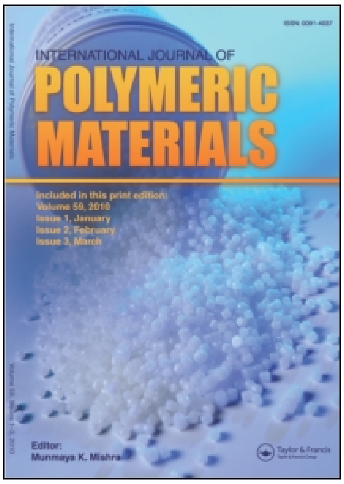

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XRD Analysis of Burnt Cotton Fabric Impregnated by Ammonium Iron (II) Sulfate Hexahydrate as a Flame-Retardant

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Ammonium iron (II) sulfate hexahydrate [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] as a nondurable finish was deposited onto cotton fabric, and its uniformity was ensured by means of squeeze rolls. By using a vertical flame test the optimum add-on values to impart flame-retardancy to the fabric was determined to be about 23.62–25.82%. The XRD analysis of ashes of impregnated samples showed the existence of iron (III) oxide. Hence it can plausibly be deduced that a reduction-oxidation reaction occurred during the combustion of the treated specimens and other elements presented in the aforementioned salt and converted to gaseous products, that is, SO_2, H_2O, CO_2, and NH_3, were eliminated during the combustion process. Hence "Gas theory" could play a significant role in justifying its flame-retardancy action. On the other hand, the presence of Fe_2O_3 dust in the consumed ashes proves the Dust or Wall effect suggested by Jolles and Jolles.

Keywords: ammonium iron (II)-sulfate hexahydrate, Dust or Wall effect, flammability, flame-retardancy, gas theory, X-ray diffraction

INTRODUCTION

Flame-retarded substances are considered to be very significant in the prevention and control of fires. They are found in building materials, curtains, carpets, bedding, baby clothes, computer cases, electrical appliances, and numerous other products [1]. A flame-retardant is a

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compound or mixture of components that when added or incorporated chemically and or physically into a polymer serves to hinder the ignition or growth of fire [2–3]. It should be mentioned that the flame-retarding component is intended to prevent a small fire from rapidly developing into a major catastrophe [1]. The term flame-retarded is often used when combustible synthetic or natural polymers become noncombustible. However, a flame-retarded substance is believed to be combustible in harsh ignition circumstances. There are several ways in which flame-retardanly may be achieved. As a rule, a flame-retardant interferes with one or more of the three factors essential to the combustion process, in other words, it interrupts the fire triangle: A combination of oxygen, fuel, and heat [2]. In practice, flame-retardants are tailored to the specific properties of the flammable material and to the common causes of fire in the materials environment. The major groups of chemicals used in the world as flame-retardants are:

1. Organic halogen compounds, especially bromine and chlorine compounds, often in combination with antimony oxides (almost half the market volume in dollars).
2. Phosphorus compounds, such as phosphate esters (about 20%).
3. Metal compounds such as alumina trihydrate, $Al_2O_3 \cdot 3H_2O$, and magnesium hydroxide, $Mg(OH)_2$ (another 20%) [1].

It should be mentioned that burning processes possess two significant steps that are present in the solid phase [4]: (I) A pyrolysis stage, in which the solid phase goes directly through the devolatilization reactions to yield volatiles (gases and tars) and a solid char fraction and (II) A combustion stage, in which the char undergoes heterogeneous reactions to yield gaseous products and an inert residue (ash).

Pyrolysis and combustion stages may be sequential or concomitant, depending on the nature of the process considered [4–5].

The aim of this investigation is to study the effect of deposited ammonium iron (II)-sulfate as a non-durable finish for imparting flame-retardancy to cotton fabric.

EXPERIMENTAL

Material

All fabrics were a plain construction, weighing 144 g/m^2, unfinished 100% cotton, laundered and dried. They were 22 cm by 8 cm strips cut along the warp direction and pre-washed in hot distilled water.

The samples were dried at 110°C for 30 min in an oven, cooled in a desiccator, and weighed with an analytical precision.

Bath Treatment

With the exception of the first set, all other samples were impregnated with suitable concentrations of ammonium iron (II)-sulfate at 20°C. Afterward they were squeeze rolled and dried horizontally in an oven at 110°C for 30 min [6–15]. They were then cooled in a desiccator and re-weighed with an analytical balance so that the suitable add-on present on the fabrics were obtained. All the specimens were kept nightlong under ordinary condition before the performance of the flammability test.

CHARACTERIZATION OF THE APPARATUS

Flammability Test

A vertical test method similar to the procedure described in DOC FF 3–71 [16] was employed to determine the flammability of thermoset fabrics. It has been designed and named as Mostashari's Flammability Tester (Figure 1). It is a rectangular aluminum frame with one of its

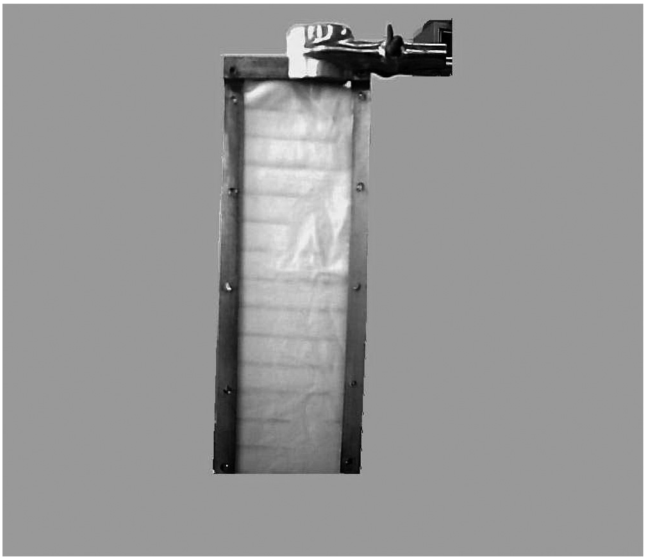

FIGURE 1 Mostashari's Flammability Tester with an untreated cotton fabric before the accomplishment of the experiment.

smaller sides missing. It has internal splits for inserting the fabric. The frame also has five holes in each of its parallel legs, so that pining inside it the fabric is possible. This method was also introduced in previously published articles [6–15].

According to the aforementioned test, an aluminum frame with the following specification has been used: Two strips of 3 mm aluminum double-sheet, 22.5 by 1.5 cm are cut, perforated, and welded at right angles to a shorter 9 cm strip. The conditions of the samples and environment were: The temperature ranged between 20°C and 22°C and the relative humidity (RH) was about $65 \pm 2\%$. All specimens were pinned tightly to the frame and held vertically in a retort stand by clamps with the lower edge 1.9 cm above the top of a Bunsen burner with a three centimeter yellow flame. Then, an ignition time of 3 s was observed. This procedure was conducted in order to avoid harsh ignition conditions. All specimens were tested with accuracy of determining the burning time of $\approx$0.1 s. Repeatability of the burning time was $\pm 5\%$ for an untreated fabric. This figure was much worse for salt-treated fabrics. This indicates the presence of inhomogeneities in the treated fabrics. The flammability test was conducted in a closed fume-cupboard prior to the completion of the combustion. However, the exhaust ventilator had been turned on for about 5 min after each burning so that the consumed toxic gases were directed away from the environment and fresh air could reach the vicinity of the experimental equipment.

XRD Analysis

X-ray diffraction (XRD) measurements were performed on a Philips PW1840 diffractometer with the use of K_a radiation of copper at room temperature. XRD patterns were recorded using an automatic divergence slit system.

RESULTS AND DISCUSSIONS

Using a vertical flammability tester the effect of the additive on the burning time of the samples was ascertained in seconds. The burning rates were calculated by means of dividing the length of the specimens (22 cm) by the burning time in seconds. These figures for untreated fabric were 25 s and 0.88 cm/s, respectively; however, for insufficient percent of ammonium iron (II) sulfate hexahydrate, upto 5% addition of the salt by the application of 0.125 M treating solution, caused complete burning at 28 s and burning rate of 0.78 cm/s.

A higher concentration of 0.6 molar of the salt caused about 21.88% by weight impregnation of the fabric. This increased the burning time upto 750–868 s and decreased the burning rate upto 0.029–0.025 cm/s, respectively. However, about 23.62–25.82% addition of ammonium iron (II) sulfate hexahydrate was sufficient to impart flame-retardancy to the cotton fabric, that is, combustion was not achieved.

Ammonium iron (II) sulfate hexahydrate has an acidic nature. The pH of its 0.1 molar solution determined via universal paper was about 5. The plausible mechanism of the flame-retardancy using these types of flame-retardants goes back to chemical theory stated by Little [17]. According to this theory, the formation of solid carbon residue rather than volatile pyrolysis products when the polymer is subjected to thermal degradation is promoted by using the acidic flame-retardants. Therefore, the decomposition of cellulose substrate could be pushed and confined through the catalytic dehydration shown as:

$$(C_6H_{10}O_5)n \rightarrow 6nC + 5nH_2O$$

It is worth mentioning that burning of the material involves two thermal decomposition processes, that is, combustion and pyrolysis [18]. Thermal decomposition of cellulose produces solid residues, liquid components, and volatile gases when it is heated without oxygen. Combustion of cellulose is an oxidation process of the heated material, which consumes flammable gases, liquids, and solid residues produced in the pyrolysis of the materials, and results in excess quantities of heat. Burning of materials may involve two different types of fires. The first type is combustion of flammable gases and volatile liquids, whereas the solid state burning is an oxidation of solid residues (mainly carbon). It should be noticed that the temperature of the volatiles flame burning is lower than that of the solid state burning [19].

The latter would cause more thermal decomposition (pyrolysis) of the materials. Thermal pyrolysis forms more flammable products, which then could fuel the burning of more materials resulting in the fire spreading. The cycle of this combustion process is self-sustainable and could cause severe damage to the materials and unexpected fatal disasters.

The pyrolysis of cellulose is a very complex chemical process and is generally believed to involve two different mechanisms [18]. One of them is a process of dehydration and charring of cellulose, resulting in water, carbon dioxide, and solid residues. According to the second mechanism, the cellulose produces nonvolatile liquid glucose by depolymerization, and glucose cleavage pursues, producing low molecular weight products, which are more flammable. In the presence of oxygen, the decomposed products of glucose will be oxidized, generating much more energy and heat to promote more cellulose cleavage. The rivalry of these two reactions exists throughout the thermal decomposition of cellulose.

The fate of cellulose during combustion has been investigated extensively [20–23]. Cellulose decomposes on heating or on exposure to an ignition source by two alternative pathways. The first, which dominates at temperatures below 300°C, involves depolymerization, water elimination, fragmentation, and oxidation leading finally to char formation. The second route happens at temperatures above 300°C and involves bond cleavage by transglycosylation, fission, and disproportionation reactions yielding tarry anhydro sugars and volatile products.

XRD Analysis

This investigation involved the X-ray diffraction (XRD) analysis with the use of K_α radiation of copper. The XRD patterns were recorded for ashes of the consumed cotton impregnated by $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and, for comparison, for ashes of Fe_2O_3 powders. The XRD patterns of the ashes demonstrate six main peaks at $2\theta = 33.175$, 35.640, 49.490, 54.095, 62.410, and 64.060 (Figure 2). These values correspond to the

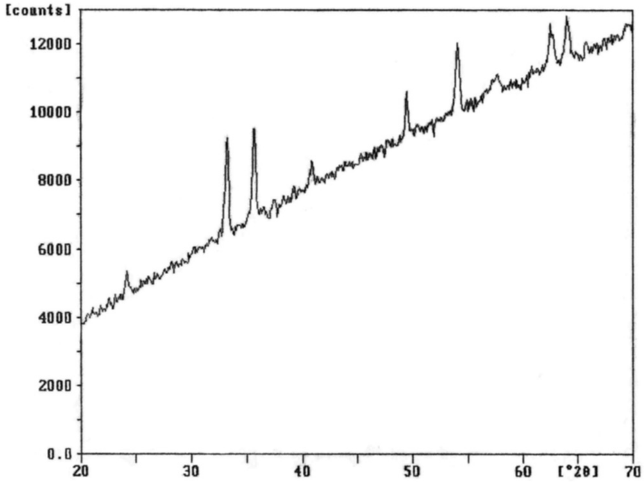

FIGURE 2 XRD pattern of the ashes of the consumed cotton impregnated by Ammonium Iron (II)-sulfate hexahydrate.

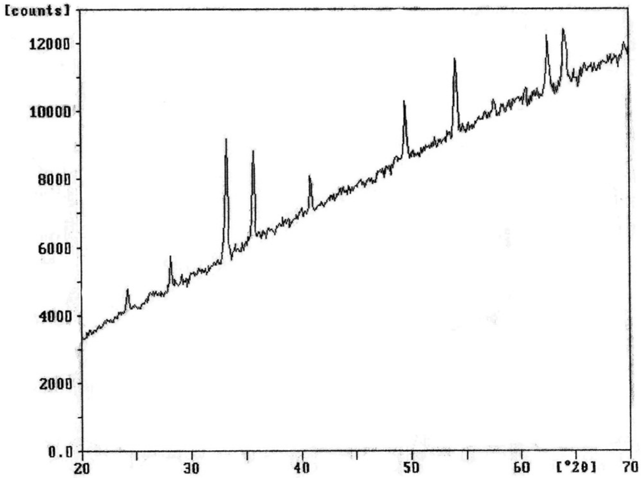

FIGURE 3 XRD pattern of pure Fe_2O_3 supplied by Merck Company.

peaks of 33.200, 35.680, 49.525, 54.140, 62.490, and 64.075 present in the pure Fe_2O_3 XRD patterns (Figure 3).

It should be noted that the XRD patterns of the ashes do not display any significant peak that would indicate the presence of other compounds such as Fe, FeO, and Fe_3O_4. It is worth mentioning that the formation of Fe_2O_3 during combustion of treated specimens is predictable. On the other hand, the flame-retardancy action of the residual Fe_2O_3 in the consumed ashes could be inferred as due to Dust or Wall effect, suggested by Jolles and Jolles [24]. That is, that a high concentration of the dust in the flame zone absorbs the heat and causes the heat dissipation, leading to lowering of temperature and consequently to retardation of the flame.

CONCLUSION

In this investigation the burning behavior of the untreated cotton fabric and the impregnated fabric with ammonium iron (II)-sulfate hexahydrate were studied. The XRD analysis of ashes of the impregnated samples illustrated the existence of iron (III) oxide. Hence, it can plausibly be deduced that a reduction-oxidation reaction occurred during the combustion of the treated specimens and other elements presented in the substrate impregnated by the salt are converted to gaseous products, that is, SO_2, NH_3, CO_2, and H_2O, which are eliminated during the combustion process. Hence “Gas theory” could play a significant role to justify the flame-retardancy action. Moreover, the action of Fe_2O_3 in the residual ashes may play the role of dust, ascribed in Dust or Wall effect, to dissipate heat from the combustion zone, according to which, heat is consumed by heating dust particles, which may assist the flame-retardancy.

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