EFFECT OF THE SPECIAL STRUCTURAL CHARACTERISTICS OF INDIVIDUAL AND MIXED COPPER AND IRON OXIDES ON THEIR ACTIVITY IN THE IGNITION REACTION OF A MIXTURE OF ISOBUTYLENE AND PERCHLORIC ACID

V. V. Bogdanova, V. F. Komarov, A. I. Lesnikovich, and V. V. Sviridov

A reaction between perchloric acid and hydrocarbons is possible under conditions of the combustion of condensed mixtures based on ammonium perchlorate and a polymeric binding combustible [1-4]. In the present work a study was made of the effect of the oxides of various metals on the autoignition temperature of a mixture of the principal gaseous product of the pyrolysis of some rubbers, i.e., isobutylene [5] and perchloric acid, to clarify the sensitivity of this process to the nature and the special structural characteristics of the solid phases. There are given below the results of a study of the effect of the preparation conditions on the activity of individual and mixed oxides of copper and iron.

The oxides were obtained by dehydration of their hydroxides at temperatures of 200-500 and 800°C for a period of 2 h. The hydroxides were precipitated from iron chloride, copper chloride (to obtain CuO-I), and copper sulfate (to obtain CuO-II). In addition, an investigation was made of the activity of the calcination products of coprecipitated hydroxides of copper and iron in the ratio Cu:Fe = 1:2.

The ignition temperature was determined in a thermostatted unit, to whose closed glass reactor (height 80, diameter 32 mm), filled with isobutylene, there was fed a pulse of 72% perchloric acid. In this case the acid was fed into a vaporizer, protecting the catalyst from the action of vaporizing HClO₄. The solid additive (50 mg) was distributed in a thin layer over the bottom of the vessel. When fresh weighed portions were used in each experiment, the determination of the ignition temperature was reproduced with an accuracy of ±0.5°C.

An x-ray investigation of the oxides was made in a URS-50IM diffractometer, using FeKα-radiation; ferromagnetic resonance spectra were recorded at room temperature in a Varian-E-12 spectrometer, in the X band. The specific surface was determined by the BET method from the absorption of carbon tetrachloride, and, for S<sub>Sp</sub> < 10 m²/g, from the low-temperature absorption of krypton.

Table 1 gives the results of a determination of the activity of the oxides in the process of the ignition of a mixture of perchloric acid-isobutylene. Iron oxide exhibited only a weak inhibiting activity, and only a sample obtained at 400°C lowered the ignition temperature by approximately 10°C. Copper oxide obtained from the hydroxide showed a considerably greater activity than analytical grade CuO.

Mechanical mixtures of the oxides differed only slightly in their activity from copper oxide obtained from the hydroxide. The calcination products of coprecipitated hydroxides, calcined at 400 and 500°C, are inactive in the ignition reaction. Samples of coprecipitated hydroxides, calcined at 200 and 300°C, have considerable activity; however, with a calcining temperature of 300°C, the activity decreases. The calcining of coprecipitated hydroxides under conditions bringing about the formation of well-crystallized copper ferrite (900°C, 8 h) leads to the formation of preparations having inhibiting properties (see Table 1).

It must be noted that the transition of iron oxide from a form which is almost indifferent in the reaction under study to an active form is accompanied by a perfecting of its structure. On the x-ray photo...
TABLE 1. Synthesis Conditions and Activity of Oxides

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination Temperature, °C</th>
<th>Specific Surface, m²/g</th>
<th>Change in Ignition Temperature, °C</th>
<th>Catalyst</th>
<th>Calcination Temperature, °C</th>
<th>Specific Surface, m²/g</th>
<th>Change in Ignition Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>200, 300, 400, 500, 800</td>
<td>137, 139, 10, 9</td>
<td>-1, -3</td>
<td>CuO</td>
<td>200</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>CuO-I</td>
<td>200, 300, 400, 500</td>
<td>Mechanical mix.</td>
<td></td>
<td>CuFe₂O₄</td>
<td>900</td>
<td>11</td>
<td>-100</td>
</tr>
<tr>
<td>CuO-II</td>
<td>300, 400, 500, 600, 700</td>
<td>38, 45</td>
<td>45</td>
<td>CuFe₂O₄</td>
<td>900</td>
<td>7</td>
<td>-15</td>
</tr>
</tbody>
</table>

*The ignition temperature in the vessel without catalyst was equal to 250°C.

Fig. 1. X-ray photos of calcination products (O denotes copper ferrite, X denotes copper oxide): a) iron hydroxides at 400°C; b-d) coprecipitated hydroxides calcined at 300, 400, and 500°C, respectively.

Fig. 2. Dependence of the g-factor on the calcination temperature of coprecipitated hydroxides (1) and on the content of copper ferrite in the calcination products (2).

of an active sample, there appear the two most intense lines of α-Fe₂O₃ (Fig. 1a), and, in the NGR spectrum,* even at room temperature, together with the quadrupole doublet of the amorphous paramagnetic product, there appear the components of a sextet characteristic for α-Fe₂O₃.

In the initial stages of the formation of crystals, α-Fe₂O₃ is probably active in reactions leading to ignition of the mixture; however, after the final formation of the crystalline phase, it loses its activity.

It is characteristic that the active functions of copper oxide are retained in the products of the low-temperature calcination of coprecipitated hydroxides. These do not contain the crystalline phases of Fe₂O₃ or copper ferrite; the absence of the latter phase is attested to not only by the x-ray photo (Fig. 1b), but also by the NGR spectra which, with a calcination temperature of the coprecipitated hydroxides up to 300°C, are similar to the spectra of the dehydration products of iron hydroxide. The appreciable fall in the activity of the products of the calcination of coprecipitated hydroxides corresponds to the start of the formation of the phase CuFe₂O₄, giving washed-out lines on the x-ray photo (Fig. 1c). However, this ferrite is still not characterized by the NGR spectrum in the form of two Zeeman sextets, corresponding to two positions of the iron ions in the lattice of CuFe₂O₄, which is observed for preparations obtained at 500°C or above, which bears witness to the poor magnetic ordering of low-temperature copper ferrite.

The growth of the degree of magnetic ordering with an increase in the calcination temperature can be followed from the position of the line of ferromagnetic resonance absorption. Figure 2, curve 1, reflects the dependence of the g factor on the temperature of the calcination of coprecipitated hydroxides, and Fig. 2, curve 2, its dependence on the amount of copper ferrite of the cubic modification formed during calcination, which is determined x-ray graphically. Taking account of the course of curve 2, it can be postulated that the steep ascent of curve 1 is due to ordering of the ferromagnetic structure of the struc-

*The results of a detailed investigation of the preparations used using the NGR method is reported in [6].