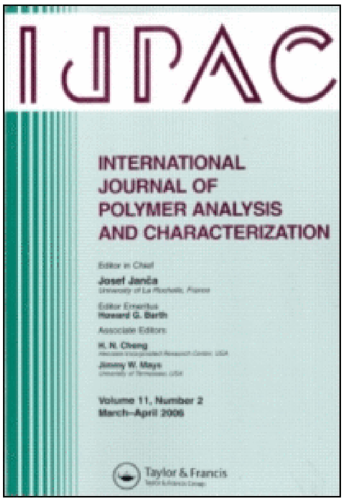

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Thermal Decomposition of Phenol-Formaldehyde Foundry Resins

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The thermal behavior of a phenol-formaldehyde foundry resin has been investigated under different experimental conditions by thermogravimetry, differential scanning calorimetry, and thermal volatilization analysis. Substances formed during curing treatments and thermal degradation were characterized by spectroscopy and chromatographic techniques. Curing conditions favor the production of a limited amount of low-molecular-weight compounds, which easily volatize. In the thermal decomposition of the cross-linked resin, the principal volatile products do not depend on the degradation atmosphere. Their relative amounts, however, depend on atmospheric conditions and extent of cross-linking of the resin.

KEY WORDS Phenol-formaldehyde resins, thermal characterization, thermal degradations

INTRODUCTION

In the foundry industry several procedures for casting metal parts are employed. With the sand casting method both inorganic and organic binders are added to fireproof sand for mold and core production. In the so-called "lost molds," binders undergo dramatic degradation during casting and the molds cannot be reused. The wide use of phenolic resins as binder for lost molds is due to their favorable properties for mass-production of high-quality castings [1].

Common fabrication processes, shell-molding, [2, 3] and hot-box, [4] require the treatment of the resin-coated sand or sand/resin/catalyst mixture at temperatures between 220° and 280°C for short times in order to obtain cured resin of the desired shape. During such treatment, in addition to the resin cross-linking, volatile compounds evolve from the molds, either produced during curing or

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already present in the starting phenolic resin. In subsequent casting operations, molten metal is poured into the mold cavity and high temperatures induce pyrolysis of the resin, with formation of decomposition products. A common feature of these processes is the diffusion of low-molecular-weight compounds into the environment.

In this paper results of an investigation on the thermal decomposition behavior of phenol-formaldehyde foundry resins under different experimental conditions are reported. Particularly, to understand the safety problems met in foundry operations, the substances evolved during curing and thermal oxidative degradation have been analyzed.

EXPERIMENTAL

Materials

A commercial phenol-formaldehyde novolak type resin Rutaphen gc 75 (Bakelite) was used. The resin was cured with hexamethylenetetramine (HMTA).

Thermal Characterization

Thermal characterization was carried out under nitrogen and in air flow (60 mL/min) with a DuPont system consisting of a Model 951 thermobalance, DSC module, and Model 2100 control unit. The experiments under vacuum were run in an all-glass system equipped with Pirani pressure gauges for monitoring the gaseous products formed during the thermal treatments of samples (thermal volatilization analysis). All experiments were performed with 10°C/min heating rate.

Volatile products of degradation were injected into a Hewlett-Packard 5890A GC connected with a Hewlett-Packard 5970 series mass selective detector. Column characteristics were the following: 12 m × 0.2 mm × 0.33 μm film thickness of cross-linked methyl silicone gum. Quantitative analysis were carried out on a Carlo Erba Fractovap 4160 GC with a capillary column Chrompack SE 52 (25 m × 0.5 mm × 0.45 μm film thickness of fused silica) using α-methylstyrene as the internal standard.

The effects of thermal treatment on the chemical structure of the resin and analysis of high-molecular-weight products of degradation were performed by FTIR spectroscopy on a Perkin-Elmer 1710 instrument.

RESULTS AND DISCUSSION

Thermal Behavior of the Resin

Thermogravimetry (TG) and corresponding derivative curve (DTG) under nitrogen flow of novolak show that volatilization occurs in several stages (Figure 1). The corresponding weight losses are reported in Table I. The first weight loss step, beginning at temperatures below 200°C, is due to volatilization of residual phenol

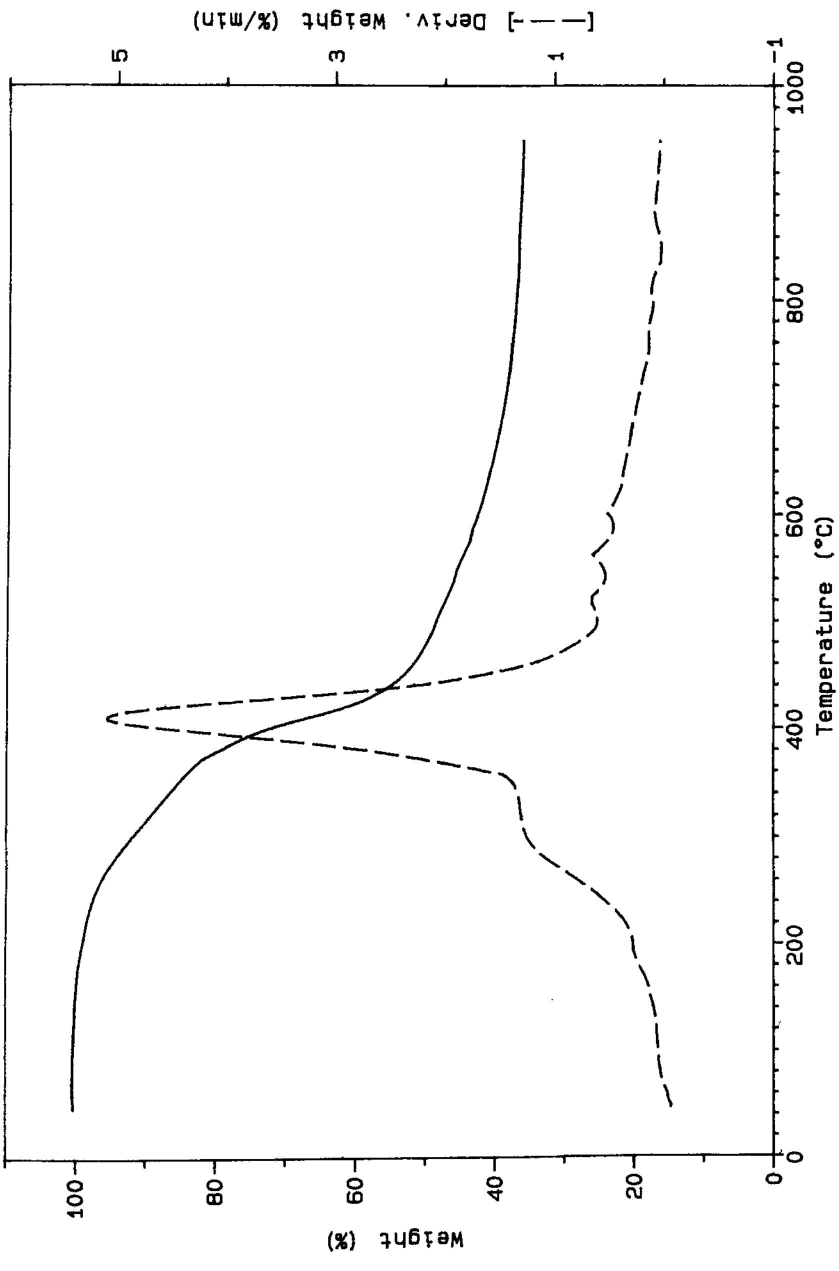

FIGURE 1 TG (———) and DTG (---) curves of novolak under nitrogen flow.

TABLE I

Relative extents of decomposition stages in nitrogen of novolak

Stage (°C)	Pure (w%)	Cured (w%)
100–230	1.8	< 1
230–350	13	1.7
350–470	38	9
470–1000	12	23

and oligomers always present in novolak-type resins [5]. The real thermal decomposition of the resin occurs in three stages, partially superimposed, and proceeds leaving a 36% charred residue at 1000°C. The temperatures of maximum weight loss, T_{max}, are 320°, 410°, and approximately 550°C, respectively. The DSC trace shows only a weak endothermic signal in correspondence of the principal process of degradation, in the range of 350–430°C, because of the competition between decomposition and cross-linking reactions.

Thermogravimetry in air flow (Figure 2) shows that the resin is fully volatilized at 630°C. Between 300 and 350°C a small (0.5%) weight increase has been attributed to absorption of oxygen from polymeric structure with formation of hydroperoxides on methylene bridges [6]. The two subsequent decomposition stages take place with peak temperatures, T_{max}, respectively at approximately 420° and 600°C. The DSC curve shows a series of exothermic peaks, the stronger being associated with the decomposition process occurring at $T > 500°C$.

The weight loss of novolak resin at $T < 300°C$ is the same independently of the fact that heating is performed in nitrogen or in air and results from the evolution of low-molecular-weight compounds present in the resin. In nitrogen, the decomposition of the polymer produces, together with the partial volatilization of the sample, cross-linking reactions which finally lead to a charred structure, stable even at 1000°C, whereas in oxygen the degradation rapidly evolves to complete sample fragmentation into volatile products.

Curing

In Figure 3 a DSC curve recorded under nitrogen pressure of the mixture novolak/HMTA of typical foundry industry composition (88/12 wt) is shown. The exothermic peak with maximum at 137°C is due to the curing reaction, which transforms the resin into a cross-linked structure.

Isothermal curings have been performed at temperatures that makes it possible to follow and measure the heat evolved during the reaction by DSC, in order to obtain conversion and rate curves. The degree of conversion is $\alpha_t = \Delta H_t / \Delta H_R$, where ΔH_R is the exothermic heat evolved during curing process per mole or reacting groups and ΔH_t the heat generated up to time t. Because ΔH_t is difficult to measure directly, the following procedure has been employed. The novolak/HMTA mixture has been cured isothermally for various times; then the samples were scanned in the calorimeter at constant heating rate and the residual heat of cross-linking, $\Delta H_{t,\mathrm{res}}$, measured. The degree of conversion is calculated

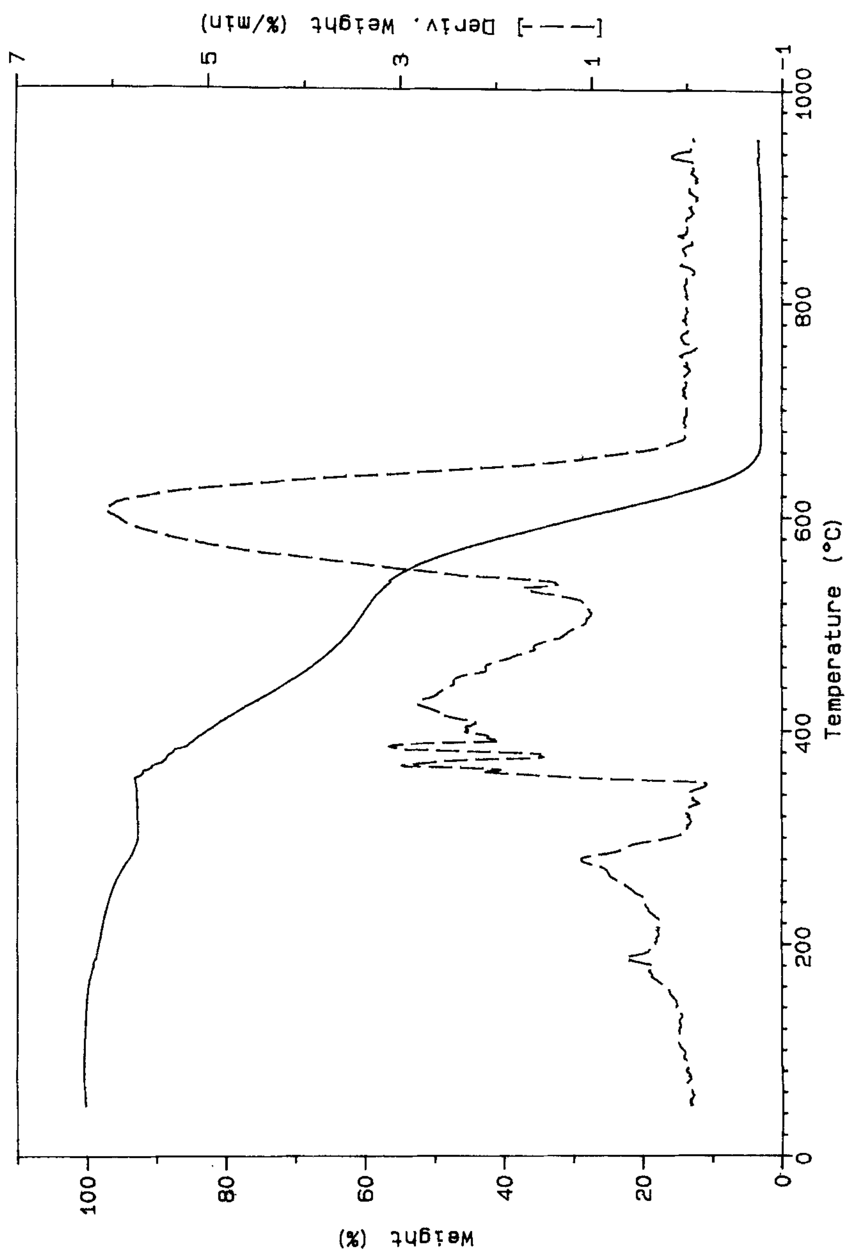

FIGURE 2 TG (———) and DTG (----) curves of novolak under air flow.

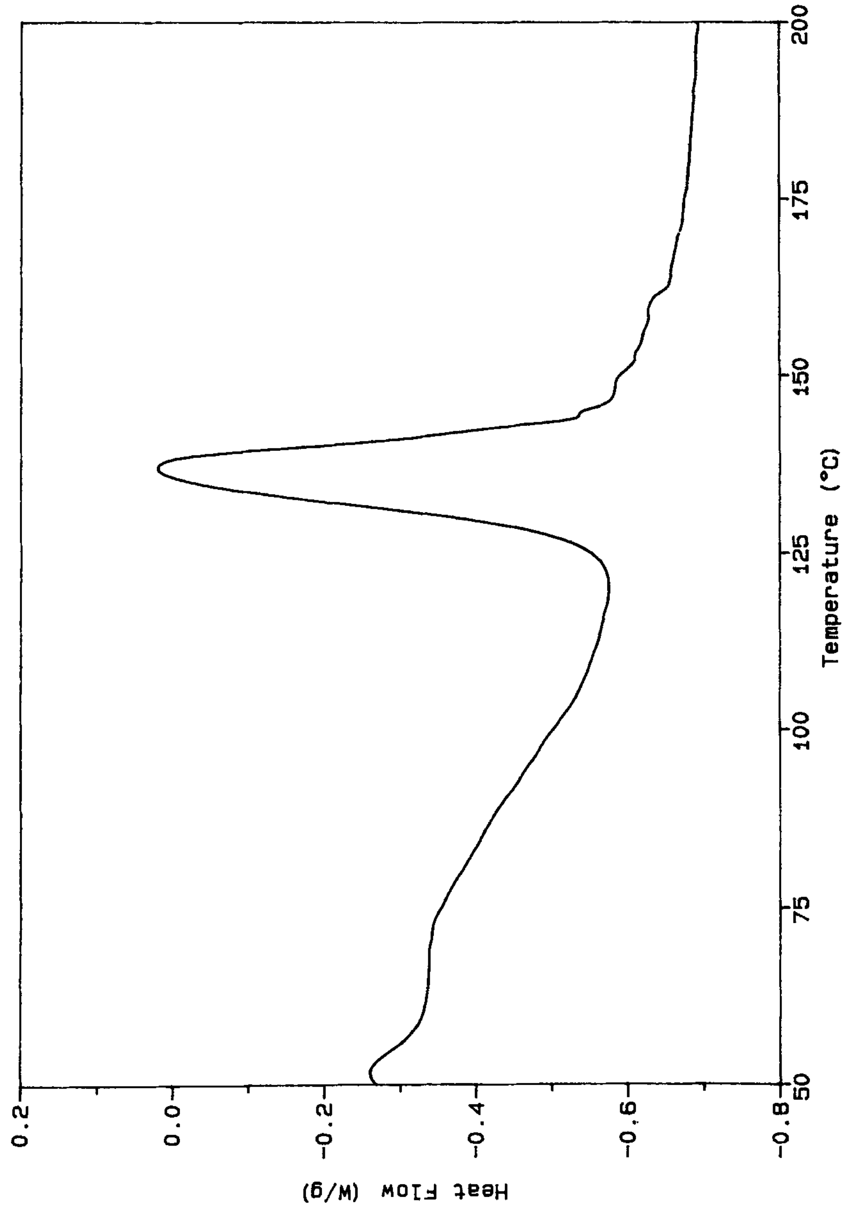

FIGURE 3 DSC curve under nitrogen pressure of the mixture novolak/hexamethylenetetramine (88/12 wt).

from the relationship:

$$\alpha_t = (\Delta H_R - \Delta H_{t,\mathrm{res}})/\Delta H_R = \Delta H_t/\Delta H_R$$

The experimental measurements were performed in a pressure DSC cell to shift out of the phenolic cure region the endothermic peak due to vaporization of products formed in the reaction (water, formaldehyde and ammonia). Figure 4 shows conversion and rate curves of isothermal curing at 110° and 130°C. At the lower temperature, the degree of conversion is less than 10% in 2 min and curing is not complete after 20 min. At 130°C total conversion is reached in about 5 min with very high rates from the beginning of the reaction. From the results we can conclude that in mold forming, where T > 200°C are easily reached, complete resin cross-linking should occur. Several novolak/HMTA mixtures with 88/12 composition have been treated at constant temperatures, in the range between 220° and 280°C, for different times, either in air or in a vacuum system. FTIR spectroscopy has confirmed for all the samples the same structural changes which

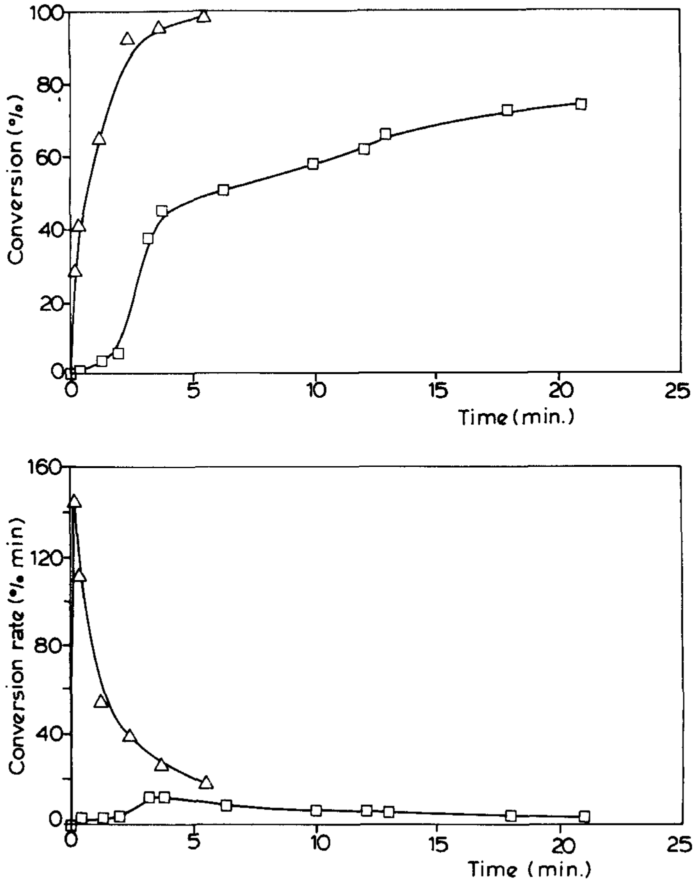

FIGURE 4 Conversion and rate curves of isothermal curing of the mixture novolak/hexamethylenetetramine (88/12 wt) at 110° (□) and 130°C (△).

are related to complete curing. The polymer network is composed of phenolic nuclei, mainly joined by methylene groups [7].

To obtain more information on curing safety problems, a mixture of novolak/HMTA 88/12 was heated at 250°C in a vacuum system for the collection of compounds evolved during the treatment. The products volatile under vacuum were analysed by GC/MS and they were found to be: ammonia and formaldehyde (from HMTA decomposition), methylamine and water (from condensation reaction), phenol, 2-hydroxy-1,3,5-trimethyl-benzene and o-(N-methylformimidoyl)phenol (present in the resin or formed in the reaction with decomposition products of HMTA). The higher molecular weight compounds, condensed on the glass walls as soon as they evaporated from the curing cell, were analyzed by FTIR spectroscopy, and showed the same structure of the novolak resin. This fraction is known to be constituted by the lower oligomers present in the novolak [5].

Thermal Degradation of Cross-linked Novolak

Thermal characterization of cross-linked novolak was performed using a resin cured with 12 wt% of HMTA, at 250°C in air for 2 min. The TG and DTG curves in nitrogen flow of the cured resin show two main decomposition stages with T_{max} at 420° and 555°C, respectively (Figure 5). The weight loss pattern is equivalent to that of the pure novolak, but the extent volatilization is lower (Table I). The small weight loss step with maximum rate at approximately 150°C is not associated with volatilization of residual phenol or oligomers, but is caused by the evolution of compounds produced during cross-linking from decomposition of HMTA or from condensation reactions. At temperatures between 230° and 380°C, volatilization of higher-molecular-weight oligomers also takes place. At higher temperatures the decomposition process is known to occur through free-radical reactions [8]. The two stages shown in the high temperature range can be related, respectively, to random homolytic scission followed by fragmentation reactions and development of further cross-linking, [9] and to subsequent partial decomposition of structures previously formed, leading to formation of a charred aromatic residue [10]. It may also be seen from Figure 5 that a 64% residue is left at 1000°C instead of 36% for pure novolak, thus showing the effect of cross-linking treatment on the thermal stability of the resin.

The nature of degradation products of cross-linked novolak was investigated by thermal volatilization analysis performed under high vacuum at 10°C/min heating rate up to 460°C. The rate curve of evolution of volatile compounds formed during sample decomposition is similar to the DTG tracing in nitrogen, with maximum rates at about 150°, 275°, and 400°C. The higher temperature stage is also characterized from the evolution of products noncondensable in liquid nitrogen, as hydrogen, methane, or carbon monoxide. The high-molecular-weight compounds formed during the decomposition also in this case were identified by FTIR as oligomers and chain fragments.

Thermogravimetry in air shows that, at temperatures below 350°C, the resin undergoes the same weight changes as in inert atmosphere (Figure 6). Complete decomposition to volatile products were reached at 700°C with a multistep process, where maximum volatilization rates were found at 420°, 557°, and 633°C. The

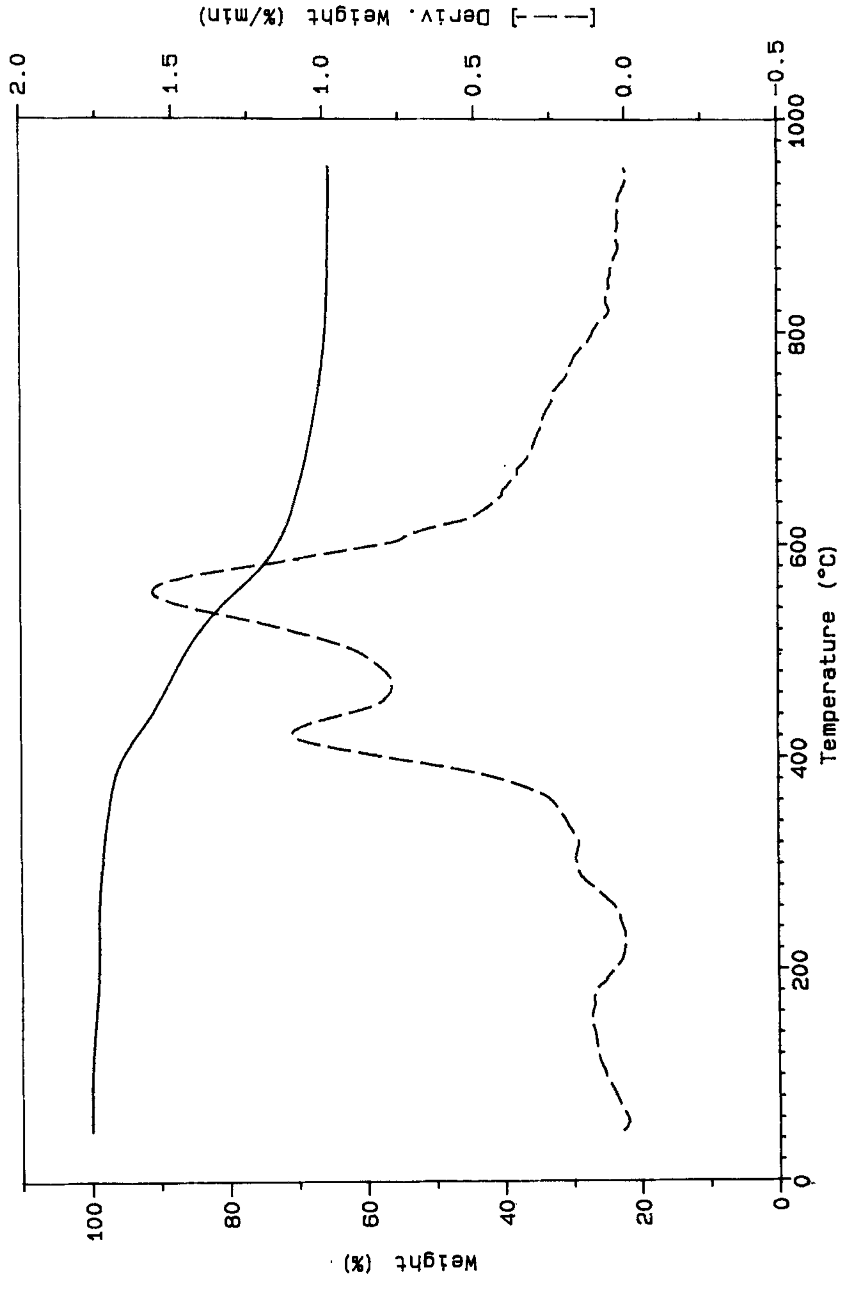

FIGURE 5 TG (——) and DTG (----) curves of cured novolak under nitrogen flow.

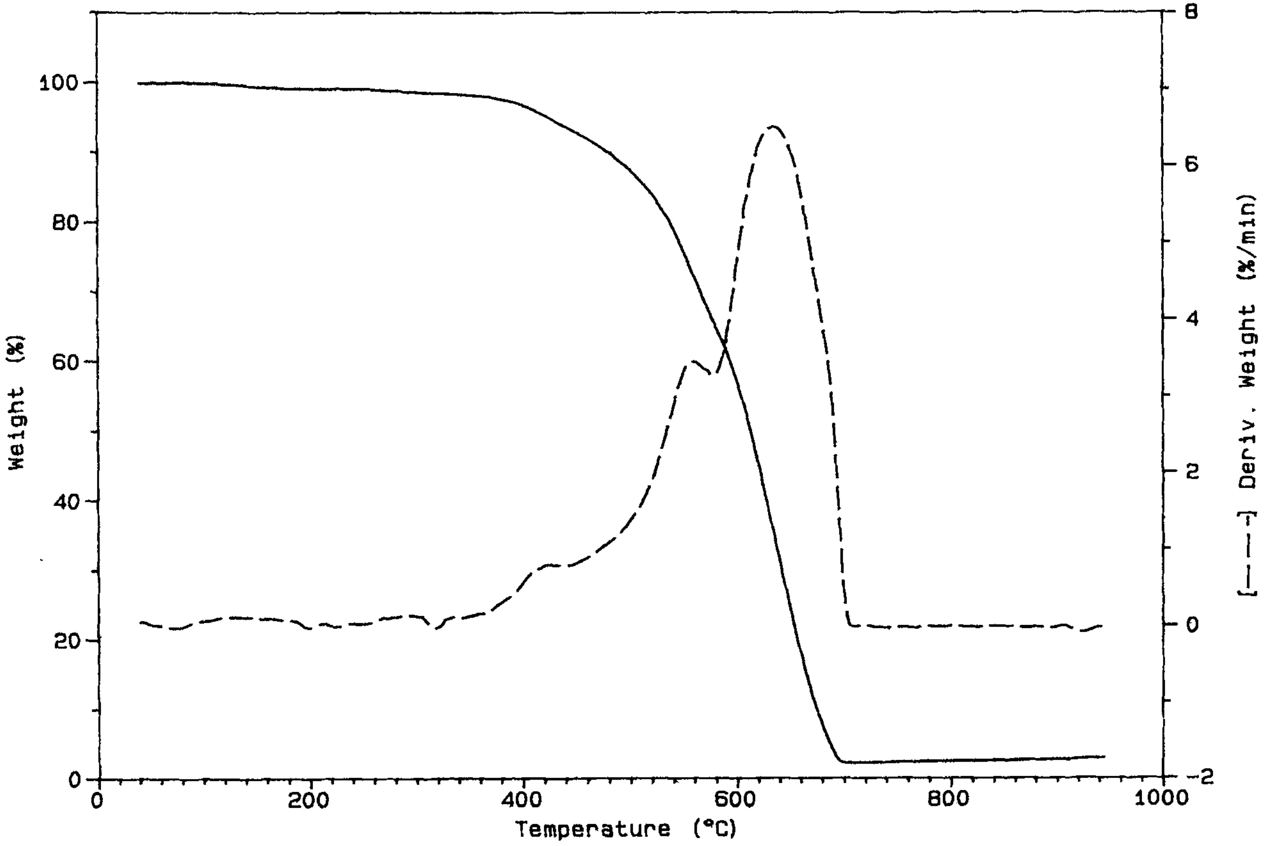

FIGURE 6 TG (———) and DTG (----) curves of cured novolak under air flow.

TABLE II

Quantitative analysis of products evolved in the thermogravimetries (TGs) of the cross-linked novolak

Product	Nitrogen (%)	Air (%)
benzene	0.4	13
toluene	5	< 0.5
m-xylene	0.7	—
phenol	1	3
o-cresol	0.3	0.8
p-cresol	10	0.5
other*	19	83
residue	64	—

*other: water, carbon monoxide, carbon dioxide, formaldehyde, xylenols, etc.

overall weight loss curve of the sample is shifted to higher temperatures in comparison with the novolak resin prior to curing.

The volatile products obtained in the TGs of the cross-linked novolak, both in nitrogen and in air, have been collected and analyzed by GC/MS. The principal ones were found to be: carbon dioxide, formaldehyde, benzene, toluene, m-xylene, phenol, o-cresol, p-cresol, and xylenols. Water, methane, and carbon monoxide are also present. These degradation products have been quantified by GC with an internal standard method and the results are reported in Table II. Toluene and p-cresol are the main volatiles formed during polymer decomposition in nitrogen, whereas in air, benzene is the most abundant.

CONCLUSION

The nature of volatile products obtained in thermal decomposition of novolak resin is substantially the same whether or not degradation occurs in air or in an inert atmosphere. Their relative amounts depends both on the extent of cross-linking and on atmospheric conditions.

In foundry processes, the evolution of products coming from the decomposition of phenol-formaldehyde resins takes place during curing and casting operations, at very different temperatures. Curing treatments favor the production of limited amounts of low-molecular-weight compounds which should easily volatilize during the treatment. However, heat and mass transfer conditions are not constant across thick samples, so that condensation and trapping of volatile products may occur. For the same reasons, the curing process in mold formation very often does not go to completion. Thermal analysis of formed foundry mold samples has shown, in fact, that unreacted HMTA is still present in thick fragments. The high temperatures reached during casting however, induce complete oxidative volatilization of the resin only on the outer mold surfaces, which are exposed to atmospheric oxygen. In the interior of molds, the resin will undergo pyrolitic decomposition, with formation of char as the main product and therefore lower amounts of volatiles.

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