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A study of the nature, cause and elimination of permanent mottle in some epoxy-resin castings used for photoelastic analysis

by

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A thesis submitted for the degree of Doctor of Philosophy of the University of Surrey

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ABSTRACT

An investigation was made into the nature of permanent non-annealable mottle in the epoxy-resin system CT200/HT901 (C.I.B.A. Ltd.) as used for photoelastic analysis.

Tensile and shear fracture specimens showed fibrilar formations, termed spicules attached to the fracture surface. Investigation of these spicules showed them to have been formed shortly prior to gel. They consisted of heavily cross-linked, fully cured resin having a higher ester content than the surrounding matrix.

The spicules were more dense than the matrix, the difference being consistent with the strain necessary to produce 0.1 stress fringes; this irregular unannealable birefringence is termed mottle.

Extraction of the insoluble fraction prior to gel showed fully cured spheres which could be the initiation points for spicular growth.

The self-diffusion constant of the phthalic anhydride hardener was determined at various temperatures and cure times.

Extent and rates of cure were determined using infra-red analysis and these were used to calculate the value of the self-diffusion constant necessary to sustain the spicule growth throughout cure.

Comparison of the calculated and experimentally determined diffusion constants showed spicule growth to be constant for about two thirds of the gel-time.

Density measurements at elevated temperatures enabled calculation of displacements in castings; differential displacements showed the
post-gel stresses to be insufficient to cause microfracture.

As spicule growth is apparently a diffusion controlled process, methods suggested for the elimination of spicules include the use of less diffusive hardeners of low exotherm coupled with low oven temperatures.
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P.1 Photoelastic effect caused by a spherical indentation.
Certain homogeneous materials, when viewed with polarised light, exhibit strain birefringence. This property can be utilised in assessing the strain extant within the materials: the relative retardation of the transmitted polarised rays being proportional to the difference between the principal stress vectors orthogonal to them.

Where the relative retardation is \((n+\frac{1}{2})\) wavelengths of the light used, total extinction occurs so that a series of black fringes are visible. This is called the photoelastic fringe pattern (fig. 1), Pl.

The force per unit area required to produce one fringe per inch is called the Stress-Optic constant. It varies with the wavelength of light used.

A two-dimensional sample is the ideal configuration and a thin sample approximates to this. Birefringence, however, obeys the law of superposition and therefore the emergent patterns caused by the sum of varying stresses through which the rays pass in a thick sample are complex and cannot be interpreted.

The original materials used for photoelastic analysis were glass, gelatine, colluloid and certain forms of Bakelite (Glyptal BT-61-893) but these are only viable when the fringe pattern can be measured
whilst the stress is being applied. For three dimensional stress analysis and the measurement of dynamic stress such as a shaft under torque or a spinning object these materials and techniques are useless.

In 1936 it was discovered that some materials, if strained above their glass transition point (Tg) and then cooled with the load still applied retained the strain on removal of the load. This is known as Stress-freezing, (1).

A large strained sample can then be sectioned and many two dimensional analyses combined to give an overall picture of the stress field. The sample must be kept below Tg during machining, diamond-tipped tools being preferred.

It has been found that Epoxy resins are amongst the most useful materials for this work having a high strength, good transparency and a convenient stress-optic constant. They are also easily machined and have Tg conveniently at 100-110°C.

A very extensively used resin is the C.I.B.A. Araldite system of CT200 hardened with Phthalic Anhydride (P.A.) HT.901. This resin is of the form:-

\[ \text{The autocatalytic effect of the hydroxyl groups which occur on the long chain molecule (n > 0) obviate the need for a separate 'initiator' but a slower reaction occurs. The highly exothermic reaction releases its heat more slowly and for small samples this can be conducted to the surface despite the low heat transfer coefficient.} \]
For large samples the heat of reaction produces more heat than the system of heat conduction and radiation can transfer to the surface and so the temperature rises internally. This system, which only cures above 95°C, may attain a temperature of more than 200°C in the centre of a cube of side 20 cm. at an oven temperature of 120°C.

A large block of cured resin often exhibits a mottled appearance when viewed with polarised light. This mottle cannot be annealed out thermally as can be temporary frozen-in stress and, the photoelastic effect being cumulative along any given light path, interferes with any fringe pattern.

This interference with the analysis of the internal stress cannot be overcome as the contribution to the stress fringe by any mottle present cannot be known before the sample is sectioned and therefore cannot be allowed for subsequently.

Mottle occurs in several forms; whorl-, needle- and star-mottle being the most common. The boundary between these forms is not strict, a gradation of effects being possible and often occurring in the same sample.

Needle-mottle has the appearance of randomly oriented needles up to 1mm. in length and obvious only under polarised light, (P2).

Whorl-mottle is visible as a series of wisps which follow a general trend of swirl or whorl. The wisps may be entire or oriented aggregates of needle-mottle, (P3).

Star-mottle occurs mostly in disc-shaped samples where it appears as a star-burst, often whorled in the centre, (P4). This and whorl-mottle can sometimes just be discerned as an orange-peel effect with
P.2 Needle-mottle.

P.3 Whorl-mottle.

P.4 Star-mottle.
ordinary unpolarised light.

Mottle is obviously of great concern in photoelastic stress analysis and its nature, cause and elimination are the subjects of this thesis.

References

Although previous workers such as McIntosh and Wolford, Blumer, Bisleb and Stattman (1-4) had developed epoxy-type casting resins as early as 1920, Lee and Neville (5, p.12) cite Castan (6) and Greenlee (7) in 1936 as the first to produce epoxy compounds which could be crosslinked to produce casting resins. Both used phthalic anhydride as the curing agent, Greenlee being the first to use the resin Di-Glycidyl Ether of Bis Phenol A (DGEBA):

\[
\begin{align*}
\begin{array}{c}
\text{O} \\
\text{C} & \text{C} & \text{O} & \text{C} \\
\text{C} & \text{O} & \text{C} & \text{C} \\
\text{C} & \text{O} & \text{C} & \text{C} \\
\text{C} & \text{O} & \text{C} & \text{C} \\
\end{array}
\end{align*}
\]

which is formed from the reaction of epichlorohydrin on 2,2-diphenol propane in the presence of NaOH (8):

\[
H-O-C-C-O-H + 2 \text{Cl-C-C-CNaOH} \rightarrow \text{Cl-C-C-C-O-C-C-O-C-C-Cl}
\]

NaOH catalyses the reaction to produce the chlorohydrin intermediate, acts as the dehydrohalogenating agent and neutralizes the HCl formed. Excesses of 2-3 times of epichlorohydrin are used with resultant yields of the lower molecular weight resins of up to 90%. DGEBA is extracted from the reaction with toluene after the remaining excess of epichlorohydrin is distilled off. Until 1969 DGEBA was made in batches but a continuous flow process is now available (9).

High M.Wt. DGEBA resins are manufactured under a pressure of 25 p.s.i. and at elevated temperature (170°C) with a 25% stoichiometric ratio of epichlorohydrin. These are solid at room temperature melting above 40°C and having the repeat index n equal to two or more. (10).
Many chlorine containing by-products are formed during the reaction but most of these are removed during the final washing. Their effect is to reduce the functionality of the resin with consequent reduction of crosslinking and increased inhomogeneity and darkening of the final cured resin. A typical chlorine content is 0.1% (DGEBA of M.W. ~850. C.I.B.A. Ltd.)

Epoxy resins react with a broad variety of reagents due to the reactivity of the epoxide ring and the hydroxyl group; Lee and Neville (5; p.5-32) list 56 distinct reactions of the epoxy group alone.

Curing (crosslinking) agents used commercially may be divided into basic and acidic types.

Organic bases such as the amines have an unshared pair of electrons in the outer orbital shell of the nitrogen atom. On approaching an epoxide group they cause a charge separation enabling the termolecular intermediate (II) to form. Subsequent addition of epoxy groups can add to the complex without increasing the charge separation (11-12).

\[
\begin{align*}
\text{ROH} & \quad \text{R-O--H} \\
\text{C-C-} & \quad \text{(C-C-)}_n \quad \text{R-O-C-C-}
\end{align*}
\]

Inorganic bases act in a similar fashion having greater initial charge separation (11).

Primary amines, having greater electron mobility, need no catalyst to initiate the charge separation (13), i.e. (Next Page).
The apparent activation energy of the reaction between DGEBA and n-butylamine is 11.6-11.8 kcal/mole; with ethylene diamine, 13.2 kcal/mole. (15) With tertiary amines slightly higher values are obtained as a result of epoxide/hydroxyl polymerization. (16)

The acid curing reagents usually employed are the Lewis acids, phenols, organic dibasic acids and anhydrides. The Lewis acids, having an empty orbital in the outer shell, react by sharing an electron pair of the epoxide oxygen atom.

A typical Lewis acid reaction sequence is: - (14)

\[
\begin{align*}
\text{R.NH}_3 + \text{C}-\text{C} & \rightarrow \text{R.NH}_2\text{C} - \text{C} \rightarrow \text{R.N} (\text{C}-\text{C})_3 \\
\text{C} - \text{C} - + \text{BF}_3 & \rightarrow \text{C} - \text{C} \rightarrow \text{n times} \quad \text{O} - \text{C} - \text{C} - \text{O} - \\
\text{C} - \text{C} - + \text{C} - \text{C} - & \rightarrow \text{C} - \text{C} -
\end{align*}
\]

with final chain termination by:

\[
\begin{align*}
\text{C} - \text{C} - + \text{BF}_2 & \rightarrow \text{O} - \text{C} - \text{C} - \text{F} \\
\text{O} - \text{C} - \text{C} - & \rightarrow \text{C} - \text{C} -
\end{align*}
\]

As this thesis is concerned primarily with anhydride cured epoxy resins, a fuller description follows of this reaction. The DGEBA used chiefly is (CT200, C.I.B.A. Ltd.) having an average molecular weight of ~850 and 2-3-hydroxyl groups per molecule.

Anhydrides do not react with epoxy groups directly, an active hydrogen containing catalyst being necessary to open the anhydride ring. Water, Lewis bases or the hydroxyl groups on the epoxy molecule
being utilizable. (I)

\[
\text{RCO}_2\text{H} + \text{ROH} \rightarrow \text{RCO}_2\text{O-R} \quad \ldots \ldots \text{(I)}
\]

Direct esterification of the hydroxides by this carboxylic acid group is a reversible reaction with the equilibrium constant << 1 in the absence of the removal of water, (Ia.)

\[
\text{RCO}_2\text{O-R} + \text{R'OH} \rightarrow \text{RCO}_2\text{O-R'} + \text{H}_2\text{O} \quad \ldots \ldots \text{(Ia)}
\]

The reaction favoured for the formed carboxyl group is direct esterification with an epoxide ring, (II).

\[
\text{RCO}_2\text{O-H} + \text{C-C-R'} \rightarrow \text{RCO}_2\text{O-C-C-R'} \quad \ldots \ldots \text{(II)}
\]

A further reaction occurs, etherification between an epoxy group and a hydroxyl (III).

\[
\text{ROH} + \text{C-C-R'} \rightarrow \text{R-O-C-C-R'} \quad \ldots \ldots \text{(III)}
\]

The extent to which this etherification occurs depends on the concentration of hydroxyl groups and the availability of epoxide rings; the esterification depending on the location of the epoxide groups and the relative concentrations of the carboxyl and epoxy groups (21). The higher reaction activation energy due to the epoxy-hydroxyl reaction is reflected in the higher overall activation energy of the higher molecular
weight resins (19): for example, 13.7 Kcal/mole. for DGEBA (M.W. = 350) and 14.4 Kcal/mole. for DGEBA (M.W. = 950).

If sufficient hydroxyls are present to open all the anhydride rings an acid-cured system would result; a lower proportion of hydroxyl groups increases the proportion of esterification.

The reactions I, II and III are those proposed by Fisch et al (18) in 1956. In 1963 reaction studies by Tanaka et al (19) suggested a termolecular transition state producing two ester links simultaneously.

\[
\text{ROH} + \text{C-C} - + \text{O=C-C=O} \rightarrow \text{RO-C-C-O-C-C}
\]

Analysis up to the gel-point (20) indicated no etherification had taken place between 70°C and 140°C (19) which agreed with the data of Fischer (22) but Dearborn et al (17) and Fisch et al (18) claim to have observed almost equal proportions of esterification and etherification.

The higher temperature reached in the initial stages of cure due to the high exotherm (typically 25-35 Kcal/mole) improve the chance of a termolecular reaction, thus a higher cure-temperature will lead to a greater proportion of ester linkages (5 p. 5-23). Tanaka et al (19) give the apparent activation energy of DGEBA (M.W. ~ 850)/phthalic anhydride as 14.4 Kcal/mole., higher than that of the polyamine cured systems.

Tertiary amines such as tri-ethanolamine are frequently used as accelerators with anhydride curing agents particularly with resins.
having a low hydroxyl content. They initiate the opening of the hydroxyl ring (22) thereby shortening the time for total cure.

The overall order of the reaction depends on the dominating reaction. Tanaka et al (19) report the initial reaction rate to be proportional to the concentration of both epoxide and anhydride giving a second order reaction: in the presence of a tertiary amine catalyst, to which they find the rate also proportional, the reaction becomes third order with an amine catalysed form of reaction II as the rate determining step. However, Feltzin and his co-workers (23) using methyl nadic anhydride found the rate to be clearly first order in catalyst and zero-order in epoxide and anhydride. They claim the rate controlling step to be the activation of the catalyst by a hydroxyl-containing co-catalyst and that Tanaka et al. (19), whilst claiming first order dependence of the reaction rate on each of the major components did not prove their data to fit a second order equation.

Their mechanism does not depend on increasing charge separation as does that proposed by Tanaka (19), Fischer (23) or Lee and Neville (24).

The gel point of anhydride cured systems has been defined experimentally by viscometric and solubility methods. The former uses the property of the change from a viscous liquid to an elastic non-flowing gel within two minutes either side of the gel point. The latter uses the sudden insolubility of a post-gel resin compared with complete miscibility in solvents such as M.E.K. and 1,4,Dioxane just before gel.

*Methyl bi cyclo (2,2,1) heptene- 2.3-dicarboxylic anhydride.*
Tanaka et al (26) derived a general equation for the gel-point in terms of the extent of reaction of reagents of various functionality. For stoichiometric ratios of an epoxide and anhydride with functionalities of four and two respectively they find the extent of reaction at the gel-point to be $1/3$ of the functional groups. The same result is obtained for a mixture of 2- and 4-functional resin with 2-functional anhydride. Any increase in the resin functionality decreases the extent of cure at gel tending to a minimum of $\frac{1}{2}$ which agrees with the calculations of Flory (29) and Stockmayer (27). Flory (29 p.360) quotes the critical extent of cure $e_c$ at gel to be $1/(f-1)$ where $f$ is the functionality of the reactants. Where the reactants have different functionalities the $(f-1)$ term becomes a summation of the $(f-1)$ term of each contributing reactant (26).

Good agreement is found between experimental and theoretical prediction of gel. Tanaka et al (26) found only 2-3% difference between their observed and calculated values for an anhydride cured system. There was little difference between high and low molecular weight DGEBA as would be expected from the distribution of the various length of molecules ($n = 0, 1, 2, 3$ etc.). Fig. (2) is taken from gel permeation studies of uncured resins of high and low molecular weight, (28).

![Fig. 2](image_url)

A comparison of methods for estimating the extent of cure will be found on p. 95.
PHYSICAL PROPERTIES

The reactions between DGEBA and phthalic anhydride are such that a large variation in the relative concentrations can be tolerated without a post-cure unreacted excess of either component. This is due to the convenient self-polymerisation of the DGEBA molecule. Even so, more highly cross-linked regions occur due to bad initial mixing or local concentration gradients caused by diffusion of P.A. to 'active' centres.

Megson (30) and Erath and Robinson (31) reason that due to differing diffusion rates of the resin mix a continuous phase is unlikely and therefore particles must grow to such a size when the surface energy repels further growth. They demonstrated a two-phase structure in epoxy-resins using carbon replicas of fracture surfaces. Electron micrographs show the particle size to remain practically constant (~0.85μ) on leaching with acetone which causes selective solution of the less cross-linked phase forming the matrix.

Sharples (33) proposed that lower molecular weight, high mobility elements are squeezed out of the growing solid. In 1966 Cuthrell (32) reported a variation of particle size with cure temperature; 90μ for 50°C and 20μ for 95°C amine-cured samples. His penetrometer measurements showed a regular fluctuation along a line perpendicular to the surface which he interpreted as a layering of what he called floccules. Electro-osmotic investigation indicated the floccules to be negatively charged with respect to the matrix with a spacing of about 0.75μ. Density calculation and experimentation were found to have a high correlation for an assumed hexagonally-close-packed arrangement of the floccules.

Cuthrell (34) considered the diffuse double layer of charge commonly associated with the colloidal nature of the floccules as well
as gravity to be the cause of this regular packing prior to gel.

Schoon (35) found similar aggregates of spherical particles in poly-methyl-methacrylate, poly-isoprene, poly-styrene and many other polymers, the typical diameter of these being 10 nM.

The cause of the mottle described in the preface has been attributed variously to external causes such as bad mixing and excess stirring near the gel-point as well as internal causes like convection, a degree of crystallisation (36) and insufficient hardener.

Spooner and McConnell (36) described needle-mottle as isostatic mottle of the order of 0.1 fringes. They demonstrated that it takes up a regular arrangement, lining up with the isoclinic lines (the locus of points at which the principal stress axis has a fixed angle to an arbitrary reference axis is known as the isoclinic for that angle; it may coincide with a stress retardation sufficient to cause a visible fringe, (P5)). They also quoted Hickson as suggesting that this apparent effect is due to the inclusion of randomly distributed fibrous elements, possibly excess hardener, which exhibit different stress-optic coefficients along and across the fibre (36a). This suggests that on a microscopic scale these fibres are anisotropic but have a random enough distribution to cause a macroscopically isotropic material for photoelastic analysis. They achieved a reduction of the mottle by ensuring complete mixing prior to curing.

Sugarman et al. (37) describe whorl-like mottle in a modified polyester and suggested that centrifuging will eliminate mottle by increasing the convection due to temperature induced density changes. Castings at 1,42 and 168 times gravity showed progressively less mottle but care had to be exercised to ensure the centrifuging did not
P.5  Isoclinic mottle.
continue long after gel as otherwise the gravitational stresses were frozen in.

Prolonged stirring for at least an hour before pouring the resin into the mould is suggested by Cook (38) to reduce the mottle. His limited success may be due to better distribution of early reaction products and lessening of thermal convection effects.

Other resin/hardener systems have been suggested: Leven (40) showed an improvement with the use of hexa-hydro phthalic anhydride (H.H.P.A.) and Kenny (41) advocated a mixture of 5 pts. MY750 (CIBA liquid DGEBA of low molecular weight), 2 pts. HT901 (CIBA P.A.) and 1 pt. HT907 (CIBA HHPA).

Chapman (39) investigated the CT200/HT901 system to confirm that mottle coincided with high cure temperature and convection before gel. He reported fringes occurring at about half the gel-time (30 mins.) which disappeared at the gel-point and a decrease in mottle which coincided with lower cure temperature for up to 3 Kg castings.

In general it seems that mottle is found more often in the centre of a casting, and that even the most optimistic of these mottle-relieving mechanisms mentioned attain no better than one stress fringe per inch.
REFERENCES.
28. Private Communication from C.I.B.A. (Duxford) Ltd.
29. Flory, Principles of Polymer Chemistry (Cornell Press, 1953).
33. Sharples, Introduction to Polymer Crystallisation (Edward Arnold, London).
THE NATURE OF THE MOTTLE

On careful examination of a mottled resin in white light it is often possible to distinguish variations in the homogeneity of the material. As these irregularities are only just discernible to the human eye, which has a resolution of about four seconds of arc, the largest features must be of the order of 25μ.

Examination of chippings with the optical microscope showed some change of refractive index in the area of the mottle but the depth of field was insufficient for a good representation to be obtained at sufficient magnification (x400).

Cubes of 1 cm. side were cut from a highly needle-mottled specimen and the faces polished on a rotating diamond-loaded turntable (grade 1μ HYPREZ). It was found that the resultant ground face was still very pitted and scratched with features of the order of 100μ, (P6).

Bars of 1cm. x 1cm. x ~5cm. were fractured both by tension on a Tensometer† and bending in a vice, the exposed surfaces then being examined under the microscope.

There are two distinct modes of fracture visible. One is a very smooth plane which is surrounded by the other, a rough cleavage. This is generally of a radial spoked appearance on superficial observation.

These two modes of fracture are well-known in the fracture of polymers being caused by fast and slow propagation of the crack front respectively, see Appendix 1.

Little difference is apparent between the surfaces due to the

† Tensometer Ltd., Type E. Extension 1mm/minute.
different types of fracture although the tensile break is usually symmetrical with the smooth plane centrally situated.

A Stereoscopic electron microscope, (Cambridge Instruments Stereoscan Type 2A) has been used and this gives a view of the surface without the distortion due to transmitted or internally reflected light besides having a considerable depth of field (>100μ at x 1000).

This instrument scans a small area of the surface with a 'flying spot' of electrons (the primary electrons). Subsequent re-emission of secondary electrons from the surface is measured and displayed on a C.R.T. scanned in the same fashion as the sample surface. Hence a picture is built up of the topography of the sample.

The ultimate resolution of this method is of the order of the wavelength of the electron (~0.1 nM) although the particular machine used has a resolution of 15 nM.

It is necessary to conduct the primary electrons to earth as otherwise the build-up of charge on the surface causes deflection of the electron beam and saturation of the instrument. The most common method of rendering non-conductive samples visible is to coat them with a conducting surface.

The epoxy-resin samples were coated with Au/Pd (60/40) in a vacuum-deposition unit. One side of each fracture surface was immersed in acetone—for four days to leach out any soluble matter and to increase the relief prior to coating.

The appearance of the various surfaces was substantially similar with the smooth plane clear of relief except for small debris from the fracture or dust from the air. The rough area had basically
the form of a tributary system, (P8-9). This is a well established form of fracture propagation in which the crack-front moves 'downstream', (Appendix 1).

It was observed that in all cases the smooth fracture starts first as the tributary system is radially distributed away from it, (P7). While all of the rough fractured areas had a tributary system there was, in some cases, a superimposition of a splinter-like formation. (P10) shows a typical boundary between fast and slow fracture regions.

These thin rods were of various cross-section from circular to elliptical to sharp edged ribbons, (P8, P10-14). These shapes are not discreet but stages in a continuum. It is noticeable that those of circular cross-section are more intimately associated with the tributary system whilst the ribbon-like ones are less dependent.

It was decided to name all these phenomena SPICULES. This was to avoid confusion with words such as fibre and whisker which have well-defined metallurgical and crystallographic connotations.

Due to the similarity in form of the samples, the surface features were measured. Step heights were easily calculated as the samples are mounted at 45° to the beam of primary electrons.

Table 1 contains a representative selection of etched and unetched samples with the spacing and height of step-features, the diameters of spicules and their lengths.

The large ribbon-type spicules frequently occur in the etched surface but have not been seen in unetched ones. The physical action of etching may reduce the diameter of smaller features and leach away the softer matrix leaving the ribbons exposed. (P12 and P14).
<table>
<thead>
<tr>
<th>Photo. No.</th>
<th>Mag.</th>
<th>Diam./Step (µ)</th>
<th>Spacing (µ)</th>
<th>Length (µ)</th>
<th>Comments</th>
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</tr>
<tr>
<td>P8</td>
<td>115</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td>mottle-free loose network</td>
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<td>&quot;&quot;whiskers</td>
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<td>8</td>
<td>&gt;80</td>
<td>&quot;&quot;</td>
</tr>
<tr>
<td>P21</td>
<td>170</td>
<td>8.5 matted</td>
<td>&gt;400</td>
<td>&quot;</td>
<td>&quot;network + whiskers</td>
</tr>
<tr>
<td>P17</td>
<td>160</td>
<td>17</td>
<td>400</td>
<td>&gt;800</td>
<td>no mottle</td>
</tr>
<tr>
<td>P24</td>
<td>205</td>
<td>10</td>
<td>100</td>
<td>&gt;500</td>
<td>needle mottle steps</td>
</tr>
<tr>
<td>Unleached</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P15</td>
<td>74</td>
<td>20</td>
<td>125</td>
<td>-</td>
<td>some mottle ribbon</td>
</tr>
<tr>
<td>P13</td>
<td>69</td>
<td>100</td>
<td>500</td>
<td>&gt;1 mm</td>
<td>&quot;          loose ribbons</td>
</tr>
<tr>
<td>P19</td>
<td>72</td>
<td>25</td>
<td>50</td>
<td>&gt;1 mm</td>
<td>&quot;&quot;filament</td>
</tr>
<tr>
<td>P23</td>
<td>123</td>
<td>5</td>
<td>c.10</td>
<td>long</td>
<td>&quot;&quot;filament</td>
</tr>
</tbody>
</table>


P.6 x 100

P.7 x 68.

P.8 x 92.

P.9 x 92.
P.18  x 255.
P.19  x 54.
P.20  x 1200.
P.21  x 105.
Light may be polarized on passing through a transparent medium by several processes. The most usual form of polarization occurs due to different rates of velocity propagation in different directions due to the various regular arrangements of atoms possible in crystalline substances.

According to the interplanar spacings within the crystal the normal propagation of the light used is more or less facilitated by the forward scattering of the wavefront on interaction with the electron clouds of the crystal material.

This inhomogeneity can also be caused in an otherwise homogeneous medium by pressure induced changes in density or refractive index (R.I.). These last are closely related by several empirical and theoretical equations, p. 45.

The necessary pressure can be externally applied or may occur as a natural result of the formation of the material during casting or mechanical forming.

A further type of polarization is caused by small spherical or rod-like inclusions having dimensions of the order of the wavelength of the light used. These, though homogeneous in themselves, present an irregular obstruction to the wavefront if they are imbedded in a matrix of a different R.I. The situation would become even more complicated if the rods were inhomogeneous as well.

Changes in density in a polymeric material may also be caused by preferential reaction at a point due to local surface activity or impurity. If more than one reaction is occurring the balance of these may be changed owing to differing temperature coefficients for each
reaction or changing mobilities of the molecular species involved within a changing thermal environment.

Convection before gelation in a thermosetting polymer is a further possible cause, the shear stresses induced by the lamina flow causing polarization. Similarly, insufficient mixing of the components or stirring too near the gel time could cause an irregular distribution of physical or chemical properties.

Spicules therefore suggest themselves as a cause of mottle; differences apparently exist between the bulk epoxy-resin matrix and the spicules. Further it is possible that inhomogeneities may exist within the spicules thereby enhancing their polarising effect.

It was therefore important to determine the conditions of cure for castings which exhibit spicules on subsequent fracture.
PART II
THE DISTRIBUTION OF SPICULES ON FRACTURE SURFACES

Over 200 fractures were made on specimens taken from castings in the form of thick and thin sheets, large and small cylinders and composite shapes such as discs with bosses and hollow rings.

It was found that, in the overwhelming majority of cases, spicular formation occurred in resins having a minimum dimension greater than 2 cm. and/or a minimum cure temperature of 140°C.

Whilst a few spicules were seen in low temperature/thin specimens, spicule fields such as in P10 were never observed.

It was most noticeable that whereas mottle occurred frequently in the centre of a large casting, the outer shell was usually relatively free of spicules. Within these large blocks the above-mentioned differences in spicular frequency was observed.

To ascertain the possible relationship between spicule growth and heat flow, a batch of five 500 g. samples was prepared with cure times around the gel-point, (previous castings had shown the gel time to be about 190 minutes at 120°C. These sample castings were made in tin-plate moulds to ensure good thermal contact when they were quenched in ice water followed by an acetone/dry ice mixture. The castings were quenched after 180,185,190,195 and 200 minutes, the first three did not quite gel and the last two gelled but were still sparingly soluble in acetone. Fig. 3 shows the position of the fracture planes in the block which was cured for 195 minutes.
Fractures 1, 2 and 3 had only the usual tributary fracture patterns and a few spicules but fracture 4 produced many spicules from both the tributary system and the flat surfaces (P25-26).

To confirm that spicule growth is primarily oriented parallel to the heat flow a large diameter, thin disc was produced (20cm. diam. x 0.5cm. thick). The cure temperature was 180°C as previous work had found this to be the inner temperature in large castings (1) and the disc would have a much lower temperature gradient if cured at the more usual 120°C. A disc was chosen as the heat flow would be predominately parallel to the axis.

The fractured samples showed spicular growth radiating axially across the thickness of the disc (P27). Their diameters range from 2 to 20μ.

The root of the spicule in P28 is seen to be an integral part of the resin although it has cracked across the base, (P29). The trough from which it has been torn shows many transverse septa. (P30). These correlate with the series of ridges on the spicule. (P31).

Two further castings were made to confirm the correlation of heat flow and spicule growth. The mould being a vertical glass tube (2.2 cm. diam. x 13 cm. long) with 2 cm. thickness of lagging around the base and along its length. Although glass has a thermal conductivity about
twice that of epoxy-resin, the thermal conductivity of the cotton wool lagging is an order less. This means that once the glass has achieved the oven temperature (120°C) the majority of the heat flow will be axial towards the free surface and enhanced by any convection before the gel point.

Both cylinders showed a high degree of whirl-mottle, one of a highly axial orientation and the other more randomly directed. An unlagged control casting was found to be almost entirely free of mottle, the small amount observed was in the form of a helix along the axis.

The higher temperature in the lagged samples apparently causes more convection and consequently more flow-induced mottle than in the unlagged control.

There can be no doubt that the spicules occur more frequently as the cure temperature rises especially in the area of the resin sample which is mottled.

The mechanism for the formation of the septa-ridge pattern is not clear but similar effects are observed in carbon and glass fibre filled resins when these are fractured, (P32,(9)), the extremely tough fibres being torn from their matrix of epoxy-resin. If the spicule were harder than the surrounding matrix with a variation in the degree of cross-linking or crystallinity along the long axis then this could account for septa-ridge formation in the slower moving rough-fracture areas.

† Thermal conductivity of resin, glass and cotton-wool are 0.005, 0.001 and 0.0005 cal/deg C/cm/sec. respectively.
The large deformation around a crack tip in such a 'tough' resin material as this lends itself to such an intermittent pattern of fracture with periodic stretch and yield following strain.

It was therefore of interest to investigate the general physical and chemical properties of the spicule as it was not known whether they were harder or softer than the matrix or even whether they were of the same material and not a crystallised by-product.

There was doubt as to whether the spicules were formed prior to gel or afterwards. If the former is the case then they will tend to align themselves with the convective flow; if the latter, it is not easy to account for the alignment except in terms of preferential reaction along the temperature gradients. These are the principal gradients for diffusion of the hardener. This means that post-gel spicule formation will depend on the slow diffusion of hardener in the resin matrix gel.

PRE-GEL SPHERES

During the cleaning of the beakers containing remains of the castings arrested near the gel point (p. 33) it was noticed that some of the resin was not completely soluble and that a milky solution resulted in the acetone. Shaking of a small piece of resin (cure time 185 minutes) in acetone gave a white solution, which persisted several days. Similar treatment of a piece of cure time 200 minutes was not noticeably soluble in the same time. The residue was centrifuged and washed with acetone several times. The milky solution revealed spherical objects under the stereo light microscope. On the Stereoscan the spheres, after Au/Pb coating, were seen to be of all sizes from 0.1 μm (100 nM) in P. 33 to 70 μm in P. 34.
Inspection shows a gradation from seemingly solid spheres through distorted spheres to collapsed spheres (P35-38) as the size increases. The small spheres have hardly any surface features, but the large one, P.34 appears to be hollow with a 1 micron thick skin. The abundance of cracks on the upper surface is not due to deformation under vacuum, as they were visible under the light microscope before coating. P36 also shows some much smaller collapsed spheres (6μ).

A further sample was viewed under the transmission electron microscope. Photographs P39-41 were taken on an electron microscope (JEM120, Japan Optics Lab.Ltd.). P40 clearly shows a split sphere of diameter 11.7μ. The hollowness of the spheres is apparent which is the general case throughout the sample.

In both the Stereoscan photographs and those from the JEM 120 it is noticed that the spheres have a propensity for forming "pearl chains", see P.35 and P.42. This phenomenon is often remarked in colloids, although the mechanism of "sticking" despite the charged double-layer at the surface (2) is not clearly understood. These "pearl-chains" occurred in the sample prepared for Stereoscan examination and may or may not occur in the resin just prior to gel.

At the stage of cure reached by the spheres the phthalic anhydride hardener (P.A.) will not have entirely reacted with the resin (C.T.200). The breaking of the epoxy and anhydride rings can be followed by infra-red spectroscopic analysis, (Appendix 2). Each chemical bond has a characteristic frequency associated with it so that a change from ring structure to the phthalate crosslink can be followed. Comparison is made of the change of the absorption intensity of reacting groups with that of an internal standard such as the absorption due to the methyl groups in the epoxy resin which do not enter into the reaction.
P.41 ~3\mu m diam.

P.42 x 6420.
Comparison of the spectra of CT 200, PA, "B" stage resin (mixed but not cured) acetone-washed and centrifuged spheres and cast resin showed a phthalate cross-link peak in the spheres' spectrum about $2/3$ the proportionate size to that in the cast resin. This line indicates that the esterification reactions I and II mentioned in the introduction have taken place. Also the shift of the broad peak around 1250 from 1260 (cyclic anhydride) to 1240 cm$^{-1}$ (aromatic ether) indicates both the opening of the phthalic anhydride ring and reaction III. The spectrum of the uncentrifuged B-stage resin shows much PA which has not yet reacted, whereas the spectrum of cast resin is identical in form (the relative peak heights are different) to that of the spheres.

It is clear that the spheres are partially reacted epoxy resin that has not attained the fully cross-linked strength. The possibility of the spheres forming chains is perfectly reasonable, this effect occurring in other polymers, although the hollow nature of some of them is not consistent with the formation of a solid denser spicule. The hollowness of the spheres is best accounted for by considering them as having been leached out by the solvent washing prior to investigation. This suggests that they are not as fully gelled as others which would be expected from a statistical view of the nucleation times.

The sphere dimension is consistent with the two-phase epoxy resin systems referred to by both Schoon (3) and Cuthrell (4) who found the included solid phase to have diameters of 100$\mu$ and 20-90$\mu$ respectively compared with the range found here of 0.1 - 70$\mu$.

There was some evidence of pre-gel chain formation in the samples notably in photographs P22 and P29 but pearl chain formation of the numbers of spicules found would indicate that the extraction of the spheres from the ungelled matrix caused considerable chain breakage.
and perhaps solution of the outer, less gelled layers.

It is conceivable that pre-gel convection is responsible for alignment of the spheres in a linear fashion. Cross-linking will be faster at the reactive and therefore hotter surface of these spheres which makes the linking of one to another, eventually to form spicules, possible as the post-gel mobility of the spheres is very small.

Further investigation into the nature of spicules was made as in the next section.
FURTHER PROPERTIES OF SPICULES

REFRACTIVE INDEX AND DENSITY

If the spicules in the resin are more cross-linked, they should have a higher specific gravity (S.G.). The usual methods of determining S.G. e.g. weighing in air and water using a Pyknometer were not applicable due to the small size of the spicules and their ability of absorbing water.

A graded density column can be used on plastics in general, but besides difficulty in locating such minute specimens (16 microns diameter and less than 1 mm long) there is a surface tension effect around such a small specimen which can cause spurious and unrepresentative results. Also the inclusion of air in cracks and in the bulk cannot be entirely disregarded when dealing with such small density changes.

Therefore an indirect method was used via the Refractive Index (R.I.). The two properties are linked by the Lorentz-Lorenz equation,

\[ \rho K = \frac{n^2 - 1}{n^2 + 2} \]  

... (1)

where \( \rho \) = density  
\( n \) = R.I.  
\( K \) = constant related to molecular weight and molecular refractivity.

An Abbe refractometer (Bellingham & Stanley Ltd.) was used to measure the R.I. of both a splinter (1 mm x 10μ) and a small (0.5 mm) cube of matrix resin by the immersion technique using a mixture of bromo-benzene (R.I. 1.56) and iodo-naphthalene (R.I. = 1.70). Successive mixtures bracketed the R.I. of the cube between R.I. = 1.5825 and 1.5896 and the splinter between R.I. = 1.5948 and 1.6025.
A mixture of R.I. = 1.5880 gave a positive Becke effect for the splinter and a negative one for the cube.

The Becke effect is the name given to the bright line along the interface between two media having differing refractive indices. The bright line appears to move into the medium with the highest refractive index when the objective lens is raised, (6).

An error of repeatability due to the transference of the fluid from microscope to refractometer of about 0.001 was noted. Values of Refractive Index are as follows:

<table>
<thead>
<tr>
<th></th>
<th>repeatability</th>
<th>reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.I. of spicule</td>
<td>1.596 ± .002</td>
<td>± .006</td>
</tr>
<tr>
<td>R.I. of cube of matrix</td>
<td>1.585 ± .003</td>
<td>± .006</td>
</tr>
</tbody>
</table>

This gives a mean difference on between the two samples of 0.01 R.I. units. Several other spicules had similar R.I. within the repeatability or higher than that of the matrix. The reproducibility was as indicated.

Differentiating equation (1) with respect to n.

\[ K(d\rho/dn) = \frac{6n}{(n^2 + 2)^2} \]  ... (2)

Assuming \( n = 1.59 \), \( \rho = 1.25 \text{ g. cm}^{-3} \) for the purpose of determining K gave (equation 1): \( K = 0.27 \)

\[ \therefore d\rho/dn = 1.72 \text{ g.cm}^{-3} \]

In this case a change of 0.01 in R.I. corresponds to a change of 0.017 \text{ g.cm}^{-3} in the density.

Using the Bykman or Gladstone/Dale equation

\[ e.g. \quad K_o = \frac{n^2 - 1}{(n - 0.4)} \quad \text{or} \quad K_o = n - 1 \]  ... (3) 

\( \delta \) (4) give \( d\rho/dn = 1.31 \) and 2.12 respectively. As the Lorentz-Lorenz equation is derived from theoretical considerations involving electron optics
and forward scattering as well as giving $d\rho/dn$ intermediate relative to the empirical equations, it is as reliable as is required.

A typical value for the pressure required to produce one stress fringe per inch is 60 p.s.i.\(^{1}\) This leads to a strain of 0.00012 inches assuming Young's modulus to be $5 \times 10^5$ p.s.i. This strain is equivalent to a line density change of $\rho[1/(0.99988) - 1]$ i.e. $\Delta\rho_1 = 0.0001 \text{ gm.cm}^{-1}$.

As for small changes, $\Delta V \sim 3\Delta L$ this leads to a bulk density change $\Delta\rho = 0.0003 \text{ g.cm}^{-3}$. Comparison of the change in density observed (0.017) and that needed to produce one stress fringe per inch shows that a 10 micron cross-section splinter perpendicular to the direction of polarised light would produce a relative retardation sufficient to produce 0.1 stress fringes.

A typical needle-whorl appearance in a three inch block corresponds to a half of a stress fringe; i.e. 0.16 fringes per inch. This is consistent with a change in density caused by preferentially cross-linked parts or oriented spicules.

**MICROTENSOMETER TESTS ON SPICULES**

Tensile test measurements were made using a Techne Microtensile Tester on twelve spicules teased carefully from a fracture surface of a 28 lb. (12.7 Kg) casting of CT200/27 p.h.r. HT901 resin. This was cured for 16 hours at 120°C and after annealing at 140°C was cooled at 1 deg. C per hour to eliminate residual stresses.

The spicules varied in diameter from 5\(\mu\) to 90\(\mu\) but the very small ones proved too difficult to mount as did the very short.

\(^{1}\) 14.22 p.s.i. = 1 Kg.cm\(^{-2}\).
The results (Table 2) and (fig. 4) show a marked increase in strength with decrease in cross-section.

**TABLE 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absolute Breaking Stress (gms)</th>
<th>Breaking Stress (p.s.i.)</th>
<th>Cross Section ($\mu^2$)</th>
<th>Youngs Modulus* (p.s.i.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spicule 1</td>
<td>38</td>
<td>12,700</td>
<td>416</td>
<td>$2.6 \times 10^5$</td>
</tr>
<tr>
<td>Spicule 2</td>
<td>280</td>
<td>10,800</td>
<td>3,700</td>
<td>$3 \times 10^5$</td>
</tr>
<tr>
<td>Spicule 3</td>
<td>269</td>
<td>8,400</td>
<td>4,570</td>
<td>omitted</td>
</tr>
<tr>
<td>Spicule 4</td>
<td>130</td>
<td>2,150</td>
<td>8,680</td>
<td>$3.5 \times 10^4$</td>
</tr>
<tr>
<td>Spicule 5</td>
<td>broke at an obvious crack</td>
<td>1,650</td>
<td>omitted</td>
<td>$4.5 \times 10^4$</td>
</tr>
</tbody>
</table>

Typical Cold 400 Kg** 5,100 $\sim 0.058 \text{ in}^2$ -

test specimens Hot 11,146 $\sim 0.058 \text{ in}^2$ -

* not compensated for decrease in area whilst under strain as the specimens are very brittle. Error $< 5\%$.

** Using a Tensometer Type 'E' at 10% elongation per minute.

It seems therefore that the brittleness and toughness of a spicule
increase as the spicule diameter is reduced. A brittle inclusion in a softer matrix would cause local deformation on cooling even if no local strain was present at hot curing temperatures. This is due to the thermal coefficient of expansion and change in volume with pressure being less for a more cross-linked resin.

Compared with the typical test specimens of unfractured resin the spicules have progressively higher breaking stresses; the thicker spicules having a breaking stress comparable with the resin cured at a lower temperature whilst the thinner ones reach and even surpass that cured at a higher temperature.

It is well known that whiskers and fibres become stronger as they become thinner. Reasons postulated include the less frequent occurrence of point defects and microcracks combined with a greater degree of perfection in the crystal lattice resulting in there being less chance of a crack propagating.

It is generally accepted that epoxy-resin spicules have no definite crystal structure, yet many polymers, especially fibres such as rubber and nylon, under conditions of stretch, tend to rearrange their structure so as to align their chains resulting in greater strength and higher density.

If this is the case, x-ray diffraction of a spicule should reveal any crystalline nature or tendency to recurring structure.

X-RAY DIFFRACTION

If the resin spicule has any regular arrangement of molecule's or chains this should be shown by X-ray diffraction studies. These will also show the presence of any crystalline inclusions, such as hardener
that have crystallised during cure, e.g. phthalic anhydride (HT901) has a freezing point of $130^\circ$C whilst castings are made at an oven temperature of $120^\circ$C.

Using a 6 inch 'Philips' X-ray diffraction camera and a Philips PW1010/25 X-ray source, spicules were irradiated for periods of up to 6 hours. All showed a broad band corresponding to an interplanar spacing of about $0.5 \text{ nm}$ (P43) with one spicule giving a very distinct pattern of 10 strong lines and many weak lines, (P44).

The broad band is shown by a large number of polymers and is generally attributed to intramolecular regularity and not crystalline arrangement.

Comparison was made between the experimentally obtained diffraction patterns from the spicules and those obtained from a selection of crystalline compounds which spicules may consist of or contain through crystallization within a casting.

The compounds compared were phthalic anhydride, phthalic acid (a possible hydrolysis product of the anhydride) and C.I.B.A. Araldite MY790 which is a diglycidyl ether of bisphenol A (DGEBA) having $n = 0$ (p. 3). The phthalic anhydride samples used were both as commercially supplied (HT901) and resublimed.

It was necessary to sublime the HT901 before diffraction as this is the form that the hardener would be in if it recrystallized during the casting. It may be noted that due to the high vapour pressure of phthalic anhydride, a considerable amount of hardener sublimes during the manufacture of large castings and crystallizes on any available cool surfaces (below its melting point of $130^\circ$C).
X-ray diffraction photographs of spicules.
The two samples have different external forms, the resublimed anhydride being long thin monoclinic crystals whilst the commercial produce is in a caked form.

First, the experimental values of the known compounds were compared with computer-generated patterns, (7).

The computer program accepts data from the diffraction pattern of a sample either as a set of Bragg diffraction angles (θ or 2θ), interplanar spacings (d) or as 'Q-factors' \((10^4/d)\). These it compares with the complete set of Q-factors calculated from the known unit cell dimensions, density and crystal system of the required comparison compound. Thus the experimental diffraction pattern of a spicule may be compared with the computed pattern of, say, phthalic anhydride: each line of the spicule pattern being compared with the nearest line to it in the anhydride.

A mean is calculated:

\[
\text{mean} = \frac{\sum_{o}^{n} (Q_{\text{ith.obs.}} - Q_{\text{nearest calc. value}})}{\text{Number of observed lines}} \times \frac{\text{No. of calc. lines}}{\text{Max. val. of } Q_{\text{obs}}}
\]

High correlation corresponds to a low calculated mean, random lines give unity.

Agreement was found between the computed and experimentally obtained results of both phthalic anhydride and phthalic acid. The diffraction patterns of the two forms of phthalic anhydride were essentially the same varying only in the intensity of the diffraction of a few lines, the difference in form being purely external.

A further investigation was made on a crystalline sample from a mixture of MY790 and HT901 which had been evaporated to dryness from acetone (Analar). Of the twenty lines in the diffraction pattern,
sixteen were directly attributable to the experimental patterns of either MY790 or HT901: all including the other four (very weak) correlated with the computer generated pattern.

The spicule pattern was found not to agree with any of the experimental or computed diffractions. Table (3) shows the agreement between the phthalic anhydride pattern and the computer which contrasts with the lack of correlation between the spicule and any other pattern.

**TABLE 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comparison Pattern (computed)</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.A. (HT901)</td>
<td>P.A. (12)</td>
<td>0.2</td>
</tr>
<tr>
<td>recrystallised P.A. (HT901)</td>
<td>P.A.</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Phthalic acid (13)</td>
<td>0.72</td>
</tr>
<tr>
<td>Spicule (P.44)</td>
<td>P.A.</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Phthalic acid</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>(experimental)</td>
<td></td>
</tr>
<tr>
<td>Spicule (P.44)</td>
<td>DGEBA (MY790)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P.A. (HT901)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>recrystallised P.A.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>See Fig. 5</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5. Comparison of X-ray diffraction data.
Fig. 5 shows on an expanded scale the experimentally determined Bragg angles with all intensities normalized to the strongest line.

The Powder Refraction Index lists all compounds so far investigated by X-ray Diffraction. The indexing is by the three strongest reflections expressed as d-spacings. The spicule has its three strongest lines at .303 nm, .249 nm and .191 nm. No correlating patterns were found in the index; special attention was paid to silicates as these might have been present as impurities in the casting release agent (Releasil No. 14) or even in air-borne dust particles that may have been introduced accidentally during mixing.

INFRA-RED SPECTROSCOPIC ANALYSIS OF THE SPICULES

An analysis of the spicules was undertaken to ascertain any chemical difference which may result from their formation. The instruments used were the Unicam S.P.200 and the Perkin Elmer 457. The samples were irradiated in the form of a KBr disc. See appendix 2.

Comparison was made between:

S1. A CT200/HT901 mix cured for 72 hours in a small (1 lb.) block in which the maximum temperature as measured by a thermocouple was 130°C in the centre.

S2. A CT200/HT901 mix cured in a large (28 lb.) block with an oven temperature of 120°C. The maximum temperature in the centre was over 210°C.

S3. 0.4 mgms of spicules (about 50 in number) in a KBr disc weighing 0.25 gms.

S4. HT901 (Phthalic Anhydride hardener).

S5. CT200 (DGEBA) of average mol. wt. ~ 900.
Infra-red spectra of cured resin
Infra-red spectrum of spicules
Infra-red spectra of P.A. and DGEBA.
The resin cured at the lower temperature (S1) has absorbance peaks at 1845, 1770, 1783, 893 and 675 cm\(^{-1}\) which are absent in that cured at up to 210°C (S2). All of these frequencies are strongly absorbing peaks in phthalic anhydride (S4) and characteristic of the anhydride ring.

The spicule spectrum (S3) has low absorbance peaks because of the low concentration of material. It shows strong similarities to the high temperature cured resin having no residual anhydride peaks which confirms the view that spicules are regions of highly cross-linked resin.

There is a higher concentration of ester linkages apparent in the spicule spectrum than either of the resin samples (1725 cm\(^{-1}\)). Compared with the internal standard at 2980 cm\(^{-1}\) (see appendix 2) the relative absorbance at 1725 cm\(^{-1}\) of the spicules is 2.15, the high temperature and low temperature resins being at 1.92 and 1.86 respectively.

Compared with the results of Tanaka and Kakiuchi (8) who found a higher ester content in resins cured at high temperatures this 11\% rise in ester content accords with the view of the spicule as a reaction centre.
From these experiments it is clear that a spicule is a region of higher cross-linked resin having a higher density than the surrounding matrix. That the spicule has more in common with epoxy-resin cured at a high temperature than that cured at a lower is shown by both the tensile tests and the I.R. analysis. These show its strength to be as high as and its proportion of the esterification reaction to be about 11% higher than the resin of higher cure temperature.

The esterification reaction requires equal molar quantities of phthalic anhydride (P.A.)/D.G.E.B.A. to sustain the reaction. In a 27 p.h.r. mix as is generally used, there are 1.44 times as many hardener molecules as resin molecules. However, the functionality of the resin is 4.4 on average compared with 2 for the hardener so that the hardener is not in excess.

The 11% rise in esterification will therefore lower the P.A. concentration in the region surrounding the spicule and a greater proportion of the curing will progress via the etherification reaction in the matrix. This results in a less dense, weaker cured resin consistent with the more open structure resulting from the etherification reaction (p. 10).

There is no evidence of crystallisation or orientation having a repeat unit of less than 30 Å. Large spacing such as that resulting from chain-folding in polyethylene is not possible in such a three-dimensional condensation polymer as epoxy-resin suggesting that the spicule is devoid of any crystallisation or similar regular arrangement of molecules or chains.

Recently, Nelson and Turner have published micrographs of phenyl-
formaldehyde fracture surfaces in which very similar spicule fields are to be seen (10). They confirm the opinion that spicules occur in the region of fast fracture propagation but claim that the formation of these lances, as they term them, is due to heat generated in the poorly conducting polymer combined with the stress waves reflected from the interfaces. They claim this stress to be sufficient to cause buckling in the area in advance of the crack front which results in secondary fractures. The buckled region then forms curls of resin as the crack opens which are perpendicular to the crack front.

This hypothesis may account for the formation of spicule-like phenomena in so far as a softened area in front of the advancing crack will amplify the structure differences between spicule and matrix. This would facilitate the removal of spicules but the hypothesis of curl formation is not borne out by the definite solidity of the spicules shown by both the tensile tests and the micrographs of the root area, P11, 28, 31.

Haward and Brough (11) consider the fibrils they found on fracturing polystyrene at room temperature to have been formed from a drawing out of softened crack-propagation area and to be solid. Their fibrils however, were much more flexible than epoxy-resin spicules and of an essentially linear polymer.

A critical factor in the formation of spicules from aggregations of spheres is the rate at which hardener can reach the reaction centres. At any time after the initiation of a sphere, the rate of reaction of anhydride at its surface must be 11% higher than the rate in the matrix. This will cause a depletion around the sphere which must be compensated for by diffusion of more hardener from the matrix.
The flux $J$ of a diffusing medium can be simply expressed in terms of the diffusion constant and the concentration gradient $dc/dx$ in one dimension; Fick's first law of diffusion:

$$J = -D \frac{dc}{dx}.$$

where $J$ is measured in moles $\cdot$ sec$^{-1}$.cm$^{-1}$, $D$, in cm$^2$.sec$^{-1}$ and $c$ in moles cm$^{-3}$.

The flux towards the sphere must therefore be equated with the extra rate of reaction of hardener at the surface of a sphere.

$$-D . \frac{dc}{dx} = \frac{11}{100} . \frac{dc}{dt}.$$

It was therefore decided to measure the diffusion of P.A. through the matrix during cure and the rate of cure to determine whether spicule formation was probable as an extension of spherical alignment.

The rate of cure is not a simple parameter to measure as it depends on concentration and the temperature which in a large block of resin is not uniform. Whilst the centre of a large block of resin may reach over 200°C, the outer regions will rise only a little above the ambient oven temperature (typically 120°C). This means the centre may have reached total cure whilst the outer shells are not even half cured.

The determination of the isothermal rate of cure can be made on small samples having essentially uniform temperature throughout and the sum of the rates of cure for the thermal history of any point will be equal to the extent of cure at that point.

It is therefore necessary to know the temperature at a number of points within the block during cure. This may be simply achieved by inserting thermocouples at appropriate points in a casting.

If the spicule has a depleted layer of hardener around it this would explain the ease with which it is torn from the surrounding matrix.
during a fracture. This ease may be further enhanced by the stress within a curing block caused by differential curing rate.

Two opposing factors come into play during cure; the density of the block becomes lower as the temperature rises but at a higher temperature the rate of cure is faster leading to a rise in density. If the density profile in a block is known, the stresses within it can be found by calculating the displacement of the resin caused by the density changes.

For the determination of the balance of the hardener during cure it will be necessary to know i) the diffusion constant D and ii) the extent of cure and the rate of cure at any time.

Calculation of the curing stresses requires a knowledge of the density at any point in a casting. This can be done if the rate of change of density with time is known for any temperature and at any extent of cure.

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PART III
DETERMINATION OF THE DIFFUSION CONSTANT

Since the discovery and subsequent availability of radioactive isotopes the easiest method of measurement of the self-diffusion of a material within itself is by labelling the diffusing species with a radioactive atom.

For determining the self-diffusion of phthalic anhydride (P.A.) the choice of isotopes is between $^3$H and $^{14}$C; the isotope of oxygen $^{18}$O has low activity and is not readily available commercially.

Tritiated substances are generally made by an exchange of the form:

$$\text{ROH} + \text{H}_2\text{O} \rightarrow \text{RO}^3\text{H} + \text{H}_2\text{O}$$

In P.A. the hydrogen atoms are all on the conjugated ring of carbon atoms which is not as readily exchanged in this fashion.

$^{14}$C was chosen because of its availability although it is not as easy to analyse as $^3$H using scintillation counting techniques. A half millicurie of phthalic anhydride was supplied by the Radiochemical Centre at Amersham. The activity of the P.A. supplied was 8.6 mC/mMole, the mass being 17.2 mgms/mC. The radiocarbon was present in the P.A. in the anhydride ring:

As the hardening of epoxy resin by P.A. is a condensation reaction the diffusion of the labelled P.A. can be followed by measuring the radioactivity after diffusion for varying times and temperatures.

$^{14}$C labelled P.A. has a higher molecular weight than unlabelled...
material due to the extra two neutrons. It will therefore diffuse more slowly on account of its extra mass and therefore greater inertia.

The ratio of the Diffusion constants due to the Isotope effect as this is called may be calculated (1) from the relationship:

\[
\frac{D'}{D} = \frac{\mu}{\mu'}
\]

\[
= \frac{148 \times 150}{148 + 150} \times \frac{148 \times 148}{148 + 148} = 1.0035
\]

\(D', D\) are the Diffusion constants of P.A. containing \(^{14}C\) and \(^{12}C\) respectively.

\(\mu', \mu\) are the reduced masses respectively.

Compared with the uncertainty associated with the statistical nature of radioactive emission this factor is small enough to be ignored.

EXPERIMENTAL METHOD - SAMPLE PREPARATION

Diffusion was carried out in glass tubes as shown in fig. (6). These were held horizontally in an oven (Pickstone Ltd.) with temperature controlled to \(\pm 1^\circ\)C and the time measured by a crystal clock (Venner). A small diameter tube was used to minimise convection and thermal gradient.

Fig. 6

'Active' resin mix | 'Normal' resin mix

'-1 cm -1 cm \rightarrow 13 cm expansion tube'

'Active' resin mix was made by diluting the radioactive P.A. with 30 gms. of commercial P.A. (C.I.B.A. HT901). This was achieved by dissolving them both in Analar grade acetone and evaporating to dryness
by means of an Infra-red lamp placed a few inches above the surface. A previous control experiment had shown a loss in mass of less than 0.0003 gms. in 30 g for the solution/evaporation cycle.

Dilution of the concentrated $^{14}\text{C}$-containing P.A. was carried out in a laboratory at A.W.R.E. Aldermaston especially equipped for handling active materials. In point of fact the $\beta$-emission from $^{14}\text{C}$ is very weak and will not penetrate laboratory glass-ware; even in open air the radiation is not detectable beyond a few cms.

The diluted 'active' P.A. was then added to 111.1 g. commercial resin (C.T. 200 C.I.B.A.) making a 27 p.h.r. mix at 100°C to minimise pre-cure (Cure time is over 60 hrs. at 100°C). This was then poured into the tubes which had previously been treated with release agent (Releasil 14). About 1 cm. was poured into each and they were cooled immediately. When they were completely hard the tubes were filled with an ordinary 27 p.h.r. mix; the bent tubes in the end seals being inserted whilst still liquid to relieve expansion on the subsequent cure cycle. The tubes were immediately cooled in an ice bath to prevent pre-cure diffusion.

Sampling is generally the most difficult stage of diffusion determination. This is due either to the difficulty of sample isolation during the diffusion of a liquid or of accurate determination of the $x$-coordinate in the small distances involved in most solid diffusions, (1-2 mm maximum).

In this experiment the ease of sampling coupled with the greater distances involved in the liquid diffusion due to the high freezing point of the resin mix greatly eased these inherent difficulties.
Sampling was done in the following manner. First the cooled cylinders of cured resin were removed from the glass moulds; for the longer cure times this was simply a matter of sliding them out, for the shorter cure times the resin had not shrunk sufficiently and the moulds had to be broken.

The cylinder was carefully cleaned of release agent using acetone and cotton-wool with the direction of cleaning towards the radioactive end to prevent contamination.

Next, the cylinders were marked with notches at 1 cm intervals to facilitate the determination of $x$, the diffusion direction coordinate. The cylinder was then placed in a vice and compressed until it split, usually axially but occasionally radially.

Samples between 1 and 15 mg were taken with a scalpel at three or four values of $x$ determined by the pilot experiments and the expediency of the crack location but always as near as possible to the axis of the cylinder.

**EXPERIMENTAL METHOD - SCINTILLATION COUNTING**

It is not possible to measure the weak $\beta$-emission from $^{14}$C directly because of its short range in air. As a result the $\beta$-emission is used to stimulate the secondary emission of light from sensitive scintillating compounds. These absorb electrons easily, transforming some of the energy absorbed into quanta of light at frequencies characteristic of the scintillator.

It has been found (2 - 3) that some of the most efficient scintillators for low energy $\beta$-emission are the substituted oxazoles; however the emitted electromagnetic spectrum is not well matched to the detected spectra of the photomultipliers (p.m.s.) which are necessary to deal with
the low light intensities obtained, (4).

Because of this a secondary scintillator is used (5) which can absorb the already stimulated excess energy from the primary scintillator by a non-radiative collision transfer mechanism (6). The secondary scintillator then returns to its ground state with the emission of light in the range of the p.m. spectrum.

Due to the high noise associated with p.m. amplification factors between $10^6$ and $10^{10}$ it is normal practice to use two matched p.m.s. within a pulse height discriminator network. This only records light pulses arriving at the p.m.s. coincidentally. Thereby any noise due to the dark current of an individual p.m. or to electron build up on the dynodes is eliminated. Cosmic radiation and natural background radiation from glassware or the solvents themselves is not eliminated and the background count is primarily due to these.

The scintillator fluid used in the following experiments was NE250 (Nuclear Enterprises Ltd.). It comprises 2,5, Diphenyl oxazole (P.P.O.) as the primary scintillator and naphthalene as the secondary scintillator in a solution of toluene and 1,4, dioxane. Toluene is an ideal solvent for scintillators having a very low quenching effect and the ability to dissolve a wide range of organic compounds.

Quenching is the absorption of either $\gamma$-emission itself or the resultant light quanta. It is little understood but is thought to be due to a non-radiative energy transfer from a scintillator during a collision or at least a short-range interaction with a quenching agent (6): subsequent re-emission is at a lower energy or outside the detected range. Due to the high quenching effect of oxygen (7), all samples counted were bubbled with a stream of nitrogen previous to
measurement. Many solvents shorten the excitation lifetime of the scintillator thus preventing transfer of energy to the secondary scintillator.

1,4-dioxane is used to take aqueous samples into solution. Although it has a small quenching effect it is lower than any other suitable solvent. NE250 mixes with up to 10% of aqueous solution although the partition coefficient is low for most inorganic salts and causes precipitation. This can be advantageous in reducing turbidity and strong colouring as long as the material being counted is not co-precipitated.

The scintillation counter used was a Beckmann LS-100. It measures $^3$H, $^{14}$C or $^{32}$P emissions as well as any combination of these. Their individual spectra overlap, fig. (7), so the ranges measured are usually as shown.

![Fig. 7](image)

All concentrations quoted here are already converted to counts per minute per milligram of resin. For example 5560 $^{20}$ cpm. is equivalent to 5560 counts per minute from a 20 minute count totalling 112,000 disintegrations having a difference from the mean of not more than 0.7 per cent.

As there is a high background count of 200 in the $^3$H region compared with that in the $^{14}$C of 18c/m/m and if a ratio of 100:1 is taken between count and background as the minimum consistent with accuracy, counts as
low as 1800 c/m/m may be used compared with 20,000 minimum for the combined spectrum.

A sample of about ~10 mg was generally used so that diffused concentrations of P.A. as low as 0.003 times that of the original 'active' resin could be counted.

The statistical confidence level used to determine the accuracy of the count is twice the standard deviation $\sigma$.

The 'active' mix gave a count of $5560^{20}_{0.7}$ c/mm compared with the theoretical 7,800 calculated from the known radioactivity at the start. This is 72% compared with the 75% claimed for NE250. Allowing for some lost during dilution and the possibility of the original activity being less than 100%, this is satisfactory and will be the value used throughout as the starting activity.

The geometry of the Beckmann LS-100 is such that an optimum peak for counting occurs when the sample tube, of low activity glass, contains about 11 mls. of fluid.

Table (4) shows the above effect, all counts are from 1 ml. samples of the same solution of uncrosslinked 'active' sample.

**Table 4**

<table>
<thead>
<tr>
<th>mls</th>
<th>NE 250</th>
<th>2.5</th>
<th>6</th>
<th>11</th>
<th>13</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.m.m.</td>
<td>$1100^{10}_{2}$</td>
<td>$1788^{10}_{2}$</td>
<td>$2586^{10}_{1.5}$</td>
<td>$2538^{5}_{3}$</td>
<td>$2212^{5}_{3}$</td>
<td></td>
</tr>
</tbody>
</table>

Before the curing cylinder of resin has gelled it is easily soluble in 1,4, dioxane and counts may be easily obtained from 1 ml. of 'active' solution in 5-10 mls. of scintillator NE 250.

Once gelled the resin is insoluble and the methods of dissolution
used result in an aqueous solution so that a maximum of 1 ml. can be used in 10 mls. NE 250.

Extensive searches for a solvent for post-cure epoxy resin proved fruitless but concentrated sulphuric acid decomposed the resin to a deep brown oil. The acid and oil mixture was too strong to use undiluted in NE 250 so it was first neutralised with solid NaOH to pH 9 followed by N/10 H_2SO_4 to pH 7 using 'universal' indicator.

This resulted in large crystals of Na_2SO_4 being formed even after dilution to 5 mls with water before neutralisation. As the total water content must be kept low to facilitate solution in the scintillator, a sample was decanted. The liquid volume loss in the neutralisation of H_2SO_4 by NaOH is about 1/3 the original volume of H_2SO_4.

1 ml. of decanted solution in the usual 10 ml. NE 250 gave 1550 cpm. This is 27.8% yield compared with uncured resin dissolved in 1,4, dioxane.

To check the effects of 'universal' indicator or Na_2SO_4 on the scintillator they were added to a solution of known count with the results below. A few drops of water were added to each tube to ensure ionic activity from the impurities.

<table>
<thead>
<tr>
<th>Control</th>
<th>Control + 1 gm. Na_2SO_4</th>
<th>Control + 4 drops</th>
<th>Control + Both of 'Universal' indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>ccm.</td>
<td>5560^10</td>
<td>5479^10</td>
<td>5594^10</td>
</tr>
</tbody>
</table>

A rise in level in the sample tubes would account for the small drop in count for those tubes containing solid but even this is only a 1.6% rise compared with the statistical uncertainty of 1%.

To test the effect of varying pH on the count of cured 'active' resin, a series of samples were made from the same 'active' cured resin dissolved in concentrated H_2SO_4 and neutralised to pH 9 as before and
then adjusted as required by N/10 H\textsubscript{2}SO\textsubscript{4}. Counts were taken as in Table (5); adjustment of the pH and the consequent counts are also shown.

<table>
<thead>
<tr>
<th>TABLE 5</th>
<th>pH10</th>
<th>pH7</th>
<th>pH2</th>
<th>Control in 1,4, Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>cmm.</td>
<td>390\textsuperscript{5} \textsubscript{5}</td>
<td>1570\textsuperscript{5} \textsubscript{3}</td>
<td>2000\textsuperscript{5} \textsubscript{2}</td>
<td>3012</td>
</tr>
<tr>
<td>% of known activity</td>
<td>7</td>
<td>28</td>
<td>36</td>
<td>100</td>
</tr>
<tr>
<td>as above with re-adjusted pH</td>
<td>2</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ccm.</td>
<td>406\textsuperscript{5} \textsubscript{5}</td>
<td>1000\textsuperscript{5} \textsubscript{2}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

P.P.O. is stable to acid hydrolysis (8) and, being a very weak base itself, is very stable to alkali hydrolysis withstanding 200°C for 2 hours in 15% alcoholic KOH (9). Therefore the evident reduction of count due to high pH number cannot be due to decomposition of P.P.O. or opening of the ring by the usual means:-

![Chemical structure](image)

In the absence of the possibility of violent quenching it was thought that some of the \textsuperscript{14}C had escaped detection before it reached the scintillator. There are three possible losses.

1. Neutralisation by NaOH, being extremely exothermic (~14 Kcals./mole), may cause some of the volatile breakdown products to evaporate.
2. Solution in c. H\textsubscript{2}SO\textsubscript{4} may release \textsuperscript{14}C as \textsuperscript{14}CO\textsubscript{2} or in some other volatile oxidation products.
3. Compounds such as Na\textsubscript{2}\textsuperscript{14}CO\textsubscript{3} or salts of organic acids formed during the violent oxidation may precipitate during neutralization or in the scintillator fluid and thus escape counting.
The first possibility that volatile radioactive compounds were driven off by the high temperature reached during neutralization was investigated in the first case by very slow ice cooled neutralization during which the temperature was never allowed to exceed 15°C. The results are given below.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>Ice cooled</th>
</tr>
</thead>
<tbody>
<tr>
<td>ccm.</td>
<td>$2218^{10}_{1.5}$</td>
<td>$2284^{10}_{1.5}$</td>
</tr>
</tbody>
</table>

This result is within the experimental error of ±1% for 10 mg samples.

A sample of the ice-cooled and neutralized mixture was then heated to 60°C and held at that temperature for 30 minutes. Subsequent counting gave $2188^{10}_{1.5}$ ccm. This is not significantly lower than before.

The second possibility was tested using the apparatus in fig. (8a).

![Diagram](image)

**Fig. 8**

A very slow stream of nitrogen impinged on the surface of the acid in which 'active' resin (10 mg) was slowly dissolving/decomposing. Any gaseous radioactive material was carried to the bubble flask where it
dissolved in the solvent.

Initially the solvents used were 2N NaOH, toluene, 1,4-dioxane and chloroform. Scintillation counting of these solutions showed no count above background radiation for any of them.

There is still the possibility that, in the second case with NaOH as the solvent, neutralisation with H₂SO₄ released $^{14}$CO₂. The other solvents used would not absorb CO₂.

$$\text{Na}_2^{14}\text{CO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + ^{14}\text{CO}_2 + \text{H}_2\text{O}$$

This was investigated by using a mixture of ethanolamine (E.A.) and ethylene glycol monoethyl ether (E.G.M.E.), as the bubble flask solvent. This is a good medium for absorbing CO₂ forming ethanolamine carbonate in the polar ether which acts as a carrier solvent for the amine carbonate and toluene based scintillator fluid. Ethanolamine is used commercially for CO₂ absorption in aqueous solution in the Girbotol process.

Once again only a background count was found confirming the fact that no volatile radiocarbon compound is evolved during neutralisation.

The method was checked by burning a known quantity of 'active' resin in a stream of oxygen. The tube was heated with a bunsen burner until the resin spontaneously ignited. A count of $496^{10}_5$ cmm. was found in the E.A./E.G.M.E. using 'active' uncrosslinked resin. Crosslinked resin yielded $152^{10}_5$ cmm. These compare very unfavourably with the known activity of $5560^{20}_7$ cmm. the cured resin having a lower count because of its higher resistance to oxidation.

Using 2 gms. of KMnO₄ to cover the resin before heating the tube to increase the concentration of available oxygen yielded a count of $684^{10}_5$ cmm.
A stream of nitrogen was used to carry over the final gaseous products and it was found necessary to interpose an air trap between the reaction tube and the bubble flask to prevent KMnO₄ reaching the scintillation medium as it is a strong quenching agent. fig. (8b).

Use of a delivery tube with a sintered glass end, fig. (8b), increased the yield to 830₁₀ cmm. whilst the addition of raschig rings and glass granules gave a maximum count of 206₅₁₀ cmm. with the uncured resin and 121₃₁₀ cmm. with cured resin. These are 37% and 22% respectively of the known available ¹⁴C count.

For uncrosslinked resin there is no necessity to use this method as it dissolves easily in 1,4, dioxane but for post-gel resin there was a lower yield than that from the acid/alkali method (66%).

The failure of this method must be due to the incomplete conversion of ¹⁴C to ¹⁴CO₂ and to the inability of the solvent medium to absorb the gases completely. This is apparently so, as increased impedance of gas flow in the bubble-flask raised the count. The highest count of 206₅ cmm. was given in a 15 cm test-tube full of raschig rings and glass granules, a single nitrogen bubble taking about 5 seconds to reach the surface from its release from the sinter surface.

The large outflow of oxygen needed for the reaction will saturate the solvent and subsequent nitrogen bubbling may not remove it completely, resulting in considerable quenching.

Possibility 3 was investigated by solvent extraction of an aqueous solution of the washed crystals with ethanolamine/toluene (1:1). This will extract ¹⁴CO₃⁻ ions from Na₂¹⁴CO₃ due to the affinity of ethanolamine for the ion. As partition of ethanolamine occurs between the aqueous and toluene layers full separation is not possible without
multiple extractions. Two separate 5 ml. portions of ethanolamine/toluene were used and counts of these and a control of active uncured resin in 1,4, Dioxane were:

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>1st extract</th>
<th>2nd extract</th>
<th>Remaining solute</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>cmm.</td>
<td>5370</td>
<td>857</td>
<td>607</td>
<td>3880</td>
<td>187</td>
</tr>
</tbody>
</table>

These are small amounts (~1%) of the total available indicating that the radioactive salts must at most be formed by a minor side-reaction or else the count comes from inclusions of solute in the crystals.

It is not possible to definitely assign reasons for the deficiency in the count from these three possibilities which seem to be the only chemical explanations. Burning the resin in an oxygen-enriched atmosphere seemed a promising method for preparing samples for counting but it is not possible to recover a sufficient proportion of emitting particles. The drop in count to 36% may be explained partially by quenching due to the large water content of the scintillator or by self-absorption of the secondary emission due to turbidity.

It was decided to use the method of dissolving in acid and subsequent neutralization to pH2 as it gave the highest count and was reproducible. Results of five independent samples gave 2061\(\pm 10\)\(_{1.5}\), 2004\(\pm 10\)\(_{1.5}\), 2010\(\pm 10\)\(_{1.5}\), 2094\(\pm 10\)\(_{1.5}\), 2073\(\pm 10\)\(_{1.5}\), the mean being 2048 ± 2%.  


CALCULATION

Fick's law of diffusion

\[
\frac{dC}{dt} = D \frac{d^2C}{dx^2}
\]

implies that the diffusion coefficient \(D\) is independent of the concentration of the diffusing species \(C\). However, Barrer (11) and others show that it is dependent on concentration and equation 1 becomes

\[
\frac{dC}{dt} = \frac{d}{dx} \left( D \frac{dC}{dx} \right)
\]

for which Matano (12) has evolved a graphical method of solution.

Fortunately this is not necessary in this case of self-diffusion as the concentration of phthalic anhydride remains constant. It is therefore possible to use the integrated forms of Fick's law which follow.

The Diffusion Constant \(D\) is most easily calculated by considering two layers of material, one of which contains a radio-active tracer, the other not.

For an infinitely thin layer containing radio-active tracer diffusing through an infinitely thick layer the solution to equation (2) is

\[
\frac{C}{C_0} = \frac{1}{\sqrt{\pi Dt}} \exp(-x^2/4Dt)
\]

For a diffusion of 1-2 cm the average concentration must not drop below 0.003 of the original concentration for an accurate count to be made (p. 70). This means that the thin layer must be approximately 0.003 cm thick. If the average diffusion were greater than this, then the thin layer would have to be correspondingly thicker.
For two finite layers the concentration at \( x \) cm from the interface is given by:

\[
\frac{C}{C_0} = \text{erf} \left( \frac{L - x}{2\sqrt{Dt}} \right) + \text{erf} \left( \frac{L + x}{2\sqrt{Dt}} \right) \quad \ldots (4)
\]

where \( L \) is the thickness of tracer-containing layer,
\( x = \) distance from interface
and \( \text{erf}(a) \) is the error function or probability integral defined as

\[
\text{erf}(a) = \frac{2}{\sqrt{\pi}} \int_0^a e^{-m^2} \, dm
\]

where \( m \) is the instantaneous value of \( a \).

The concentration \( C \) at a distance \( x \) from the interface after time \( t \) for two infinite layers is given by:

\[
\frac{C}{C_0} = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] \quad \ldots (5)
\]

where \( C_0 \) is original tracer concentration with the boundary conditions:

- at \( t = 0 \); for \( x > 0 \), \( C = 0 \)
  - for \( x < 0 \), \( C = C_0 \)
- at \( t > 0 \); for \( x > 0 \), \( C = f(x, t) \)
  - for \( x < 0 \), \( C = f^*(x, t) \)

'Infinite' layers of a material with a low diffusing distance of a few microns need only be a few cm thick but it was estimated that in the hot resin the average diffusion would be in the order of a few cm because of the surface depletion noted by Cuthrell (13) and that equation (4) would apply.

It was found during pilot experiments, however, that the diffusing species rarely reached more than 1.5 cms from the interface in a countable quantity. This means that equation (5) may be used which facilitates calculation by eliminating lengthy interpolation formulae
which must otherwise be used with the error integrals. Fig. (9) shows an idealised diffusion profile for different times of diffusion.

![Diagram of concentration profile](image)

As long as the decrease of concentration of the diffusing species at \( x = 0 \) and the increase at \( x = 2x_o \) are very small then equation (5) holds (11). It can be seen that the concentration at the interface remains at \( 0.5C_o \).

The diffusion of phthalic anhydride will diminish during the reaction for two main reasons. Firstly some of it will react with the resin so reducing the concentration and secondly, having reacted, the path of diffusion will steadily increase. Hence the values of the diffusion constant obtained will decrease with time of cure, extrapolation to zero giving the true self-diffusion constant. The values obtained after any time may be taken as average values of the diffusion constant for the reaction up to that point.

A small error will occur due to the diffusion of crosslinked resin which has already reacted with tracer-containing anhydride. The cross-section of this diffusing species will be at least five times that of the unreacted anhydride and it will be in an excited state (see p. 10), readily reacting to attain an even greater volume.

It is estimated that its contribution to the total diffusion will be less than 1% as its concentration at the beginning of the reaction is small and its diffusion constant less than 1/25 that of the anhydride.
Three sets of data were experimentally determined, the results being tabulated in Table (6). The values of $\text{erf}(x)$ were obtained from the Mathematical Tables of Abramowitz and Stegun.

$C_0$ was taken as 5,560 cm$^2$ for 1,4, dioxane-soluble counts whilst for those for which it was necessary to use c.$\text{H}_2\text{SO}_4$, $C_0$ was taken as 3,700 cm$^2$.

$x$ was measured to 0.1 mm where possible but in any case to 0.2 mm. Where a sample was greater than 0.1 mm in the x direction, $x$ was estimated for the centre of mass of the sample.
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Solvent</th>
<th>Diffusion $x$ (cm)</th>
<th>Concentration $C$ (cmm)</th>
<th>$\text{erf}^{-1}(1 - 2(C/C_0))$</th>
<th>Diffusion Constant $10^5 \times D$ (cm$^2$·sec$^{-1}$)</th>
<th>Average $D \times 10^{-5}$</th>
<th>$\log(Ave. D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>Dioxane</td>
<td>0.08</td>
<td>1286</td>
<td>0.5194</td>
<td>0.2076</td>
<td>0.2248</td>
<td>6.352</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.26</td>
<td>300</td>
<td>1.1368</td>
<td>0.2421</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>130</td>
<td>Dioxane</td>
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<td>934</td>
<td>0.6803</td>
<td>0.5290</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>280</td>
<td>1.1607</td>
<td>0.5498</td>
<td>0.5549</td>
<td>6.744</td>
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<td></td>
<td></td>
<td>0.63</td>
<td>~54</td>
<td>1.7700</td>
<td>0.5860</td>
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<tr>
<td>150</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>0.18</td>
<td>1275</td>
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<td>1.876</td>
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<td></td>
<td>0.32</td>
<td>965</td>
<td>0.4531</td>
<td>2.309</td>
<td>2.126</td>
<td>5.328</td>
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<tr>
<td></td>
<td></td>
<td>0.58</td>
<td>432</td>
<td>0.8425</td>
<td>2.194</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1.3</td>
<td>143</td>
<td>1.2492</td>
<td>5.01</td>
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<tr>
<td>180</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>0.22</td>
<td>1213</td>
<td>0.3153</td>
<td>2.254</td>
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<tr>
<td></td>
<td></td>
<td>0.74</td>
<td>321</td>
<td>0.9624</td>
<td>2.737</td>
<td>2.55</td>
<td>5.4065</td>
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<tr>
<td></td>
<td></td>
<td>1.15</td>
<td>~59</td>
<td>1.5174</td>
<td>2.659</td>
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</tr>
</tbody>
</table>
Cure time 60 minutes

<table>
<thead>
<tr>
<th>Time (°C)</th>
<th>solvent</th>
<th>Cure time (min)</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
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</thead>
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<tr>
<td>110</td>
<td>Dioxane</td>
<td>0.075</td>
<td>1809</td>
<td>0.3202</td>
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<tr>
<td></td>
<td></td>
<td>0.3</td>
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</tr>
<tr>
<td></td>
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<td>0.3639</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.88</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>Dioxane</td>
<td>0.14</td>
<td>1722</td>
<td>0.3512</td>
<td>1.104</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.27</td>
<td>944</td>
<td>0.6753</td>
<td>1.110</td>
<td>1.107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67</td>
<td>473</td>
<td>0.9701</td>
<td>3.30</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>H₂SO₄</td>
<td>0.24</td>
<td>912</td>
<td>0.4848</td>
<td>1.709</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.36</td>
<td>588</td>
<td>0.7064</td>
<td>1.804</td>
<td>2.337</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.98</td>
<td>~94</td>
<td>1.3810</td>
<td>3.497</td>
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</tr>
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<td></td>
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<td>1.70</td>
<td></td>
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<tr>
<td>180</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>550</td>
<td>0.7390</td>
<td>3.196</td>
<td>5.70</td>
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<td></td>
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<td>1.4</td>
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<td>1.2875</td>
<td>8.2</td>
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</tr>
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<td></td>
<td></td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cure time 40 minutes</td>
<td>Dioxane</td>
<td>Dioxane</td>
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</tr>
<tr>
<td>----------------------</td>
<td>---------</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>150</td>
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<td>1.00</td>
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<td>150</td>
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<td></td>
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<td></td>
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<td>1.70</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.33</td>
<td>1.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.60</td>
<td>1.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.60</td>
<td>1.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CASTING STRESSES

THEORY

For a knowledge of the distribution of stresses within a casting it is necessary to know the displacement vectors along the stress paths. Photoelastic measurements are not available due to the impossibility of stress-freezing a large block which would continue to cure during the stress-freezing method. Also this method gives zero stress readings in cases of homogeneous compression or tension whilst the object of the experiment is to ascertain whether the cure stresses are greater than the strength of the material.

If the density is known at any point in the casting it is possible to calculate the displacement between any two points in it. In a cylinder the radial stress is simply:

\[ \text{stress} = \frac{du}{dr} \cdot \text{Bulk Modulus} \quad \ldots(1) \]

where \( u \) = displacement, \( r \) = radius.

By measuring the temperature-\( v \)-time relationship for any point in the casting during cure and correlating this with the known rate of change of density at any temperature and the degree of cure at any time, it is possible to calculate the density-\( v \)-time relationship for any point in the block.

Thus at time \( t \) the density \( \rho \) equals the initial density + the sum of the rate of change of \( \rho \) for \( t_0 = 0 \) to \( t \)

\[ \rho_t = \rho_o + \sum_{i=0}^{t} \frac{\partial \rho_i}{\partial T_i} \cdot \Delta t \]

where \( \rho_o, \rho_i, \rho_t \) = initial density, density at time \( i \) and time \( t \).

However the rate of change of density depends on both the
Consider the point $t_x$ in fig. (10). The degree of cure $C_t$ at time $t$ is the sum of the instantaneous rates of cure at each temperature multiplied by the time spent at this point.

$$C_t = \sum_{0}^{t_x} \int \frac{\alpha C_{Ti}}{\alpha t} dt. \quad \ldots(3)$$

**Fig. 10.** Typical cure schedule.

The parameter for percentage cure used is the relative infra-red absorption (ABS) at 1760 cm$^{-1}$. The choice of this parameter is discussed on page 95. The relationship between ABS and time may be considered exponential as in fig. (11).

**Fig. 12**

For this type of decay curve:

$$\text{ABS} = A \exp(-Bt) \quad \ldots(4)$$

where $A = \text{ABS}_{\text{max}} - \text{ABS}_{\text{min}}$

or $\text{ABS}_{t=0} - \text{ABS}_{t=\infty}$

The first derivative:

$$\frac{d(\text{ABS})}{dt} = -B \times \exp(-Bt) = -B(\text{ABS}) \quad \ldots(5)$$
Thus for each isothermal cure there is a different value for B which uniquely represents the slope at any point.

Similarly, the change of density with time may be considered as another exponential decay from the initial value to the final value. The figs. 12a & b demonstrate the transform used to obtain the more easily handled slope constant $b$.

![Fig. 12](image)

In fig. (12b), $\rho_x = (\rho_f - \rho_t)b_x t$ and $\frac{d\rho_x}{dt} = -b_x(\rho_x)$ ...(6), (7)

Comparing fig. (12a and b)

$\rho_x = \rho_f - \rho_t$

from which $\frac{d\rho_x}{dt} = -\frac{d\rho_t}{dt}$ ...(9)

$\therefore b_t = -b_x$ ...(10)

Thus, $\rho_x = A_p \exp(-b_x t)$ ...(11)

and $\frac{d\rho_x}{dt} = -b_x A_p \exp(-b_x t)$ ...(12)

The positive value of $b$ indicates an increase of density with time as would be expected during a cure.

Thus the density at any point during cure can be found from:-

1) A knowledge of the point's thermal history up to that time.

2) A knowledge of the extent of cure obtained from the thermal history and known rate of cure at any temperature and degree of cure.
3) A knowledge of the rate of change of density at any stage of cure for any given temperature.

**EXPERIMENTAL (1)**

**8Kg Castings.** Temperature measurement in large castings during cure.

The change of temperature with time for various points in the casting were measured by thermocouples supported at chosen points during the cure cycle.

The casting was a right cylinder of weight about 8 kg. This is well above the size at which mottle is said to occur. The larger the block is, the greater will be the exotherm and therefore the greater will be the curing stresses.

Fig. (13a) shows the design of the cure apparatus: fig.(13b), the distribution of thermocouples.

---

**Fig.13**

---

- a) Mould of sheet steel 0.6 mm thick.
- b) Close fitting lid of sheet steel.
- c) Thermocouple supports of hardwood. The lower disc is a slide fit into the mould which minimises the sublimation of hardener.
- d) Copper Constantan thermocouples having their leads fixed into
their support (c) with the sensitive junction at a depth of 10 cm.

e) Porcelain junction blocks enabling repeated experiments to be made without disturbing the main leads to the recorder.

f) Epoxy-resin mix of composition:

\[
\left\{ \begin{array}{l}
5,457 \text{ g. of CT200 at } 116.8^\circ \text{C} \\
1,474 \text{ g. of HT901 at } 140^\circ \text{C}
\end{array} \right\} = 120^\circ \text{C}.
\]

The mould was 20.25 cms in diameter so that to make a right cylinder 7900 g of resin mix was used.

For a temperature gradient of $80^\circ \text{C}$ the heat conductivity of the copper used was 65 calories per hour and that of the constantan, 30 calories per hour. In a cure of an 8 kg casting, six pairs of thermocouple wires caused a lowering of the temperature of the casting by 0.025 deg. C. If all the heat loss occurred in the cylinder of diameter 1 cm around the wires, a drop of only 0.3 deg. C would occur. As the gradient assumed is the maximum which occurs over any wire and the average drop is less than 30% of this the error in temperature caused by the perturbation of the system by the thermocouples was less than 0.1 deg. C.

The distribution of the thermocouples at a depth of 10 cm. (fig. 13b) is as below:

<table>
<thead>
<tr>
<th>Thermocouple Number</th>
<th>Radius from Centre. (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>2.7</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>6.6</td>
</tr>
<tr>
<td>5</td>
<td>8.6</td>
</tr>
<tr>
<td>6</td>
<td>9.75</td>
</tr>
</tbody>
</table>
Each thermocouple was composed of heat-welded pairs of 0.062" diameter constantan and 0.022" diameter copper. The constantan was chosen as the thicker of the pair to provide stiffness and therefore stability of position whilst the thinnest copper available was used to minimise heat loss; it will be seen that three times as much heat loss was due to the copper wires even though they have only an eighth of the surface area compared with constantan.

The oven temperature was controlled at 120°C with an Ether 'Transitrol' set to override the oven thermostat. The operating voltage of the oven was controlled with a 'Variat' transformer to reduce the surge of heat experienced in the oven under full mains pressure thus reducing the variation of oven temperature at the casting surface. A fan was fitted in the oven to improve heat distribution.

From the porcelain connectors, a common constantan wire and six lacquered copper wires were led through a heat seal in the oven roof to a six-channel recorder (Honeywell Brown Electronik) where they were connected to the appropriate channel.

Preliminary measurement of temperature distribution around the mould in the oven showed an improvement due to these modifications in the oven performance from ±5 deg. C to ±0.5 deg. C at 120°C and ±1 deg. C at 180°C. The highest temperature was underneath the mould even after placing it on a perforated aluminium tray to increase air flow against the base.

Thermocouple no. 1 was calibrated against a standard thermometer and the others calibrated against this: a constant deviation was noted for each thermocouple throughout the temperature range which was allowed for in all subsequent calculations.
Each thermocouple was selected in turn by the recorder, the time interval between each being 42.6 seconds giving 4.26 minutes between each pair of readings for any particular thermocouple.

The resin/hardener system was made in a separate container with thorough mixing by an electric stirrer with the screw well below the surface to avoid air bubbles.

The time required for mixing, stirring, filling the mould and positioning it in the oven with its lid bearing the thermocouples was three minutes.

Corrected temperature against time curves are shown for each thermocouple in fig. (14). This was drawn by the graph plotting attachment of the I.C.L. 1905 series computer on which all the calculations were made in this thesis, appendix 3, program 2b.

Three experiments were made using the above method. The exotherm of the first was higher than anticipated and exceeded the normal range of the recorder. Modification of the recorder by increasing the resistance in the bridge circuit gave two switched ranges, 0 - 200°C and 130 - 330°C. The new range was calibrated as before and two further castings made. Comparison of these two showed excellent agreement the casting used for the calculations having a slightly better distribution of thermocouple radii giving wider coverage of the casting.

**EXPERIMENTAL (2) Small castings**

To find the rate of change of density during cure or the extent of cure at various points in the casting during the cure it was impractical to use many 8 kg blocks, sectioning them at appropriate times of cure. In any case it is not possible to cool such a block
to below a curing temperature in less than an hour due to the low conductivity of the material.

Therefore a series of experiments was made in which small and therefore isothermal castings were cured at different temperatures and at various times ensuring minimum sublimation of hardener by restricting evaporation with close-fitting lids. With these small samples that could be cooled throughout in under 30 seconds it was possible to measure any required parameters.

Moulds were constructed from steel channel; the ends of the moulds were treated with release agent and end-pieces were cast in situ. These were easily removed and made the release of castings easy and facilitated multiple use of the mould. fig. (15).

Five series of castings were made keeping the oven temperature constant at 120, 140, 160, 180 and 200°C. In general, two samples were removed from the oven at each of a range of cure times (Table 7). A brief drop of 10°C in oven temperature occurred at each withdrawal but the heat content of the oven and moulds was sufficient to recover this drop within 20 seconds. A thermocouple placed within a small casting registered a temporary drop of 1°C returning to the preset temperature within 30 seconds.

TABLE 7

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>80,170*, 247,365,483,623,743,858,1537*, 4492*</td>
</tr>
<tr>
<td>140</td>
<td>35,96,143,232,392,517,740,1327*</td>
</tr>
<tr>
<td>160</td>
<td>62,115,227,360,486,1144,2619,3944</td>
</tr>
<tr>
<td>180</td>
<td>38,96,130,174,243,343,1275,2546</td>
</tr>
<tr>
<td>200</td>
<td>20,40,61,82,100,121,180,465</td>
</tr>
</tbody>
</table>

* only one sample.
A further six series of small castings were made in which the oven temperature was controlled to simulate the temperature environment of the thermocouples used in the previous experiment. These enabled the calculated values to be checked with the experimental determinations of the rate of change of density and degree of cure.

The oven was controlled again by the Ether 'Transitrol'. Fig (16) shows the method of operation. A synchronous motor rotates the interchangeable disc a about x at a predetermined rate, in this case 1 r.p. day. A spring-loaded arm b, pivoted at c, translated the differing radii r of the disc into corresponding positions of the pointer on scale d. This position was sensed photoelectrically and, if the oven temperature was too low, a mercury relay switch was activated giving power to the oven. If the temperature was high the relay was deactivated and the oven cooled by heat loss to the environment. A variation of ±1°C about a mean was achieved.

Paper discs were made, Fig. (16), with the time and temperature axes inscribed upon them. This was previously determined for the temperature radii correlation and deduced from the geometry of the transitrol for the time axis.

![Paper disc pattern](image)
A circular graph was plotted on these discs of the six temperature-time curves known from the large block experiment. From these patterns aluminium discs were made with the central hole and locating slot being made first to ensure accurate centering with no eccentric 'run-out'. Each disc was run on the transitrol and checked with the actual thermocouple temperature cycle and any necessary adjustments were made until the simulated cycle was accurate to within 1°C throughout.

RATE OF CURE PARAMETER

It was necessary to choose a parameter for the extent of cure. The first to suggest itself was the tensile breaking stress of the material. A jig was made to manufacture tensile testing samples of the shape recommended by A.S.T.M., fig. (17a).

An initial series of breaking stresses was done on a Tensometer, Type E, of a number of small castings cured at 120°C to ensure as large a spread of the extent of cure as possible. The samples were strained at 10 mm/min (50% / min.) to ensure a brittle fracture with minimal relaxation of the resin structure.

The results Fig.17b. showed an initial low value with an enormous increase in breaking stress initially, flattening out to a steady value. Comparison of the stress-strain relationships of the individual specimens showed a greater extension before break for the less crosslinked resin. Thus, once gelled, the resin became less elastic but showed no increase in ultimate strength. The method was therefore not suited to determine a parameter of cure.
As the toughness of the material appeared to increase with cure the hardness of the material was next measured on a pyramidal 'Hardness' tester (Vickers). Hardness is an empirical measurement of the extent of penetration of a loaded diamond pyramid, in this case 0.66 inches across, into the surface under examination. It depends on many parameters including the elasticity, toughness, surface condition and frictional properties of the material. The loading of the diamond is fairly critical; too large a load producing too small a change in penetration with varying 'Hardness'. Too small a load leads to inaccuracies due to surface irregularities and is very sensitive to elasticity effects.

Table (8) shows the variation in hardness between a newly gelled sample and a fully cured one.

**TABLE 8**

<table>
<thead>
<tr>
<th>LOAD (Kg.)</th>
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<th>2.5</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
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<tr>
<td>fully cured</td>
<td>not</td>
<td>64.1</td>
<td>71.5</td>
<td>72.6</td>
<td>74.2</td>
</tr>
<tr>
<td>vis.</td>
<td></td>
<td>72.4</td>
<td>69.1</td>
<td>74</td>
<td>±5</td>
</tr>
<tr>
<td>newly gelled</td>
<td>not</td>
<td>74.2</td>
<td>73.2</td>
<td>73.2</td>
<td>71.5</td>
</tr>
<tr>
<td>vis.</td>
<td></td>
<td>67</td>
<td>±10</td>
<td>74.2</td>
<td>86.7</td>
</tr>
<tr>
<td></td>
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<td>85.4</td>
<td>81</td>
<td>±6</td>
<td>±6</td>
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<td></td>
<td></td>
<td>81.8</td>
<td>79.3</td>
<td>83.6</td>
<td>72.6</td>
</tr>
</tbody>
</table>

Therefore, (fully cured) - (newly gelled) = \( \pm 14 \pm 10 \) @ 2.5 Kg. and \( 8.4 \pm 6 @ 5 \) Kg.

A loading above 5 Kg was found to be too large as the change in hardness was only 4.6 units and below 10 Kg the error of repeatability is comparable with the overall change in the parameter.

Several papers exist in the literature quoting infra-red or near infra-red spectroscopy as a method of producing a parameter for cure, the level of the absorption of a characteristic band for a reacting
group being an indication of the state of cure. Due to differences in concentration from one sample to another it is usual to compare the absorption of a reacting group relative to that of a non-reacting group.

Dannenberg (14) and Serboli and Golowski (15) compared the change of the epoxy group band at 4540 cm\(^{-1}\) with the band due to the first overtone of the aromatic C-H stretching mode at 6000 cm\(^{-1}\) to measure the state of reaction. They showed that the epoxy value of a resin (Moles of epoxy groups per 100 g resin) to be directly proportional to the relative absorption of these bands for a wide range of DGEBA resins cured with ethylene diamine (14) and phthalic anhydride (15).

That is to say

\[
\frac{\text{ABS} @ 4540 \text{ cm}^{-1}}{\text{ABS} @ 6000 \text{ cm}^{-1}} = \text{constant (conc. of epoxy groups)}
\]

Dannenberg also quotes the epoxy band at 8700 cm\(^{-1}\) to be useful if that at 4540 cm\(^{-1}\) is disturbed by neighbouring absorption bands.

Feltzin et al. (16), using the absorption at 1600 cm\(^{-1}\) due to aromatic flexure note the strong dependence of the rate of cure on the temperature using the change of the band at 920 cm\(^{-1}\) due to the epoxy group. This frequency was not recommended by Dannenberg for amine cures due to interference from other bands but it is relatively isolated with anhydride curing agents. Feltzin also showed the absorption at full cure to be independent of the temperature cycle taken to achieve this state. A half-cured low-temperature cure subjected to a high temperature subsequently attains the same final absorption.

Comparison of I.R. spectra of uncured and cured resins show the epoxy group absorption at 920 cm\(^{-1}\) to be unsuitable for the hardener used as there is a band due to anhydride hardener at 910 cm\(^{-1}\). However
at 1770 cm\(^{-1}\) there is a band due to the carbonyl stretch in the anhydride
group. Using the band due to C-H stretch mode of the methyl groups in the
bisphenol propane component of the DGEBA molecule at 2980 cm\(^{-1}\) as an
internal standard, the spectra of the series of small castings cured at
120\(^\circ\)C were measured using KBr discs on the Perkin Elmer 337 spectro-
photometer. For the method see Appendix (2).

Absorption values were read from these after first assessing the
base line of the absorption as in fig. (18). As absorbance is a
parameter of energy, the difference between the base line and the peak
absorptions gives the total energy of absorbance at that wavelength.

![Absorbance graph]

A good exponential fit was found using a 'least squares' method from
a programme by Deily (17) on the ICL 1905. Fig. (19) shows the good fit
obtained against a computer-generated curve derived from the points
themselves. (Appendix 3). The approximation to an exponential decay
so found allows the slope of this graph to be used confidently as a
parameter for rate of cure.

Spectra S6 to 16 show a typical set of spectra obtained for the
particular set of the first series of small castings cured at 120\(^\circ\)C.
Absorbance - Time curves for small castings of various oven temperatures.

Fig. 19
The relative absorptions from all the sets of spectra corresponding to cure temperatures of 120, 140, 160, 180 and 200°C were analysed by the least squares fit program previously mentioned (appendix 3, program 1). The slope constants were as follows:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Slope constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°C</td>
<td>4.5284. \times 10^{-3}</td>
</tr>
<tr>
<td>140°C</td>
<td>7.0063. \times 10^{-3}</td>
</tr>
<tr>
<td>160°C</td>
<td>1.2659. \times 10^{-2}</td>
</tr>
<tr>
<td>180°C</td>
<td>2.0714. \times 10^{-2}</td>
</tr>
<tr>
<td>200°C</td>
<td>3.0306. \times 10^{-2}</td>
</tr>
</tbody>
</table>

The relative absorbance at the beginning of cure was taken as 223%. These values were used in the calculation of stress in large castings, appendix 3 program 4.

The relative absorption of the second series of small castings was also measured; the results are compared with the absorbance corresponding to the extent of cure calculated by the computer, appendix 3, program 4. Comment on the correlation of the two sets of results is left until the final discussions, see Table 16.

Experimental method (3) Density Measurements.

Two factors combine, making it necessary to measure the density of the resin at an elevated temperature.

Firstly, the density difference between uncured and fully cured
resin is only 0.01 g.cm\(^{-1}\) at room temperature and this would require an accuracy of \(\pm 0.0001\) g.cm\(^{-1}\) to detect the difference of density between cured and uncured resin.

Secondly, and more important, the glass transition temperature Tg of the resin is 110°C when fully cured and at a lower temperature with less highly cured resin. In spite of the higher rate of change of density with temperature of cured resin, the change of slope at Tg causes the similarity of density between cured and uncured resins at room temperature.

Above Tg the resin obeys the usual form of equation for expansion.

\[ \rho_T = \rho_{120}(1 - C_1(T - 120) + C_2(T - 120)^2 \ldots) \]

where \(\rho_T\) and \(\rho_{120}\) are densities at \(T^\circ\text{C}\) and 120°C respectively.

\(C_1\) and \(C_2\) \ldots etc. are constants determined empirically.

Terms after the first have been ignored as the relationship proved essentially linear between 120°C and 200°C, the range investigated.

It was decided to measure the density of all the samples at 120°C as this was well above the Tg and yet low enough to enable samples to achieve equilibrium without excessive post-cure.

The density change for total cure can be seen to be about 0.1 g.cm\(^{-1}\) so that accuracy of 0.001 g.cm\(^{-3}\) was sufficient to give a useful change during cure. Determination of density at 120°C is not practicable using the usual methods: weighing in air and liquid has inherent problems of temperature stabilisation in an open balance and air convection around the balance which were not easily surmountable. A pyknometer cannot be used due to the lack of reproducibility and a graded density column at
120°C is not only unstable but due to the much reduced viscosity of available liquids with $\rho = 1 -1.15$ at 120°C, the method requires constant calibration and would not be convenient for the large number of samples that were to be investigated.

The method chosen finally was a relative one entailing direct measurement at 20°C and then measurement of the change in volume from 20°C to 120°C.

It was found that by far the best and also quickest method at room temperature was weighing in air and then in water.

After weighing in air the samples were suspended on a loop of hair (18) and immersed in conductivity water at 20°C. Hair was found to give the most reproducible results due to its low water absorption and the very small surface tension effect ($\pm 0.0001$ g.). The density at 20°C was calculated from the standard formula.

$$\rho_{20} = \frac{\text{Mass in air}}{\text{Mass in water/}\rho_{H_2O \ at \ 20^\circ C}}$$

Repeatability was $\pm 0.0007 \text{ g.cm}^{-3}$, an error of 1 mg producing an error of 0.00025 g.cm$^{-3}$ which makes the method inherently accurate. Samples were examined for air bubbles before use and discarded if they were present.

For determining the change of volume from 20°C to 120°C the sample a (3 cm x 4 mm x 5 mm) was immersed in mercury b in a pyrex glass cell c with a 'Quick-fit' ground glass stopper d containing a capillary tube e, fig. (20). A quartz cell would have been preferable but it was not possible to obtain a quartz capillary tube bored to the accuracy required and the large and sudden temperature rise precluded the use of a glass stopper because of the variation in coefficient of expansion.
The stopper/capillary had a concave base to eliminate air bubbles when the cell was assembled. Mercury was chosen because of its high heat conductivity which ensured the shortest possible time for the resin to attain equilibrium and also because of its inert behaviour with regards to solubility in the resin. This was especially important in the samples which were not fully gelled. The top of the samples were chamfered as indicated to prevent slightly softened resins from blocking the capillary.

It was found that, after assembling the cell and capillary, the level of mercury was a few cm above the top of the stopper and thus clear of any irregular variation in capillary cross-section caused by the joining of capillary and stopper.

The capillary radius was determined by measuring the length of a known weight of mercury at a known temperature and therefore volume per gram. Two cells were used; table 9 gives the relevant masses and lengths etc.

<table>
<thead>
<tr>
<th>TABLE 9</th>
<th>Mass (g)</th>
<th>Capillary radius (cm)</th>
<th>Volume (cm$^3$)</th>
<th>Coeff. of expansion (linear)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>27.3465</td>
<td>0.454</td>
<td>3.0095</td>
<td>$99 \times 10^{-6}$</td>
</tr>
<tr>
<td>Cell 2</td>
<td>24.5369</td>
<td>0.458</td>
<td>3.0771</td>
<td></td>
</tr>
</tbody>
</table>
The method of determining the density of the resin at $120^\circ C$ was as follows. First the cell and capillary were cleaned with c. $HNO_3$, alcohol and distilled water and dried at $105^\circ C$ in the oven. Next the cell was filled with mercury to just above the bottom of the ground joint and the sample placed in the top; the capillary was used to push the sample under the surface and the ground joint locked by twisting.

The cell and stopper were then immersed in a water bath controlled at $20^\circ C \pm 0.1^\circ C$ by a thermostat (Grant SB3).

The height of the mercury column was measured, relative to a horizontal line f inscribed on the capillary, using a travelling microscope(Precision) which measured accurately to $\pm 0.001\text{cm}$. 

The cell was then transferred to an oil-bath controlled at $120 \pm 0.2^\circ C$ by a thermostat. An experiment with a cell containing a resin sample containing a thermocouple showed that equilibrium was reached in 7 minutes.

When the resin had reached equilibrium temperature the mercury level was again measured relative to the horizontal mark with a travelling microscope accurate to $\pm 0.005\text{cms}$. 

Samples of low cure times which had therefore not reached the gel point occasionally melted during this process but they generally adhered to the side of the cell and only on one occasion blocked the capillary. In the event of uncured resin remaining in the cell it was first cleaned with 1,4-dioxane and then c.$H_2SO_4$ to ensure complete removal before reuse of the cell.

The change in level was thus determined for a temperature rise from $20^\circ C$ to $120^\circ C$. This change in level is due to the change in volume of the sample, mercury and the capillary and cell.
RESULTS AND CALCULATION

The changes in volume of the relevant materials are as follows:

Sample ........................ \( \frac{M_s}{\rho _{r20}} - \frac{M_s}{\rho _{r120}} \)

Mercury in cell ........... \( \frac{M_m}{\rho _{m20}} - \frac{(M_m - M_l)}{\rho _{m120}} \)

Cell .......................... \( V_c \cdot C_g \cdot \Delta T \)

Capillary .................... \( \pi r^2 l (1 - C_g T_{ave}) \)

where:-

\( M_l = \pi r^2 l (1 - C_g T_{ave}) \rho _{mta} \)

\( M_r = \) mass of sample (g)

\( M_m = \) mass of mercury (g)

\( M_l = \) mass of mercury in the capillary of length \( l \) at \( 120^\circ C \) (g)

\( \rho _{r120}, \rho _{r20} = \) density of resin at \( 120^\circ C, 20^\circ C \) (g.cm\(^{-3}\))

\( \rho _{m120}, \rho _{m20} = \) density of mercury at \( 120^\circ C, 20^\circ C \) (g.cm\(^{-3}\))

\( \rho _{mta} = \) density of mercury at \( T_{ave} \) (see below)

\( V_c = \) Volume of cell (cm\(^3\))

\( C_g = \) coefficient of volume expansion of pyrex glass

\( \Delta T = \) change in temperature during experiment

\( T_t, T_b = \) temperature of mercury at top and bottom of mercury column \( l \)

\( r = \) radius of the capillary (cm)

\( l = \) change in height of mercury column (cm)

\( T_{ave} = \) average temperature of mercury in capillary

\( = \frac{T_b - T_t}{ln(T_b/T_t)}, \) for radiating heat loss at equilibrium.

Equating volume changes:-

\( \Delta V(\text{capillary}) = \Delta V(\text{mercury}) + \Delta V(\text{sample}) - \Delta V(\text{Cell}) \)
i.e.,
\[
x^2(1 + C_gT_{ave}) = \frac{M_m - M_1}{\rho_{m120}} - \frac{M_m}{\rho_{m20}} + \frac{M_r}{\rho_{r120}} - \frac{M_r}{\rho_{r20}} - V_cC_g\Delta T
\]

This rearranged to:
\[
\rho_{r120} = \frac{M_r}{V(1 + \rho_{mta}/\rho_{m120})} - \frac{M_m(\rho_{m20} - \rho_{m120})}{(\rho_{m20}, \rho_{m120})} + \frac{M_r}{\rho_{r20}} + V_cC_g\Delta T
\]
\[
(13)
\]

An accuracy of 0.001 g.cm\(^{-3}\) is required to ensure reliable determination of the density during cure. The accuracy of each measurement to ensure this degree of accuracy was calculated and compared with the actual experimental repeatability, table 10.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Typical Value</th>
<th>Error producing a variation of 0.001 g.cm(^{-3})</th>
<th>Tolerance of Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>l</td>
<td>8 cm.</td>
<td>0.1 cm</td>
<td>0.001 - 0.005 cm according to microscope used</td>
</tr>
<tr>
<td>C_g</td>
<td>9.9 x 10(^{-6})</td>
<td>10(^{-6})</td>
<td>10(^{-7})</td>
</tr>
<tr>
<td>r</td>
<td>0.049 cm</td>
<td>0.00025 cm</td>
<td>±0.0001 cm</td>
</tr>
<tr>
<td>M_m</td>
<td>30 g.</td>
<td>0.1 g.</td>
<td>&lt;0.0002 g.</td>
</tr>
<tr>
<td>M_r</td>
<td>1 g.</td>
<td>0.0012 g.</td>
<td>&lt;0.0001 g.</td>
</tr>
<tr>
<td>(\rho_{r20})</td>
<td>1.23 g.cm(^{-3})</td>
<td>&lt;0.001 g.cm(^{-3})</td>
<td>0.0007 g.cm(^{-3})</td>
</tr>
<tr>
<td>(\rho_{m20})</td>
<td>13.5 g.cm(^{-3})</td>
<td>&lt;0.003 g.cm(^{-3})</td>
<td>max. temp. dependent error = 0.0005 g.cm(^{-3})</td>
</tr>
<tr>
<td>(\rho_{m120})</td>
<td>13.5 g.cm(^{-3})</td>
<td>&lt;0.003 g.cm(^{-3})</td>
<td>max. temp. independent error = 0.0001 g.cm(^{-3})</td>
</tr>
<tr>
<td>(\rho_{mta})</td>
<td>13.5 g.cm(^{-3})</td>
<td>&lt;0.04 g.cm(^{-3})</td>
<td>0.001 g.cm(^{-3})</td>
</tr>
</tbody>
</table>

It can be seen that the critical measurement is that of the density of the resin at 20°C. The next most critical is the radius of the capillary which produces an uncertainty of ±0.0002 g.cm\(^{-3}\).
It was realised that the variation in the height of mercury above the sample would lead to compression of the sample and a consequent change in volume. The maximum column height found in any experiment was 37.5 cms which causes an excess pressure of about 7 p.s.i. Even with uncured resin this leads to a change in volume at 120°C of less than $5.10^{-5}\text{cm}^{-3}$ the total effect of which is lower than the other errors considered: it has therefore been ignored in the calculations.

Table 11, lists the temperature of cure $T$, time of cure $\text{TIME}$, mass of resin $M_R$, height of mercury column $L$, changes in volume of mercury and resin $DVR$ and $DVM$, initial and final density of the resin RO20 and RO120.

These values of $\rho_{120}$ were used to generate the slope constant $b_x$ in equation 7, p 87. This was achieved using the least squares fit program, Appendix 3 program 1.

Comparison of the experimental points and the curve generated from equation 6 is shown by Fig. 20a. The same density-$v$-time values were compared with polynomials of order 1-6 generated from an ICL program (E2LSQFIT) but the exponential decay curve was found to be more accurate.

The values obtained for the slope constant $b_x$ from the exponential program were used in the program which calculates stresses in the large castings.

<table>
<thead>
<tr>
<th>Temperature of cure of small castings</th>
<th>$b_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°C</td>
<td>$2.26706 \times 10^{-3}$</td>
</tr>
<tr>
<td>140°C</td>
<td>$8.59045 \times 10^{-3}$</td>
</tr>
<tr>
<td>160°C</td>
<td>$1.67115 \times 10^{-2}$</td>
</tr>
<tr>
<td>180°C</td>
<td>$3.01673 \times 10^{-2}$</td>
</tr>
<tr>
<td>200°C</td>
<td>$5.31006 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Table 11  Density results for the first set of small castings.

<table>
<thead>
<tr>
<th>T</th>
<th>TIME</th>
<th>MR</th>
<th>L</th>
<th>DVR</th>
<th>DVL</th>
<th>RO20</th>
<th>RO120</th>
<th>CELL</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>80</td>
<td>0.4332</td>
<td>8.524</td>
<td>0.06252</td>
<td>0.05141</td>
<td>1.2300</td>
<td>1.0446</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>247</td>
<td>0.8549</td>
<td>10.925</td>
<td>0.1053</td>
<td>0.04471</td>
<td>1.2290</td>
<td>1.0738</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>365</td>
<td>0.5890</td>
<td>8.588</td>
<td>0.06030</td>
<td>0.04847</td>
<td>1.2340</td>
<td>1.0835</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>483</td>
<td>0.7540</td>
<td>9.359</td>
<td>0.07611</td>
<td>0.04669</td>
<td>1.2360</td>
<td>1.0957</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>623</td>
<td>0.9431</td>
<td>9.650</td>
<td>0.08335</td>
<td>0.04332</td>
<td>1.2290</td>
<td>1.1060</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>743</td>
<td>0.6628</td>
<td>7.954</td>
<td>0.05903</td>
<td>0.04748</td>
<td>1.2330</td>
<td>1.1110</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>858</td>
<td>1.0525</td>
<td>9.736</td>
<td>0.08622</td>
<td>0.04209</td>
<td>1.2330</td>
<td>1.1162</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>1537</td>
<td>0.8423</td>
<td>8.317</td>
<td>0.06543</td>
<td>0.04581</td>
<td>1.2350</td>
<td>1.1269</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>4492</td>
<td>1.0910</td>
<td>9.097</td>
<td>0.07950</td>
<td>0.04210</td>
<td>1.2310</td>
<td>1.1299</td>
<td>1</td>
</tr>
<tr>
<td>140</td>
<td>35</td>
<td>0.8742</td>
<td>12.345</td>
<td>0.11907</td>
<td>0.04457</td>
<td>1.2300</td>
<td>1.0535</td>
<td>1</td>
</tr>
<tr>
<td>140</td>
<td>96</td>
<td>0.8832</td>
<td>10.509</td>
<td>0.09453</td>
<td>0.04773</td>
<td>1.2310</td>
<td>1.0877</td>
<td>2</td>
</tr>
<tr>
<td>140</td>
<td>143</td>
<td>0.7915</td>
<td>9.372</td>
<td>0.07859</td>
<td>0.04638</td>
<td>1.2340</td>
<td>1.0993</td>
<td>2</td>
</tr>
<tr>
<td>140</td>
<td>252</td>
<td>0.6317</td>
<td>7.915</td>
<td>0.05016</td>
<td>0.05174</td>
<td>1.2340</td>
<td>1.1154</td>
<td>2</td>
</tr>
<tr>
<td>140</td>
<td>392</td>
<td>0.6912</td>
<td>7.503</td>
<td>0.05136</td>
<td>0.05111</td>
<td>1.2300</td>
<td>1.1270</td>
<td>2</td>
</tr>
<tr>
<td>140</td>
<td>517</td>
<td>0.7624</td>
<td>7.724</td>
<td>0.05313</td>
<td>0.05024</td>
<td>1.2290</td>
<td>1.1287</td>
<td>2</td>
</tr>
<tr>
<td>140</td>
<td>740</td>
<td>0.8997</td>
<td>8.116</td>
<td>0.06347</td>
<td>0.04318</td>
<td>1.2310</td>
<td>1.1298</td>
<td>1</td>
</tr>
<tr>
<td>140</td>
<td>1327</td>
<td>0.7155</td>
<td>7.542</td>
<td>0.05429</td>
<td>0.04686</td>
<td>1.2350</td>
<td>1.1292</td>
<td>1</td>
</tr>
<tr>
<td>160</td>
<td>62</td>
<td>0.8764</td>
<td>9.681</td>
<td>0.08639</td>
<td>0.04490</td>
<td>1.2290</td>
<td>1.0962</td>
<td>2</td>
</tr>
<tr>
<td>160</td>
<td>115</td>
<td>1.0132</td>
<td>9.615</td>
<td>0.08750</td>
<td>0.04236</td>
<td>1.2290</td>
<td>1.1152</td>
<td>2</td>
</tr>
<tr>
<td>160</td>
<td>227</td>
<td>0.8812</td>
<td>8.175</td>
<td>0.06666</td>
<td>0.04466</td>
<td>1.2330</td>
<td>1.1278</td>
<td>2</td>
</tr>
<tr>
<td>160</td>
<td>360</td>
<td>0.7651</td>
<td>7.690</td>
<td>0.05725</td>
<td>0.04591</td>
<td>1.2340</td>
<td>1.1297</td>
<td>1</td>
</tr>
<tr>
<td>160</td>
<td>486</td>
<td>0.8180</td>
<td>7.922</td>
<td>0.06054</td>
<td>0.04556</td>
<td>1.2330</td>
<td>1.1299</td>
<td>1</td>
</tr>
<tr>
<td>160</td>
<td>1240</td>
<td>0.5940</td>
<td>6.764</td>
<td>0.04341</td>
<td>0.04924</td>
<td>1.2310</td>
<td>1.1294</td>
<td>2</td>
</tr>
<tr>
<td>160</td>
<td>318</td>
<td>0.7726</td>
<td>9.045</td>
<td>0.06475</td>
<td>0.04597</td>
<td>1.2300</td>
<td>1.0992</td>
<td>2</td>
</tr>
<tr>
<td>160</td>
<td>96</td>
<td>0.8291</td>
<td>8.451</td>
<td>0.06013</td>
<td>0.04894</td>
<td>1.2330</td>
<td>1.1226</td>
<td>2</td>
</tr>
<tr>
<td>180</td>
<td>130</td>
<td>0.8113</td>
<td>8.117</td>
<td>0.06112</td>
<td>0.04945</td>
<td>1.2330</td>
<td>1.1282</td>
<td>2</td>
</tr>
<tr>
<td>180</td>
<td>174</td>
<td>0.6459</td>
<td>7.434</td>
<td>0.04490</td>
<td>0.05262</td>
<td>1.2350</td>
<td>1.1294</td>
<td>2</td>
</tr>
<tr>
<td>180</td>
<td>243</td>
<td>0.7069</td>
<td>7.413</td>
<td>0.05185</td>
<td>0.04763</td>
<td>1.2320</td>
<td>1.1299</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>20</td>
<td>0.7532</td>
<td>9.440</td>
<td>0.07621</td>
<td>0.04997</td>
<td>1.2300</td>
<td>1.0907</td>
<td>2</td>
</tr>
<tr>
<td>200</td>
<td>40</td>
<td>0.7849</td>
<td>8.241</td>
<td>0.06368</td>
<td>0.04854</td>
<td>1.2350</td>
<td>1.1184</td>
<td>2</td>
</tr>
<tr>
<td>200</td>
<td>61</td>
<td>0.8556</td>
<td>7.973</td>
<td>0.06425</td>
<td>0.04291</td>
<td>1.2360</td>
<td>1.1260</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>82</td>
<td>0.6900</td>
<td>7.508</td>
<td>0.05118</td>
<td>0.05135</td>
<td>1.2310</td>
<td>1.1280</td>
<td>2</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>0.7176</td>
<td>7.354</td>
<td>0.05197</td>
<td>0.04674</td>
<td>1.2350</td>
<td>1.1294</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>121</td>
<td>0.9081</td>
<td>8.122</td>
<td>0.06780</td>
<td>0.04091</td>
<td>1.2340</td>
<td>1.1299</td>
<td>1</td>
</tr>
</tbody>
</table>
Fig. 20a  Density - Time curves for small castings at various temperatures
It was also necessary for the purpose of stress calculation in the large blocks to know the coefficient of expansion of the resin at temperatures above 120°C.

This was measured by determining the density of samples of uncured, partly cured and fully cured resin at 180°C, 150°C and 120°C using the same method as before with the oil bath at these temperatures. If the resin sample is not fully cured it will, of course, undergo partial cure at these elevated temperatures.

The height of the mercury column was therefore noted 7 minutes and 12 minutes after immersion. The height at immersion was then estimated from the change in height with time. The results are shown in fig. (21). The values used in the stress calculation were:

<table>
<thead>
<tr>
<th>% Cure</th>
<th>Coefficient of Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8 . 10⁻³</td>
</tr>
<tr>
<td>40*</td>
<td>1.55 . 10⁻³</td>
</tr>
<tr>
<td>100</td>
<td>1.35 . 10⁻³</td>
</tr>
</tbody>
</table>

* as measured by infra red analysis

The same method was used to determine the density of the second set of small samples in which the cure had been simulated by controlling the oven temperature, table 16.
Discussion. Diffusion during cure.

The diffusion of phthalic anhydride within an epoxy resin matrix is true self-diffusion with respect to constant concentration but the presence of epoxy resin monomer molecules originally and then larger molecules due to the polycondensation reaction as the cure progresses makes the effective path travelled by an average diffusing molecule progressively larger and always larger than the parameter \( x \) which is measured for the determination of \( D \).

This increase in the value of \( x \) which is reflected by the gradual increase in the viscosity of the system results in a lowering of the true self-diffusion constant of phthalic anhydride. This is apparent in fig.22 where the values of \( \log D \) for the higher temperatures are lower than would be expected from a linear relationship as given by equation 14.

It is therefore not possible to obtain accurate instantaneous values of \( D \) throughout cure but extrapolation to \( t = 0 \), fig.22 gives a reasonable estimate of \( D \) at the beginning of the reaction after which \( D \) steadily falls with onset of the curing reactions, tables 6 and 12.

Table 12

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diff. Constant at ( t = 0 ) cm(^2) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>(~1 \times 10^{-5})</td>
</tr>
<tr>
<td>130</td>
<td>(~4 \times 10^{-5})</td>
</tr>
<tr>
<td>150</td>
<td>(~7 \times 10^{-5})</td>
</tr>
<tr>
<td>180</td>
<td>(~10 - 20 \times 10^{-5})</td>
</tr>
</tbody>
</table>

It has been found that diffusion, being a rate process, is dependent on temperature and is related exponentially, (20):

\[
D = A \cdot \exp(-\Delta H/RT)
\]
Fig. 22  Log Diffusion constant - 1/Temperature.
where \( \Delta H = \) activation energy (K\,cals\,mole\(^{-1}\)).

\[ R = \text{gas constant} \quad \text{(cals}\,\text{deg}C^{-1}\text{mole}^{-1}) \]

\[ A = \text{constant}. \]

Fig. 22 shows plots of \( \log D - 1/T \); the slope of this being 
\[-\Delta H / 2.303 R. \]

From the data compiled it is found that:

- \( \Delta H = 16.5 \text{ Kcal.mole}^{-1} \) for \( t = 90 \) mins.
- \( \Delta H = 16.0 \text{ Kcal.mole}^{-1} \) for \( t = 60 \) mins.
- \( \Delta H = 14.7 \text{ Kcal.mole}^{-1} \) for \( t = 40 \) mins.

Self-diffusion constants found for the different temperatures and
times of cure can be seen to be similar to those associated with the
self-diffusion of solutions and liquids including metals above their
melting points, table 13, (20).

**TABLE 13**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Self diffusion (10^5\text{cm}^2\text{sec}^{-1})</th>
<th>(\Delta H) kcal.mole(^{-1})</th>
<th>Temperature of determination (^\circ C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NaCl}^- ) in ( \text{H}_2\text{O} )</td>
<td>1.54</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>Mercury</td>
<td>1.6</td>
<td>1.0</td>
<td>25</td>
</tr>
<tr>
<td>Gallium</td>
<td>1.67</td>
<td>1.12</td>
<td>30.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>4.2</td>
<td>2.43</td>
<td>98</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>1.41</td>
<td>3.3</td>
<td>25</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.21</td>
<td>2.1</td>
<td>25</td>
</tr>
<tr>
<td>n.Dicetly</td>
<td>0.3</td>
<td>5.6</td>
<td>100</td>
</tr>
<tr>
<td>n.pentane</td>
<td>4.14</td>
<td>1.6</td>
<td>0</td>
</tr>
</tbody>
</table>

The activation energy for this diffusion is rather higher than
for these other diffusion processes being close to the energy of
activation of the condensation reaction itself, p.11. Therefore it
is probable that the reaction is largely diffusion controlled.

It was suggested previously that the growth of spicules was a
diffusion controlled process and that the reaction causing formation
of the spicules as distinct from the general rate of reaction was
balanced by the diffusion of extra hardener to the spicule surface.
If one considers the diffusing layer in fig. 23.

![Diagram](image)

The total flux from 0 to \( x \) for each \( \text{cm}^2 \) of the spicule surface is:

\[
J = D \int_0^x \frac{dC}{dx} \cdot dx
\]

Now, for \( C = C_i \) (instantaneous conc.)

at \( x = 0 \)

and \( C = 0 \) at \( x = x \)

\[
J = D \int_0^{C_i} \left( \frac{dC}{dx} / \frac{dC}{dx} \right) \cdot dC
\]

\[
= DC_i^{0}
\]

\[
= DC_i
\]

This total flux to the spicule must be equal to or greater than

\( \sim 11\% \) of the rate of cure at any time for the spicule to sustain the

\( \sim 11\% \) higher hardener content found by infra-red analysis, p. 55.

\[
\therefore -C_i D \geq \frac{11}{100} \cdot (C_o \cdot \text{rate of cure}).
\]

or

\[
D \geq \frac{11}{100} \cdot (C_o / C_i) \cdot \text{rate of cure}.
\]

Instantaneous values of \( D \) were calculated from the computer

program (appendix 3, program 4) at one minute intervals during cure for

1 mm annuli perpendicular to the axis of the cylindrical casting.

Fig. 24 compares the diffusion constant calculated to be necessary to

sustain spicule growth with the experimentally determined average diffusion

constant at 110, 130, 150 and 180°C for times of 0, 40, 60 and 90 minutes.

At the gel point \( D \) becomes about three orders lower than immediately

before gel and so the spicule-forming reaction will cease. This is in

accordance with the observation that the mottle present at gel does not

become any more extensive during or after post-cure.

The computer program calculates the gel time (time of one quarter of

the reaction) to be 60 minutes in the centre of the casting increasing to
62 minutes at the outer edges.

Before the gel point it would seem that $D_{ave}$ is marginally too small to sustain spicule growth for the full 60 minutes up to gel time, fig.24. However, the curve of $D_{ave}$ - Temperature for 40 minutes indicates that $D$ is sufficiently greater than is required for growth for most of the pre-gel period. No diffusion constant was measured for the 40 minute cure period at $110^\circ C$ but it cannot be lower than those for 60 or 90 minutes. A reasonable extrapolation for the value of $D$ at $110^\circ C$ is $5.10^{-6}$ so that $D_{ave}$ is large enough to allow spicules to grow for this period, after which the diffusion to the surface will gradually diminish. This slow change in the external surface hardness may be the explanation of the microtensometer tests which showed the spicules to be stronger as their cross-section diminished, p.48.

It has been reported that mottle can first be seen in a 14Kg mass of curing resin at approximately half the gel time (19). Decreasing the temperature up to gel so that the critical value of the diffusion constant for spicule growth is reached earlier should effect a decrease in both the size and the frequency of the spicules.

If the resin temperature is kept below $110^\circ C$ there should be only a very small chance of spicule growth but the increased viscosity at this temperature increases the chance of mottle due to bad mixing and stirring shear stresses, p.15.

A longer gel time will also facilitate the growth of spicules if the diffusion constant is only marginally less than that required for growth. In this case, spicules of lower ester concentration may occur; the critical factor being their rate of initiation.

Many workers use hexa-hydro phthalic anhydride (HHPA) as a hardener due to its lower melting point and consequent lower mixing temperature
Fig. 24  'D' - temperature.  

D_c = 0 mins  
D_c, 40 mins  
D_c, 60 mins  
D_c, 90 mins  

D calculated to sustain spicule growth
even though the fringe constant, p. 2, is reduced by one half which means
a doubling of the loads applied during the stress freezing process.

The success of this hardener in reducing mottle could be due to the
lower diffusion constant occasioned by its larger bulk.

\[
\begin{align*}
P.A. & \quad H.H.P.A. \\
\end{align*}
\]

However, the fully hydrogenated benzene ring in the structure of
HHPA being less rigid than the conjugated ring in phthalic anhydride (P.A.)
allows more relaxation of stress under strain which results in the need
for greater loads in use to produce the same photoelastic effect.

All other anhydride hardeners reported have either aliphatic side
chains on the conjugated rings or have unsaturated ring systems. These
modifications inevitably lead to stress relief and the low fringe constant.
Discussion  Cure parameters and stress calculations.

Using the values on pages 110, 117 of relative absorption and the rate of change of density; the rate of cure, total cure at one minute intervals throughout the cure, density and the resultant displacement and strain were calculated using program 4, appendix 3.

Figs. 25 - 27 show the change during cure of the cure rate, the displacement and the density of resin along the radial plane of the thermocouples.

The rate of cure (proportion of total cure per minute) reaches a maximum of $6.13 \times 10^{-3}$ after 150 minutes in the centre of the casting at 177.5°C although the casting eventually reaches a maximum temperature of 200.8°C after a further 90 minutes, fig. 25. The cooler outer regions of the casting do not cure at such a high rate as the centre but cure at a greater rate after about 200 minutes due to the centre having spent its potential reactivity more quickly in the early stages of cure.

Table 14 shows two useful parameters of full cure. At the time of maximum rate of cure for the casting's centre the extent of cure is seen to be 69.3% whilst at the thermocouple furthest from the centre (6) the extent of cure is only 45.4% at its own maximum rate of cure.

<table>
<thead>
<tr>
<th>Radius of thermocouple</th>
<th>Minutes to reach 95% cure</th>
<th>Minutes to reach 98% cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>216</td>
<td>246</td>
</tr>
<tr>
<td>2.7</td>
<td>217</td>
<td>248</td>
</tr>
<tr>
<td>4.0</td>
<td>218</td>
<td>249</td>
</tr>
<tr>
<td>6.6</td>
<td>234</td>
<td>261</td>
</tr>
<tr>
<td>8.6</td>
<td>263</td>
<td>335</td>
</tr>
<tr>
<td>9.75</td>
<td>393</td>
<td>534</td>
</tr>
</tbody>
</table>
Fig. 25 Cure rate-time for 8Kg casting.
Clearly it is only the outside 2 cm of the block which needs to be cured for 7 hours; the inside has reached 98% cure in 5 hours and 95% in 4 hours. The usual practice of raising the temperature of the oven to 140°C after 4 hours would seem to affect only the skin of the casting.

Theoretically the gel point occurs at 25% of total cure, p.13. The time calculated by the computer program from the experimental data is:

Table 15

<table>
<thead>
<tr>
<th>Radius (cm)</th>
<th>Time to reach 25% cure (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>60</td>
</tr>
<tr>
<td>2.7</td>
<td>60</td>
</tr>
<tr>
<td>4.0</td>
<td>61</td>
</tr>
<tr>
<td>6.6</td>
<td>61</td>
</tr>
<tr>
<td>8.6</td>
<td>61</td>
</tr>
<tr>
<td>9.75</td>
<td>62</td>
</tr>
</tbody>
</table>

This is in excellent agreement with the practical experiments of Fife et al. (19) which gave 60 minutes as the gel time for a 10 Kg casting mixed and cured at the temperatures used for computer data.

The displacement - time curves, fig. 26 show an initial shrinkage (positive displacement value) throughout the casting until the gel time when the outside annuli expand due to the cure shrinkage having a greater effect on the density than the rise in temperature. The slope of these curves is du/dr; a positive slope corresponding to a positive strain or tension and a negative slope to a compression where u is the displacement.

Up to the gel point the resin is still liquid and therefore undergoes no compression or tension. At the gel point the displacement is very close to zero having a maximum here of $6.10^{-4}$ cm.cm$^{-1}$. 
Therefore the annuli are assumed to be 1 mm wide at gel for the purpose of evaluating the displacements thereafter. The maximum displacements during the cure cycle occur at the end as might be expected; the maximum value is $3 \times 10^{-2} \text{cm/cm}$.

Whilst the predominant strain within the block during cure is seen to be tensile the following features should be noted.

The strain is greatest at the edge of the casting except in the immediate post gel period when the temperature expansion and cure-shrinkage effects are similar and small waves of tension and compression appear near the outside of the block. These herald far larger displacements which from 90 to 140 minutes cause a small compressive strain in the centre up to a radius of 4 cms and a much larger tensile strain which increases continuously to the outside of the block. The maximum strain of $8 \times 10^{-4} \text{cm/cm}$ occurs at radius 9.4 cms after 160 minutes.

To determine the actual stresses within the block it is necessary to know the modulus of elasticity (either Young's or Bulk) of the material at that temperature and degree of cure.

The value for Young's modulus for fully cured resin usually used in photoelastic analysis is 3000 p.s.i. at $130^\circ\text{C}$. This value gives 2.4 p.s.i. as the stress at maximum strain. As the temperature at the point of maximum strain is $156^\circ\text{C}$ and the extent of cure only 67%, the true modulus will be less than this resulting in a lower strain.

At $130^\circ\text{C}$ the tensile breaking stress of cured resin is 225 p.s.i. (19). Unless the tensile breaking stress falls to the order of 1 p.s.i., the curing stresses will not cause any internal microcracks or stress failure.
Immediately post-gel, the elastic modulus of the resin will be much reduced which will also tend to decrease the stress.

Fig. 27 shows the density falling at the beginning of cure after which there is a continuous rise to the final value of 1.13 g.cm\(^{-3}\) at 120°C. Minimum density is reached earlier in the outer regions of the block than the centre; 60 minutes at r = 9.75 cm and 160 minutes at r = 0.8 to 6.6 cm. The inset of Fig. 27 shows the density changes just after gel to correspond to the small waves of compression and tension.

Table 16 compares the experimental and calculated data obtained for the relative absorption and density of the second set of small castings which underwent simulated cure cycles, p.94.

The relative absorption could be measured to ±1% which produced an error in the %cure value of ±1%.

At extents of cure of more than 95%, the relative absorption of the infra-red spectrum is small and an error of ±2% is found. From 50-95% the calculated extent of cure is within 1% and below this the calculated value is consistently 2-3% lower than the experimental value. This is due to the increased mobility of the reactants prior to gel which causes an increased cure rate.

Comparison of the density determinations gives an overall error of ±2% which compares favourably with the errors in the estimation of cure by infra-red analysis.

The calculation of density and displacement throughout cure for any regular casting of epoxy-resin at any oven temperature is thus possible with no modification of the program. It is necessary only to know the temperature-time profiles of up to six thermocouple implants and their distance from the centre of the casting.

The program may be used with other polymer systems if the rate
Fig. 27  Density - time for thermocouple radii.
<table>
<thead>
<tr>
<th>No. of simulated thermocouple</th>
<th>Cure time mins.</th>
<th>Relative absorption %</th>
<th>% cure experimental</th>
<th>% cure calculated</th>
<th>density at 120°C experimental</th>
<th>density at 120°C calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>132</td>
<td>40.8</td>
<td>38</td>
<td>1.063</td>
<td>1.060</td>
</tr>
<tr>
<td></td>
<td>225</td>
<td>9</td>
<td>95.9</td>
<td>96.2</td>
<td>1.125</td>
<td>1.129</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>3</td>
<td>98.6</td>
<td>99.6</td>
<td>1.126</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>~1</td>
<td>99.6</td>
<td>100</td>
<td>1.133</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>123</td>
<td>44.8</td>
<td>42.0</td>
<td>1.067</td>
<td>1.065</td>
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<tr>
<td></td>
<td>140</td>
<td>80</td>
<td>64.1</td>
<td>62.95</td>
<td>1.094</td>
<td>1.094</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>33.3</td>
<td>85.0</td>
<td>85.1</td>
<td>1.122</td>
<td>1.121</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>14</td>
<td>93.7</td>
<td>95.4</td>
<td>1.129</td>
<td>1.129</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>5</td>
<td>97.7</td>
<td>99.3</td>
<td>1.128</td>
<td>1.130</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td></td>
<td>1.131</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>126</td>
<td>41.7</td>
<td>1.064</td>
<td>1.064</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>17</td>
<td>91.5</td>
<td>1.125</td>
<td>1.127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>~2.5</td>
<td>99.5</td>
<td>1.129</td>
<td>1.130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>-</td>
<td>100</td>
<td>1.132</td>
<td>1.130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>163</td>
<td>24.6</td>
<td>1.045</td>
<td>1.044</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>105</td>
<td>51</td>
<td>1.073</td>
<td>1.078</td>
<td></td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>51</td>
<td>76.9</td>
<td>1.114</td>
<td>1.112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>18</td>
<td>92.9</td>
<td>1.127</td>
<td>1.127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>255</td>
<td>8</td>
<td>97.7</td>
<td>1.129</td>
<td>1.130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>317</td>
<td>4</td>
<td>99.4</td>
<td>1.131</td>
<td>1.130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>390</td>
<td>-</td>
<td>99.8</td>
<td>1.130</td>
<td>1.130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1380</td>
<td>-</td>
<td>100</td>
<td>1.132</td>
<td>1.130</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of change of density and coefficients of expansion are known and if a measure of the extent of cure is available. These values will need only a change in the exponential slope constant data if the rates of change follow an exponential decay. If they have any other relationship which is representible mathematically then a modification of the program will be necessary.
1. Permanent mottle occurs in epoxy-resins (used in photoelastic analysis) especially in castings having a minimum dimension of greater than 2 cm and/or a resin temperature during cure of greater than 140°C. It occurs most frequently in the centre of a casting and cannot be annealed out as can cooling stress.

2. Mottle has several appearances: whorled, needle-like and forming a star from the casting centre. These may be interrelated. It can sometimes be just observed by the naked eye as an 'orange-peel' effect without polarised light.

3. Tensile and shear fracture surfaces often show fibrilar projections especially in mottled samples. These phenomena have been termed spicules.

4. Spicules have various cross-sections from a narrow ellipse to a circular form. Their diameters range from 1-100 μm: their lengths being from 10-100 times the diameter.

5. Experiments designed to show the alignment of spicules to the casting isotherms were inconclusive.

6. Centrifuged solutions in acetone of marginally pre-gel resins showed permanently insoluble spheres from 1-100 μm in diameter. Infra-red analysis showed these to be fully cured spheres of epoxy-resin. They compare in dimensions with the spheres in the two-phase systems discussed by both Schoon and Cuthrell. They had a tendency to pearl-chain formation which could be interpreted as a first step towards spicule formation.

7. A correlation between the ridge pattern on a spicule and the septa in the trough from which it had been torn was observed. This was seen to be similar to the septa-ridge formation found in fractured glass-fibre reinforced epoxy resins. It suggests that the spicule differs from the surrounding matrix before fracture.
8. Determination of the refractive index of both spicules and their matrix showed a difference of 0.01 R.I. units. This was shown to correspond to an increase in density of 0.017 g.cm\(^{-3}\). Such a change in density corresponds to a strain sufficient to produce 0.1 stress fringes. This apparent stress would not be annealable.

9. Measurement of the breaking stress of spicules showed an increase in strength with decrease in cross-section. The strength of the thinner spicules reached and tended to surpass the bulk breaking strength of epoxy-resin.

10. X-ray diffraction photographs of individual spicules showed the usual amorphous ring typical of polymers. One particular spicule showed a pattern of 10 strong lines and many very weak lines on leaving for a very long exposure, 6 hours. Comparison of these with both experimental and computer calculated patterns showed that the pattern was not due to crystallised hardener, resin or phthalic acid (the hydrolysis product of the hardener). The cause of the pattern was not ascertained.

11. Infra-red analysis showed spicules to have a higher ester content than cured resin. This accords with the view of the spicule as a reaction centre. As such, the local temperature would be raised and so facilitate hardener diffusion towards it.

12. The self-diffusion constant of phthalic anhydride during cure was determined using \(^14\text{C}\) - containing hardener as a tracer with post-diffusion scintillation counting.

13. Ungelled samples were counted in dioxane using a proprietary scintillation fluid, NE250. Several methods were tried for counting gelled samples; that used finally being solution in c.H\(_2\)SO\(_4\) with subsequent neutralisation before counting with NE250. Quenching of the scintillation in the neutralisation method was constant at 33.5%.

14. An integrated form of Fick's law of diffusion was used to determine the average self-diffusion constant. (see Table 6, p.82-84).
15. The activation energy for diffusion was found to be \(15 \text{ kcal.mole}^{-1}\) which is close to the activation energy of the condensation reaction itself. This suggests a largely diffusion controlled reaction.

16. The flux at a spicule surface necessary to sustain the higher hardener content consistent with the increased esterification found was equated with the maximum flux available calculated from the diffusion constant, the rate of cure and the extent of cure, see \(^{22}\).

17. It was found that, for two thirds of the gel time, the self-diffusion was high enough to sustain this growth but reduced gradually to the gel-point. This produces a gradual change in properties of the resin from the centre of the spicule to the surrounding matrix. This may account for the increase in tensile strength of the smaller spicules and the deformation in the septa-ridge formation associated with the tearing of spicules from a fracture surface.

18. The dynamics of cure were investigated by calculating the rate of change of displacement (strain) throughout cure in an 8 kg right cylindrical casting. This necessitated the determination of the rate of change of density and extent of cure with time of small isothermal castings. The temperature of six thermocouples implanted along the central plane of the casting was recorded showing a peak exothermic temperature of \(200.8^\circ\text{C}\). The oven temperature being \(120^\circ\text{C}\).

19. The rate of change of density at \(120^\circ\text{C}\) was found by determining the density of the isothermal castings at \(20^\circ\text{C}\) and their change in volume when raised to \(120^\circ\text{C}\). This method was shown to be inherently accurate to \(0.0015 \text{ g.cm}^{-3}\). The density was shown to follow a good exponential relationship with time during cure.

20. The rate of change of density with temperature was determined similarly for uncured, 40\% cured and fully cured resin.
21. After rejecting tensile breaking strength and hardness as parameters of cure, infra-red analysis was used. An exponential relationship was found between the relative absorption measured and time.

22. The displacement, density, rate and extent of cure of a curing casting was calculated using a program written in Algol for an I.C.L. 1905F series computer.

23. The extent of cure and rate of cure were used to determine the value of the self-diffusion constant necessary to sustain spicule growth throughout cure.

24. The outside of the casting required a further 160 and 300 minutes to reach 95 and 98% cure respectively compared with the inner 8cm.

25. Gel time was calculated as 60-62 minutes which agreed very closely with the experimentally observed value.

26. After a small tension and compression wave from the centre of the casting at gel time, the predominant displacement causes a tensile strain throughout the casting during the rest of the cure.

27. Up to the gel point the density of the resin decreases until the increase in density due to advancing cure becomes greater than the decrease due to temperature rise.

28. The strain caused by differential displacement leads to a maximum stress of 1 p.s.i. compared with a tensile strength of 225 p.s.i. for fully cured resin. It is clear therefore that mottle is not due to post-gel curing stresses caused by differential cure in various parts of the casting.

29. Mottle is probably caused by polarisation of light by the spicules, this may be either form polarisation or strain birefringence due to inhomogeneity of density.

30. Mottle, i.e. spicule growth, may be minimised by using minimum oven temperatures and low reactivity hardeners (large molecules, low exotherms).
REFERENCES

18. Private Communication, B. Crook, University of Surrey.
APPENDIX 1

THE FRACTURE OF POLYMERS

In general polymers undergo brittle fracture below their glass transition point (Tg) and ductile fracture above it. For epoxy resins Tg is around 100°C; this is the temperature at which the coefficient of expansion shows a sharp rise with rising temperature.

The Griffith criterion for fracture from a flaw at the surface is derived from equating the critical stress at fracture T with γ, the surface energy of the new fracture faces so formed. (1) He assumed the flaw to be ellipsoidal at the crack tip, fig. (1a).

\[ T = \left( \frac{2E\gamma}{\pi C} \right)^{\frac{1}{2}} \]

where
- \( E \) = Young's Modulus
- \( C \) = Depth of flaw
- \( \gamma \) = Surface Energy;

Fig.1

(a) Griffith type.          (b) Barenblatt type.

This formula holds well for brittle fracture in glasses or polymers at low temperatures but at normal temperatures Yoffé (2) showed a correction factor of about 0.5 - 0.6 was required to achieve good agreement. Berry (3) found the fracture strength to depend dominantly on the critical strain and in 1964 showed that in viscoelastic materials, such as epoxy resins, much mechanical energy is dissipated by deformation around the crack-tip so that for a known system the surface energy term \( \gamma \) is too large (4). A better correlation with experiment is achieved by
modifying the equation so that it includes the energy stored at the crack tip.

Barenblatt (5) correlated fracture with the finite cohesive stress at a smoothly opening slit under plane stress assuming perfect plasticity at the crack tip. The cohesive force is assumed to be proportional to the separation distance (δ) within the crack and the function of strain (σ) and δ summed over the length of the crack is found to equal twice the surface energy. fig. (1b) and fig. (2).

\[ 2\gamma = \int_{0}^{\delta} \sigma(\delta) d\delta \]

This treatment yields the Griffith equation as a special case for plane stress. Barenblatt is open here to the same criticism as he addressed to Griffith that for small cracks, for which the Griffith critical stress tends to infinity, the size of the crack tip is small enough to render his inherent assumption of a linear flaw continuum invalid. This is due to the finite size of molecules within the bulk.

Orowan (6) pointed out that the stress at the crack tip over an area of atomic dimensions must equal the theoretical bond-strengths. His treatment gives the same values for critical stress as Griffith.

The development of a fracture under constant strain is slow at first; speeding up as the stress increases due to the progressively reduced cross-section.

Robert and Wells (7), assumed the dynamic stress state around the tip of a two-dimensional crack of finite length to be the same as for
static conditions; they derived the velocity of crack propagation \( v_c \).

\[
v_c = 0.38\left(\frac{E}{\rho}\right)^{\frac{1}{2}}
\]

where \( \left(\frac{E}{\rho}\right)^{\frac{1}{2}} \) = the velocity of longitudinal propagation of sound waves in the medium \( \left( v_1 \right) \).

\( \rho \) = stress at tip.

As \( \mu = E/(2(1-\nu)) \), where \( \mu \) is the shear modulus and \( \nu \) is Poisson's ratio, the shear velocity \( v_s \) is approximately 0.6 \( v_1 \).

Yoffé (2) and Craggs (8) point out that at speeds approaching the maximum theoretical the highest stress concentration moves away from its normal position axially in front of the crack tip to two maxima at ± 60° fig. (3).

![Fig. 3](image)

This leads to zig-zag propagation of the crack with eventual bifurcation. In metals and crystalline structures Berry (4) claimed that this zig-zagging is due to the crack meeting screw dislocations and other lattice defects. These do not occur as such in polymers but similar irregularities may occur in any polymers of more than one phase.

In viscoelastic polymers such as epoxy resins there is a relaxation time associated with the applied strain which effectively reduces the stress in the material under constant strain. This is of the order of minutes to hours according to temperature but at room temperature this is many orders greater than the total fracture cycle time (30 secs.) with the result that no appreciable ductile fracture (tearing) occurs.
Spicules may be formed either by change of crack direction around harder more cross-linked regions or as a natural product of irregular propagation. The smooth area where the crack starts in the fracture of a resin sample is that in which the Griffith criterion is obeyed; the rougher region where $v > v_1$ becoming sensitive to subtle changes in structure which are made apparent by the formation of many steps and spicules.
REFERENCES

2) Yoffe, Phil.Mag. 42 739, (1951).
3) Berry, Fracture by Averbach et al. (Wiley 1959) p.262.
APPENDIX 2

I.R. ANALYSIS

Infra-Red spectroscopic analysis is useful for the analysis of organic molecules; the interactions between the vibrations of the bonds normally extant in organic molecules and electromagnetic radiation occurring between 350 cm\(^{-1}\) and 4000 cm\(^{-1}\), the Infra-red region.

Characteristic frequencies of absorption exist for each type of bond, e.g. C-O, C=C, C=O, O-H, N-H etc., Table 1. These may be accounted for by the natural bending and stretching frequencies of the bond. Linear combinations of the frequencies occur which give rise to the combination bands.

**TABLE 1**

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bending Mode</th>
<th>Stretching Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - C</td>
<td>Far I.R.</td>
<td>800 - 1200</td>
</tr>
<tr>
<td>C = C</td>
<td>Far I.R.</td>
<td>1580 - 1700</td>
</tr>
<tr>
<td>C - H</td>
<td>1300 - 1475</td>
<td>2700 - 3300</td>
</tr>
<tr>
<td>C = O</td>
<td>Far I.R.</td>
<td>1640 - 1850</td>
</tr>
<tr>
<td>C - O</td>
<td>Far I.R.</td>
<td>900 - 1300</td>
</tr>
<tr>
<td>O - H</td>
<td>1200 - 1450</td>
<td>3000 - 3750</td>
</tr>
<tr>
<td>N - H</td>
<td>1500 - 1650</td>
<td>3000 - 3750</td>
</tr>
</tbody>
</table>

Whilst all bonds of one type have similar frequencies, yet the adjoining atoms also affect the vibration of the bond either by affecting the electron density of the bond or by a 'damping' effect. This effect may alter the vibrational frequency by several hundred wave-numbers.

Hence different frequencies are characteristic of for example the C=O bond in ketones, aldehydes, acids, ethers etc. An even more subtle
effect may be caused by slightly changed atomic environment. 
E.g.,

Benzoic acid  Phthalic anhydride

\[ C=O \text{ stretch at } 1680-1720 \text{ cm}^{-1} \] \[ C=O \text{ stretch at } 1760-1780 \text{ cm}^{-1} \]

The bandwidth of the spectra peaks is due to mechanical factors such as the slit width of the spectrometer and the dispersive power of the prism or grating whilst molecular factors include rotational broadening in gaseous and liquid samples and the effect of neighbouring atoms in multifunctional molecules.

A quantitative analysis through direct measurement of intensity is critically dependent upon the spectral response of the detector so that as a consequence most I.R. spectrometers are twin beam instruments. This obviates the necessity for absolute measurement which would have to proceed with an exact knowledge of the detector response.

The radiation from the source is split into two parts by an angled mirror, one beam passing through the sample, the other being a reference beam. The two beams are sampled in turn by a rotating or vibrating mirror.

If there is no absorption in the sample beam the intensity falling on the detector is constant and after A.C. amplification no output signal is produced.

With the presence of an absorbing sample in the beam the resulting chopped input to the detector is amplified, the resultant output being used in a feedback loop to reduce the intensity of the reference beam.
This is commonly achieved with a servo motor driving a 'comb' which progressively blocks the reference beam. On equalization of the twin beam intensities no further signal is output and the amount of backing off required is displayed, usually as an output to a chart recorder calibrated directly in transmittance or absorbance. The time axis of the recorder being coupled to the dispersive element yields a spectrum of wave-number of the radiation against the absorbance of the sample.

In the event of a high sample absorbance some improvement can be made by permanently impeding a portion of the reference beam so that the change in intensity recorded on the chart is physically as large as possible; the absorbance being logarithmic, a more accurately measurable band is read when the relative absorbance is low. In this case higher gain is needed, a variable gain control being employed. In its turn the higher gain results in more damping being necessary to counteract the higher signal/noise ratio. A slower chart speed is employed to nullify the slower response of the instrument.

If the sample is a gas it can be held in the beam in a parallel ended cell. Liquids are usually held as a thin film between polished NaCl or KBr plates; these do not absorb in the infra red region having absorption-free windows down to 650 cm\(^{-1}\) and 400 cm\(^{-1}\) respectively.

Solid samples, if thin enough, (0.01 to 0.1 mm.), can be measured directly otherwise they may be ground to a mull with a carrier liquid such as liquid paraffin (Nujol) or hexa-chloro-butadiene of which the spectra are known and may be allowed for on subsequent analysis of the spectrum. The resultant mull is placed between the plates as before, the object being to reduce scattering.

An alternative technique is to grind a few mgms. of the sample
solid with a few hundred mgms. of dry pure KBr and pressing under vacuum in a die (fig. 1) with a load of 20-30 tons per sq. inch. The disc so-formed is transparent and yields good absorption spectra. There are cases where this technique may alter the spectrum but for the resin-hardener system in this thesis a comparison of the H.C.B. spectra and that from a KBr disc showed them to be indistinguishable.

![Diagram of the die press](image)

The spectrometers used for this work were the Unicam S.P.200 and the Perkin-Elmer 337 and 457. They are all twin-beam machines, the latter being slower in operation than the S.P.200 but more sophisticated producing greater resolution due to their narrower slits and therefore more accurate absorbance readings.
APPENDIX 3

COMPUTER PROGRAMS USED IN THE CALCULATIONS

All programs were written in the Algol programming language and run on the I.C.L. 1905F series digital computer in the computer centre of the University of Surrey.

1. Curve fitting by means of an exponential least squares algorithm

N pairs of variables (X,Y) where X was time and Y either density or absorbance were fed into two arrays X[0:N] and Y[0:N].

The curve fitting procedure by Deily (p.98) was used in which a Taylor series modification of the classical least squares method is utilised to approximate a solution to the system of non-linear equations of condition. "After each iteration, the statistic Esquared is computed as a measure of goodness of fit. Commencing with the second iteration, the successive values of Esquared are differenced, and when the difference in absolute value becomes less than epsilon, the calculations cease. If the number of calculations necessary to achieve this result exceeds lmax, a flag is set to a non zero value and the procedure is terminated."

Epsilon was set at $10^{-12}$ and lmax to 1000. The solution is in the form:

$$Y = A \cdot \exp(B \cdot X) = C$$

For an exponential decay in which B is always negative the curve is as in fig. 1. It may be noted that the maximum value of Y is $(A-C)$ greater than the minimum value of Y. This was used throughout to make the minimum value of the Y-variable zero and therefore the maximum value equal to $(A - C)$. 
2. **Graphic display**

Both graphic display programs utilise the I.C.L. 1905 plotter package SPLOT. This produces a diagram as dictated by the program accurate to 0.005 inches in both X and Y directions.

(a). **Density/Absorbance versus Time**

This program plots out N points of form \((X,Y)\) where \(X\) is time and \(Y\) is either density or absorbance for each cure temperature of the first series of small blocks, i.e. 120, 140, 160, 180, 200°C, p. 93. The values for \((A - C)\) and \(B\) determined by program 1 were used to plot a continuous curve of the function \(Y = (A - C) \exp(-BX)\) for values of \(X\) at five minute intervals up to 1000 minutes, figs. 19 and 20a.

(b). **Temperature versus Time**

This program plots the temperature-time curves read from the cure cycle of the large castings stress experiment. N points are plotted for each thermocouple position, there being more points where the rate of change of temperature was greatest.

3. **Density calculations**

This program calculates the density at 120°C of the resin samples
according to equation 13. The main body of the program includes the data on the two cells used.

The data read are the densities of mercury at 120°C (ROLH), the average temperature of the capillary MDT, (ROLG) and at 20°C (ROLC); the temperatures of the two density determinations (120°C and 20°C) and the ambient temperature above the oil bath at the top of the mercury column in the capillary (24°C).

For each specimen the data supplied was the number of the cell, 1 or 2, an identification number, (e.g. 120.0080 is the sample cured at 120°C for 80 minutes), the mass of resin, MR, the total mass of the cell and contents, MT, the change in height of the column, L, and the initial density of the resin as determined at 20°C, R020.

The results printed out are the temperature of cure; time of cure; MR;L; DVR and DVL, the changes in volume of resin and mercury; R020 and R0120, the density of the resin at 20 and 120°C; and the cell number, 1 or 2; Table 11.

4. Stress calculation

This calculates the stress at any point on the plane including the six thermocouples. The data used was as follows:

a. Initial and final time in minutes, TIMIN and TIMAX.
b. Radius of the casting in cm, RBLOCK.
c. 808 zeros to initialize arrays if TIMIN = 0, or 808 values for the arrays from their value at TIME = an integer in the case where TIMIN = an integer + 1.
d. Radii of six thermocouples from the centre of the casting, RA[1-6].
e. Time - temperature points from thermocouples 1 to 6 proceed by the number of points M for each thermocouple; e.g. A[K,J,I] where
K is the thermocouple number; \( J \) is 0 for time and 1 for temperature and \( I \) is the order number of the point in the array and less than \( M \).

f. Maximum value of absorbance \( \text{ABSMAX} \) from the \( (A-C) \) value in program 1.

g. Density of uncured resin at \( 120^\circ \text{C} \), ROSTART.

h. Slope constant in \( \rho_{120} = a \cdot \exp(-b \cdot \text{TIME}) + C \), RB[1 to 6].

The program assigns this data into arrays or variables and sets all other variables necessary for the calculation to zero.

For each one minute step in time the stress across each 1 mm annulus from 1 to 100 is calculated as follows:

For the radius equals \( R \) cm (\( M \) mm):

1. The temperature \( T \) at point \( R \) is found by interpolating between the known temperatures \( \text{TH} \) and \( \text{TL} \) of the thermocouples either side of point \( R \), \( \text{RH} \) and \( \text{RL} \). \( \text{TH} \) and \( \text{TL} \) are found by interpolating in the corresponding arrays \( A[K,J,I] \). As the temperature drop across the block varies as in fig. 2, the interpolation used was the root mean square.

![Fig. 2](image)

\[
T = \frac{(\text{RL}-R) \cdot \text{TH}^2 + (\text{RH}-R) \cdot \text{TL}^2}{(\text{RH} - \text{RL})}
\]

2. The extent of cure \( \text{TOTCURE}[M] \) for radius \( R \) was found by estimating the amount of cure during all the one minute periods up to that under consideration. This was done using equation 5, p.86, with
A = relative I.R. absorption at 1770 cm\(^{-1}\) of uncured resin and B obtained by interpolating between known B values of the thermocouples above and below radius R, in the array RB|appropriate| . The amount of cure for one minute is then \(B(1-\text{TOTCURE}[M])\). fig. (3) where \((1-\text{TOTCURE}[M])\) is the normalised parameter of the absorption. Thus full cure corresponds to \(\text{TOTCURE}[M] = 1\).

3. At this point the rate of change of density with temperature \(\text{ROCO}\) is determined for the extent of cure equal to \(\text{TOTCURE}[M]\). This is the value obtained from interpolating the results on p.120 fig. 4. This value of the density coefficient is used to convert the density, which is calculated by the program at 120°C, to the density at the temperature of the point at radius R. The maximum error produced by linear interpolation will be approximately 1% and thus the error in the final displacement which is proportional to the cube root of the density will be less than 0.3%.

4. Using the known temperature at the point at radius R the density at this time can be found. First, the slope constant B at \(\text{TIME}\)
is determined by interpolating between the slope constants experimentally obtained for the temperatures 120, 140, 160, 180 and 200°C. It is important to note that the slope constant here relates to density at 120°C.

As the slope constant changes slightly during the one minute period under consideration the root mean square of the values of B at TIME and TIME-1 is taken as the average for the one minute period where the time from the beginning of cure is TIME.

Due to the transformation of the axes of the rate of change of density with time, \( \rho R \), the range of density change from the B-value obtained is

\[
\rho_{\text{cured}} - \rho_{\text{uncured}} = 0.1026 \text{ g cm}^{-3}
\]

Thus \( \Delta \rho = B_{\text{ave}} \cdot (1.13 - \rho_{\text{time-1}}) \) per minute.

and \( \rho_{\text{time}} = \rho_{\text{time-1}} + \Delta \rho \).

This is the density at 120°C, the working temperature for the calculation from the known rates of change of density and absorbance. Therefore the density \( \rho_T \) at the resin temperature for radius R is

\[
\rho_T = \rho_{\text{time}} (1 - 0.0001 [M] \cdot (T - 120)).
\]

5. The thickness of the annulus is now calculated so that the rate of change in displacement with radius \( du / dr \) may be found. The displacement of the annulus R may be taken to be the change in thickness from time = 0 or any time such as the gel time.

Consider a cube of side \( r \) units. After some amount of cure the side becomes \( r + dr \). Their respective volumes are \( r^3 \) and \( (r - dr)^3 \).

\[
\text{Density} = \frac{\text{mass}}{\text{volume}} \text{ and the mass remains constant, shrinking cube.}
\]
Therefore \( \rho r^3 = (r - dr)^3 \rho r^3 dr \),
so that \( r - dr = r(\rho r / \rho r - dr)^{\frac{1}{3}} \).

Therefore the change in thickness (displacement) of annulus \( R \) is
\[
R = 0.1(1 - (\text{density of uncured resin at } 120{\degree}C / \rho r)^{\frac{1}{3}})
\]

6. The rate of change of displacement is found simply by taking
the difference between the displacement for radius \( R \) and radius \( R - 1 \).

7. From this, a substitution of known values for Young's Modulus
can give the radial stress in the curing resin casting at points
initially 1 mm apart at 1 minute intervals throughout cure for
any casting of CT200 / HT901 epoxy resin for which a temperature
profile at several points in the casting are known.
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