EVOLUTION OF GASES FROM REFRACTORY MIXTURES
ON THE BTSO PHENOL-FURFURAL BINDER

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Translated from Ogneupory, No. 4, pp. 4—6, April, 1995.

Original article submitted November 15, 1993.

Using the BTSO phenol-furfural binder as an example, the main regularities of the evolution of volatile phenolic resins from refractory mixtures are considered. The evolution of gases is treated as being a result of two competitive processes, namely, the evaporation of volatile components and their combination into a solid or gel-like phase.

Removal of the volatile components from binder films distributed over the surface of the refractory powder occurs in two stages. The first stage is characterized by a constant rate of the removal of volatile components, which is restricted by the diffusion resistance of the vapors in the air layer directly at the surface of the fluid film and, in accordance with Gardner’s equation, is directly proportional to the vapor pressure over the film [7].

Due to the volatilization of the binder and the simultaneous interaction of free phenols and phenol oligomers with the surface of the refractory powder, the viscosity of the polymer film gradually increases, and the system loses fluidity and acquires concentration. The second stage of the formation of the polymer film is begun, i.e., a period when the rate of removal of the volatile substances is decreased.

Table 1 presents characteristics of substances volatilizing from the BTSO binder and their content in the free binder.

<table>
<thead>
<tr>
<th>Component</th>
<th>Admissible concentration, mg/m³</th>
<th>Boiling temperature, °C</th>
<th>Pressure of saturated vapor at 150°C, P, Torr</th>
<th>Approximate content in free binder, c, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>10</td>
<td>162</td>
<td>400</td>
<td>5</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.1</td>
<td>&gt; 240</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Dioctylphthalate</td>
<td>0.5</td>
<td>340</td>
<td>&lt; 1</td>
<td>30</td>
</tr>
</tbody>
</table>

* Summed shale phenols contain 10—15% monoatomic phenols and 85—90% biatomic phenols, mostly alkyl resorcinols. In accordance with TU 38.10935-77 the mass share of fractions distilled below 240°C does not exceed 4—9%.

** For resorcinol.

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Evolution of Gases from Refractory Mixtures

Taking into account that a multicomponent system obeys Raoult's law and the gases are ideal, we can determine the share of each component in the vapor mixture  

\[ V_i = \frac{c_i P_i^0}{\sum c_i P_i^0} \]

Using the data of Table 1 we obtain the following approximate composition for the vapor above the BTSO binder: 94% furfural, 5% phenols, and 1% dioctylphthalate.

The actual vapor mixture should differ from that calculated theoretically, because the summed shale phenols have a complex composition, which changes during their polycondensation with aldehydes in the process of binder synthesis. Chromatographic analysis of the vapor mixture over the BTSO binder gives 80% furfural, 16% phenols, and 4% dioctylphthalate.

Figure 1 shows the kinetics of the removal of volatile components from the refractory mixture containing periclase of fraction finer than 0.5 mm with 6% BTSO binder. In the experiments a thin layer of the mixture (< 1 mm) was placed in a Petri dish under an air hole. Different samples of the BTSO binder were produced in the laboratory of the St. Petersburg Technological Institute and at the Slantsy Plant.

It can be seen from Fig. 1 that even in the first few hours the volatilization rate of the refractory mixture on the BTSO binder decreased. This is explained by the comparatively low content of volatile constituents in the binder and the beginning of gel formation in the polymer film on the surface of the refractory powder. Our results allow us to evaluate the relative loss of mass of the BTSO binder during the first hour of volatilization at 0.8%. Knowing the composition of the vapor mixture we can determine the shares of individual components in the total loss of mass, namely, 0.64% furfural, 0.13% phenols, and 0.03% dioctylphthalate.

The maximum amount of volatile components that can evolve from the refractory mixture on the BTSO binder during a lengthy period (1 – 2 days) is at most 6% of the binder mass, including 4.8% furfural, 1.0% summed shale phenols, and 0.2% dioctylphthalate. Thus, furfural is the main volatilizing phase, whereas the plasticizer volatilizes very slightly. Though phenols are also gasified, they mostly remain in the structure of the polymer film.

In order to give a more exhaustive characteristic of the effect of the processes in condensed phases on the gas evolution from refractory mixtures on the BTSO binder, we determined the time changes in the phenol concentration in the vapor phase above the refractory mixtures under the condition when the removal of gases was insignificant. The binder was deposited on periclase powder of a fraction finer than 0.5 mm in an amount of about 6%. The compositions were periodically blown through with dry air (at a low flow rate), the loss of mass was determined by weighing, and the change in the mean concentration of phenols in the air was determined by the photoeotorimetric method. The total amount of air blown through the refractory mixture was 200 liters, the amount of removed volatile substances was very low, the total loss of mass in aging was 0.9%, and the concentration of phenols in the vapor phase decreased severalfold (Fig. 2).

Figure 3 shows the kinetics of volatilization from a freshly prepared composition of periclase and 6% BTSO binder and the same composition preliminarily held for 1 day in an air-tight vessel. In both cases a thin layer of the mixture