INCOMBUSTIBLE CHEMICAL FIBRES

FIREPROOF VISCOSE FIBRES

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A modifying bath composition was developed for manufacture of fireproof viscose fibres used for fabrication of textiles with a fireproofing effect and resistant to laundering. The existence of a chemical reaction in the viscose fibre (VF)—Pyrofax (PF) system was demonstrated and the mechanism of action of PF in thermolysis and combustion was determined. Multicomponent bath compositions were developed for manufacturing fibres with high oxygen indexes and a high yield of carbonized residue which can be promising as reinforcing systems in creation of PCM and for fabrication of carbon fibres.

The use of combustible polymer materials including chemical fibres, for fabrication of consumer articles (carpets, floor coverings, upholstery and curtain fabrics, work clothes, etc.) used in the interiors of schools, hospitals, sanatoria, children's institutions, hotels, offices, and vehicles, are prohibited by international convention. However, viscose fibre, characterized by high inflammability and combustibility — its oxygen index (OI) is equal to 19 vol. % — is widely used for fabricating such articles.

Thermolysis of cellulose is accompanied by two competitive processes — dehydration and depolymerization, which are difficult to separate in a certain temperature region. Carbonized substance, water, carbon dioxide, and other products are formed in dehydration of viscose fibres, and beginning at approximately 250°C and higher, levoglucosan appears in the products of thermal degradation. With further delivery of heat, levoglucosan rapidly decomposes with liberation of hydrogen, methane, carbon monoxide, etc. The problem of reducing the combustibility of cellulose materials is thus related to directed alteration of the chemical process in thermolysis [1, 2], and it can be solved by using different methods of modification of viscose fibres.

Since viscose fibre has a well-developed internal surface that favors diffusion into the bulk of the fibre and can swell in treatment with solutions of reagents, we modified the fibre with aqueous solutions of flame retardants (FR).

A phosphorus-containing compound — Pyrofax (PF), N-methylol-3-(dimethylphosphonyl)propionamide, (CH₃)₂P(O)(CH₂)₂C(O)NHCH₂OH, and a nitrogen-containing compound, metazin (MTZ), obtained as a result of esterification of some melamine methylol groups >CNCH₂OCH₃, were used as the FR. These compounds were selected because of the concentration of combustion inhibitors in them — phosphorus and nitrogen, their degradation in the range of indexes of the stages of thermolysis of a protected fibre (Table 1), and the presence of methylol groups in the molecules capable of chemically reacting with the hydroxyl groups of the fibres.

The viscose fibres were modified in water baths containing from 10 to 40 wt. % PF or MTZ or a mixture of PF and MTZ in the presence of an acid catalyst — phosphoric acid (PA). Modification consisted of the following stages: impregnation at 20°C for 1 min, drying, heat treatment at 160°C for 5 min, washing with water at 60°C with detergents (2%) for 5 min to eliminate unreacted product.

The diffusion—sorption processes and degree of preservation of the fireproofing effect were quantitatively and qualitatively evaluated with the following equations:

\[
\frac{\text{Amount of FR retained by fibre after laundering, wt. %}}{\text{Amount of FR retained by fibre after impregnation, wt. %}} \times 100 = \text{Efficiency of reaction of FR with fibre (Eₚ), %}
\]

\[
\frac{\Delta \text{OI, vol. %}}{\Delta \text{C, wt. %}} = a
\]

TABLE 1. TGA Data for Viscose Fibers (VF)

<table>
<thead>
<tr>
<th>Composition of material</th>
<th>Basic stages of thermolysis</th>
<th>Weight loss, %, at the temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_\text{r}$, °C</td>
<td>$m_\text{i} - m_\text{f}$, %</td>
</tr>
<tr>
<td>VF</td>
<td>245-340</td>
<td>10.5-69.0</td>
</tr>
<tr>
<td>PF</td>
<td>50-405</td>
<td>1.0-54.3</td>
</tr>
<tr>
<td>MTZ</td>
<td>50-390</td>
<td>1.0-83.0</td>
</tr>
<tr>
<td>VF+30% PF</td>
<td>240-310</td>
<td>11.0-53.0</td>
</tr>
<tr>
<td>VF+8% MTZ</td>
<td>230-315</td>
<td>13.5-59.0</td>
</tr>
<tr>
<td>VF+30% PF+8% MTZ+2% PA</td>
<td>230-280</td>
<td>11.0-40.0</td>
</tr>
<tr>
<td>VF+15% PF+4% MTZ+1% PA</td>
<td>230-290</td>
<td>14.0-45.0</td>
</tr>
</tbody>
</table>

The efficiency of PF, determined both by gain in weight and by OI (Table 2), was relatively high. This is due to the chemical reaction between the methylol groups of the PF and the hydroxyl groups of the cellulose:

$$\text{Cell.OH} + \text{HOCH}_2 \cdots \rightarrow \text{Cell.OCH}_2 \cdots$$

According to the IR spectroscopic data, the existence of such a reaction was confirmed by the decrease in the intensity of the 3420 cm$^{-1}$ peak corresponding to stretching vibrations of the OH groups in the modified fibre in comparison to the starting fibre, while additional incorporation of OH groups with PF in the fibre should on the contrary have increased the intensity of this peak. In addition, the intensity of the peak of vibrations of C—O—C groups increased in the modified fibre (1158 cm$^{-1}$).

PF is partially hydrolyzed at the amide bond in the water baths with formation of phosphinic acid, as the change in the pH of the bath to 2.5 indicates. The phosphinic acid esterifies the hydroxyl groups in the cellulose, and the phosphates form

$$\begin{align*}
\text{H}_2 \text{O} & \quad \text{HN} \cdots \text{CO} \cdots \rightarrow \text{H}_2 \text{N}+\text{COOH}\cdots
\end{align*}$$

in thermolysis and combustion decompose with the formation of a double bond and regeneration of the acid, which again participates in the reaction. As a result of this, stable conjugated structures arise in the cellulose, and a large number of double bonds can be obtained with one molecule of phosphinic acid [3].

Carbonized residue, whose amount is significantly higher in thermolysis of the modified fibre (47%) than in thermolysis of the starting fibre (31%), is formed from these conjugated unsaturated structures. The yield of volatile products decreases correspondingly, and the yield of incombustible products — water vapors — increases, since dehydration processes predominate in thermolysis of fireproof viscose fibre. For this reason, PF-modified fibres have high OI: 29-30.5%. It should be noted that increasing the amount of PF above 19 wt. % is not very effective, since the OI changes insignificantly (Table 2). For this reason, for practical purposes, baths with a 30% concentration of PF should be used.

The efficiency of the reaction of viscose fibre and MTZ and the OI of the fibres modified with MTZ are low and not very dependent on the concentration of the bath (Table 1). This indicates that only a small part of the MTZ enters the chemical reaction by formation of cross-links between the OH groups of neighboring macromolecules of cellulose and the methylol