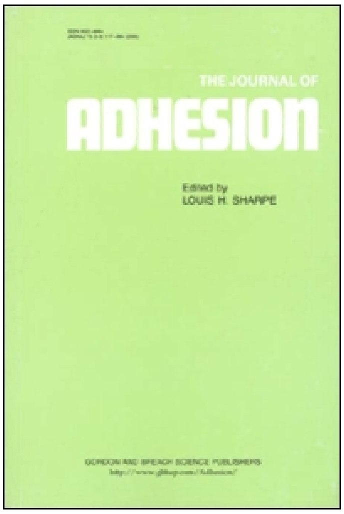

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A Possible In-Situ Thermal History Indicator for Uncured Film Adhesives†

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A range of epoxy formulations, typical of aerospace adhesives, containing a pyrazolone dye, has been shown to undergo a reaction which results in a change in colour of the formulation. The rate of reaction depends greatly on the particular epoxy resin. The extent of reaction may be determined by direct colour measurement or by chromatographic analysis of the remaining dye level. The possible use of this reaction as an in-situ thermal history indicator is discussed.

KEY WORDS Colour change; colour measurement; epoxy resins; film adhesives; in-situ thermal history indicator; reactive pyrazolone dye

INTRODUCTION

Film adhesives are increasingly being used in structural aircraft applications. Adhesives in this form afford various advantages including ease of use, since only heat and pressure are required to effect cure. However, one of the disadvantages of this form is the

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short shelf life (commonly 6 months at −18°C or around 20 days at 15°C). Transport of the adhesive from the manufacturer's plant to the point of use thus presents significant logistics problems. Assurance that the adhesive to be used is still within life (despite its often unknown thermal history in transit) is of considerable importance, especially in view of the critical applications in which these materials are now employed.

Currently, acceptance criteria of adhesives are based on specified mechanical tests of bonded joints. Considerable attention is being given to development of chemical characterisation procedures, mostly based on chromatographic techniques, which are principally aimed at detecting batch-to-batch variations in the adhesive formulation[1] but which also can be used in assessing the extent of ageing (or advancement) which has occurred during and since manufacture.[2,3]

Another approach to the question of thermal history assessment has been the inclusion of some suitable indicating device in the adhesive packaging.[4] This method has the advantage of providing a simple, if somewhat empirical, indication of thermal history without the need for chemical analysis and expert interpretation of the results.

In the course of studies on changes in physical and chemical properties during ageing of an uncured structural film adhesive it was observed that the colour of the adhesive (green) altered gradually during ageing.[3] The origin of this colour change and the possibility of its use as a simple but direct built-in indicator of the thermal history of the adhesive is the subject of the present work.

EXPERIMENTAL

Samples of various epoxy resins were obtained from Shell Chemical (Aust.) Pty Ltd, Ciba-Geigy Australia Ltd and Dow Chemical (Aust) Ltd. The 2,4-tolylene diisocyanate-dimethylamine adduct (TDI-DMA) was prepared according to the method of Nawakowski.[5] A sample of C.I. Solvent Yellow 72 was obtained from Morton Chemical, U.S.A., while samples of C.I. Solvent Yellow 16 and C.I. Solvent Red 8 were provided by BASF Australia Ltd. All these dyes are substituted pyrazolones. High performance liquid chromatography (HPLC) analysis indicated a high level of purity.

Colour differences obtained by ageing an uncured nitrile/epoxy adhesive film were determined with a Gardner XL 10 Colorimeter according to standard procedures.[6] Ultraviolet-visible spectra were measured on a Hitachi EPS 3T UV-Vis spectrophotometer while infrared spectra were obtained on a Perkin Elmer 580B spectrophotometer. Proton nuclear magnetic resonance spectra were determined on a JEOL model FX-90Q Fourier transform instrument.

Combinations of the various compounds of interest were prepared by thorough mixing with a pestle and mortar or, in some instances, by the use of a small triple roll mill. Samples from these batches were weighed into separate, lightly-stoppered vials and kept at the desired temperature. They were removed at suitable intervals and either analysed at once or stored at −18°C until required.

Samples for thin layer chromatography (TLC) were dissolved in tetrahydrofuran (THF), applied to precoated plates (Merck silica gel GF_{254}) and eluted with the appropriate solvent system. A standard was included on each plate to allow for variations between plates. For samples containing Solvent Yellow 72 or Solvent Yellow 16 the solvent system was petroleum ether (40–60)/acetone $7+3$ while for samples containing Solvent Red 8 the system was THF/methanol $11+9$. Plates were scanned, at 370, 390 and 535 nm for Solvent Yellow 72, Solvent Yellow 16 and Solvent Red 8 respectively, using a Zeiss PMQ II UV-Vis spectrophotometer with TLC scanning attachment. These wavelengths correspond to maxima in the UV-Vis spectra of these dyes, as determined from separate measurements on dilute dye solutions.

For comparison, some samples were assessed by means of two component analysis (2CA) by absorption spectrophotometry. Samples were dissolved in THF and absorbances measured at 370 and 410 nm from spectra recorded between 340 and 500 nm. Assuming that only one product from the dye was formed (a reasonable assumption for most of the reaction according to TLC results) the concentrations of the unreacted dye and the dye product were determined from application of simultaneous equations to Beer's Law. Values of the absorption coefficients for the dye and the product were determined from standard solutions initially and after complete reaction. Results from this method agreed well with those from TLC analysis down to about 20% residual dye. Deviations at the higher extents of reaction are most probably due to the fact that more than one product is eventually formed.

For HPLC a modified Varian 8500 system was used in the reverse phase, gradient elution mode using THF/water as the solvent and a Zorbax CN analytical or preparative column. The UV detector was either an Altex model 153 or Beckman model 165 at wavelengths of 280 and 365 nm.

RESULTS AND DISCUSSION

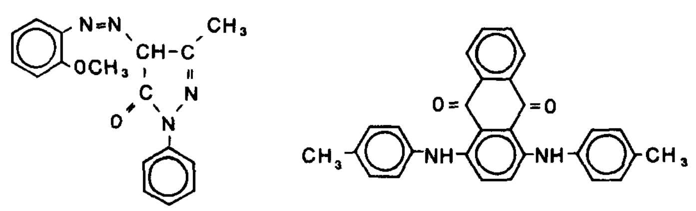
The Colour Change and its Origin

In the course of ageing of an epoxy-nitrile structural film adhesive it was observed that the green colour gradually became bluer over about 5 weeks at ambient temperature. Another, thicker grade of the same adhesive, initially a golden yellow, was found to become a more lemon-yellow over about 3 weeks at ambient temperatures. The UV-Vis spectra of the green adhesive showed maxima at about 415, 610 and 645 nm. On ageing, the first of these shifted gradually to about 390 nm while the other two peaks were unchanged.

The colouring agents in the two adhesives were isolated by TLC and identified by IR analysis as, in the case of the green adhesive, a combination of a yellow dye (Solvent Yellow 72) and a blue dye (Solvent Green 3) and, in the case of the yellow adhesive, the same yellow dye alone (Figure 1).

TLC studies on the green adhesive showed that the yellow dye disappeared during ageing and, by the end of the reaction, a number of other components appeared at Rf values suggestive of higher polarity and/or molecular weight. Evidently, the dye reacts with one or more of the adhesive components until all the dye is consumed (dye content of the adhesive is less than 0.1% by weight) after which no further colour change occurs, as shown by direct colour measurements (Figure 2). No change in the blue dye was noted.

The composition of this adhesive, previously determined,[7] is given in Table I. Mixtures of various combinations of these components (but using Epon 834 in place of Epon 836 for convenience of handling) were made as a means of identifying the reactive ingredients. It was found that the combination of epoxy

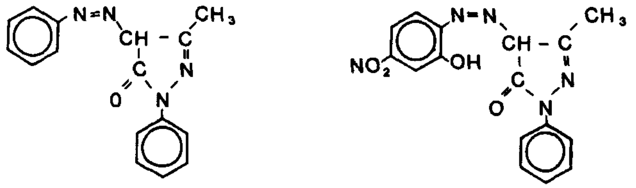


4-(2'-methoxyphenylazo)-3-methyl-1-phenyl-5-pyrazolone

C.I. Solvent Yellow 72

1,4di(4-methylphenyl)diamino 9,10 anthraquinone

C.I. Solvent Green 3



4-phenylazo-3-methyl-1-phenyl-5-pyrazolone

C.I. Solvent Yellow 16

4-(2'-hydroxy-4'-nitrophenylazo)-3-methyl-1-phenyl-5-pyrazolone

C.I. Solvent Red 8

FIGURE 1 Structural formulae of dyes.

resin, yellow dye (Solvent Yellow 72) and curing agent gave the same TLC profile on ageing as the adhesive itself.

It was thought that this colour change might be usable as the basis of an in situ thermal history indicator. Accordingly, some investigations have been conducted with other epoxy resins and curing agents, typical of adhesive formulations, and other closely related dyes. In addition, some attention has been given to the rate of the change. These studies have been undertaken in an attempt to elucidate the nature of the reaction responsible for the colour change and to delineate its likely usefulness as a thermal history indicator.

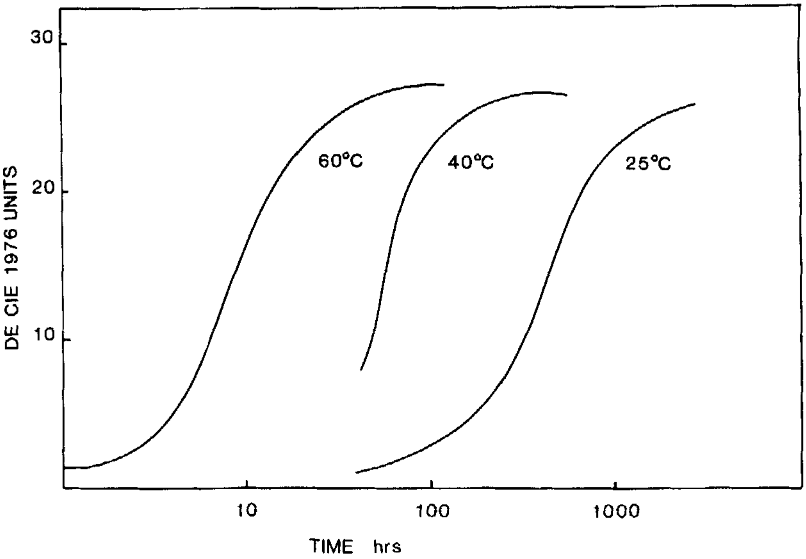


FIGURE 2 Rate of colour change of a green structural film adhesive at various temperatures.

TABLE I
Approximate overall composition of nitrile/epoxy adhesive film

Component	% by weight
DGEBA epoxy resin	78
Carboxy-containing nitrile rubber	13
Adduct of 2,4-tolylene diisocyanate/ dimethylamine (TDI-DMA)	5
Soluble dye	0.1
Polyester fibre mat	4

Other Resins, Curing Agents and Dyes

Mixes containing tetraglycidyl methylene dianiline, triglycidyl(4-aminophenol) or an epoxy cresol novolac (Ciba Geigy's MY 720, ERL 0510 and ECN 1235 respectively), in place of Epon 834, were examined. These mixes were all in the proportion epoxy resin:dye:curing agent 100:2:4 and were held at 60°C for 30 hours and then analysed by HPLC using the UV absorbance at 365 nm,

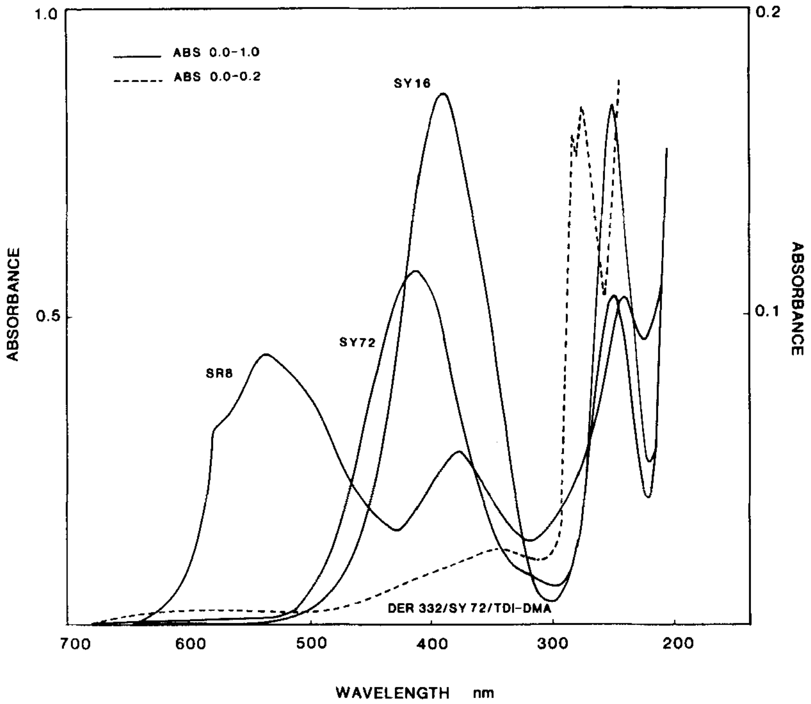


FIGURE 3 UV-Vis spectrum of dye solutions and of DER 332/SY72/TDI-DMA mixture after 18 h at 60°C. Solutions 1.3×10^{-4} g/ml in THF.

where the contribution from the epoxy resins is negligible (Figures 3 and 4). In all cases, evidence was apparent of a reaction between dye and either epoxy or an epoxy adduct leading to a reduction in the height of the dye peak and the appearance of other peaks, but the rates clearly differed significantly. By comparison, a mixture containing phenyl glycidyl ether as the epoxy compound showed no reaction after 18 hours at 60°C.

A mixture of dicyandiamide (dicy) and 3-(chlorophenyl-)1,1-dimethylurea (Monuron) 2:1 was used in place of the TDI-DMA adduct in an Epon 828 mix. The same pattern of HPLC peaks was formed after about 20 hours at 60°C. Mixes containing either dicy or Monuron alone gave no reaction under these conditions.

Two other dyes closely related to Solvent Yellow 72 in structure (see Figures 1 and 3) were examined. Based on the time to 50%

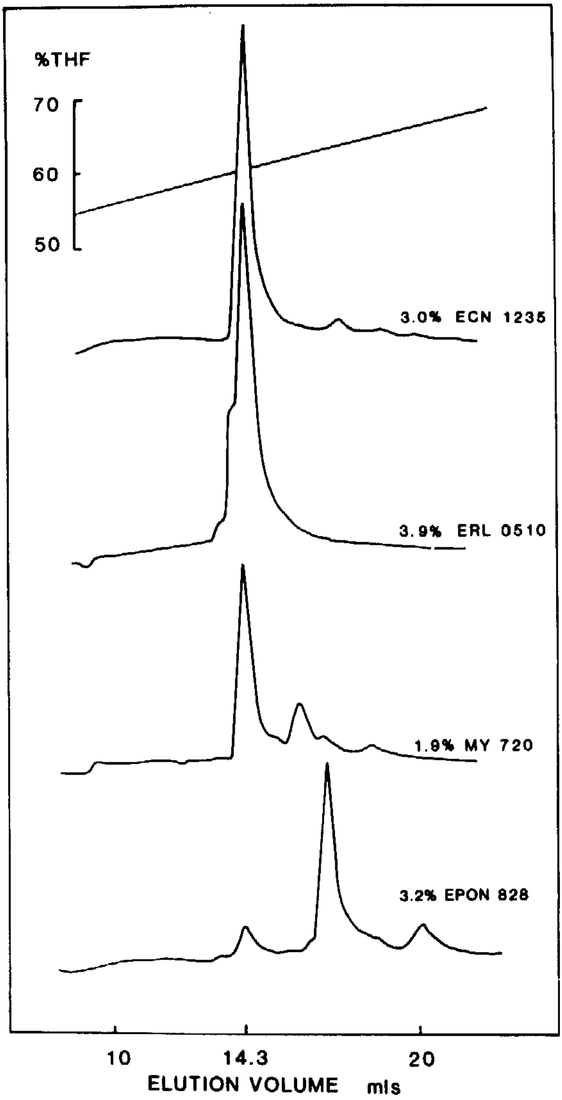


FIGURE 4 HPLC analysis of resin/SY72/TDI-DMA mixes 100:2:4 after 30 h at 60°C using UV detector at 365 nm. Dye elutes at 14.3 mls. Concentration of solutions and resin identity as indicated.

TABLE II
Time to 50% reduction in height of the dye peak (TLC)

System	Temperature, °C	Time
Epon 834/SY72[a]	50	72 hrs
Epon 828/SY72[a]	50	31 hrs
Epon 828/SY72[a]	35	6.5 days
Epon 828/SY72[a]	23	60 days
Epon 828/SY72[a]	61	10 hrs
Epon 828/SY16[a]	60	22 hrs
Epon 828/SR8[a]	60	≫75 hrs
Epon 828/SY72[b]	50	36 hrs
Epon 828/SY72[b]	38	5.2 days
Epon 834/SY72[a]	60	32 hrs*
Epon 834/SY72[c]	60	32 hrs*

[a] Resin/dye/TDI-DMA 100/2/2
[b] Resin/dye/TDI-DMA 100/2/5
[c] Resin/dye/TDI-DMA 100/2/0.5
* Determined by 2CA

consumption of the dye, Solvent Yellow 16 was slightly less reactive than Solvent Yellow 72 while Solvent Red 8 was substantially less reactive (Table II). In addition, it was found that the latter was more reactive in the absence of the curing agent than in its presence, which was not the case for the two yellow dyes.

Efforts were made to isolate and identify the principal product from the Epon 834/Solvent Yellow 72/TDI-DMA mix. This proved difficult since its Rf value in the TLC analysis coincided with that of the $n = 1$ epoxy oligomer. Use of a variety of solvents failed to displace the product peak sufficiently to obtain a pure sample. Also, the product was a very strong UV absorber and the amount of material applied to the plate was very small. Similar problems arose in separation attempts by HPLC and GPC. Accordingly, studies were made using a lower molecular weight DGEBA resin, Dow's DER 332 which is approximately 98% monomer. However, it was found that higher molecular weight compounds were generated as some chain extension and/or cross-linking occurred in competition with the dye reaction. Small amounts of two products were finally collected, from the DER 332 mix, using a preparative HPLC column followed by TLC separation (Peaks 1 and 2 of Figure 5).

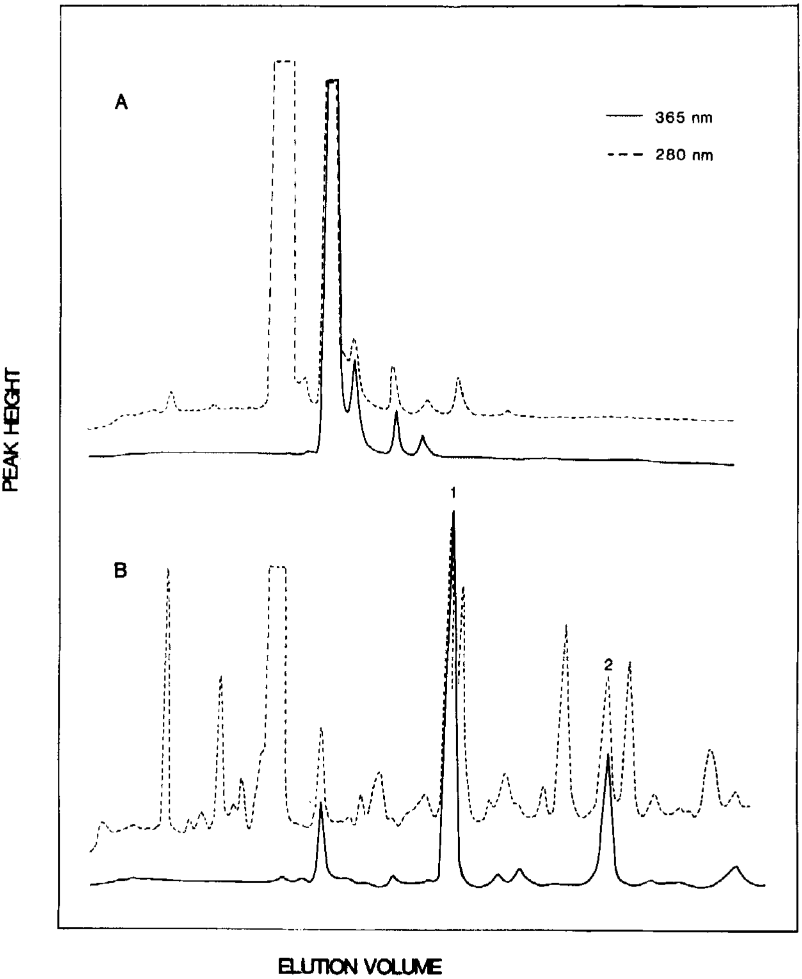


FIGURE 5 HPLC analysis at 365 and 280 nm of DER 332/SY72/TDI-DMA 100:5:7. A. Initial mixture. B. After 72 h at 60°C. Material at peaks labelled 1 and 2 collected for spectroscopic analysis.

NMR and IR analyses of these components suggested that they were still mixtures rather than single compounds. However, no absorptions attributable to TDI-DMA fragments were evident and hence it seems that the products are formed from the dye and epoxy, although the presence of the curing agent is required.

The Rate of the Dye Reaction

Some investigation was undertaken of the rate of the reaction and the effect of certain variables. The rate was determined from TLC measurements, assessing both the disappearance of the dye peak and the appearance of the principal products. Results for Epon 828 and Epon 834 systems at 50°C are shown in Figure 6. Results for a range of other systems are summarised in Table II, using the time to 50% reduction in the dye concentration as a measure of rate.

As indicated in Figure 6, the Epon 828 system reacts significantly faster than the Epon 834 system and the shape of both curves suggests an autocatalytic reaction. In addition, there appears to be

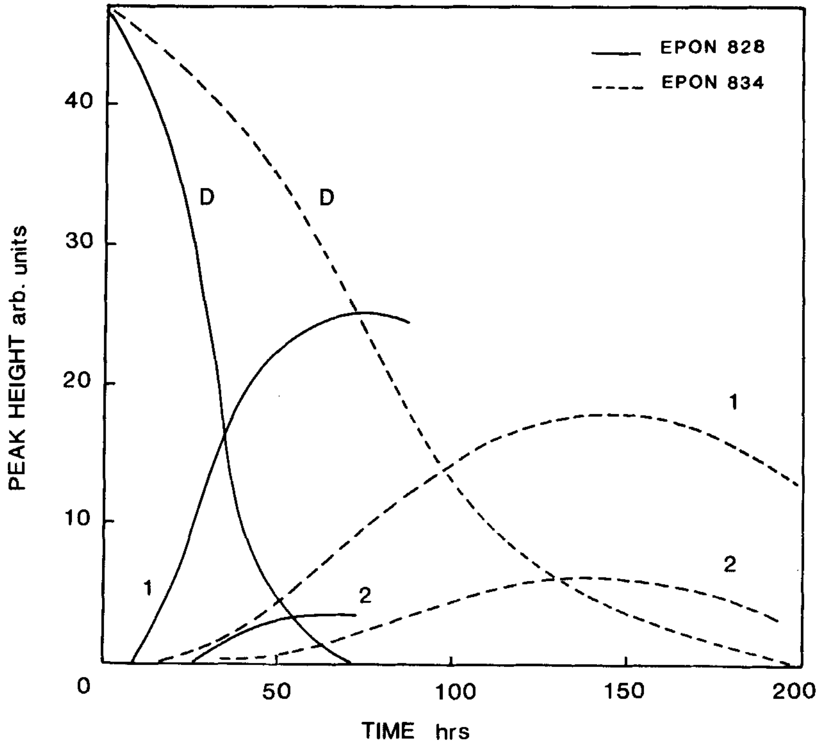


FIGURE 6 Rate of dye consumption and product formation from TLC studies on resin/SY72/TDI-DMA mixes 100:2:4 held at 50°C. D, Dye peak. 1 and 2, first and second products respectively.

an induction period before the principal product is formed in detectable amounts and this product is evidently consumed by further reaction, as indicated by the decrease in concentration after longer heating times. In considering why Epon 828 is about twice as reactive as Epon 834 under these conditions various differences can be noted. The viscosity (at 25°C) differs by about 50% for these two resins and the epoxy equivalent weight is about 190 and 250 g/eq for 828 and 834 respectively. The solubility of the TDI-DMA in the two resins was determined as about 2.0% at 50°C in each case. The hydroxyl content of 834 is about 2.5 times greater than in 828. Detailed rate studies have not been undertaken for the other epoxies shown in Figure 4 but it is clear that the other three are less reactive than DGEBA resins under the particular conditions employed.

The temperature dependence of the rate of the Epon 828 system has been investigated to some extent (see Table II). An increase of more than 40-fold was found in the time to 50% reduction in the dye peak height between 50 and 23°C. This implies an activation energy of approximately 40 kJ/mol which is commensurate with that of catalysed epoxy reactions (less than 50 kJ/mol).

Data for the other dyes are included in Table II. As previously noted, both these systems were less reactive than Solvent Yellow 72 and in the case of Solvent Red 8 a more rapid and extensive reaction occurred in the absence of the TDI-DMA (Figure 7). It was also noted that in some instances samples containing Solvent Red 8 solidified under conditions in which samples with the yellow dyes were still syrupy. This suggests the Solvent Red 8, or trace impurities therein, catalysed the cure. The presence of a hydroxyl group in Solvent Red 8 (see Figure 1) may be significant in this regard.

The effects of an increase in TDI-DMA content are included in Table II. A curing agent content of 5 parts per hundred of epoxy resembles that used in actual adhesive formulations. It is seen that the rate of the dye reaction is virtually independent of the TDI-DMA content over the range examined.

Figure 8 shows the time to 50% reaction for all systems, including the direct measurement of colour change of the adhesive (from Figure 2). Clearly, the temperature dependence is broadly similar in

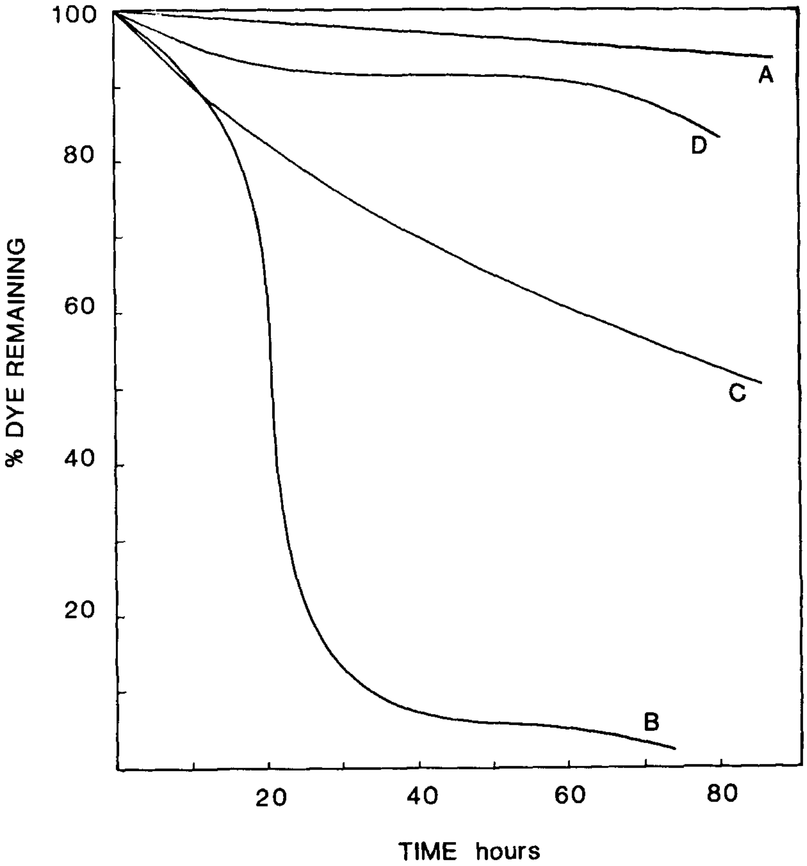


FIGURE 7 TLC analysis of the rate of dye consumption in Epon 828 for Solvent Yellow 16 and Solvent Red 8 at 60°C. A, Epon 828/SY16 100:2. B, Epon 828/SY16/TDI-DMA 100:2:2. C, Epon 828/SR8 100:2. D, Epon 828/SR8/TDI-DMA 100:2:2.

all cases. It is interesting to note that the adhesive, which is based on Epon 836, changes more rapidly than the Epon 828 systems. However, the adhesive also contains a toughening agent and fibre support (Table I) so that such factors as viscosity and solubility of the TDI-DMA may be affected and specific catalytic effects may be introduced.

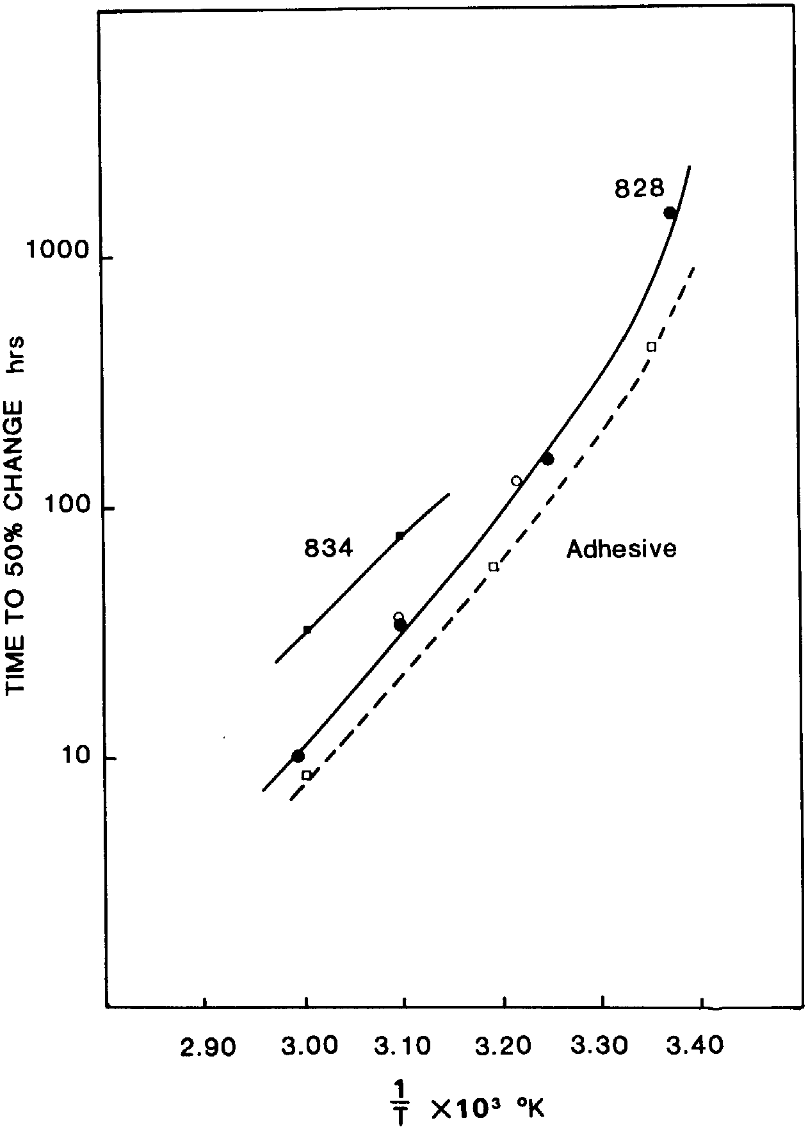


FIGURE 8 Time to 50% reaction for various resin mixes. Solid lines, dye consumption; broken line, colour change of green structural film adhesive. ● Epon 828/SY 72/TDI-DMA 100:2:2. ○ Epon 828/SY 72/TDI-DMA 100:2:5. ■ Epon 834/SY 72/TDI-DMA 100:2:2.

A Thermal History Indicator

It has been demonstrated that in epoxy formulations containing a pyrazolone dye a reaction occurs which produces a change in colour of the formulation. The extent of the reaction can be determined by direct colour measurement or by chromatographic analysis of remaining dye or product levels. The reaction has been shown to occur with a range of epoxy resins, of types commonly used in aerospace adhesives, but at a rate which depends on the particular resin. Curing agents may be the adduct of 2,4-tolylenediisocyanate and dimethylamine or the combination dicy/Monuron but not dicy alone. Candidate resin/curing agent combinations thus encompass a large proportion of the types of formulations used in structural aerospace applications.

An in-situ indicator based on a reaction such as that outlined here offers a definite advantage over any other type of indicating device included in the packaging. Since the reaction giving the colour change is an epoxy reaction, its activation energy can be expected to be similar to that of the advancement reactions for which it is serving as an indicator; this would not be the case for an indicator based on some other type of reaction. This point is of particular significance in the integration of time and temperature which comprises the thermal history of the sample.

In its simplest form a thermal history indicator based on these reactions would serve as a visible signal for unsuspected delays or losses of "dry ice" in transit between manufacturer and user. (On long journeys the container is frequently refilled with "dry ice" on route and thus its presence when the destination is reached is no guarantee the contents were frozen at all times on the journey.) This application would be facilitated by selection of a dye giving a conspicuous colour change.

To form the basis of a qualitative thermal history indicator the full cooperation of the adhesive manufacturers would be required. Firstly, the amount of dye incorporated may need to be increased, or an alternative dye used, which would react in a time commensurate with the shelf life of the adhesive, to ensure that the amount of unreacted dye remaining at the end of the recommended shelf life is sufficient to be determined with adequate accuracy. Secondly, since the formulations are proprietary mixtures and the nature of the resin influences the rate of reaction, a calibration curve for each adhesive, and possibly for each batch, would have to be provided. In its simplest form this could relate colour, determination by a standard procedure, to time at ambient temperature.

The effect of the presence of the reaction product from the dye reaction on the performance of the cured adhesive would need to be assessed. Since the amount would be small (perhaps 1%) no major effect on such properties as strength or glass transition temperature would be expected but such aspects as the long term durability and moisture uptake would need to be considered.

This approach could also form the basis of a thermal history indicator for fibre-reinforced composite prepregs, the matrices of which are of similar composition and which suffer from the same type of limited shelf life problems. In that case a dye would need to be incorporated, since none is currently used, and the assessment would need to be on solutions of the extracted matrix to separate it from the colour dominating effect of the fibre.

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