

## COMBUSTION PATHWAY OF COTTON FABRICS TREATED BY AMMONIUM SULFATE AS A FLAME-RETARDANT STUDIED BY TG

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The effect of ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$  on the flammability of 100% cotton woven fabric (plain  $144 \text{ g m}^{-2}$ , the number of yarns 21 per 10 mm) has been of interest in this study. The laundered bone-dried, massed fabrics were impregnated with suitable concentration of aqueous ammonium sulfate solutions by means of squeeze rolls, drying and conditioning. Afterwards the specimen's resistance to burning has been determined. The optimum add-on value of ammonium sulfate to impart flame-retardancy to cotton fabric was in a range about 10.55–13.62 g anhydrous salt per 100 g fabric.

Thermogravimetry (TG/DTG) of the pure cotton and the treated one with the above-mentioned sulfate as well as for pure salt were also accomplished and their TG curves were compared and commented to detect the combustion's pathway of the supported substrate. TG data confirm major mass loss in treated cotton. It occurred well below at a punctual duration of the thermal degradation zone of the polymer. So fewer flammable volatiles and more char could be produced during combustion. The results obtained are in compliance with gas dilution theory and also chemical action theory.

**Keywords:** ammonium sulfate, chemical action theory, flame-retardancy, flammability, gas dilution theory, TG

### Introduction

Each year, fires cause about 300000 deaths in the world and most of these occur at home. Residential fires comprise 75% of fires in the United States and burns are the fourth leading cause of unintentional injury related to deaths [1]. In our modern environment we are surrounded by a wide range of highly combustible materials, which under the right conditions readily ignite and burn vigorously. These materials include both natural (e.g. wood, cellulosic materials, etc.) and man-made polymers (e.g. polyester, nylon, etc.) [2]. Idea of impartation of flame-retardancy into the materials is dated back to 450 B.C. when the Egyptians used alum to reduce the flammability of wood. About 200 B.C., the Romans applied a mixture of alum and vinegar to reduce the combustibility of wood [3].

The development of flame-retardant polymers has been an important area of research over the last 40 years. The drive for new materials can be attributed to the consumer's products and also governmental regulations for fire safety in many countries [4]. With the objective of reducing the flammability of the polymeric materials, some substances are added in order to delay or even extinguish the combustion [5].

Flame-retardants are defined as chemicals that modify pyrolysis reaction of polymers or oxidation reactions implied in the combustion by slowing down or by hindering the burning process. The flame-retardant can act in various ways i.e. physically or chemi-

cally, or both. In fact many types of flame-retardants are used in consumer products such as inorganic flame-retardants, which are mainly phosphorus, antimony, aluminium and boron-containing compounds, chlorides and bromides, etc. [6]. It is mentionable that ammonium compounds are known to provide some flame resistance, besides this, the use of some sulfates such as  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{ZnSO}_4$  and  $\text{MgSO}_4$  etc. in extinguishers or as fire-proofing agents has also been cited in the scientific literature [7, 8].

Among different substances, the flammability and flame-retardancy of cotton fabric have been extensively studied and comprehensive reviews are available [9–15]. The main purpose of this work is to evaluate the effect of ammonium sulfate as a non-durable flame-retardant for cotton fabric. In addition the thermogravimetry (TG) of the deposited salt into cotton fabric was carried out, and its effectiveness on the cotton's substrate during the combustion process has been judged.

In fact TG technique played an important role in this investigation. In general this method could provide beneficial data for the evaluation and development of flame-retarding agents [5]. Therefore the affection of treatments on the combustion's pathway of the substrate could be deducible.

Regarding to ammonium sulfate it is extensively used as a fertilizer or as a fertilizer component. This salt is also the principal component in the powder material used in fire extinguishers [9]. The disadvantage

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of this chemical is its easily leach out properties. This salt also finds use in qualitative analysis for the detection of barium and strontium [10].

In the flame-retardants systems, ammonium sulfate is stated to act as an acidic salt via a dehydration mechanism, during the thermal decomposition, directing the degradation pathway of cellulose towards more char production and fewer inflammable volatiles [11]. In fact we decided to prove the proceeding of lowering the combustion's temperature when this salt was added to the cotton substrate, so that its catalytic action to push this process during combustion could be detected via TG.

However we planed to find out a combined justification for its flame-retardancy action via Gas Dilution and Chemical Action Theories.

## Experimental

### Materials

#### Sample preparation

All specimens used in this article were a 'woven' plain construction, unfinished 100% pure cotton fabric with a density of  $144 \text{ g m}^{-2}$ , the number of yarns were 21 per 10 mm, tex value of warp was 35 and for weft was 42. The samples were pre-washed with hot distilled water and dried. The fabrics were  $22 \times 8$  cm strips cut along weft direction. They were then dried horizontally at  $110^\circ\text{C}$  for 30 min in an oven, cooled in a desiccator and massed by an analytical balance.

With the exception of the first bunch, several bunches of specimens were impregnated by different concentrations of ammonium sulfate solutions at  $20\text{--}22^\circ\text{C}$  i.e. sets (B, C, D, E).

The impregnations into the fabrics were completed by means of squeeze rolls and the samples were then dried horizontally in an oven at  $110^\circ\text{C}$  for 30 min.

Afterwards the fabrics were cooled in a desiccator and re-massed with analytical precision, so that the suitable add-on values presented into the specimens were obtained. The treated samples were kept nightlong under an average of relative humidity ranged between 65 and 67% and an average temperature ranged between  $20$  and  $22^\circ\text{C}$  before the accomplishment of the flammability test, so that their humidity regain had been obtained during this period.

### Methods

#### Flammability test

A vertical flame spread test method for the estimation of the fabric's combustibility has been developed and named as Mostashari's flammability tester (Fig. 1). It was introduced in the corresponding author's ac-



**Fig. 1** Mostashari's flammability tester during the combustion. A low addition of flame-retardant was applied into the fabric, prior to the accomplishment of the flammability test

cepted article in this journal [12]. The above-mentioned tester has also been described in the previous published investigations [13–26]. The conditions of the fabrics and environment in the test were in average temperature ranged between  $20$  and  $22^\circ\text{C}$  and relative humidity (RH) ranged between 65 and 67%.

#### Thermogravimetry (TG)

TG is a technique, which 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 [27]. It indicates how the flame-retardant affects the pyrolysis, i.e. to produce more char rather than flammable volatiles.

In our investigation thermal analysis was carried out for different samples; i.e. pulverized untreated cotton fabric (1.7697 mg), and flame-retarded cotton fabric at the optimum sufficient content to impart flame-retardancy (1.8165 mg) and also for pure ammonium sulfate (1.9087 mg). By using TG analyzer (TGA V5.1A DuPont 2000), all of the specimens were heated from room temperature ( $20^\circ\text{C}$ ), upto  $600^\circ\text{C}$  in the presence of air; so that the combustion's pathway of the supported substrate could be monitored. The applied heating rate was  $10^\circ\text{C min}^{-1}$ . It is mentionable that the fabrics were scratched by a razor blade, so that their pulverization could be achievable.

## Results and discussion

Several experiments were accomplished to find out the optimum efficient content of ammonium sulfate applied as a flame-retardant into the cotton fabric. The tabulated results revealed that a bath of 0.4 molar solution of the afore-mentioned salt caused a fairly sufficient addition to impart flame-retardancy for cotton fabric. It can be concluded from the subsequent data that about 10.55–13.62% addition of  $(\text{NH}_4)_2\text{SO}_4$

per 100 g fabric is around the optimum add-on value to donate flame-retardancy to a cotton fabric.

The individual TG slopes and the comparative TG curves of untreated cotton and the treated one with optimum addition of the salt and also for the pure ammonium sulfate are shown in Figs 2–5, respectively.

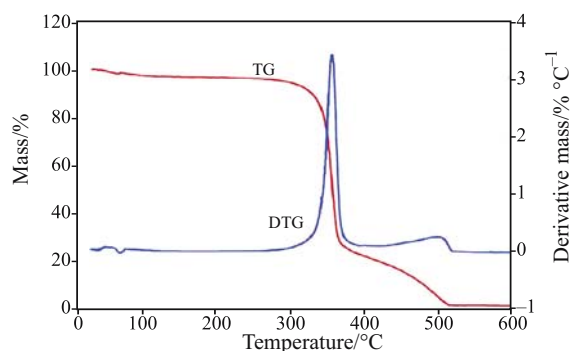


Fig. 2 TG and DTG of untreated (UT) cotton fabric

TG curve of pure cotton fabric (Fig. 2) demonstrates three stages: in the initial stage, where the temperature range is below 300°C, the most important changes are in some physical properties and little mass loss. Here, the damage to the cellulose occurs mostly in the amorphous region of the polymer. However the main pyrolysis stage occurs in the temperature range of 300–370°C. In this stage, the mass loss is very fast and significant. In fact most of pyrolysis products of cellulose are formed at this stage. According to the scientific literature [28], glucose is one of the major products generated, together with all kinds of combustible volatile gases. At 370°C the pyrolysis of char happens. Above this temperature dehydration and charring reactions continues more obviously. So the mass decomposition dehydration and probably decarboxylation could be obtained, and more water, carbon dioxide and other residues could be released. Hence the enrichment of carbon content during the formation of char in the decomposed products is the resultant. In overall it may be rationalized that: the pyrolysis of cellulose will start from its amorphous regions and continues to crystalline regions. However it seems that the exact temperature ranges of pyrolysis may vary depending on different cellulosic materials and various experimental circumstances [28].

It is noticeable that the applied salt used as a flame-retardant in this article, i.e. ammonium sulfate, decomposes by heating in two stages that can be summarized as [9]:

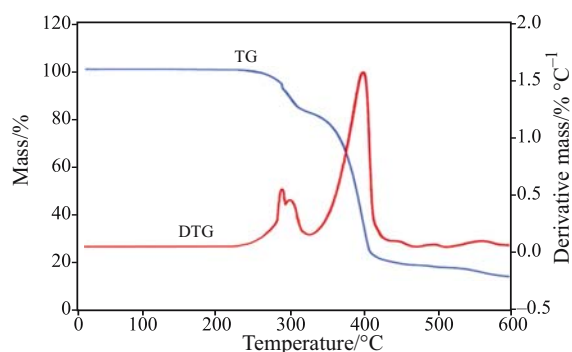
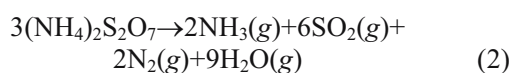
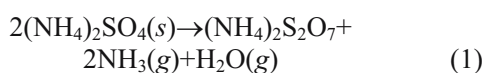


Fig. 3 TG and DTG of pure ammonium sulfate

Figure 3 shows TG/DTG curves of the thermal decomposition concerning pure  $(\text{NH}_4)_2\text{SO}_4$  in dynamic air atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ .

Referring to the TG curve concerning untreated cotton specimen, it started a rapid decomposition at 330°C and lost 98% of its mass at 500°C leaving a little ash, Figs 2 and 5, (curve a). However, the treated conditioned specimen began to lose a spectacular mass at 235°C, Figs 4 and 5, (curve c). It is noticeable that the major mass loss for untreated cotton started at 340°C and about 70% of its mass has been lost at this temperature. Though the treated sample lost the majority of its mass rather smoothly and below the degradation region of cellulose, Figs 4 and 5, (curve c); so it can be deduced that the applied salt functions as a catalyst at the combustion's temperature of the polymeric substrate. This is discussed hereinafter in the chemical action theory in this article. Moreover the action of ammonium sulfate is via losing its constitute elements as:  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$  gases in a punctual duration of the thermal degradation zone of cellulose. Hence these data are beneficial to justify its flame-retardancy.

It is worthy to mention that Figs 3 and 5, (curve b) present that the pure salt lost majority of its mass i.e. the afore-mentioned gases, most likely in a similar manner compared with cellulose, that is: around 400°C.

Therefore the effect of the flame-retardancy of ammonium sulfate via 'gas dilution theory' would

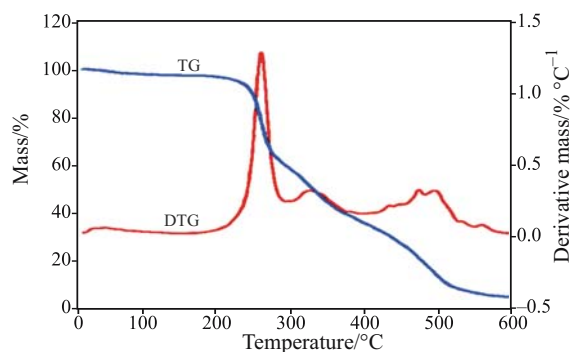
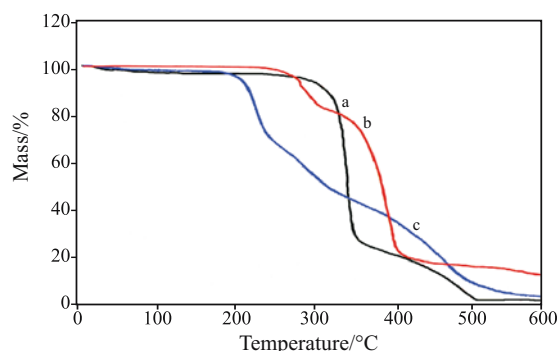


Fig. 4 TG and DTG cotton fabric treated by ammonium sulfate at the optimum addition for flame-retardancy

**Table 1** The effect of deposited ‘ammonium sulfate’ on the flame-retardancy imparted to cotton fabric (woven plain 144 g m<sup>-2</sup>)

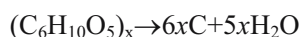
Set*	Treating solution molarities	Percent (add-on) after drying at 110°C	Burning time/s (sd**)	Burning rate/cm s <sup>-1</sup>	Char length/cm	State of the fabric***
A	untreated	–	25±1.08	0.88	–	CB
B	0.275	5.00	24±1.41	0.92	–	CB
C	0.3	7.02	4.66±1.52	1.67	7.8	PB
D	0.4	10.55	–	–	1.2	FR
E****	0.5	13.62	–	–	–	FR

\*Each experiment was reported five times and the results are averaged. \*\*sd stands for standard deviation. \*\*\*CB stands for completely burned, PB stands for partly burned, and FR stands for flame-retarded. \*\*\*\*Confirmatory tests applying excessive quantities of ‘ammonium sulfate’. Note 1: For flame-retarded (FRs) specimens the char length ≤2.0 cm. Note 2: Percent (add-on) means the mass of add-ons for treated dry cotton fabrics ×100


**Fig. 5** TG comparative curves: a – pure untreated cotton fabric, b – pure ammonium sulfate, c – treated cotton fabric by ammonium sulfate at the optimum addition for flame-retardancy

also be justifiable [29–31]. According to this theory the action of some flame-retardants is because of the generation of inert or not easily oxidizable gases such as CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, 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 the combustion process, and or to play the role of a blanket, which prevents or makes very difficult the access of the air oxygen.

As it has been indicated hereinbefore, in the introduction, the applied ammonium sulfate has an acidic nature, so the treated cellulosic substrate could be pushed through a catalytic dehydration process during the thermal decomposition as shown in the following reaction:



In general the dehydration is catalyzed by the presence of dehydrating agents such as acidic or neutral species that form Lewis acids at high temperatures. They are effective and stable in flame-retardants at normal temperatures and function only on heating and show to be ideal for commercial purposes [32].

In addition, the generation of water molecules considered by ‘chemical action theory’ as well as ‘gas dilution theory’ could be rationalized [31].

Ultimately the results of the third and fourth rows of Table 1 show under the optimum limit addition of this salt, a decrease in the burning time and an increase in the burning rate was the outcome. This observation is in favor of the literature stated by Reeves and Hammons [33]. They recognized that the inefficient quantities of certain flame-retardants accelerate the burning process of fabrics, i.e. by deposition of inadequate amounts of some flame-retardants, the imperfect rapid burning deformation occurred and a decrease in burning time and an increase in the burning rate were the resultant. Plausibly this is due to the relative rigidity donated to the cotton substrate by the use of some additives such as the afore-mentioned salt. It seems that the heat feedback into the bulk’s surface of the cellulosic substrate makes it susceptible to participate in a rapid, uncompleted surface combustion. However if sufficient quantities of the above-mentioned salt are deposited into the cotton fabric, the char conducts away the heat from the cellulosic substrate at a comparable rate, which is being supplied by the flame, so the flame-retardancy is achieved.

## Conclusions

In this investigation the effect of ammonium sulfate deposited into cotton fabric as a flame-retarding agent has demonstrated a desirable performance to donate flame-retardancy, i.e. between 10.55–13.62% addition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> manifested a fairly efficient add-on value to achieve the target of flame-retardancy. It is assigned that the action of this salt is through losing its constitute elements as: NH<sub>3</sub>, SO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O i.e. generation non-flammable gases at the flaming zone of the burning polymer, is likely to play a role to achieve this goal. This assumption could be rationalized by the evidential TG. It has been monitored that the major loss of mass in treated cellulose happened



very smoothly at a punctual duration of the polymer's combustion zone, i.e. the treatment has affected the pyrolysis process of the substrate to produce more char. As a result; fewer flammable volatiles could be produced. Therefore the 'gas dilution theory' concerning its effect is explicable. Moreover the 'chemical action theory' concerning its acidic nature through the catalytic dehydration of cellulose causing to char could also be justifiable.

Due to leaching out properties of this salt, and probably the poor affectation of the above-mentioned deposited salt on the handle, aesthetic and unfair mechanical characteristics imparted to the fabric, it may not be used for garments. However choosing cotton fabric, as a handy polymeric substrate and also by using our flammability tester a reliable and economical rapid detection for the efficiency of organic and inorganic flame-retardants could be applicable. Furthermore the synergistic effect by mixing this salt with phosphorus compounds may also be offered, experienced and detected. Ultimately the obtained results may be put in practice for other commercial applications such as: wood, insulators, plastics and polymers, etc.

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