

THERMOGRAVIMETRIC ANALYSIS OF A CELLULOSIC FABRIC TREATED WITH NICKEL SULFATE HEXAHYDRATE AS A FLAME-RETARDANT

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The effect of nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) on the flammability of cotton fabric was investigated and the optimum add-on value of nickel sulfate for imparting flame-retardancy to cotton fabric was calculated (as 11.8-14.3 g anhydrous salt per 100 g fabric). Thermogravimetric analyses of pure cotton, treated cotton and pure salt were accomplished, and their thermograms were compared. The results obtained agree with the Gas theory expressing water expulsion over a certain duration of the thermal degradation zone of cellulose. In fact, this occurs over a desirable range, prior to the initiation of cellulose thermal decomposition.

Keywords: nickel sulfate, flame-retardancy, thermogravimetry, Gas theory

INTRODUCTION

Nowadays, the necessity of reduced flammability in different products, such as plastics, textiles, insulators, etc., has been stressed by the governmental legislations of numerous countries, which is mainly the result of the deaths caused by ignition, obviously connected to the flammability of the materials. Also, mention should be made of other hazards that may be caused by fire, such as the combined effect of smoke and toxic gases generated during fire accidents.

Quite noticeably, over half of such accidents are caused by the above-mentioned side effects.^{1,2} It has also been reported that, annually, residential fires kill between 15 and 20 thousand people in the United States alone.³

As far as inorganic compounds are concerned, several inorganics – including $\text{Mg}(\text{OH})_2$, ZnSnO_3 , Sb_2O_3 and borates – have been considered as a major group of flame-retardants applied in Europe in 2003, representing 36% of the total chemicals sold for such purposes.^{4,6}

The present investigation analyzes the influence of nickel sulfate hexahydrate on the flame-retardancy imparted to cotton fabric. Therefore, its efficiency as a hydrated salt in liberating water in the vicinity of the thermal decomposition zone of the impregnated cotton has been investigated. Mention should be also

made of the fact that this salt is a monoclinic emerald-green crystalline salt that dissolves easily in water and ethanol.⁷ On heating, it loses water and, above 800 °C, it decomposes into nickel oxide and SO_3 . Its density is of 2.03 g/cm³, so that the generation of sulfur dioxide during the thermal degradation of cotton substrate, occurring around 350 °C, seems improbable.

Another important observation is that, on the evaporation of a solution of nickel oxide or basic carbonate in dilute sulfuric acid, nickel sulfate heptahydrate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) is separated as green prismatic crystals; this salt is isomorphous with the Epsom salt. On heating, it gradually loses water, giving hexa-, tetra- and di-hydrate and finally, above 280 °C, a yellow anhydrous salt.⁸

EXPERIMENTAL

A bath method treatment for nickel sulfate impregnation on cotton fabric was developed. The washed, bone-dried and weighed specimens (“woven” structures weighing 178 g/m²) of unfinished 100% pure cotton were dipped into a bath of 0.4 molar solution of nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), a value resulted from several experiments, as indicated in Table 1. After the treatment, the specimens were horizontally dried in an oven, at 110 °C, for 30 min, cooled in a desiccator and re-weighed on an analytical balance, then conditioned over the whole night, at an average

relative humidity between 65 and 67%, and average temperatures between 20 and 22 °C, prior to the accomplishment of the flammability test. With the exception of the first set, all other sets of specimens were impregnated with suitable concentrations of nickel sulfate hexahydrate solutions at 20-22 °C, for 10 min, under the following conditions:

Set B: Dipped into 100 mL of a 0.30 M NiSO₄·6H₂O solution and stirred.

Set C: Following the same procedure with a 0.4M NiSO₄·6H₂O solution.

Set D: Following the same procedure with a 0.5M NiSO₄·6H₂O solution.

The application onto the fabrics involved dipping, emerging, squeezing by rolls and, finally, horizontal drying in the oven at 110 °C, for 30 min.

Table 1
Effect of deposited nickel sulfate on the flame-retardancy imparted to cotton fabric
(woven 178 g/m²)

Set*	Treating solution (Molarities)	Percent (add-on) drying 110 °C and weighing	Burning time (sec)	State of fabric**	Char length (cm)	Burning rate (cm/sec)
A	Untreated	—	31.0	CB	—	0.70
B	0.30	7.4	30.3	CB	—	0.72
C	0.40	11.8	—	FR	1.2	-
D***	0.50	14.3	—	FR	0.8	-

* Average value of 5 tests for each set

** CB stands for completely burned, FR stands for flame-retarded

*** Confirmatory tests, applying excessive quantities of the additives

Flammability Test

A vertical test method for the estimation of fabric's combustibility, designated as Mostashari's Flammability Tester (Fig. 1), was applied, for both fabrics and the environment parameters, under the following experimental conditions: average temperature between 20 and 22 °C, relative humidity (RH) between 65 and 67%. The method is similar to the procedure⁹ described in DOC FF 3-71.

The tester has been described in previous investigations.¹⁰⁻²²



Figure 1: Mostashari's Flammability Tester with a treated fabric inserted and pinned in its internal splits, prior to the fulfillment of the flammability test

Thermogravimetric Analysis (TGA)

Thermogravimetry measures the mass change of a sample as a function of temperature, in the scanning mode, or as a function of time, in the isothermal mode.²³ Hence, for better understanding the role of nickel sulfate on the flame-retardancy imparted to

cotton fabric, it was decided to consider the obtained thermogravimetric data for pure cotton, pure nickel sulfate hexahydrate and conditioned cotton treated with the above-mentioned salt (containing 12.8% anhydrous nickel sulfate). A thermogram was obtained for each specimen with a TGA V5.1A Dupont Thermal Analyzer, used to determine the mass loss during thermal decomposition. Thermal analysis made use of pulverized pure cotton fabric, cotton fabric treated with nickel sulfate and pure hydrated nickel sulfate. Noticeably, the fabrics were scratched by a razor blade, which permitted their pulverization. The specimens were heated from 20 to 600 °C, in the air, at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

The experimental results are given in Table 1. Vertical flame tests were performed carefully to determine the effect of add-on quantities on burning times (in sec). The states of the fabrics after testing are listed and defined as: CB for completely burned and FR for flame-retarded. The burning rates were calculated by dividing the length of the specimen (22 cm) by the burning time. Char lengths are given in centimeters. The experimental results support the conclusion that an amount of anhydrous nickel sulfate between 11.8-14.3% is quite efficient for imparting flame-retardancy to cotton fabric.

The comparative curves of cotton, untreated and treated with the hydrate salt as flame-

retardant, are plotted in Figure 2.

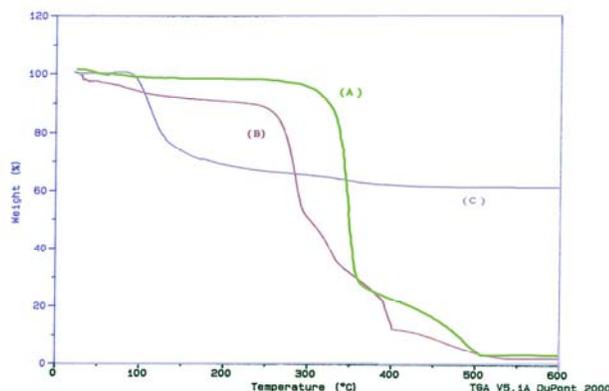


Figure 2: Thermograms of: A) pure pulverized cotton fabric, B) fabric treated with nickel sulfate hexahydrate and C) fabric treated with pure nickel sulfate hexahydrate

The untreated specimen evidenced rapid decomposition at 330 °C, losing 98% of its mass at 500 °C and releasing a small amount of ash (curve A), while the treated and conditioned specimen showed a spectacular mass loss starting with 250 °C (curve B). Quite interestingly, the major mass loss for untreated cotton occurred at 340 °C, when about 70% of its mass was lost. Curve C shows that the hydrated salt lost its hydration water quite far from the thermal decomposition zone of cellulose. No further spectacular mass loss was observed with increasing temperature. However, the treated sample lost most of its mass, its hydration water included, over the degradation temperature range of cellulose (curve B). Hence, one may assume that the flame-retardancy action of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ occurs *via* losing its hydration water over a pre-established duration of the thermal degradation of cellulose.

To conclude, the flame-retardancy of hydrated nickel sulfate is supported by the Gas theory,^{1,3,24} according to which the action of some flame-retardants is caused by the generation of inert or not easily oxidizable gases, such as CO_2 , SO_2 , H_2O , NH_3 , etc. These gases may be generated in the vicinity of the inflamed specimen, so that the adjacent atmosphere will be changed, either by diluting the flammable gases produced during combustion, or by acting as a blanket, which prevents or makes the access of the oxygen from the air very difficult. Actually, the migration of hydration water from the pure nickel sulfate

hexahydrate occurs at a low temperature, however, when the cellulosic fabric is treated with this salt, the conditioned and treated fabric resists mass loss at low temperatures. The reason may be the hydrogen bonding formed between the hydroxyl groups of cellulose and of the nickel sulfate hexahydrate, where it is linked *via* its hydration molecules. Therefore, water migration temperature is shifted towards 250 °C, occurring at an established duration of cellulose thermal degradation. Hence, the Gas theory should be rationalized. Also, the above-mentioned effect could result from the endothermic evaporation of water in the combustion zone of the cotton substrate. Therefore, insufficient heat is propagated to feed back the other part of the polymer bulk, *i.e.* the further burning process could be stopped and the target of flame quenching achieved.

CONCLUSIONS

The nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) deposited on cotton fabrics as a flame-retarding agent evidenced a desirable flame-retardancy, an 11.8-14.3% addition to the cellulosic fabric appearing as an efficient treatment for achieving this. Possibly, its action involves the loss of the hydration water in the combustion zone of the polymer, as evidenced by the thermogravimetric analysis, according to which the loss of hydration water in treated cellulose occurred over a pre-established duration of the polymer's degradation zone, which agrees with the Gas theory.

Due to its non-durability and, possibly, to the low extent to which the above-mentioned deposited salt affects, during handling, the aesthetic and mechanical properties of the fabric, it may not be recommended for garments. However, choosing cotton fabric as a handy cellulosic substrate could be beneficial for a reliable and rapid economical detection of the efficiency of organic and inorganic flame-retardants, such as the aforementioned chemical. Furthermore, the synergistic effect may be also experienced and detected by mixing this salt with appropriate amounts of different substances. Ultimately, the obtained results may be applied for other commercial uses, such as flame-retardancy of insulators, plastics or other polymers, etc.

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