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THE SUPERIORITY OF HYDRATED ZINC AND NICKEL *VERSUS* HYDRATED SODIUM SULFATE IN THE FLAME-RETARDANCY OF CELLULOSIC FABRICS

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Some hydrated sulfates, namely $ZnSO_4$, $NiSO_4$ and Na_2SO_4, have been selected and deposited onto cotton fabrics, for investigating their effectiveness as flame-retardants. A vertical flame spread test was then accomplished and the specimens' degree of resistance to burning was assessed. An efficient quantity of $ZnSO_4$, expressed in dry salt per 100 g fabric, has been determined over the 11.2-16.3 g range. For $NiSO_4$, this value was obtained over the 11.8-14.3 g range. In spite of this close resemblance, the incorporation of Na_2SO_4 over about 25.2% (almost twice as much as the above-mentioned quantities) showed no trace of flame-retardancy. Thermogravimetric analyses of both pure cotton and cotton treated with the aforementioned salts were accomplished, the thermograms being compared and interpreted. The results obtained for zinc and nickel sulfate suggest that the expulsion of the hydration water present in treated cellulose occurred well below the desirable range, prior to the thermal degradation of the cotton substrate. However, the application of sodium sulfate decahydrate to the cotton fabric illustrated an overlapped curve in the cellulose thermogram. Quite significantly, the loss of hydration water for the last mentioned salt occurred approximately in the same temperature zone of the thermal decomposition range of the polymer, where it showed no advantage in imparting flame-retardancy. Meanwhile, the thermograms for hydrated $ZnSO_4$ and $NiSO_4$ showed mass loss at high temperature, below the above-mentioned zone, which involves the catalyzation of the substrate thermal degradation; hence, their combustion retardation can be controlled.

Keywords: sodium sulfate decahydrate, zinc sulfate heptahydrate, nickel sulfate hexahydrate, combustibility, flame-retardancy, thermogravimetry

INTRODUCTION

Inorganics, including $Mg(OH)_2$, $ZnSnO_3$, Sb_2O_3 etc., represent one of the major groups of materials used as flame-retardants in Europe. These salts account for about 36% of the total of chemicals sold in Europe[1-3] in 2003 for this purpose. Still, the use of some sulfates, such as $Al_2(SO_4)_3$ and $ZnSO_4$, as fire extinguishers or as fire-proofing agents was also reported.[4] The present study investigates the effect of selected non-durable sulfates on the combustibility of cotton fabrics (woven cotton, 178 g/m^2). To this end, three hydrated sulfates with different levels of hydration water, namely $Na_2SO_4 \cdot 10H_2O$, $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ were chosen, for possibly demonstrating the potential of $Na_2SO_4 \cdot 10H_2O$ for a higher content of hydration water for imparting flame-retardancy.

Mention should also be made of some previously published studies on the effectiveness of selected inorganic compounds as flame-retardants, when impregnated on the cotton fabric.[3,5-17]

EXPERIMENTAL

All fabrics (woven structures weighing 180 g/m^2, unfinished 100% cotton) were laundered and dried. The specimens, 22×8cm strips cut along the weft direction, were pre-washed in hot distilled water, then oven-dried horizontally at 110 °C for 30 min, cooled in a desiccator and weighed with analytical precision.

With the exception of the initial set of fabrics, all the other samples were impregnated with suitable concentrations of $ZnSO_4·7H_2O$, $NiSO_4·6H_2O$ and $Na_2SO_4·10H_2O$, respectively.

The samples were then oven-dried horizontally at 110 °C for 30 min, cooled in a desiccator, re-weighed on an analytical balance and conditioned prior to the accomplishment of the flammability test. The average temperature ranged between 20 and 22 °C and relative humidity (RH) – between 65 and 67%.

Flame spread test

A vertical test method – Mostashari's Flammability Tester (Figs. 1, 2) – for the estimation of fabric flammability, described elsewhere,[3,5-17] was applied, at an average temperature ranging between 20 and 22 ºC and relative humidity (RH) – between 65 and 67%.

The tester, a rectangular aluminum frame cut on from one of its smaller sides, has an inner groove for inserting the fabric. The frame also has five holes in each of its parallel legs, so as to pin the fabric inside it. According to the aforementioned procedure, an aluminum frame with the following specifications has been applied: two strips of 3 mm aluminum double-sheet, 22.5x1.5 cm, perforated and welded at the right angles to a shorter 9 cm strip. The specimens were then cut, 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 3 cm yellow flame of a Bunsen burner, at an ignition time of 3 s. This procedure was conducted for avoiding harsh ignition conditions. After a 3 s ignition time at the bottom edge, the total burning time (up to 0.1 s) was determined with a stop-watch. It should be mentioned that the ignition time was subtracted from the total combustion duration, the rest being reported as the burning time. The standard deviation of the burning time was of ±1.06 for an average of 5 tests, when the untreated samples were burned. However, for the "salt-treated fabrics", this figure was around ±1.30. In fact, the pad squeeze process evidenced some variability. The char length was measured after each test to the nearest cm. The flammability test was conducted in a fume-cupboard, with the fan switched off, prior to the fulfillment of combustion; however, the exhaust ventilator was turned on for about 5 min after each burning, so that the toxic gases were conducted away and fresh air could enter the experimental apparatus.

It is worth mentioning that the burning rates could be calculated by dividing the length of the combusted samples, in cm, by the burning time, in seconds. Noticeably, too, the method was established[18] by resemblance with the procedure described in DOC FF3-71.

Thermogravimetric analysis (TGA)

Thermogravimetry provides a specific representation of the thermal changes occurring within a specimen system.[19] Therefore, the flame-retardancy of the treated specimens (having correlative optimum concentrations of sulfates) was estimated by thermal analysis, then compared with that of the untreated sample. For each sample, a thermogram was obtained on a TGA V5 1A DUPONT 2000 thermal analyzer, permitting to determine mass loss during thermal degradation.

To carry out the thermal analysis, a pulverized pure cotton fabric and fabrics treated with $ZnSO_4$, $NiSO_4$ and Na_2SO_4 were employed. The fabrics were starched by a razor blade, so that their pulverization could be performed.

Figure 1: Mostashari's Flammability Tester with a treated fabric inserted and pinned in its inner groove splits, prior to the accomplishment of the flame spread test

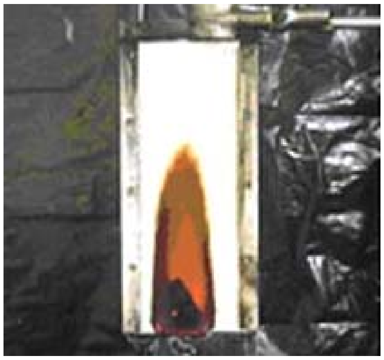

Figure 2: Mostashari's Flammability Tester with a treated cotton fabric during the experiment

All samples were heated from 20 to 600 °C, in air, at a heating rate of 10 °C/min. The TGA and DTG curves of the untreated cotton fabric are illustrated in Figure 3, while Figure 4 plots the comparative thermograms for both untreated and treated cotton samples.

RESULTS AND DISCUSSION

The experimental results are listed in Table 1. The vertical flame spread test was carefully conducted to determine the effect of the additives on the burning time values. The burning rates were calculated by dividing the sample length (22 cm) by the burning time (in seconds). The tabulated results, expressed in moles of anhydrous sulfates per 100 g of fabric, show that the optimum addition required to impart flame-retardancy to the cotton fabric was of approximately 0.08% for zinc and nickel sulfates. By contrast, a large loading of 0.18% Na_2SO_4 was inefficient in achieving the same goal.

Table 1
Effect of selected sulfates on the flammability of cotton fabric (woven, 178 g/m^2)

Sample set no*	Treating solution (molarity)	Percent loading (anhydrous sulfate)	Corresponding mole, %	Burning time, s	State of fabric**	Char length, cm	Burning rate, cm/s
1	Untreated	—	—	31.0 s.d. (±1.06)	CB	—	0.548
2	***$ZnSO_4$ (0.45)	13.75	0.0851	—	FR	1.1	—
3	***$NiSO_4$ (0.45)	13.05	0.0843	—	FR	1.2	—
4	Na_2SO_4 (1.00)	25.20 (Non-effective)	0.1774	33.6 s.d. (±1.30)	CB	—	0.506

*Each experiment was repeated five times and averaged
** CB – burned; FR – flame-retarded
*** Optimum addition of zinc and nickel sulfate to impart flame-retardancy

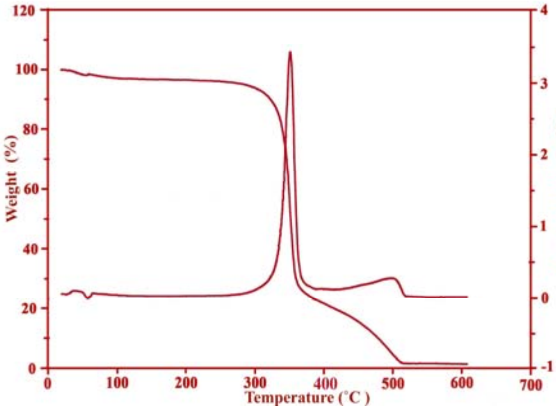

Figure 3: TGA and DTG curves of untreated (UT) cotton fabric

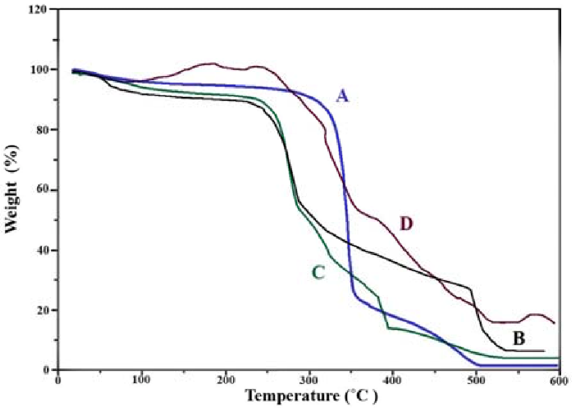

Figure 4: TGA curves of: A – pure pulverized cotton fabric; B – fabric treated with zinc sulfate heptahydrate; C – fabric treated with nickel sulfate hexa-hydrate; D – fabric treated with sodium sulfate deca-hydrate

The comparative thermograms of the untreated and treated cotton with optimum additions of flame-retardants and sodium sulfate (appearing as an inefficient addition), shown in Figure 4, demonstrate that the untreated cotton started a rapid degradation at 330 °C, losing 98% of its mass before 500 °C (curve A). The specimens treated with optimum additions of zinc sulfate and nickel sulfate displayed a spectacular mass loss at around 250 °C (curves B and C, respectively).

In fact, the thermograms illustrated that the samples treated with $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ degraded before the thermal decomposition range of cellulose, *i.e.* that the thermograms of cotton impregnated by $ZnSO_4 \cdot 7H_2O$ and/or $NiSO_4 \cdot 6H_2O$ demonstrated that the mass loss of the samples started at suitable temperatures, well below the thermal decomposition zone of the cotton substrate. That is why, they catalyze the polymer's combustion along its punctual duration, so that their flame-retardancy should be taken into consideration. Meanwhile, curve D, illustrating the degradation of the cotton treated with $Na_2SO_4 \cdot 10H_2O$, was almost overlapped by that for cellulose, which supports our idea that the sodium sulfate decahydrate-supported cotton fabric may be considered as a non flame-retarded sample.

Mention should also be made of the fact that some flame-retardants act to liberate the inert or not easily oxidisable gases, such as H_2O, NH_3, CO_2 and SO_2, around the inflamed materials. Hence, the combination of fuel, oxygen and heat necessary to sustain the burning process could be interrupted,[20,21] because of the atmospheric alterations in the vicinity of the inflamed sample, which resulted in the dilution of the inflammable volatiles produced during combustion. The other role of these gases is to act as a blanket, which prevents the access of air oxygen to the flame zone or makes it very difficult.[20-22] Therefore, the essential factor sustaining the burning process, *i.e.* oxygen, could be absent and fire failure might occur.[23] However, the application of sodium sulfate decahydrate, despite the presence of ten moles of hydration water per one mole in the salt, appeared as ineffective in inducing flame-retardancy, as due to the loss of the water present in its molecules at around the same temperature of the substrate thermal degradation zone.

The thermograms also show that the fabrics treated with nickel and zinc sulfate hydrates have been less stable thermally, to be possibly assigned to the weakened hydrogen bonding, in relation with their hydration water. In fact, their metals have a rather high electronegativity, of 1.8 and 1.6 by Pauling's scale, respectively.[24,25] Consequently, their sulfates are less ionic. By contrast, sodium electronegativity is of only 0.9 by Pauling's scale, which makes its sulfate more ionic. Hence, the cotton fabric treated with the last mentioned salt can be more stable thermally and does not tend to lose its hydration water over a punctual duration of cellulose thermal degradation. A similar deduction may refer to the untreated cotton fabric, which stands between the $ZnSO_4$ and $NiSO_4$ treated samples, on the one hand, and the Na_2SO_4 treated specimen – on the other.

Ultimately, the TGA results could be probably explained by the Lewis acidic effects of the zinc and nickel sulfates, *versus* the non-Lewis acidic character of sodium sulfate.

A very simple mechanism describing the role of these salts as flame-retardants considers the total decomposition of the cellulosic substrate, according to the reaction shown below:[26]

$$\mathbf{-(C_6H_{10}O_5)_n-} \longrightarrow \mathbf{(6C + 5H_2O)_n}$$

Dehydration is catalyzed by the presence of dehydrating agents such as acidic or neutral species forming Lewis acids at high temperatures. They are efficient and stable in flame-retardants at normal temperatures and function only on heating.

Although the above-mentioned reaction seems to be the major source for the generation of water vapors, to comply with the Gas theory, the release of hydration water may have only a small contribution, which could also explain the mass loss of the treated sample at around 100 °C, with minimum effects on flame-retardancy.

CONCLUSIONS

The positive effect of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) and nickel sulfate hexahyrate ($NiSO_4 \cdot 6H_2O$) applied to impart flame-retardancy to cotton fabric has been investigated. The thermogravimetric analysis of the treated fabric illustrated that cellulose dehydration in the presence of these salts occurred over a desirable temperature range, well below the thermal degradation zone of the substrate. However, sodium sulfate decahydrate appeared ineffective as a flame-retardant, which may be understood in terms of the inert gases released at the punctual temperature of the degradation zone, as compared to the fabric treated by zinc and nickel sulfates. Despite this, although with ten moles of hydration water, sodium sulfate decahydrate appeared as ineffective, once its hydration water had been almost entirely lost over the same temperature range as that of the cellulose thermal degradation zone.

Moreover, the acidic nature of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ made them susceptible to acting as catalysts, and suitable as flame-retardants for cellulose. Ultimately, due to their easy wash and, probably, to their poor handle, aesthetic and mechanical properties, these salts could not be used for garments. However, the results obtained may be applied for some other commercial purposes (insulators, plastics, polymers etc.).

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