

THERMOGRAVIMETRY OF DEPOSITED AMMONIUM ALUMINUM
SULFATE DODECAHYDRATE USED AS FLAME-RETARDANT
FOR COTTON FABRICS

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The effect of ammonium aluminum sulfate dodecahydrate on the flammability of 100% cotton fabric (woven with a density of 144 g/m²) has been studied. The laundered, total dried, weighed fabrics were impregnated with a suitable concentration of aqueous ammonium aluminum sulfate dodecahydrate solutions by squeeze rolling and dried at 110 °C for 30 min. They were then cooled in a desiccator, re-weighed with analytical precision and kept under ordinary conditions overnight, prior to the fulfillment of the vertical flame test, applied for determining the specimen's resistance to burning and flame spreading. The optimum add-on value of the salt to impart flame-retardancy to a cotton fabric ranged between 9.82 and 12.16 g anhydrous salt per 100 g fabric. Furthermore, thermogravimetry of both pure cotton and cotton treated with the above-mentioned additive, as well as of pure salt, was accomplished and their TG/DTG curves were compared and commented. The results obtained agree with the Dust or Wall Effect Theory, and with the Gas Dilution Theory.

Keywords: ammonium aluminum sulfate dodecahydrate, Dust or Wall Effect Theory, flame-retardancy, flammability, Gas Dilution Theory, thermogravimetry

INTRODUCTION

In the 21st century, natural and synthetic polymeric materials are used in extremely large areas and under ever more demanding environmental conditions. However, fire hazards associated with the use of these polymers, causing life losses and property destruction, are of particular concern for governmental regulatory bodies, consumers and industrial manufacturers.¹

According to the U.S. Fire Administration of the Department of Homeland Security,² between 1992 and 2001, an average of over 4,200 people were killed by fires each year in the United States and 25,000 were injured (excepting victims of the attacks on September 11, 2001). Flame-retardants are substances used in plastics, textiles, electronic circuits etc., to prevent fire spreading.³ The development of flame-retardant materials for household appli-

cations is mainly driven by the consumers' increasing safety awareness and by environmental concerns.¹

One of the most important textiles, containing mainly cellulose, is cotton, cotton fabrics holding a major share on the textile market. As they are highly inflammable, the development of successful flame-retardant systems for cotton is of major interest. Therefore researchers have studied the pyrolysis mechanism of both untreated and flame-retarded cotton fabrics.⁴

The flame-retardant may act in various ways, *i.e.* physically, chemically, or both. In fact, many types of flame-retardants are used in consumer products as inorganic materials, mainly phosphorus, antimony, aluminium and boron-containing compounds, chlorides and bromides, etc.⁵ As known, ammonium compounds provide some flame-resistance;

besides this, the use of some sulfates such as $\text{Al}_2(\text{SO}_4)_3$, ZnSO_4 and MgSO_4 etc., in extinguishers or as fire-proofing agents has been also cited in the literature.^{6,7}

The present work studies the effect of ammonium aluminum sulfate dodecahydrate as a flame-retardant system during the thermal decomposition of cotton fabric.

EXPERIMENTAL

Materials

All specimens used in the investigation – woven plain constructions, unfinished 100% pure cotton fabric with a mass of 144 g/m^2 – were pre-washed with hot distilled water and dried. The fabrics were cut as $22 \times 8 \text{ cm}$ strips along weft direction, then dried horizontally at $110 \text{ }^\circ\text{C}$ for 30 min in an oven, cooled in a desiccator and weighed by an analytical balance.

With the exception of the first bunch, several sets of specimens were impregnated with solutions of different concentrations of ammonium aluminum sulfate dodecahydrate, at $20\text{-}22 \text{ }^\circ\text{C}$.

The impregnation into the fabrics was completed by squeeze rolling, after which the samples were dried horizontally in an oven at $110 \text{ }^\circ\text{C}$, for 30 min.

Further on, the fabrics were cooled in a desiccator and re-weighed with analytical precision, so that the add-on values suitable for the specimens were obtained. The treated samples were kept overnight at a relative humidity between 65 and 67%, at an average temperature between 20 and $22 \text{ }^\circ\text{C}$, prior to the accomplishment of the flammability test, so that their humidity was re-established during this period.

Methods

Flammability Test

For the estimation of fabric combustibility, a vertical flame spread test method – Mostashari's Flammability Tester – (Fig. 1) was developed, as described in previous papers.⁸⁻¹⁹ The test method followed the procedure described²⁰ in DOC FF 3-71. The average temperature ranged between 20 and $22 \text{ }^\circ\text{C}$ and relative humidity (RH) – between 65 and 67%.



Figure 1: Mostashari's Flammability Tester with lowly treated cotton fabric after the accomplishment of the experiment

Thermogravimetry (TG)

Thermogravimetry, measuring 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,²¹ indicates how the flame-retardant affects pyrolysis, by producing more char than flammable volatiles.

Thermogravimetry plays an important role in the study of flame-retardants in polymers, as it provides important information for the evaluation and development of flame-retarded polymeric systems.²²

In the present investigation, thermal analysis was carried out for different samples, namely pulverized untreated cotton fabric and flame-retarded cotton fabric, at an optimum salt content, to impart flame-retardancy, as well as for pure salt. TG curves have been obtained for each specimen with a TG V5.1A DUPONT 2000 Thermal Analyzer. All specimens were heated from room temperature ($20 \text{ }^\circ\text{C}$) up to $600 \text{ }^\circ\text{C}$, in the presence of air, at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. Mention should be made of the fact that, prior to

thermogravimetric analysis, the fabrics were scratched by a razor blade, which permitted their pulverization.

RESULTS AND DISCUSSION

The optimum efficient content of ammonium aluminum sulfate dodecahydrate applied as a flame-retardant to the cotton fabric was obtained as the major outcome of the experiment. The experimental results, summarized in Table 1, permit to identify the burning characteristics of the specimens. Vertical flame spread tests were carefully conducted to determine the increasing quotient of the burning time (in sec. – column 4). The burning rates were calculated in cm/s, by dividing the length of the burned fabrics by their burning times, as shown in column 5. Char lengths are given in column 6, in cm. The fabric condition (after the tests) is illustrated in column 7; CB means completely burned, while FR stands for flame-retarded. It can be deduced from the above results that the efficient quantity of

ammonium aluminum sulfate dodecahydrate as a flame-retardant for cotton fabric, expressed in g per 100 g dried fabric, is of about 9.82%. This add-on value represents an efficient amount for imparting flame-retardancy to the cotton fabric. The plausible mechanism of such flame-retardancy is likely to be explained by the Dust or Wall Effect Theory. It should be also mentioned that the formation of Al_2O_3 during the combustion of treated specimens has been predicted. On the other hand, the flame-retardancy action of the Al_2O_3 that remained in the consumed ashes could be assessed, due to the Dust or Wall Effect Theory proposed by Jolles and Jolles.²³ According to this theory, “if a high enough concentration of dust is present in the air, no flame can propagate”. This phenomenon is possibly caused by the absorption and dissipation of heat by inert dust, thus causing a diminished temperature to be produced in the polymer bulk, defined as the Dust or Wall Effect.^{23,24}

Table 1
The effect of deposited ammonium aluminum sulfate dodecahydrate on cotton fabric flame-retardancy

Set ^a	Treating solution molarities	Percent (add-on) after drying at 110 °C and weighing	Burning time, (sec) Sd ^b	Burning rate, cm/s	Char length, cm	State of fabric ^c
A	Untreated	-	25 (± 1.08)	0.88	-	CB
B	0.15	5.39	20 (± 1.41)	1.1	-	CB
C	0.175	6.94	6 (± 1.52)	0.91	5.5	PB
D	0.2	9.82	-	-	0.2	FR
E ^d	0.25	12.16	-	-	0.1	FR

^a The results represent the average values obtained after five experiments; ^b Sd stands for standard deviation;

^c CB stands for completely burned, PB stands for partly burned and FR stands for flame-retarded;

^d Confirmatory tests applying excessive quantities of ammonium aluminum sulfate dodecahydrate;

Note 1: For flame-retarded (FRs) specimens, char length ≤ 2.0 cm.

The effect of the flame-retardancy of ammonium aluminum sulfate dodecahydrate can be also explained by the Gas Dilution Theory.²⁴⁻²⁶ According to this theory, 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 to dilute the flammable volatiles produced during combustion, or to play the

role of a blanket, which prevents or makes very difficult the access of the air oxygen. The TG/DTG curves of the treated fabric evidence a significant mass loss occurring around 260 °C, which is about 70 °C below to the thermal degradation zone of the untreated cotton fabric.

In fact, the thermogravimetry method was applied to measure the effects of additives on the thermal degradation and charring behavior of cotton fabric, including the initial degradation temperature, the peak of

degradation temperature and the residue obtained. Thermogravimetry results for untreated cotton and for cotton treated with an optimum addition of salt, as well as for the pure ammonium aluminum sulfate dodecahydrate, are shown in Figures 2 to 5.

The TG/DTG curves of pure cotton fabric (Fig. 2) evidence three stages: in the initial stage, at temperatures below 300 °C, the most important changes occur in some physical properties, along with a slight mass loss. Here, the cellulose damage occurred mostly in the amorphous region of the polymer. However, the main pyrolysis stage occurred over the 300-370 °C temperature range. In this stage, the mass loss is very fast and significant. In fact, most of the cellulose pyrolysis products are formed in this stage. According to literature data,²⁷ glucose is one of the major products generated, together with all kinds of combustible volatile gases. At 370 °C, char pyrolysis occurs. Above this temperature, dehydration and charring reactions continue more obviously, so that mass decomposition, dehydration and probably decarboxylation would result, while more water, carbon dioxide and other residues could be released. Hence, there results an increase in the carbon content during char formation in the decomposed products. It may be therefore concluded that cellulose pyrolysis will begin from the amorphous regions and continue in the crystalline regions. However, it has been

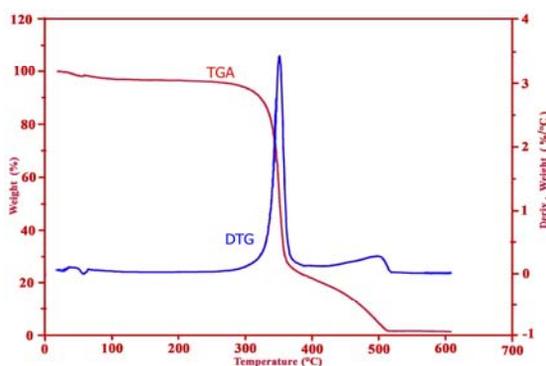


Figure 2: TG/DTG curves of untreated (UT) cotton fabrics

noted that the exact temperature ranges of pyrolysis may vary, depending on the different cellulosic materials employed and on the various experimental circumstances applied.²⁷

Figure 3 plots the TG/DTG curves of the thermal decomposition of pure ammonium aluminum sulfate dodecahydrate in dynamic air atmosphere, at a heating rate of 10 °C/min.

According to the TG curves of the untreated cotton specimen, it started a rapid decomposition at 330 °C and lost 98% of its mass at 500 °C, leaving small amounts of ash (Figs. 2 and 5, curve A). However, the treated conditioned specimen lost its mass rather smoothly and below the degradation region of cellulose (Figs. 4-5, curve C), wherefrom it can be deduced that the applied salt works as a catalyst at the combustion temperature of the polymeric substrate.

Moreover, the action of ammonium aluminum sulfate dodecahydrate involves losing its constituent compounds, such as NH₃, SO₂, N₂, CO₂ and H₂O gases in a punctual duration of the thermal degradation zone of cellulose, which confirms its flame-retardancy. It is worth mentioning that, as may be observed in Figures 3 and 5 (curve B), the mass of pure salt decreased, the afore-mentioned gases being emitted, probably, like in the case of cellulose, *i.e.* around 400 °C.

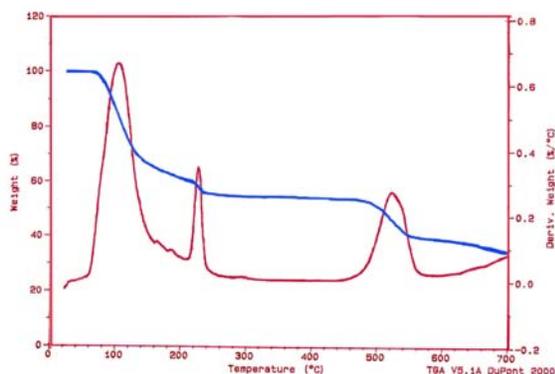


Figure 3: TG/DTG curves of pure ammonium aluminum sulfate dodecahydrate

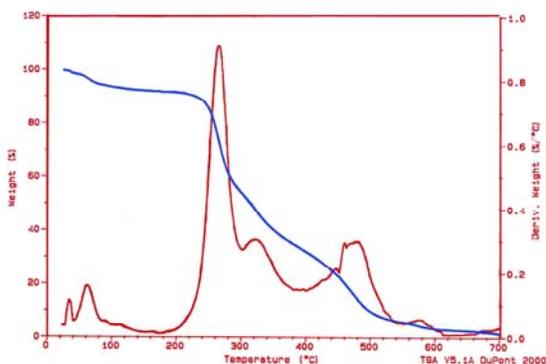


Figure 4: TG/DTG curves cotton fabric treated by ammonium aluminum sulfate dodecahydrate at an optimum addition for flame-retardancy

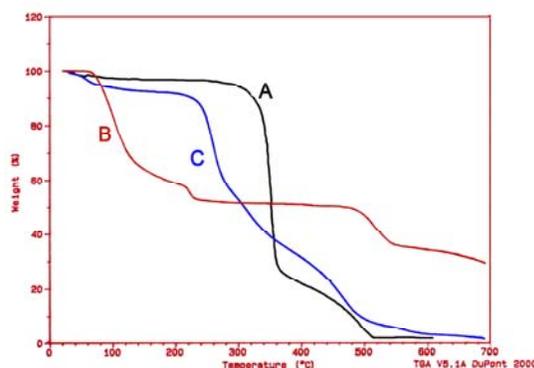


Figure 5: TG comparative curves: A – pure untreated cotton fabric; B – pure ammonium aluminum sulfate dodecahydrate; C – cotton fabric treated by ammonium aluminum sulfate dodecahydrate at an optimum addition for flame-retardancy

CONCLUSIONS

Ammonium aluminum sulfate dodecahydrate was employed to grant flame-retardancy to cotton fabric.

The results obtained showed that the optimum add-on value of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in imparting flame-retardancy to cotton fabric ranged between 9.82 and 12.16%.

It is assumed that the action of this salt involves losing its constituent compounds, namely NH_3 , SO_2 , N_2 , CO_2 and H_2O , which are non-flammable gases within the flaming zone of the burning polymer, possibly playing the role of inert or not-easily oxidizable media, thus permitting flame-retardancy. It seems that the formation of Al_2O_3 during the combustion of the treated specimens may act either as dust or as a wall, absorbing and dissipating the heat from the combustion zone and causing a decrease in temperature, so that flame-retardancy is achievable – which may be evidenced by thermogravimetry.

The choice of cotton fabric as a handy polymeric substrate may be useful for a reliable and beneficial detection of most flame-retardants, including the salt used in this study.

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