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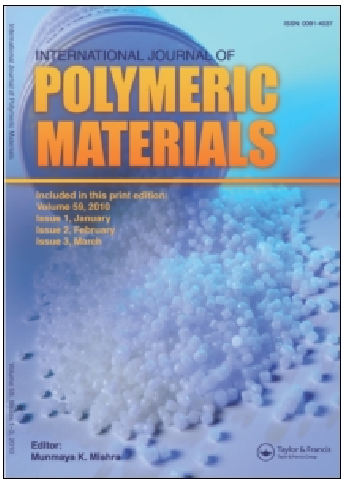

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Detection of Magnesium Oxide in the Ashes of a Burnt Cellulosic Fabric Treated by Magnesium Chloride Hexahydrate as a Flame-Retardant

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The authors investigated the effect of magnesium chloride hexahydrate [Mg $Cl_2{\cdot}6H_2O$*] as a nondurable finish on the flammability of 100% cotton fabric (woven construction, weighing 144 g/m*^{2}*. The laundered bone-dried, weighed fabrics were impregnated with various concentrations of the aqueous aforementioned salt solutions by means of squeeze rolls and drying in an oven at 110°C for 30 min. The specimens were then cooled in a desiccator, re-weighed with an analytical balance, and kept under standard conditions before the fulfillment of the vertical flame test. The optimum add-on values to impart flame-retardancy expressed in g anhydrous magnesium chloride hexahydrate per 100 g fabric were about 6.73% to 8.30%. The ashes of the treated specimens were subjected to X-ray diffraction analysis (XRD), and the result was compared with data for MgO powder. The existence of MgO was detected in the ashes. The results obtained for magnesium chloride hexahydrate are in favor of the "Gas Theory," "Free Radical Theory," and also "Dust or Wall Effect Theory."*

Keywords: dust or wall effect, flame-retardancy, flammability, free radical theory, gas theory, magnesium chloride hexahydrate, X-ray diffraction

INTRODUCTION

Most polymers and cellulosic fibers as organic materials are very sensitive to flame. Therefore the improvement of their flame retardancy has

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become more and more important in order to comply with the safety requirements.

The burning process comprises five fundamental steps, which are: heating, decomposition, ignition, combustion, and propagation [1–2]. Flame retardancy can be achieved by the disruption of the burning process at any of these stages that can lead to the termination of the process before actual ignition occurs. The most expeditious method used to acquire flame retardancy is the incorporation of flame-retardants that can interfere with the combustion during a particular stage of the process, so that the resulting system shows a satisfactory behavior [1].

The familiar additives used as flame-retardants are inorganics such as halogenated substances and phosphorous compounds [3–5]. In addition, boric acid, ammonium phosphates, ammonium sulfate, zinc chloride and borate, antimony oxide, and dicyanodiamide have also been applied as flame retardant additives [5–8]. Depending on the nature of the additives, they can act chemically or physically in the solid, liquid, gas phase. For example, halogenated compounds are said to function primarily by a vapor phase flame inhibiting mechanism through radical reaction, whereas phosphorous compounds reduce the formation of flammable carbon-containing volatiles by increasing the conversion of polymeric materials to a char residue during pyrolysis [2,9].

In search of environmental and health safety of fire retardants, there is also an increasing attention on the application of metallic hydroxide additives.

Metallic hydroxides provide efficient flame retarding effects by:

1. Releasing a significant amount of water that they contain at high temperatures and hence diluting the amount of volatiles fuels available to sustain the combustion during a fire.
2. Absorbing heat from the combustion zone, which reduces the prospect of continued burning.
3. Producting a char during buring that results in further flame-retardant protection and less smoke generation.
4. Generating a metal oxide coating that can act as an insulating protective layer during combustion [1,10].

The aim of this investigation is to study the effect of deposited magnesium chloride hexahydrate as a non-durable finish for the impartation of flame-retardancy to the cotton fabric, moreover XRD analysis of the ashes of consumed treated specimens has been of interest in this research project.

EXPERIMENTAL SECTION

All fabrics were a “plain” construction, weighing 144 g/m^2, unfinished 100% cotton, laundered and dried. They were 22 × 8 pm strips cut along the warp direction and pre-washed in hot distilled water. The samples were then dried horizontally at 110°C for 30 min in an oven, cooled in a desiccator and weighed with an analytical precision.

With the exception of the first set, all other samples were impregnated with several independent concentrations of magnesium chloride hexahydrate at 20°C. Afterward they were squeeze rolled and then dried horizontally in an oven at 110°C for 30 min. 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 of the specimens were kept nightlong under ordinary conditions before the fulfillment of the flammability test.

The aforementioned method has also been described in previous investigations, including in this journal [11–25].

CHARACTERIZATION OF THE APPARATUS

Flammability Tester

A vertical test method following the procedure described in DOC FF 3-71 [26] was employed to determine the flammability of thermoset fabrics. It has been designed and named as Mostashari’s Flammability Tester (Figures 1–3).

XRD Analysis

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

RESULTS AND DISCUSSION

By using our vertical flammability tester we ascertained the effect of the deposited salt on the burning time of the samples in seconds. The burning time and rate for untreated fabric were 25 s and 0.88 cm/s, respectively. For insufficient percent of the salt, that is, upto 5.8% addition by the application of 0.25 M treating solution, an average of completely burning at 20 s and burning rate of 1.10 cm/s was obtained. However, about 6.73–8.30% of its addition is fairly sufficient to impart flame-retardancy for the cotton fabric.

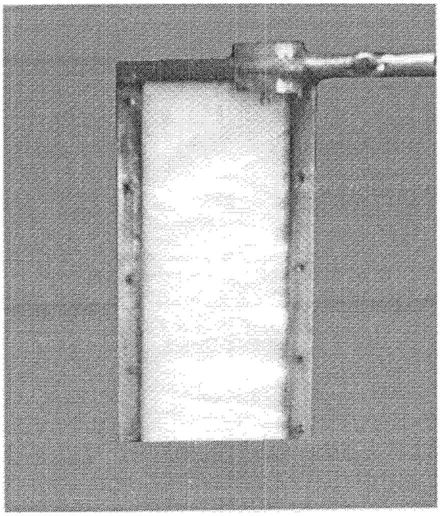

FIGURE 1 Mostashari's flammability tester with an untreated cotton fabric before the accomplishment of the experiment.

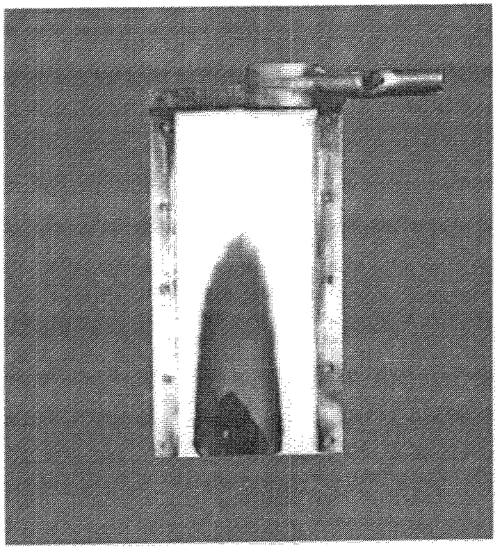

FIGURE 2 Mostashari's flammability tester with a treated cotton fabric during the test.

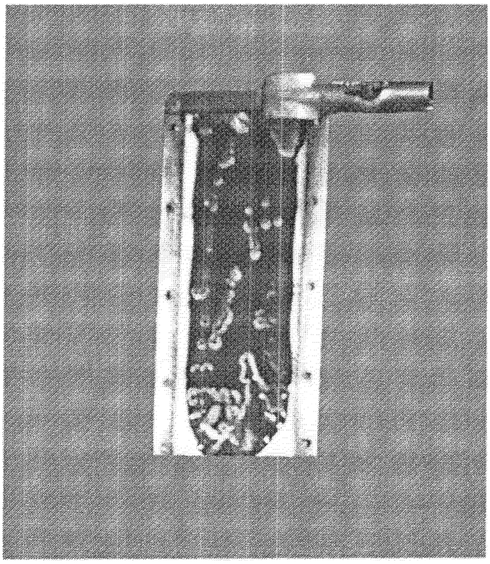

FIGURE 3 Mostashari's flammability tester with a low-addition of the impregnated salt, at the completion of the flaming. (The after-glow has also been illustrated.)

In fact, magnesium chloride hexahydrate has an acidic nature; the pH of its 0.1 molar solution determined via a universal paper was about 5. The plausible mechanism of the flame-retardancy by using these types of flame-retardants is referred to as Chemical Theory, stated by Little [27]. According to this theory, the formation of solid carbon residue rather than volatile pyrolysis products when the polymer is subjected to thermal degradation is catalyzed by using dehydrating flame-retardants such as acidic species. Therefore the decomposition of the cellulosic substrate could be promoted and confined through the following catalytic dehydration:

$$(C_6H_{10}O_5)_x \rightarrow 6C + 5H_2O$$

It is noticeable that the mode of action of halogen-containing compounds to act as flame-retardants is in compliance with the Free-radical theory [27–28]. According to this theory, the mechanism taking place in the gas phase during combustion is believed to involve the formation of high-energy $^\bullet$OH, $^\bullet$H, $^\bullet$O$^\bullet$ and alike radicals formed during combustion, which can support the aforementioned process, so that their removal or conversion can help to suppress the flame. To achieve this target it would be beneficial if these active radicals could be converted to less active ones. In fact, this suppression is believed to occur via chlorine or bromine compounds when applied as flame-retardants:

$$RX + {}^{\bullet}H \rightarrow HX + {}^{\bullet}R \quad (X = Cl \text{ or } Br)$$

It is mentionable that $^{\bullet}R$ is a less active radical than $^{\bullet}H$. It is also noticeable that the aforesaid halogenated flame-retardants absorb the required quantities of energy and the bonds between carbon and halogen will break homolytically. The free halogen atoms formed by this process react with the polymer's hydrogen atoms, and hygrogen halide molecules are generated. These molecules also play an important role in stopping the chain reaction that occurs during the propagation of fire or combustion process. They may, for instance, inhibit the generation of $^{\bullet}OH$ radicals [28–29].

$$^{\bullet}OH + HX \rightarrow H_2O + {}^{\bullet}X$$

Then the newly formed free halogen radical regenerated HX via capturing free hydrogen radical present in the gaseous phase or by reacting with the polymer's body:

$$^{\bullet}H + {}^{\bullet}X \rightarrow HX$$
$$RH + {}^{\bullet}X \rightarrow HX + {}^{\bullet}R$$

Various other reactions are proposed in the literature. The major overall effect is that the heavy halogen atoms withdraw energy from the combustion-propagation zone or from the burning region.

Thus the generated HX ultimately acts as a negative catalyst. After all, hydrogen halides as non-flammable gases could also form non-combustible protective gas layers interfering with the availability of air oxygen, so stopping the combustion process is the result [29–31].

It is worth mentioning that burning of a material involves two thermal processes, that is, combustion and pyrolysis [32]. Regarding to the thermal decomposition of cellulose, it produces solid residues, liquid components, and volatile gases when it is heated without oxygen. Combustion of cellulose is an oxidation process of the compound under heat, 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 based on the nature of the fires may involve two different types: gas state and solid state.

The first type is combustion of flammable gases and volatile liquids; however, the solid state burning is an oxidation of solid residues (mainly carbon). It is noticeable that the temperature of the gas phase burning is lower that that of the solid-state burning [33].

It is generally agreed that free radicals play a significant role in the complicated reaction mechanism of gas-phase combustion. In fact reactive combustion radicals such as $^{\bullet}$OH, $^{\bullet}$O$^{\bullet}$, $^{\bullet}$OR and alike take part an important role in the chain reaction of combustion. Their formation is strongly endothermic, but when they react with each other or with other reactive species present in the gas phase, a large amount of heat is released back into the combustion zone [15,29]. The pathway of the hydrated magnesium chloride deposited into the rich oxy-containing substrate, that is, cotton fabric, after losing its water molecules and chlorine radicals in the combustion propagation zone, leads to generate magnesium oxide.

Hence at this stage a profound investigation of the remained ashes has been of interest for continuing of this study.

After the treated specimen burned down completely the ashes of the treated cotton with insufficient amount of magnesium chloride were collected.

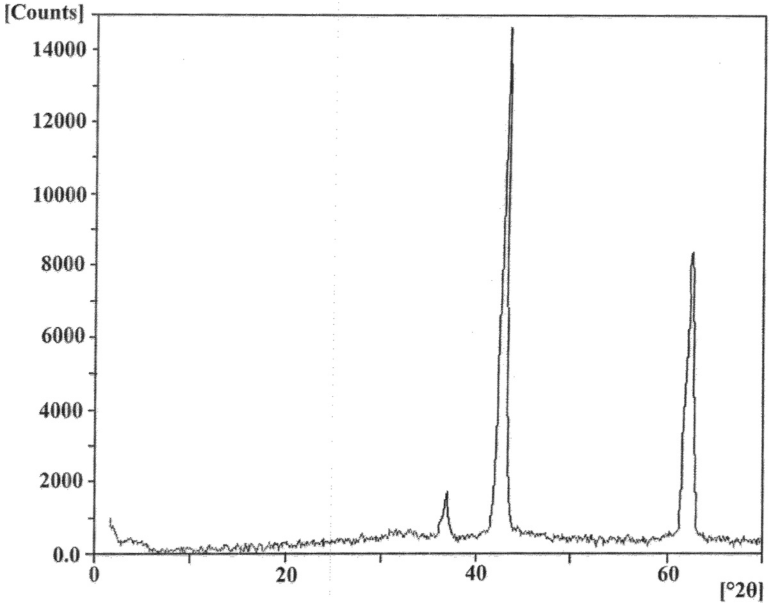

FIGURE 4 XRD pattern of the consumed ashes of a cotton fabric impregnated by magnesium chloride hexahydrate.

This investigation involved an X-ray diffraction (XRD) analysis. The XRD patterns were recorded for ashes of consumed cotton impregnated by $MgCl_2 \cdot 6H_2O$ and, for comparison, for ashes of MgO powders. The XRD patterns of the ashes demonstrate two main peaks at $2\theta = 42.925$ and 62.310 (Figure 4). These values correspond to the peaks of 42.845 and 62.250, present in the pure MgO XRD patterns (Figure 5). Note, the XRD patterns of the ashes do not display any significant peak that would indicate the presence of other compounds such as $MgCl_2$ and Mg (Figures 6 and 7). It is mentionable that the formation of MgO during combustion of treated specimens has been predicted. On the other hand the flame-retardancy action of the remained MgO in the consumed ashes could be explained by the Dust or Wall Effect Theory suggested by Jolles and Jolles [34]. According to this theory "if a high enough concentration of dust is present in the air, no flame can propagate." This phenomenon happens by the absorption and dissipation of heat by the inert dust, causing a diminished temperature to be fed back into the bulk of polymer. It is named as Dust or Wall Effect [28,34]. The aforementioned suggestion seems to be in accordance with the "Thermal Theory." It suggests, "the heat of combustion can be dissipated away from the unburnt medium with a rate equal to the rate of heat addition to the bulk of the fuel" [35]. Therefore

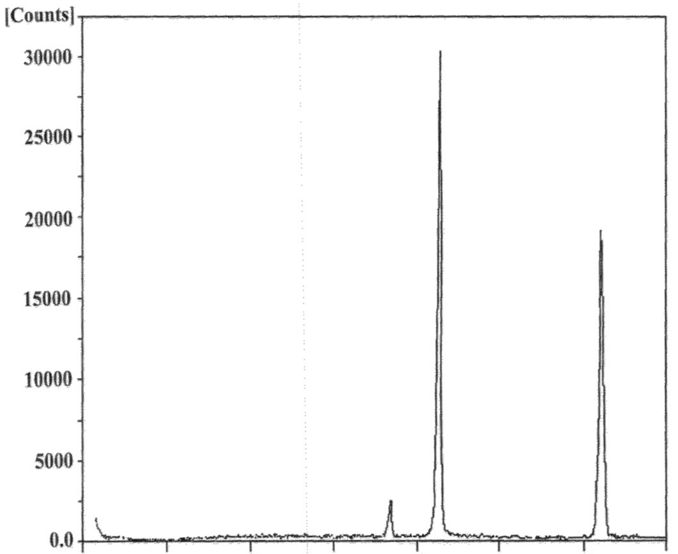

FIGURE 5 XRD pattern of pure MgO specimen.

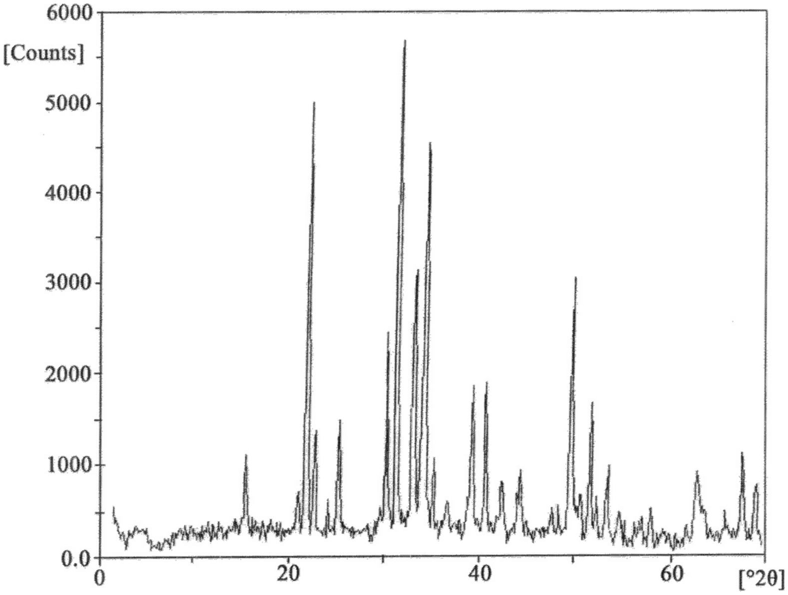

FIGURE 6 XRD pattern of pure $MgCl_2$ specimen.

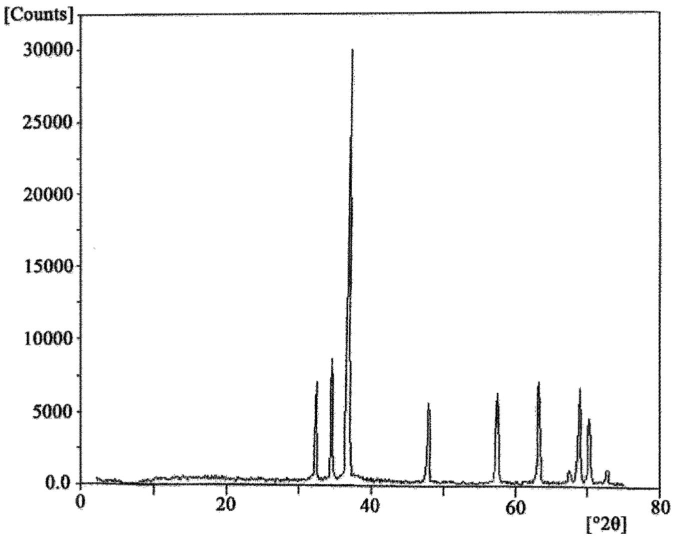

FIGURE 7 XRD pattern of pure magnesium specimen.

the target of flame-retardancy is achievable. Ultimately, the generation of this oxide as an insolating protective layer may assist the formation of coating at the surface of the substrate, leading to a snuffing out the flame.

CONCLUSION

In this study the capability of hydrated magnesium chloride to impart flame-retardancy to the cotton fabric has been attributed to the generation of chlorine radicals ascribed in “Free Radical Theory.” Apart from the aforesaid assumption, the pathway of the deposited salt during the combustion, verifies an oxidation-reduction process due to the access of atmospheric oxygen to the burning medium.

The existence of magnesium oxide in the consumed ashes of impregnated samples by XRD analysis verified this hypothesis. However, no traces of metallic magnesium and/or magnesium chloride were detected in the ashes. The failure of combustion by using the aforementioned salt can be considered on the basis of Free Radical Theory supporting the inhibiting action of chlorine radicals during the combustion process leaving magnesium oxide in the consumed ashes.

The latest-mentioned material performs the role of a heat dissipater indicated in thermal “Thermal Theory.” This oxide may coat the substrate as an insolating protective layer during the combustion process, leading to a snuffing out the flame.

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