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DETECTION OF COPPER(II) SULFATE'S UNIFORMITY AND ITS THERMAL BEHAVIOR IN FLAMMABILITY OF COTTON FABRIC

Spectrophotometric and TG analysis

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Blue vitriol (copper(II) sulfate pentahydrate), $CuSO_4{\cdot}5H_2O$ has been chosen and investigated for its effectiveness as a flame-retardant, when impregnated into cotton fabric (cotton with a plain structure; woven 180 g m^{-2}, with 22 numbers of yarns per 10 mm). Using the vertical flame test, the extent of resistance to burning of the specimens has been determined. The impregnation was accomplished via dipping and stirring of bone-dried, weighed fabrics into the individual and suitable concentrations of the salt at room temperature. Afterwards the samples were squeeze rolled and dried horizontally at 110°C for 30 min in an oven and cooled in a desiccator and reweighed with an analytical precision. They were then kept under ordinary conditions overnight prior the fulfillment of the vertical flame test. The efficient quantities of the aforesaid salt expressed in g per 100 g dry fabric have been determined in an average figure of 12.75%. Estimation of uniformity in a selected sample was carried out via a spectrophotometer and results are in favor of the heterogeneous distribution of the salt in the fabric's middle sectors. However initial and final parts of specimen showed to be rather uniformed. Thermogravimetric analysis of the pure cotton and the treated ones with insufficient and effective amounts of the salt were fulfilled and their thermograms were compared and commented. The results obtained for the effect of copper(II) sulfate comply with 'The Dust or Wall Effect Theory'. This action is also assigned to the condensed phase retardation.

Keywords: *condensed phase retardation, copper(II) sulfate pentahydrate, dust or wall effect theory, flame-retardancy, flammability, thermogravimetry*

Introduction

Nowadays most polymeric materials used in modern applications are flame-retarded. This target may be achieved by addition of chemical(s) that will interfere with one of the three requirements of combustion; i.e. heat, fuel and oxygen. These chemicals are known as fire or flame-retardants [1]. They will reduce or delay the propagation of flame through mass or surface of polymeric materials. In this regard one of the major groups used as flame-retardants in Europe are inorganic materials such as: $Mg(OH)_2$, $ZnSnO_3$, Sb_2O_3 and borates [2–4].

Hitherto, the use of some sulfates such as $Al_2(SO_4)_3$, $ZnSO_4$ and $MgSO_4$, etc. in extinguishers or as fire-proofing agents have been cited in the scientific literatures [5, 6].

The present study was accomplished for the investigation of the effect of blue vitriol or copper(II) sulfate, finishes (nondurable) on the flammability of cotton fabric (cotton plain 180 g m^{-2}). It is noticeable that the X-ray diffraction study of blue vitriol has shown that; in the penta-hydrate form, four water molecules are coordinated to the central copper in a square planar arrangement, but the fifth molecule is held by hydrogen bonds between a sulfate ion and a coordinated water molecule. This salt is a blue crystalline efflorescent solid, soluble in water. It is applied in electroplating, electrotyping and as a mordant in calico printing, as a constituent of green pigments, in white washing and as germicide and fungicide. For the last purpose, it is applied in the solution form mixed with milk of lime (Bordeaux mixture) [7]. There are different comments about the destination of $CuSO_4{\cdot}5H_2O$ on being warmed. One of the latest reliable scientific literature indicates that: 1 mol H_2O is released from it at 110°C, 2 mol H_2O at 140°C, 1 mol H_2O at 280°C and 1 mol H_2O is released at 810°C $CuSO_4$, i.e. at this temperature it transforms to $CuSO_4$.

$CuSO_4$ decomposes to $Cu_2O(SO_4)$ and releases SO_3 at 870°C. Finally $CuO(SO_4)$ decomposes to CuO and SO_3 [8]. It is mentionable that the corresponding author has tested selected different inorganic compounds to be used as flame-retardants for cotton fabric and the results have been published in recent years [4, 9–11].

Experimental

Materials

All fabrics were of 'woven' construction weighing 180 g m^{-2}, with 22 numbers of yarns per 10 mm,

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unfinished 100% cotton, laundered and dried. The samples were 22 cm by 8 cm strips cut along the left direction and pre-washed in hot distilled water. The specimens were then bone-dried horizontally at 110°C for 30 min in an oven, cooled in a desiccator and weighed by an analytical balance. The drying process was repeated until to reach a constant mass before the finishing treatment.

With the exception of the first bunch, all other bunches of fabrics were impregnated with suitable concentrations of $CuSO_4{\cdot}5H_2O$. Afterwards the fabrics were squeezed rolled and dried in an oven at 110°C for 30 min. The treated samples were then cooled in a desiccator, re-weighed with analytical precision and kept overnight under ordinary conditions before the fulfillment of the flammability test. The laboratory's environment was in average temperature ranged between 20 and 22°C and the relative humidity (RH) ranged between 65 and 67 %.

Characterization of the appartus

Flammability tester

A vertical test method for the estimation of the fabric's combustibility has been originated and named as Mostashari's flammability tester (Fig. 1). It is a rectangular aluminum frame cut on from one of its smaller sides. It has internal splits for inserting the fabric. The frame has also five even numbers of holes in each of its parallel legs, so that pining of the fabric has been possible inside it. This method was also introduced in the previous published articles [4, 9–11]. According to the aforementioned test, an aluminum frame with the following specification has been applied: two strips of 3 mm aluminum double-sheet, 22.5 by 1.5 cm are cut, perforated and welded at right angles to a shorter 9 cm strip. The conditions of the samples and environment were in average temperature ranged between 20 and 22°C and the relative humidity of 65±2%. The fabrics were conditioned overnight before the accomplishment of the flammability test. It is noticeable that all specimens were pinned tightly to frame and held vertically in a retort stand by clams with the lower edge 1.9 cm above the top of a Bunsen burner with a 3 cm yellow flame, and an ignition time of 3 s was observed. This procedure was conducted in order to avoid the harsh circumstances of ignition. The accuracy of the burning time was determined close to the nearest 0.1 s with a stopwatch and the 'char length' was measured to the nearest cm for all of the samples. The flammability test was conducted in a put out fume-cupboard prior the fulfillment of the combustion; however, the exhaust ventilator had been turned on for about 5 min, after each burning. It is mentionable that the aforesaid procedure resembles to the description in DOC FF 3-71, which has left an impression for originating this method [12].

Fig. 1 Mostashari's flammability tester with a treated fabric inserted and pinned in its internal splits, during the fulfillment of the combustion test. A sensor of a thermocouple is inserted at the end of the frame

Methods

Determination of uniformity via spectrophotometry

Pad squeeze process is known to give a certain amount of variability [4, 9–11]. At this stage, it was decided to check the salt content in different selected fragments of one individual specimen with a low add-on treatment of copper(II) sulfate. Due to blue appearance of the treated fabric, the distribution of the additive throughout the sample was examined. A spectrophotometer Junior Model 35 (PerkinElmer) with λ_{max}=620 nm was used, and a piece of treated cotton fabric with a treatment by 0.15 molar $CuSO_4{\cdot}5H_2O$ solution was chosen.

The selected sample was cut into four counterbalanced portions. Bunches A and D were related to the initial sectors of the fabric respectively. Whereas bunches B and C were related to the middle parts of the specimen. The counterbalanced pieces of fabrics were dried in an oven at 110°C for 30 min, cooled in a desiccator and weighed with analytical precision. The drying process was repeated until to reach a constant mass. They were then put into a 100 mL conical flask containing 50 mL of distilled water, then boiled for 30 min and cooled. Each remained extracted solution was transferred into a 100 mL volumetric flask and diluted with distilled water to the appropriate volume. 10 mL of this solution was transferred into another 25 mL volumetric flask. Then 5 mL concentrated ammonia solution was added into each container. Afterwards they were diluted with distilled water to the appropriate volume. A dark-blue complex was formed, so that the concentration of pure $CuSO_4$ in it could be determinable. Total add-on percent concerning $CuSO_4$ regarding insufficient salt to impart flame-retardancy was related to 4.32% of anhydrous $CuSO_4$. The beginning and final sectors of the fabric had 4.24 and 3.5% anhydrate $CuSO_4$ and the middle sectors had 4.38 and 5.39% anhydrate $CuSO_4$, respectively. These show that the initial and final parts of a specimen were rather uniform and had fewer percentages of additives. However, the middle sectors of the treated fabric illustrated to be rather heterogeneous.

Measuring of combustion's temperature

In order to have a better understanding about the temperature of combustion, the sensor of a thermocouple was inserted nearly at the end of the frame. So that the temperature of aborted inflamed fabric was, compare with those untreated ones.

Thermogravimetric analysis (TG)

Thermogravimetry 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 [8]. For a better understanding about the role of copper(II) sulfate on the flame-retardancy of cotton fabric, it was decided to fulfill thermogravimetric analysis of pure cotton and the treated ones with the above-mentioned salt. To carry out investigation a TG: V5A DUPONT 2000 thermal analyzer was used, so that the estimation of mass loss of samples during their thermal degradation could be detectable. To accomplish thermal analysis, pulverized pure cotton and the treated ones with insufficient amount and extra quantity of copper(II) sulfate for impartation of flame-retardancy were examined.

To fulfill this intention the fabrics were scratched by a razor blade so that their pulverization could be achievable. It is mentionable that all of the specimens were heated from 20 to 510°C in air. The applied heating rate was 10°C min^{-1}.

Results and discussion

The experimental results are listed synoptically in Table 1. Vertical flame test was carefully conducted to ascertain the add-on values on the subject of to the burning times in sec (column 5). In column 6 the states of the fabrics after the fulfillment of tests are given: CB stands for completely burned, FR means flame-retarded. The char lengths in cm are illustrated in column 7. It can be attributed from the experimental results expressed in moles of copper(II) sulfate per 100 g dry cotton fabric that, the optimum add-ons required to impart flame-retardancy is approximately 0.06% (column 4). In column 8 the burning rates are calculated by means of dividing the length of the combusted samples in cm by the burning times in sec. The results of the 3rd row show that inadequate amounts of the additive as a flame-retardant i.e. 6.31% of mass of the fabric or 0.04% of corresponding moles of the salt's present at 110°C decreased the burning time and increased the burning rate. This result is in favor of the literature stated by Reeves and Hammons [13]. They recognized that the inefficient quantities of certain flame-retardants, accelerate the burning process of fabrics, i.e. by using inadequate quantities of some flame-retardants, the imperfect rapid combustion takes place and a decrease in the burning time and an increase in the burning rate is the resultant. Plausibly this is due to the relative rigidity donated to the substrate by the application of some additive such as the above mentioned salt, which concentrates the heat feedback into the bulk's surface of polymer, so that makes it susceptible to participate in a rapid, uncompleted combustion. In fact, the imperfect burning of the whole length of fabric took only 19 s in comparison with duration of 31 s for untreated fabric. Moreover, by putting the sensor of a thermocouple at the end of burnt specimen, which possessed insufficient salt, the combustion's temperature was determined.

Whereas untreated fabric showed the maximum temperature of 205°C, this figure for the treated fabric with insufficient quantities of the aforementioned salt was only 99°C. Furthermore, the thick char residue formed during the burning process supports this hypothesis. However if sufficient quantities of the above-mentioned salt are used, it conducts away the heat from fabric at a comparable rate, so that at which it is being supplied from the polymer's body, therefore the flame-retardancy is obtained.

Table 1 The effect of copper(II) sulfate on the flame-retardancy imparted to cotton fabric (plain 180 g m^{-2})

Bunch no.*	Treating solution molarities	Add-on of salt/%	Related anhydrous moles/%	Burning time/s	State of the fabric**	Char length/cm	Burning rate/ cm s^{-1}
1	untreated	–	–	31.0 s.d. ±1.06	CB	–	0.70
2	0.15	6.31	0.04	13.5 s.d. ±1.27	CB	–	1.62
3	0.20	9.41	0.06	–	FR	1.3	–
***4	0.25	12.75	0.08	–	FR	0.5	–

*Each experiment was repeated five times. **CB stands for completely burned and FR stands for flame-retarded. The standard deviation for completely burned of untreated and treated samples were ±1.06 and ±1.27, respectively, ***Confirmatory tests using excessive quantities of copper sulfate

The above-mentioned reported temperatures are 30–50% less than the actual combustion temperature because considerable amount of heat as dissipated into the environment. Our TG curves are in favor of this deduction [14].

As it has been narrated in the introduction, the efflorescent salt looses water in different stages, unto 810°C. These temperatures seem to be relatively far away from the combustion and thermal degradation zone of cotton substrate, which is 350°C [15]. However the chemical ($CuSO_4$), remains intact at this temperature. Therefore, this salt in the combustion and thermal degradation zone of cotton substrate could act as a dust or wall, so that to dissipate the heat from the combustion zone i.e. the heat may be conducted away from the flaming treated fabric by dust of the remained salt. This effect is declared in the scientific literature as dust or wall effect theory [16]. According to this theory if a high enough concentration of dust is present in the flame's adjacent atmosphere, no flame can propagate. It is due to the absorption and dissipation of heat by the inert dust, causing a lowering of temperature. On the other hand, it seems that the action of the above-mentioned salt is due to its acidic nature (the pH value of its 0.1 M solution measured by a pH-meter was 3.15). Therefore the acidic nature of the salt, especially under heating condition, plausibly is to act as a dehydrating agent. The required moisture to sustain the above-mentioned role can probably be supplied by the humidity regain, subject to the fabric's conditioning process at temperature ranged between 20 and 22°C and the relative humidity (RH) of 65±2% and may also be obtained via the remained crystallization water of the salt. This complies with the catalytic molecular rearrangement via a carbonium ion mechanism [16]. So the removal of water from the cellulose molecules is the resultant. Hence the flame-retardation by the confinement of cellulose to carbon and water vapor occurs.

By all means the condensed phase retardation during the thermal degradation of cotton substrate can be explainable [15, 18]. The decomposition process via the catalytic dehydration is shown below:

$$(C_6H_{10}O_5)_x \rightarrow 6xC+5xH_2O$$

Thermogravimetric analysis of treated fabrics with two different contents of the salt was also fulfilled. The comparative curves of untreated cotton fabric and the treated ones are illustrated in Fig. 2. It is mentionable that curve A is related to the fruitless treatment, i.e. for the fabric treated by 0.15 M blue vitriol solution. Curve B is ascribed to the treatment by 0.25 M blue vitriol, which donated an excessive concentration of the salt for impartation of flame-retardancy to cotton fabric.

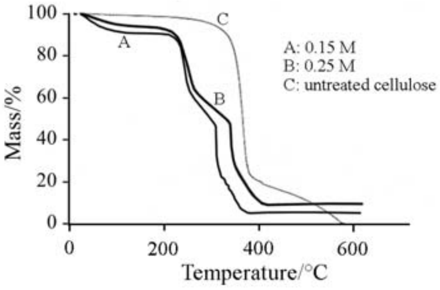

Fig. 2 TG comparative curves of untreated and treated cotton fabrics with the different content $CuSO_4$

Untreated cotton sample started a rapid thermal degradation at 330°C and lost nearly 98% of its mass at 500°C, leaving a little ash. However, the treated samples with low and high add-on of the salt illustrated three major mass losses at 240°C for both treated specimens, 350 and 370°C for low treated, 340 and 400°C for high treated sample respectively. Apparently, the crystallization water of blue-vitriol, which may be liberated in the vicinity of inflamed fabric, does not play a crucial role as an inert or not easily oxidizable atmosphere. This is due to the similarity between the behavior of losing crystallization waters for effective and ineffective quantities of the additive present in the samples. Instead of this, the relative vicinity of mass loss regarding to the treated fabric with extra content of additive, which is rather adjacent to the decomposition zone of cotton which show a desirable punctuality, seems to be the most crucial steep to justify the effectiveness of copper(II) sulfate on the flame-retardancy of cotton fabric.

Conclusions

In this investigation, the effect of copper(II) sulfate on the combustibility of cotton fabric has been studied and commented. However, this treatment is acidic and therefore degrades cotton and because of its possible irritative effect to skin it cannot be used for garments. However choosing cotton, as a handy polymeric substrate could be beneficial for a rapid assessment to detect flame-retardancy of chemicals. So these chemicals could be used in some appropriate applications such as fire extinguishers, etc. As it has been indicated in the introduction, the above-mentioned salt requires 810°C to be totally decomposed into CuO, SO_3; therefore in this investigation it is improbable to loss SO_3 in the flaming substrate. So, the intact $CuSO_4$ in the treated cotton`s substrate plays the role of dust or wall for absorption and dissipation of heat at the combustion zone of the substrate. Hence, the Dust or Wall Effect Theory is explicable to justify its action.

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