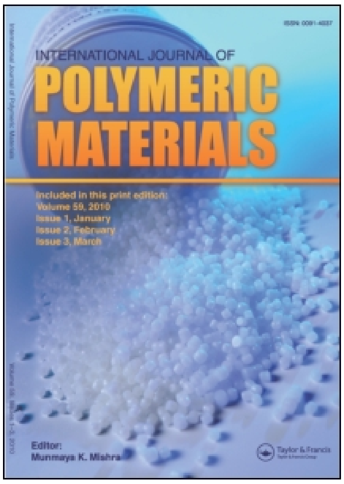

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A Combination of Red Phosphorus-Zinc Chloride for Flame-Retardancy of a Cotton Fabric

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In this investigation, the combination of red phosphorus with zinc chloride was found to be effective for flame-retardancy of a pure cotton fabric. The fabrics were dipped in individual aqueous suspensions of red phosphorous and/or the zinc chloride; meanwhile, some sets were impregnated with appropriate admixed solutions of both chemicals. The vertical flame spread test was accomplished to characterize the flammability of the specimens. A suitable synergistic effect was then experienced by using an admixed bath containing 0.15 formal red phosphorous and 0.15 formal zinc chloride solutions to impart flame-retardancy to a cotton fabric. The optimum mass of the mixture required to donate flame-retardancy was about 5.6 g anhydrous additives per 100 g fabric. The results obtained are mainly in favor of Free Radical Theory.

Keywords: flame-retardancy, flame-retardant, free radical theory, red phosphorous, zinc chloride

INTRODUCTION

Halogenated chemicals combined with synergists (e.g. antimony trioxide (Sb_2O_3), melamine and their derivates), and/or red phosphorus are among the flame-retardant agents currently used for polyamides. Moreover, halogen compounds are generally recognized as effective flame-retardants for polymeric materials [1].

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Halogenated flame-retardants apparently act in the vapor phase by interfering with free-radical chain reactions in the flame. Chlorine containing flame-retardants are less expensive, offer good light stability, but require high amounts to achieve the required flame-retardancy. They are thermally less stable and more corrosive to the equipment as compared to brominated ones [2]. These materials introduce halogens into the combustible matrix and, during combustion, release various halide species, including hydrohalides that react with free radicals. Highly reactive combustion products thereby suppress combustion [3].

On the other hand, there are several advantages to phosphorus compounds when utilized as flame-retardants. They possess high flame-retardant efficiency, less production of corrosive, toxic gases in flames, and less destruction to the earth's environment. When burning, the phosphorus-based flame-retardants form foamed cellular crusts as barriers between flame and the underlying polymer, which results in prolongation of burning time or extinguishing of fire [4]. Phosphorus compounds enhance the effectiveness of the halogens. Lyons suggested that phosphorus oxyhalides may be formed that are more effective radical traps than the halogen or halogen compounds by themselves [5].

As regards the nature of flame-retardancy concerning phosphorous compounds in conjunction with halogen components, the synergistic effect of zinc chloride and red phosphorous on the flame-retardancy of a cotton fabric was investigated. It should be mentioned that while the additive effect is the sum of the individual actions, the effect of synergism is higher than this sum [6].

EXPERIMENTAL

Materials and Methods

All fabrics were a plain (woven) construction of unfinished 100% cotton fabric weighing $150\,g/m^2$ laundered and dried. They were then cut along the warp direction in 22×8 cm strips and pre-washed in hot distilled water. Afterwards the samples were dried horizontally at 110°C for 30 min in an oven, cooled in a desiccator, and weighed with an analytical precision.

With the exception of the first set, all other sets of specimens were dipped independently at 20–22°C and stirred for 5–10 min with suitable concentrations of red phosphorous or zinc chloride and/or their combinations. They were then rendered uniform by means of squeeze rolls. Afterwards they were dried horizontally in an oven at 110°C for 30 min. The fabrics were then cooled in a desiccator and reweighed with an analytical balance. All the samples were kept overnight under ordinary laboratory conditions before the performance of the flammability test, so their humidity was regained during this period. The laboratory's environment was an average temperature ranged between $20 \pm 2°C$ and the relative humidity (RH) ranged between $65 \pm 2\%$.

Method (Flame Spread Test)

A vertical flame spread test method by impression from the procedure described in DOC FF 3-71 [7] was designed and developed to determine the flammability of fabrics. It has been originated and named as Mostashari's Flammability Tester. This method was introduced in the corresponding author's published articles [8–15,25]. The description of this tester has also been introduced in the author's published article in this journal [16].

RESULTS AND DISCUSSION

When the combinations of red phosphorous-zinc chloride were used, no uniformity could be observed during the burning process. This indicates uneven impregnation onto the fabric, due to the presence of inhomogeneities in the pad-squeezing process which caused certain amounts of variability. The experimental results are summarized to identify the burning characteristics of the treated samples in Table 1. Vertical flame spread tests were carefully conducted to clarify the effect of additives on the burning times; these data are given in column 5.

In column 6 the states of samples at the completion of testing are shown: CB for completely burned, PB for partly burned and FR for flame-retarded. The char lengths in cm are illustrated in column 7. The burning rates are calculated by means of dividing the length of fabrics by their burning times in sec, these data are given in column 8. The add-on percents of red phosphorous, zinc chloride and their combinations are shown in column 9. It can be deduced from the experimental results in the ninth column that the efficient quantity of red phosphorous as a flame-retardant expressed in g per 100 g dried fabric is about 4%. This figure for zinc chloride-treated fabric is about 7.34%. Moreover, the data concerning the combination of 0.15 F red phosphorous and 0.15 F zinc chloride showed about 5.6% gain on the weight of samples. This addition is an efficient amount for imparting flame-retardancy to a cotton fabric. The plausible

TABLE 1 The Synergistic Effect of Deposited Red Phosphorous-Zinc Chloride on the Flame Retardancy Imparted to Cotton Fabric (Woven 150 g/m^2)

Set* no	Treating solution red phosphorous (Formalities)	Treating solution zinc chloride (Formalities)	Treating solution admixed bath red phosphorous: $ZnCl_2$ respective (Formalities)	Burning time (sec)	State of the Fabric**	Char length (cm)	Burning rate (cm/s)	Percent add-on 110°C and weighing
A	untreated	–	–	27	CB	–	0.81	–
B	0.3	–	–	16.3	CB	–	1.35	2.3
C	0.35	–	–	4	PB	3.6	0.9	3
D	0.4	–	–	–	FR	1.5	–	3.95
E	–	0.25	–	15.5	CB	–	1.42	4.97
F	–	0.3	–	–	FR	1.2	–	7.34
G	–	–	0.125–0.125	17	CB	–	1.29	4.17
H	–	–	0.15–0.15	1	FR	2.0	–	5.6
***1	–	–	0.175–0.175	–	FR	0.5	–	6.95

*Average of 5 tests for each set of samples.
**CB completely burned, PB for partly and FR flame-retarded.
***Confirmatory tests using excessive amounts of the additives.
Note: For flame-retarded (FR) samples char length $\leq$2.0 cm.

mechanism of such flame-retardancy seems to be in favor of Free Radical Theory [6,17].

In general the mode of action of halogenated flame-retardant is based on the formation of the hydrogen and hydroxyl free radicals by breaking of chemical bonds in the polymer. They are high in energy and will act as fuel during the combustion process. The radical mechanism takes place in the gas phase and is interrupted by halogenated flame-retardants. The exothermic processes concerning generation of especially reactive radicals such as H and OH, are thus stopped, the system cools down and the supply of flammable gases is reduced and eventually completely suppressed. The chemistry of the FR system will govern as to when the FR system will start trapping the high-energy free radicals. Hence Free Radical Theory could be justified [2,18].

$$RX^\bullet \longrightarrow R^\bullet + X^\bullet$$

$$X^\bullet + RH^\bullet \longrightarrow R^\bullet + HX$$

$$HX + H^\bullet \longrightarrow H_2 + X^\bullet$$

$$HX + OH^\bullet \longrightarrow H_2O + X^\bullet$$

It is noticeable that $X^\bullet$ radicals formed by series of reaction are low in energy.

It is noticeable that zinc chloride used in the above-mentioned synergism has a low melting point of 365°C as an anhydrous salt. The bond Zn−Cl is partly ionic and partly covalent [19].

Although zinc chloride serves as flame-retardant, it promotes smoke and glowing [20]. It should be mentioned that in this work, when $ZnCl_2$ was combined with red phosphorous on the cotton fabric, no afterglow was observed during the flammability test.

Overall, although it seemed a spectacular effect happened by using red phosphorous by itself as a flame-retardant, its synergism (using an admixed bath of 0.15 F red phosphorous and 0.15 F zinc chloride) donated 5.6% dry add-one to the fabric. This addition is proven to be a sufficient quantity for impartation of flame-retardancy to the cotton fabric.

The tabulated results show that inadequate amounts of red phosphorous and/or zinc chloride decreased the burning times and hence increased the burning rates, which agrees with the general trend reported by Reeves and Hammons [21].

It is worthy to notice that the synergistic effect between elements and their related compounds to achieve flame-retardancy has currently gained a great significance. The synergism of nitrogen-phosphorous, antimony-halogen, phosphorous-halogen, and phosphorous-silicon has also been mentioned in the scientific literature [22–30].

CONCLUSION

The red phosphorous/zinc chloride binary combination system is an effective flame-retardant for cotton fabric. This is due to their assicity to increase the formation of solid char rather than volatile combustible products when the polymer is subjected to thermal decomposition. The Free Radical Theory seems to be involved in this action. Moreover, because of the production of inert or not easily oxidizable gases, i.e. HCl and H_2O generated during the combustion, they are likely to play some role in the above-mentioned synergism. That is, vapors generated in the flame zone modify the atmosphere in the burning process in the fabric's vicinity and reduce the flammable volatiles produced or may play the role of a diluent. Thus they prevent or make very difficult the accessibility of the atmospheric oxygen into the burning zone, so the goal of flame-retardancy could be achieved. The low addition of this combination is advantageous to avoid physical and mechanical deleterious properties such as poor-handle of the fabric substrate.

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