*Journal of Thermal Analysis, Vol. 41 (1994) 1495-1499*

# ALKYD-BASED-THERMOSETTING RESIN
## Calorimetric investigations of the curing process

*J. M. Saiter, N. Delahaye, M. Liziard and L. Podgorski**

LECAP, Faculté des Sciences, 76821 Mont-Saint Aignan, Cedex, France
*CTBA, 10 Avenue Saint Mandé, 75 021 Paris, France

## Abstract

In this work, the rate of cure of different oxidative drying oil modified alkyd resins are investigated by DSC measurements. We determine, from the Kissinger equation, the apparent activation energy of the curing process. We show that this activation energy depends on the curing duration and that these variations lead to the determination of a time constant, characteristic of the material.

**Keywords:** alkyd resins, DSC, Kissinger method

## Introduction

Alkyd-based resins are generally used as wood protective varnishes and stains. Figure 1 shows a typical example of the binder structure of such a resin, R' is the siccative oil. In fact a commercial alkyd resin formulation is more complicated, and siccative elements (Co, Zr ..), which are catalysts, are added, and finally the formula can be modified with some organic materials as U.V. absorber, light stabilizers .. To resume, Fig. 2 shows the complexity of the formulation of an oxidative drying oil modified alkyd resin. According to D. E. Vesper *et al.* [1], the binder cures through absorption of atmospheric oxygen by the double bonds of the unsaturated fatty acid. A radical chain reaction of the hydroperoxides formed causes the polymers to crosslink. New carboxyl and hydroxyl groups are also formed through oxidation reactions. Condensation reactions of these functional groups also contribute towards crosslinkage. For a commercial alkyd resin formulation, the liquid to solid state transformation is not only dependent on the curing temperature and duration, but depends on other parameters (water content, illumination ...). So, the real structural mechanisms which lead to the final film are certainly more complicated [2–4]. This work deals with the determination, from calorimetric investigations, of parameters depending on the curing process and on the alkyd resin formulation.

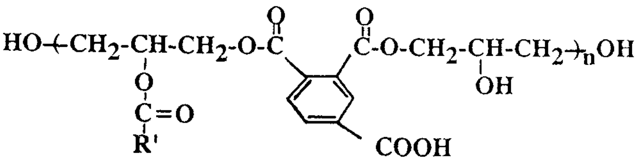
*John Wiley & Sons, Limited, Chichester*
*Akadémiai Kiadó, Budapest*

## Experimental

Oil modified alkyd resins used in this study are commercial ones. The first one called $R_1$ is modified with an organic UV absorber, the second $R_2$ is $R_1$ plus a Hindered Amine Light Stabilizer. In order to obtain a film, a controlled thickness (30 μm) of liquid is deposed on a substract, and kept at a constant temperature in air ambiance, and without illumination. Calorimetric measurements are performed on a DSC (Perkin Elmer system 7). Calibration is achieved from the determination of the temperature and the energy of fusion of indium.

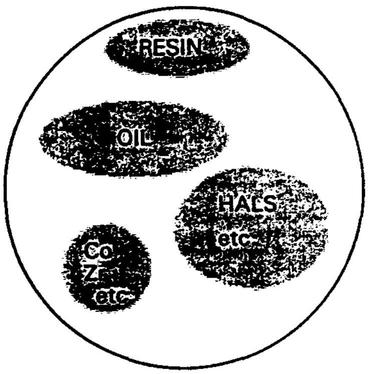
## Results and discussion

Figure 3 shows typical enthalpic curves obtained on such resin for a given curing duration ($D_c$) and curing temperature ($T_c$). At first we observe the glass transition phenomena at $T_g$ = 5°C ($T_g$ is determined from the onset temperature). For annealing time lower than ≈1000 h, $T_g$ is observed by a small change of the base line in a great temperature interval and never as an endothermic peak. This indicates that a large dispersion of molecular weight exists in such



$R' = C_5H_{11}\text{-}CH_2\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}$

**Fig. 1** Chemical structure of a typical alkyd resin



OIL MODIFIED ALKYD RESIN

**Fig. 2** Real commercial alkyd resin composition

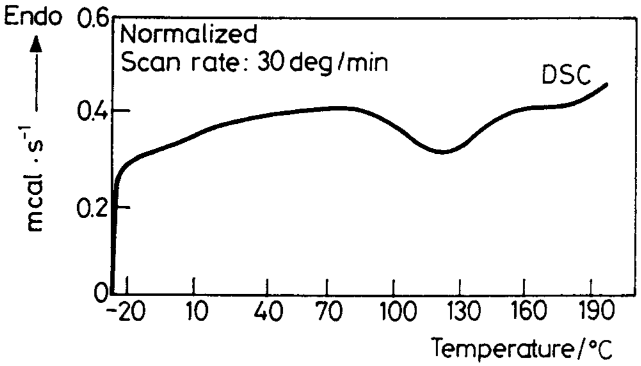


**Fig. 3** Typical enthalpic curve obtained on alkyd-based thermoset

material. For temperatures greater than 80°C, two successive exothermic reactions occur. The first one is associated with the curing reaction (characterized by $T_m$), while the second one is the beginning of the degradation (oxidation) of a part of the polymer (observed from thermogravimetry measurements) [1]. We have to notice that, for a given value of $D_c$ and $T_c$, the first exothermic peak observed during a scan corresponds to the fraction of material which has not been transformed during $D_c$.

Because of the mass loss at the end of the cure peak, the energy of reaction may not be easily determined, and because of the low signal at $T_g$, the glass transition temperatures cannot be used to follow the cure kinetics.

According to the Kissinger equation [5], Fig. 4, shows the variations of $\ln(V/T_m^2)$ *vs.* $1/T_m$ for $T_c = 40$°C and for different $D_c$ values ($V$ is the heating rate).

For each curing duration, the slope leads to the determination of an apparent activation energy ($E_a$). Then the variations of $E_a$ with $D_c$ are reported on Fig. 5.

In order to describe these variations, we propose the following relationship

$$E_a = E_{inf} + (E_o - E_{inf})e^{-t/\tau}$$

where $E_{inf}$ is the apparent activation energy when the cure is achieved, $E_o$ is the apparent activation energy at $D_c = 0$ h, and $\tau$ a characteristic time constant. By numerical interpolation, the fit of the data (full line on Fig. 5) leads to the results reported in Table 1. For both resins, if $E_o$ are identical and $E_{inf}$ are practically the same, the values obtained for $\tau$ are differents. That means that the initial and final rate of cure are practically the sames, only the cure kinetics change. So, from these results, we notice that the effects of light stabilizing agents lead to an increase of the duration of the liquid to solid transformation, in other words to a cure retardation effect. How to overcome this effect by proper reformulation of the drying catalysts was not the scope of this study.

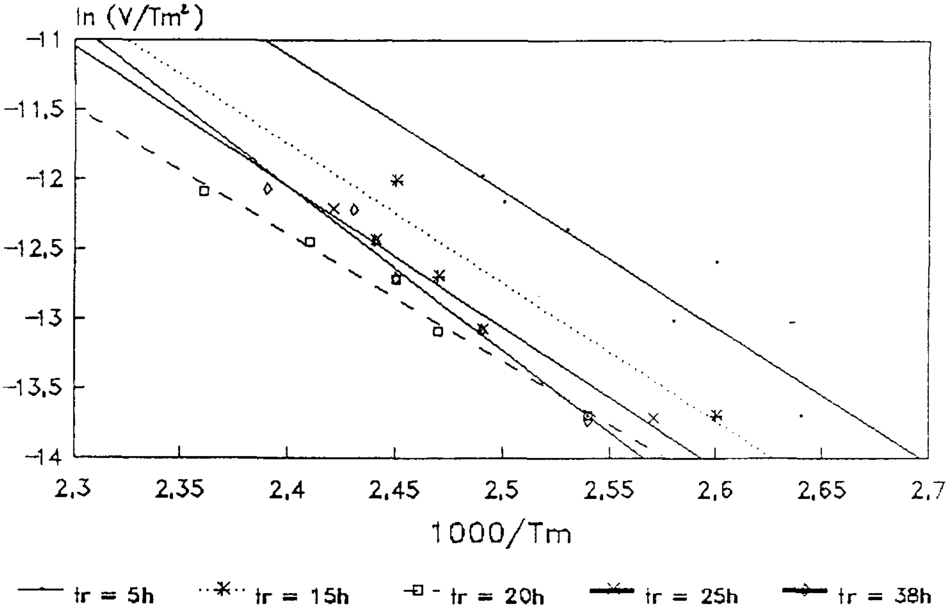


**Fig. 4** Kissinger plot of the variations of $T_m$ with the heating rate for $R_1$, and for different values of $D_c$, and for $T_c$ = 40°C

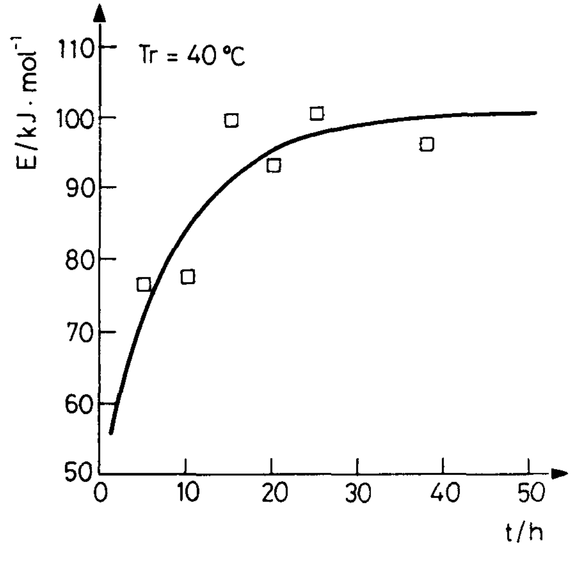


**Fig. 5** Variations of the apparent activation energy with the curing duration $D_c$, □ are the data, — is the fit

Table 1 Values of $E_o$, $E_{inf}$, and $\tau$ obtained on two different alkyd resin formulations

| | $E_{inf}$ / kJ·mol$^{-1}$ | $E_o$ / kJ·mol$^{-1}$ | $\tau$ / h |
|---|---|---|---|
| $R_1$ | 101 | 50 | 9 |
| $R_2$ | 110 | 50 | 20 |

## Conclusion

In this work, we have shown that differential scanning calorimetry can give numerical informations about the modifications of the curing kinetics of different alkyd-based thermosets. In a first approach, the use of the Kissinger plot seems to be appropriated and allows the determination of an apparent activation energy depending on the curing duration. The dependences can be described by a simple law, which leads to the knowledge of different parameters and particularly to a time constant. The value of this time constant depends on the nature of the different agents included into the resins.

## References

1 D. E. Vesper and K. Hedden, Euro. Coat. J., 1 (1990) 34.
2 G. P. A. Turner, Introduction to paint chemistry and principles of paint technology, third Edition, Chapman and Hall Ed., N. Y., 1988.
3 P. Grandou and P. Pastour, Peintures et vernis - les constituants, Herman Ed., 1987.
4 J. H. Hartshorn, J. Coatings Technology, 54 (1982) 53.
5 H. E. Kissinger, J. Res. National Bureau Stand., 57 (1956) 217.

**Zusammenfassung** — In vorliegender Arbeit wurde mittels DSC-Messungen die Aushärtung verschiedener, mit Hilfe von oxidativen trocknenden Ölen modifizierter Alkydharze untersucht. Die scheinbare Aktivierungsenergie des Aushärtungsprozesses wurde anhand der Kissinger-Gleichung ermittelt. Es wurde gezeigt, daß diese Aktivierungsenergien von der Aushärtungsdauer abhängen und daß diese Änderungen zur Bestimmung einer Zeitkonstante führen, die für die Substanz charakteristisch ist.