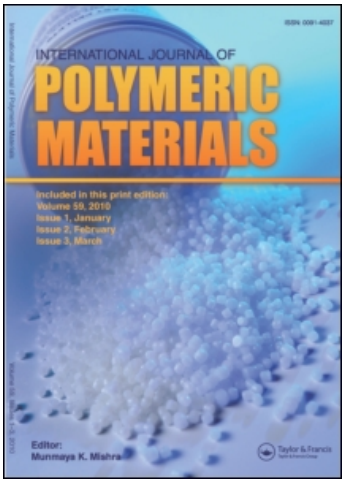

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Ammonium copper (II) phosphate [$CuNH_4PO_4$] was synthesized by means of a multiple bath method and deposited onto a laundered and dried weighed cotton fabric (woven plain construction, 180 g/m^2). This was followed by means of squeeze rolls and drying at 110°C for 30 min. The specimens were then cooled in a desiccator, re-weighed with analytical precision and kept nightlong under ordinary conditions, before the performance of the vertical flame test. The optimum addition of $CuNH_4PO_4$ to impart flame-retardancy to cotton fabric was about 13.96%. The outcomes of the vertical flame test are in compliance with Dust or Wall Effect Theory. The estimation of inhomogeneity's distribution in different parts of a selected specimen was accomplished via spectrophotometric analysis and the results express the heterogeneous distribution of the salt in various sectors of the fabric.

Keywords: ammonium copper (II) phosphate, dust or wall effect theory, flame-retardancy, spectrophotometric analysis

INTRODUCTION

Most organic materials usually undergo flaming combustion when ignited by an open flame. Once a portion of the material undergoes the flaming process, the charred residue will often be consume, through a solid-state glowing or smoldering oxidation. It is worth mentioning that all textiles including cotton fabric are susceptible to ignition. Hence to develop flame-retardant fabrics that meet minimum legislative safety

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standards is considered to be very important in the prevention and control of fires. Among fatalities due to ignition of clothing, the elderly are most at risk. Deaths due to clothing fires such as choking by smoke and toxic gases are obviously linked with other hazards caused by fires. Therefore the necessity for diminished flammability in consumer products such as building materials, carpets, curtains, fibers, and fabrics is in great demand. Cotton fabric as a handy cellulosic texture has a high susceptibility to react through solid–state glowing or smoldering oxidation as well as flame. Due to its popularity, it was decided to investigate the effect of synthesized ammonium copper (II) phosphate as phosphorus-nitrogen containing material upon its flame-retardancy. Furthermore the salt's distribution after the pad squeeze process on the cotton fabric has also been of interest in this study.

EXPERIMENTAL SECTION

Materials

All specimens were of plain construction, 180 g/m^2 of unfinished 100% pure cotton, laundered and dried. The fabrics were 22 cm by 8 cm strips cut along the weft and pre-washed in hot distilled water. The samples were then dried horizontally at 110°C for 30 min in an oven, cooled in a desiccator and weighed in an analytical balance.

Bath Treatment

Different sets of specimens were dipped and impregnated with suitable concentrations of 1.0 and 1.25 molar of sodium dihydrogen phosphate (NaH_2PO_4) solutions at 20–22°C. The applications were followed by squeeze rolling and drying horizontally in an oven at 110°C for 30 min. Afterwards, the fabrics were impregnated with admixed baths of the appropriate molarities of copper (II) sulfate ($CuSO_4{\cdot}5H_2O$), ammonium chloride (NH_4Cl) and aqueous solution of 1M ammonia (NH_3). The precipitation was accomplished following a similar procedure for ammonium zinc phosphate cited in the literature [1]. It should be mentioned that total volume of each bath was 100 ml. The treated samples were again squeeze-rolled and dried horizontally in an oven at 110°C for 30 min. They were then immersed in separate dishes of tap water and distilled water containing 0.1 molar ammonia to remove sodium hydrogen sulfate from the fabric and also to avoid the formation of undesirable hydrolysis equilibrium yielding $CuHPO_4$.

The equations are shown below:

$$NaH_2PO_4 + CuSO_4 \rightarrow CuHPO_4 + NaHSO_4 \quad (1)$$

$$CuHPO_4 + NH_4OH \rightarrow CuNH_4PO_4 + H_2O \quad (2)$$

$$CuNH_4PO_4 + H_2O \leftrightarrow CuHPO_4 + NH_4OH \quad (3)$$

Finally the samples were again dried horizontally in an oven at 110°C for 30 min, cooled in a desiccator and re-weighed with analytical precision. It should be mentioned that the specimens were conditioned nightlong in a relative humidity ranging between 65 and 67% and an average temperature ranging between 20°C and 22°C before the performance of the Vertical Flame Test.

Flammability Test

A vertical test method following the procedure described in the literature [2] was originated and named Mostashari's Flammability Tester. The description of this tester is presented in the author's previous article in this journal [3].

Determination of Inhomogeneities Distribution of Ammonium Copper (II) Phosphate via Spectrophotometric Analysis

Pad squeeze process is known to give a certain amount of variability [4–11]. 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 ammonium copper (II) phosphate. Due to the blue appearance of the treated fabric, the heterogeneous distribution of the additive in the sample was examined. A spectrophotometer JUNIOR Model 35 (Perkin-Elmer) with $\lambda_{max} = 620$ nm was used,

TABLE 1 Spectrophotometric Determination Concerning the Distribution of Ammonium Copper (II) Phosphate in Different Sectors of a Treated Cotton Fabric

Sector Additive %	A	B	C	D	E	F	G	H	Total Additive %
Spectrophotometric Analysis	5.32	5.66	6.15	6.33	4.96	5.08	5.70	5.74	5.65
Drying at 110°C and weighing	5.64	6.00	6.51	6.92	5.25	5.38	6.04	6.10	5.98

and a piece of fabric having 6.10% of the salt was chosen. The selected sample was cut into eight equal-sized portions. Batches A-H correspond to each individual sector of the fabric (Table 1). The equal-sized pieces of fabric were dried in an oven for 30 min, cooled in a desiccator and weighed in an analytical balance. They were then put into individual 100 ml conical flasks containing 20 ml 0.1M H_2SO_4 and boiled so the $CuNH_4PO_4$ molecules could break down, forming $CuSO_4$ solution. Each solution was neutralized by adequate amounts of concentrated ammonia solution. Then 10 ml additional volume of ammonia was added to each flask, so that a dark blue complex was formed. Each solution was transferred into a 100 ml volumetric flask and diluted by distilled water to 100 ml. Ultimately, total add-on percent of $CuNH_4PO_4$ was obtained in each piece by spectrophotometric analysis (Table 1).

RESULTS AND DISCUSSION

Apart from spectrophotometric analysis, which is discussed hereafter, it is worth mentioning the different baths using several concentrations of the aforementioned treating solutions were put in practices for the detection of flammability of the treated cotton fabrics. The obtained results via our vertical flammability tester ascertained the positive effect of ammonium copper (II) phosphate on the burning time. Meanwhile the burning rates were calculated by means of dividing the length of the combusted samples by the burning time in sec. These figures for untreated fabric were 31 sec and 0.70 cm/sec respectively. Interestingly, by the use of insufficient percent of this salt, i.e. up-to 7.74% addition by the application of 1.0 M treating solution into the fabric, a complete burning of 22.5 sec was experienced. Moreover, the burning rate average increased up-to 0.97 cm/sec. Nevertheless, using a higher percent of the treating baths, i.e. the concentration up to 1.25 M, caused about 13.96% deposition into the cotton fabric. In fact, a fairly sufficient impartation of flame-retardancy has been experienced at this range of deposition. As it has been mentioned, below the optimum level 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 [12]. They distinguished that insufficient amounts of certain flame-retardants accelerate the burning process of fabrics, i.e., by deposition of inadequate quantities of some flame-retardants, accelerated burning, a decrease in burning time, and an increase in the burning rate was the outcome. Plausibly this is due to the relative rigidity imparted to the cotton substrate by the application of some additives such as the

aforementioned salt. It seems that the heat feedback into the surface of the cellulosic substrate makes it susceptible to participate in a rapid, incomplete surface combustion. However if sufficient amounts of the above-mentioned salt are deposited into the cotton fabric it conducts the heat from the cellulosic substrate at a comparable rate controlled by the flame. Hence the flame-retardancy is achieved. In other words, the role of dust or wall described in Dust or Wall Effect Theory stated by Jolles and Jolles [13] could be justified. The action of $CuNH_4PO_4$ in the combustion's zone is likely to be similar to the role of $ZnNH_4PO_4$ during the burning process [1]. It seems that under ignition conditions, ammonium copper (II) phosphate loses water vapor and ammonia as well. Therefore copper (II) pyrophosphate is the result:

$$2CuNH_4PO_4 \rightarrow Cu_2P_2O_7 + 2NH_3 + H_2O$$

This copper (II) pyrophosphate tends to play a role as a dust or wall in the combustion's zone [13]. This action is assigned to the absorption and dissipation of heat, causing a lowering of temperature, so that flame-retardancy is achievable (14).

In regard to spectrophotometric data concerning the distribution of $CuNH_4PO_4$ deposited into a selected cotton fabric, the results are given in Table 1. They indicate the presence of inhomogeneities in the treated fabric. However, the percent addition via drying at 110°C and weighing was slightly above the determined add- on percent obtained via spectrophotometric analysis. This may be due to the hydroscopic properties of the treated cotton fabric to sustain a little moisture, and partly due to minor experimental errors.

CONCLUSION

Ammonium copper (II) phosphate as a phosphorus-nitrogen containing compound displayed an acceptable flame and glow retardancy, probably because of the synergism between these two elements. It may be deduced that its efficiency relies on Dust or Wall Effect Theory. Spectrophotometric analysis of deposited salt in different pieces of the same specimen of a treated cotton fabric proved the presence of inhomogeneities concerning its distribution. These data support the suggestion that the pad squeeze process causes a certain amount of variability. A Furthermore, differences between the obtained additive percents via drying at 110°C and weighing and spectrophotometric data is explained by moisture pickup and partly due to experimental errors.

Due to the poor effect of the above-mentioned deposited salt on the handle, aesthetic and poor mechanical characteristics imparted to the fabric, it can not be used for garments. Other applications in other polymeric materials such as wood and insulators may be practical.

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