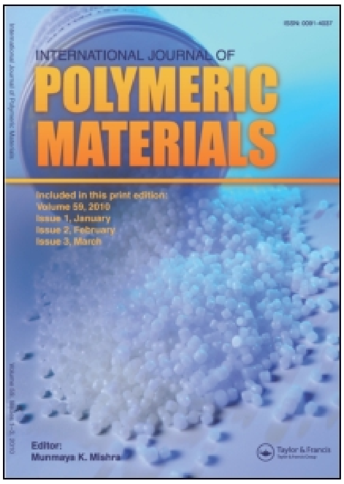

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Synergistic Effect of Sodium Polymetaphosphate-Urea on the Flame-Retardancy Imparted to a Polyester Fabric

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The synergistic effect between sodium polymetaphosphate (Calgon) and urea on the flame-retardancy of a polyester fabric (plain construction weighing 160 g/m^2) is described in this study. The laundered bone-dried weighed specimens were impregnated with suitable concentrations of individual aqueous sodium polymetaphosphate (Calgon) or urea solutions and some sets were impregnated with appropriate admixed solutions of both chemicals. A vertical flammability test was then carried out. An acceptable synergistic effect was obtained using an admixed bath containing 0.4 molar sodium polymetaphosphate and 4.0 molar urea solutions for imparting flame-retardancy to a polyester fabric. The optimum weight of the mixture needed to impart flame-retardancy was about 36.52 g anhydrous additives per 100 g fabric. The results obtained are in favour of "phosphorus-nitrogen synergism" required to retard the flame. They comply with "chemical theory," "gas theory," and "condensed phase retardation."

Keywords: chemical theory, condensed phase retardation, flame-retardancy, gas theory, sodium polymetaphosphate (Calgon), synergism, urea

INTRODUCTION

The significance of the incorporation of flame-retardants into composite materials has become more and more important. The need to comply with safety requirements in several consumer products, and to reduce the flammability of organic materials, textiles, and soon have also been recognized by governmental legislations in many countries [1]. Hence the necessity for diminished combustibility and reduced flammability in consumer composites in various applications such as building

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materials, automotive components, aerospace, polymers, textiles, and soon is in great demand these days. Virginia Department of Fire Programs announced that: The U.S. has one of the highest fire death rates in the industrialized countries for 1998; the U.S. fire death rate was 14.9 deaths per million population. Between 1994 and 1998, an average of 4,400 Americans lost their lives and another 25,100 were injured annually as the result of fires [2]. Furthermore, a U.S. Fire Administration Study released on March 31, 2005 showed that more than 3,000 die in residential fires each year [3]. The cost both in human lives and in financial terms of fires caused a pressure on the industries to develop flame-retarded products that meet minimum legislative safety standards.

Among the aforementioned materials, textiles usually undergo flaming combustion when ignited by an open flame. Once an amount of the material is consumed by the flaming reaction, the charred residue will often continue to react through a solid-state glowing or smouldering. In fact, all textiles, with few exceptions, are flammable and a fire hazard is probable. It is worthy to mention that the elderly are at high risk of fatality because of the ignition of clothing. While fatalities due to clothing fires are obviously linked with the flammability of textiles, there are other hazards caused by fires including the combined effects of smoke and toxic gases. The major effect of smoke is to reduce visibility and to make escape from the vicinity of the fire more difficult [4].

Overall, the necessity for decreased flammability and minimized combustibility in consumer products has gained a great significance nowadays.

Most flame-retardant treatments formulations and additives were developed in the 1950–1980 period [5], and those possessing current commercial interest have been very recently reviewed. In general, a flame-retardant is a component or mixture of compounds that when added or incorporated chemically into a polymer serves to hinder the ignition or growth of fire [6]. It should be mentioned that the flame-retarding component is intended to prevent a small fire from rapidly developing into a major catastrophe [7]. However, a flame-retarded substance is believed to be combustible in the intense ignition circumstances. It is noticeable that different inorganic compounds including $Mg\ (OH)_2$, $ZnSnO_3$, and so on had been categorized as an important group of flame-retardants used in Europe in 2003 at 36% level of total chemicals sold for this purpose. It is also mentionable that the value of halogen-based organics and phosphorus-based chemicals had been forecasted to be used as 26% and 38%, respectively [8–9].

One of the most interesting subjects of flame-retardancy is the synergism between elements and their related components. The synergism of nitrogen-phosphorus, antimony-halogen, phosphorus-halogen, and so on has also been mentioned in the scientific literature [10–17]. While the additive effect is the sum of the individual actions, the effects of synergism are higher than this sum [18]. In this regard, very early use was made of antimony oxide in conjunction with chlorine-containing compounds, the methods being somewhat empirical, but attempts were then made in various publications to explain the favorable outcome [19]. It is worthy to notie that antagonism in the flame-retardation of polymers is less known and documented [20]. The purpose of this investigation is to prove the influential synergistic combination of sodium polymetaphosphate (Calgon) or "Graham's Salt (Na_6 P_6O_{18})" and urea deposited as a nondurable finish for the flame-retardancy imparted to a polyester fabric.

EXPERIMENTAL

Materials and Methods

All samples were plain construction fabrics weighing 160 g/m^2, unfinished 100% polyester, laundered and dried. The specimens were 8 × 22 cm strips cut along the weft direction and pre-washed in hot distilled water. The fabrics were then dried horizontally at 110°C for 30 min in an oven, cooled in a desiccator, and weighed accurately with analytical precision. This method has also been developed and introduced in previous investigations [11–12,21–32].

Bath Treatment

With the exception of the first set, all other sets of specimens were dipped independently at 20–22°C and stirred for 10 min in suitable concentration solutions of calgon or urea or their combinations by means of "squeeze" rolls, and then dried horizontally in an oven at 110°C for 30 min. They were then cooled in a desiccator and reweighed with an analytical balance. The treated fabrics were kept overnight under ordinary conditions before carrying out the vertical flammability test, so that some humidity was regained during this period. The laboratory's environment was in average temperature ranging between 20°C and 22°C and the relative humidity (RH) ranged between 65 and 67%.

CHARACTERIZATION OF THE APPARATUS

Flammability Tester

A vertical test method following the procedure described in DOC FF 3-71 [33] was employed to determine the flammability of the fabrics.

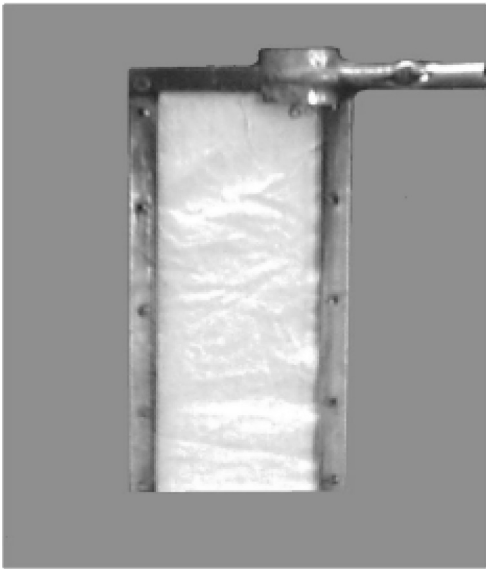


FIGURE 1 Mostashari's Flammability Tester with an untreated fabric before the accomplishment of the experiment.

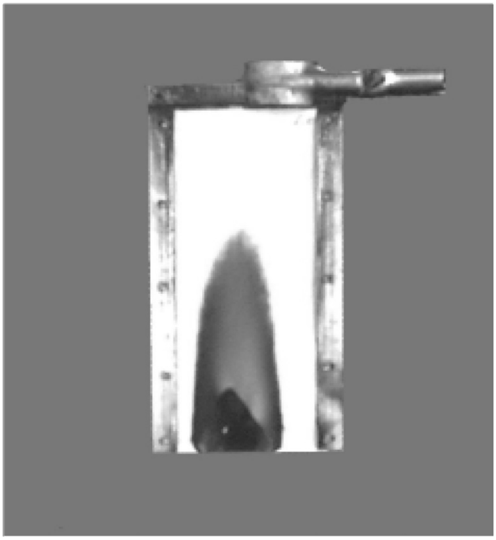


FIGURE 2 Mostashari's Flammability Tester during the burning experiment.

It has been designed and named as Mostashari's Flammability Tester (Figures 1 and 2). The aforementioned method has also been described and published in previous investigations [11–12,21–32].

RESULTS AND DISCUSSION

The experimental results are summarized to identify the burning characteristics of the specimens in Table 1. Vertical flame tests were carefully conducted to determine the add-on values on the burning times in seconds in column 6. The state of the specimens after the accomplishment of tests are illustrated in column 8, CB means completely burned, FR stands for flame-retarded. The burning rates in cm/s, calculated by means of dividing the length of the burned fabrics by their burning times, are given in column 9. It can be deduced from the experimental results in the fifth column that the efficient quantity of sodium polymetaphosphate (calgon) as a flame-retardant expressed in g per 100 g dried fabric is about 43.65%. The figure for urea treated fabric has also been determined as 46.51%. Moreover, the results of the fifth column illustrate that the combination of 0.4 M, sodium polymetaphosphate and 4.0 M urea donated about 36.52% weight gain to the specimens. This add-on value is an efficient amount for imparting flame-retardancy to the polyester fabric. The plausible mechanism of such flame-retardancy seems to be in favor of the *Chemical Theory* stated by Little [34].

According to this theory, the flameproofing action of some chemicals is to promote the formation of solid char rather than volatile pyrolysis products. In fact, the experimental observations showed a black carbonaceous texture remaining after the completion of the burning process, that is, the remaining carbonaceous texture indicated the outcome of the thermal decomposition because of a catalytic dehydration in which carbon and water are produced. In other words, during the thermal degradation, the carbon content present in the fiber has been confined to the solid phase. Consequently the decomposition process occurred via the catalytic dehydration process yielding water vapor and char. It is mentionable that urea has high nitrogen content of 46.7%, [35], but it has a little effect on the flame-retardancy. It is noticeable that the mode of action of nitrogen-containing flame-retardants is still not well understood in the scientific literature [36]. Nevertheless, there are some explanations to clarify the performance, which indicate that nitrogen-based flame-retardants such as melamine and melamine derivatives act by intumescence [19]. The gases by-products of intumescence are mainly CO_2 and NH_3, which are liberated in the vicinity of the thermal degradation zone of the

TABLE 1 Synergistic Effect of Deposited Sodium Polymetaphosphate (Calgon)-Urea on the Flame-Retardancy Imparted to a Polyester Fabric (*Plain* $160\,g/m^2$)

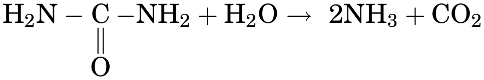
Set no.[*]	Treating solution Calgon formality	Treating solution urea molarity	Treating solution (admixed bath) Calgon-urea-respective formality and/or molarity	Percent add-on drying at 110°C and weighing	Burning time	Char. length (cm)	State of the fabric[**]	Burning rate (cm/s)
1	Untreated	—	—	—	12.0	—	CB	1.83
2	0.60	—	—	39.08	36.1	0.6	CB	0.61
3	0.65	—	—	43.65	—	0.2	FR	—
4	—	8.0 at 50°C	—	43.95	60	—	CB	0.36
5	—	9.0 at 50°C	—	46.51	2	1.3	FR	—
6	—	—	0.35, 3.5	46.51	45.5	—	CB	0.48
7	—	—	0.4, 4.0	36.52	—	—	FR	—

[*] Average of 5 tests for each set of samples.

[**] CB completely burned and FR flame-retarded.

substrate, making the material swell and form an isolating char on its surface. This complies with the *Gas Theory* [34]. According to this theory the action of some flame-retardants is due to the generation of inert or not easily oxidizable gases such as CO_2 NH_3, H_2O, and so on. These gases may be liberated in the vicinity of the inflamed fabric. Hence the adjacent atmosphere will be modified or diluted from the flammable gasses produced during combustion. The aforementioned effect causes oxygen depletion around the flaming material, so that the flame snuffs out.

The desired reaction of urea seems to be accomplished via the following equation [37]:



$$H_2N-\underset{\underset{\displaystyle O}{\|}}{C}-NH_2 + H_2O \rightarrow 2NH_3 + CO_2$$

The required water to sustain the aforementioned reaction, when urea is used by itself, may probably be supplied by the humidity regained during this fabric's conditioning process. However, if urea is applied in conjunction with sodium polymetaphosphate, a synergistic effect on the flame-retardancy between sodium polymetaphosphate-urea is achievable. As mentioned above earlier several authors have demonstrated the synergistic effect of phosphorus-nitrogen compounds, although many of them pointed out an individual mechanism to clarify the role of each additive.

In industry, sodium polymetaphosphate is incorrectly called sodium hexametaphosphate [38]. This name is wrong because it does not contain six $[PO_4]$ units and is a high molecular weight polymer, $(NaPO_3)_2$, which usually has a mean weight of 12000–18000, and up to 200 $[PO_3]$ units in the chain. Although mainly made up of long chains, it does contain up to 10% of ring metaphosphates and a little crosslinked material [39].

In fact, sodium polymetaphosphate (calgon) as a phosphorus-containing compound has also demonstrated a tendency towards flame-retardancy. Troitzsch [36] stated that such compounds mainly influence the reactions taking place in the condensed phase. They are particularly effective in materials with high oxy-content, such as cellulose and oxygen containing plastics, and are converted by thermal decomposition to phosphoric acid, which in the condensed phase extracts water from the pyrolyzing substrate, causing it to char. That is: the phosphoric acid formed, esterifies and dehydrates the oxygen-containing polymer and causes charring. However, Jolles and Jolles [40] stated that phosphorus compounds form phosphoric acid on heating, which coat the surface of the polymer as a stable coating material and cause it to become a carbonaceous residue. Overall, it seemed that no spectacular effect happened by using the individual aforementioned additives. Despite this, their synergism by using an admixed bath of 0.4 M sodium polymetaphosphate and 4.0 M urea donated 36.52% dry add-on to the fabric. This addition is proven to be about sufficient quantity for imparting flame-retardancy to the polyester fabric.

CONCLUSION

The combination of sodium polymetaphosphate (Calgon) and urea deposited onto a polyester fabric to impart flame-retardancy confirmed an acceptable synergism performance. This is due to their collaboration to promote the formation of solid char rather than volatile combustible products, when the polymer is subjected to thermal decomposition. Hence, the chemical theory and the "condensed phase retardation" may be involved to justify this action. Moreover, the "gas theory" because of the intumescence and subject to the production of inert or not easily oxidizable gases, seems to play some decisive role in the aforementioned synergism. These gases modify the atmosphere in the fabric's vicinity and reduce the flammable gases produced during the combustion, or play the role of a cover. So they prevent or make very difficult the access of the atmospheric oxygen, therefore the goal of flame-retardancy is achieved.

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