Effect of Deposited Ammonium Bromide as Flame-Retardant on the Flame-Retardancy Imparted to Cotton Fabric

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In this work, the effect of ammonium bromide as a non-durable finish on the flammability of 100 % cotton fabric, (woven construction, weighing 160 g/m^2) has been investigated. The laundered bone-dried, weighed fabrics were impregnated with suitable concentrations of aqueous ammonium bromide solutions by means of squeeze rolls and dried at 110°C for 0.5 h. Afterwards they were cooled in a desiccator, reweighed with an analytical precision and kept under ordinary conditions before the fulfillment of the vertical flame test. The optimum add-on values to impart flame retardancy expressed in g anhydrous ammonium bromide per 100 g fabric were about 6.64-7.81 %. The results obtained follow the free radical theory.

Key Words: Flammability, Aluminium bromide, Flame-retardancy, Free radical theory, Mohr analytical method.

INTRODUCTION

Flame-retardants should inhibit or even suppress the combustion process. Depending on their nature, flame-retardants can act chemically and or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process. They may intercept heating, decomposition, ignition or flame spread[1]. The main requirement for all flame-retardants is to decrease the rate and intensity of combustion of the material and as a consequence, to decrease the formation in rate and toxic substances such as carbon monoxide, soot and in some cases, hinder the generation of hydrogen cyanide. Modern safety standards require self-extinguishing capability of a product when it is exposed to the most common sources of fire found in its normal surroundings[2].

A substance must fulfill several requirements as a flame-retardant. A flame-retardant must be inexpensive, stable to heat and in some cases to light and preferably colourless. It must not drastically change the physical and mechanical properties of the final product and it must be stable at temperatures at which the product is formed. It should decompose around

the same temperatures at which the polymer itself begins to decompose, which is normally between 200 and 300ºC[3-6].

Another requirement is that the flame-retardant does not itself release toxic substances that might be toxic either immediately or in the long run[2]. In case of halogen compounds, the effectiveness of halogen-containing flame-retardants increases in the order F < Cl < Br < I. It is suggested that fluorine and iodine-based flame-retardants are not used in practice because they interferes with the combustion process at the right point. Fluorine cannot become effective as a radical interceptor in the gas phase because of its strong bond to carbon. Iodine in contrast is attached to carbon so loosely that it is liberated by even a negligible energy supply. As a result, the polymer's properties (*e.g.* light stability) are affected and the flame-retardant effect is already lost in the combustion's temperature range or in the zone of pyrolysis[1].

Of the two remaining halogens, bromide is the more effective since its weaker bonding to carbon enables it to interfere at a more favourable point in the combustion process. It is assumed, moreover, that the effective agent, HBr, is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone. In contrast with it, HCl, which is formed over a wider temperature range and is present at lower concentrations, is thus less effective[7]. Therefore flame-retardants containing bromine are usually more effective, on a molar basis, than those containing chlorine. On the other hand, bromine atoms are much heavier than chorine atoms.

Despite the high cost of bromine relative to chlorine and a significant increase in the mass of the polymer caused by bromine compounds, brominated flame-retardants are often preferred[2]. In order to meet both the flame-retardancy and desired mechanical properties of the product, most bromine containing flame-retardants are used as additives, usually should not be more than 30 % of the mass of the final product.

The aim of this study is to investigate the effect of deposited ammonium bromide as a non-durable finish for the impartation of flame-retardancy to cotton fabric. It is also suggested that ammonium bromide is used as a flame-retardant especially for chipboard. It is also used in manufacturing photographic chemicals and emulsions[8].

EXPERIMENTAL

All fabrics were a woven construction, weighing 160 g/m^2, unfinished 100 % cotton, laundered and dried. They were 22 × 8 cm strips cut along the warp direction and pre-washed in hot distilled water. The specimens were dried at 110ºC for 0.5 h in an oven, cooled in a desiccator and weighed with analytical precision.

Bath treatment: With the exception of the first bunch, all other samples were impregnated with suitable concentrations of ammonium bromide at 20ºC. Afterwards they were squeeze rolled and dried horizontally in an oven at 110ºC for 0.5 h and then they were cooled in a desiccator and reweighed with an analytical balance so that the suitable add-on presented into the specimens were obtained. The treated fabrics were kept over night under ordinary conditions before the fulfillment of the flammability test, so that the humidity regain could be obtained during this period.

Determination of uniformity *via* Mohr analytical method: Pad squeeze process is known to give a certain amount of variability[9-19]. At this stage, it was decided to check the salt content in different selected fragments of one individual specimen with a related add-on treatment of ammonium bromide. So a piece of finished cotton fabric, 22×8 cm, with a treatment by 0.35 M ammonium bromide solutions was chosen.

The selected specimen was cut into four counterbalanced portions. Sets A and D were related to the initial and final sectors of the fabric, respectively. However sets B and C were related to the middle parts of the sample. The counterbalanced pieces of fabrics were dried in an oven at 110ºC for 0.5 h, cooled in desiccator and weighed in an analytical balance. They were put into a 100 mL conical flask containing 50 mL of distilled water. Afterwards they were boiled for 0.5 h by hot distilled water. The specimen was cooled and shaken. Each extracted solution was transferred into a 100 mL volumetric flask and diluted with distilled water to the appropriate volume. The amount of anhydrous ammonium bromide in the finish was calculated by titration of bromide anion *via* Mohr method.

The bromide anions were determined by titration with a standard 0.01 normal solution of $AgNO_3$, using 5 % K_2CrO_4 solution as an indicator. The beginning and final sectors of the fabric showed to possess 6.43 and 6.00% anhydrous ammonium bromide. However the middle sectors of the sample showed to possess 6.42 and 6.14 % anhydrous salt, respectively. These show that the initial and final sectors of the specimen were rather heterogeneous. However the middle parts of the finished fabric illustrated to be rather uniform.

Flammability test: A vertical test method for the estimation of the fabric's combustibility has been originated and named as Mostashari's flammability tester[13-19]. It is a rectangular aluminium 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 as pining of the fabric has been possible inside it. This method was also introduced in the previous published articles[9-11,13].

In this test, an aluminium frame with the following specification has been applied. Two strips of 3 mm aluminium double-sheet. 22.5×1.5 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 22ºC and the relative humidity of 65 ± 2 %. The fabrics were conditioned overnight before the accomplishment of the flammability test. It is suggested that all specimens were pinned tightly to frame and held vertically in a retort stand by clamps with the lower edge 1.9 cm above the top of a Bunsen burner with a 3 cm yellow flame and then 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 for all of the samples and also the char length was measured to the nearest 0.1 cm. 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.

RESULTS AND DISCUSSION

The experimental results are given in Table-1. It can be attributed from the experimental results that about 6.64 % of ammonium bromide in the dried sample are efficient to impart flame-retardancy to the fabric. It is also noted that the mode of action of bromine containing compounds to act as flame-retardants comply with the free-radical theory[12,20]. According to this theory, the mechanism taking place in the gas phase during combustion is believed to involve the formation of high-energy OH, H, O and the like radicals formed during combustion which can support the afore-mentioned process, so that their removal or conversion can help to suppress the flame. To achieve this target it would be beneficial if these active radicals could be converted to less active ones. Actually this suppression is believed to occur *via* chlorine or bromine compounds when used as flame-retardants:

$$RX + {}^{\bullet}H \rightarrow HX + {}^{\bullet}R \qquad (X = Cl \text{ or } Br)$$

It is worthwhile to mention that R is a less active radical than H. It is also noted that brominated flame-retardants absorb the required quantity of energy and the C-Br bonds will break homolytically. The free bromine atoms formed by this process react with the polymer's hydrogen atoms, generating hydrogen bromide molecules. These HBr molecules also play a significant role in hindering the chain reaction that occurs during the propagation of fire or combustion process. They may, for instance, inhibit or deactivate ${}^{\bullet}$OH radicals as follows:

$$^{\bullet}OH + HBr \rightarrow H_2O + {}^{\bullet}Br$$
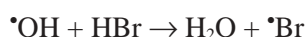
The newly formed free bromine radical regenerates HBr *via* capturing free hydrogen radical present in the gaseous phase or by reacting with the polymer's body:

$$^\bullet H + {^\bullet Br} \rightarrow HBr$$

$$RH + {^\bullet Br} \rightarrow HBr + {^\bullet R}$$
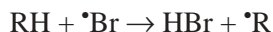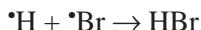
The major overall effect is that; the heavy bromines atoms withdraw energy from the combustion-propagation zone or from the burning region[2,12].

TABLE-1
EFFECT OF DEPOSITED AMMONIUM BROMIDE ON THE
FLAME-RETARDANCY IMPARTED TO COTTON FABRIC
(WOVEN CONSTRUCTION WEIGHING 160 g/m^2

Set No.*	Treating solution NH_4Br (M)	Per cent (add-on) drying at 110ºC and weighing	Burning time (s)	Char length (cm)	NH_4Br (%) (exp)**	Bromine (%) (exp)**	State of fabric
1	Untreated	-	30	-	-	-	CB
2	0.20	3.34	17	-	3.11	2.54	CB
3	0.25	4.54	12	17	4.29	3.50	PB
4	0.30	5.71	4	5	5.51	4.50	PB
5	0.35	6.64	-	-	6.25	5.10	FR
6	0.40	7.81	-	-	7.56	6.17	FR

*Average of 5 tests for each set, **Exp = experimental data *via* Mohr method,
***CB = completely burnt, PB = partially burnt, FR = flame-retarded

Conclusion

In this work, the action of ammonium bromide deposited as a flame-retardant into cotton fabric has been investigated. Its capability can be attributed to the generation of bromine free radicals ascribed in free radical theory. Due to non-durability, the aforementioned deposited salt on the handle, aesthetic and mechanical properties of the fabric, cannot be recommended for application in garments. However, selecting cotton fabric as a polymeric substrate may be useful for a reliable and beneficial detection of most flame-retardants. Moreover the synergistic effect between flame-retardants could be economically assessed with cotton fabric using the orginated vertical test method. Ultimately the obtained results may be put in to practice for some other commercial purposes such as insulators, plastics and polymers.

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