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A THERMOANALYTICAL STUDY OF THE CURE OF XYLOK 225 RESIN

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ABSTRACT

The cure of Xylok 225 resin with a range of concentrations of hexamethylene tetramine has been studied by DTA, DTA–TG and DSC. The process has also been followed by IR spectroscopy. Two reaction peaks were observed during the cure, an exotherm occurring near to 150°C and an endotherm near to 250°C. The exotherm appeared to be affected by the concentration of hexamethylene tetramine, at a low concentration (4.8%) its onset was delayed until near 190°C, whilst at a higher concentration (13.0%) the heat of reaction was diminished.Both the exothermic and endothermic phases of cure were accompanied by evolution of volatiles.

INTRODUCTION

The Xylok resins are a group of high performance thermosetting resins marketed by Albright and Wilson Ltd. They are the condensation products of aralkyl halides, or ethers, with phenols, and in some instances other aromatic compounds. An example of a resin of this type is the condensation product of α,α′-dimethoxy-*p*-xylene with phenol, the reaction being catalysed by a small amount of stannic chloride. The product may be cured by heating it with hexamethylenetetramine (hexamine) or with an alternative crosslinking agent.

The resin studied in this paper, Xylok 225 (Fig. 1), is used with hexamine as a curing agent as a binder in moulding powders[1]. Because of their recent origin little has been reported of the curing mechanism of Xylok resins although a chemistry very similar to that of the phenolic resins can reasonably be anticipated.

Thermal analytical techniques have been widely used to study the curing reactions of resin systems and the cure of epoxy[2, 3] and polyester[4, 5] systems have been particularly well reported.

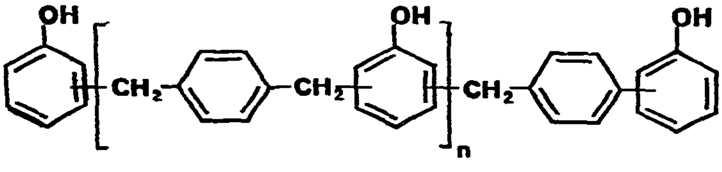

Fig. 1. Xylok 225 resin structure.

Attention has also been given to the cure of phenolic resins, Burns and Orrell[6] reported DTA studies of cure of novalacs with hexamine and Era et al.[7] used DSC to determine the heats of reaction and activation energies of a phenolic system. King et al.[8] have used pressure DSC in their studies of the cure of phenolic resins.

The chemistry of the hexamine/phenol hardening process in Xylok 225 is influenced by many factors. In this study the aim was to assign the observed thermal transitions to the physical and chemical reactions taking place during the curing process, using thermal analytical techniques in conjunction with IR spectroscopy.

EXPERIMENTAL

Reagents

Xylok 225 resin was supplied by Albright and Wilson Ltd. Hexamethylenetetramine was supplied by BDH Ltd. Both reagents were dried in vacuo at 100°C over P_2O_5 before sample preparation. Indium, melting point $T_m = 156°C$ was supplied by the U.S. National Bureau of Standards.

Sample batch production for DTA studies

Resin and hexamine were each ground to pass through a 300 mesh. Two samples of resin/hexamine mixtures (4:1 by weight) were prepared and one of these, together with a sample of resin, and one of hexamine, were stored over phosphorus pentoxide in vacuo.

Sample batch production for DSC studies

Resin/hexamine mixtures of 5, 10 and 15 parts of hexamine per hundred parts of resin were prepared by grinding in a Perkin-Elmer vibrating mill. The samples were stored over phosphorus pentoxide in vacuo.

Differential thermal analysis

A Stanton–Redcroft LDTA model 671 was used for DTA studies and 23 mg samples were used in sealed aluminium pans. Vacuum dried alumina was used as a reference material. A heating rate of 10°C min^{-1} was used for the DTA studies.

Differential scanning calorimetry

A Perkin-Elmer DSC-1B was used for the DSC studies. The calibration of the instrument was performed by measuring the T_m and latent heat of fusion of indium. Sample weights of the resin/hexamine mixture were in the range 10.00–19.00 mg, and each sample was weighed into an aluminium pan and closed hermetically with a lid. Thermograms were recorded at a range setting of 8 $mcal^{-1}$ (33.5 mJ sec^{-1}) and a heating rate of 4°C min^{-1}. Areas under the power vs. time curves were measured using a PCD Digital Data Reader XAE 6. The results of four samples at each concentration of hexamine were averaged.

Combined differential thermal analysis and thermogravimetric analysis

A Stanton–Redcroft TR-02 thermobalance was used for this analysis. A 60 mg sample was heated at 10 °C min^{-1} in air.

IR spectroscopy

2–5 mg of sample were ground with 200 mg of anhydrous potassium bromide and a disc prepared from the mixture. The absorption spectra were recorded on either a Unicam SP 200 or a Perkin-Elmer 577 spectrophotometer.

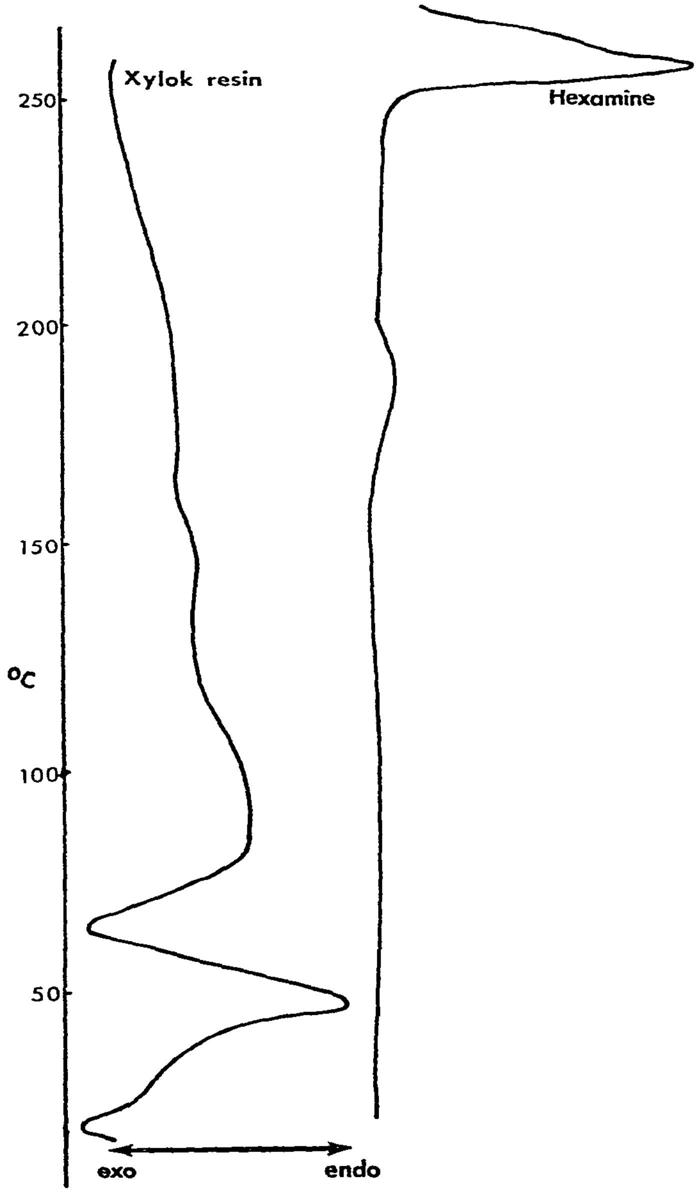

Fig. 2. DTA thermograms of Xylok 225 and hexamine.

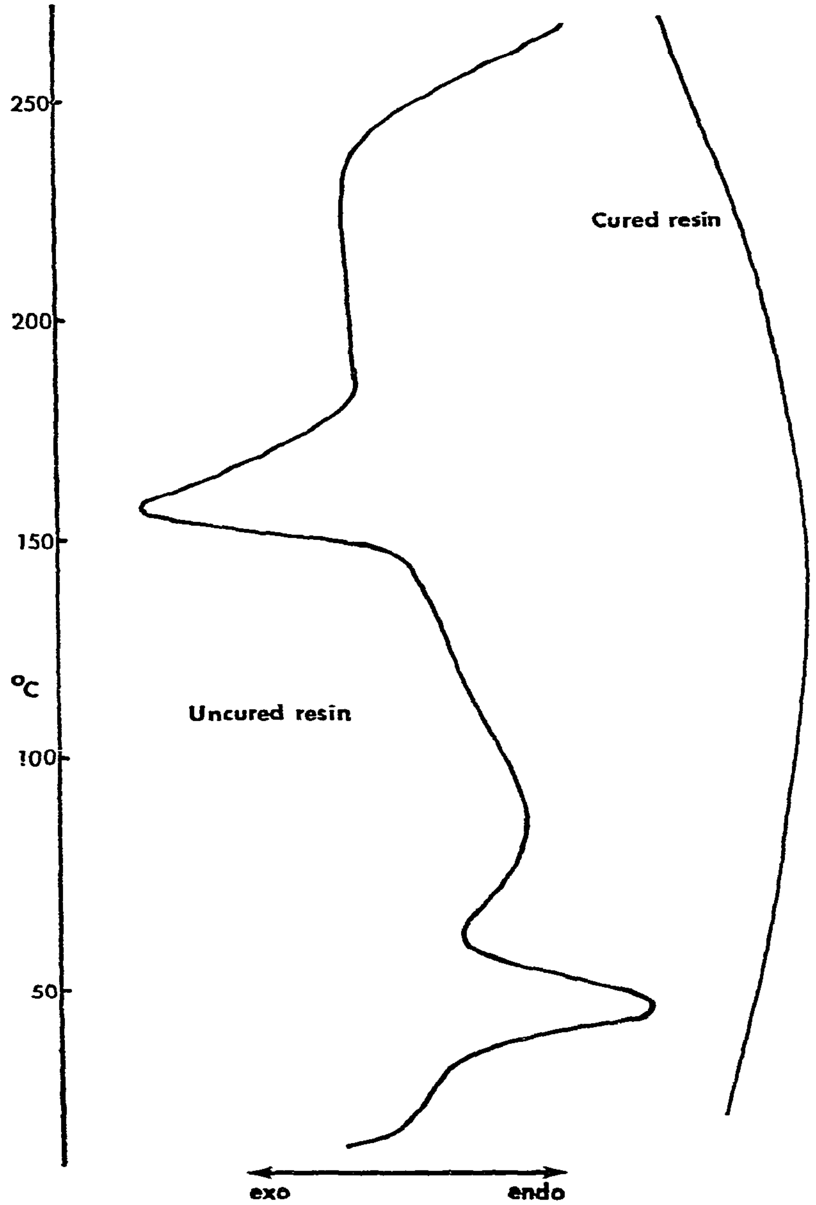

Fig. 3. DTA thermograms of Xylok 225 resin/hexamine 4:1 mixture, uncured and cured.

RESULTS AND DISCUSSION

The DTA thermograms of Xylok 225 resin, hexamine, a Xylok 225 resin/hexamine (4:1) mixture and of the cured mixture were obtained and are shown in Figs. 2 and 3. Comparison of the DTA traces enabled the major thermal features of these systems to be identified and they are summarised in Table 1. Noteworthy is the strong exotherm, occurring between 150 and 160 °C, observed only in the DTA of the Xylok 225 resin/hexamine mixture, which is attributable to the primary curing reaction. A second curing stage begins around 220–260 °C and in this region the

TABLE 1

THE THERMAL FEATURES OBSERVED FOR XYLOK 225 RESIN AND HEXAMINE

(See Figs. 3 and 4.)

Thermogram feature			*Material*				*Comments*
Endotherm	*Exotherm*	*Temperature (°C) (uncorr.)*	*Xylok 225*	*Hexamine*	*Xylok 225 + hexamine (4:1)*	*Xylok 225 + hexamine (4:1) after cure*	
Strong		50 peak	Present	Absent	Present	Absent	May be due to free phenol melting
Strong		100 broad peak	Present	Absent	Present	Absent	Resin melting point observed on hot stage microscope = 110°C
V. weak		150 peak	Present	Absent	Not observed	Absent	
—	V. strong	157 peak	Absent	Absent	Present	Absent	Curing reaction
Strong		220–250 start	Absent	Absent	Present		Secondary curing step and melting endotherm of unreacted hexamine
Strong		280 peak	Absent	Present	Absent		Hexamine melting point. Lit. value 285°C

DTA trace shows a marked endotherm. Simultaneous DTA–TG (Fig. 4) showed that the exotherm (150–160°C) and the endotherm (220–260°C) were both accompanied by weight loss in the latter case of over 10% of sample weight.

Following the study of the cure using DTA the primary step was re-examined by DSC. The exotherm in the region 150–160°C was selected as suitable for study in sealed aluminium cruicibles, for TG indicated that this phase of the reaction was accompanied by a small weight loss. Study of the secondary phase, which occurs above 220°C, was deferred subject to the availability of a pressure DSC. For the DSC studies three concentrations of hexamine were used, 4.8%, 9.1% and 13.0%

(equivalent to 5, 10 and 15 parts of hardner for hundred parts of resin). Typical DSC thermograms are shown in Fig. 5, a comparison of which reveals two interesting features of the curing process. Firstly, the curing exotherm of the 4.8% formulation occurs at about 190°C, 40°C above the exotherms observed for the formulations with higher concentrations of hexamine, and secondly the peak height of the 13.0% formulation is much reduced, the sample weights being approximately equal.

These points of difference were confirmed when the peak temperatures and peak areas from the DSC thermograms of a number of runs at each concentration were averaged (see Table 2). Using the latent heat of fusion of indium to calibrate the DSC instrument the heats of reaction for the primary phase of the exotherm at the three concentrations of hexamine were estimated and are collected in Table 2. It appears that the heat of reaction is dependent upon the hexamine concentration and that the addition of 13.0% suppresses the reaction in some way, whilst a lower concentration (4.8%) delays the reaction, in all cases however the reaction remains very exothermic.

To gain a further insight into the chemical processes revealed by the thermal phenomena, the changes in the IR absorption spectrum of the system was studied by heating samples of the Xylok 225 resin/hexamine (4:1) mixture to different stages of the cure throughout the range 35 to 292°C as shown in Fig. 6, and retrieving the product for examination. Table 3 summarises the major features of the IR spectra obtained. The two endotherms at low temperatures (35 and 110°C) observed in

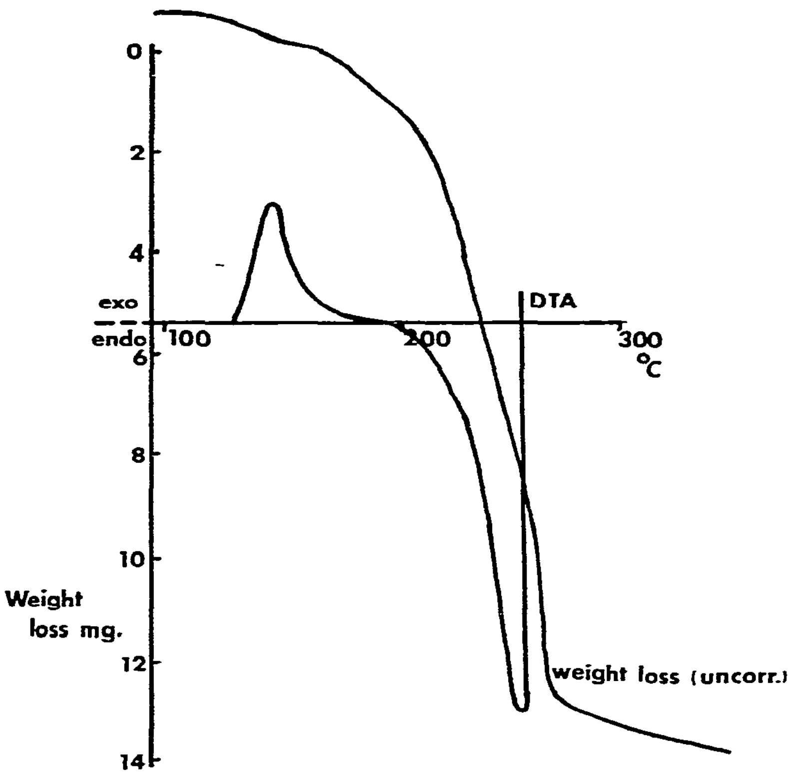

Fig. 4. Simultaneous TGA and DTA thermograms of Xylok 225 resin/hexamine (4:1) mixture.

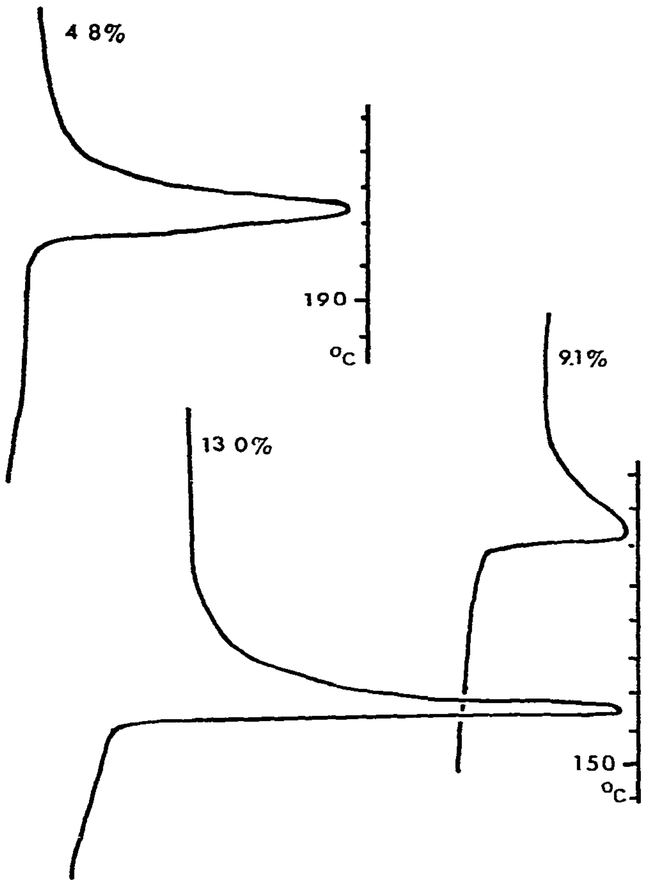

Fig. 5. DSC thermograms of the endothermic phase of the cure of Xylok 225 resin with hexamine (%).

TABLE 2

AVERAGE PEAK TEMPERATURES AND AVERAGE HEATS OF REACTION OF XYLOK 225 RESIN/HEXAMINE MIXTURES, DERIVED FROM DSC THERMOGRAMS

Hexamine in mixture (wt %)	*Peak temperature of cure (°C)*	*Heat of reaction (of mixture) (−Jg^{-1})*	*Heat of reaction (of resin) (−kJ mole^{-1})*	*Heat of reaction (of hexamine) (−kJ mole^{-1})*
4.8	190.2	116 ± 10	73.2	326
9.1	151.8	116 ± 10	76.4	162
13.0	154.5	39 ± 6	26.6	41.6
20.0	157[a]			

[a] Uncorrected from DTA thermogram.

both Xylok 225 resin and 4:1 resin/hexamine mixture are evidently physical changes, for no change in the IR spectra of the samples from that of the starting materials was observed. The melting point of Xylok 225 resin was found to be 100°C and so this explains the higher temperature endotherm. Samples of the mixture which

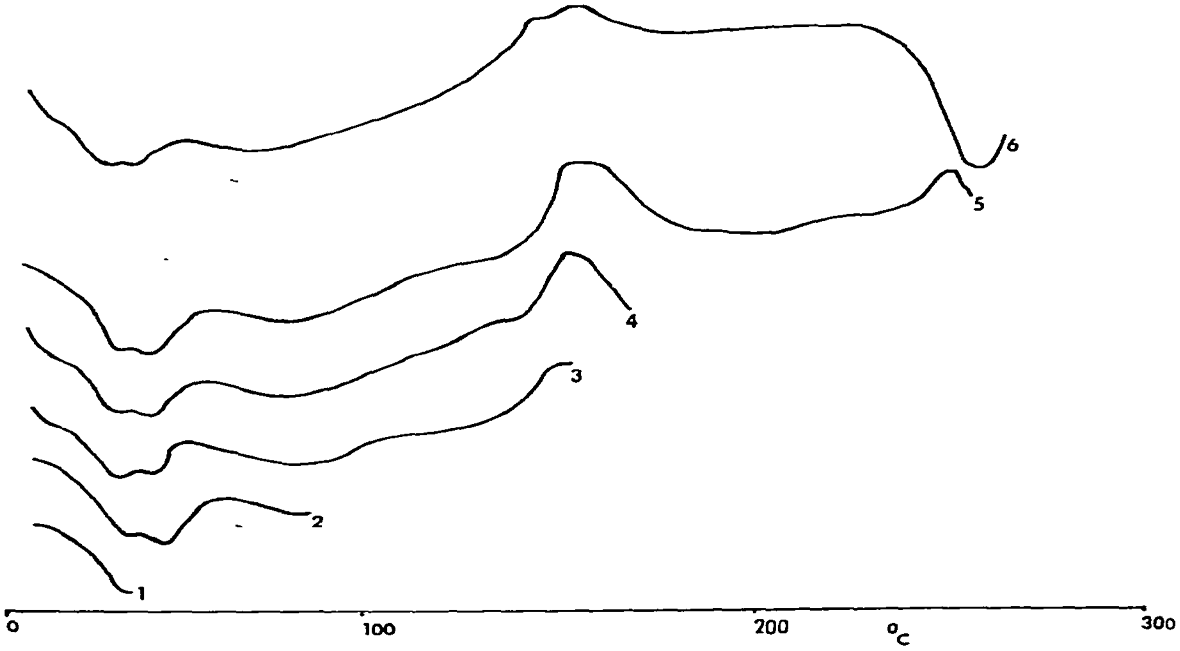

Fig. 6. DTA thermograms of Xylok 225 resin/hexamine (4:1) mixtures used for IR spectroscopy (see Table 3).

had passed through the exotherm in the region 150–160°C had IR spectra giving progressive band broadening and weakening as the samples were heated to higher temperatures, a clear indication of crosslinking. Some sharp absorption bands attributable to carbon–nitrogen bonds were retained in the sample heated to the highest temperature (292°C), and were probably indicative of an excess of the crosslinking agent.

The DSC samples were also retrieved after thermal analysis and their IR absorption spectra determined. Again the major absorption bands were broader and weaker than those observed in the starting mixtures but sharp bands attributable to crosslinking bonds were retained in the 13% formulation and to a lesser extent in the 9.8% formulation (Table 4).

The information derived from this study relating to the precise nature of the chemical changes occurring in the resin during the course of the hexamine cure is relatively meagre but is not inconsistent with the following interpretation based upon the well established stages of the cure of phenolic resin with hexamine[9]. The strong exotherm near to 150°C arises from the reaction of the phenolic rings in the Xylok resin with hexamine, leading to the formation of dimethylamino bridges (Fig. 7). These may condense to methylazomethine bridges at an elevated temperature with the loss of volatiles and this reaction probably accounts for the strong endotherm observed above 220°C.

Harris[1] has reported that the reaction of free *ortho* and *para* positions of phenolic rings in the Xylok prepolymer with hexamine is rapid, and Zinke[10] has confirmed the presence of methylazomethine groups in hexamine-cured phenolic

TABLE 5

CHANGES IN THE IR SPECTRUM OF XYLOK 225 RESIN/HEXAMINE (4:1) MIXTURE DURING THE COURSE OF DTA (SEE FIG. 6)

Sample No. (T °C)	*Assignment of major absorption bands (frequency cm^{-1})*										
	Phenolic hydroxyl (3500)	*Methylene stretching (2900)*	*Aromatic C=C in plane deformation 1600*	*Methylene deformation (1460)*	*(1440)*	*C–N stretching (1380)*	*(1240)*	*C–O stretching (1340)*	*(1200)*	*C–N deformation (1000)*	*Comments*
1 (35)	Broad and sharp	Sharp and strong	Sharp	Sharp	Sharp	V. sharp	V. sharp	Sharp	Broad and strong	Sharp and strong	Identical IR, spectrum to the origin mixture
2 (100)	Broad and sharp	Sharp and strong	Sharp	Sharp	Sharp	V. sharp	V. sharp	Sharp	Broad and strong	Sharp and strong	Identical IR, spectrum to the origin mixture
3 (157)	Broadening	Strong	Broadening	Sharp	Sharp	Sharp	Sharp	Absent	Weak shoulder	Sharp and strong	Xylok bands broadening
4 (170)	Broadening and weakening	Strong	Broadening and weakening	Sharp	Sharp	Sharp	Sharp	Weak shoulder	Weak shoulder	Sharp and strong	Absorption attributable to benzene rings is reduced indicating cross linking
5 (250)	Broad and weak	Broad and weak	V. broad	Broad	Shoulder	Sharp	Sharp	Absent	Weak shoulder	Sharp and strong	Spectrum lacks definition and is typical of cross linked resin. Some C–N bands sharply defined
6 (292)	Broad and weak	Broad and weak	V. broad	Very weak	Absent	Absent	Sharp	Absent	Absent	Sharp	

TABLE 4

SIGNIFICANT FEATURES OF THE IR ABSORPTION SPECTRA OF XYLOK 225 RESIN SYSTEM

Frequency (cm^{-1})	*Assignment*	*Xylok 225*	*Hexamine*	*Xylok 225 after heating to 160°C*			
				+ 4.8% hexamine	*+ 9.1% hexamine*	*+ 13% hexamine*	*+ 20% hexamine*
3500	Phenolic hydroxyl	Broad and sharp	Absent	V. broad	V. broad	V. broad	Weak and broad
2900	Methylene stretching	Weak	Sharp and strong	Weak and broad	Weak and broad	Weak and broad	Weak and broad
1600	Aromatic C=C in-plane deformation	Sharp	Absent	Broad	Broad	Broad	Broad
1460	Methylene deformation	Sharp	Sharp	Broad	Broad	Broad	Broad
1440	Methylene deformation	Sharp	Sharp				
1380	C–N stretching	Absent	V. sharp	Absent	Sharp	V. sharp	Weak
1340	C–O stretching	Sharp	Absent	Absent	Absent	Absent	Absent
1240	C–N stretching	Absent	V. sharp	Absent	Absent	V. sharp	Sharp
1200	C–O stretching	Broad and strong	Absent	V. broad	Broad	Absent	Absent
1000	C–N deformation	Absent	Sharp and strong	Absent	Absent	Sharp	Sharp

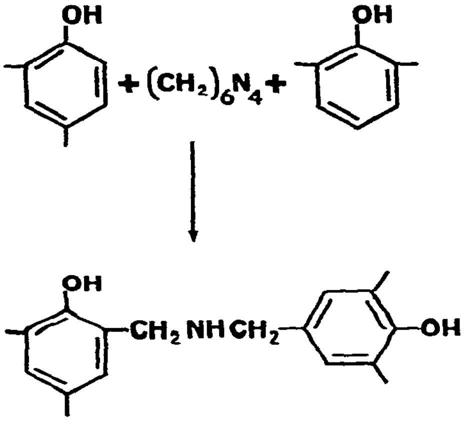

Fig. 7. Formation of dihydroxydibenzylamine grouping in phenolic resin.

resins. After 1000 h at 250°C Harris[11] observed a decline of 35% in the nitrogen content of hexamine cured Xylok 225 resin, which was probably due to the breakdown of azomethine groups to methylene groups. Such a process could account for the weight losses observed during TG above 220°C.

The IR absorption bands at 1380 and 1240 (C–N stretching) and 1000 (C–N deformation) observed in the spectra of Xylok resin cured with 9.8% or more of hexamine (Table 4) may be attributable to dimethylamino groups formed in the first stage of the cure.

CONCLUSION

The reaction of Xylok 225 resin with hexamine has been studied using DTA, DSC and IR spectroscopy. The cure was found to involve two distinct phases, a strong exotherm at near to 150°C followed by a strong endotherm above 220°C. The hexamine concentration dependance of the exotherm was identified.

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