THE THERMAL DECOMPOSITION PRODUCTS OF PHENOL-FORMALDEHYDE LAMINATES
PART 1. THE PRODUCTION OF PHENOL AND RELATED MATERIALS

by

W. D. WOOLLEY AND ANN I. WADLEY

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SUMMARY

The phenolic products from the thermal decomposition of phenol-formaldehyde laminates have been studied by gas chromatography and mass spectrometry at temperatures between 300 and 550°C in nitrogen and air. The main phenolic components have been identified as phenol, o- and p-cresols, 2:4- and 2:6-xylenols and 2:4:6-trimethyl phenol. The maximum yields of the phenols are obtained at 460°C in nitrogen. The presence of air greatly reduces the quantities of the phenolic products. It is shown that in fires the phenolic laminates could, under certain conditions, generate hazardous amounts of phenolic products.

The results of three experimental fire tests are recorded to show that the concentrations of phenol and cresols appear to be lower than expected and, in these tests, not hazardous in comparison with the carbon monoxide.

KEY WORDS: Gas chromatography, mass spectrometry, pyrolysis, thermoplastic resin, toxic gas.

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PART 1. THE PRODUCTION OF PHENOL AND RELATED MATERIALS

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1. INTRODUCTION

a) General Introduction

Phenol-formaldehyde resins are now used widely in the building industries particularly in the laminated surface boards\(^1,2\). The resins are also used as adhesives in bonded board such as wood-waste board, chipboard, particle board and various plywoods and in moulded form in many electrical fittings.

When involved in fires, phenol-formaldehyde resins may release toxic gases in addition to carbon monoxide. The resins are known to release formaldehyde\(^3\) and various phenolic materials\(^3,4,5\) under certain decomposition conditions but the contribution of these materials to the toxicity of fire gases is unknown.

The work outlined in this report (Part 1) was undertaken to study by gas chromatography and mass spectrometry the release of phenol and related materials from phenol-formaldehyde laminates in order to evaluate the possible hazards of these products*.

Five different commercial laminates have been obtained for these tests. For convenience these will be labelled alphabetically, i.e. types A to E. It is known that the laminates are normally built up of a phenol-formaldehyde resin laminated with paper or fabric and possibly containing various inert fillers. The thin layer of decorative urea and melamine formaldehyde added to the boards for improved scratch and heat resistance has been physically removed for these tests. The results given in this report for the laboratory experiments refer only to the phenol-formaldehyde laminate.

By using a type of pyrolysis chromatography, it is shown that all five commercial laminates give very similar chromatographic patterns. This analytical procedure confirms that the laminates are similar in chemical structure and composition.

*The production of formaldehyde, carbon monoxide and carbon dioxide from the laminates will be recorded in a future publication (Part 2)
By using mass spectrometry and chromatographic retention time studies (by direct seeding), the main phenolic products have been chemically classified as phenol, cresols, xylenols and trimethyl phenol.

Detailed experiments to quantitatively monitor the release of these compounds at temperatures between 300 and 500°C in nitrogen and air have been undertaken with Type A laminate. This data is recorded graphically as the yields of phenolic compounds (by weight) versus the decomposition temperature in the two atmospheres.

A suitable method for analysing the phenolic content in the gases from model and full scale fires is given. Some preliminary results from three trial fires in a 50 m³ experimental chamber involving laminate A* are briefly recorded.

Finally, for comparison with other work, the toxicity factors of the phenolic compounds obtained from the thermal decomposition work are recorded.

b) Chemistry of phenol-formaldehyde resins

The detailed chemistry of the production of phenol-formaldehyde resins (phenoplasts) can be found in a number of excellent articles. A brief survey of the chemistry will be given here since it is relevant for understanding the origin of the decomposition products.

The reaction, or condensation, between phenol and aldehydes has been known for very many years. In general, aldehydes will condense with phenolic compounds providing that there are free ortho and para positions in the benzene ring. Formaldehyde is the most widely used aldehyde because of its high reactivity and relatively low cost.

The reaction of formaldehyde with phenol is relatively slow. Catalysts (acidic or basic) are used to accelerate the reaction but also determine the type of phenoplast which is formed.

With alkaline catalysts the primary reaction products are phenol alcohols and are usually termed 'resoles'. Acidic catalysts produce diphenyl methane derivatives, possibly via phenol alcohol intermediates, and are termed 'novolaks'.

The essential difference between the two primary reaction products is that the resoles can be condensed further by heat alone, whereas the novolaks require additional formaldehyde usually as paraformaldehyde or hexamethylene-tetramine.

*With decorative surface
(i) The resoles

The resoles (termed the A stage resin) represent the initial condensation product of phenol and formaldehyde in alkaline solution. The methylol groups (-CH₂OH) enter the benzene ring in ortho and para positions relative to the phenolic hydroxyl group. Depending on the amount of formaldehyde used, the series of methylol derivatives given below may be formed.

In the curing stages (B and C stages) of the resoles the methylol groups of the phenol alcohols condense (by elimination of H₂O) with vacant reactive positions in the benzene rings (ortho and para) to give methylene bridge structures but some methylol groups may condense with one another to give ether structures as shown below.

In this way complex structures, cross linked in the ortho and para positions can be built up. Depending on the temperature of the curing process the ether links may lose formaldehyde giving further methylene bridges.

(ii) The novolaks

Novolaks are prepared in acid solution usually with a molar excess of phenol. It is likely that the initial products are phenol alcohols, as in the resoles, but these condense (by elimination of water) to give a series of long chain compounds joined with methylene bridges (again ortho and para in the benzene rings) with the type of structure as shown below.
For curing, the novolaks are condensed with more formaldehyde in alkaline solution (as for the resoles) or can be mixed with hexamethylene-tetramine. This latter material provides both the formaldehyde for cross linking and the ammonia for catalyst. The resulting cured resin is a complex cross linked system, similar in many ways to the cured resoles.

c) Decomposition products of phenol-formaldehyde resins

Madorsky et al.\(^9\) were amongst the first workers to study the decomposition products of phenol-formaldehyde resins. In this work the phenolic resin was decomposed 'in vacuo' at temperatures between 360 and 1200°C. Mass spectrometric analysis of the volatiles showed the presence of hydrogen, carbon monoxide, carbon dioxide, various unsaturated and saturated hydrocarbons, acetone, propanols and butanol.

In 1960, Heron\(^4\) studied the thermal and thermal-oxidative decomposition products of a phenol-formaldehyde resin and detected, by gas chromatography involving retention experiments, phenol, o- and p-cresol, 2:4- and 2:6-xylenol, 2:4:6-trimethyl phenol and mesitylene. He also observed that the oxidation products were very similar to those from an inert atmosphere. This was explained on the basis that the diffusion of air to the resin was insufficient to prevent some purely thermal decomposition taking place.

More recently in 1966, Shulman and his co-workers\(^3\) studied the decomposition of a phenol-formaldehyde resin 'in vacuo' at temperatures between 200 and 800°C using a mass spectrometer. In addition to hydrogen, carbon monoxide, carbon dioxide, methane, benzene and toluene, Shulman also identified phenol, cresols, xylenols and formaldehyde. Formaldehyde was only detected between 250 and 400°C with a maximum rate of formation at about 325°C. Phenol, cresols and xylenols were formed between 425 and 600°C with a distinct maximum rate of formation at about 460°C in each case.

The work of Madorsky, Heron and Shulman indicate only the general types of products generated during the thermal and thermal oxidative decomposition of certain phenolic resins. The present study, outlined in this report was necessary in order to study the products (both qualitatively and quantitatively) from commercially used and fully cured phenolic laminated building boards.

2. EXPERIMENTAL

a) The decomposition system

The decomposition apparatus is essentially the same as used in studies of the decomposition products of PVC\(^10,11\). For convenience the essential features of the apparatus are shown in Fig.1 and outlined briefly below.
Samples of the phenolic resin (15 mg) are placed into the ceramic boat and introduced into the furnace by the influence of an external magnet on the steel plug P. During the decomposition a flow of dry air or nitrogen is maintained through the tube and carries the volatile decomposition products along the heated outlet tube and into a heated stainless steel gas sampling valve coupled in the usual way to a research gas chromatograph. During a collection period (30 minutes) the air or nitrogen from the furnace is directed through the collecting loop (stainless steel tubing, 3.2 mm O.D.) and condensable materials are trapped from the gas stream by surrounding the loop with a refrigerant (isopentane cooled with liquid nitrogen). The collection temperature is monitored by a thermocouple, silver-soldered to the base of the loop, and controlled manually (at temperatures down to -160°C) simply by raising or lowering the liquid nitrogen vessel. Some experiments are recorded using liquid nitrogen (-196°C) directly as a refrigerant but only with nitrogen as the furnace carrier gas. During the collection period an internal bypass in the valve maintains the supply of helium to the chromatograph.

After collection, the valve is turned to the inject position, the refrigerant is removed and replaced quickly by a fluidised sandbath thermostatted at 150°C. In this way the trapped products are vaporised quickly and carried by the helium into the chromatograph for analysis.

The stainless steel valve and flow lines coupling the valve to the furnace tube and chromatograph respectively are controlled at about 100°C in order to avoid problems from the absorption and condensation of products prior to chromatography.

b) Chromatography

A Hewlett Packard 5750 Research Chromatograph fitted with simultaneous dual flame ionization and thermal conductivity detectors was used. For sensitivity reasons products were monitored by the flame ionization detector. The products were separated using a Porapak Q column using either a long or short temperature programme. The long programme was designed for a complete separation of the products and the short programme for a relatively rapid analysis of the phenols only. The two operating conditions of the column are given below.

Porapak Q, 2 m x 3.2 mm i.d. stainless steel. Helium carrier gas at 40 ml/min.

Long programme : 50°C to 260°C at 4°C/min
Short programme : 150°C to 260°C at 4°C/min

For quantitative analysis of the phenolic compounds, peak areas were determined using a Hewlett Packard 3370A automatic integrator with print out facilities.
coupled directly to the chromatograph. For mass spectrometry, samples were collected from the output of the non-destructive thermal conductivity detector and analysed using an A.E.I. MS10C2 mass spectrometer. Details for the collection, storage and mass spectrometric analysis of samples eluted from the chromatograph have been outlined in a separate publication\textsuperscript{12}.

c) Materials

Five different commercial laminates were obtained for the experiments. In all cases the top decorative surface (melamine and urea formaldehyde) was physically removed from the phenol-formaldehyde base. The remaining laminate was then divided into fragments of between 2 and 3 mg in weight. A total sample weight of 15 mg was used in all the phenolic estimations.

The phenols, cresols and xylenols used for seeding were obtained commercially as technical grade.

d) Experimental fire tests

The general experimental details of the three preliminary fire tests are recorded with the results in section 3(c). The complete experimental data including the permanent gas analyses and compartment temperatures will be given in a future publication\textsuperscript{13}.

The phenol-formaldehyde laminate used in these tests was Type A (1.5 mm thick) complete with decorative surface.

3. RESULTS

a) General laminate tests

In order to compare the decomposition products of the commercial boards, samples (15 mg) of the five different sheets were decomposed at 500°C in a stream of nitrogen (100 ml/min at 20°C). The products were collected using liquid nitrogen (−196°C) directly as a refrigerant and injected into the chromatograph as outlined in the experimental section. The chromatographic traces, using the long temperature programme (from 50°C at 4°C/min) with flame ionization detection, of laminates A to E are shown in Fig.2 to 6 respectively. All traces were recorded using the same recorder deflection, i.e. chromatograph range 10\textsuperscript{2}, attenuation 16. For convenience the peaks are numbered in Fig.2. A total of 45 components can be clearly detected in the traces but some fine detail may be lost during the duplication processes.

The chromatographic patterns are very similar in all five cases suggesting that the laminates are chemically similar in structure and composition. Further the traces can be divided into two sections. Firstly, an intense region (peaks 36-44) which is later shown to be due to phenolic compounds and, secondly, a
general pattern of minor products clearly visible up to peak 35 but then masked by the relatively large quantities of the phenolic products.

The general products (i.e. excluding peaks 36-44) are due partly to the decomposition of the phenolic resin and also, and more probably, due to the decomposition of the paper laminate and will be investigated at a future date.

Although the pattern of the phenolic products is similar in all five cases, the absolute amounts vary between samples. This may be a reflection on the experimental deviation between experiments, a problem associated with using samples at 15-mg levels of a non-uniform material or genuine discrepancies arising from different percentages of resin in each sample. The content of inert fillers in each sample is unknown. This problem will be discussed further in a later section.

b) Retention time studies

The long temperature programme used in Fig.2 to 6 (from 50°C at 4°C/min) was designed to give an effective separation of all products, but phenolic materials were eluted after 45 minutes. Consequently the cycle time between experiments was rather long. For retention studies and general analysis of phenols under various decomposition conditions, a short temperature programme (from 150°C at 4°C/min) was developed. With this modified programme the phenols were eluted after only 24 minutes with little or no loss in resolution; it was however necessary to operate the temperature of the collecting trap at -20°C instead of -196°C in order to prevent low molecular weight products interfering with the phenol estimations. A typical chromatographic trace of the decomposition products of Laminate A, again at 500°C in nitrogen, with product collection at -20°C is shown in Fig.7. As can be seen, the intensities of components eluted at the start of the trace are greatly reduced without interfering with the phenolic compounds. For comparison purposes the phenolic peaks of Fig.7 are numbered as in Fig.2. No attempts were made to correlate other general peaks but peak 22 is quite distinct in the short programme.

Samples of phenol, all cresols, all xylenols, all ethyl phenols and 2:4:6-trimethyl phenol were obtained for retention time and direct seeing experiments. Peak 36 was readily identified as phenol and confirmed by direct seeding, i.e. by adding phenol to the furnace during a decomposition experiment and noting that the peak height increased without doublet formation. The retention times of the other phenolic compounds were then obtained by direct chromatography in the normal manner using phenol as a reference material. The use of the reference material ensured that slight deviations in the chromatographic flow rate or in the start of the temperature programme did not affect the
retention times. In this way peak 38 was identified as o-cresol, peak 39 as m- or p-cresol, peak 40 as 2:6-xylenol, peak 41 as 2-ethyl phenol or 2:4-xylenol and peak 44 as 2:4:6-trimethyl phenol or 3:4-xylenol.

Direct seeding experiments by adding small quantities of each material in turn to the boat during decomposition experiments, calculated to give an approximate 50 per cent increase in the peak height in each case confirmed peak 40 as 2:6-xylenol, peak 41 as 2:4-xylenol and tentatively identified peak 44 as 2:4:6-trimethyl phenol. It was not possible to differentiate between m- and p-cresol in this way.

c) Mass spectrometry

For mass spectrometry samples of peaks 36, 38, 39, 40, 41 and 44 were taken from the exit port of the thermal conductivity detector using a freezing technique with ice as the refrigerant\(^{12}\). The operating conditions of the A.E.I. MS1002 mass spectrometer are given in Appendix 1. The Appendix also records the mass spectra of the various components giving the six most intense ion peaks of each spectra with intensities assuming the base peak to have an intensity of 1000 arbitrary units. Possible chemical structures of the materials are shown based upon spectral information compiled by Cornu & Massot\(^{14}\). For convenience the identifications are given in Table 1 together with the relevant retention data.

The mass spectrometry confirms the direct seeding identifications as given in Table 1 of peaks 36, 38, 40 and 41. It has not been possible to differentiate between m- and p-cresol but since peaks 40 and 41 have been positively identified as 2:6- and 2:4-xylenol respectively and since xylenols with a methyl group in the meta position are absent then it is very probable that the material is p-cresol. In future, in this report, peak 39 will be termed p-cresol.
Table 1
Retention and mass spectrometric data of phenolic compounds

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention data (by direct seeding)</th>
<th>Mass spectrometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>phenol</td>
<td>phenol</td>
</tr>
<tr>
<td>38</td>
<td>o-cresol</td>
<td>cresol*</td>
</tr>
<tr>
<td>39</td>
<td>m- or p-cresol</td>
<td>cresol*</td>
</tr>
<tr>
<td>40</td>
<td>2:6-xylenol</td>
<td>xylenol*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ethyl phenol*</td>
</tr>
<tr>
<td>41</td>
<td>2:4-xylenol</td>
<td>xylenol*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ethyl phenol*</td>
</tr>
<tr>
<td>44</td>
<td>2:4:6-trimethyl phenol</td>
<td>trimethyl phenol*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>methyl ethyl phenol*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>propyl phenol*</td>
</tr>
</tbody>
</table>

*elucidation of isomeric configuration not possible by mass spectrometry under these conditions

Peak 44 was tentatively identified as 2:4:6-trimethyl phenol by direct seeding experiments. The material was chosen for retention studies by inference from the known presence of 2:4- and 2:6-xylenol. Mass spectrometry confirmed the material to be a trimethyl, methyl ethyl or propyl substituted phenol with a total of 22 possible isomers. Some of these isomers may have retention times very similar to that of 2:4:6-trimethyl phenol and the identification of the material although not completely conclusive, will be accepted in this report.

For convenience the final identifications of the phenolic components are marked on Fig. 7.

d) Quantitative analysis of products from Laminate A

The release of phenol, o- and p-cresol and 2:4- and 2:6-xylenols from Laminate A were studied in nitrogen and air atmospheres at temperatures between 300 and 550ºC. The release of 2:4:6-trimethyl phenol was not monitored. In all cases analyses were undertaken using the short temperature programme of the chromatograph with product collection at -20ºC. The areas of peaks 36, 38, 39, 40 and 41 were obtained using the automatic on line integrator. In the doublet peaks (38-39 and 40-41) the integrator interprets each area of the doublet by extrapolating the centre valley towards and perpendicular to the baseline. In this report, total cresols and total xylenols (from total areas of doublets
38-39 and 40-41 respectively) are used in product studies and hence errors from the incorrect interpretation of the divisions between the peaks of the doublets are avoided.

For peak area calibrations, known amounts of phenol in methanol were injected into the inlet port of the chromatograph in the usual manner. The calibration graph of integrator counts (i.e. peak area) plotted as a function of the weight of phenol (in mg) is shown in Fig.8. The same calibration graph was used for the cresols and xylenols since it is known that the relative flame ionization sensitivities (on a weight basis) of materials of a homologous series containing an appreciable number of C-C and C-H bonds, are, in general, very similar. Figure 9 shows the release of phenol, total cresols (o- and p-) and total xylenols (2:4- and 2:6-) over 30 minute periods plotted as functions of temperature. As can be seen there is a distinctive maximum value in each case at about 460°C.

For the decompositions in air, chromatography shows the same relative distribution of the phenolic products as in nitrogen but the yields are greatly reduced in quantity as shown in Fig.10, plotted for comparison purposes on the same scale as Fig.9. Figure 10 shows distinctive maximum values at 450°C.

The total yields of all phenolic materials (i.e. total phenol, cresols and xylenols) have been extracted from Fig.9 and 10 and are shown directly in Fig.11. From this figure it is clear that under the worst possible decomposition conditions, i.e. about 460°C in a relatively inert atmosphere, Laminate A could release 7.3 weight per cent (1.1 mg from 15 mg of laminate) as total phenolic material.

e) Experimental fire tests

An experimental fire chamber (approximately 4.5 x 4.5 x 2.5 m high) fitted with heated gas sampling lines and associated equipment for general studies of combustion gases from fires was available for three trial experiments involving phenol-formaldehyde laminates. The general results of these tests are recorded below and in Appendix 2 but the complete experimental data including the carbon monoxide content, the oxygen deficiency and the temperatures of the combustion gases will be recorded in a future publication.

The compartment was ventilated by a vertical slit, 1.88 m high and either 210 or 565 mm wide and the 59 kg of phenolic laminate (type A with decorative surface, 1.5 mm thick) located on the inside walls of the compartment. A cellulosic fire crib (266 kg) was used as the main fuel.
For the estimations of the phenols, the combustion gases were sampled using a heated stainless steel tube (100°C) from the top of the ventilation slit and bubbled (at 1 l/min) through 50 ml of cold methanol for 1 minute intervals at known times after the start of the fire. In this way the phenolic products of the combustion gases could be obtained in methanol and stored for future gas chromatographic analysis.

For chromatography the 50 ml samples were chilled and concentrated at 50°C under slightly reduced pressure by bubbling air through the samples and extracting the methanol solvent to waste with a filter pump. In this way the samples were concentrated to less than 2 ml and then made up accurately to 2.0 ml giving a theoretical concentration factor of 25. Samples (5 µl) of the concentrated materials were then injected into the chromatograph with a syringe and analysed with integrator facilities using the fast temperature programme.

For calibration purposes known weights of phenol were dissolved in 50 ml samples of methanol and concentrated to 2 ml as outlined above. These calibration standards were prepared to cover the concentration range up to 5000 p.p.m. of phenol in the fire gases and were calculated assuming that 1 mg/l of phenol at 25°C is equivalent to 260 p.p.m. Hence by sampling the combustion gases at 1 l/min for 1 minute, 1000 p.p.m. of phenol for example would give 3.85 mg of phenol in the 50 ml of methanol.

The calibration graph of phenol (in p.p.m.) against the integrator counts (i.e. peak area) is shown in Fig.12. For these tests the chromatograph was attenuated to a more sensitive range (Range 10) than used in the small scale work and the integrator counts between the two series of work are not directly comparable. In Fig.12 the additional point at 5000 p.p.m. (labelled 'dilute') is an analysis of a calibration mixture prior to concentrating to 2 ml with the integrator counts multiplied by 25. This comparison technique suggests that little or no phenol is lost during the methanol extraction. Unfortunately, there was insufficient chromatographic sensitivity to extend this comparison below 5000 p.p.m.

Calibration experiments were undertaken using phenol only. However, as mentioned in an earlier section, phenol, the cresols and the xylenols have equivalent sensitivities (on a weight basis) to flame ionization detectors. Hence, Fig.12 can be easily converted to cresol and xylenol calibration simply by correcting the p.p.m. scale. For example, 1 mg/l of phenol and 1 mg/l of cresol in the combustion gases are equivalent to 260 and 230 p.p.m. respectively and hence for cresol calibration the phenol p.p.m. scale reading is multiplied
by 0.88 (i.e. 230/260). Summaries of the experimental conditions and the detected concentrations of phenol and cresols at various times after the start of the fire are given in Appendix 2 for the three fire tests (P1, P2 and P3). Xylenols were not detected. Essentially test P2 was a duplicate run of P1 but with reduced ventilation. Test P3 was a 'blank' experiment to monitor the production of phenols and cresols from wood alone. These tests will be discussed further in a following section.

4. DISCUSSION

a) General discussion

The observed phenolic products, namely phenol, o- and p-cresols, 2:4- and 2:6-xylenols and 2:4:6-trimethyl phenol from the decomposition of the laminates in nitrogen are in good agreement with the expected products from a phenolic resin having the general type of structure shown below:

\[
\begin{align*}
\text{CH}_2 & \quad \text{H} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

During the decomposition, thermal cracking of the methylene links can take place giving, via radical intermediates, phenols substituted in the ortho and para positions relative to the phenolic hydroxyl group. The close similarities between the observed and expected products also tends to confirm that the resins are prepared from phenol itself rather than substituted phenols.

The general structure given above is somewhat ideal and the resins may contain methylene ether structures as explained in section 1(b). At the temperatures of decomposition used in this report (300 to 500°C) these ether links probably eliminate formaldehyde and form normal methylene links. It is unlikely that this formaldehyde is released since it would immediately condense with any vacant ortho or para sites in the benzene rings giving further cross linking and eliminating water. Water is also probably eliminated by the direct condensation of phenolic hydroxyl groups giving ether links directly between benzene rings. This latter type of ether link would not of course eliminate formaldehyde.

It is now fairly well established\(^5\) that the methylene group is relatively vulnerable to oxidation forming, via hydroperoxides, benzophenone (i.e. diphenyl ketone) type of structure. These sites may degrade further with chain scission.
forming a variety of phenols and related compounds.

In this present work, the oxygen appears to greatly reduce the quantities of the phenolic materials without appreciably altering the relative amounts of phenol, cresols and xylenols. It seems probable that, as suggested by Heron, these materials are generated not by an oxidative route but by some purely thermal reaction taking place because of limited air diffusion to the resin. This is further substantiated by the temperature distribution of products in air and nitrogen. One would expect oxidation processes to generate the phenolic compounds at much lower temperatures than in nitrogen. Certainly there is a slight difference between the maximum yields of products in air and nitrogen (450 and 460°C respectively) but this is insignificant. The presence of air does not apparently alter the production of phenols in the 300 to 450°C region.

In general the maximum yields of products observed at about 460°C are in good agreement with the experiments of Shulman.

No attempts have been made to determine the maximum yields of phenols from laminates B to E in this work. The general evaluation of the products from all the laminates at 500°C in nitrogen showed that the amounts of phenolic products from each laminate might be different but only one experiment was performed in each case for this evaluation. It is evident from Fig. 9 that the experimental points from Laminate A are scattered considerably in the 475 to 550°C region and a quantitative comparison of product formation for each laminate based on one experiment only is clearly unreliable.

A solution to the problem is to perform several experiments for each laminate in the 425-500°C region in order to find the maximum yield in each case but this is beyond the scope of this report.

b) Toxic evaluation

In previous work the toxic potential of the decomposition products of plastics has been evaluated by calculating a toxicity factor (T), first introduced by Tsuchiya and Sumi, and defined as

\[ T = \frac{C_E}{C_F} \]

where \( C_E \) = experimental concentration in p.p.m. (at 25°C) produced from 1 gram of material in a metre cube

\( C_F \) = concentration in p.p.m. fatal in a short exposure.
Unfortunately very little information is available on the toxic inhalation hazards of phenolic compounds. Phenol and the cresols are widely used in industry and concentrated solutions can cause serious injury by burns if allowed to contact the skin\textsuperscript{17}. In contact of this kind, usually by spillage, the phenols are also rapidly absorbed through the skin and can cause serious systemic injury or death.

In vapour form, the maximum allowable concentration (M.A.C.) for phenol and all cresols has been recommended as 5 p.p.m. An odour threshold of phenol has been quoted as about 0.05 p.p.m. and a level of 0.13 p.p.m. has been reported as unpleasant\textsuperscript{17}. Similar odour thresholds of the cresols are unknown but are probably of the same order as for phenol itself. It is interesting to note that the M.A.C. is very much greater than the odour threshold.

The concentrations of phenol and the cresols in vapour form in the atmosphere likely to be fatal in short exposures are unknown. Also, the mode of injury from these vapours is not clear but may follow the same route as in acute phenol poisoning from spillages with injury to the kidneys, liver, pancreas, spleen and lungs\textsuperscript{17}.

In 1967, Rasbash\textsuperscript{20} showed that an empirical relationship exists for toxic materials such that the D.S.E.C. (dangerous in short exposures) in p.p.m. is approximately 20 times the M.A.C. (also in p.p.m.). In all of the 20 examples quoted, the D.S.E.C. was never less than 20 times the M.A.C. but in many cases considerably greater. This factor of 20 tends to err on the side of safety in handling toxic gases and a more realistic value is probably between 20 and 200.

In this way, the concentrations likely to be fatal in a short exposure (D.S.E.C. or $C_f$ for this report) for phenol and the cresols lie between 100 and 1000 p.p.m. It should be noted that at 25$^\circ$C, the maximum concentrations of phenol, o- and p-cresols by vapour pressures at 460, 320 and 140 p.p.m. respectively. However, in fires, the decomposition gases are generated at high temperatures and subsequently cool to temperatures approaching ambient and may hold (in mist form) effective concentrations much greater than theoretically possible from vapour pressure data.

There appears to be little or no documented information regarding the toxic hazards of the xylenols. It is usually thought that the toxicity of phenolic compounds decreases with increased substitution. Sax\textsuperscript{21} reports the toxicity of 3,5-xylenol as being similar to that of xylene (M.A.C. of xylene 200 p.p.m.). This is a very different order of magnitude to the toxicity of phenol and the
cresols (M.A.C. 5 p.p.m.) and rather surprising since the toxicology of
phenol and the cresol appear to be quite similar. On the basis of the
empirical relationship by Rasbash\textsuperscript{20}, the D.S.E.C. (or \(C_p\)) value for
3:5-xylenol therefore lies between 4000 and 40,000 p.p.m. The authors regard
this value as being somewhat large and in this report a \(C_p\) value for the
xylenols intermediate between that of cresol and xylene will be used, namely
500 to 5000 p.p.m.

For the calculations of the toxicities, the maximum yields of phenolic
materials from Laminate A occur at a decomposition temperature of 460°C in
nitrogen. These maximum yields are 0.315, 0.475 and 0.29 mg (from 15 mg of
laminate) for phenol, total cresol and total xylenol respectively. The
maximum toxicity factors (\(T\)) for these materials and the relevant intermediate
numbers in the calculations are shown in Table 5.

Table 5

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield per 15 mg of resin (mg)</th>
<th>Yield per gram of resin (mg)</th>
<th>(C_E)* (p.p.m.)</th>
<th>(C_p) (p.p.m.)</th>
<th>Maximum toxicity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>0.315</td>
<td>21.0</td>
<td>5.46</td>
<td>100-1000</td>
<td>5.47 x 10(^{-2}) to 5.47 x 10(^{-3})</td>
</tr>
<tr>
<td>total cresols</td>
<td>0.475</td>
<td>31.6</td>
<td>7.30</td>
<td>100-1000</td>
<td>7.30 x 10(^{-2}) to 7.30 x 10(^{-3})</td>
</tr>
<tr>
<td>total xylenols</td>
<td>0.29</td>
<td>19.3</td>
<td>3.86</td>
<td>500-5000</td>
<td>7.72 x 10(^{-3}) to 7.72 x 10(^{-4})</td>
</tr>
</tbody>
</table>

Since the toxicology of phenol, cresols and xylenols appear to be similar,
the combined toxicities of mixtures of the vapours are probably additive. The
total additive toxicity factor (\(T\)) from Table 5 lies between 1.35 x 10\(^{-1}\) and
1.35 x 10\(^{-2}\) which is relatively large. The toxicity factor, for example, of
hydrogen chloride from a commercial UPVC\textsuperscript{10} is 2.25 x 10\(^{-1}\) and less for
plasticised PVC. If decomposed under the worst possible conditions (i.e. at
temperature near 460°C in an inert atmosphere) the toxic hazards from the
production of phenolic materials from Laminate A could approach the same order
of magnitude as that of hydrogen chloride from plasticised PVC.

\*At 760 mm Hg and 25°C

- phenol 1 mg/m\(^3\) = 0.26 p.p.m.
- cresol 1 mg/m\(^3\) = 0.23 p.p.m.
- xylenol 1 mg/m\(^3\) = 0.20 p.p.m.
c) Experimental fire tests

Because of the possibility of producing relatively large quantities of phenolic materials from the thermal decomposition of phenolic resins, a series of three trial fire experiments involving Laminate A were undertaken*. Fire test P1 contained a cellulosic fuel loading of 266 kg with 59 kg of phenolic laminate (maximum calculated yield in nitrogen at 460°C of 4.25 kg of total phenolics). Small concentrations of phenol (145 and 72 p.p.m.) were detected at 10 and 15 minutes respectively. No cresols were detected.

In test P2, the ventilation was reduced to 210 mm with the same fuel and phenolic loadings. The concentrations of phenol were somewhat larger in this test and some cresol was detected. Fire test P3 was a duplicate run of P2 but without phenolic laminate in order to examine phenol production from the cellulosic loading alone. The maximum concentrations of phenol and cresols in test P2 are 260 and 150 p.p.m. respectively, and somewhat less if one subtracts the blank values for wood alone (test P3).

Although the concentrations quoted for test P2 are in the 'dangerous for short exposure' levels, it must be remembered that these are the concentrations in the undiluted fire gases from the compartment. These gases also contain carbon monoxide ($C_F = 5000$ p.p.m.)$^{22}$ at concentrations up to about 8 per cent$^{13}$ (i.e. 80,000 p.p.m.), and hence the contribution of the phenolic materials to the overall toxicity of the fire gases is small.

In general there appears to be a distinct discrepancy between the expected (i.e. from thermal decomposition work) and the observed concentrations of the phenolic material from the fire tests. It is possible that the phenols are generated in the fire compartment but are quickly consumed by the flame. A further decrease of the ventilation to the compartment could produce much higher concentrations of phenolic products in the fire gases. Alternatively, the consumption of the phenols, even in fires of very low ventilation, may be sufficient to eliminate the toxic hazard of the materials. It is certainly clear that further large scale work is required to clarify this important point.

5. CONCLUSIONS

(1) A type of pyrolysis chromatography shows that 5 different commercial phenolic laminates are similar in chemical structure and composition.

(2) The production of phenol, o- and p-cresols and 2:4- and 2:6-xylenols has been studied from the thermal and thermal oxidative decomposition of a

*See Appendix 2
phenolic laminate between 300 and 550°C. There is a maximum yield of phenolic products in an inert atmosphere at 460°C. Under these conditions the laminate produces 7.3 weight per cent of total phenolic material.

(3) The presence of air greatly decreases the yields of phenols. Further, the phenols which are formed in air are thought to be derived from some purely thermal decomposition (i.e. inert decomposition) which is taking place due to limited oxygen diffusion to the resin.

(4) The thermal decomposition data predicts that the phenols from the decomposition of the laminate in fires could under the worst possible conditions, be a hazard in fire gases.

(5) Three trial fire tests show that the phenolic concentrations in fires are much lower than expected and under these conditions not hazardous in comparison with carbon monoxide.

(6) Further large scale fire tests are required to study the production of phenols at different ventilation and fuel loading parameters to confirm and explain conclusion 5.

6. REFERENCES


(13) STAARK, G. W. V. F.R. Note. To be published.


(22) Carbon monoxide, hygenic guide series. American Industrial Hygiene Association, 14125 Prevost, Detroit 27, Michigan, U.S.A.
APPENDIX I

Mass spectra were recorded at 70 eV using a trap current of 50 µa. The batch inlet system was operated at 100°C and the analyser tube flanges at 120°C. The six most intense ion peaks are shown for each spectrum excluding 28+, 32+ and 44+ which are invariably present in the background when operating with the fast leak. The amplifier range and the type of leak (i.e. fast or slow) are given with each spectrum.

Peak 36. Recorded on fast leak. Range 25

<table>
<thead>
<tr>
<th>m/e</th>
<th>Intensity</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>310</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

Mol wt 94

*Impurity from peak 36 (phenol)

Peak 38. Recorded on fast leak. Range 25

<table>
<thead>
<tr>
<th>m/e</th>
<th>Intensity</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>780</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>292</td>
<td></td>
</tr>
<tr>
<td>94*</td>
<td>218</td>
<td></td>
</tr>
</tbody>
</table>

Mol wt 108

*Impurity from peak 36 (phenol)

Peak 39. Recorded on fast leak. Range 10

<table>
<thead>
<tr>
<th>m/e</th>
<th>Intensity</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>970</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>94*</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>240</td>
<td></td>
</tr>
</tbody>
</table>

*Impurity from peak 36 (phenol)
### Peak 40. Recorded on fast leak. Range 10

<table>
<thead>
<tr>
<th>m/e</th>
<th>Intensity</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>107</td>
<td>1000</td>
<td>( \text{CH}_3 ) (xylenol)</td>
</tr>
<tr>
<td>122</td>
<td>590</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>108</td>
<td>540</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>77</td>
<td>360</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>79</td>
<td>280</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>91</td>
<td>250</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
</tbody>
</table>

Mol wt 122

---

### Peak 41. Recorded on fast leak. Range 10

<table>
<thead>
<tr>
<th>m/e</th>
<th>Intensity</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>107</td>
<td>1000</td>
<td>( \text{CH}_3 ) (xylenol)</td>
</tr>
<tr>
<td>108</td>
<td>560</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>122</td>
<td>560</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>77</td>
<td>330</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>121</td>
<td>280</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
<tr>
<td>79</td>
<td>260</td>
<td>( \text{C}_6 \text{H}_5 ) (ethyl phenol)</td>
</tr>
</tbody>
</table>

Mol wt 122

---

### Peak 44. Recorded on fast leak. Range 2.5

<table>
<thead>
<tr>
<th>m/e</th>
<th>Intensity</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>107</td>
<td>1000</td>
<td>( \text{CH}_3 ) (trimethyl phenol)</td>
</tr>
<tr>
<td>136</td>
<td>830</td>
<td>( \text{CH}_3 ) (methyl ethyl phenol)</td>
</tr>
<tr>
<td>121</td>
<td>710</td>
<td>( \text{CH}_3 ) (methyl ethyl phenol)</td>
</tr>
<tr>
<td>91</td>
<td>590</td>
<td>( \text{C}_6 \text{H}_5 ) (propyl phenol)</td>
</tr>
<tr>
<td>77</td>
<td>470</td>
<td>( \text{C}_6 \text{H}_5 ) (propyl phenol)</td>
</tr>
<tr>
<td>135</td>
<td>240</td>
<td>( \text{C}_6 \text{H}_5 ) (propyl phenol)</td>
</tr>
</tbody>
</table>

Mol wt 136
APPENDIX 2

Fire Test P1
Cellulosic fire load 266 kg
Phenolic laminate 59 kg
Ventilation slit 565 mm

<table>
<thead>
<tr>
<th>Sample time (min)</th>
<th>Integrator counts ($10^3$)</th>
<th>p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenol</td>
<td>Total Cresol</td>
</tr>
<tr>
<td>5</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>10</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fire Test P2
Cellulosic fire load 266 kg
Phenolic laminate 59 kg
Ventilation slit 210 mm

<table>
<thead>
<tr>
<th>Sample time (min)</th>
<th>Integrator counts ($10^3$)</th>
<th>p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenol</td>
<td>Total Cresol</td>
</tr>
<tr>
<td>5</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>25</td>
<td>130</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>45</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

< 25 x $10^3$ counts
< 40 p.p.m.
< 35 p.p.m.
Fire Test P3

Cellulosic fire load 266 kg
Phenolic laminate zero
Ventilation slit 210 mm

<table>
<thead>
<tr>
<th>Sample time (min)</th>
<th>Integrator counts (x $10^3$)</th>
<th>p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenol</td>
<td>Total Cresol</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>65</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$\phi < 25 \times 10^3$ counts

$x < 40$ p.p.m.

$y < 35$ p.p.m.
To Waste

Gas Chromatograph

Isopentane Gas Sampling Valve

Liquid Nitrogen

Collecting Loop

Helium Carrier Gas

Brass Unions and Mounting Bracket

Glass Test Tube

Collecting Loop

Isopentane

Liquid Nitrogen

Dry air or nitrogen

Oven

Ceramic Boat

Pyrex Tube

Rubber Cap

A

P

Tubes and Areas Marked == are Heated by Electric Tape

FIG. 1. THE DECOMPOSITION SYSTEM
FIG. 2. THE DECOMPOSITION PRODUCTS OF LAMINATE A AT 500°C IN NITROGEN
FIG. 3. THE DECOMPOSITION PRODUCTS OF LAMINATE B AT 500°C IN NITROGEN
FIG. 4. THE DECOMPOSITION PRODUCTS OF LAMINATE C AT 500°C IN NITROGEN
FIG. 5. THE DECOMPOSITION PRODUCTS OF LAMINATE D AT 500°C IN NITROGEN
FIG. 6. THE DECOMPOSITION PRODUCTS OF LAMINATE E AT 500°C IN NITROGEN
FIG. 7. THE DECOMPOSITION PRODUCTS OF LAMINATE A WITH FINAL IDENTIFICATIONS OF PHENOLIC COMPONENTS
FIG. 8. CALIBRATION GRAPH FOR PHENOL
FIG. 9. THE PRODUCTION OF PHENOL, CRESOLS AND XYLENOLS FROM LAMINATE A IN NITROGEN
FIG. 10. THE PRODUCTION OF PHENOL, CRESOLS AND XYLENOLS FROM LAMINATE A IN AIR
FIG. 11. THE PRODUCTION OF TOTAL PHENOLIC MATERIAL FROM LAMINATE A IN NITROGEN AND AIR
FIG. 12. FIRE TEST CALIBRATION FOR PHENOL