used without reference to R161, but was used exclusively for a study of the effect of heating rates in SR780.

The problem of the homogeneity of powder coatings is a difficult one; some attempts were made to find a solution.

Microscope examination alone did not produce a useful result; then the powders were stained with acid dyes and washed, in the hope that the basic hardener would be stained more deeply of the two components and would stand out in the microscope. The actual appearance was ambiguous, some deeply dyed small particles could be seen in R165 - more than in R161, but then, there were more small particles in R165.

In the event, the problem was put aside until a more suitable means of solution could be envisaged.

Another set with a limited application is represented by R170-173.

These are powder coatings pigmented with carbon black/filler to assist in examining the effect of pigmentation. R170 is pigmented to give a glossy film; R171-173 are pigmented to give matte films. It was found that differences existed in melting and reaction and these are discussed in more detail in Chapter 4. Unfortunately, the binder free from pigment was not available for study.

TABLE 3:1

SPECIFICATIONS OF EPOXY RESINS

	Epikote 1055	Epikote 3003
Epoxy molar mass	800–900	725–825
Melting point °C	64	57
Specific heat J/g/deg	2.1	2.1
Density g/ml	1.19	1.19

****

TABLE 3:2

SPECIFICATIONS OF HARDENERS

	Dicyandiamide	o–Tolylbiguanide
Molecular Weight	84.08	191
Melting point °C	209–211	139
Density g/ml	1.404	1.0
Particle size um	<40	<75

****

TABLE 3:3

COMPOSITION OF STANDARD POWDER COATINGS

Component	R160	R161	R162	R163	R164	R165
Epoxy resin						
Epikote 3003		955	955	955	955	955
Epikote 1055	52.1					
o–Tolylbiguanide		45	45	45	45	47
Dicyandiamide/catalyst	3.9					
Acrylic flow additive			10			
Carbon black				20		
Blanc fixe				300		
TiO	44.0				700	
Resin/Hardener Content %	56.0			75.8	58.8	

APPENDIX 3:1

LIST OF POWDER COATINGS USED IN THE EXPERIMENTS

R160. Used extensively in detailed studies of the kinetics of reaction in a furnace at different constant temperatures, for the study of the effect of variations in the heating rate on thermograms in the SR625, and for a study of a comparison of oven and instrumental runs to a final constant temperature to establish whether an instrumental run can forecast oven cure.

R161. Used principally for studying the effect of pigmentation - not itself pigmented.

R162. Used to establish the effect of small additions of a flow control agent to R161, and to examine the effect of particle size.

R163. Used to establish the effect of one kind of pigmentation - a carbon black/barytes mixture.

R164. Used to establish the effect of one kind of pigmentation - titanium dioxide.

R165. A laboratory-prepared copy of R161, used mainly to establish the effect of variation in heating rate on the thermogram in SR780.

R170-173. Used to establish the effect of addition of matting agent to a black-pigmented formulation.

CHAPTER 4

METHODS OF STUDY OF THE KINETICS OF POWDER COATINC CURE

SPECTROSCOPY

Vibration spectroscopy can be used to identify characteristic groups participating in the cure reaction, and be used to follow their changes to monitor the reaction. The technique has been used to study curing reactions in solution, but a question arises about the value of vibrational spectroscopic methods in studies of powder coatings. Relevant groups in an epoxy powder coating are; epoxy at 915 cm^{-1} (C-O stretching vibration); secondary amine at 1650-1550 cm^{-1} (N-H deformation vibration); secondary alcohol at 1240 cm^{-1} (C-O stretching and O-H in-plane deformation vibration); alkane at 1380 cm^{-1} (aliphatic C-C stretching frequency in $C-CH_3$ - actually a doublet); aromatic ring stretching frequency at 1510 cm^{-1}; cyano at 2150 cm^{-1}(-C=N stretching frequency); another alkane absorbance at 2965 cm^{-1} (C-H stretching frequency in $C-CH_3$). The absorbance at 1510 cm^{-1} may be used as a reference, if it is accepted that the ring is not broken during the reaction; otherwise an alkane absorbance can be used with some assurance of stability. Some authors, it should be noted, have observed aromatic ring fracture in certain epoxy reactions, but this is not commonly encountered.

The usual technique for measurement in the infra-red region is the solution mode. The reactants are dissolved in a suitable solvent (tetrahydrofuran is commonly used), allowed to react at ambient or elevated temperature, and the absorbance measured in an IR spectrophotometer. The reactants are therefore present as isolated molecules and a reasonable degree of homogeneity of the reactants is attained.

This cannot be assured with a powder coating because the reactants are less mobile than in a solution, and because of the very large differences in viscosity, viscosity changes may determine reaction paths; solvent effects may be important in a solution and insignificant in a powder. States of aggregation may be different in the two modes, and homogeneity may not be complete in a powder.

In this work, two possible methods of using vibration spectra to study powder cure were studied;
(a) absorbance changes from dispersions in a KBr disc, (b) changes in reflectance spectra, using Raman and then Fourier Transform IR.

SPECTRAL ABSORBANCE CHANGES IN DISPERSIONS IN A KBR DISC

An attempt was made to effect a compromise between solution and powder. The powder, finely ground, was dispersed at a low concentration in spectroscopically pure KBr and formed into a thin disc under pressure. It was assumed that in the path of the beam of the spectrophotometer, the powder would give rise to the usual triad of effects - reflectance/absorbance/scatter, which is imposed on any radiant beam in all circumstances when two surfaces of different refractive indices occur. It was also assumed that the scatter and reflectance effects would remain constant because the refractive index difference powder/KBr would remain unchanged, but that the absorbance would change with the progress of the chemical cure reaction in the powder, and that these changes could be monitored.

The spectra of the disc samples were obtained in a Perkin Elmer Model 983 spectrophotometer. The discs were then removed, and heated to 180° at a known heating rate for a number of sequential intervals, 1, 2, 5 and 10 minutes, after each interval shock-cooled, then inserted in the spectrophotometer to record the spectrum again.

As an example of what can be achieved, Figure 4:1 is presented. This is the spectrum of Epikote 3003 obtained in a KBr disc. All the bands of interest in identifying the material are present. Thus, as examples, 2960, 2163 and 915 cm^{-1}. However, the spectrum also shows up one of the difficulties encountered in doing such a quantitative study, because the epoxy absorbance at 915 cm^{-1} is so small.

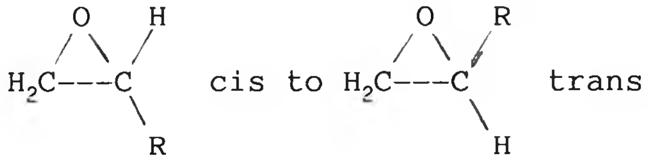
Trials were run for KBr discs containing (a) Epikote 1004 (the resin alone), (b) the pigmented resins R160 and R164, containing dicyandiamide and o-tolylbiguanide respectively. The discs were examined as prepared and after heating them for 5 minutes at 173°.

In the 1004 example, the 915 cm^{-1} absorbance was very small, and a quantitative measurement was of dubious significance; no 915 cm^{-1} was present in the R164 sample, a band was present at 875 cm^{-1}. In R160, a small 915 cm^{-1}

absorbance was present, but this disappeared on heating, to be replaced by a band at 892 cm^{-1}.

These results do not present a very consistent picture, or one easy to analyse. The 875 – 892 band is something of a puzzle. The only group that in any way fits appears to be a substituted aromatic ring, but not the 1,4 substitution known to exist in an epoxy resin, but 1,3 or 1,2,4, as though the ring had been further substituted.

An alternative explanation is, that the band represents cis-trans isomerism about the epoxy group, as follows:



Then the puzzle is, why does the 875-892 cm^{-1} band appear initially in R164 and not in 1004 or R160? Why does the 915 cm^{-1} band occur in R160, but then disappears on heating, to be followed by the appearance of the 875-892 cm^{-1} band?

A tentative explanation may be, that the epoxy groups are of different configurations initially in R160 and R164, but that on heating the residual epoxy groups (those which have not reacted with an amine) assume the other configuration in R160 by detachment, rotation and re-attachment. The explanation is very tentative indeed, but any other solution does not at present come to mind.

However, the spectra obtained from the KBr discs were of such poor quality that quantitative results could not safely be derived; the spectra are complex and a more rigorous analysis might be helpful, so a check to try and derive a quantitative result was made.

Mixtures of Epikote 1004 and dicyandiamide were made up and thoroughly mixed in a laboratory coffee mill, each mixture being incorporated into a KBr disc as before, and the spectra recorded in the Perkin Elmer spectrophotometer.

Absorbance ratios were measured as 2150:2963 and 915;2965 cm^{-1} ratios, where 2150 cm^{-1} is the stretching frequency of $-C{\equiv}N$ and 2965 cm^{-1} is C-H stretching frequency in $C-CH_3$.

These ratios were chosen for the following reasons. The 2150:2965 ratio represents the relative amounts of resin and dicyandiamide and consequently as a logarithmic ratio should correspond to the dicyandiamide content in the mixture - the ratio should be linear with the dicyandiamide content. The 915:2965 ratio represents epoxide:alkane and should be constant in all mixtures.

The results of the spectrophotometric measurements are given in Table 4:1.

In brief, the 2150:2965 ratio is not linear with dicyandiamide content and the 915:2965 ratio is not constant. In all probability, the error lies in supposing that the effective thickness of the absorbing layer in the discs is constant. For the different mixtures, probably particle size and number of particles in the beam were not constant, and so the application of the Beer-Lambert law was invalid.

Accordingly, the disc method was deemed to give erratic results unsuitable for quantitative work.

SPECTRAL ANALYSIS BY REFLECTANCE TECHNIQUES

In early experiments, aluminium foil was coated with the powder coating and the coating fused. Foil was appropriate because it could be flattened, on a very flat glass surface for example, and additionally stuck down with double-sided adhesive tape. Flatness is essential for reflectance measurements.

The first technique was the use of Multiple Internal Reflectance, with the appropriate probe head feeding to the 983 spectrophotometer. In this method, the IR beam is directed at an angle at the surface of the film, penetrates it to a shallow depth (the depth depending on the incident beam angle and refractive index of the material), is reflected back to the surface, reflected again into the film and so on until after a finite number of penetration / reflectance cycles, it arrives at a detector and is passed to the spectrophotometer, where a spectrum is recorded. The multiple reflectance path obviously gives greater sensitivity than a single reflectance.

Films were prepared from Epikote 1004,R160 and R164 by laying down a uniform layer of powder, melting, and then shock-cooling to give a smooth, continuous film surface.

Here again, the quality of the results was poor. In the 1004 sample there was no sign of the 915 cm^{-1} band nor in the R164, and only a trace, not meaningfully measureable, in the R160 sample.

The method had to be discarded as insensitive.

The next method used was Raman Spectroscopy, in which the energy levels of molecules are explored by examining the frequencies present in radiation scattered from molecules. A monochromatic laser beam in the visible region is focused on the specimen and radiation scattered at 90° to the incident beam measured. The scattered radiation may be at a lower frequency than the incident and is of low intensity - this is Stokes radiation. Some incident photons may collect energy from excited molecules and emerge with a higher energy - this is anti-Stokes radiation, also of low intensity. Analysis of the spectrum of the scattered radiation (detected in a photomultiplier) is not simple; intensity at specific wavelengths is important. An interesting consequence of the photon/collision/scatter phenomenon is, that absorbance bands present in transmission/reflectance IR often do not appear in Raman spectra.

The Raman spectra of the sample prepared on aluminium foil as described in the previous section were obtained through the kind collaboration of Dr. Mark Sceats of the Physical Chemistry department of Sydney University. In the result, it was felt that Raman spectroscopy was not applicable to the actual samples examined for a number of reasons. In the first place, strong fluorescence occurred on illumination in the laser beam, probably because of the presence of impurities, which could not be eliminated; a frequency of 488 nm was the best tried. This fluorescence varied from point to point on the surface, and bubbles (very difficult to remove) caused interference. Finally, the rather intense incident beam used probably caused thermal curing of a fresh or partially cured sample, as could be seen from the change of the spectrum with time. The best example of a spectrum is shown in Figure 4:2 - representing an uncured epoxy resin.The absorbance at 915 cm^{-1} has shifted to 965 cm^{-1} and is obscured by background noise. In partially cured samples this absorbance could not be distinguished from the noise.

In view of these limitations, it was decided not to proceed with a technique which initially had seemed very promising.

A final spectral analysis tried was the technique of IR Photoacoustic Fourier transform spectrophotometry. In this work, the photoacoustic facility was not utilised, and so the method became one of diffuse reflectance, with Fourier Transform analysis of the absorbance spectrum.

The samples for analysis were prepared and studied in DTA sample pans, so that thermal analysis could be performed on each sample after recording the spectrum. In each experiment, a pan was charged with 6 mg of powder, and either melted, or heated at a specific temperature and time and then submitted for measurement in the FTIR. The resulting spectrum was then examined for changes in absorbance and amplitude.

The bands monitored in an initial set of experiments were the following;

1510 cm^{-1} - aromatic ring bond stretching.

1380 cm^{-1} - aliphatic C-C stretching in $(CH_3)_3$

915 cm^{-1} - C-O-C bending in an epoxy.

The 1510 cm^{-1} band was thought to remain constant, but would change if the aromatic ring was opened. The 1380 cm^{-1} absorbance is unlikely to change, so the 1510:1380 ratio should indicate if the 1510 cm^{-1} absorbance decreased because of ring opening. The 915 cm^{-1} absorbance was presumed to decrease consistently throughout the heating cycle.

A selection of spectra obtained in the initial survey is shown in Figures 4:3 to 4:7, in which the spectrum for 4:3 is typical for an epoxy resin (Epikote 3003); the 3003/SP710 mixture (Figure 4:4) serves as a reference for the cross-linking mixtures; then the 3003/SP710 mixtures (Figures 4:5 4:7) illustrate the effect of heating on the spectrum. From these latter, the degree of conversion of the system may be derived.

The 3003 spectrum shows the aromatic C-H stretch frequency at 1510 cm^{-1} and also the C-H deformation vibration of the C-CH groups between the aromatic rings in the epoxide chain.

The 1380:1510 ratio is reasonably constant at 0.65, except that the one minute cure of 3003/710 at 0.71 is something of an anomaly, compared to the 3003/710 uncured mixture at 0.63. It probably indicates an experimental deviation. This appears to be borne out by the circumstance that the addition of 5% of SP710, not itself possessing a

1380 cm^{-1} absorbance has a smaller 1380:1510 ratio than the simple 3003, when what would be expected would be an increase in the 1510 cm^{-1} absorbance because of the extra aromatic content from the tolyl radical in SP710, and a decrease in the 1380 cm^{-1} absorbance because of the absence of a contribution from SP710.

In the 915:1380 ratio, there is a decrease in the ratio on addition of SP710. This is reasonable because 5% of the original 3003 containing epoxide has been replaced by a compound containing no epoxide, and also increased the aromatic content from the tolyl radical. The ratio falls progressively with time of oven heating, as would be expected if epoxide is consumed in the curing reaction.

If we now take the 915:1380 ratio of the 3003/710 mixure of 0.96 as representing an unreacted system, then values of this ratio referred to 0.96 will give the fraction of reactive material remaining, that is the $(1-\alpha)$ value, from which the α conversion may be derived. This has been done and is reported in the last column of Table 4:2.

Considering the thermal analysis figures for the mixtures referred to earlier, the conversion figures derived therefrom are 0.15 for one minute, 0.53 for two minutes and completion at ten minutes. This does not compare exactly with the conversion values reported on the basis of spectral absorbances of 0.29, 0.60 and 1.00.

Several repeat experiments were run, but regrettably the verdict had to be that consistent, repeatable results could not be obtained. The variation in absorbance ratios and in conversion values was such as to inhibit any clear conclusions to be drawn with confidence.

It appears, therefore, that although good quality spectra could be obtained, the 915 cm^{-1} absorbances in the later stages were difficult to measure with any accuracy, and the method is not suitable for precise quantitative work.

THERMAL ANALYSIS: INSTRUMENTS AND THERMOGRAMS

Phase changes and chemical reactions proceed with the absorption or evolution of heat (phase changes such as melting/cooling and glass/rubber transition, according to whether the ambient temperature is rising or falling) or evolution of heat only (chemical reactions); in the latter case, however, there may well be an overall evolution of heat or no change at all, even though a chemical reaction is proceeding, for example in a condensation reaction resulting in the evolution of water, when the endotherm due to water evaporation may just balance the exotherm due to the chemical reaction.

The heat evolved in a chemical reaction is referred to as the enthalpy of reaction and is defined by the equation:

$$\Delta E=\Delta H-T.\Delta S$$

where ΔE is the Gibbs free energy

ΔH is the enthalpy

ΔS is the entropy change

This indicates clearly that the term "enthalpy" can only be applied to a reaction proceeding at a constant oven temperature. In thermal analysis, the commonest procedure is to run an experiment at a steadily increasing temperature, and so the heat evolved, recorded as an exotherm, is not the enthalpy of reaction but simply the heat evolved over a certain temperature range.

If the technique adopted is to raise the oven temperature rapidly to a preset temperature and to hold this temperature constant, then the heat evolved over the isothermal part of the reaction plot is the enthalpy of that part of the reaction proceeding over that isotherm.

However, measurement of enthalpy or heat of reaction is conveniently performed instrumentally by Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC), two instruments with slightly different modes of operation. Both have this in common, that the sample, usually of the order of 10 mg in weight is held in an oven and subjected to a heating regime, either a continuously rising temperature, or to a preset temperature and held there. The thermal energy absorbed in a phase change or evolved in a chemical reaction is measured by outputting the sample temperature change accompanying these phenomena to a recorder.

To consider the instruments in more detail. The DTA comprises an oven in which the sample is placed, in a pan. The pan sits on a small platform (of about the same diameter as the pan, in order to avoid heat loss) accompanied by another pan/platform combination in a side-by-side configuration. This second pan contains an inert material of approximately the same thermal capacity as the sample. The inertness refers to an absence of heat absorption/evolution in the reference in the temperature range in which the properties of the sample are of interest. The oven heating regime is controlled such that the reference and sample rise in temperature at a steady pre-set rate. This temperature is recorded instrumentally as a line from which the sample/reference temperature may be read at any point in the process; another recorder pen traces the differential temperature between sample and reference material. This differential temperature first rises (in an exotherm), achieves a maximum, then falls back to the reference material temperature as the reactants are exhausted and the reaction heat is dissipated. In the DTA, the area enclosed by the reaction trace and the base line is a function of the heat evolved. Its actual value can only be obtained by referring the measured area to that for a reference material of which the heat absorbed over approximately the same temperature limits is known; that is, the endotherm at a melting point is usually the reference, and this may be measured in a precision calorimeter. For the powder coatings used in the present study, Indium is a suitable material. Indium has a melting energy of 28.6 Jg^{-1} at 156.6°. If an endotherm is prepared under exactly the same conditions as for the test sample (principally the rate of heating), then unit areas of the resulting endotherm can be assigned an energy value, and this, multiplied by the area of the sample exotherm gives the thermal energy of the sample. Usually, in a DTA, the temperature line on the recorder is in millivolts (the amplified output of the thermocouple) and has to be converted to a temperature by use of conversion tables.

Examples of DTA instruments are Models 785 and 780 by Stanton Redcroft; Model 785 is essentially as described above, but 780 is more complicated in that the support platforms are attached to the lower end of a rod suspended fron one arm of a microbalance, so that weight changes may be monitored simultaneously with thermal changes. It so happens that epoxy resins do not change significantly in weight in a thermal experiment since there is no volatile product of reaction of amine and epoxy. If the material has not been thoroughly dried out, however, moisture will be observed to evaporate from the damp powder. All samples in the present study are stored over fresh silica gel.

Turning to the DSC. Here the measurement is directly in terms of thermal energy evolved or absorbed, but instrumentally the arrangement is much the same as for the DTA.

Temperature differences between sample and reference are again monitored, but the area under the output trace on the recorder reads directly in energy change. The ordinate of the endotherm or exotherm therefore is proportional to the rate of heat transfer dq/dt. Another helpful difference is that the temperature line reads directly in degrees, so that no conversion is necessary. The design of a DSC cell is shown in Figure 4:8.

Commercial instruments operating as Differential

Scanning Calorimeters are the Perkin-Elmer DSC 1, the Mettler TA3000 and the Stanton Redcroft 625. The Mettler and the 625 have been used in the present study.

The Mettler TA3000 is an advanced instrument, programmed by computer to produce different kinds of data. It is particularly characterised by having a liquid nitrogen reservoir incorporated, so that cooling to ambient after a run is rapid (and can be controlled to give, for example, glass transition temperatures on the cooling run, and also at sub-ambient temperatures).

The Stanton Redcroft 625 is very similar to the SR780, except that

(a) the temperature output to the recorder has been linearised;

(b) the design of the sample pan platforms has been modified so as to facilitate conversion of a differential temperature measurement to an energy record. Thus, at a 100 µV setting on the primary differential temperature amplifier the ouput to the recorder is 10 mW.

Comparison of DTA and DSC runs on a standard sample have not shown up any important differences in heat evolution, peak and start and final temperatures. However, because of the direct reading of heat evolution and temperature in a DSC, it might be thought that this instrument would be favoured to the exclusion, more or less, of a DTA in experimental work. Interestingly enough, in the papers published in the Journal of Thermal Analysis where use of a thermal analysis instrument is reported, a DTA figures as prominently as a DSC, if not more so.

Because of the similarity of the thermograms, it is clear that the advantage of a DSC lies mainly in its convenience of use.

The actual result of a thermal analysis experiment will now be considered to establish what data of significance in evaluating thermal properties can be extracted.

For this purpose, the thermogram of R160 is presented, prepared on a Mettler TA3000. This was chosen because the experiment is programmed, and it is interesting to see how the programme deals with some ambiguities in analysis, not often discussed in the literature.

First of all, the complete thermogram is shown in Figure 4:9.

Heat evolution is represented by deviation from (and return to) a base line, that is a line which indicates the specific heat of the sample relative to that of the reference. This line necessarily increases with temperature.

In Figure 4:9 the first peak is of course an endotherm indicating the melting of the resin. Because of the shallow slope of the base line as the falling temperature limb of the endotherm is approached, and the initial gradual rise of the limb, measurement of the melting temperature is not possible with precision. Consequently, one has to make a choice based on some criterion and adhere to it in comparing different materials.

In the present case, the Mettler programme has taken the point at which the initial horizontal base line begins to slope at a small angle, and records this temperature as 43°. Anyone familiar with this class of epoxy resin would be unlikely to accept this figure, since a melting point determination in the usual melting point instrument would give a reading in the 60's. Additionally, repeat experiments would not always show quite the same shallow slope, and a different instrument would give a different result.

The method used in this thesis is to take the initial falling temperature limb of the endotherm as a fixed reference because it usually approximates quite well to a straight line. If this line is then extrapolated back to intersect the drawn continuation of the base line in the neighbourhood of the endotherm, a fix is obtained to which repeat experiment have given results in agreement to one degree. Changes in the initial base line slope do not then have a significant effect on the melting temperature estimate. The method is shown in Figure 4:10 to give a value of 69°.

The same problem arises with all the other change points that one can identify. The Mettler gives 105° for the start of the exotherm, for example (Figure 4:9), whereas the nore realistic value would be 172° (using the revised procedure discussed above), or 147° (taking the point at which the exotherm shows a marked deviation from the base line). The fact is, the base line is steadily increasing so to involve the slope of the base line as a reference point as Mettler does, is not, in the Author's view, acceptable.

However, there is one temperature which can reasonably be accepted as certain, and that is the temperature of occurrence of the peak of the endotherm and exotherm. Kissinger (1) shows that this is the temperature at which the maximum rate of reaction occurs, and it is a useful identifier of resins and processes. It is sensitive, for instance, to the rate of heating of the sample - increasing as the rate of heating increases. In the present instance, these temperatures are 72° for the endotherm and 205° for the exotherm.

Before going on to consider energy calculations, there is a factor of interest in the thermogram that merits a brief mention, and this is the slight protruberance (arrowed) that occurs on the rising temperature limb of the endotherm just where it rejoins the base line. Its position leads one to suppose that it is the melting point of a secondary constituent, and this may well be the activator known to be present in the dicyandiamide cross-linked system. The peak temperature of the not-well defined protruberance is 97°.

ENERGY CHANGES, ACTIVATION ENERGY AND ORDER OF REACTION.

As can be seen from the thermogram, the ordinates of any point represent work in milliwatts, that is, joules per second. If the area of the endo- or exotherm is calculated in seconds for the base and milliwatts for the verticals as an integral, then the area is in joules, that is, energy units, and this is the thermal energy absorbed in melting or evolved in a reaction, between the two temperature limits indicated on the thermogram.

Calculation of these areas with sufficient precision is something of a problem. In the present case, the areas to be taken into account are clear enough, but sometimes it is difficult to decide what part of an approach to an endo- or exotherm should be included, because of the length and shallowness of the approach. A common method is to cut out the shape, weigh it, then compare with a reference of known energy, such as indium, tin or benzoic acid, preferably appearing within the same temperature limits (certainly so, if a DTA is being used). Another method is to employ a computation of the area with Simpson's rule, namely;

$$A=\{3.3[F+L+4\Sigma_{odd}+2\Sigma_{even}]\}$$

where F and L are the first and last ordinates, the base being divided into equal intervals in seconds;

Σ_{odd} is the sum of the odd ordinates

Σ_{even} is the sum of the even ordinates

then the area is converted into mW x seconds using a conversion factor for ordinates, mms to mW, and the answer is in joules, which is divided by the mass.

Although this is common practice. however, it is not strictly correct. The reason may be seen by referring to Figures 4:10 and 4:11, for here an attempt has been made to establish a base line taking into account the fact that the specific heat at constant pressure C_p, changes during the melting or reaction. The base line, therefore, must change in some manner. The assumption in most calculations is that the base line under the exotherm is formed by joining the before and after portions with a straight line, but this is fairly certain to be incorrect. The problem is, what form this portion of the base line should adopt. If the fore and aft parts are extrapolated into the exotherms, they do not meet, but can be joined by a step, and on the whole this is thought to be the best solution. Mettler have done this, putting the step at half way into the exotherm for symmetry, and also smoothed it into a curve. The area is then programmed by integration.

The values given by this method are:

For the endotherm 12.2 joules g^{-1}

For the exotherm 63.8 joules g^{-1}

If a rapid check is required, endo- and exotherm can be made into straight-sided triangles and the area measured directly. The method gives a surprisingly good result if the baseline changes are ignored.

Reference has already been made to the fact that the thermal energy calculated above is not the enthalpy of reaction, and if it is required to estimate this, a paper by Richardson provides one solution (2).

Referring to the thermogram of R166 in Figure 4:12, two temperatures have been selected, T_1 (400K) and T_2 (538K) respectively above and below the exotherm temperature limits.

If we write;

Heat content of products at T_2, H_2

Heat content of reactants at T_1, H_1

and extrapolate the C_p (>583K) line back to intersect the ordinate to T_1, we have an intercept

$$H_2 \text{ products at } T_1$$

then the heat content change ΔH of the system referred to T_1 is:

$$\Delta H = H_{2(400K)} - H_{1(400K)}$$

and this is the true enthalpy of the reaction at 400K. The great merit of this treatment is, that it avoids the problem of establishing the true trace of the C_p curve underneath the exotherm. The values of H are obtained from the calculated C_p's, that is $C_p = \Delta H/\Delta T$ along the base line,

and

$$C_{p1} = 0.7676 \text{ Jg}^{-1}$$

$$C_{p2} = 3.3146 \text{ Jg}^{-1}\text{deg}^{-1}$$

and from

$$\Delta H = (C_{p1} - C_{p2})T$$

we have, by substituting the values above and putting $T = 400K$, $\Delta H = -101.9 \text{ Jg}^{-1}$ and this is the enthalpy of reaction at 400K, or to be explicit, this is the enthalpy of the reaction if it were performed at a constant furnace temperature of 400K.

The Mettler gives -106.57 Jg^{-1} for the thermal energy evolution over the given temperature limits.

From a single exotherm, not much can be deduced about reaction kinetics if only because with a constantly changing temperature - if a constant heating rate regime is being employed, the value of the rate constant cannot be derived, since this refers to a constant temperature.

A more suitable procedure is to make repeat experiments at a series of different heating rates. Then, selecting a given degree of conversion, α, for all the different temperatures, we have:

$$\ln(d\alpha/dt) = E/R(1/T)+\ln(Af(\alpha))$$

where $f(\alpha)$ is assumed not to be a function of temperature, that is, the mechanism does not change over the temperature limits considered.

In this expression, α is a constant and so is $f(\alpha)$. Thus, a plot of $\ln(d\alpha/dt)$ versus $1/T$ for the several experiments should yield a straight line of slope E/R and an intercept of $\ln(Af(\alpha))$. Thus, the activation energy may be obtained. This procedure is repeated for different values of α to confirm (or otherwise) that E is indeed constant. Having obtained an average E value over the whole reaction, this value and values of $d\alpha/dt$ and T can be substituted into the equation, giving $Af(\alpha)$ as a function of α. Then, if $\ln(Af(\alpha))$ is plotted against $\ln(1-\alpha)$ and gives a straight line, this has a slope of n.

An alternative method for the estimation of n is provided in the pioneering paper by Kissinger (1), which many have discussed without essentially disputing the conclusions thereof.

In effect, he deduces the reaction order from the degree of symmetry of the exotherm, the symmetry being given by a numerical value, the shape factor S, such that:

$$n = 1.26S^{\frac{1}{2}}$$

In the illustrations in the paper, he shows that for a reaction order of unity, the symmetry of the exotherm is at a maximum; as the order decreases, the symmetry deteriorates. The manner in which it does so is, that the rising temperature limb assumes the same curve for all values of n; as n decreases, the falling temperature limb falls more and more sharply until at a (nominal) value of n=0, the limb is a vertical straight line.

Kissinger (1) shows a number of exotherms for inorganic materials, e.g., magnesite and halloysite, where the exotherms differ in symmetry and consequently reaction order. Thus kaolinite has good symmetry and gives n=1.06; calcite has defective symmetry and gives n=0.33.

A simple method of calculating S is to obtain a measure of symmetry by considering the deviation of the falling temperature limb from superposition on the rising limb. Thus, if the straight portion of the rising limb is extrapolated to meet the extrapolated line of the falling limb, the horizontal distance between the two lines and a vertical from the centre of the peak should be the same for perfect symmetry, but differing from unity as the symmetry deteriorates.

This is illustrated in Figure 4:13, where the degree of symmetry is given by the ratio b:a. In Figure 4:13, a is 22.5 mm and b is 26.0 mm, that is, n is not exactly unity. Its value is given by :

$$n = 1.26 \times (26/22.5)^{\frac{1}{2}} = 1.35$$

This, of course, is an overall reaction order, individual stages may have a smaller or greater reaction order.

FOLLOWING A REACTION BY THERMAL ANALYSIS.

It is accepted that the thermal energy represented by the exotherm in thermal analysis is the total heat evolved in the underlying reaction. If a series of experiments on a single material is performed at a constant temperature on samples withdrawn from an oven at progressively longer intervals, then the area of the exotherms would be expected to decrease in step with the length of time in the oven and would represent the amount of material remaining after the measured intervals, that is, the value of $(1 - \alpha)_i$ at t_i.

From start to finish of the oven heating we would have a complete history of the progress of the reaction.

It so happens that other workers, particularly Prime (3) have tried to utilise a sequence of runs at different heating rates and then analysed the exotherm to derive ΔH at a given temperature and so α values at increasing t values. However, this ignores the fact that in such an experiment, the reaction order may vary with heating rate, and this may well not be revealed by the data collected. However, the real objection to Prime's method is that simpler but analogous methods are available and are commonly used in preference.

Another method used is to heat a given sample in a DTA or DSC very fast to a final isothermal and use the isothermal part of the thermogram for analysis, since a very fast heating rate attains the isothermal at a low α value, thus providing a relatively long time over which the temperature is constant, starting from a low α value.

However, it is the Author's experience that such a procedure always produces a long curve in the temperature line as the isothermal is approached, and this may substantially reduce the extent of the isothermal portion.

The best solution appears to be to place the sample in a preheated oven and to measure the time to attain the preset temperature. Samples may then be withdrawn and thermally analysed in the usual way. It is important that the samples are small - for rapid heating, and that entry to, and withdrawal from, the oven is performed in such a manner that does not lead to significant cooling of the oven.

In the present thesis, the experimental technique is to use a horizontal tube furnace, with a 6 mg sample held in a DTA pan, entry and exit being effected with a long, thin wire arm which seals the oven on forward motion. The pan always arrives at the same spot in the tube, which has been monitored for retention of the set temperature.

An example of the results one obtains is shown in Figure 9:1 in Chapter 9 for a set of five samples of an epoxy resin, the exotherms only being shown.

It is apparent that the heat evolution changes correspond to expectation - the longer the oven dwell time, the smaller the area of the exotherm. A convincing aspect of the exotherms is, that the initial, terminal and peak temperatures are all approximately the same. Any substantial difference would cast doubt on the validity of the method.

In view of the Kissinger treatment of the peak temperature, described in Chapter 8, the fact that it is constant is an assurance that the same reaction (constant energy of activation) is being considered.

The method has been used at four temperatures and the results are presented and discussed in Chapter 10.

With respect to the time for the 6 mg sample to equilibrate to the isothermal, this was usually less than 50 seconds; even at the highest test temperature of 180°, and represents only a small fraction of the total isothermal of 600 seconds.

TABLE 4:1

ABSORBANCE RATIOS : EPIKOTE/DICYANDIAMIDE MIXTURES IN KBr DISCS

Mixture No.	% Dicyandiamide	Ratio	
		ln 2150:ln 2965*	ln 915:ln 2965
0	0	–	0.72
1	4.31	1.0	0.73
2	2.91	0.97	0.75
3	1.96	0.94	0.77
4	0.99	0.72	0.65
5	0.50	0.48	0.67

****

TABLE 4:2

ABSORBANCE RATIOS AND DSC CONVERSIONS

Sample	Ratio of Absorbances		Conversion
	ln 1380:ln 1510	ln 915:ln 1380	
3003	0.67	1.0	
3003/SP 710	0.63	0.96	
3003/SP 710 Cured			
1 Minute	0.71	0.68	0.29
2 Minutes	0.63	0.38	0.60
3 Minutes	0.61	0.00	1.00

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1. H.E. Kissinger, Reaction kinetics in DTA, Anal. Chem., 1957,, vol. 29, 1702.
2. M. J. Richardson, Quantitative interpretation of DSC results, Plastics and Rubber; Materials and Applications, 1970, September, 162.
3. R. B. Prime, E. Sacher, Kinetics of epoxy cure. 2. Bisphenol-A diglycidyl ether/polyamide, Polymer, 1972, vol. 13, 455.

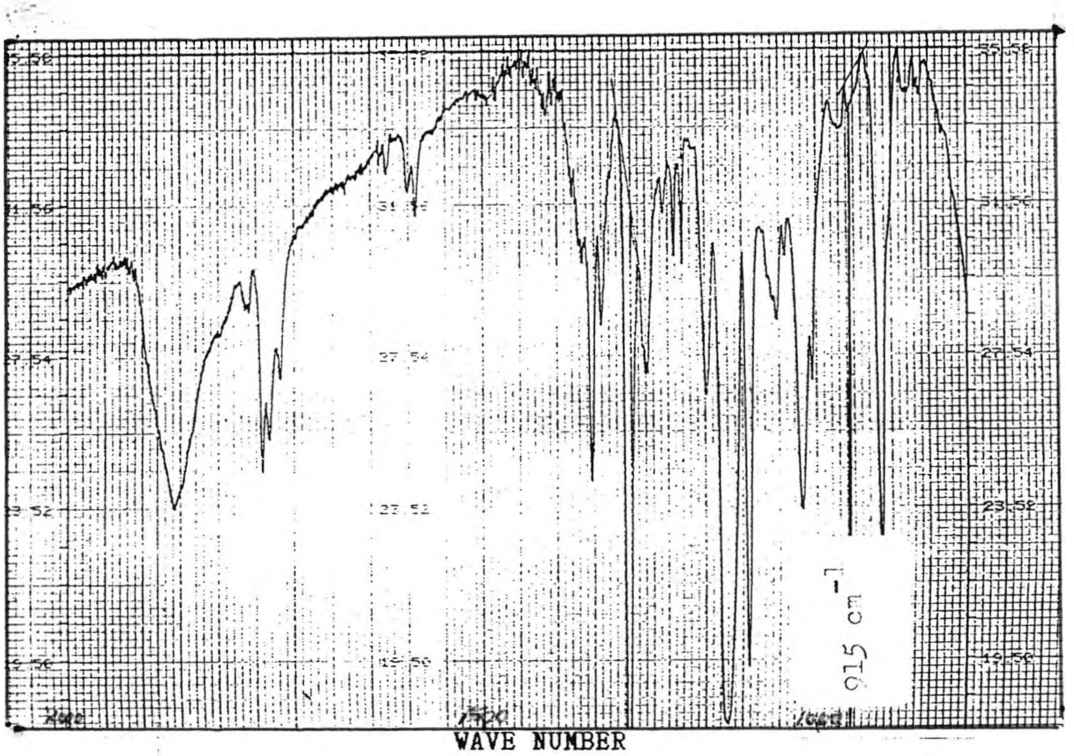


FIGURE 4:1 SPECTRUM OF 3003

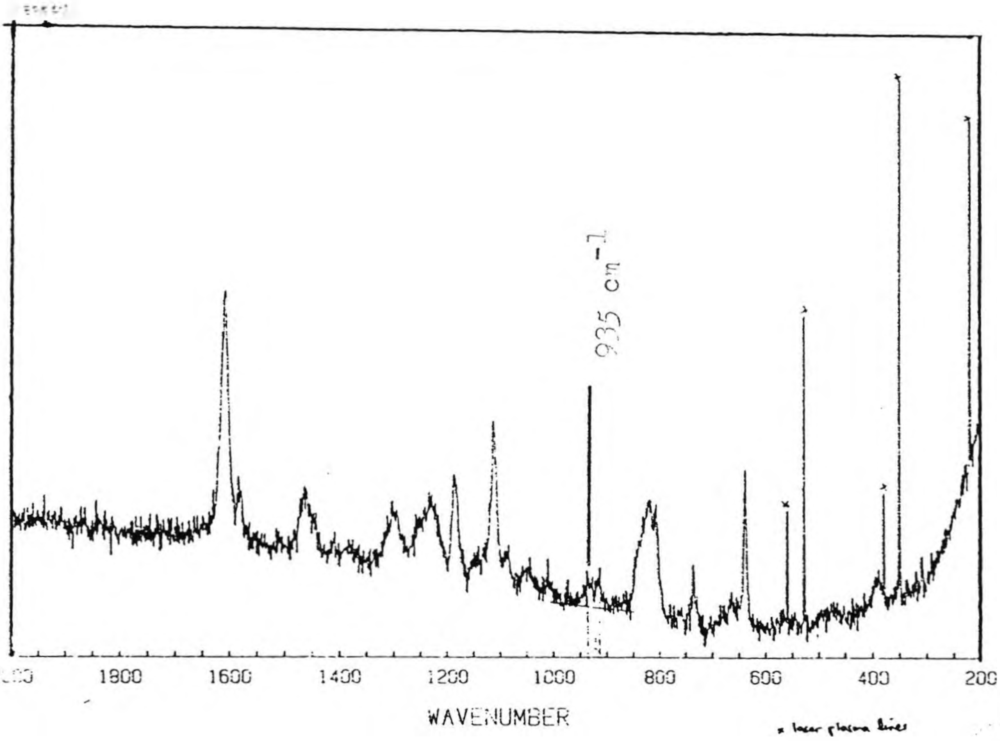


FIGURE 4:2 RAMAN SPECTRUM OF R160

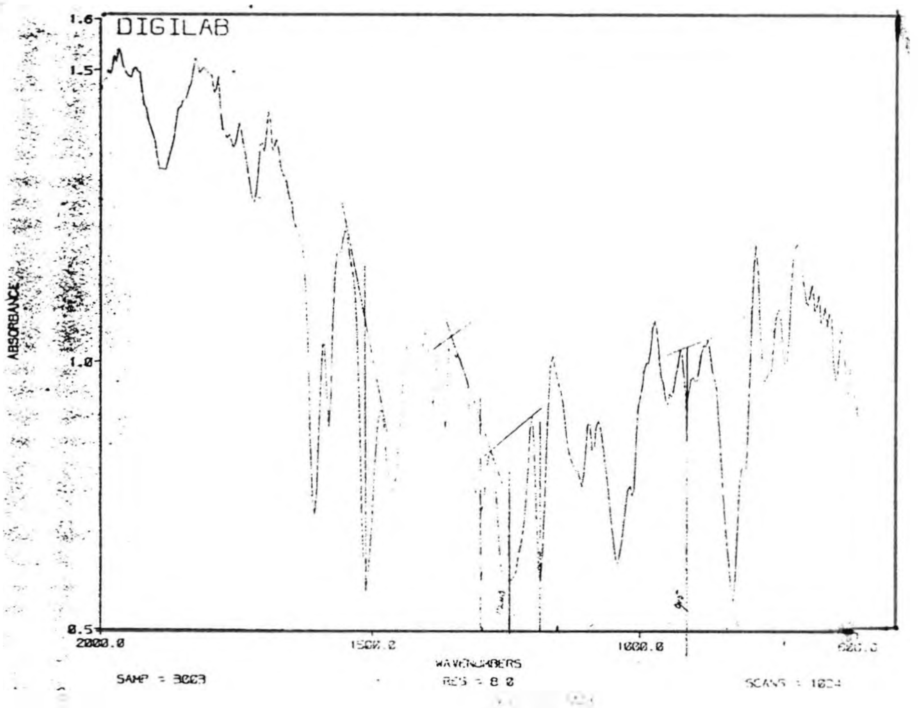


FIGURE 4:3 FTIR SPECTRUM OF 3003

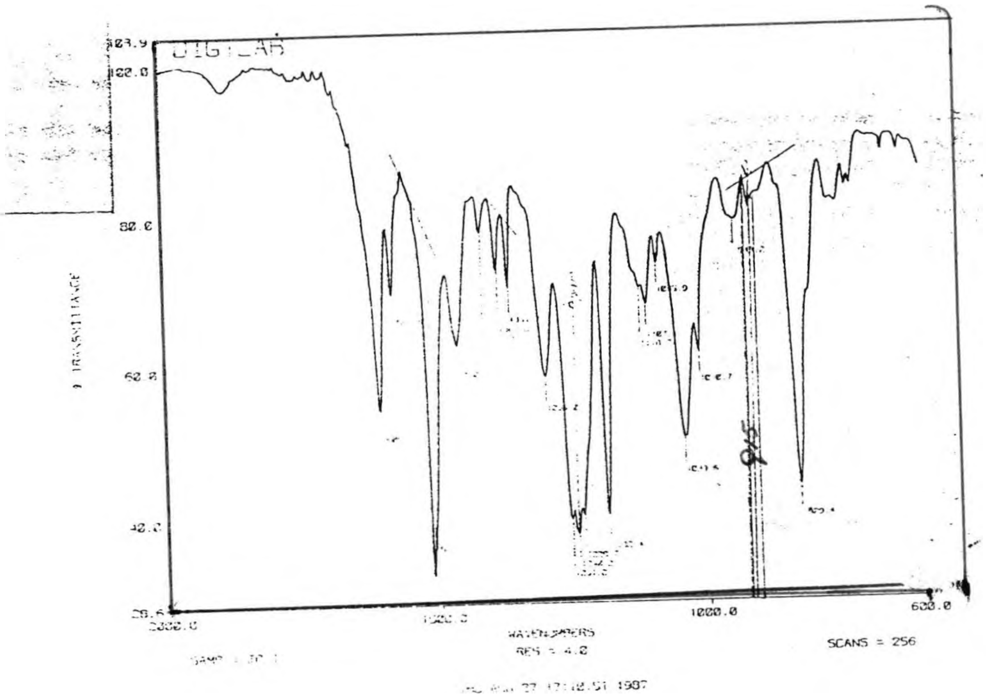


FIGURE 4:4 FTIR SPECTRUM OF R165

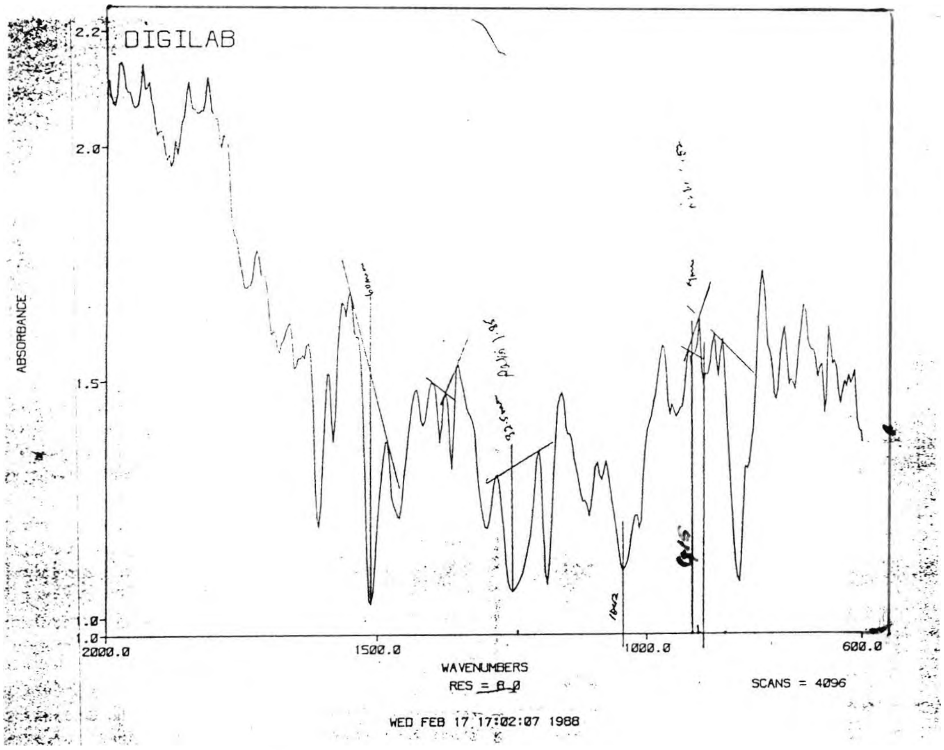


FIGURE 4:5 FTIR SPECTRUM OF R165; 1 min

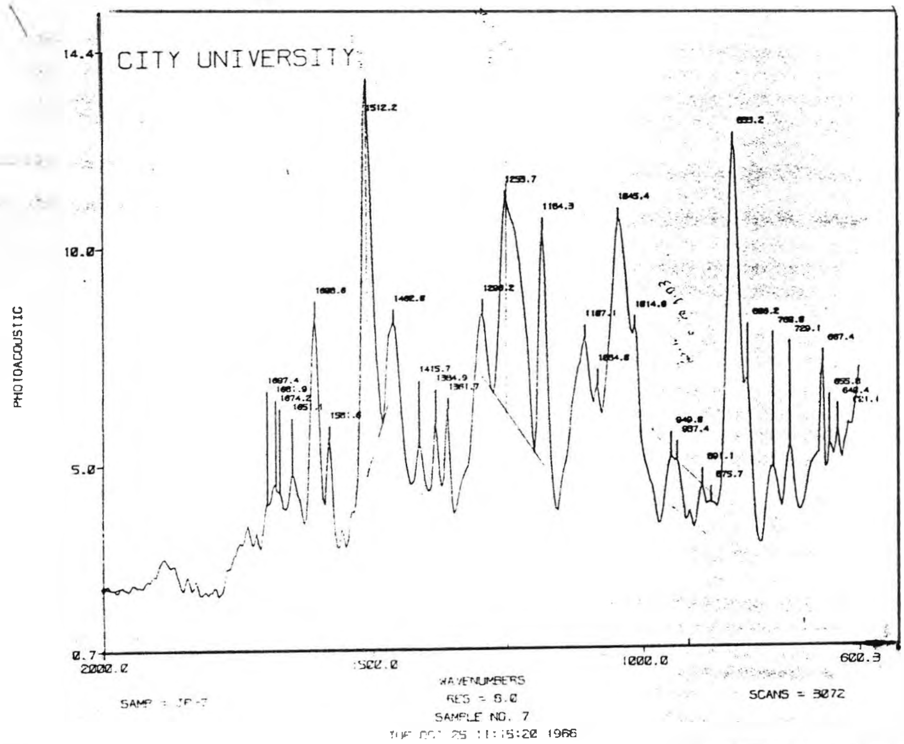


FIGURE 4:6 FTIR SPECTRUM OF R165; 2 min.

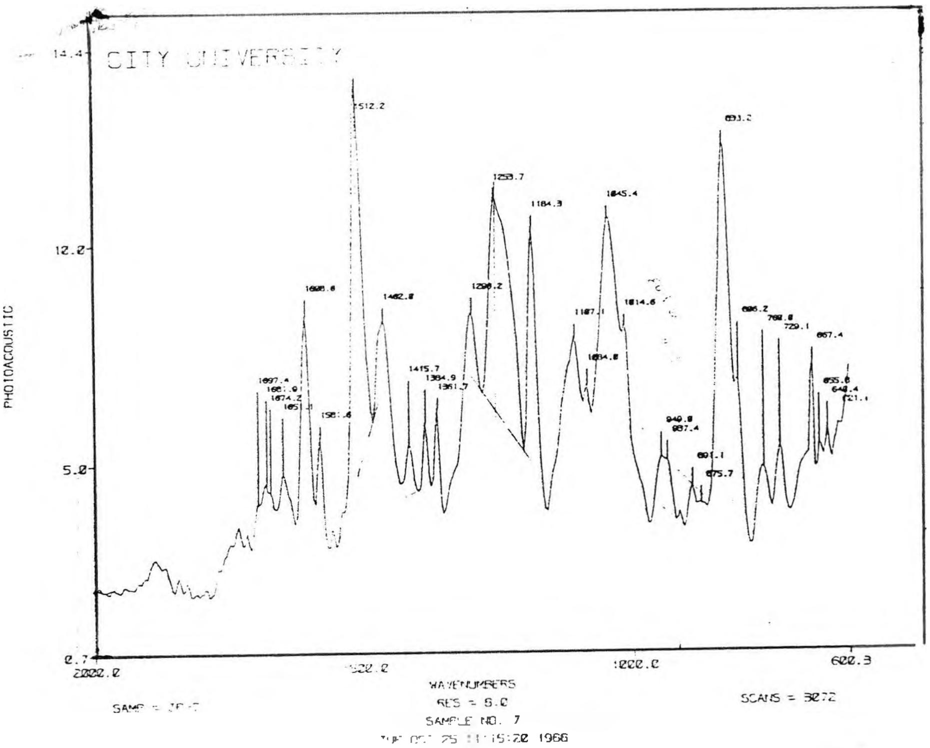


FIGURE 4:7 FTIR SPECTRUM OF R165; 10 min

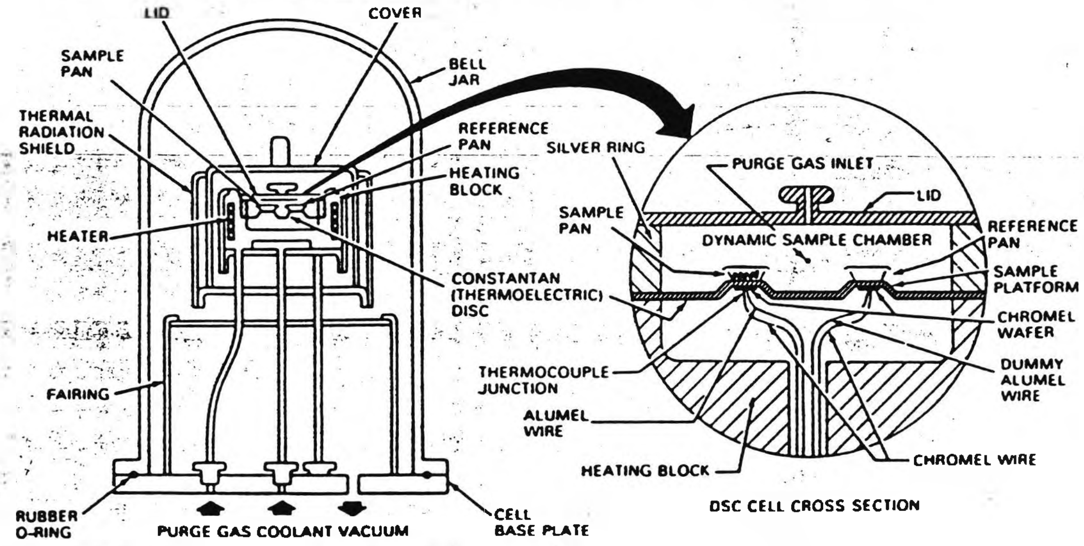


FIGURE 4:8 ILLUSTRATION OF A DSC CELL

4:8

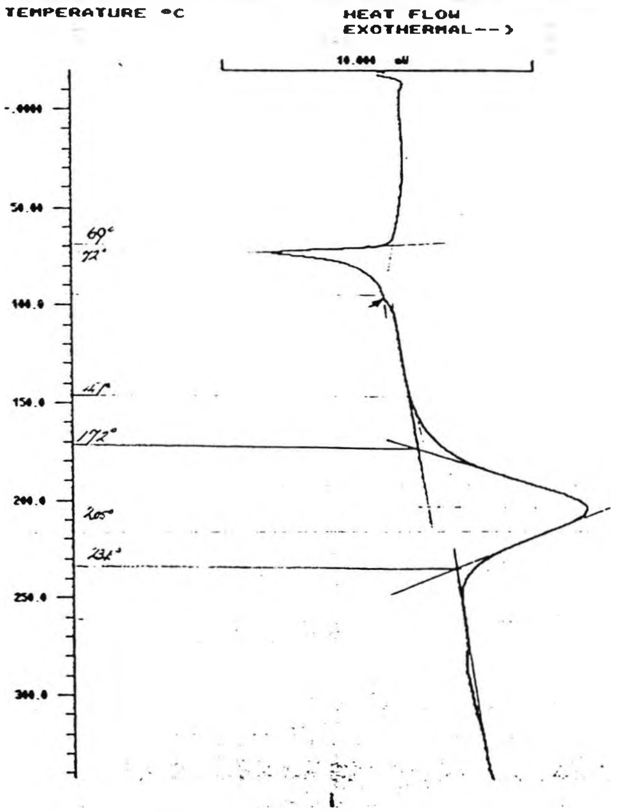


FIGURE 4:9 METTLER TA3000 THERMOGRAM OF R160

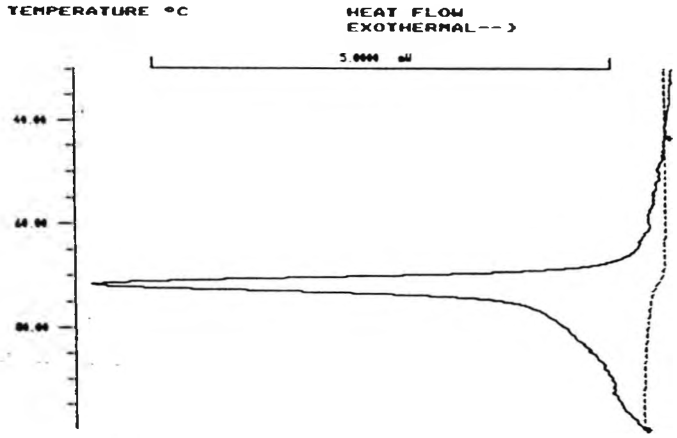


FIGURE 4:10 ENDOTHERM OF R160 SHOWING BASE LINE

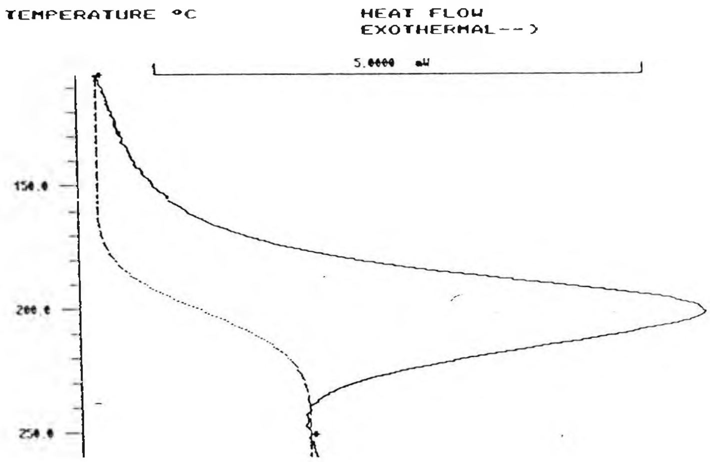


FIGURE 4:11 EXOTHERM OF R160
SHOWING BASE LINE

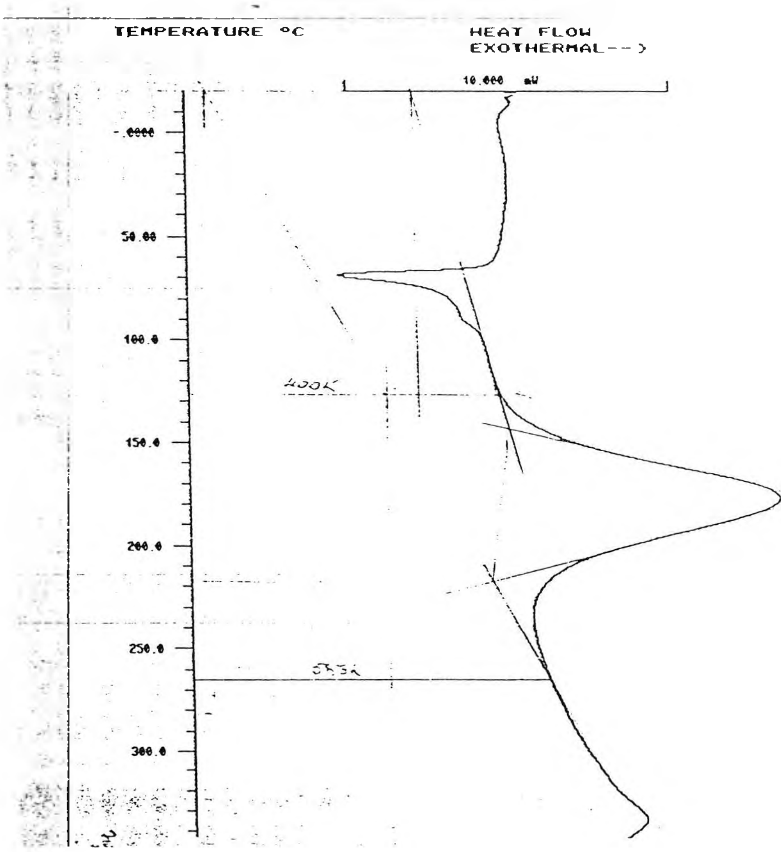
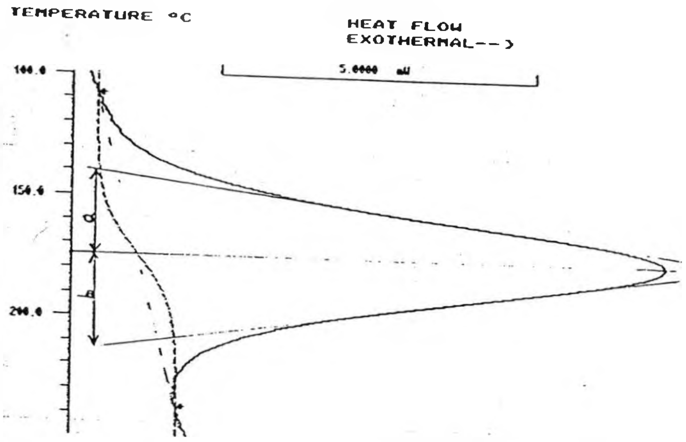


FIGURE 4:12 THERMOGRAM OF R166



ΔH EXO	mJ	1065.7
ΔH	J/G	106.57
PEAK TEMP.	°C	175.5

FIGURE 4:13 CALCULATION OF SYMMETRY OF EXOTHERM OF R166

CHAPTER 5

THE EFFECT OF POWDER PARTICLE SIZE ON THERMAL PROPERTIES

An important difference in the properties of solvent-thinned paints and powder coatings lies in the circumstance that in solvent-thinned paints the reactants are in solution, and consequently in molecular form; in powder coatings, the reactants are present as particles, large in terms of molecules and of an uncertain homogeneity. Reaction in the powder must take place by a diffusion mechanism in a melt of relatively high viscosity. It is reasonable to suppose that the size of the powder particles will have some effect on the reaction, because of the nature of the transmission of heat in a powder, which is also a diffusion mechanism.

Without going into detail on the subject, it is worth noting the diffusion equation relating to heat transmission is:

$$\delta T/\delta t = (k/\rho c).V^2 T \qquad (1)$$

where k is the thermal conductivity, c the specific heat and ρ the density. If the material itself generates heat, then the equation is modified to allow for this, but for the present purpose, it is not necessary to consider this.

The rate of temperature rise, then, is inter alia an inverse function of the density, and the effective density of a powder is related to its particle size. In addition, a difference in the rate of rise of temperature will affect the recorded thermal properties, as will be shown in Chapter 8.

A literature reference has been found that deals, in part, with this question. This is in Sacher (2), who mixed an epoxy resin with dicyandiamide in 10% excess of stoichiometric, melted the mixture, then ground it, separately, into two samples of different particle size. One sample of the mixture had a mean particle size less than 125 µm, the other a particle size in the range 250-500 µm. The mixtures were then submitted to thermal analysis in a differential scanning calorimeter, particularly for measurement of reaction order, rate constant and energy of activation. The results showed a remarkable effect of particle size - a 10^6 increase in the rate constant from fine to coarse, a 1:2 drop in energy of activation, and a roughly 2:1 increase in reaction order.

These truly remarkable effects indicate that in comparing the thermal properties of powders, it is important to make the comparison at equal particle sizes, otherwise differences in thermal properties may be ascribed to chemical differences rather than to unmeasured particle size differences.

It was obviously important to establish whether Sacher's findings were applicable to the powder coatings under study in the present thesis.

Accordingly, the R162 kibble was used for manipulation. R162 is the unpigmented mixture of Epikote 3003 and o-tolyl biguanide containing a flow-control additive.

EXPERIMENTAL

MEASUREMENT OF THE EFFECT OF PARTICLE SIZE AND SAMPLE MASS ON THERMAL PROPERTIES.

The kibble was ground in a laboratory coffee mill, and a portion taken and sieved through a stainless steel mesh. The portion passing through the mesh was designated R162F and the retained portion R162C. They were examined in the microscope, photographed, and analysed for particle size. The photomicrographs are shown in Figure 5:1 and 5:2. R162F had a mean particle size of 60µm, and R162C one of 195µm.

The powders were then analysed in a Mettler TA 3000 DSC, at two sample masses, namely, about 6 mg and 13 mg respectively. The programme used was for Kinetic Analysis, and after cooling, the programme for Transition Temperature was run on the same sample.

The numerical results are shown in Table 5:1, and the thermograms for the kinetic analysis and transition temperature in Figures 5:3 to 5:10. The latter are presented in extenso to illustrate the nature of the material provided by the Mettler and to facilitate an alternative conclusion to the one presented in the following section.

The tabular data are arranged in pairs according to sample masses, the approx 6 mg of R162F and R162C together and the 13 mg masses of the two together.

DISCUSSION AND CONCLUSIONS

Within each pair of equal weight samples, the thermal properties are to all intents and purposes equal, with the exception of the glass transition temperatures of the 6 mg pair. As between each pair, however, there are significant differences. The energy change is 10 Jg^{-1} greater for the heavier pair, the energy of activation about 3 Kcal $mole^{-1}$ greater and the peak temperature about 1.5 degree smaller.

This result is most surprising, and flatly contradicts Sacher's conclusions and indeed what common sense would indicate to be most likely to happen, not to say nullifying the conclusion drawn from the heat transfer equation discussed earlier.

An important circumstance is, that the results clearly indicate a decisive effect on the reaction order from the sample weight alone. This is unexpected, although it is easy to see that other thermal properties might be affected by sample weight, since in the instrument oven the same amount of heat is being supplied to a sample irrespective of its volume, hence a larger volume will tend to heat up more slowly than a smaller volume. Heating rate has an effect on thermal properties because of a concomitant effect on viscosity changes. It was anticipated, in view of Sacher's paper, and in view of the conclusions drawn from the heat transmission equation, that any effect from sample volume differences would be overshadowed by the particle difference effect, but this has not happened.

What the data in Table 5:1 appear to indicate is, that a change in reaction mechanism has occurred on changing sample weights; the change may be small, but according to

Table 5:1 it is real - all the measured properties are different, and it is difficult to provide an adequate reason for this. Parenthetically it may be mentioned that a very small effect from the particle size can be extracted if one considers that in each pair, in the majority of measurements, the coarse figure is higher than the fine one.

However, in the present case the particle size effect is negligible, and sample volume is of predominant importance.

REFERENCES

1. H. Morgenau and G. M. Murphy, Mathematics of Physics and Chemistry, p 232, Van Nostrand, New York.
2. E. Sacher, Kinetics of Epoxy Cure: Bisphenol-A epoxy/dicyandiamide. Polymer, 1973, Vol. 14, 91.

TABLE 5:1

THERMAL ANALYSIS : EFFECT OF PARTICLE SIZE

TWO SAMPLE WEIGHTS : R162F AND R162C

IDENTITY	SAMPLE WEIGHT Mg	ΔH J/g	Tg °C	E Kj/mol	n	PEAK °C
R162F	6.2	46.53	91.40	68.93	0.60	181.3
R162C	5.75	46.89	100.56	68.32	0.80	181.3
R162F	12.85	59.62	97.55	77.16	1.11	179.8
R162C	13.0	59.76	98.51	79.59	1.15	179.8

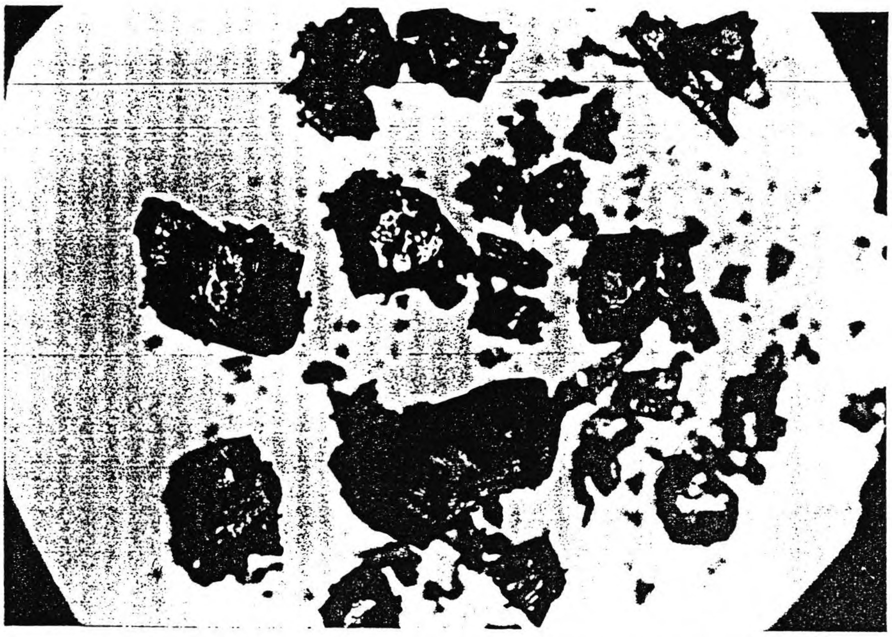
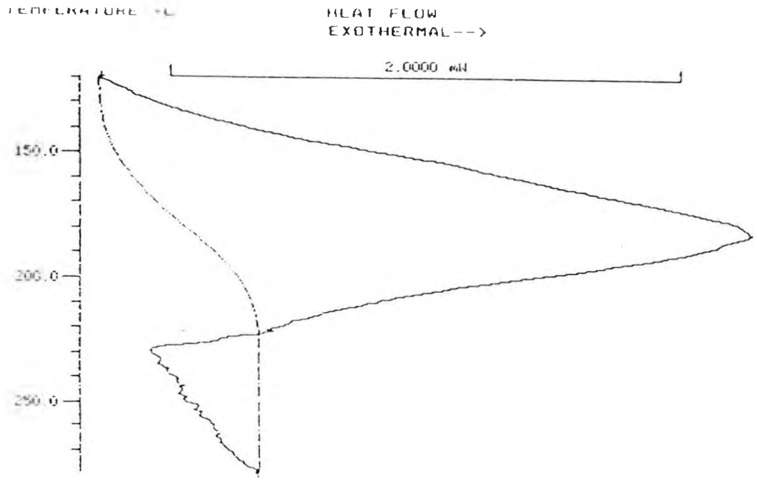


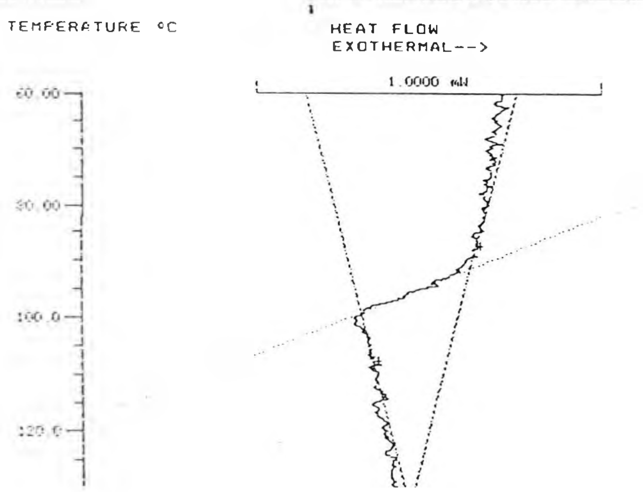
FIGURE 5:1 FINE PARTICLE FRACTION R162F

FIGURE 5:2 COARSE PARTICLE FRACTION R162C



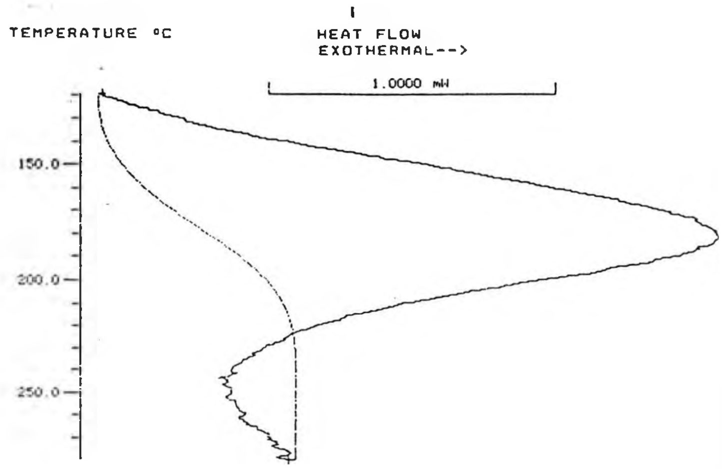
ΔH EXO mJ	288.51
ΔH J/G	46.534
PEAK TEMP. °C	181.3
REACT. ORDER	0.60
CONF. LIMIT	0.07
E A KJ/MOL	68.93
CONF. LIMIT	4.25
LN Ko	14.09
CONF. LIMIT	1.21

R162

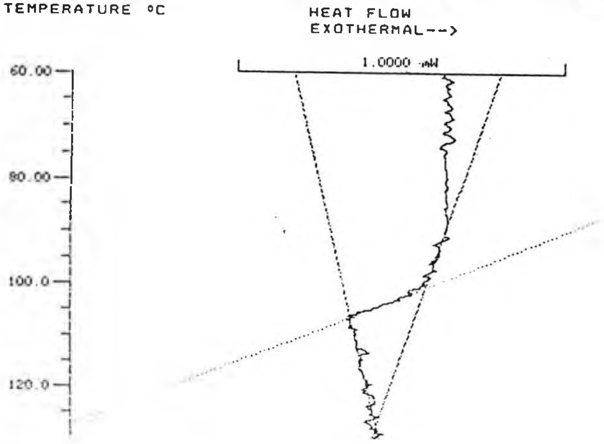


ΔCP J/G*K		0.308
GTRANS	°C	91.40
GTRANS	°C	95.22
GTRANS	°C	99.04

FIGURE 5:3 HEAT OF REACTION
FIGURE 5:4 Tg MEASUREMENT
R162F:6 mg

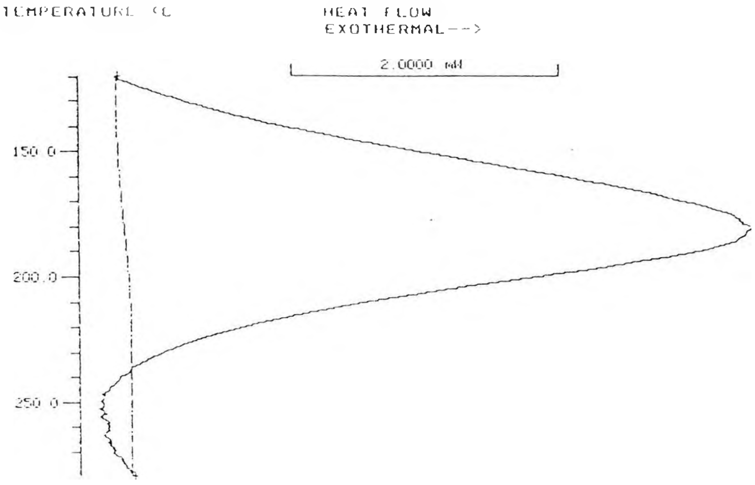


ΔH EXO	mJ	269.32
ΔH	J/G	46.83
PEAK TEMP.	°C	181.3
REACT. ORDER		0.80
CONF. LIMIT		0.08
E A	KJ/MOL	68.32
CONF. LIMIT		4.49
LN Ko		14.03
CONF. LIMIT		1.28



ΔCP	J/G*K	0.236
GTRANS	°C	100.56
GTRANS	°C	103.39
GTRANS	°C	106.21

FIGURE 5:5 HEAT OF REACTION
FIGURE 5:6 Tg MEASUREMENT
162C:6 mg



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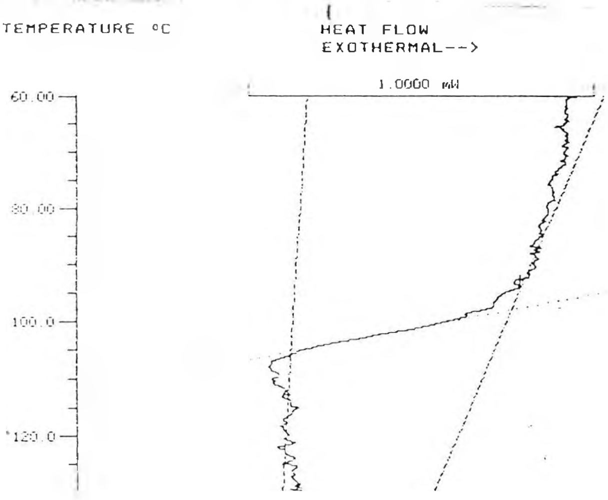
ΔH EXO       mJ            766.07
ΔH           J/G           59.616
PEAK TEMP.  °C              179.8

REACT. ORDER                 1.11
CONF. LIMIT                  0.03
E A      KJ/MOL             77.16
CONF. LIMIT                  1.59
LN Ko                       16.27
CONF. LIMIT                  0.45
```



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ΔCP J/G*K                   0.287

GTRANS      °C              97.55
GTRANS      °C             101.20
GTRANS      °C             104.83
```
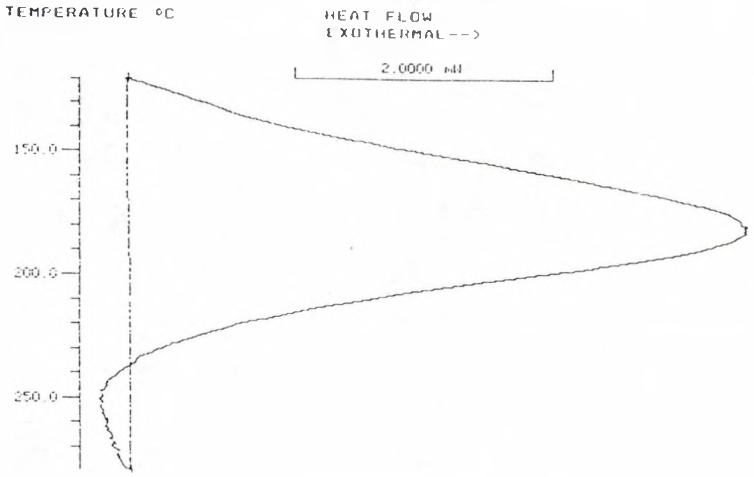
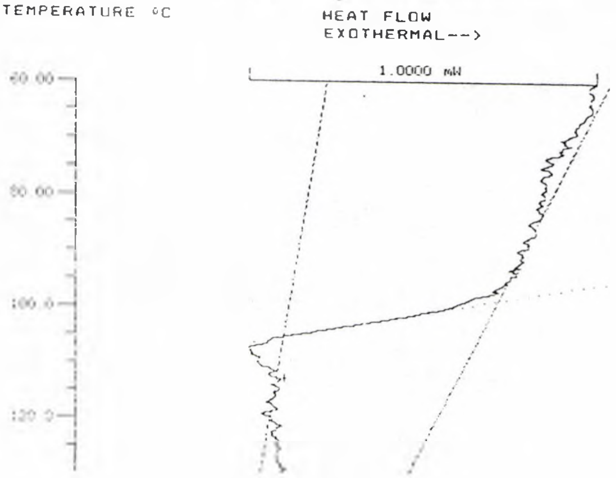

FIGURE 5:7 HEAT OF REACTION
FIGURE 5:8 Tg MEASUREMENT
R162F:13 mg



ΔH EXO	mJ	782.80
ΔH	J/G	59.756
PEAK TEMP.	°C	179.8
REACT. ORDER		1.15
CONF. LIMIT		0.04



ΔCP J/G*K		0.267
GTRANS	°C	98.51
GTRANS	°C	101.83
GTRANS	°C	104.96

FIGURE 5:9 HEAT OF REACTION
FIGURE 5:10 Tg MEASUREMENT
R162C: 13 mg

CHAPTER 6

THE EFFECT OF PIGMENTATION AND OF THE ADDITION OF FLOW CONTROL AGENT

The object of the experiment was to establish whether thermal analysis could detect an effect from the presence of a pigment on the cure of an epoxy resin in a powder coating. Such effects have been observed by Simpson (1) for TiO_2 pigmentation by dielectric measurements.

The series R161 to 164 was prepared with this in mind. R161 is a mixture of resin and hardener - epoxy resin 3003 and o-tolylbiguanide, but made commercially; additionally, an acrylic flow-control agent was incorporated in R162. In R163, the pigmentation was a mixture of carbon black and barium sulphate; in R164, the pigmentation was with TiO_2 alone.

First of all, the effect of pigmentation on the melting of the resin, Series R161-164, was examined, on the grounds that strong adsorption of, say, a component of the resin (most probably of lower molecular weight, but also the low molecular weight hardener) on to the pigment surface might be detectable in the melting experiment. R160, a quite different formulation, was also studied, since this material was most extensively reported in the Thesis.

EXPERIMENTAL

The measurements were made on the thermograms from SR625, after the kibbles had been reduced to a fine powder in a laboratory grinder.

EFFECT OF PIGMENTATION ON THE ENDOTHERMS OF R161 TO R164

Samples R163 and R164, containing less resin per unit weight of powder coating than R161 would be expected to show smaller endotherms than R161, and the interest of the experiment was to establish whether, taking account of pigmentation, anomalies in the melting energy, if present, could then be used to give information on the effect of pigmentation.

The thermograms obtained are shown in Figures 6:1 to 6:4, and the derived data are tabulated in Table 6:1 and 6:2.

All four thermograms consist of a melting endotherm followed by a reaction exotherm.

The peak melting point of R160 at 72° is distinctly higher than for R161-164 (mean 67.7°), confirming the presence of different resins. The peak melting temperature is quoted because it is measureable with some precision, whereas the true m.pt at the commencement of the endotherm is difficult to measure with equal precision because of the nature of the base line at that point.

At higher temperatures, after the completion of the endotherm, there is a curious feature for all four samples just before the development of the exotherm. This appears as a horizontal shelf, followed by a short, rapid fall which then becomes less steep until the exotherm appears. It can be regarded as a protruberance on a smooth curve between endotherm and exotherm, perhaps representing either (a) the melting of a much higher molecular weight fraction than the average in the resin. or (b) the melting point of a mixture of hardener and resin, or some component of the resin; the hardener itself has a much higher melting point. The feature cannot be due to the melting point of a catalyst, e.g in a dicyanamide-hardened R160, because it occurs also in R161-164, which do not contain a catalyst.

EFFECT OF THE ADDITION OF A MATTING AGENT.

In order to obtain more information on the nature of this feature, a series of powder coatings, R170-173, was studied. These are powder coatings which are pigmented with carbon black and contain a filler, very like R163, and differ only in that R170 gives a glossy film on cure whilst the others give matte films.

The thermograms of the set are shown in Figures 6:5 to 6:8.

The thermograms take the usual form of a melting endotherm followed by a reaction exotherm. The rising temperature limb of the endotherm has a second, much more distinct feature as in R160-164. In R170 (Figure 6:5), the feature is a step, as previously noted for R161-164; but in the other three endotherms the appearance of the feature is decidedly different; it is, in fact a true protruberance, representing a second, very small, endotherm.

The media in R170-173 are all very similar epoxy resins; the only known difference lies in the pigmentation;

indeed, the pigmentation difference is minor; all contain about the same amount of carbon black and filler, as in R163, but in R171-173 a matting agent has been added. In solvent-thinned paints, a matte effect can be obtained by increasing the pigmentation, but this is not done in powder coatings. Reduction of gloss is by incorporation of a specific matting agent, and this is usually fine silica, in quite small amount.

The inference is, then, that modification of a powder coating, in this case by addition of this quite small amount of matting agent, affects the melting of the base resin. It is not easy to see how this occurs. A tentative suggestion is, that the silica adsorbs a fraction of the resin and releases it only at higher temperatures than the normal melting temperature of the bulk resin. That is, the "step" in R170 may have quite a different explanation from the secondary endotherm peak in R171-173.

EFFECT OF PIGMENTATION ON THE EXOTHERMS

In R170 (glossy black), in addition to the feature on all the endotherms, there are shoulders on the exotherms on both limbs, visible but not pronounced. On R171-173 (matte black), however, the shoulder on the falling temperature limb is very marked, so much so, that a Kissinger symmetry analysis to obtain order of reaction would be pointless. Here again, one has to ask whether the presence of silica is alone responsible for the distortion.

If one analyses the shape in more detail, it can be seen, that as the material cools from attaining a half reaction, a second reaction occurs, which results in stopping the cooling for a short time; the cooling then resumes after the second, minor, reaction is complete.

A related phenomenon, but at the start of the exotherm, is discussed in Chapter 8, where the effect of different heating rates on the thermogram is reported. For the resins described in Chapter 8, however, these shoulders appear only at the higher heating rates, and are associated consequently with a change in cure characteristics (Kissinger) with increasing heating rates, and not with pigmentation, since the R165 powder used therein is a clear one.

We are left with the conclusion that certain kinds of pigmentation, and also faster heating rates, have the common property of affecting the cure characteristics of powder coatings.

EFFECT OF PIGMENTATION ON THE HEAT OF REACTION

The actual values of the heats of reaction in R161-164 are given in Table 6:1. Of course, these values decrease progressively from R161 to R164 because the content of reacting binder also decreases, per unit of total mass. The question that must be answered is, does the heat evolution correspond simply to the reduction in resin/hardener content, i.e can the influence of pigmentation be detected in the exotherm?

As a preliminary, consider the system showing a lower heat of reaction simply because of the lower binder content; that is, does the fraction (1-x) content of binder correspond to (1-x) fraction of heat evolved? The calculated values for this hypothesis are given in Table 6:1.

The data show, that on this basis, discrepancies exist and are large. For R163 (carbon black/filler), the measured value was 48.84 Jg^{-1} and the calculated one 62.64; for R164 (TiO_2 only), the measured value was 31.38 Jg^{-1} and the calculated one 46.92. In both cases, a discrepancy of 14-16 Jg^{-1} exists; that is, significantly less heat is actually evolved in pigmented systems than in non-pigmented ones, relative to the binder content.

However, this may be too simplistic a view of the phenomenon, and a more detailed analysis was carried out. In effect, unit weight of a binder in a pigmented film on being heated evolves, say, ΔH units of heat. This is distributed between unit weight of binder and the pigment present, and raises pigment to the same final temperature; the pigment does not, of course, contribute any thermal energy.

It is possible, on this basis, to calculate what the maximum temperature of the sample should be, assuming a knowledge of sample composition and the specific heats of the components.

Suppose the composition and properties of the sample are:

Binder x g per g sample;

Pigment (1-x)g per g sample;

Specific heat of binder C_1 $Jg^{-1}deg^{-1}$;

Specific heat of pigment $C_2Jg^{-1}deg^{-1}$;

Heat evolved per 1g binder ΔH joules.

This quantity of heat raises the temperature of sample and binder through ΔT degrees;

For the binder;

Heat required $C_1.\Delta T.x$

For the pigment;

Heat required $C_2.\Delta T.(1-x)$.

Then $\Delta H=C_1.\Delta T.x + C_2.\Delta T.(1-x)$

$=\Delta T\{C_1.x + C_2.(1-x)\}$

$=\Delta T\{x(C_1-C_2)+C_2\}$

or $\Delta T=\Delta H/\{x(C_1-C_2) + C_2\}$

But the temperature rise from xg of binder alone, if not pigmented, would be;

$$\Delta T_1 = \Delta H/x.C_1$$

and the temperature rises can be compared to establish whether the presence of pigment reduces the temperature rise on account of immobilising reactive groups by preferential adsorption on the pigment surface.

To use the equation, it is necessary to calculate the specific heats of binder and pigments. This has been done by the standard method of running thermograms of the pigments and binder against a reference of known or measured specific heat and using the slopes of the differential temperature lines for the calculation. The differential temperature lines for R161, 163 and 164 are shown in Figures 6:9 and 6:10, where the transition temperatures are also visible. It can be seen that the slopes are greater after the Tg than before - as would be anticipated. Similar thermograms were run for the pigments.

The calculation of temperature rises in this work is confined to R161/164 since TiO_2 is of principal interest to the Author.

Using the differential temperature slopes, C_1 for R161 (that is, the binder alone) was 1.03 $Jg^{-1}deg^{-1}$ below 160° and 2.06 above. For TiO_2 the values were 0.56 $Jg^{-1}deg^{-1}$ below 153° and 1.29 above. For the record, R163 gave a value of 1.77 $Jg^{-1}deg^{-1}$ and R164 1.96 in the relevant temperature range.

Inserting the values given above in the appropriate equations, and taking the higher of the values for the specific heats:

$$\Delta T_1 = \Delta H/(0.588x2.06) = 0.8256\Delta H \text{ deg}$$

$$\Delta T_2 = \Delta H/\{0.588x0.77)+1.29\} = 0.5738\Delta H \text{ deg}$$

$$\text{The ratio } \Delta T_2/\Delta T_1 = 0.6950$$

The actual value of ΔH is not important for the moment, since all that is required to determine the correctness of the value of 0.6950 for the ratio of the heights of the exotherms at the peak temperatures, referred to a common mass for the binder, is the ratio itself, not the individual values.

Turning to the thermograms of R161 and 164, the mass for 164 is 6.8mg, giving 3.984mg for the binder content.

The height of the exotherm at the peak temperature is 33.5mm. For R161, the corresponding height is 94.5mm for a mass of 7.0 mg, or 53.98mm for 3.98mg. Then the ratio of heights is 33.5/54.0=0.6210.

On the basis of using the larger of the two specific heats in the appropriate equations, then, there is a small effect on the exotherm from the presence of TiO_2 pigmentation.If the difference between 0.6210 and 0.6950 is significant, then this implies a slight retardation of cure attributable to the presence of pigment.

Finally, an examination was made of the possibility of pigmentation having an effect on the order of reaction. This might be possible if, as already suggested, pigment immobilised part of the reactive groups by adsorption and released them later at a higher temperature.

The method used was that of Kissinger, described in Chapter 4, where he employs the symmetry of the exotherm to derive an estimate of the reaction order, n, such that;

$$n=1.26S^{1/2}$$

where S is the symmetry, defined as the ratio between the extrapolated limbs of the exotherm and the vertical through the points of intersection of the extrapolated limbs.

On measurement;

R161 gave the ratio b/a of 1.36, n=1.47;

R162 gave the ratio b/a of 1.267, n=1.42;

R163 gave the ratio b/a of 1.3539, n=1.47;

R164 gave the ratio b/a of 1.02, n=1.27.

Here again, there seems to be a distinct effect from TiO_2.

Overall, then, there seems to be good reason to accept that inclusion of TiO_2 in the epoxy powder coating does affect the cure characteristics.

SIGNIFICANCE OF THE GLASS TRANSITION TEMPERATURE

The glass transition temperatures of the powder coatings are also reported in Table 6:1, and these of course are related to the degree of cross-linking, so a high peak temperature and a high Tg could imply that a slight retardation of reaction occurs, perhaps through adsorption of reactive groups on to TiO_2, followed by a more complete cross-linking because the adsorbed groups become released on raising the temperature, and then react (as primary amines?) sheltered from earlier reaction by adsorption.

TiO_2 is well known for its ability to adsorb active groups; the strength of such adsorption being dependent, among other things, on the presence of adsorbed water.

EFFECT OF THE INCORPORATION OF A FLOW CONTROL AGENT.

The other variant in the R161-164 set is the acrylic flow control agent incorporated in R162. The object of using this material is to reduce the viscosity of the powder at the melting point so that the particles may more readily flow to form a uniform film. At first sight, the reduction in melting point between R161 and R162, from 69.0° to 67.0°, might indicate an unique effect from the agent on the melting point of the resin; however, the remaining formulations R163 and R164 also possess a similar lowered melting point, so this cannot be attributable to the flow agent alone; the difference of 0.5° between the melting points of R162 and R163 and R164 is probably insignificant, given the difficulty of precise measurement of the endotherm peak.

In repeat experiments, however, the heat of reaction of R162 was always less than that of R161. In Table 6:1, in the quoted example, the heat of reaction has been reduced by 7.25% for an addition of flow agent of no more than 1%, a large disproportionation.

The flow control agent used is a low molecular weight acrylic, of which the function is to plasticise the resin at higher temperatures, to secure a smoother film after melting than might be attained in its absence. It is not unreasonable to postulate that flow being promoted would facilitate reaction, render the resin and hardener molecules more mobile and perhaps tend to increase the speed of reaction; that is, start the reaction at a lower temperature and attain the peak temperature in a shorter time. None of these postulates is, however, realised. The only measureable result is the reduction in the heat of reaction referred to.

A tentative explanation can be offered on the basis of what is involved in manufacture. It will be recalled that the last process in manufacture is passage of the initial mix through a plastics extrusion machine, where the mix is held in a hot barrel - usually about 100° - for a minute or so. It is possible that for the more sensitive formulations, a dwell at this temperature for such a time may well cause the powder to react slightly. If reaction is facilitated by the presence of the flow control agent, then although all the powders will show consequently a reduction over the heat of reaction on subsequent test, the one containing the flow agent will be more affected - as appears to be indicated by the lower reaction heat actually measured. That the R161 to 164 series is particularly sensitive to warming is well known, and even room temperature storage for a few months usually results in a reduction in heat of reaction. This is attributable to the presence of the fast acting hardener o-tolylbiguanide.

CONCLUSION

Pigments, specifically carbon black, blanc fixe and titanium dioxide, appear to have a measureable effect on the endotherms of the relevant powder coatings, by reducing the melting point slightly, and reducing also the heat of melting, but not beyond what is calculable on the basis of pigment loading; titanium dioxide gives the greatest reduction.

Silica used as a matting agent does have an effect, most noticeably in the development of a second endotherm after the one relating to the melting of the resin.

The pigments show a detectable influence on exotherms, both by reducing the heat of reaction (after allowing for the pigment loading) and by increasing the exotherm mid-point temperature; both effects are indicative of a slight retardation in cure characteristics due to the presence of pigment.

Silica as a matting agent has a marked effect on the exotherm, notably by producing a shoulder on the falling temperature limb of the exotherm, indicative of the existence of a minor cure reaction prior to the main cure reaction.

REFERENCES

1 D. L. Taylor, L. A. Simpson, Use of dielectric analysis to monitor the cure of powder coatings, Paint Resin, 1986, Vol. 56, 21.

TABLE 6:1

THERMAL PROPERTIES OF POWDER COATINGS

	R160	R161	R162	R163	R164
Melting Point °C					
Resin Peak	72.0	69.0	67.0	67.5	67.5
Minor Peak	88.5	83.5	86.5	85.0	83.0
Inflexion Pts. °C					
Exotherm Starts	145.5	110.0	109.5	106.0	115.0
Exotherm Mid Pt.	191.0	160.5	161.5	158.5	172.5
Exotherm Ends	230.5	236.5	224.5	219.5	228.5
Heat of Reaction J/g					
Measured	68.56	79.74	74.05	48.84	31.38
Calculated				62.64	46.92
Tg, Cured Film °C	103.0	91.0		89.0	93.5

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Specific Heats

R161 1.03 – 2.06 J/g/deg.C

TiO_2 0.56 – 1.29 J/g/deg. C

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TABLE 6:2

MELTING POINTS

		Energy of Melting J/g			
	R160	R161	R162	R163	R164
As measured	22.4	16.93	16.21	10.53	10.94
[Resin Content %	56.9			75.8	58.8
Energy allowing for pigment	39.65	16.93	16.21	7.98	6.43
Per g. binder				13.90	18.61

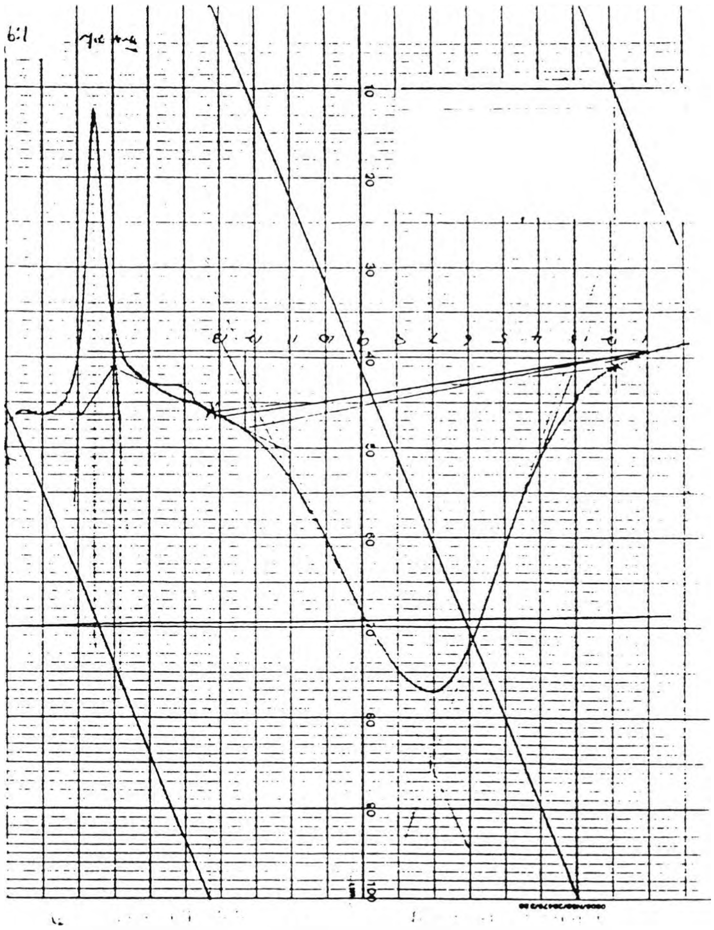


FIGURE 6:1 THERMOGRAM OF R161

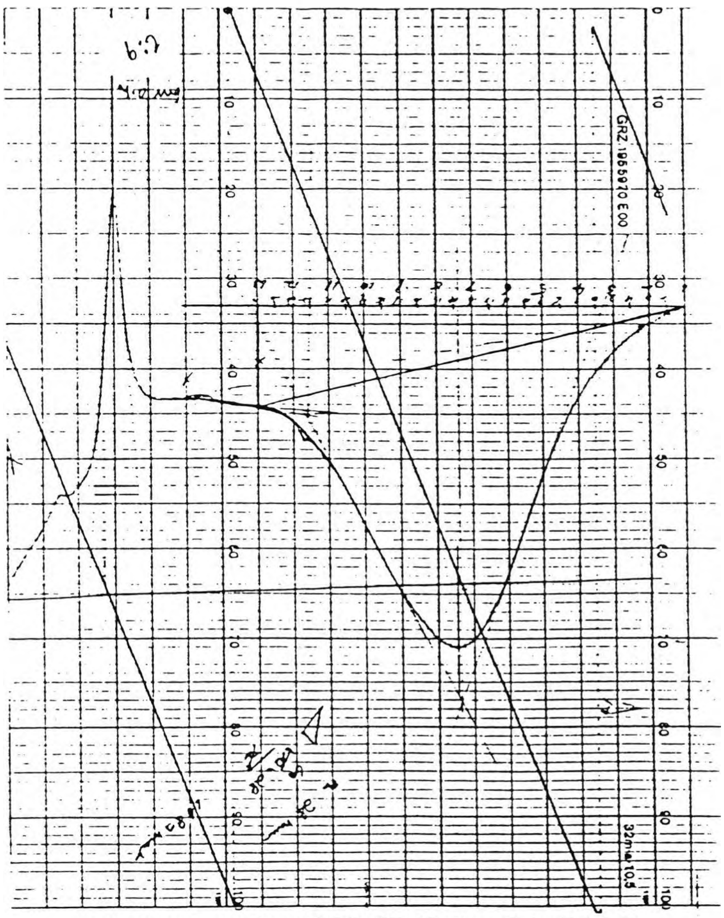


FIGURE 6:2 THERMOGRAM OF R162

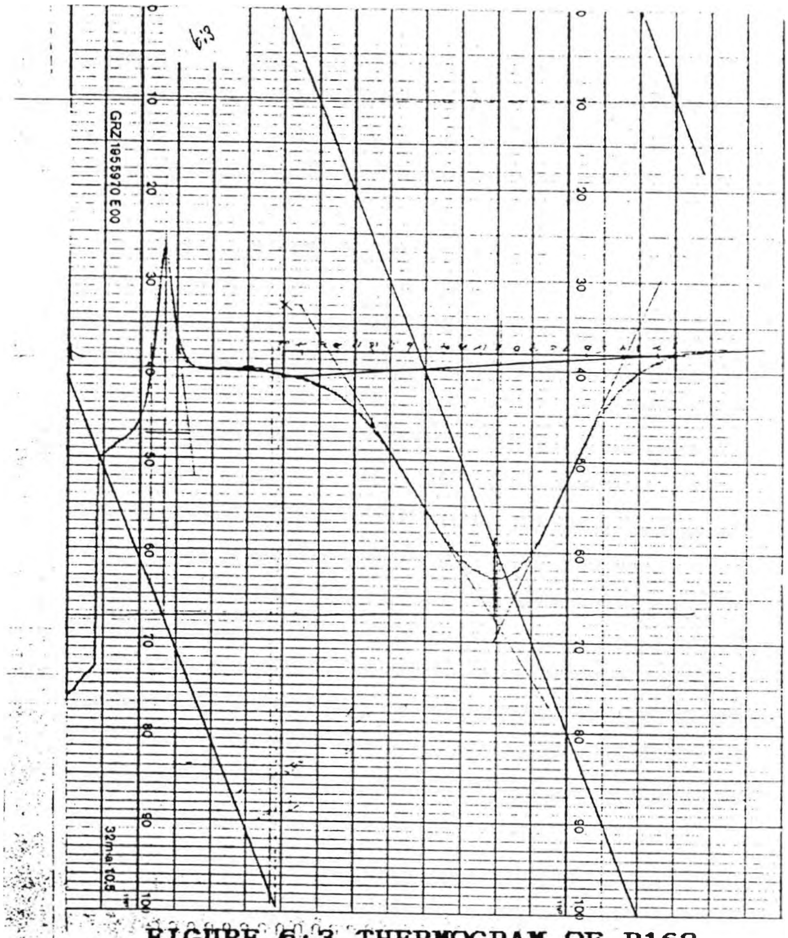
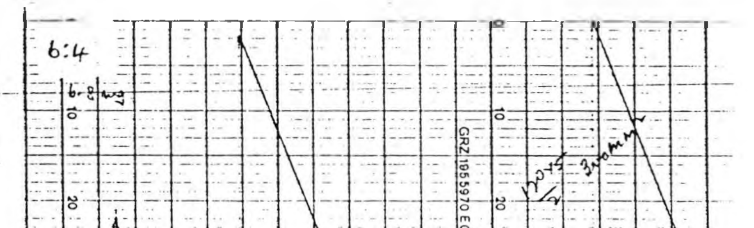


FIGURE 6:3 THERMOGRAM OF R163



DTA 85		
SAMPLE R164	DATE 20.5.85	RUN No. 1
HEATING RATE 10°/M FURNACE No. – CHART SPEED 1 CM/M SENSITIVITY 100/50 ATMOSPHERE N2 FLOW RATE 40 REFERENCE Al2O3 10 mg HOLDER Pt OPERATOR	CRUC. + S. CRUC. WT. S. 6.8 mg. WT. RESIDUE PACKING & DILUTION REMARKS ΔH 29.82 Jg⁻¹	

FIGURE 6:4 THERMOGRAM OF R164

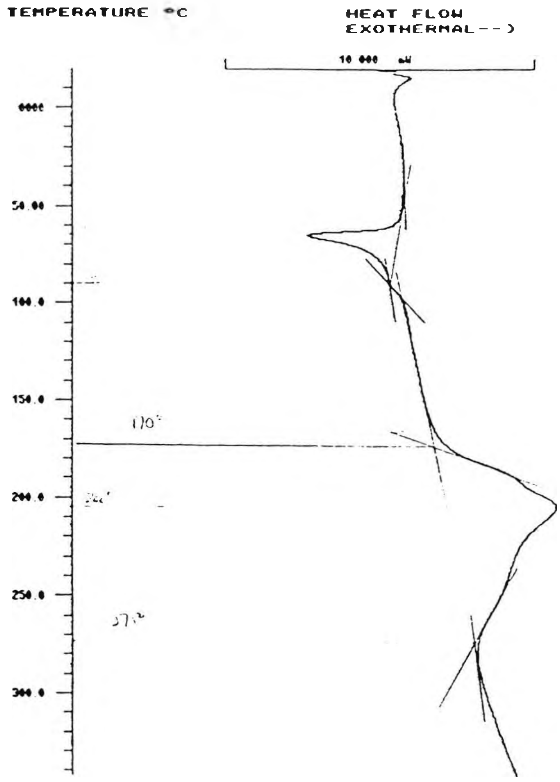


FIGURE 6:5 THERMOGRAM OF R170

IDENT. NO 34
WEIGHT mG 16.45

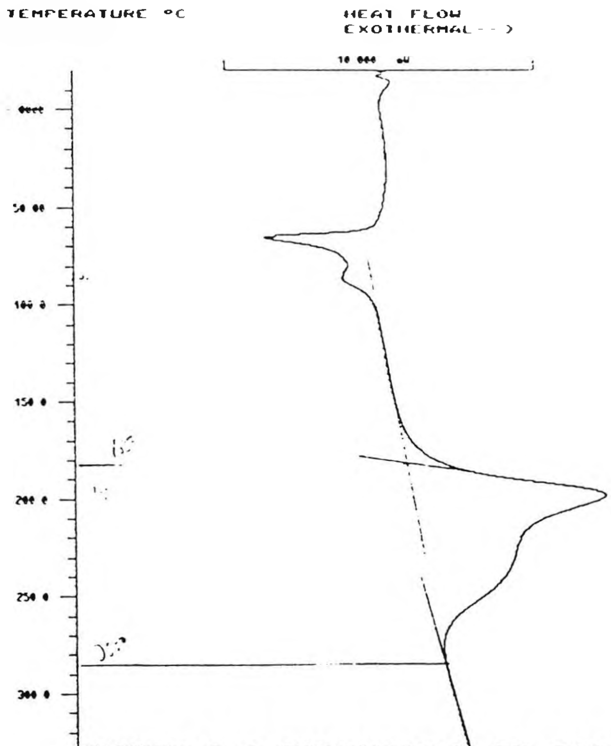


FIGURE 6:6 THERMOGRAM OF R171

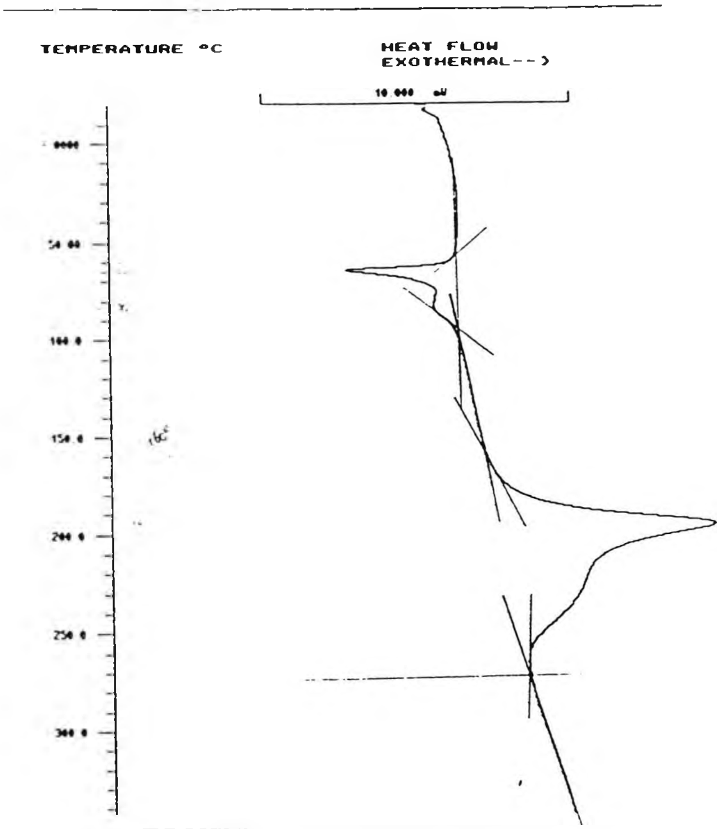


FIGURE 6:7 THERMOGRAM OF R172

IDENT. NO.	43
WEIGHT mG	9.95

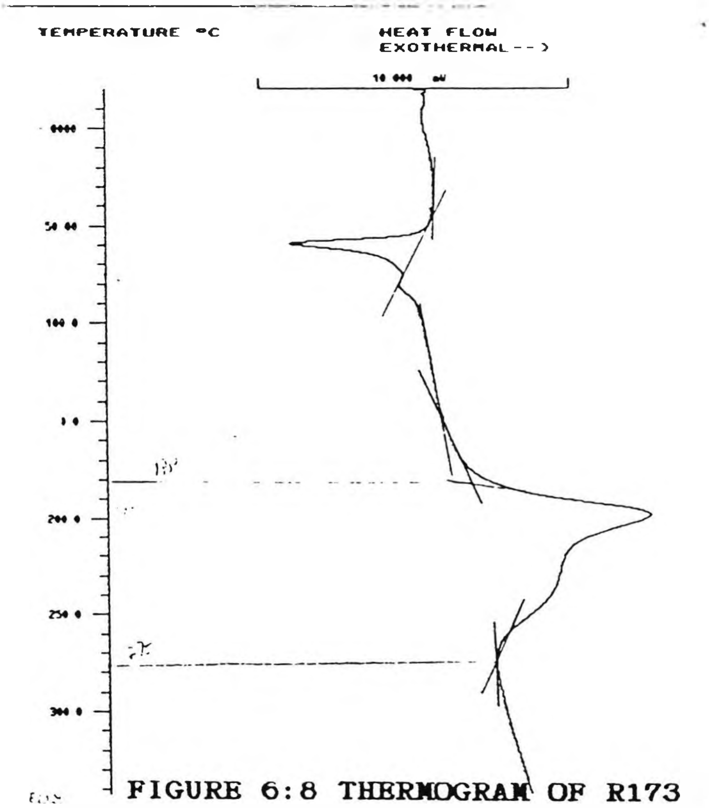


FIGURE 6:8 THERMOGRAM OF R173

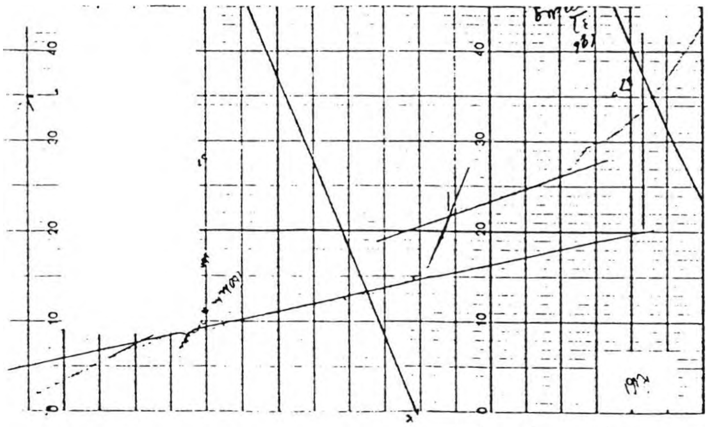


FIGURE 6:9 Tg MEASUREMENT R161

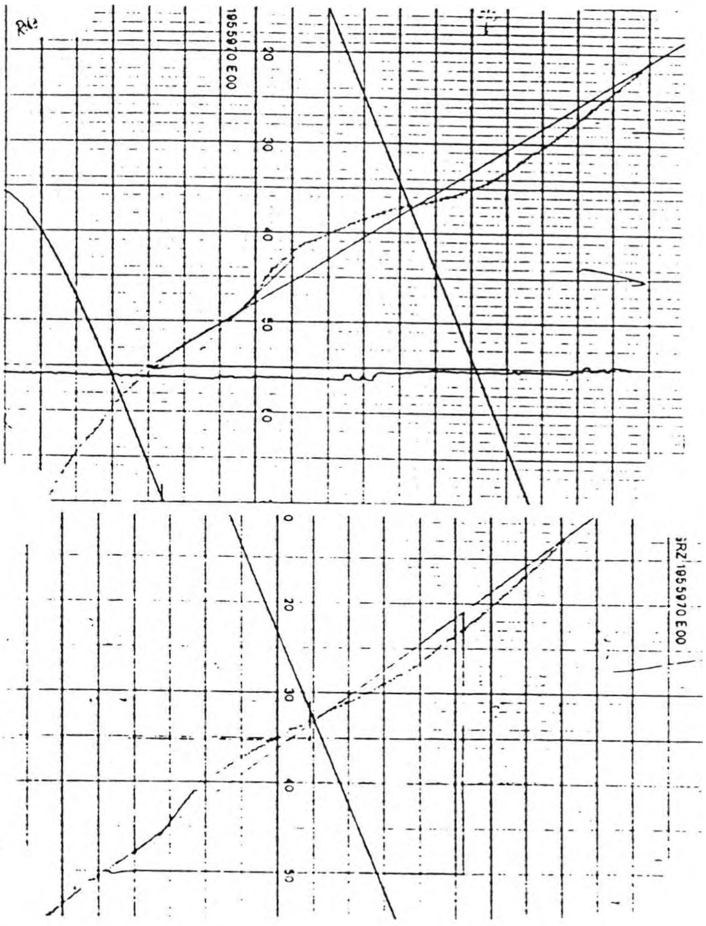


FIGURE 6:10 Tg MEASUREMENT R163, R164

CHAPTER 7

INSTRUMENTAL ISOTHERMAL KINETICS

The isothermal kinetics of the powder coatings are worth studying, principally to examine curing in infra-red cycles, where heating rates can be very fast before settling to an isothermal by reducing the intensity of the radiant source. It is, however, difficult to perform this experiment in an infra-red oven because the rate of heating prevents convenient sampling.

Isothermal runs should permit a more precise measurement of thermal properties such as energy of cure (in the case of a constant temperature run measureable as the enthalpy), activation energy and reaction order. In addition, because the melt viscosity and hence molecular diffusion rate are related to temperature, glass transition temperature measurement might throw light on the effect of cure temperature on cross-linking density.

EXPERIMENTAL

USE OF THE METTLER TA3000 TO STUDY THE ISOTHERMAL KINETICS OF CURE OF R160 AND R165

The standard R160 and freshly prepared R165 powders were used in the experiment for thermal analysis, using a Mettler TA3000 DSC.

For R160, a straightforward run was made on the instrument at a series of constant temperatures to give the

ΔH of the sample, which was measured on the relevant thermogram. This was followed by measurement of the transition temperature again on a straightforward run at 10 degrees per minute, with measurement of the Tg from the thermogram. The constant temperatures used were 150°, 160°, 170° and 180°.

For the R165 powder, the Mettler Peak Temperature programme was used at five constant temperatures, namely, 150°, 160°, 170°, 180° and 190°. In this programme, the instrument itself analyses and measures the exotherm and prints out the enthalpy. This was followed by a glass transition temperature programme, where again the instrument measures the transition(s) and prints out the value(s). The plurals are put in brackets here, because the instrument seems intent on finding as many as possible, providing perhaps a superfluity of information, and leaving it for the experimenter to decide which is the true glass transition - usually the lowest of the three the instrument prints out

Finally, for R165 only, an instrumental Kinetic Analysis programme was run, followed by a programmed glass transition run. The object was to characterise the R165 in as much detail as possible, since values of heat energy change, reaction order, activation energy and peak temperature are provided by the instrument, and then Tg can be measured. The value of the Tg should represent a fully cured film, and should act as a reference for the transition values found in the constant temperature runs.

Plots of enthalpy and glass transition values against temperature are given in Figures 7:1 and 7:2, and the derived data are given in Tables 7:1 and 7:2.

DISCUSSION AND CONCLUSIONS

The most striking conclusion from the results obtained in this part of the study is, perhaps, the marked dependence of the enthalpy and glass transition on the constant cure temperature. The data in Table 7:1, for any temperature below 180°, show that cure is not complete, in the sense that all the reactivity of the reactants is exhausted. Since the recommendation for R160 is that cure should be at 180° for 10 minutes, then heating at any lower temperature - supposing that this could be done (as it could be in a fast infra-red oven) - would not produce the same molecular structure as at 180°. This is confirmed by an examination of transition temperatures. It is taken as axiomatic that a different transition temperature implies a different structure - either because reactivity has been terminated by limitation of diffusion, or because reaction patterns differ, arising from the presence of at least five reactive couples in the system.

In Figure 7:1, the Tg can be seen to be approaching a maximum, although the enthalpy plot still has some way to go before attaining a maximum. The data in Table 7:2 and in Figure 7:2 for R165 are similar to those obtained for R160, but allusion is made in Table 7:2 to the reference run. The idea here is, that the ΔH obtained at 10DPM should represent the fully cured state, and this could be identified in the isothermal runs. In fact, the value of 70.1 J/g found in the reference run is exceeded above 160° in the isothermal run, the value going up to 111.3 J/g at 190°, the maximum constant temperature examined. The inference is, that the system posesses greater reactivity at a constant temperature attained very rapidly than in a run at a much slower heating rate, even though the temperature continues to rise in the latter case.

The Tg plot is not as smooth in Figure 7:2 as in 7:1, and all one can say by way of generalisation is that the lower values of Tg are grouped together in the 150-170° range, rising to a maximum of about 107° at 180-190°. The enthalpy plot is roughly parallel, but again has not reached a maximum.

For an explanation of these phenomena, one turns to the effect of heating rate and temperature on melt viscosity of the powder. The faster the rate of heating, the lower the melt viscosity of the powder at any given temperature, on the descending part of the viscosity curve, and the better the promotion of the diffusion-controlled reaction at the attained temperature. In the reference run of Table 7:2, a much slower heating rate occurs than in the isothermal runs, where the low mass sample is placed in a preheated oven, consequently one would not expect the viscosity to be as low in the reference run at any attained temperature as at the same isothermal.

Then again, on attaining any given temperature in the reference run in the 150-190° range, the degree of conversion will already be greater than at the same temperature in the isothermal run, and this alone has an effect on the measured rate of reaction.

These two circumstances together would appear to be sufficient to explain why the ΔH values are greater for the isothermal runs, since they indicate that (a) there are more reactive couples available in the isothermal runs at a given temperature, and (b) a fast reaction starts almost immediately the sample is put into the preheated oven.

Finally, the kinetic analysis programme of the Mettler provides additional information on the R165 reaction. The reaction order calculated by this method is 1.01, and the activation energy 88.3 Kj/mole; for a sample weight about 12 mg, this gives a value in reasonable agreement with that of 1.10 reported in Chapter 5 for the larger weight sample of R162.

In conclusion, it seems that a constant temperature analysis of the reaction in the DSC does not yield the detailed information on the course of the reaction that such a study hypothetically provides, since the intermediate stages in the reaction (measurement of degree of reaction) are not readily available. It was with this observation in mind that the experimental method of Chapter 9 was devised to analyse the degrees of reaction.

However, what the material in this chapter shows is:

(1) the large sensitivity of the epoxy system in powder form to the reaction temperature, and

(2) that at the different cure temperatures, the values of the Tg obtained show that the structure of the final product is different at the different temperatures.

TABLE 7:1

THERMAL ANALYSIS OF R160 AT CONSTANT TEMPERATURE

Number	Temperature	ΔH J/g	Tg °C
6160	150°	37.96	73
8160	160°	44.71	83
9160	170°	69.10	94
10160	180°	90.96	99

****

TABLE 7:2

THERMAL ANALYSIS OF R165 AT CONSTANT TEMPERATURE

Number	Temperature	ΔH J/g	Tg °C
2165	150°	42.14	103
3165	160°	68.79	101
4165	170°	90.25	97.1
5165	180°	97.07	106.5
7165	190°	111.3	106.9

****

Reference Run at 10DPM

Number	ΔH J/g	Tg °C	n	E Kj/mole	Peak Temp
8165	70.14	102.5	1.01	88.27	175.1°C

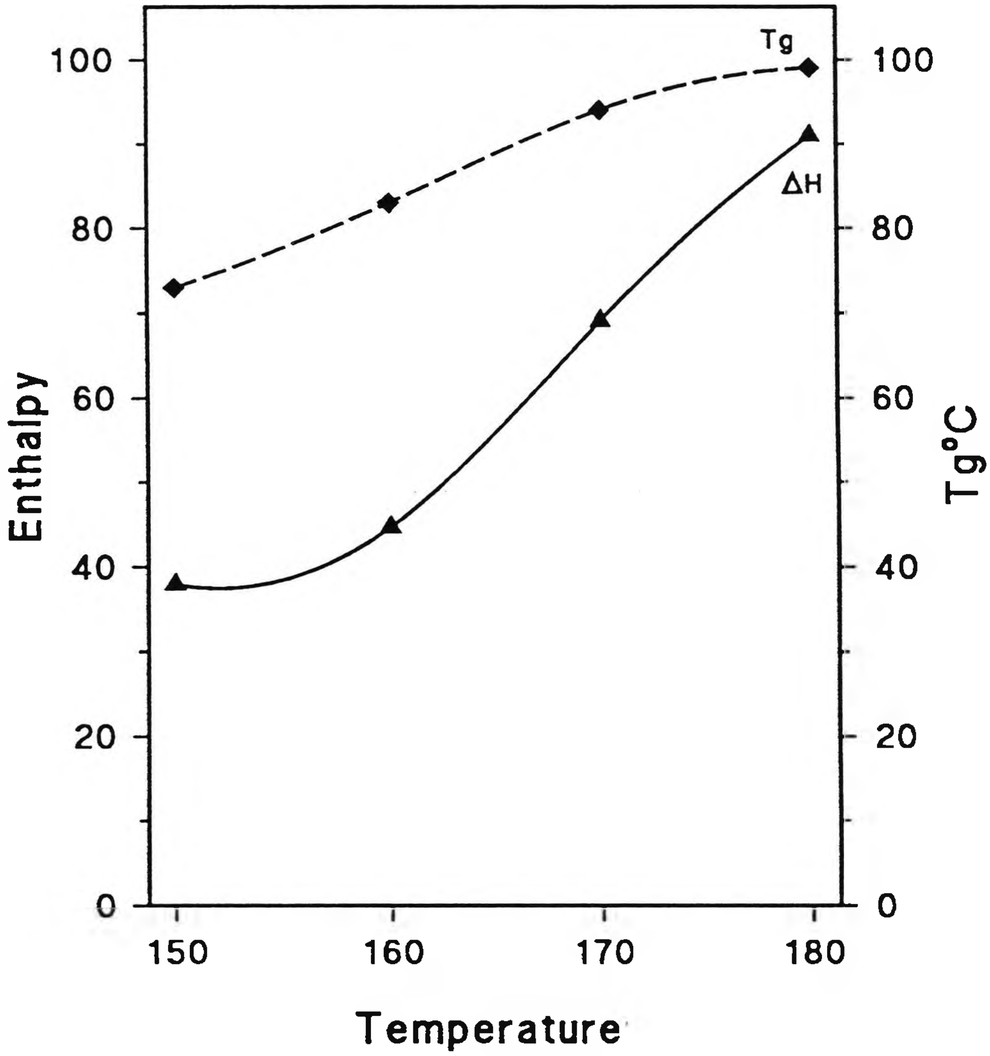


FIGURE 7.1 RELATIONSHIP OF ENTHALPY OF REACTION AND GLASS TRANSITION TEMPERATURE TO TEMPERATURE OF CURE

R160

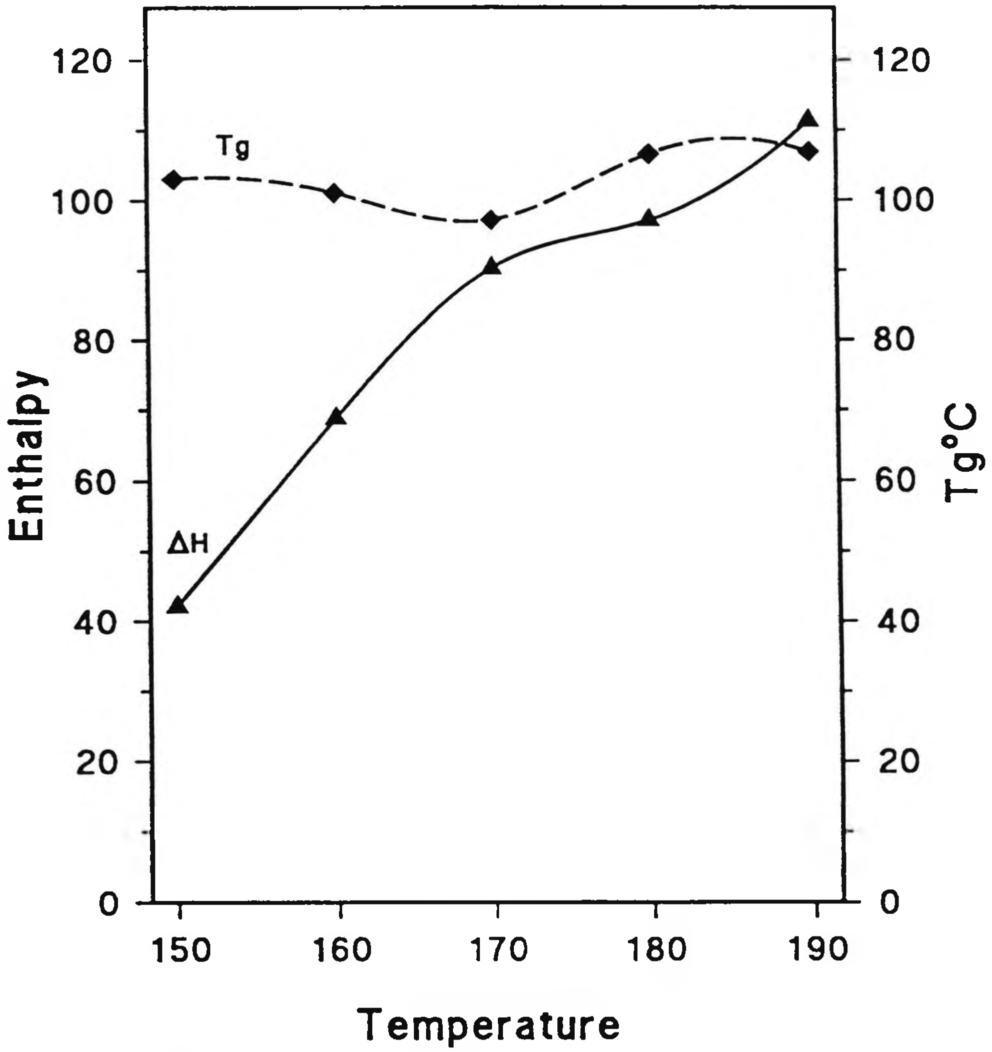


FIGURE 7.2 RELATIONSHIP OF ENTHALPY OF REACTION AND GLASS TRANSITION TEMPERATURE TO TEMPERATURE OF CURE

R165

CHAPTER 8

EFFECT OF VARIATION IN THE RATE OF HEATING ON THE THERMOGRAM

It is a common observation, that when thermal experiments on a material are run at different heating rates, the appearance of the thermogram differs according to the heating rate. Almost invariably, the base length (time interval) is shorter the faster the heating rate, and the height of the endotherm or exotherm (temperature, cooling or heating) is greater.

Explanations for this phenomenon refer to the existence of a temperature lag between sample and furnace or to the natural consequence of reaction proceeding by an activation mechanism.

What was of interest in the present context was whether the variation in heating rate affected cure characteristics and cure kinetics, because in industrial practice, oven and above all radiant energy cure, certainly proceed at varying heating rates, according principally to metal thickness and final temperature in the case of oven cure, and to metal thickness and (above all) to colour in the case of infra red cure. It is well known that when metals of different thicknesses or paints of different colours (in infra red), are used, changes in heating schedules can be difficult to establish, especially because establishing a satisfactory curing schedule depends on some empirical test, like film hardness. The present Author once observed a radiant heating schedule being determined as the point just short of a copious evolution of smoke from the paint film - a kind of test not uncommon though rarely admitted.

Because of the practical importance of the influence of the heating regime, the subject has been studied in some detail in this work.

EXPERIMENTAL

STUDY OF VARIATION IN THE HEATING RATE ON THE THERMAL PROPERTIES OF R160 : FIRST SERIES.

The first series of experiments with the R160 formulation were made with the Stanton Redcroft 625 (SR625). Sample weights were 6+/-0.1 mg, sensitivity was 100µV/50mV, the chart speed was 3 centimetres per minute (CPM).

The thermograms from this set are not illustrated here, but those for the second set are presented later. The two sets were very similar, but those of set 1 are tabulated in Table 8:1

DISCUSSION

The data show that, as expected, the temperatures of onset of the peaks of endotherm and exotherm increase with the rate of heating, as do the temperatures of termination of exotherms, while the lengths of the bases (time) decrease with the rate of heating. It so happens, that calculation of the area of the exotherm, to obtain the energy of reaction gives an approximately constant value. Perhaps it ought to be exactly constant, but termination and commencement of an exotherm do not always yield precise values, because of the frequent very shallow slopes of the differential temperature line at these points, so some variation usually occurs. In fact the area is 5480.8mm^2 with a standard deviation of 462.2mm^2.

Of the temperatures quoted as start, peak and end of cure, the start temperature is not very reliable, but since the temperature at which the reaction starts is of some practical importance - obviously an oven set at below the thermogram start temperature would give an inconveniently slow cure - the mean value of those tabulated is taken as a characteristic value; this is 148.1°SD11.51°, and interestingly insofar as the evidence may be trusted, there does not seem to be a strongly marked drift upwards at the higher heating rates. On the whole, then it may be assumed that at about 150° the reaction starts off at a reasonable speed.

The sample temperature at which about half the reaction is completed, somewhat ambiguously labelled the peak temperature, does appear to be related to the rate of heating, the relationship being a smooth curve, as shown in Figure 8:1.

One may briefly explain the effect of the heating rate as follows. Suppose we have two heating rates plotted as straight lines of different slopes in the illustration of Figure 8:2. In the same time interval Δt the movement along the heating rate lines are represented by the distances AC and DF respectively. But to attain the points C and F, the lines AC and DF may be resolved into the abscissa AB and DE and the ordinates BC and EF of a triangle of which AC and DF are the hypotenuses. At the lower heating rate because the rate constant is smaller, the degree of conversion is smaller, consequently to attain the same degree of conversion (completion), the material at the lower heating rate will take longer than that at the higher rate. However, as the illustration also shows, in the interval Δt the material at the higher heating rate has passed to a higher temperature, and this will be the case at completion. The higher heating rate then produces a shorter heating time to attain a higher end temperature.

The temperature and time differences are indeed quite striking. For example, a cure at 2DPM requires 33 minutes spread over 66 degrees; at the maximum examined heating rate of 40DPM, the cure time is only 2.4 minutes but spread over 137.5 degrees, and the final attained temperature is 286°. Of course, one does not normally allow a stoving paint to heat up indefinitely, but the approach to a nominal cure temperature can be fast or slow and before reaching the set temperature, different degrees of conversion will occur, according to the heating rate.

This question is treated in later chapters.

The plot of cure times versus heating rates shown in Figure 8:1 represents a smooth curve, falling rapidly in the 2-15 DPM range but then tending to level out thereafter. Interestingly, a plot of log of cure times versus DPM gives a quite good straight line.

STUDY OF THE EFFECT OF VARIATION IN THE HEATING RATE ON THE THERMAL PROPERTIES OF R160 : SECOND SERIES.

The 2 - 15DPM region attracted attention because of the rapid changes occurring there, so a further examination was made to see what light could be thrown on this.

Accordingly, the experiment was repeated on a slightly reduced scale, namely at 5, 10, 15, 20 and 25DPM, using a fresh delivery of R160 powder coating, 6+/-0.1mg of sample, and taking particular care to obtain good quality thermograms. These are shown in Figures 8:4 to 8:7 and the derived data given in Table 8:2.

The same features appear in these thermograms as in the first set, namely an increasing heating rate producing a shorter cure time to a higher temperature, a greater height to the exotherm (a higher differential sample temperature).

For an analysis of the effect of heating rate, the method of Kissinger (1) was employed. A detailed account of the method is given in APPENDIX 3, but for convenience, a condensed version is included here.

In summary, the Kissinger method makes use of the peak temperature to calculate activation energies. It analyses heat flow into the reactive and reference samples and demonstrates that peak differential deflection occurs when the reaction rate is a minimum. Further, from the elementary rate equation

$$d\alpha/dt=A(1-\alpha)^n.\exp-E/RT \quad (8:1)$$

he showed that the rate of heating function can be incorporated to give

$$d^2\alpha/dt^2=d\alpha/dt\{E\phi/RT^2-An(1-\alpha)^{n-1}.\exp-E/RT\} \quad (8:2)$$

Since the value of $(1-\alpha)^{n-1}$ is very nearly equal to unity, inserting this value into equation 8:2 and differentiating gives:

$$d(\ln\phi/T_m^2)/d(1/T)=-E/R \quad (8:3)$$

from which E may be calculated. From this equation, it appears that at any one temperature for a series of exotherms at different heating rates (ϕ being the heating rate), the following relationship should hold:

$$\ln(\phi/T_m^2)=E/RT-\ln(AR/E) \quad (8:4)$$

Then a plot of $\ln(\phi/T_m^2)$ versus 1/T should give a straight line of slope E/R and an intercept ln(AR/E). This has been done for the second SR625/R160 set, the calculation being set out in Table 8:3, and the plot obtained therefrom according to the Kissinger method in Figure 8:12.

The plot gives two straight lines of different slopes, with a point of inflexion between 10 and 15DPM, or rather one should say a break at this point. This is some confirmation of the observation that stimulated the second trial, namely that there is a change in mechanism in the epoxy cure reaction as the heating rate is increased. One might almost say there is a hiatus whilst the mechanism changes over a small temperature range.

First of all, it is possible to calculate the activation energies for the two parts of the plot, and these are 11.79kcal mole^{-1} for the 5-10DPM region and 23.49kcal mole^{-1} for the 15-25DPM region.

DISCUSSION

On the basis of the Kissinger equation, there can be no doubt of a change in kinetics as the heating rate is increased.

As for an explanation, this is difficult without a more systematic study, but a tentative suggestion is the following. First of all one should take into account the changes in viscosity that are so marked a feature of the curing process of powder coatings, especially the effect of heating rates on the rapidity and magnitude of such changes. According to Meyer (2), there is an order of magnitude difference between the minimum viscosity at 5DPM and 20DPM from about 10^4 to 10^3 Pa.s, and on account of this difference, it is suggested that at faster heating rates, some change occurs in which groups react. For example, dicyandiamide and similar compound are chemically complex, they contain both primary and secondary amine groups, and in the epoxy resin both epoxy and hydroxy groups occur. Then again hydroxy radicals are in any case formed during the cure reaction, available for reaction later if the reactant mobilities become high enough. It also ought not to be overlooked that some evidence exists for a transformation of dicyandiamide to melamine during the initial stages of the reaction (3). What is proposed by the Author is this; that in rapid heating, the viscosity falls so fast that on account of the greatly increased mobility of the reactants at an early stage, readily reacting groups like primary amines and chain end epoxy groups are quickly used up, but then slower reacting groups like secondary amines and hydroxyls which have a lower mobility as the viscosity rises rapidly and which in any case react at a higher activation energy, now do so, a process detected by the higher activation energy shown in the Kissinger treatment.

Finally, the R160 data were re-examined to see whether more information on kinetics could be extracted.

First of all, the exotherms were analysed to construct the usual α vs. t curves from $\alpha=\Delta A/A$ on the thermogram, and the results are given in Table 8:3, with the actual plots in Figures 8:8 to 8:10. The plots all show the familiar S-shape, all well separated except that the 20 and 25DPM plots are very close together. Because of the steepness of the plots at the higher heating rates, it is difficult to measure slopes with any conviction, so an example has been made of the 5DPM curve.

The slopes, $d\alpha/dt$ were measured at six points and used to calculate k at each point (Table 8:4). Then a plot of lnk vs. 1/T gave a reasonable straight line, as shown in Figure 8:11. From the slope, calculated by linear regression analysis, E was calculated to be 11.83Kcal mole^{-1}.

STUDY OF THE EFFECT OF THE VARIATION OF THE HEATING RATE ON THERMAL PROPERTIES OF R165

The possibility was next examined that other powder coating formulations might show the broken line in the Kissinger plot, and R165 was chosen for this purpose. This was a powder coating made up in the laboratory by thorough mixing of Epikote 3003 and 5% o-tolylbiguanide, both first ground to very fine powders before mixing and then mixed in a coffee grinder. The ingredients and the mixture were kept in a desiccator over fresh silica gel. Six-mg samples were heated, separately, at 5, 10, 20 and 25DPM in the SR780, the SR625 not then being available for use.

DISCUSSION

The Thermograms obtained are shown in Figures 8:13 to 8:14, and again the usual dependence of peak temperature on heating rate appears. What is novel, however, is the undoubted appearance of two exotherms, not one (as in the other powder coatings examined). First of all, to establish the reality of the existence of two exotherms, consider an experiment on the effect of heating rate variation on the thermogram of resin 3003, as shown in Figure 8:16, where, of course an endotherm, not an exotherm can only be obtained.

The endotherms show the same progression in height as for the endotherms and exotherms of the powder coatings, but what is most important for the present purpose is that immediately following the termination of the endotherm, the differential temperature follows a horizontal line, it does not continue to drop as does the post-endotherm line in the R165 set; this holds for the 3003 even at the highest rate of heating of 25DPM. The horizontal post-endotherm in 3003 forms a shoulder in the thermogram, and this represents, of course, the specific heat of the post-melting resin, necessarily greater than the specific heat of the solid.

In a separate experiment, the heat of melting of the 3003 resin was found to be 17.37 J/g in a SR625 run.

To return to the resin endotherm. It is reasonable to suppose that the ratio of specific heats of the material before and after melting should stand in some constant ratio, and indeed in the 2-20DPM set this is approximately correct, the ratios being 0.22, 0.23 and 0.26, giving a mean of 0.24; however the 25 DPM value does not fit in, giving a ratio of 0.54 - a difference difficult to explain.

To return to the R165 set, examination of the melting exotherm will show up a "kink" or part shoulder on the falling temperature line at about where one would expect to find the shoulder on the 3003 resin, but then the differential temperature line continues downward, most definitely at 20 and 25DPM but also at 10DPM to form a first exotherm.

For confirmation of the existence and significance of the two exotherms, the paper by Duffy, Hui and Hartmann (4) referred to in Chapter 2 was studied. These authors prepared thermograms of a number of complex amino compounds, which they describe as "hindered" amines and for which they anticipate two sequential exotherms, which could be attributed, in certain cases at least, to reaction of primary then secondary amine groups; in extension, the first exotherm might refer to the formation of a linear polymer which is still soluble. This initial linear polymer formation is quite a feature of commercial resin production. It is used as a stable form of cross-linking agent.

In view of the complex structure of the o-tolyl biguanide used in the R165 formulation, the first hypothesis for the existence of two exotherms is that the first relates to the reaction of the primary amine groups in the compound and the second to reaction of the secondary amine groups. It should be noted that there are four secondary amine groups in the molecule to one of primary amine.

The formula of o-tolylbiguanide is given below:

$o\text{-}CH_3.C_6H_4NH.C(=NH).NH.C(=NH).NH_2$

The Kissinger analysis is given in Table 8:5, and a plot of the data in Figure 8:17. The lines relating to first and second exotherms are separate and have different slopes and intercepts.

From the slopes it is possible to calculate the energies of activation and collision frequencies in the two sets.

The activation energies are:

For exotherm 1, $E=9.3854$ Kcal $mole^{-1}$

For exotherm 2, $E=13.004$ Kcal $mole^{-1}$

indicating, as would reasonably be anticipated, the second, higher temperature reaction operates at a higher activation energy than the lower one.

The collision frequencies are:

For exotherm 1, $A=5.790\times10^{3}\ s^{-1}$

For exotherm 2, $A=9.3747\times10^{3}s^{-1}$

Continuing with the DHH treatment, it is now possible to calculate the rate constants for the two reactions, which they use to identify the nature of the reactions.

Using the standard Arrhenius equation:

$$k=A\exp-E/RT$$

it was found at 298K that the values of k were;

For exotherm 1, $k=7.5793\times10^{-5}s^{-1}$

For exotherm 2, $k=2.8281\times10^{-6}s^{-1}$

The ratio of the two is 26.81:1.

Duffy, Hui and Hartmann identify their ratio of 9:1 with reaction by primary then secondary amines, though commenting that Rinde, Chiu, Morse and Newey (5) in NMR studies found a ratio of 19:1 for primary and secondary amines. The ratio quoted here for the R165 set might seem to to be gratifyingly close to the latter value especially since primary and secondary amines are present in o-tolylbiguanide.

However, a caveat should be entered.

Rinde et al examined compounds containing primary amines less complex than the o-tolylbiguanide. In the R165 set, both primary and secondary amine groups exist together in a single compound and must compete with one another for the initial reactive sites. Consequently, classification of the two exotherms in the R165 set as originating in reaction of primary and then secondary amines is not satisfactory. A tentative conclusion could be that the first exotherm can be attributed to a larger proportion of primary amine reacting and the second exotherm to a larger proportion of secondary amine in the mixture.In the first stage, reaction of the primary amine and the epoxy groups of the resin produces, in effect, a very large secondary amine molecule, which necessarily reacts more slowly - as the difference in the k values indicates, and with a higher energy barrier to reaction.

After the first rapid reaction of the primary amine group, the more readily reactive part of which is used up in forming the first exotherm, the reaction of the predominantly secondary amine fraction produces a larger total energy because there are four such groups to the single primary group, and this shows up in the larger size of the second exotherm.

Perhaps a remaining puzzle is why no indication of two exotherms appears in the R160 set. The cross-linking agent in this powder coating is dicyandiamide or an accelerated dicyandiamide, to some extent confirmed by the fact that the start temperature is higher for R160 than for R165. To make some attempt to clarify the issue a little more, the formula of dicyandiamide is given below to compare with that for o-tolylbiguanide given earlier:

$$NC.NH.C(=NH).NH_2$$

The differences are; the substitution of the tolyl group for the cyano group and the double length of the aliphatic chain in o-tolylbiguanide. Thus the ratio of primary to secondary amine is 2:1 in the latter, not four to one. It is well known that dicyandiamide has been abandoned for use in powder coatings for several reasons, one being its slowness of reaction, and it may be that its structure ensures that there is not a great deal of difference in the reactivities of primary and secondary amine.

An interesting, if minor effect, of the variation in heating rate, is the sample differential temperature change as the heating rate is increased; it has no real practical value but serves to show the real effect of heating rate variation. The method of measurement is described in APPENDIX 2, and results for the SR625/R165 set are given in Table 8:6 and plotted in Figure 8:18. They show the variation as a smooth curve rising to a maximum at about 25DPM. Data and a plot for Indium are also given, and show the same effect. The actual values are of course negligibly small compared to the furnace temperature at any one heating rate.

Finally, some comments on the practical aspects of the effect of variation in heating rates may not be out of place.

Such variation will be encountered, for example in industrial curing schedules, when light and heavy metal parts are passed simultaneously through an oven or submitted to IR radiant elements - a matter discussed at greater length in Chapter 10.

Perhaps the most marked effect occurs in radiant heat cure, where differences in colour of the paint are of crucial importance. Differences can be dramatic.

In a laboratory experiment, panels coated with, respectively, black and white powder coatings were submitted to quartz envelope short wave radiant emitters with a peak emission at about 1.5µm, with thermocouple leads attached to the reverse of the panels; the output from the thermocouples, after amplification, was passed to a recorder, so that a continuous record of temperature was obtained from ambient. The white panels heated up at 4.8DPM and the black ones at 31.25DPM - a more than 6:1 difference in heating rates. In practice, on attaining 180°, radiant elements would be switched out to maintain this temperature.

However, the data in Table 8:3 clearly show that differences in heating rates produce different curing regimes in a stoving paint. In this discussion, colour is unimportant, it merely serves to visualise what could happen if any one of a number of factors, colour among them, are varied in the course of industrial processing.

Suppose we were concerned with an actual stoving process, where it was required to heat up to an isothermal and hold thereat for a certain time, and suppose precision of cure were asked for. Normally, in a camel-back oven for example, set at slightly above the selected temperature, the schedule would call for, say, 10 minutes at 180°, and this is all that would be taken into account, for a powder coating for example. However, if the heating regime is considered in detail, there is first the heating-up period, when at some point cure starts, the isothermal run and then the cooling period as the product is taken from the oven; in all these three parts of the cycle, the paint film is curing, and the question is, what is the contribution that each part of the cycle makes to the total cure?. We have information on the contribution of the first cycle, at least, from the data presented in this chapter. The data for SR625/R165 were used to establish what degree of conversion had been attained by the powder coating when it had reached 180° for the different rates of heating examined, and the results are given in Table 8:7. The contribution made by the first part of an oven cure cycle to total cure is clear in the data.

At 5DPM, cure is virtually complete when 180° is reached, but at 25DPM only an eighth of complete cure has occurred. These two heating rates roughly correspond to the difference between black and white panels referred to earlier; in a radiant cure cycle, where the heating rate is constant, the effect of product thickness or paint colour is obviously dramatic.

A point should be made about heating rate differences in IR and oven cure. An object heats up at a rate determined by the instantaneous difference between itself and the heating element. In oven cure, where the ambient oven temperature is usually at, or slightly above, the final set temperature, heating rates are not constant, because the temperature difference, object-oven, is continually decreasing, so that the heating rate continuously falls. In radiant element cure, however, the radiant element temperature is so far above final set temperature - for example a quartz element would be at about 1500°, that to all intents and purposes the heating rate is constant.

Whilst IR cure schedules are more sensitive to changes in the nature of the product, then, oven schedules can also be affected by product changes.

To establish the complete history of cure in an oven requires rather different experimental techniques from the ones described here, and these will be found in Chapter 9.

DISCUSSION AND CONCLUSION

The experimental material in this chapter clearly shows that the heating rate in a thermal experiment has an important effect on the kinetics of cure of an epoxy system, irrespective of the kind of instrument employed (DTA or DSC) and allowing for differences in resin and cross-linking agent identity and mixture formulation.

The principal effect, and one most important from the point of view of use in industry is that the time to attain a given degree of cure is dependent on the rate of heating; the faster the rate, the smaller the degree of cure when the oven pre-set temperature is attained (and the shorter the time to complete the cure). Whenever the production situation is such that changes in heating rate may be anticipated from a change in product dimensions or colour (in IR cure), then a change in oven setting will be required, or a change in conveyor speed if the product line is fully automated; in the case of IR cure, a change in emitter power or a larger/smaller emitter/product distance may be required.

These questions of the practical significance of heating rate in production are dealt with in more detail in Chapter 9.

Turning to more theoretical matters, two important conclusions on mechanism have emerged from the experiments. The first is, that an analysis due to Kissinger has shown that the rate of heating has an effect on mechanism, and the data show a change of some kind from the 5-15 DPM region to the 20-40 DPM region, accompanied by a corresponding change in the activation energy for reaction.

Secondly, for one system at least, that is the one containing o-tolyl biguanidine as cross-linking agent, two exotherm peaks are present in the thermogram. The peaks are the more prominent according to the rate of heating - the faster the rate, the more prominent; at 5DPM two peaks are not really distinguishable, from 10 DPM they are just present and then grow progressively larger, relative the one to the other, as the heating rate increases. The postulate advanced in explanation is, that the amine curing agent can be described as hindered, in the sense that rapid reaction of the primary amine groups "hinders" the reaction of the original, and the newly formed, secondary amine groups. The reality of the existence of two peaks is in part confirmed by the circumstance that the endotherm of the resin alone does not show a continuous fall on its falling temperature limb, though this is what happens in the mixture to form the first of two exotherms.

If we attempt some explanation for the phenomena observed, the most marked measureable change in behaviour for epoxy/polyfunctional amine cross-linking agent mixtures is the viscosity of the melt as the temperature is raised. Referring to Meyer (2) and his data on powder coating viscosity; at 5 DPM, the viscosity falls from a start value of (approximately) 10^5 Pa.s to a minimum of 0.7×10^2 Pa.s in

6 minutes, whereas at the highest studied heating rate of 40 DPM, the change is from 10^5 Pa.s to 7 Pa.s in just one minute. It is a curious coincidence - perhaps no more than that - that in Meyer's diagram of viscosity against time, the peaks of curves 15 - 40 DPM lie on a good straight line, whereas the peaks at 5 and 10 DPM are not on the same straight line, but on another, making a point of inflexion in the 5 - 40 DPM data. A table of results derived from Meyer's data is given in Table 8:8.

In the light of the discussion on viscosity in relation to heating rate, it may be of interest to relate an anecdote relevant to the discussion. A complaint was made to the Author (at the time a consultant) that a system recommended by him was giving unsatisfactory results, in particular of the gloss of the cured powder coating, although the cure temperature specified was rigidly adhered to. On investigation, it was found that the curing schedule employed a batch oven; the coated product was loaded into the oven when ready at an unknown start temperature (from the previous cycle) and then the heaters turned on to bring the final temperature up to the specified one. The film produced was of low gloss and quite unacceptable. The reason was, of course, that at the very low rate of heating attained, flow of the powder was poor and incomplete, so that full fusion of the powder granules was not obtained - the viscosity of the coating not having fallen low enough before cure set in to produce complete flow.

A far more detailed and systematic study would be required to establish the mechanism of the effect of these viscosity changes, but there can be no doubt that viscosity changes and heating rate effects are related.

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APPENDIX 1

CALCULATION OF THE ENERGY ABSORBED/EVOLVED IN THE DEVELOPMENT OF AN ENDO/EXOTHERM

FROM THE INSTRUMENTAL ENERGY SETTING

The Stanton Redcroft 625 has a maximum output of 10 mW at the 100 µV setting of the differential temperature amplifier.

Let the recorder sweep setting be s mV, at a chart width of 250 mms; then the height h mms at a distance a mms along the endo/exotherm baseline corresponds to

$$hs/250 \text{ mV}$$

$$\text{or } h/25 \text{ mW}$$

If the chart speed is v cm/min or 10v/60 mms/sec, then a mms corresponds to 6a/v seconds.

The total energy defined by the area of the endo/exotherm is Σha mm^2

$= (\Sigma ha) \times 6/25vm$ J/g, where m is the mass of the sample.

In an example, for the first series SR625/R160, where the mean area of the exotherms was 5480.8 mm^2, the sample mass was 6 mg and the chart speed 3 cm/min, the area corresponds to the following energy

$$\Delta H = (6 \times 5480.8)/(25 \times 3 \times 6) = 73.08 \text{ J/g}$$

APPENDIX 2

CALCULATION OF THE PEAK DIFFERENTIAL TEMPERATURE OF AN ENDOTHERM OR EXOTHERM

Let the maximum height of endo- or exotherm be h mms on a recorder paper width of 250 mms, and a sweep of s mms.

Then h mms corresponds to

$$hs/250 \text{ mv}$$

and the 250 mm sweep corresponds to the maximum output of the thermocouple amplifier of 100 µv.

The chromel/alumel thermocouple has an output of 4.28 mv for 100 deg, so 100 µv corresponds to 0.0237 deg, and the recorded height on the recorder paper corresponds to

$$0.0237h/250 = 9.346h\times10^{-4} \text{ deg}$$

In an example, SR625/R160/10DPM recorded a maximum height of 44 mms, giving a maximum differential peak temperature of 0.0411 deg.

APPENDIX 3

DERIVATION OF THE KISSINGER EQUATION

Kissinger first proves (as is commonly accepted) that the temperature at which maximum deflection occurs in a thermogram corresponds to the maximum reaction rate.

Starting with the conventional rate equation

$$dx/dt=A(1-x)^n.\exp-E/RT \qquad 8A3:1$$

and differentiating, we have:

$$E\phi/RT_m^2=An(1-x)^{n-1}\exp-E/RT_m \qquad 8A3:2$$

Integration of 8A3:1 by parts according to Murray and White (6) gives a rapidly converging series, and dropping all terms after the second gives:

$$1/(n-1).(1/(1-x)^{n-1}-1)=ART^2.\exp-E/RT(1-2RT/E) \qquad 8A3:3$$

Combining equations 8A3:2 and 8A3:3 and simplifying:

$$n(1-x)_m^{n-1}=1+(n-1).RT_m/E \qquad 8A3:4$$

This equation does not contain the heating rate ϕ, except in the sense that T_m increases with heating rate. However, the product $(1-x)_m^{n-1}$ is not only independent of ϕ but very nearly equal to unity, so writing this value into equation 8A3:2, differentiating and neglecting small quantities gives:

$$d(\ln\phi/T_m^2)/d(1/T_m)=-E/R \qquad 8A3:5$$

and this is the Kissinger equation used in Chapter 8.

TABLE 8:1

EFFECT OF THE HEATING RATE ON THE THERMAL PROPERTIES of R160 POWDER COATING

Heating Rate	M.Pt	Temperatures of Exotherms				Tg	Cure Time
DPM	°C	Start	Peak	End	Duration	°C	Minutes
2	60.8	119.7	172.0	192.0	66.4		33.2
5	67.4	163.0	184.3	207.9	59.8		11.4
10	68.8	136.0	193.8	227.0	79.9	100.5	8.3
15		145.4	200.4	242.5	94.4	96.6	5.3
20	71.6	135.4	206.8	255.0	107.7	101.2	4.8
30	72.3	145.0	215.6	269.0	121.9	105.1	3.3
40	72.6	163.8	226.6	285.6	137.5		2.4

****

TABLE 8:2

KINETICS OF REACTION : SR625/R160 : 2nd SERIES

Interval	Conversion/Temperature				
Seconds	5DPM	10DPM	15DPM	20DPM	25DPM
10				0.01/140	0.01/144
20	0.003/140	0.006/132	0.007/132	0.06/160	0.05/171
30				0.15/180	0.14/198
40	0.015/145	0.03/142	0.03/147	0.37/200	0.47/223
50				0.74/220	0.95/248
60	0.035/150	0.06/152	0.07/161	0.95/240	1.00/253
70				1.00/260	
80	0.065/155	0.12/162	0.16/175		
100	0.106/160	0.23/172	0.34/191		
120	0.166/160	0.41/182	0.67/205		
140	0.245/170	0.66/192	0.91/220		
160	0.346/175	0.87/202	1.00/235		
180	0.465/180	0.97/212			
200	0.599/185	1.00/222			
220	0.723/190				
240	0.827/195				
260	0.898/200				
280	0.946/205				
300	0.977/210				
320	0.992/220				
340	1.00/248				

TABLE 8:3

KISSINGER ANALYSIS : SR625/R160 : 2nd SERIES

Heating Rate DPM	1/T.10 K	$(\mathrm{Ln}\phi/T_m^2)$ K
5	2.305	−14.72
10	2.174	−14.05
15	2.110	−13.90
20	2.090	−13.60
25	2.055	−13.25

****

TABLE 8:4

DATA FOR THE CALCULATION OF ACTIVATION ENERGY

$(1-\alpha)$	T °C	1/T.10 K	Gradient.10	Ln k.10
0.85	115	2.58	2.938	3.46
0.70	130	2.48	5.263	7.52
0.50	150	2.36	5.519	11.04
0.30	170	2.26	5.990	20.00
0.20	180	2.21	4.026	20.13
0.10	190	2.16	2.810	28.13

****

TABLE 8:5

KISSINGER ANALYSIS : SR780/R165/5–25DPM

Heating Rate	1st Exotherm		2nd Exotherm	
DPM	1/T.10	Ln (ϕ/T_m^2)	1/T.10	Ln(ϕ/T_m^2)
5			2.3256	−14.6129
10	2.8217	−13.5306	2.2442	−13.3989
20	2.6674	−12.9455	2.1395	−13.3394
25	2.6539	−12.7381	2.1093	−13.1975

TABLE 8:6

MAXIMUM DIFFERENTIAL PEAK TEMPERATURE IN SR625

Heating Rate DPM	Differential Peak Temperature	
	R 160	Indium
2		0.350
5	0.045	0.528
10	0.638	0.740
20	1.213	0.915
25	1.225	–
30	–	0.920

****

TABLE 8:7

PROPORTION OF CURE COMPLETED ON REACHING 180°C SR780/R165/5–25DPM

Heating Rate DPM	% Cured
5	99.98
10	74.00
20	26.00
25	12.50

****

TABLE 8:8

VISCOSITY CHANGE IN AN EP/PES POWDER COATING (AFTER MEYER)

Heating Rate DPM	Max/Min Change Pa.s	Time Max–Min Minutes
5	10 /0.7.10	6
8	10 /0.4.10	4
10	10 /0.3.10	2
15	10 /0.1.10	2
20	10 /0.09.10	1.5
40	10 /0.07.10	1.0

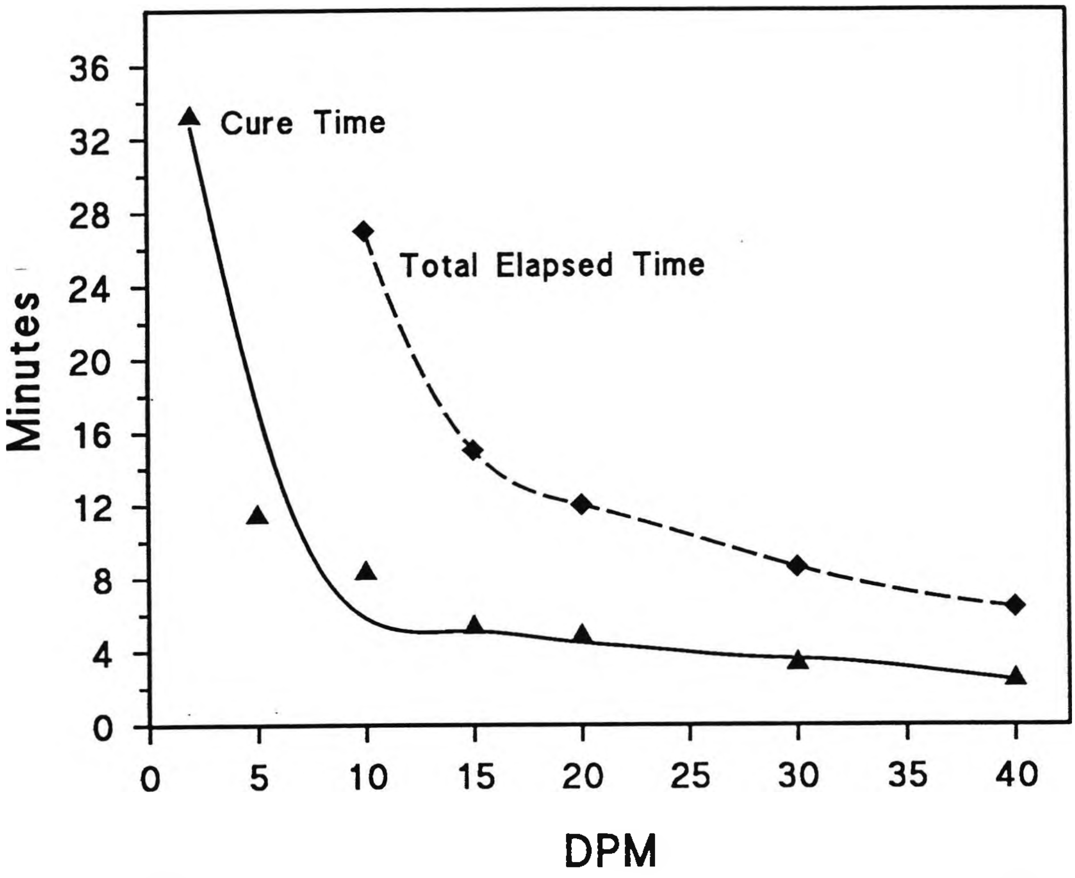


FIGURE 8.1 Dependence of Cure Time on Rate of Heating
SR625/R160/2-40 DPM
Ist. Series

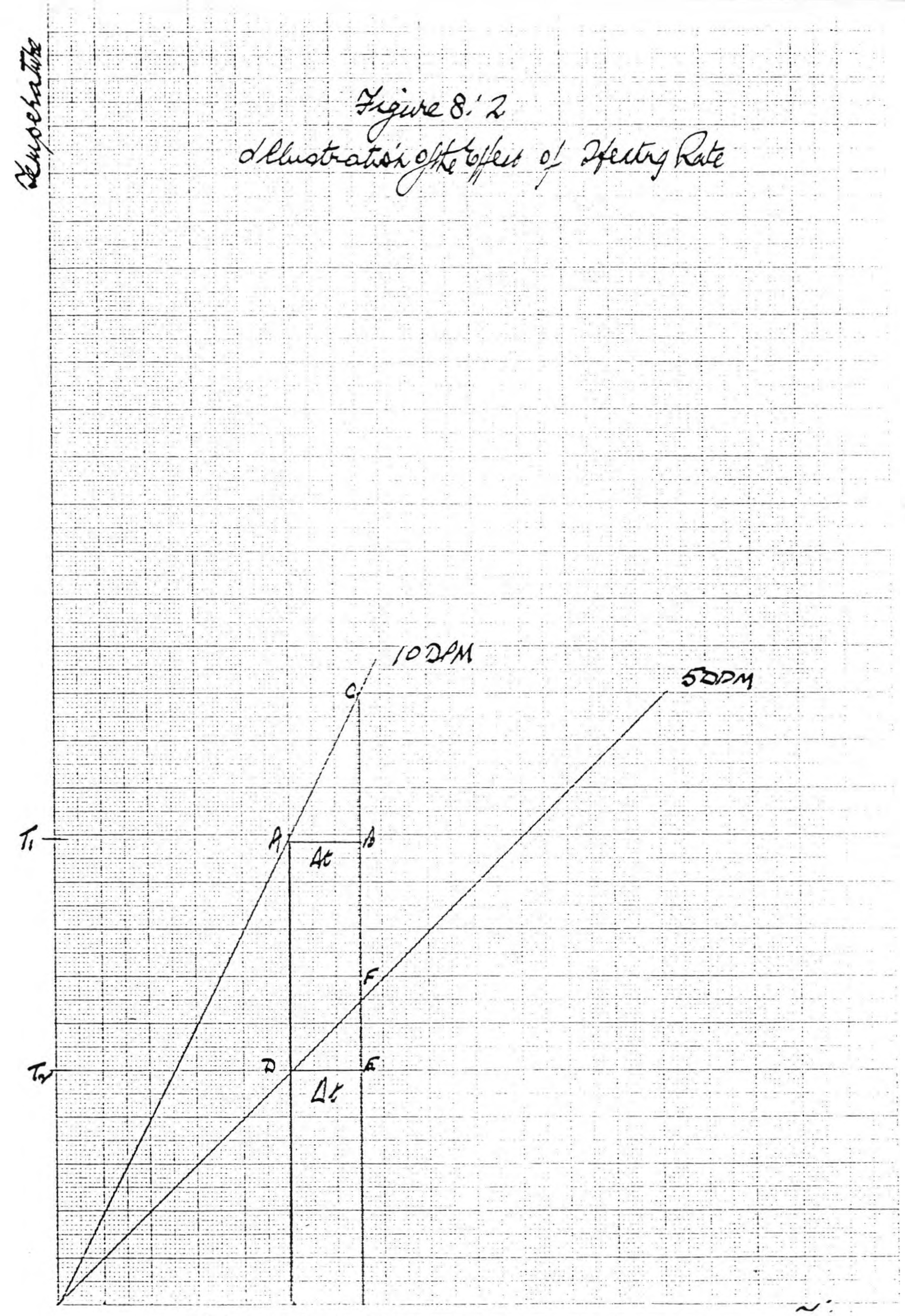


FIGURE 8:2 ILLUSTRATION OF THE EFFECT OF HEATING RATE

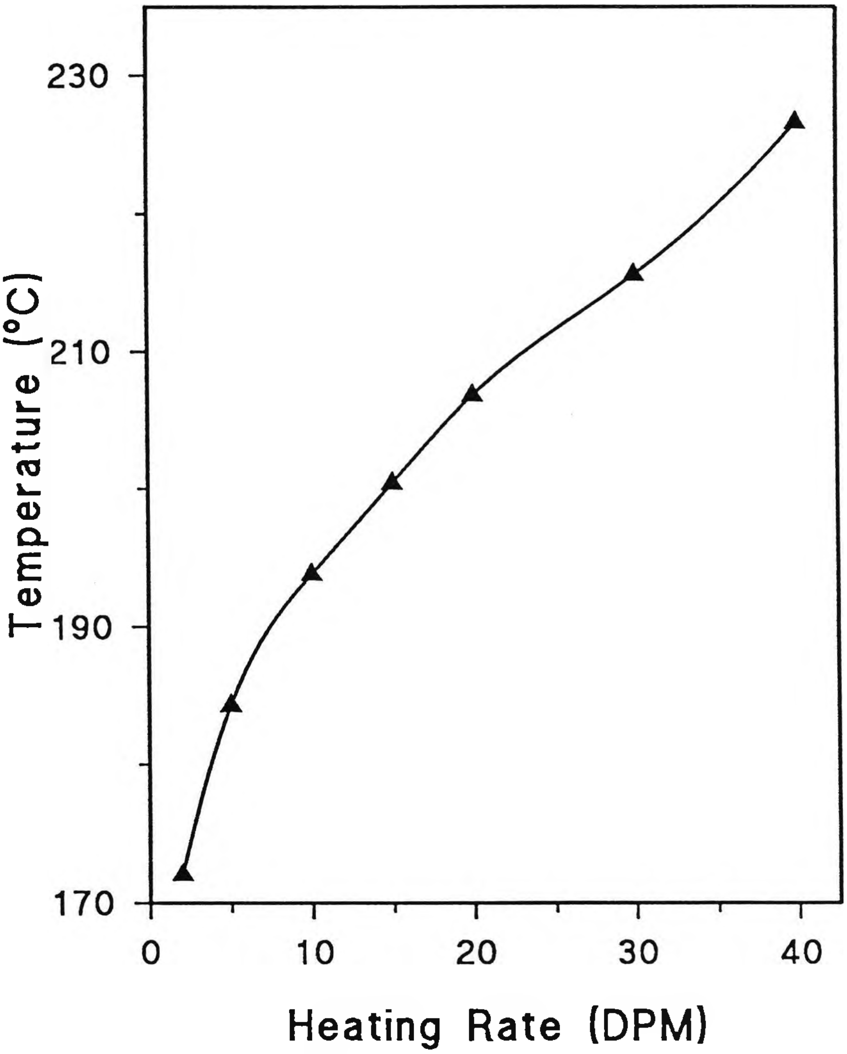


FIGURE 8.3 Peak Temperature versus Heating Rate
Ist Series

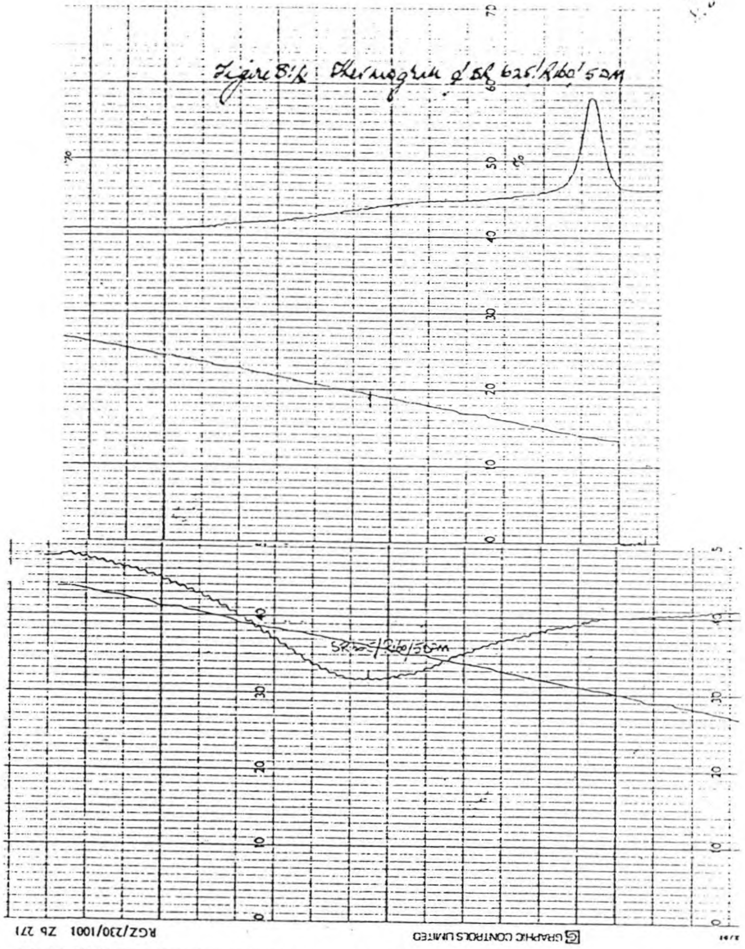


FIGURE 8:4 THERMOGRAM OF SR625/R160/5DPM

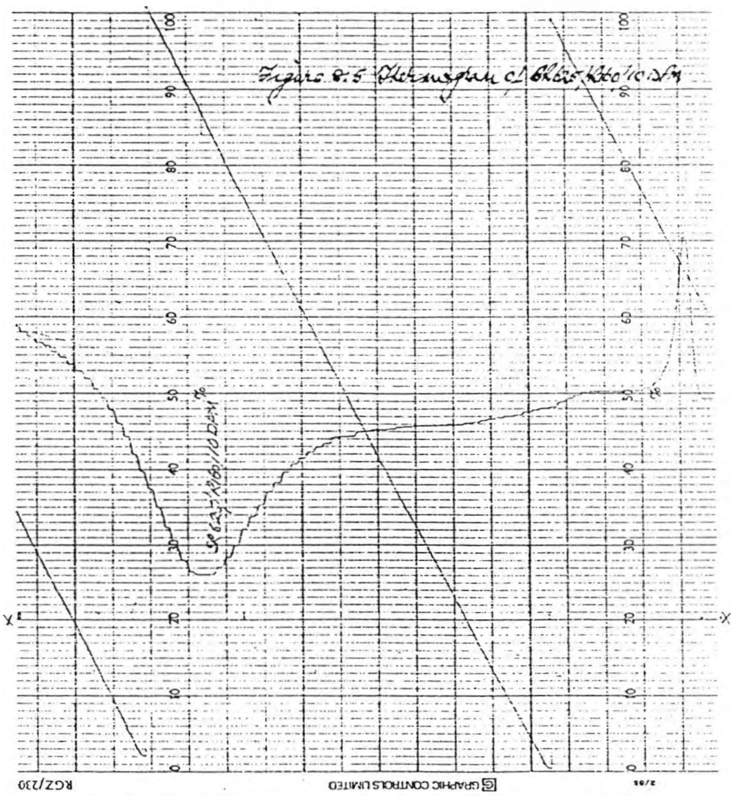


FIGURE 8:5 THERMOGRAM OF SR625/R160/10DPM

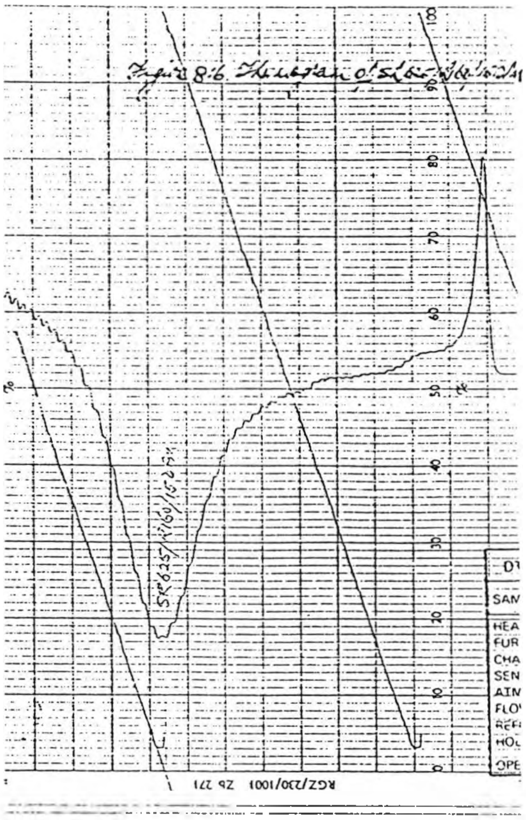


FIGURE 8:6 THERMOGRAM OF SR625/R160/15DPM

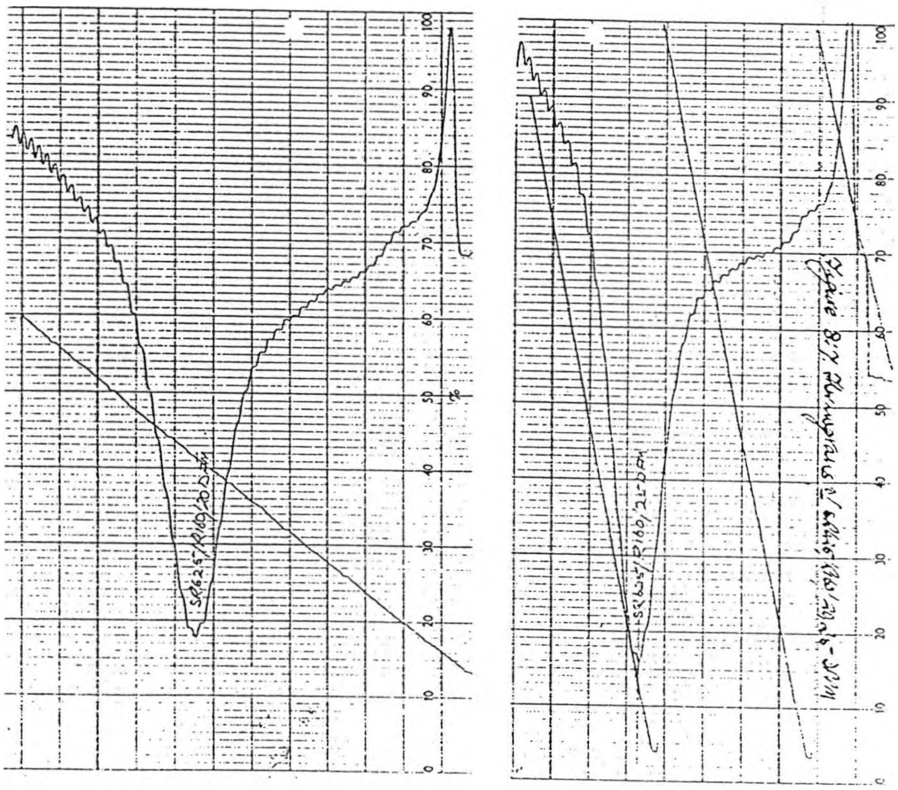


FIGURE 8:7 THERMOGRAMS OF SR625/R160/20, 25DPM

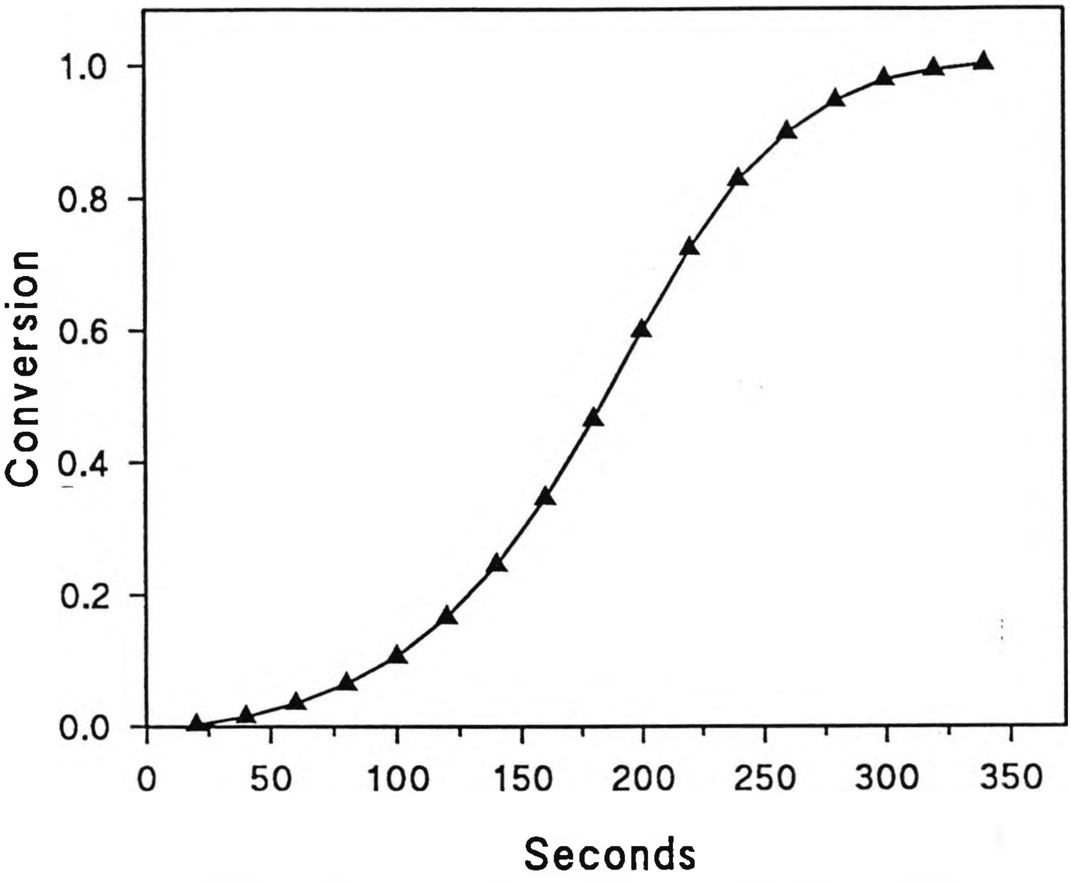


FIGURE 8.8 Conversion versus Time
SR625/R160/5 DPM

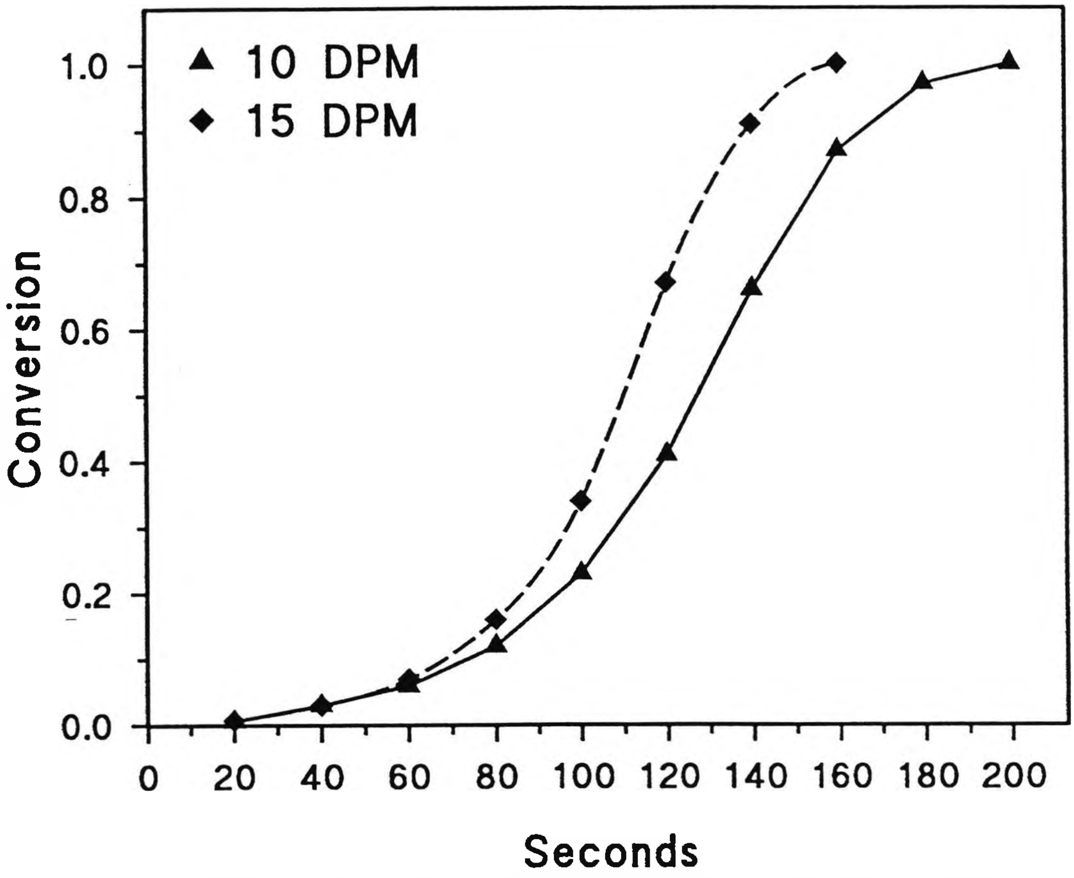


FIGURE 8.9 Conversion versus Time
SR625/R160/10, 15 DPM

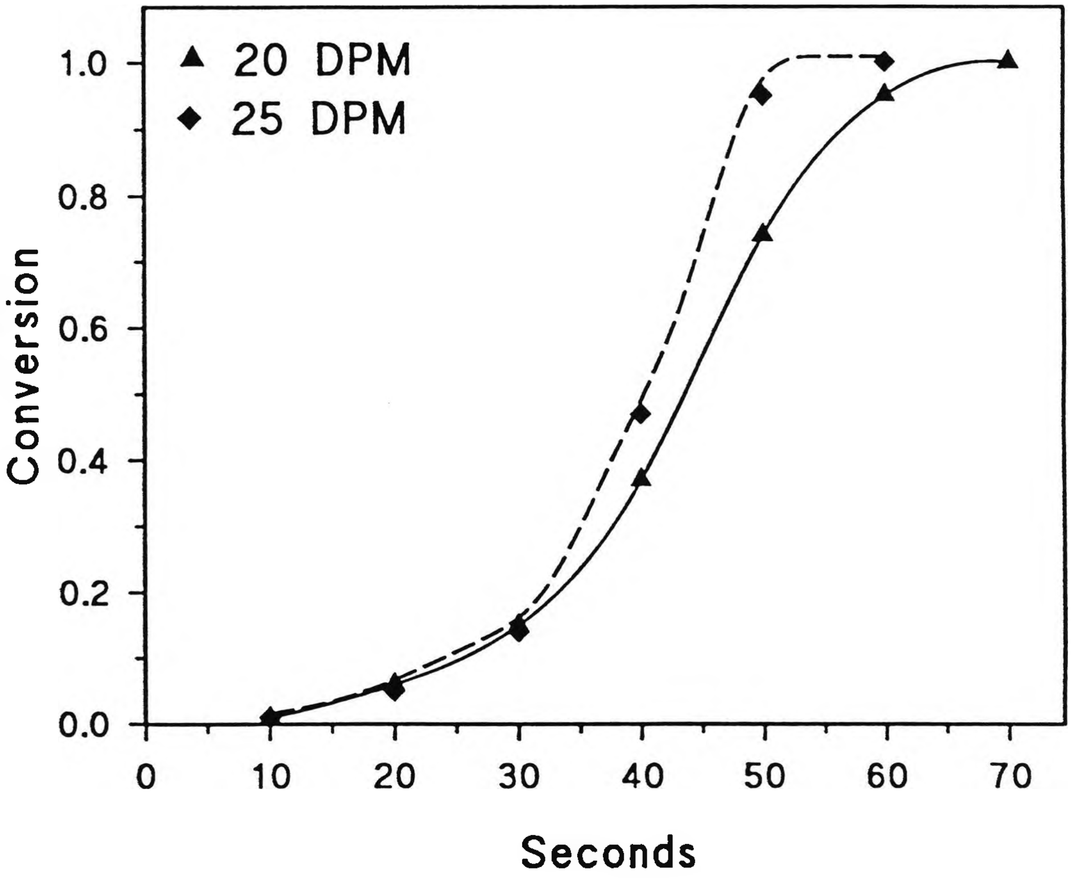


FIGURE 8.10 Conversion versus Time
SR625/R160/20, 25 DPM

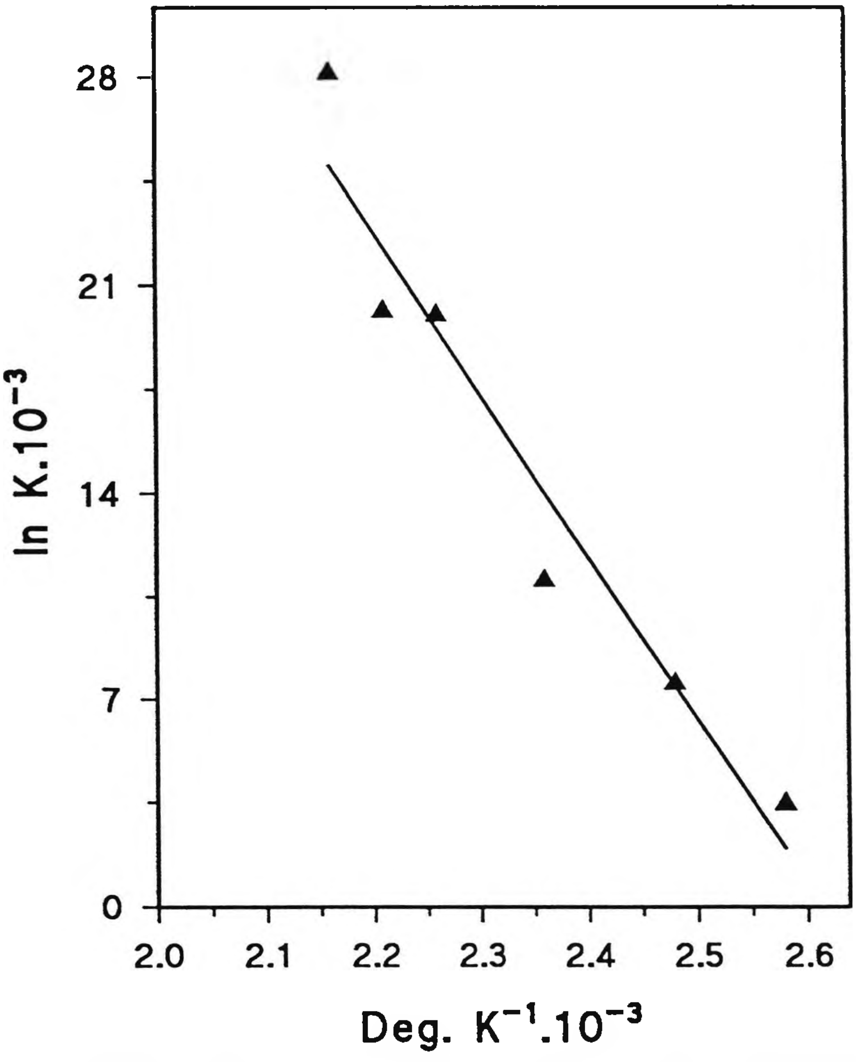


FIGURE 8.11 Calculation of Energy of Activation
SR625/R160/5 DPM

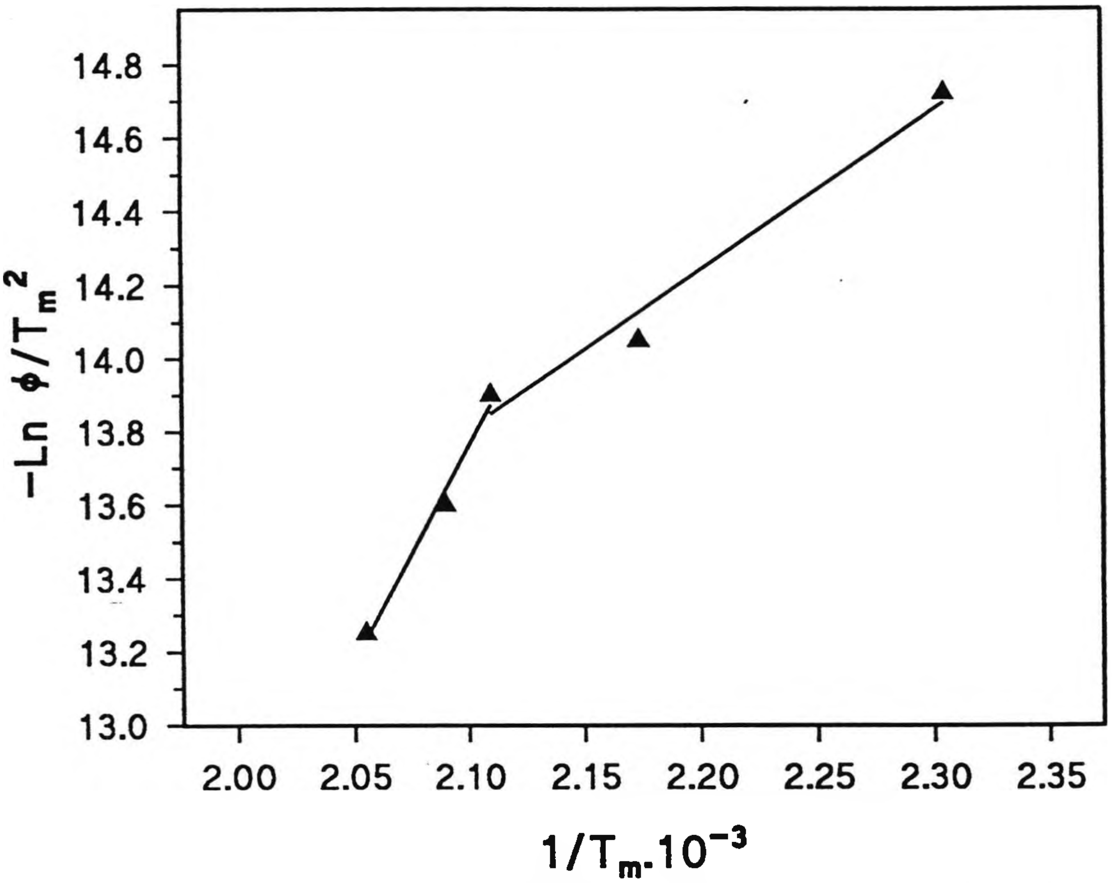


FIGURE 8.12 Kissinger Analysis of SR625/R160 2nd. Set

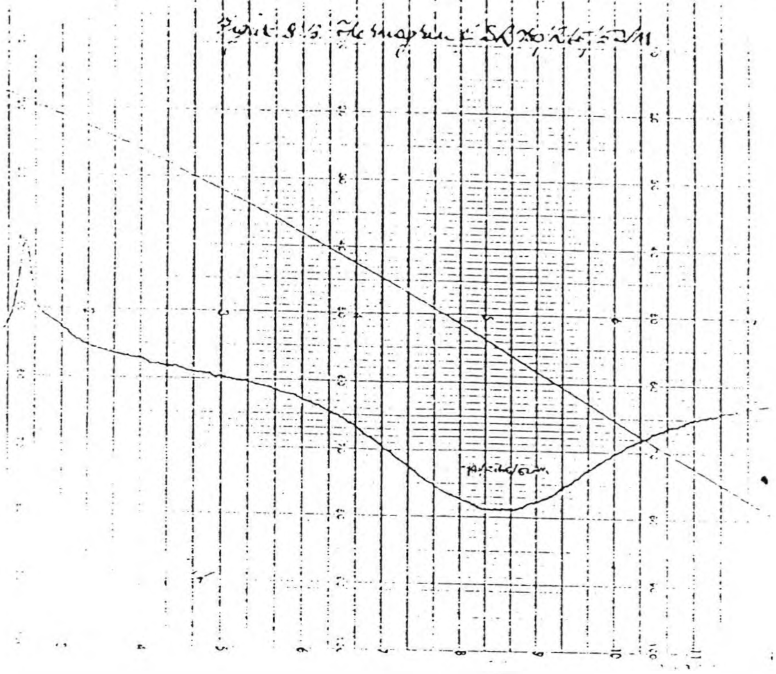
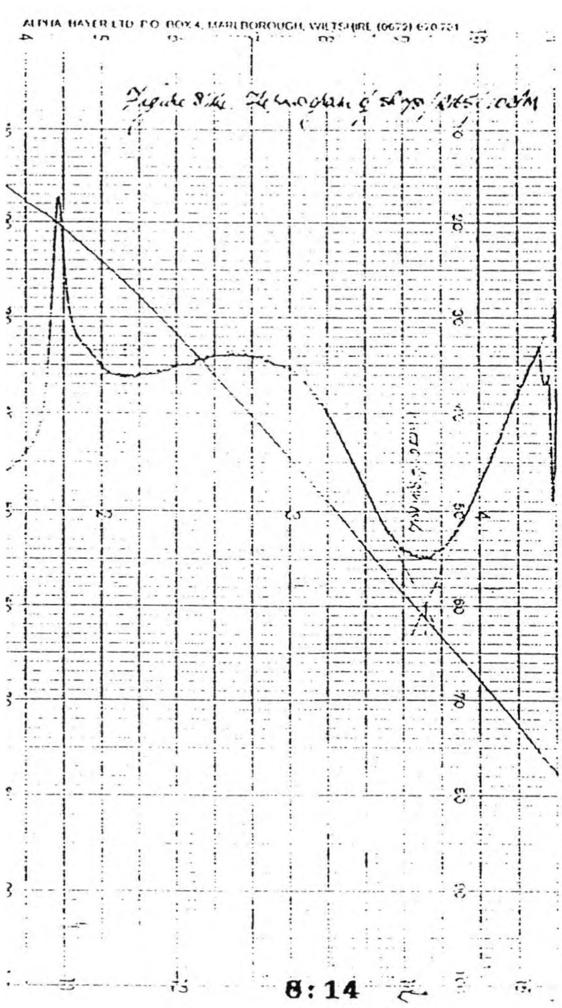


FIGURE 8:13 THERMOGRAM OF SR780/R165/5DPM



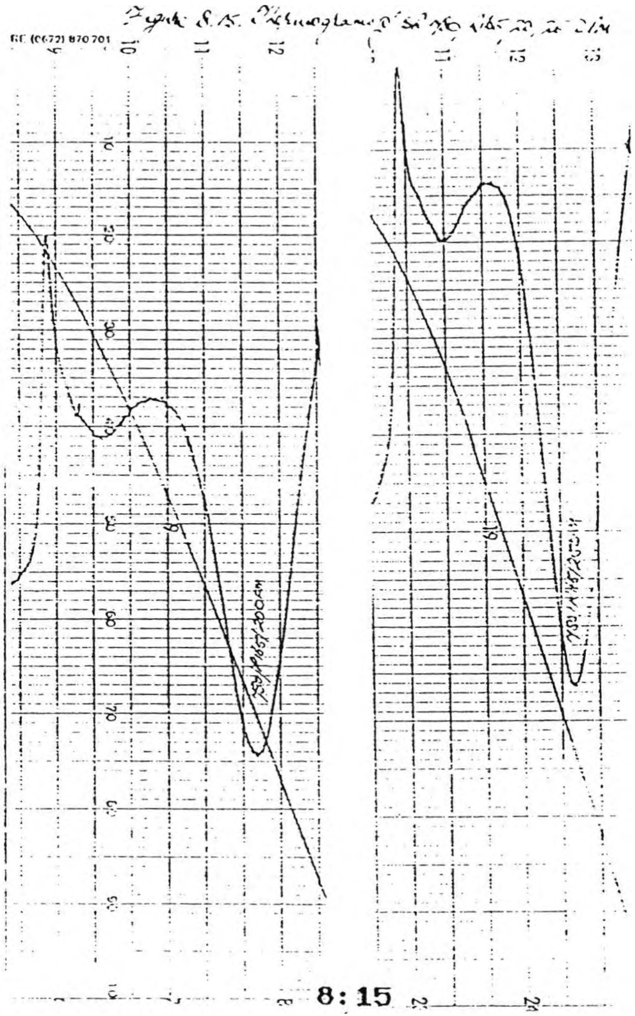


FIGURE 8:14 THERMOGRAM OF SR780/R165/10DPM
FIGURE 8:15 THERMOGRAMS OF SR780/R165/20, 25DPM

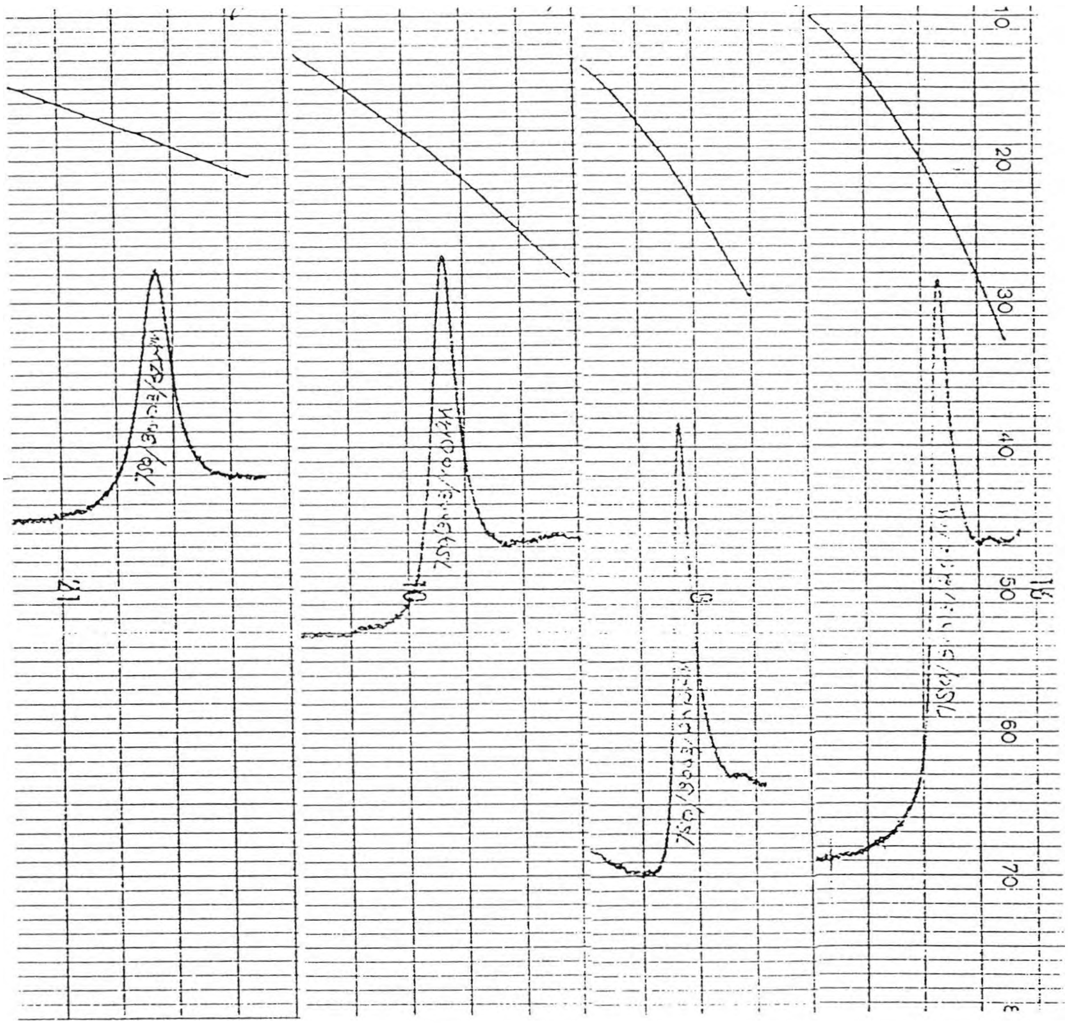


FIGURE 8:16 ENDOTHERMS OF 3003 AT 5, 10, 20 and 25DPM

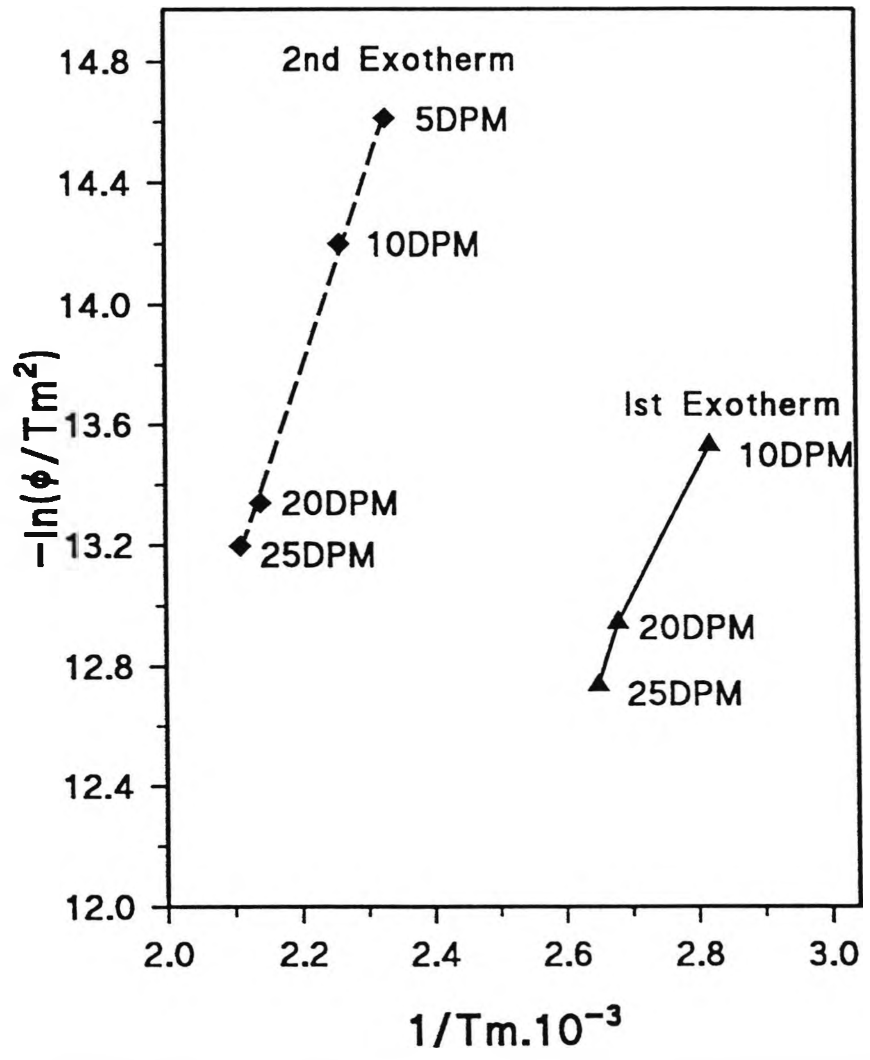


FIGURE 8.17 Kissinger Analysis of SR780/R165 Two Exotherm Set

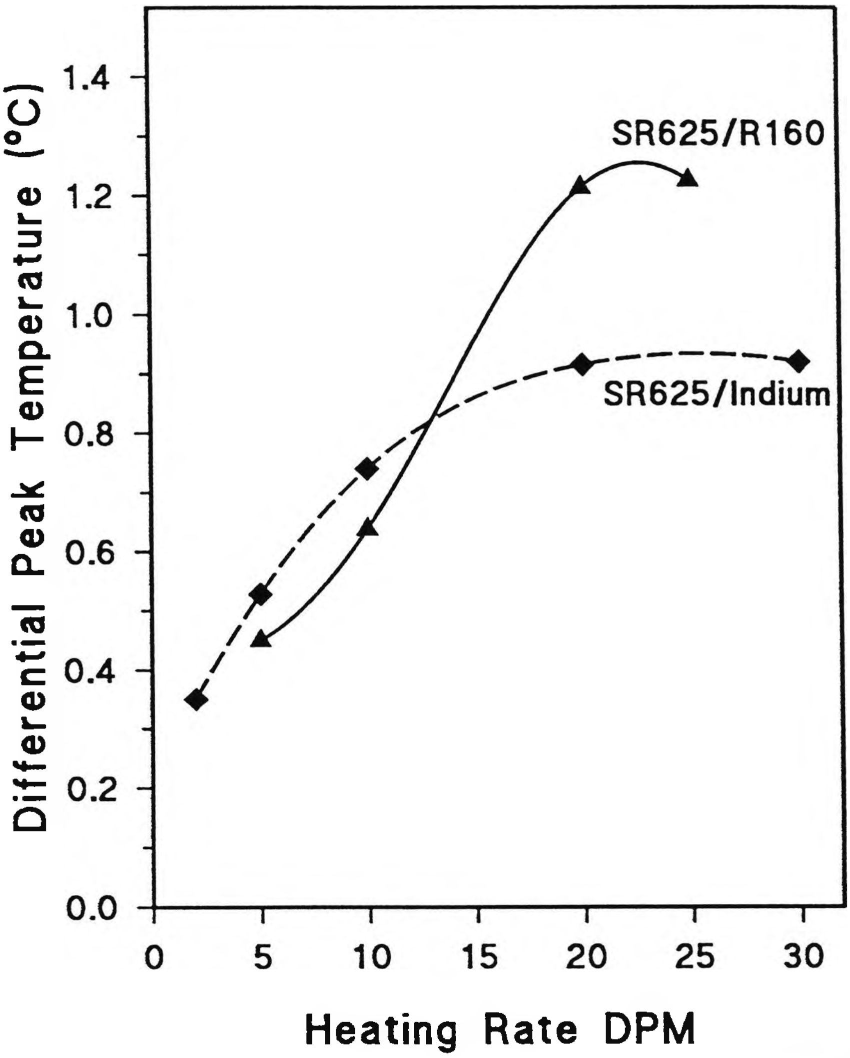


FIGURE 8.18 Maximum Differential Peak Temperature SR625/R160, Indium

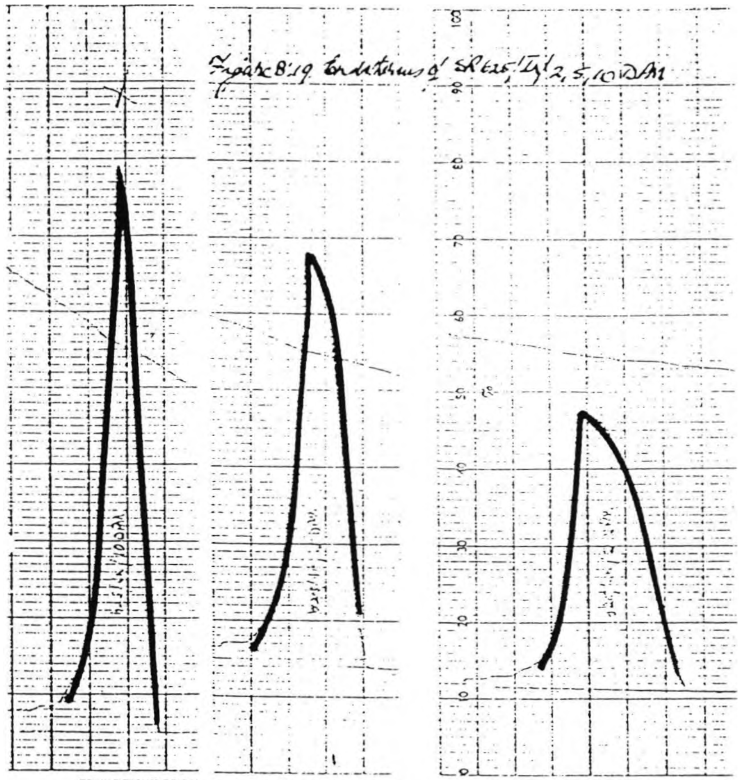


FIGURE 8:19 ENDOTHERMS
SR625/In/10,5,2DPM

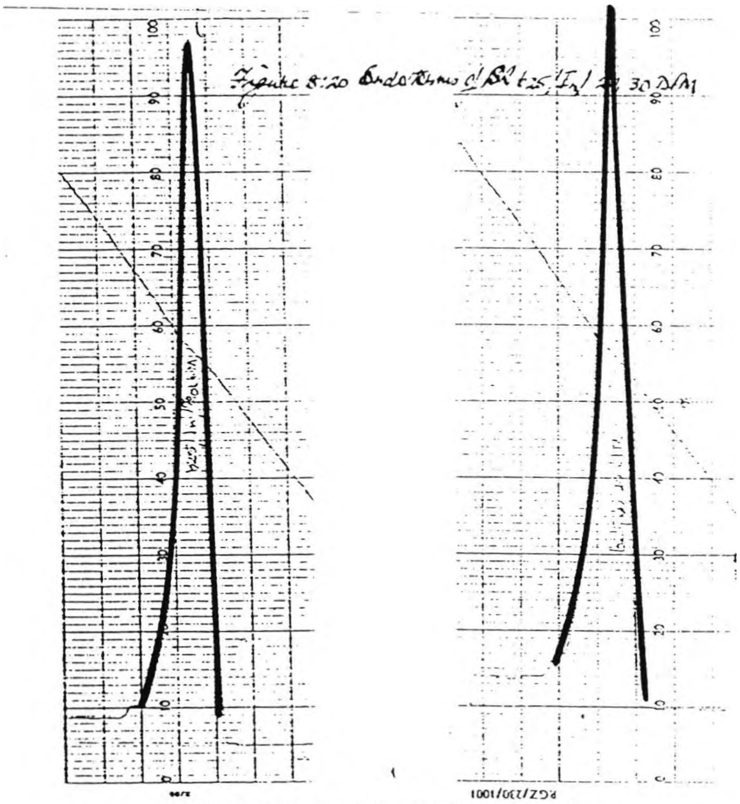


FIGURE 8:20 ENDOTHERMS
SR625/In/30,20DPM

CHAPTER 9

OVEN ISOTHERMAL KINETICS

The most rational way to study the kinetics of a reaction is to subject the reacting mixture to a constant furnace temperature, then the standard kinetic equation can be applied. If one simply heats the mixture to a pre-set temperature one is, of course, passing through all the intermediate temperatures; at each step, the reaction is controlled by a different rate constant, k, which progressively increases; thus, the start of the reaction is no longer applicable for an analysis using the standard kinetic equation, and a true k value cannot be calculated. Furthermore, if a series of pre-set temperatures is being investigated, then each temperature is being reached at a different heating rate, and, as the preceding studies have shown, this means that the reactant mixture attains the individual temperatures at different degrees of conversion, so again one does not have a reliable zero time for the application of the standard rate equation.

This technique, that is, insertion of a sample into a furnace at a pre-set temperature, was examined in Chapter 7, but in the end was considered to be inadequate, principally because the intermediate steps in the reaction are not readily measureable.

Then again, a practical matter in instrumental usage. In the isothermal programme for the Mettler TA3000 at the point of insertion of the sample into the pre-heated furnace, one removes the furnace lid and inserts the loaded sample pan, then closes the lid back on the furnace; this operation must take not more than 15 seconds, to prevent the escape of hot air and cooling of the furnace.

However, the sample pan has a bubble protruberance on the underface of its floor which is meant to engage with a corresponding depression in the furnace floor, and finding this and securing the pan into it is no easy task; the point is, one cannot be sure how much heat is lost or what the true start temperature of the furnace is after this operation, a fumble could make a difference.

The ideal method of study would be an instantaneous elevation to the pre-set temperature, and this of course is not possible. What is needed therefore is some technique that positively minimises heat loss during sample insertion and provides knowledge of the time to attain the pre-set temperature. For this purpose, the following experimental set-up was devised.

An Eurotherm cylindrical furnace was set on its side and a Pyrex glass tube inserted in the cylinder as a lining; the temperature set by means of the furnace control. The sample pans were 3 mm diameter flat-bottom ones as used in the Stanton Redcroft instruments. These were inserted and withdrawn from the furnace by means of a thin stainless steel rod with a loop at one end to hold the pan, so that it could be pushed in and withdrawn by moving the rod, itself running in a cylindrical metal sleeve, close-fitting to prevent imprecision in placement of the pan. The rod carried stops to limit its movement forward, so as to locate the pan in exactly the same place in the furnace at every trial; additionally, it carried a circular heat shield which moved up to the furnace mouth when the rod was moved forward so as to prevent heat loss from the furnace.

The exact position of the pan (and the length of movement of the rod) was established as that position attaining and holding the relevant pre-set temperature. This was determined by placing a thermocouple under the glass tube at about half-way along its length and setting the furnace control to attain and maintain the requisite temperature at that point.

EXPERIMENTAL

MEASUREMENT OF DEGREE OF CONVERSION AT TIMED STAGES DURING THE NEAR-ISOTHERMAL CURE OF AN EPOXY POWDER COATING.

The powder coating chosen for the study was R160.

Samples 6+/-0.1 mg were loaded into pans used in the SR625, and after the furnace temperature had stabilised, placed one at a time in the loop of the positioning rod and pushed into the furnace, with closure of the heat shield. After a timed interval, the rod was withdrawn, the pan lifted out and shock-cooled by placing on a cold, massive iron plate.

It has been noted elsewhere in the Thesis, that a characteristic of industrial oven practice is, that cure continues after removal of the painted product from the oven; the object of the shock-cooling was to eliminate this portion of the cure cycle and obtain a real value for the extent of conversion of the powder in the furnace at the specified temperature. A check established that cooling was effected in 10 seconds.

After each experiment, the positioning rod was moved forward, with the heat shield closing off the furnace mouth, and the temperature allowed to recover before the next experiment, as indicated by the thermocouple thermometer, and only then was the next pan inserted. By this means, the heat loss from opening and closing the furnace was minimised.

As to the uniformity of the temperature to which the sample was subjected, it was noted in a preliminary experiment that a pan loaded with about 6 mg of resin took about 30 seconds to attain the pre-set temperature; this was established in a series of trials with the thermocouple tip dipping into the resin held in a pan pushed along to the correct position in the furnace. This is not an instantaneous rise in temperature, but it is a known value, and could be used in a calculation if required.

Each loaded pan after cooling was placed in an SR625 DSC and analysed at 10 DPM. This gave a thermogram from which the energy change (interpreted as the enthalpy) during cure could be calculated, and translated into degree of cure.

The method used is shown in Figure 9:1. Here, a series of 6 mg samples of powder was taken (not R160) and submitted to the heating/analysis cycle described above. At each treatment time in the oven, the relevant exotherm is of smaller area than the previous one, and each exotherm as a fraction of the initial one from a sample not heated represents (1−α), that is the residue of the active cure, from which the energy change (enthalpy) may be calculated.

This is a more valid method of exploring kinetics than the common practice of slicing up a non-isothermal exotherm into sequential parts and calculating the degree of cure from proportional areas, because in this method, the exotherms relate to a constant temperature and so to constant rate constants.

The data on degrees of cure versus time are given in Tables 9:1 to 9:4 for the four temperatures studied, namely 159°, 163°, 167.5° and 181°. Plots of α versus t are given in Figures 9:2 to 9:5 for the four temperatures.

DISCUSSION AND CONCLUSION

The plotted curves of degrees of conversion against time in Figures 9:2 to 9:5 present a most unusual appearance; they do, in fact show the course of the reaction as a series of steps; this is not so marked for the reaction at 181°, but the rapidity of reaction at this temperature may obscure curve fluctuations.

The first explanation that occurs is, that the result is spurious and arises from random errors in timing or handling the sample, or in not allowing the furnace temperature to equilibrate after an insertion/withdrawal cycle. This explanation, however, seems to be unacceptable, when one considers the uniformity of occurrence of the steps. These are quoted in Table 9:6 as the temperature of commencement of the step and the time of occurrence.

Two sets are given each for the runs at 159° and 167.5°, and one each for runs at 163° and 181°.

If one considers the way in which the steps are characterised, that is by drawing tangents to the two parts of the step and finding the point of intersection, then the agreement can be described as good, for comparison of the first steps with one another and the second steps with one another, for both temperature and time. There is a small tendency for the temperature to move upwards, and the time to move downwards, as the furnace temperature is raised.

Thus, taking mean values, at 159° the steps occur at α0.56 and t6.1 minutes for the first step, and for the three higher temperatures α/t 0.495/4 - 163°, 0.72/4.6 - 167.5°, 0.72/3 - 181°; for the second step the values were, in the sequence as before, 0.8/10.2 - 159°, 0.635/6.3 - 163°, 0.89/9.7 - 167.5°.

Whilst it is true that to obtain the smooth stepped curves, a smooth curve has been drawn through a scatter of individual points, for two curves at least, the points exactly define a stepped line, that is, all the points are on a stepped line. This circumstance, and the uniformity of the steps at the four temperatures surely indicate the real existence of steps in the line and point to some sort of complexity in the course of the epoxy resin cure reaction.

Putting aside for the moment further discussion of this topic, the question arises how the data are to be treated in order to extract quantitative data on reaction parameters?

The solution adopted is admittedly only capable of providing an approximate answer, but hopefully yields some useful information.

First of all, a graph has been made of the logarithm of (1−α) against time, to permit calculation of the rate constant k from:

$$d\alpha/dt = k(1-\alpha)^n$$

$$-\ln(1-\alpha) = kt + C$$

if n is taken as unity.

This equation can be used in the present instance because temperatures are constant.

The graphs are given in Figures 9:6 to 9:9, where 9:6 is from the means of the values for 159°, 9:8 is from the means of the values for 167.5°. The plots do not, of course, give a very convincing straight line. However, to leave the situation at that stage would prevent a discussion of kinetics, so a straight line has been drawn through the points to represent, hopefully, the postulated smoothly running principal reaction.

From this line, it is now possible to calculate the rate constant, with the result shown in Table 9:7. These values, in turn, can be plotted as logarithms against the reciprocal of the temperature, to obtain the energy of activation from:

$$\ln k = \ln A - E/RT$$

The plot is quite a good straight line, and the slope yields a value of 92.6 Kj/mole for the energy of activation, which compares quite well with the value of 88.3 Kj/mole obtained in the instrumental isothermal experiments of Chapter 7. The conclusion must be, that if one wishes to obtain the activation energy, a set of isothermal runs in the Mettler TA3000 will produce an acceptable result, despite the criticisms voiced by the Author originally of the method, but the stepwise method described in this chapter reveals the unexpected behind the conventional.

The most interesting problem posed by the nature of the kinetic curves described in this chapter is, of course, why the curves are stepped.

A completely satisfying and detailed explanation of the mechanism of reaction of epoxy/polyamine blends, even simple ones, has not been provided. As Barton writes (1); complex parallel or sequential reactions requiring more than one rate constant may be involved. Autocatalytic in the beginning, the rate may become diffusion controlled as the viscosity of the system increases; opening of the epoxy ring may be followed by homopolymerisation, with further epoxy reaction with other species to form addition products.

However, some explanation must be attempted, otherwise no progress can be made.

First of all, there is the possibility of the applicability of one of the oscillating reactions described by Atkins (2), including the Lotka-Volterra cycle, the Prigogine cycle and the Noyes cycle.

The Lotka-Volterra cycle is particularly interesting and has the following mechanism;

(a) $A + X \rightarrow 2X$; $d[A]/dt = -k_a[A][X]$

(b) $X + Y \rightarrow 2Y$; $d[X]/dt = -k_b[X][Y]$

(c) $Y \rightarrow B$; $d[B]/dt = k_c[Y]$

where steps (a) and (b) are autocatalytic. The concentration of A is held constant by supplying it to the reaction vessel as needed. B plays no part in the reaction once it has been produced, and so it is unnecessary to remove it. These constraints leave [X] and [Y], the concentrations of the intermediates as variables.

One can tentatively identify A with hydroxyl, since this remains fairly constant, being reacted by amine and also regenerated in the epoxy/amine reaction, then X and Y could be the amines.

The following mechanism based on a series of individual events is now proposed:

(a) There first occurs an energetic reaction of primary amine/cyanogen with epoxy, catalysed by hydroxyl on the epoxy chain (3), the energetics being greater because the alcohol is polysubstituted (4) and related to the structure of the polyamine (5). The epoxy concentration is reduced, the hydroxyl concentration increased, and the primary amine/cyanogen concentration reduced.

(b) The secondary amine, present as such, or formed from the primary amine/epoxy reaction, reacts with residual epoxy and hydroxyl to reduce the epoxy concentration, and both increase and decrease the hydroxyl concentration - this latter being an accelerator. The energetics of this second reaction are less vigorous than the first, hence the existence of the step in the kinetics curve - that is, the reaction slows down from the initial period. But the increasing tertiary amine content tends to produce an increase in the rate again, because tertiary amine is itself an accelerator (6).

We thus have a plausible explanation for the first step in the kinetics curve.

A second step is more difficult to identify.

Some residual epoxy probably remains for reaction with any secondary amine which may remain - and this is now a hindered amine, so steric factors and increasing viscosity may well produce this second step; acceleration beyond this point to the completion of the reaction (and it is not large) may be due to the extra tertiary amine produced. The explanation has to be tentative because an analysis of a mixed powder is so difficult; above all, following the changing concentrations of the three species of amine is particularly difficult, the IR spectra of the three being practically indistinguishable.

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TABLE 9:1
EXAMPLE OF THE CALCULATION OF DEGREE OF CONVERSION TO CORRESPOND TO FIGURE 9:1

Number	Time Minutes	Exotherm Area Mm^2	Fraction of Initial Exotherm $(1-\alpha)$
1	0	1976	1.0
2	2	1682	0.85
3	4	1288	0.65
4	6	891	0.45
5	8	672	0.34

****

TABLE 9:2
KINETICS OF REACTION AT CONSTANT TEMPERATURE
FOUR OVEN TEMPERATURES

Oven Time	Degree of Reaction					
Minutes	Ser.1	Ser.2	Ser.3	Ser.4	Ser.5	Ser.6
1	0.11	0.05	0.16	0.27	0.19	0.10
2	0.17	0.13	0.24	0.31	0.49	0.49
2.5				0.30		
3	0.26	0.26	0.28	0.49	0.45	0.72
3.5				0.64		
4	0.37	0.49	0.45		0.59	0.92
4.5				0.58		
5	0.35	0.47	0.51	0.72	0.73	0.92
6	0.51	0.58	0.52	0.69		
7	0.54	0.59	0.64	0.75	0.80	0.95
8	0.58		0.66	0.78	0.90	
9		0.69	0.68	0.86		
10		0.78	0.83	0.90	0.94	0.95
11				0.90		
12	0.84	0,84	0.91			
14	0.84		0.94		1.00	
16	0.92			1.00		
18	0.92					

Series 1 and 2 at 159°, Series 3 at 163°, Series 4 and 5 at 167.5°, Series 6 at 181°.

TABLE 9:3
POINTS OF INFLECTION

Oven Temperature	Points of Inflection α/time 1st	 2nd
159°	0.59/6.20	0.78/9.8
	0.52/6.0	0.81/10.6
163°	0.495/4.0	0.635/6.3
167.5°	0.69/4.2	0.88/9.2
	0.74/5.0	0.91/8.2
181°	0.72/3.0	

****

TABLE 9:4
RATE CONSTANTS AT FOUR TEMPERATURES

Temperature K	Rate Constant $sec^{-1} 10^{-3}$
432°	2.3404
435	3.0900
440.5	3.7800
453	9.2449

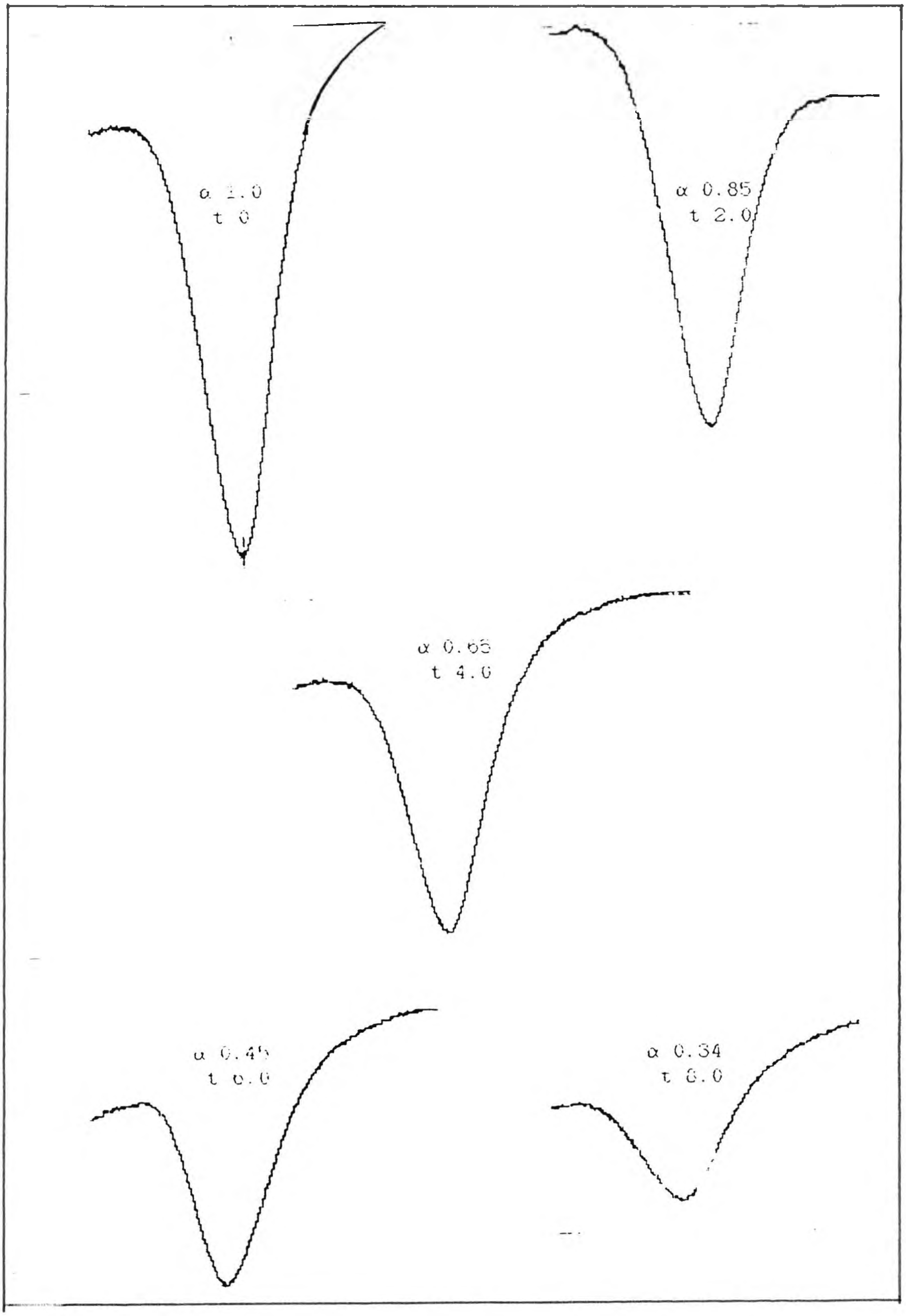
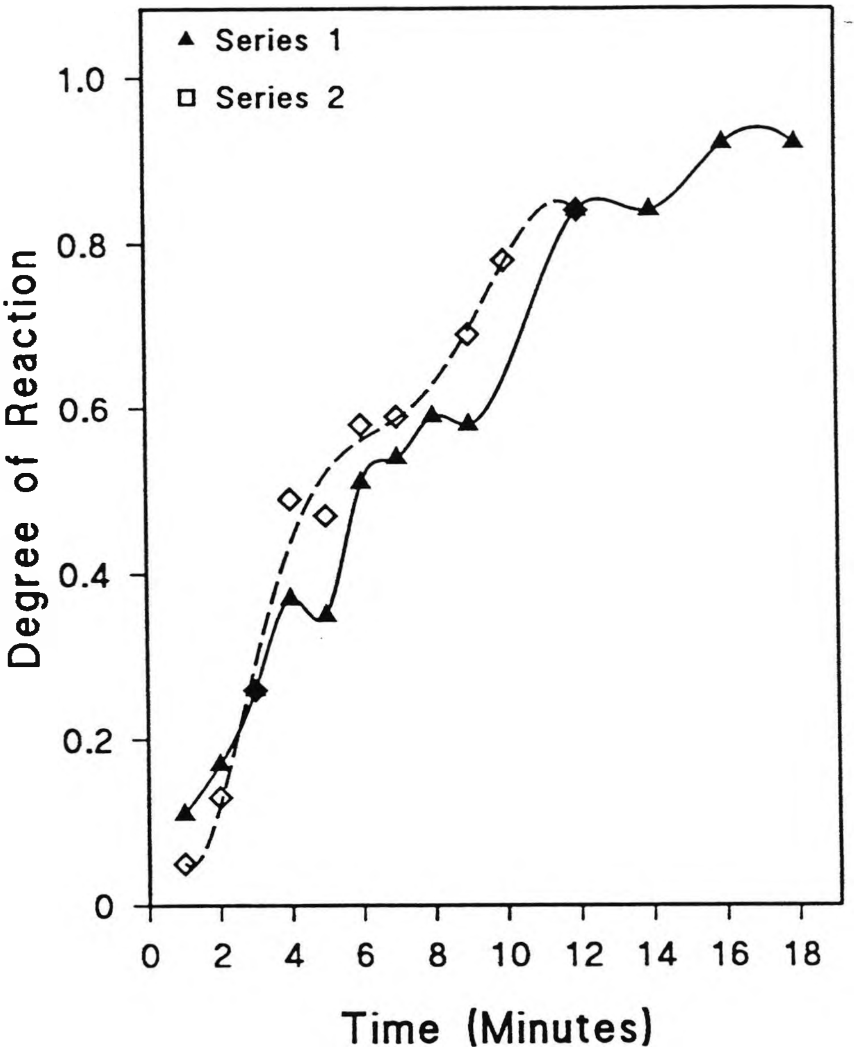


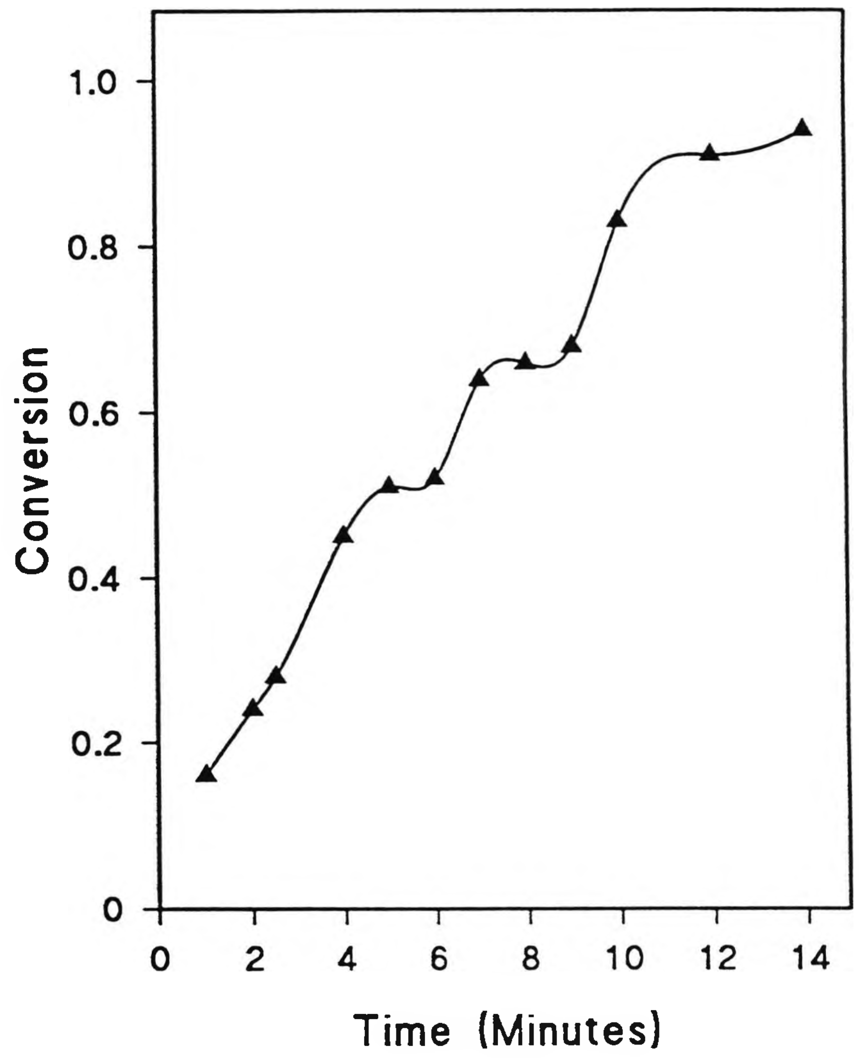
FIGURE 9:1 CALCULATION OF DEGREES OF CONVERSION



Kinetics of Reaction at Constant Temperature

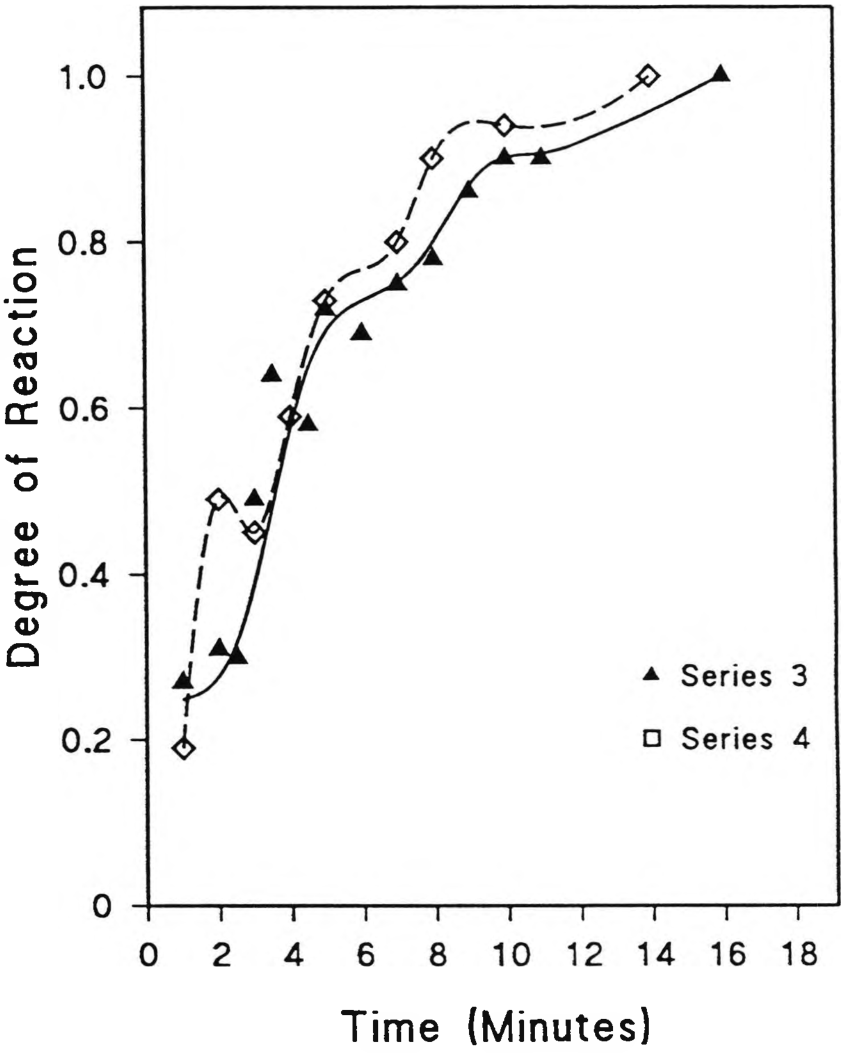
Two Oven Experiments at 159°C

FIGURE 9.2



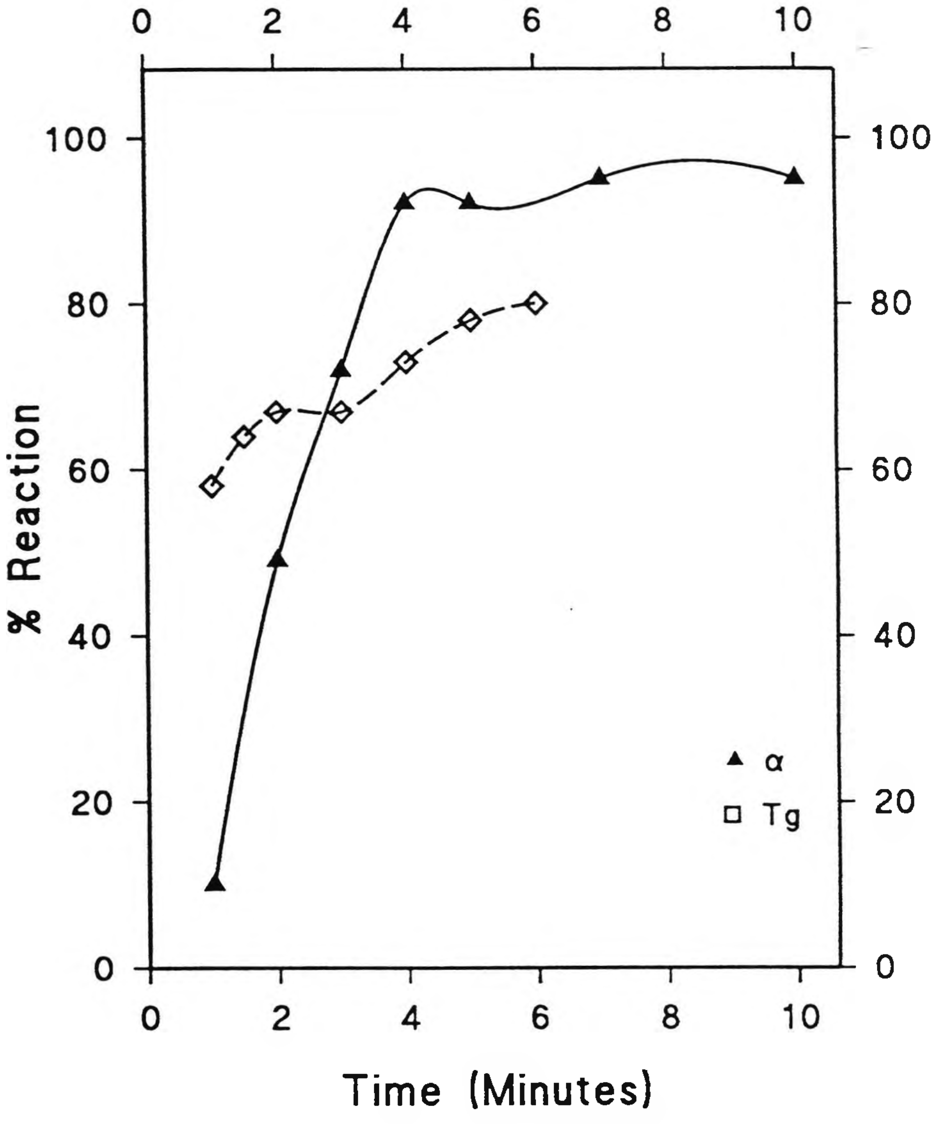
CONVERSION versus TIME at 163°C

FIGURE 9.3



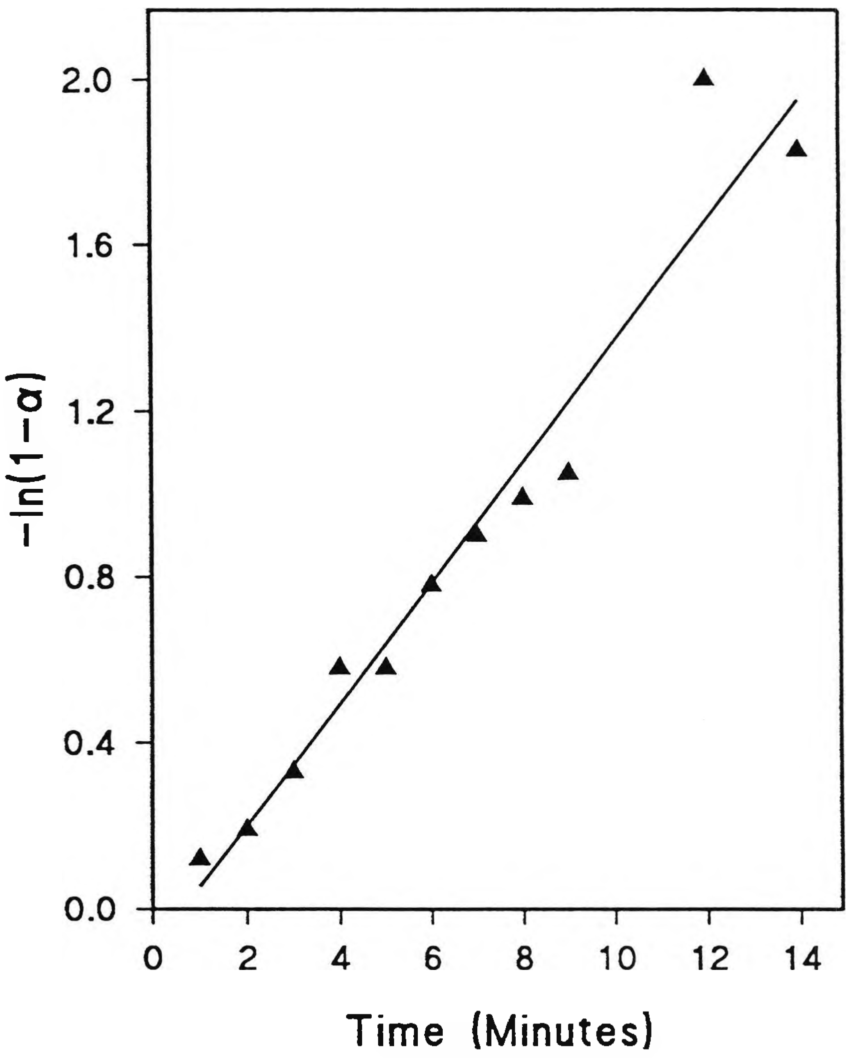
Kinetics of Reaction at Constant Temperature
Two Oven Experiments at 167.5°C

FIGURE 9.4



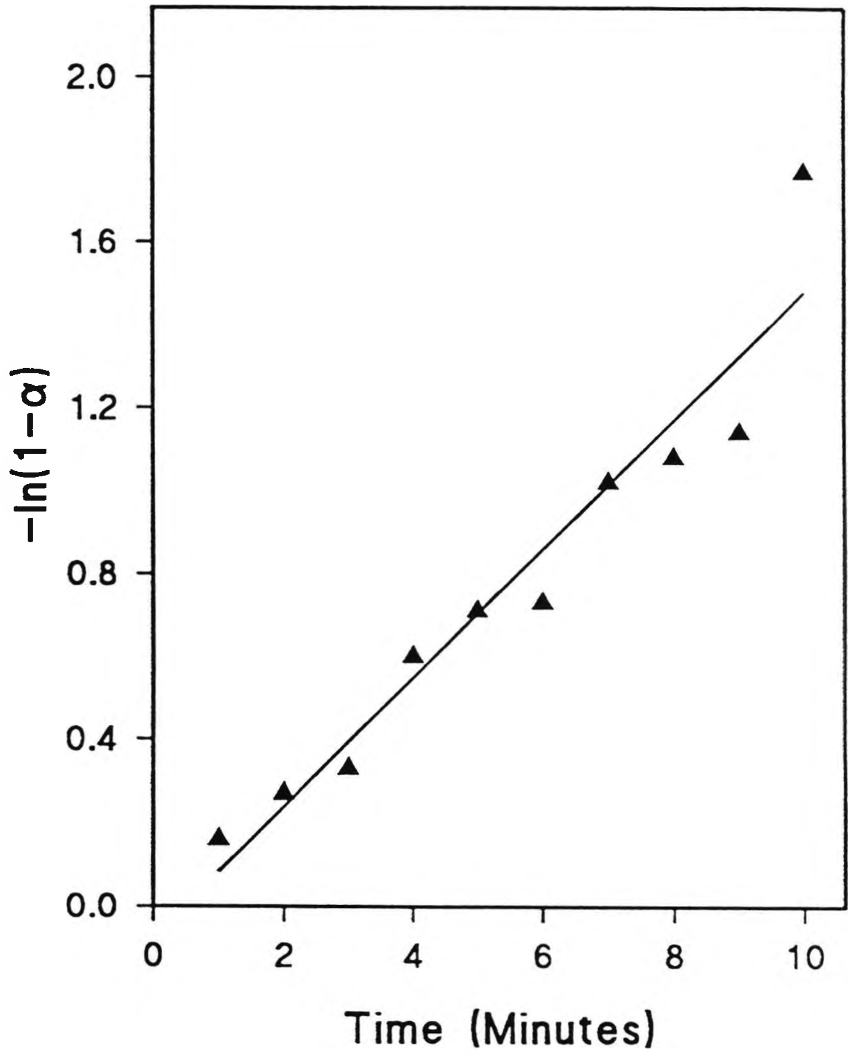
Kinetics of Reaction at Constant Temperature
oven experiment at 181°C

FIGURE 9.5



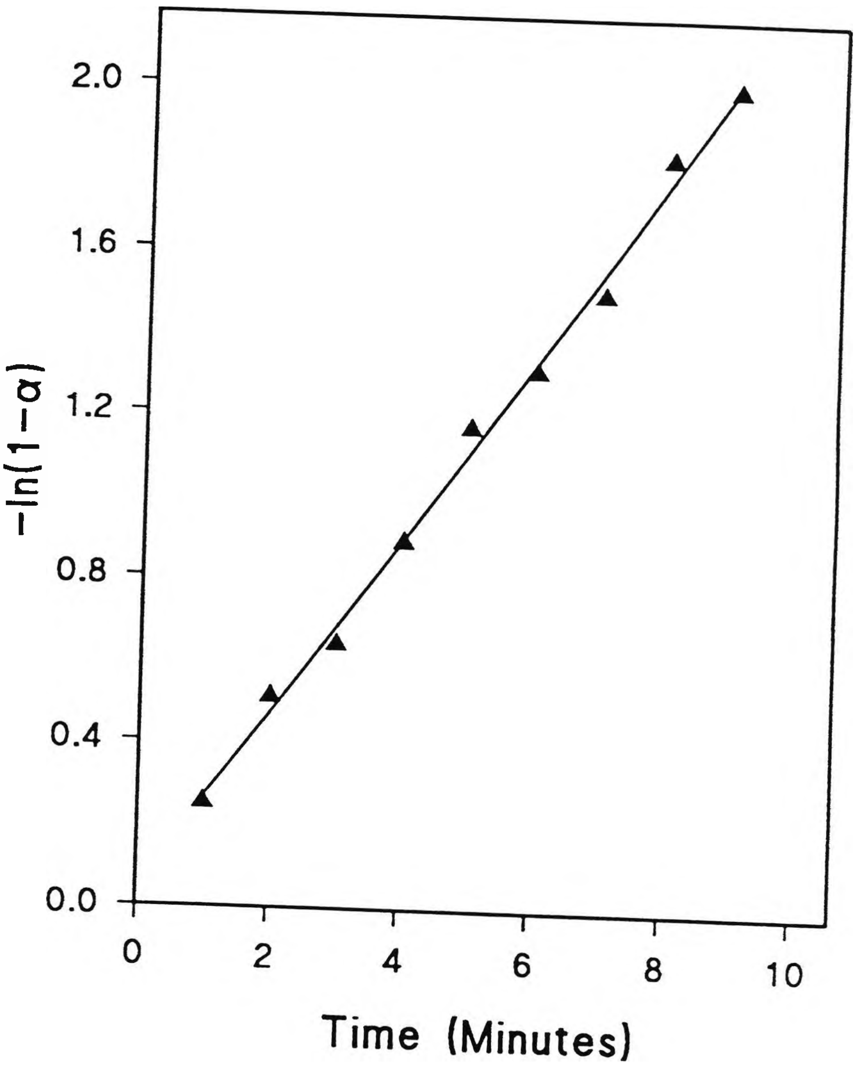
Calculation of k:159°C

FIGURE 9.6



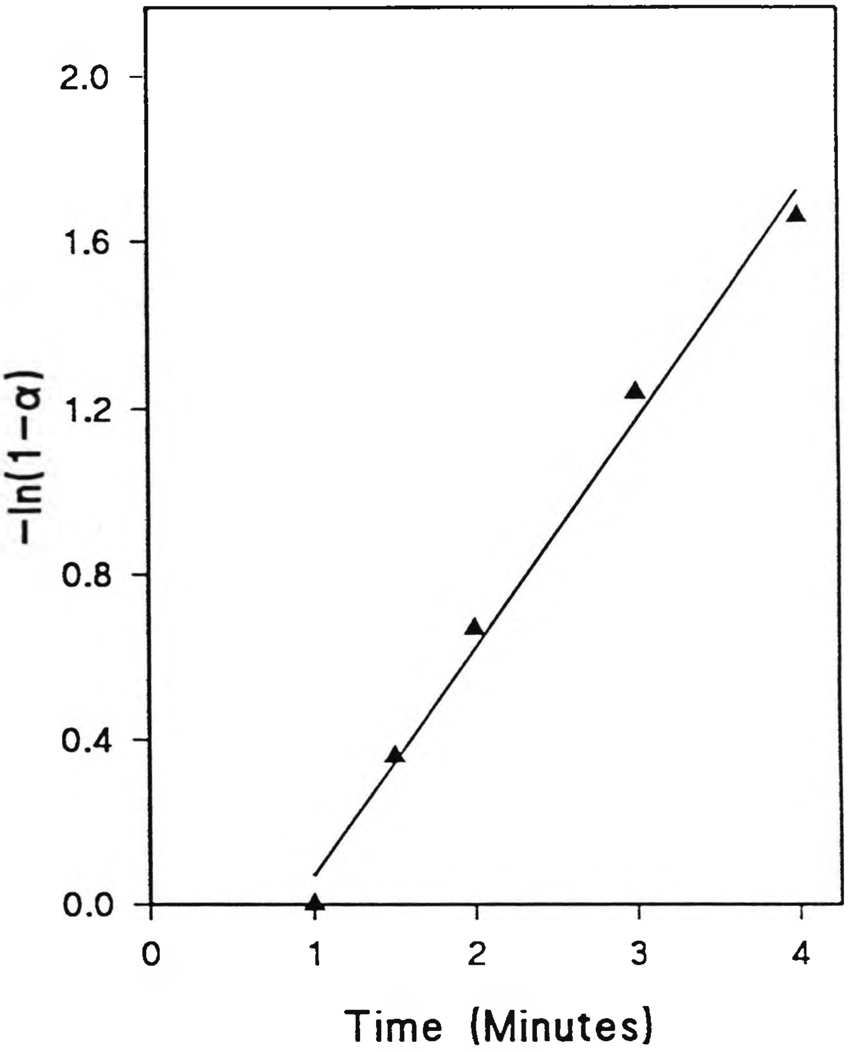
Calculation of k:163°C

FIGURE 9.7



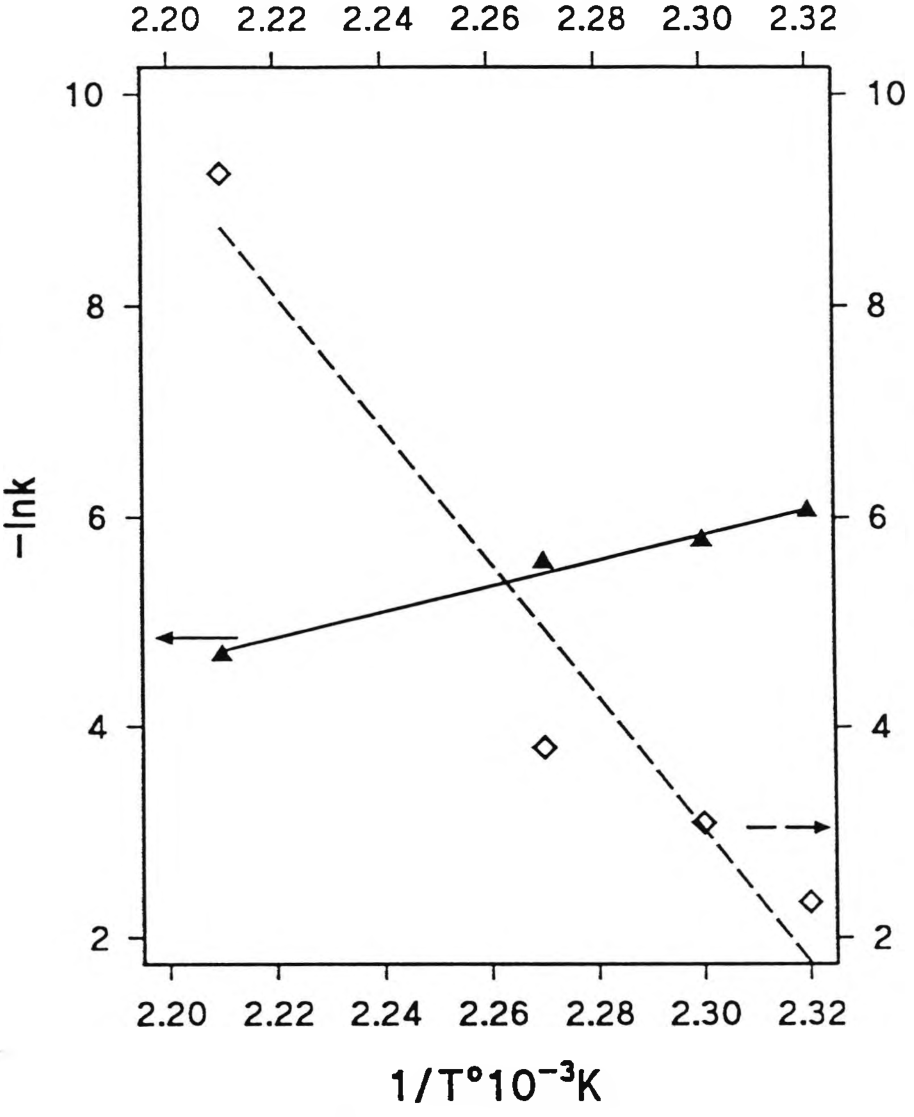
Calculation of k:167.5°C

FIGURE 9.8



Calculation of k:181°C

FIGURE 9.9



Calculation of Activation Energy

FIGURE 9.10

CHAPTER 10

OVEN HEATING STUDIES

The final experiment represented an attempt to relate thermal analysis to practical cure conditions in a constant temperature oven; a common industrial oven of this kind is a camel-back oven where an overhead chain conveys the painted product up an angled entry tunnel into a horizontal tunnel maintained at a constant air temperature, and then out through a downward sloping exit tunnel; by this means, escape of warm air from the central portion is minimised..

The oven temperature is adjusted by varying the heat input, and the time to which the product is submitted to the set temperature is changed by varying the speed of the conveyor chain. A common specification for the cure of a coating is so many minutes at a specified temperature, for example, 10 minutes at 180° is usual for an epoxy powder coating.

The manufacturer of the powder coating will, of course, have established the suitability of this schedule by employing some test indicating completeness of cure of the coating, such as film hardness, solvent resistance, and more frequently nowadays, thermal analysis. Most often, the test is performed by coating a number of thin metal panels with the test material, placing them in a thermostatted oven, and withdrawing them one by one at timed intervals and measuring their properties; this is continued until one panel shows a satisfactory degree of hardness - or whatever is the criterion of cure. The temperature of the panels can be monitored, so that not only the total dwell time in the oven, but also the true time at the set temperature can be monitored for guidance.

However, the product is not invariably a thin metal panel in industry. It may be a much heavier metal sheet, or even a relatively massive casting, and the question may be asked whether the specified x minutes at y degrees cure time is adequate. It might be thought that measurement of surface temperature (relatively easily done) would suffice, provided that the oven temperature was raised sufficiently to attain the desired value. A limitation here is, that heavier gauge means slower heating, and slower heating does not give the same conversion curve as fast heating. In particular, the degree of conversion when the object reaches the uniform temperature tunnel is a function of heating rate, and unless the conversion curve is recorded, this will be missed. Realistically, it is improbable that a production engineer would have at his disposal the means for constructing a conversion curve and so the temperature rise curve in itself would be misleading. The time to attain the set temperature might be the same for all metal thicknesses if the surface temperature were unaffected by the mass of metal behind it, and it is possible that this occurs in infra-red heating, where heating rates are faster than in oven heating.

Another aspect of slow heating rates which may be of importance is, that such slower heating may eventually cure the coating but is certain to reduce the gloss of the powder coating film. This is well known, and occurs because a slow heating rate does not reduce the viscosity sufficiently to produce good flow between the particles of powder which are curing and hardening at the same time. Thus, the curing of powder coatings, on whatever thickness of metal, is not to be recommended in batch ovens, which may cool off substantially between loads. The constant temperature camel-back oven is thus ideal for securing consistency in powder coating film properties, but is not so important for stoving paints in general.

The present study seeks (i) to establish what effect metal thickness has on rate of rise of surface temperature in a constant temperature oven, on the rate of reaction of a standard powder coating, and whether a simple rule relating acceptable cure kinetics to metal thickness can be derived, of use in an industrial situation, and (ii) to study the use of an infra-red oven in which heating rates vary, but not necessarily according to metal thickness.

The infra-red oven used in the latter was the IRIS Mk. 2 of the Electricity Council, constructed in the form of a cube standing on legs. The cube comprised two side walls, a closed back and a pivoted door in the front with a solid floor and a partly open roof. Demountable IR emitter modules can be placed against the side walls and facing inwards, the distance between them, and between each set on the side walls and a centrally placed panel, can be varied. Each module comprises an array of IR emitter units, the total ouput of any module being 6 KW, and the units are switchable in pattern to reduce output and consequently the temperature of the test panel. The latter is suspended between the modules and can be rotated by a motor-driven turntable in the roof.

Three kinds of emitter are available;

quartz envelope short wave bulbs with a maximum emission at 1.2 µm;

medium wavelength silica tubes with a maximum emission at 2.6 µm;

metal sheathed long wave tubular elements with a maximum emission at 3.0 µm;

ceramic long wave emitters with a maximum emission at 4.0 µm.

In the brief study reported here, only the quartz envelope bulbs were used, with 0.8 mm panels coated with black and white epoxy powder coatings, respectively.

It is, of course, well known, that colour is the determining factor in IR heating, and it was of interest to determine what quantitative effect colour had on heating rate and maximum temperature and rate of cure of the powder coatings.

EXPERIMENTAL

MEASUREMENT OF SURFACE TEMPERATURE OF METAL PANELS OF DIFFERENT THICKNESSES IN A CONSTANT TEMPERATURE OVEN

An ordinary (Gallenkamp) laboratory oven was used in the experiments to determine temperature profiles for the three metal thicknesses and also to measure conversion of the epoxy powder coatings. Steel panels were used as substrates, of thickness 0.8, 2.0 and 3.0 mm respectively, and two final temperatures, viz 182° and 146°, though conversions were only measured at 182°.

To obtain temperature profiles, an alumel/chromel thermocouple was stuck to the panel surface, the tip being in contact with the surface and a heat-resistant aluminium-pigmented adhesive tape, applied a little way from the tip, and holding the tip in contact. The thermocouple was taken back to a temperature indicator and outputted to a recorder, giving a continuous reading of the metal surface temperature.

The oven was pre-set to give the 182° or 146° final temperature for all three metal thicknesses. When the pre-set temperature had been attained, the panel with attached thermocouple (at room temperature - usually about 20°) was slid quickly on to a shelf in the oven and the door closed. The recorder then wrote out the temperature profile as the panels heated up.

The profiles at the two test temperatures are shown in Figures 10:1 and the numerical data derived therefrom in Table 10:1. It was thought best to combine the two kinds of profile on one graph to see whether there was any correspondence between them.

The illustrations and numerical data show that the profiles of the 0.8 and 2.0 mm panels are more like one another than either is to the 3.0 mm profile; both the thinner panels heat up faster than the 3.0 mm panel.

A problem is, how to give this difference a numerical value, since the rate is nowhere a constant value. However, the curves look very like exponential curves of a certain kind, and a possible solution is:

$$T=1-A\exp(-kt)$$

$$\ln T=\ln A-kt$$

$$dT/dt.(\ln T)=-k$$

$$1/T.dT/dt=-k$$

$$dT/dt=-kT=k(1-A\exp(-kT))$$

$$\ln(dT/dt)=\ln k+\ln A-kt$$

If the equation is applicable, a plot of ln(dT/dt) against (t) should give a straight line of slope k, which could be used to characterise the curve.

A test was made of this by measuring (dT/dt) as the tangents to the curves at four times, viz 1, 3, 5 and 7 minutes, and the values are reported in Table 10:2. The logarithms are plotted against times and the result shown in Figure 10:5.

The plots are not straight lines, with the doubtful exception of the 3 mm panel at 182°, for which a slope for characterisation of the curve of 0.4702 can be calculated. The other plots are shallow curves; the equation above is not exactly obeyed, and one cannot use (k) to characterise the curves.

However, the curves can to a certain extent be analysed. The three plots for 0.8 and 2 mm panels at 182° and the plot for the 0.8 mm panel at 146° are closely parallel and grouped together and differentiated, as a group, from the plot for the 3 mm panel at 182°. This implies that panel thickness is the most important factor in determining heating rates in the oven, even when different final temperatures are being used.

As a generalisation, then, the 1 mm thickness difference in the 0.8-2mm range has a certain effect, but the additional 1 mm increase to 3 mm has a much more important effect.

This is shown in the illustrations of course, but in Table 10:2 the (dT/dt) values may at first glance seem to be anomalous, in that the thickest panel shows the fastest heating rate. This is explained by the fact that a given time corresponds to different temperatures for the different panels, and if this is rectified by comparison at a fixed temperature, in this case 120° in Table 10:2, then the heating rates will be seen to correspond to the panel thicknesses.

As to the failure of the heating rate to conform to the equation above, this is no doubt because of the complexity of heat diffusion kinetics in a panel.

According to the chapter on Heat Transmission in Kemp's Engineers' Handbook, the mechanism of transmission of ambient heat into a panel is that the surface heats up initially at a rate corresponding to the temperature difference between surface and ambient, this difference continuously decreasing; thus, from the outset the rate is not linear but is likely to be some exponential function. Then at some point, the advancing heat fronts from front and back of the panel will meet and reduce the rate of transfer of heat from surface to interior, and a change in heating kinetics is likely, so a priori there is likely to be an effect from panel thickness, and a simple equation is not applicable for the whole of the temperature profile.

However, in a private communication from research personnel at the Electricity Council, it was suggested that repeated experiments had shown no effect from panel thickness - a circumstance contradicted by the work described in this chapter and by previous extensive tests by the Author.

Perhaps the explanation is, that for thin panels the panel thickness is not important (confirming the Electricity Council assertion), but for thick panels the Kemp mechanism becomes more important.

What is important in the present case is how paint film cure is affected by panel thickness, and experiments were devised to test this, simulating industrial practice.

MEASUREMENT OF CURE KINETICS OF AN EPOXY POWDER COATING IN OVEN AND INFRA-RED HEATING CYCLES

Panels of three different thicknesses were coated with R160 powder coating to a final film thickness of 60 µm and inserted into the laboratory oven; the panels were at room temperature, the oven was preheated to 182°.

After a measured interval, the panel was removed, whilst still hot, and a sample of the coating - softened by the heat - was scraped off; a 6 mg sample was cut, weighed, and placed in a thermal instrument pan for analysis. The process was repeated at progressively greater intervals on freshly prepared panels until a sufficient number of experimental points had been obtained.

The results in terms of fractional conversion against time are given as numerical data in Table 10:1 and as plots on the relevant temperature profiles in Figures 10:2 to 10:4.

The data represent fractional conversion against time for three different, non-linear heating rates. The plots are closer together for the 0.8 and 2 mm panels and different from the plot for the 3 mm panel - confirming that panel thickness has an effect on film cure

. To find a single figure to quantify this difference is again difficult, so an empirical analysis is made.

The most important figure from a practical point of view is the time to produce complete cure, usually determined in a physical test open to wide variation. In thermal analysis, theoretically complete cure is at infinite time, and one is often not sure that the last specimen, assumed completely cured, is not in fact giving a slight perturbation to the recorder line, or in fact, if the line is perfectly smooth, one has not over-shot the point of complete cure by an uncertain margin, so the safest procedure appeared to be to take the time to attain 0.9 fraction conversion, which can be immediately read off from the (α) versus (t) plot.

In addition, the oven was set for 182°, so the time to attain this temperature was of interest, indicating how long the material was at a constant final temperature. The attainment of this final temperature is a little difficult to fix accurately because of the shallow slope of the temperature line as it approaches 182°, so as a useable compromise a temperature of 180° was selected for the measurement.

Finally, it was of interest to establish whether a more rigorous analysis of the thermal analysis curve could be made to obtain a figure for the effect of panel thickness. This was done by measuring the slope of the curves at three different temperatures, viz 157°, 172° and 178° and plotting the ($d\alpha/dt$) values at each temperature against the conversions (α) for each panel thickness to permit, perhaps, calculation of a set of rate constant values, since in:

$$d\alpha/dt=k(1-\alpha)^n$$

for any one temperature, k is a constant, and should be calculable from the slope of ($d\alpha/dt$) versus ($1-\alpha$) if (n) is taken as unity. These calculations were made.and the results plotted.

The plots were totally uninformative and could not be interpreted as providing values for k and n; they were not linear. The reason probably lies in the inaccuracy of measurement of degree of conversion; this arises from the method of the experiment, principally the uncertain delays in handling, inserting cold panels, removing hot panels which were difficult to hold and manipulate, and cutting off the film, which again was not easy to do. The conversion values quoted probably represent the limits of tolerance. However, the thinner panels are quite distinctly different from the 3 mm panel. From Table 10:3, the simplest measurement and probably the most informative is the time to reach 0.9 conversion, because this is what the practical production engineer would most want to know, and it is clear that panel thickness does have a systematic effect because the 3 mm panel takes roughly 40% longer than the thinner panels to attain this degree of conversion. For real practical use, it would be helpful if a simple relationship could be shown to exist between time to cure and panel thickness. A plot has been made of these variables in Figure 10:6 which shows them to lie on a curve.

On the available data, interpolation between 0.8 mm and 3 mm is possible, and perhaps some moderate extrapolation also. The curve is a further illustration of the fact that panel thickness does affect cure kinetics.

It would be valuable if one could select a heating rate in thermal analysis which gave the same result as an oven run, despite the fact that in thermal analysis one uses a constant heating rate and an oven operates a continuously decreasing one. Of course, if a thermal analysis instrument were sufficiently sophisticated, one could envisage programming it to give the same temperature profile as an oven and therefore all the requisite information for a cure cycle in the oven. This is not yet possible, to the knowledge of the Author, at least, and another approach is necessary.

The new approach attempted in this work is shown in Figure 10:7, with numerical data in Table 10:4. In Figure 10:7, the reaction profiles for the 0.8 and 2 mm panels are drawn and at five selected degrees of conversion, namely 0.2, 0.4, 0.6, 0.8 and 1.0, bars are drawn across defining the times to attain those degrees of conversion at these heating rates, namely 5, 10 and 15 degrees per minute (DPM); the data come from Chapter 8. The intention was, to note whether the profiles would pass through the bars at approximately the same DPM at all degrees of conversion, so defining the one that could be used to give, within limits, the actual conversion profile; the thermogram so obtained, together with those relating to the other metal thicknesses, could permit of the extraction of kinetic data in a way not possible with the actual conversion profiles themselves, always granted that actual and match thermograms did not deviate so much as to render the exercise pointless. As can be seen in Figure 10:7, the 0.8 mm profile always falls within the 5-10 DPM limits, the 2mm profile falls just outside, the 3 mm profile completely outside.

The actual DPM values on which the 0.8 mm profile falls are given in Table 10:4. On the whole, the values are not so different at each bar, and the mean value of 8.7 DPM would give a reasonable result, as is indicated by the "reconstructed" profile drawn at 8.7 DPM through each bar-shown as a dotted curve.

The reconstructed curve at 8.7 DPM is quite a good fit for the 0.8 mm profile, except at the final stage, when approaching full cure, when it would give a value of 14 minutes against the original of 16 minutes. This is surely an acceptable result, and if we take 0.9 conversion as the termination, the result is even better. The profiles at 2 and

3 mm cannot be so well matched, so the prospect of extracting kinetic data from a set of model profiles is not realisable in this case, at least.

The final subject to be dealt with is infra-red cure of an epoxy powder coating on panels where two coatings were examined, one white and the other black.The method has already been described.

Numerical data on temperature profiles are given in Table 10:5 and on cure in Table 10:6, the corresponding plots in Figures 10:8 and 10:9

Figure 10:8 shows the remarkable effect of colour on heating rates, and this at an emitter:panel separation of 35 cm; any nearer approach and the black coating would be unmeasureable. The white coating attains 200° in 200 seconds; the black coating in 40 seconds. The test of exponential fit was applied to the white coating to see whether the profile would fit

$$\ln(dT/dt)=-kt$$

and the result is shown in Figure 10:10. The plot is more a shallow curve than a straight line, and it cannot be said that the equation is obeyed. IR heating was thought to be more likely to fit the equation than oven heating, because of the difference in emitter/ambient temperatures in the two cases. In oven heating, the ambient/panel surface temperature difference is about 200° and continuously diminishing; in IR heating, the quartz bulb filament temperature is at about 1500°, giving a temperature difference of about this figure, and whilst this also diminishes continuously, one would not have thought that the effect would have been as great as in oven heating.

Colour also has a dramatic effect on cure kinetics of the epoxy coating applied to the 0.8 mm panels used. The data are given in Table 10:6 and the conversion profile in Figure 10:9.

First of all, there are differences in the times to cure. For the white panel, the time is 5 minutes; for the black, 1.5 minutes. What is most interesting is, that the conversion profiles in no way resemble those from oven heating, and are indeed not easy to interpret.

The oddity arises in that the plots continuously rise, there is no reduction in cure rate as the end approaches, as would be expected from adherence to first order kinetics, and as is observed in thermal instruments and in oven heating. A much more detailed study is required before explanation could be offered.

A further point to note is, that if the 5 minute white curve is correlated with the extrapolated temperature profile, cure was achieved at about 220°, whereas correspondingly the black attained cure at 260°, with imminent danger of flaming from volatiles released by the heat in interaction with ambient oxygen.

Reverting to the reaction profiles of Figure 10:9, the 5 - 15 heating rate bars have been drawn in as for oven heating to show that for the white coating a not very good simulation could be obtained in a thermal instrument at about 13 DPM; the final cure would not correspond. For the black coating, a run in the 20 - 30 DPM range would cover some part of the cure.

DISCUSSION AND CONCLUSION

The object of the work reported in this chapter was to simulate industrial practice in oven heating as well as, if possible, to confirm whether metal thickness had any effect on heating characteristics, the magnitude of any side effect, and to establish further whether differences in heating characteristics were reflected in differences in rates of cure of powder coatings applied on different thicknesses of metal.

As to the effect of metal thickness, panels 0.8 and 2 mm thick show no significant effect on heating rate in a constant temperature oven, but then a 3 mm panel does differ from the thinner ones, so above 2 mm, thickness does begin to have a noticeable effect. The heating rate curves do not permit of a simple mathematical analysis, which would facilitate a description of these effects.

Paint coatings applied to these panels also show an effect from metal thickness, although experimental difficulties prevent precision in analysis. There is no doubt, however, that the thickest panel, at 3 mm, gives a much slower rate of cure to the applied coating than the thinner panels.

Infra-red cure of black and white powder coatings demonstrates the importance of colour in determining the rate of heating and the rate of cure; black heats up much faster under a quartz bulb, and cures much faster. The reaction curve does not then appear to correspond to first order kinetics.

TABLE 10:1

TEMPERATURE AND REACTION DATA

OVEN HEATING TO 146° AND 182°

THREE PANEL THICKNESSES

TIME	OVEN at 146°		[----------OVEN at 182°				-----------]	
	0.8 mm Panel		0.8 mm Panel		2.0 mm Panel		3.0 mm Panel	
	Temp.	α	Temp.	α	Temp.	α	Temp.	α
0	35°		20°		20°		20°	
1	82°		116°		116°		70°	
2	108°		145°		146°		105°	
3	122°		159°	0.07	160°	0.06	130°	0.05
4	131°		168°	0.12	168°	0.10	145°	0.075
5	137°		173°	0.20	174°	0.15	156°	0.10
6	140°		177°	0.35	177°	0.225	163°	0.14
7	143°		179°	0.46	179°	0.325	169°	0.19
8	144.5°		180.5°	0.58	180°	0.43	173°	0.27
9	145°		181°	0.68	181°	0.535	176°	0.36
10	146°		182°	0.785	182°	0.625	178°	0.45
11				0.86		0.71	179°	0.54
12				0.92		0.79	180°	0.625
13				0.96		0.86	180.5°	0.71
14				0.985		0.91	181°	0.90
15				1.0		0.95		
18						1.0	182°	
20								0.96

****

TABLE 10:2

OVEN HEATING RATES

TIME MINUTES	dT/dt VALUES 146°	 182°		
	0.8 mm Panel	0.8 mm Panel	2.0 mm Panel	3.0 mm Panel
1	34.50	41.70	33.30	45.71
3	11.04	12.41	8.33	18.72
5	4.66	5.39	3.81	
7	2,55	2.00	1.75	4.60
9				2.12
At 120°	12.0	50.0	40.7	26.5

****

TABLE 10:3

ANALYSIS OF THE CONVERSION PROFILES OF FIGURES 10:2 to 10:4

TEMPERATURE	0.8 mm Panel	2.0 mm Panel	3.0 mm Panel
157°			
(1−α)	0.925	0.935	0.90
dα/dt. 10 sec .	0.77	0.53	0.50
172°			
(1−α)	0.80	0.80	0.75
dα/dt. 10 sec .	1.6	1.4	1.3
178°			
(1−α)	0.535	0.38	0.445
dα/dt. 10 sec .	2.3	1.5	1.5
TIME to 0.9 α Min.	11.6	13.7	17.5
CONVERSION at 180°	0.58	0.46	0.70

****

TABLE 10:4

COMPARISON OF DSC AND OVEN HEATING CONVERSION RATES

FRACTIONAL CONVERSION		DSC HEATING RATE to EQUALISE CONVERSIONS DPM
0.2		8.8
0.4		9.8
0.6		8.4
0.8		7.9
	MEAN	8.7

****

TABLE 10:5

TEMPERATURE PROFILES OF WHITE AND BLACK COATINGS

IR SHORT WAVE EMITTER : 35 cm SPACING

R160 : 0.8 mm PANEL

TIME SECONDS	TEMPERATURE WHITE	TEMPERATURE BLACK
0	25°	25°
20	72°	150°
40	108°	200°
60	130°	
80	148°	
100	162°	
120	173°	
140	160°	
180	195°	
200	200°	

TABLE 10:6

CONVERSION PROFILES OF WHITE AND BLACK COATINGS

IR SHORT WAVE EMITTER : 35 cm SPACING

R160 : 0.8 mm PANEL

TIME SECONDS	CONVERSION	
	WHITE	BLACK
30		0.23
60	0.07	0.47
90		1.0
120	0.11	
150	0.75	
240	0.85	
300	0.96	

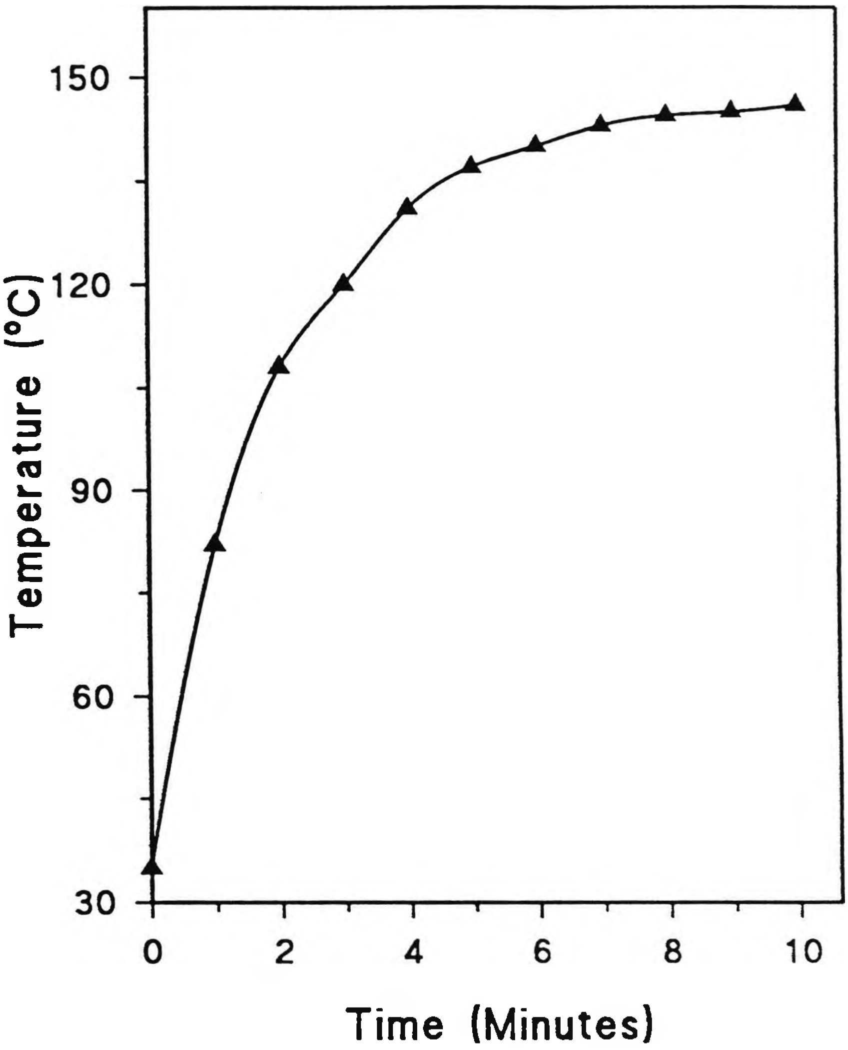


FIGURE 10.1 Temperature Profile
0.8 mm Panel/146°C

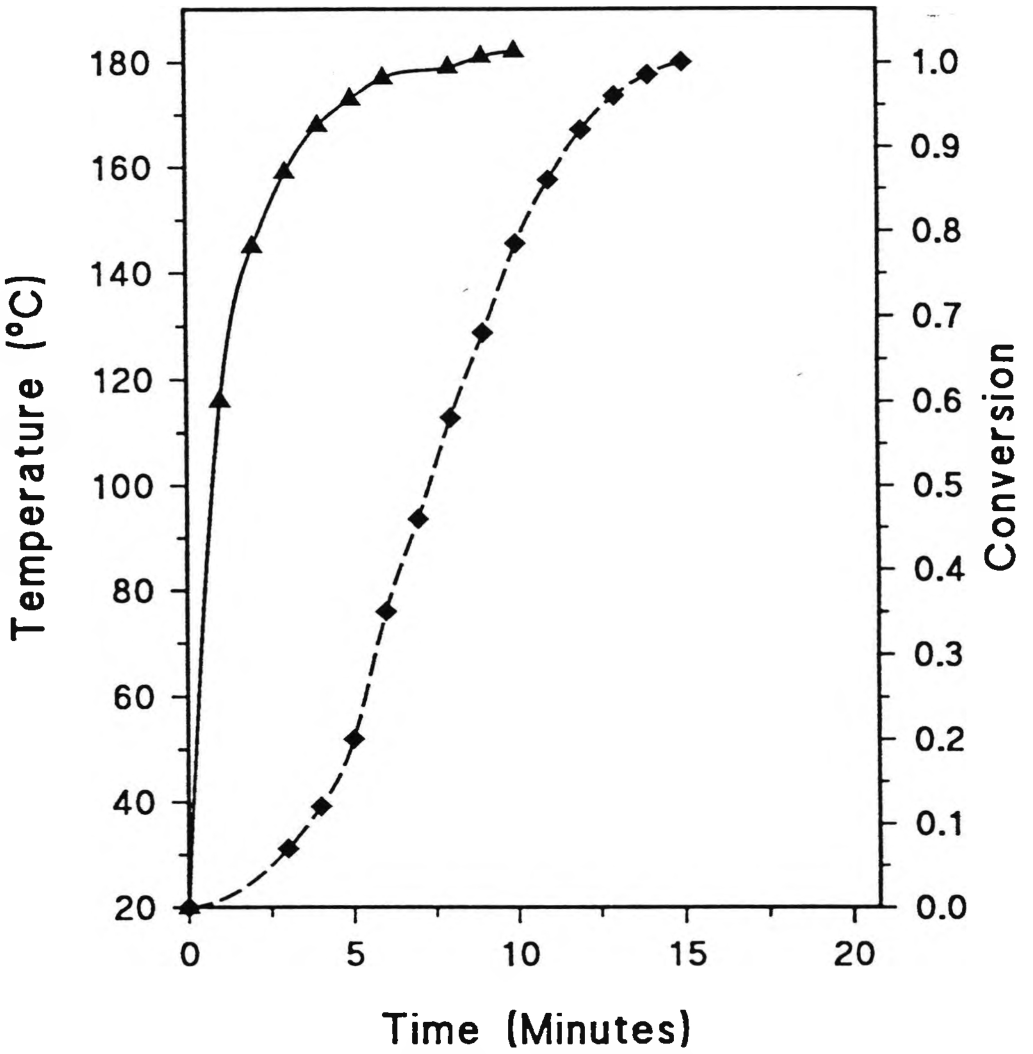


Figure 10.2 Temperature and Conversion Profiles
0.8 mm Panel/182°C

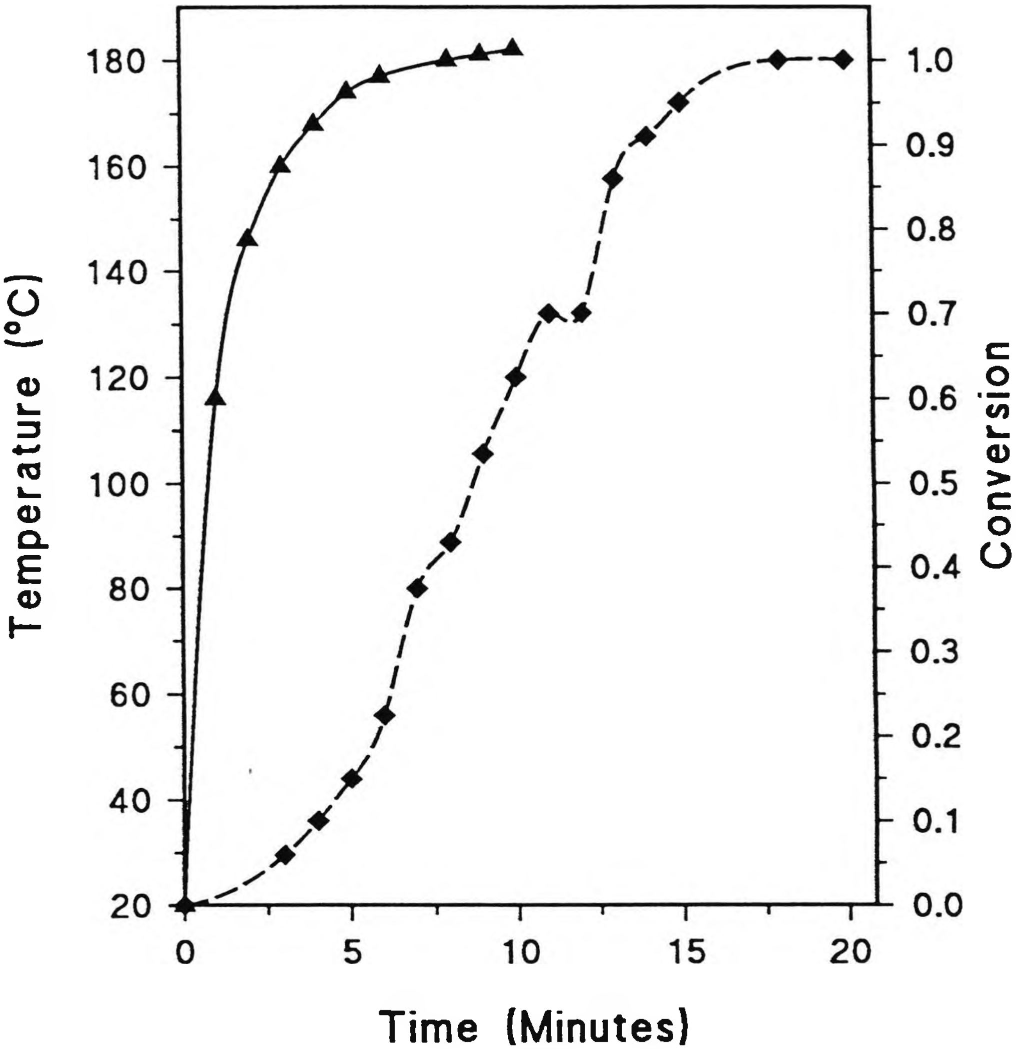


Figure 10.3 Temperature and Conversion Profiles
2.0 mm Panel/182°C

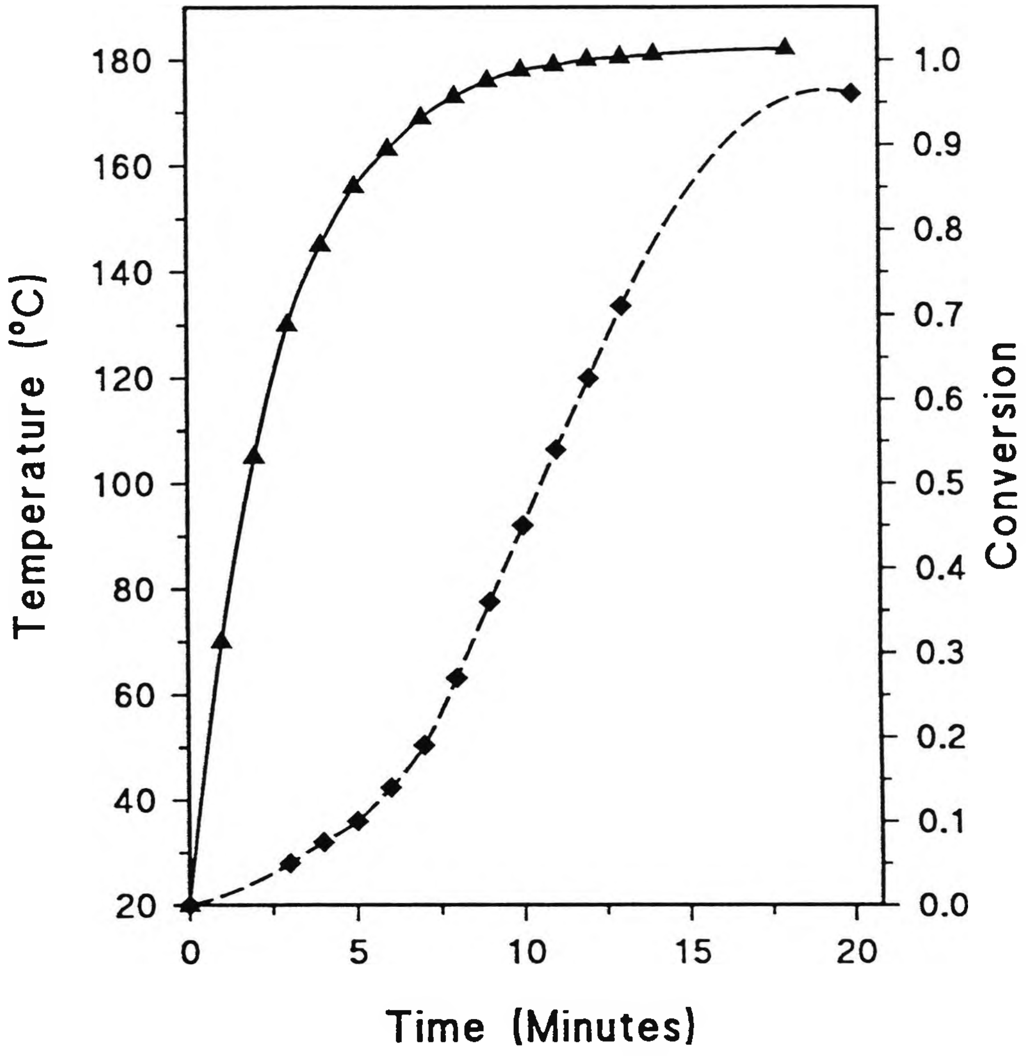


Figure 10.4 Temperature and Conversion Profiles
3.0 mm Panel/182°C

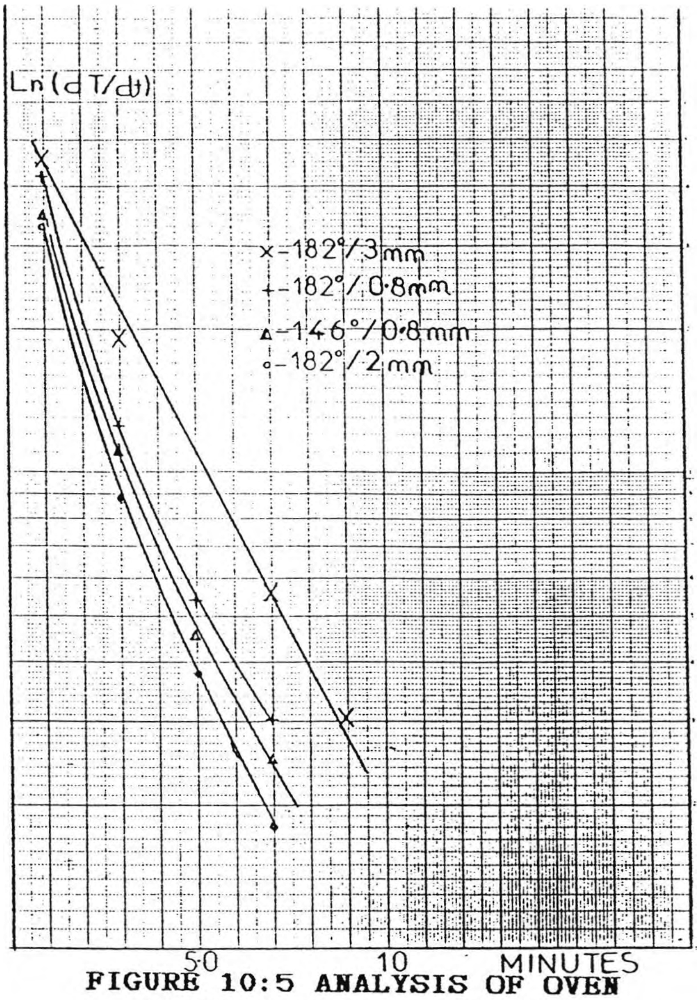


FIGURE 10:5 ANALYSIS OF OVEN HEATING RATE KINETICS

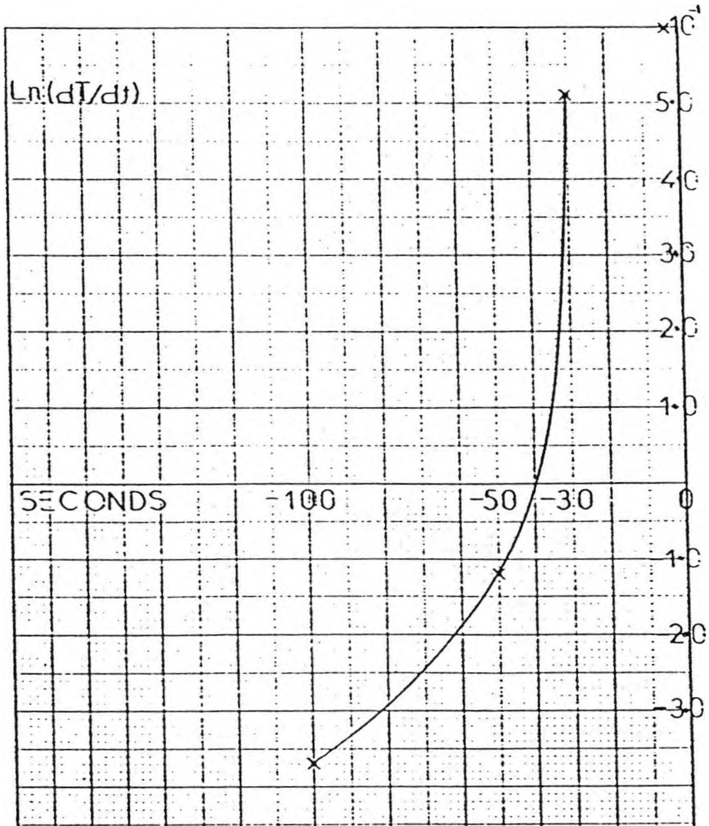


FIGURE 10:10 ANALYSIS OF IR HEATING RATE KINETICS

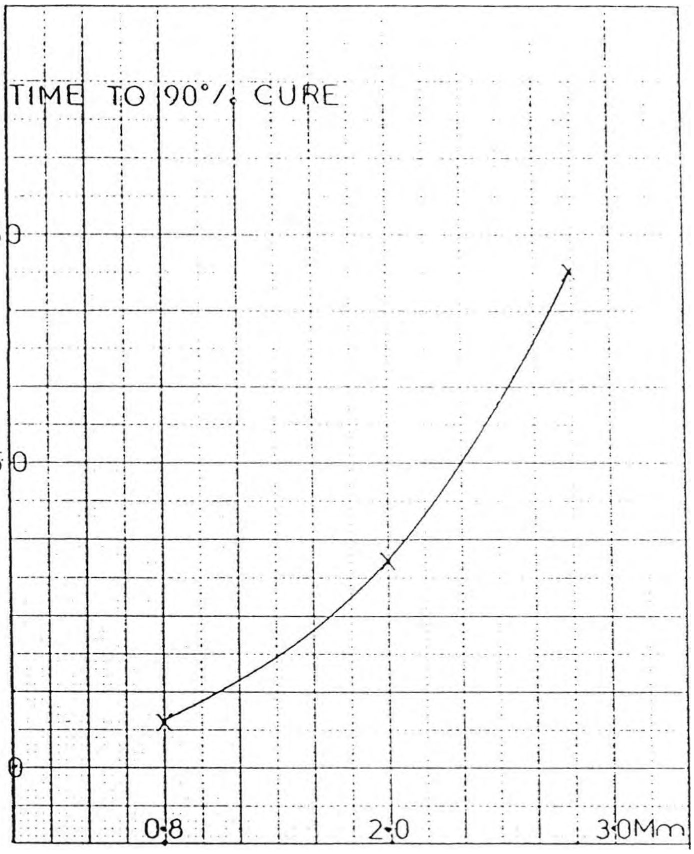


FIGURE 10:6 DEPENDENCE OF CURE TIME ON PANEL THICKNESS

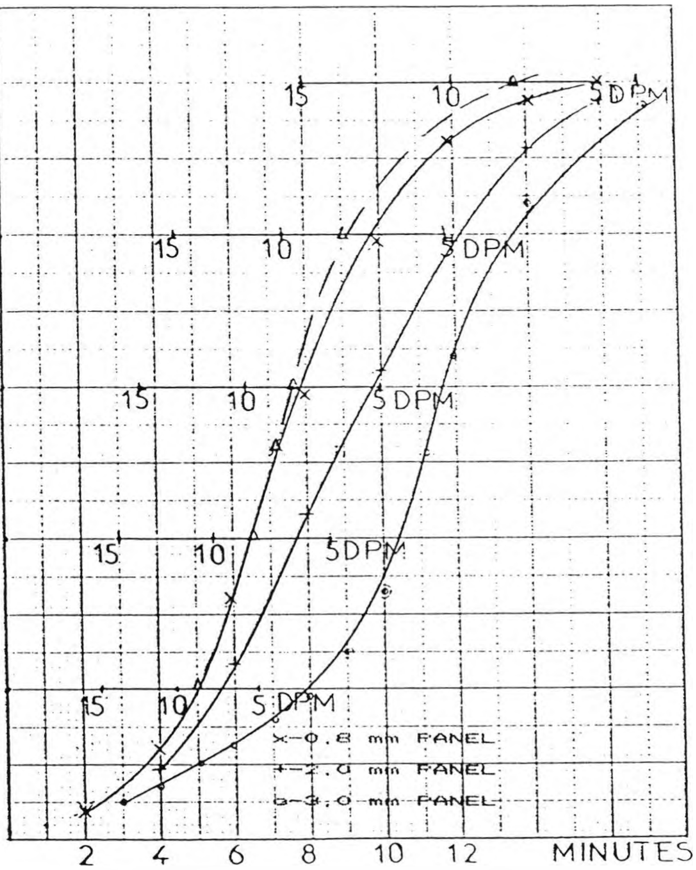


FIGURE 10:7 RELATIONSHIP OF OVEN AND DSC PROFILES

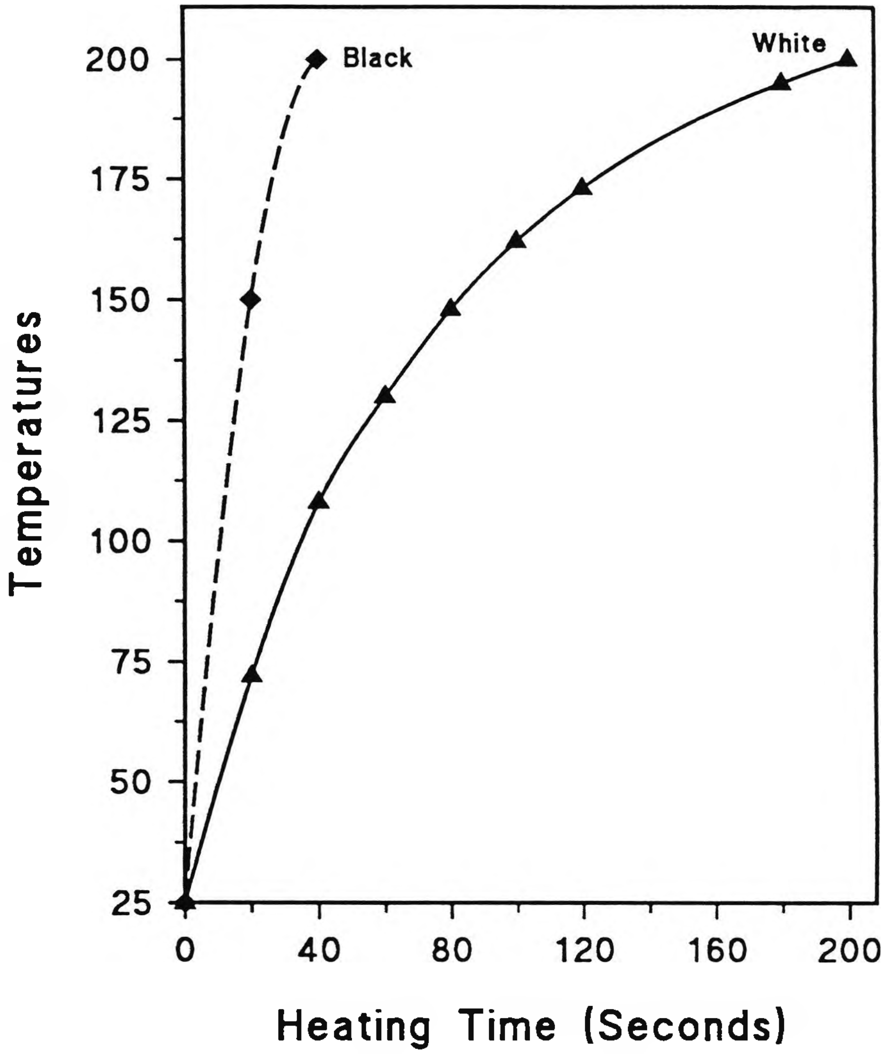


Figure 10.8 Temperature Profiles of White and Black PC films R160/0.8mm Panel

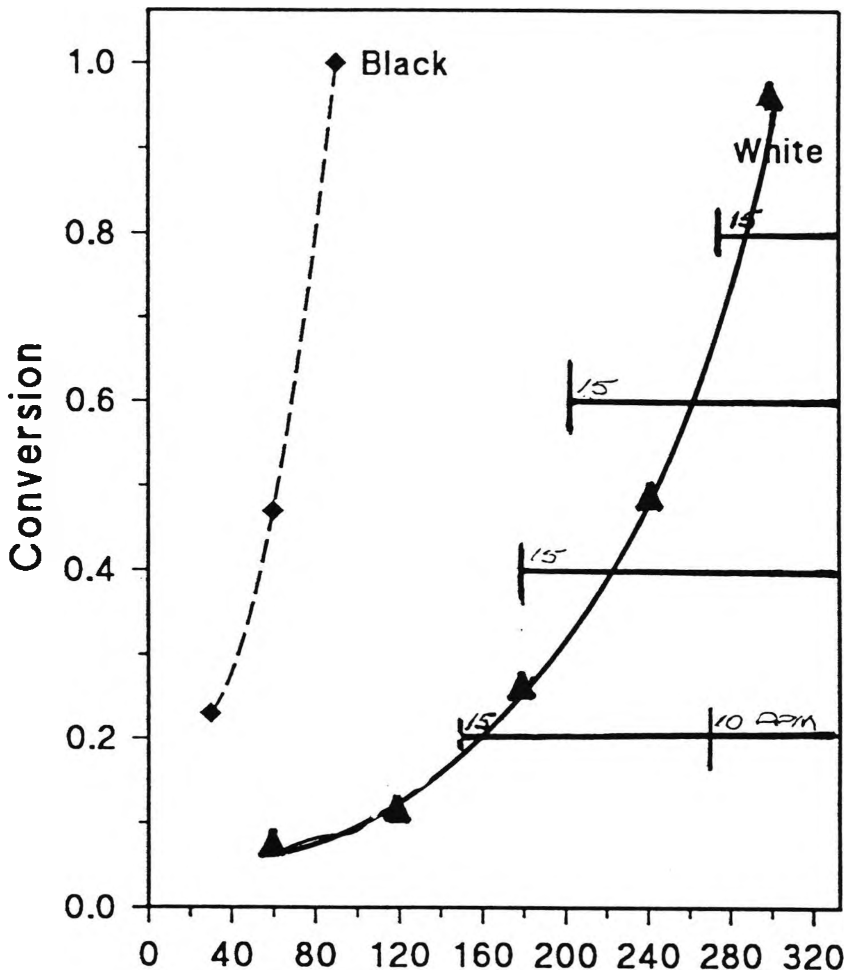


FIGURE 10.9 Conversion Profiles of White and Black PC films R160/0.8mm Panel

CHAPTER 11

OVERVIEW OF THE RESULTS OF THE THESIS

The principal aim of the present study was to assess the behaviour of the relatively complex hardeners (namely dicyandiamide and o-tolylbiguanide) used for the cure of the epoxy resins in a powder coating formulation. A particular interest lay in the effect of variation in the heating rate in dynamic DSC experiments or oven heating.

The analytical methods used in the study were spectroscopic analysis and thermal analysis.

As the data in Chapter 4 show, a determined effort was made to apply spectroscopic analysis to the problem, and in at least one method, namely FTIR spectroscopy, a very good result at first appeared to have been attained. Large variations found in repeat analyses of the same sample, however, led to the conclusion that spectroscopic data could not form the basis of an accurate study of the behaviour of hardeners in epoxy resin cure.

The Author may at this point perhaps be permitted a note of puzzlement as to the validity of the spectroscopic analytical results on similar systems reported in the literature. In all the important papers discussed in Chapter 2, for example Acitelli, and Barton, no experimental details are quoted for the spectroscopic method, so it is impossible to determine reproducibility of the experimental results. Some authors, of course, use low molecular weight model compounds, of which the reaction products remain soluble, and so spectroscopy is much simpler.

The thermal analysis results obtained in this work have been rewarding. and show that the method does form the basis of an accurate study of the behaviour of hardeners in epoxy resins.

The results described in this Thesis are for

(a) a dynamic DSC study of an epoxy / o-tolylbiguanide formulation, with and without addition of a flow control agent;

(b) a study of the effects of pigmentation on the epoxy/o-tolylbiguanide system;

(c) isothermal studies of the epoxy / o-tolylbiguanide and epoxy/dicyandiamide systems;

(d) studies of the effect of variation in heating rate on the epoxy/o-tolylbiguanide and epoxy/dicyandiamide systems;

(e) a study of oven and instrumental isothermal reactions in epoxy cure;

(f) an industrial epoxy cure simulation experiment.

In the dynamic DSC study on an epoxy/o-tolylbiguanide/flow control agent system at two sample weights, 6 mg and 13 mg, and two particle sizes, about 125 µm and above 250 µm, the differences that are observed in heats of reaction, glass transition temperature and peak temperature, are related to sample size and not at all to particle size. There is even a significant effect on order of reaction (according to a Kissinger exotherm curve symmetry analysis). These observations are contrary to those anticipated on the basis of a consideration of heat flow theory and also from a paper by a respected author (Sacher) that there would be a large difference in kinetics according to particle size. It was concluded, that for comparison of different systems, use of a constant mass of sample is of paramount importance, otherwise differences in important properties might be found that did not, in fact, exist.

Another system variation examined in the present study was pigmentation. No effect on the endotherm of an o-tolylbiguanide/epoxy formulation is observed when silica (a matting agent) or titanium dioxide (a pigment) is used as a filler/pigment. Use of both, however, affects the exotherm, suggesting a small effect on the chemistry of reaction, presumably because of the selective adsorption of one or more components of the binder (the low molecular weight fraction of the epoxy resin) or the (low molecular weight) hardener on the pigment. This observation is confirmed by a small reduction in the reaction order when a Kissinger exotherm curve symmetry analysis is performed.

Isothermal analysis experiments were carried out with systems containing dicyandiamide and o-tolylbiguanide. The runs at each temperature were taken to completion of cure, and it was found that for both systems the heats of reaction and glass transition temperatures increase progressively with increase in constant temperature. The Tg for the dicyandiamide formulation increases to a larger extent than for the o-tolylbiguanide system. Because the increase in the heats of reaction is a little surprising, a dynamic run was made on the o-tolylbiguanide formulation, and this gave a lower Tg than the value found in the lowest temperature isothermal run. Since the Tg can be taken to be indicative of the structure of the system, the results suggest that different reaction chemistries are taking place at the different temperatures.

The effect of heating rate variation was examined for the dicyandiamide formulation. Two sets of similar experimental results were obtained, and the data show that there is a remarkable reduction in cure rates with increasing heating rates. Presumably this is because of the reduction in viscosity at faster heating rates leading to a promotion of the cure reaction. If the experimental data were analysed according to the Kissinger method (using the peak curve temperature to calculate energies of activation), a plot of the Kissinger parameters shows a distinct break in the 10-15 degree per minute (DPM) region, clearly indicating a change in chemistry, with different activation energies for the regions above and below the 10-15 DPM region.

The effect of heating rate variation on the o-tolylbiguanide formulation was also followed by DTA. This provided the illuminating result of two exotherms of successively higher peak temperatures, becoming more pronounced as the heating rate increased. After measurement of energies of activation, it is concluded that the exotherms correspond to a first reaction of predominantly primary amine hydrogen followed by reaction of predominantly secondary amine hydrogen.

A comparison of oven and instrumental isothermal reactions was made in this study. The oven experiment permitted measurement of degrees of conversion of the systems in a more convincing manner than is possible in dynamic DSC experiments. The resultant reaction curve has two steps superimposed on the basic S-shaped one. These steps were found at about the same degrees of reaction at all four temperatures examined. The results can be explained if the reaction is a cyclic one, first an energetic reaction of primary amine/cyanogen with epoxy, catalysed by hydroxyl, then the reaction of secondary amine with residual epoxy and hydroxyl to reduce the epoxy concentration and both increase and decrease the hydroxyl concentration; the energetics of this second step would be less vigorous than the first and the reaction would slow down from the initial period - hence the existence of the first step in the curve. Then since tertiary amine increases from the primary/secondary amine reaction, and since tertiary amine is an effective catalyst for the continuing reaction, the reaction rate speeds up. The second step is difficult to identify chemically, but could arise from an interaction of viscosity increase and etherification processes.

Finally. an industrial simulation experiment was carried out to see whether the observations made in instrumental studies could be detected in oven runs. Using three different metal thicknesses coated with a constant thickness of powder coating led to three different heating rates for a dicyandiamide/epoxy formulation. No important correspondence was noted between instrument and oven, and using DSC results to predict oven kinetics was inconclusive. What was of interest, however, was that working to a final oven temperature of 180°, the degree of conversion of the powder coating is found to be a function of panel thickness, that is, of heating rate.

In conclusion, thermal analysis has been shown to provide valuable insights into the complexity of the chemistry of the cure of epoxy/amine powder coatings, but is not sufficient itself to simplify the complexity.