SUPERIORITY OF LITHIUM BROMIDE OVER LITHIUM CHLORIDE USED AS FLAME-RETARDANTS ON COTTON SUBSTRATES

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The effect of lithium bromide as compared to lithium chloride, as non-durable finishes, on the flammability of 100% cotton fabric (woven construction, weighing 151 g/m^2) has been investigated in the present article. The laundered, bone-dried, weighed specimens were impregnated with suitable concentrations of aqueous lithium bromide and/or lithium chloride solutions by means of squeeze rolls and then dried at 110 °C for 30 min. Afterwards they were cooled in a desiccator, re-weighed with an analytical balance and kept under ordinary conditions before carrying out the vertical flame test. The optimum add-on values conferring flame retardancy, expressed in g anhydrous lithium bromide and lithium chloride per 100 g fabrics, were found to be about 3.85% and 7.5%, respectively. The thermogravimetric analysis (TGA) of pure cotton and of the fabrics supported by salts at optimum additions was performed and the thermograms were then compared and commented. The results obtained proved the superiority of lithium bromide in imparting flame retardancy as compared to lithium chloride. Overall, the additions comply with *Free radical theory* in explaining flame-retardancy. The results may provide some beneficial data and assessments to be put into practice for commercial purposes, such as in the dope of insulators, plastics and polymers.

Keywords: flammability, lithium bromide, lithium chloride, flame-retardancy, *Free radical theory*

INTRODUCTION

Fabrics made from cellulosic fibers are generally good absorbers of liquids and vapors. Moreover, when wet, their durability increases. However, they have a tendency to wrinkle easily and have been found to be extremely flammable. Even at a low ignition temperature, cotton may be ignited in about 2 seconds. Once ignited, it burns quite readily, that is, it may support combustion after ignition starts in the open air. Besides, the removal of the ignition source could produce the afterglow. In fact, the carbonaceous residue continues to combust the fabric until it is eventually decomposed entirely into a fluffy ash. The flammability characteristics of its fiber are reasonably poor.[1]

To overcome this deficiency, flame-retardants could be added to this material. Flame-retardants are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion zone by slowing down or by inhibiting the burning process. They can act in various ways, *i.e.* physically or chemically. Many types of flame-retardants are used in consumer products. They are mainly phosphorus, antimony, aluminum and boroncontaining compounds, chlorides and bromides etc.[2]

Halogen-containing flame-retardants became more often used in the 1970s. The 1980s witnessed a high increase in the use of brominated systems. Currently bromine-based flame-retardants are the most widely used of the halogen systems. In the early 1990s, approximately 150000 metric tons of halogen-based flame-retardants were consumed annually worldwide, which is more than 25% of the total flame-retardant market.[3]

Halogen-containing flame-retardants (FRs) have been used in engineering thermoplastics and epoxy resins to improve their thermal stability and fire resistance performance.[4] 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 and their compounds are more expensive than chorine components.

However, despite the high cost of bromine compared to chlorine, and despite a significant increase in the mass of the polymer caused by the application of bromine compounds, the brominated flame-retardants are generally preferred.[5] Halogenated flame-retardants are postulated to function primarily by a vapor phase flame inhibition mechanism through radical reaction.[6]

The aim of this research is to investigate the superiority of flame-retardancy of lithium bromide *versus* lithium chloride as non-durable flame-retardants imparted onto cotton fabric.

EXPERIMENTAL
Material
All fabrics (unfinished 100% cotton, plain construction, weighing 151 g/m2) have been laundered and dried. They were cut into 22 × 8 cm strips, along the warp direction, and pre-washed in hot distilled water. The samples were then dried in an oven, at 110 °C for 30 min, cooled in a desiccator and weighed with an analytical balance.

Bath treatment
With the exception of the first set, all the other samples were impregnated with suitable concentrations of lithium bromide and/or lithium chloride at 20 °C. Afterwards, they were squeeze-rolled and dried horizontally in an oven, at 110 °C for 30 min, [7-18] cooled in a desiccator and re-weighed with analytical precision so that suitable add-on values could be obtained.

Flammability test
A vertical tester for determining the flammability of fabrics – Mostashari's flammability tester – was designed. The procedure performed was similar to that described in DOC FF 3-71[19] (Fig. 1).

Figure 1: Mostashari's flammability tester with a treated cotton fabric during the test

This method has also been mentioned in some previous articles.[7-18]

Thermogravimetric analysis
Thermal analysis was carried out on untreated cotton fabrics and on those treated with lithium bromide and/or lithium chloride, by using a Thermogravimetric analyzer (TGA V5.1A DUPONT 2000). All of the samples were heated from room temperature up to 600 °C in the presence of air.

RESULTS AND DISCUSSIONS
The experimental results are listed in Table 1. The vertical flame test was carefully conducted to ascertain the add-on values as related to the burning time period, in seconds (column 5). In column 4, the percents of lithium bromide and/or lithium chloride are given, respectively. In column 6, char lengths are illustrated. In column 7, the states of the fabrics after carrying out the tests are given. CB stands for completely burnt, PB – for partially burnt and FR – for flame-retarded.

It can be deduced from the above-mentioned experimental results that the optimum addition values to impart flame-retardancy to cotton fabrics, expressed in g anhydrous lithium bromide and lithium chloride per 100 g samples, were individually obtained as about 3.85% and 7.5%, respectively. It is noteworthy that the mode of action of halogen-containing compounds as flame-retardants is in compliance with the *Free radical theory*.[20] According to this theory, the mechanism taking place in the gas phase during combustion process is believed to involve the formation of high-energy OH, H, O and similar radicals formed during burning, which can support the afore-mentioned process, so that their removal or conversion can help to put out the flame.

More precisely, to achieve this target, it would be beneficial if these active radicals could be converted to less active ones. In fact this suppression is believed to occur by chlorine and/or bromine compounds when applied as flame-retardants as follows:

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

Table 1
Comparison between the effect of deposited lithium bromide and lithium chloride on the flame-retardancy
imparted to cotton fabric (woven construction weighting 151 g/m^2)

Set No*	Treating solution LiBr (molarity)	Treating solution LiCl (molarity)	Percent (add-on) drying at 110 °C and weighing	Burning time (S)	Char length (Cm)	State of the fabric**
1	Untreated	—	—	27	—	CB
2	0.10	—	2.71	14.3	—	CB
3	0.15	—	3.85	—	1.4	FR
4***	—	0.70	5.30	7	—	CB
5	—	0.75	5.60	3	3.2	PB
6	—	0.80	7.50	—	1.0	FR

*Average of 5 tests for each set. **CB stands for completely burnt, PB for partly burned and FR means flame-retarded. *** Confirmatory tests using excessive quantities of salts. Note: For flame retarded (FR) samples char length ≤ 2.0 cm.
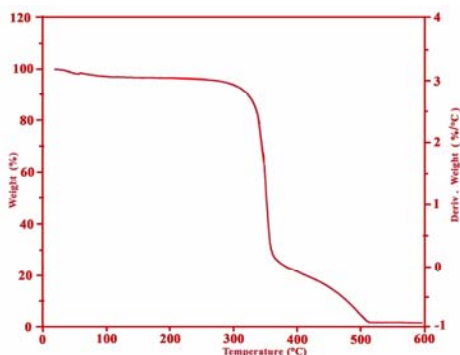

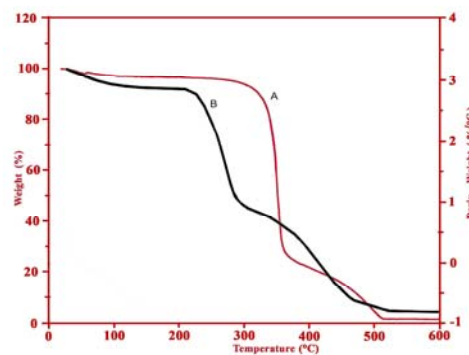Figure 2: TGA spectra of untreated (UT) cotton fabric

Figure 3: TGA spectra of flame-retarded cotton fabric treated at optimum addition of LiCl to achieve flame-retardancy
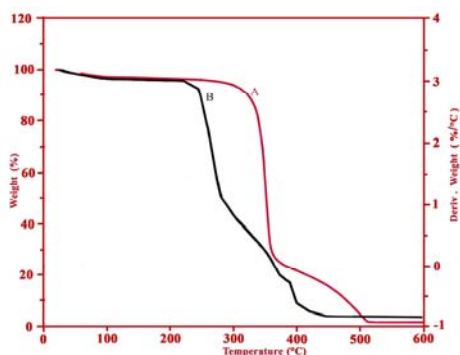

Figure 4: TGA spectra of flame-retarded cotton fabric treated at optimum addition of LiBr to achieve flame-retardancy
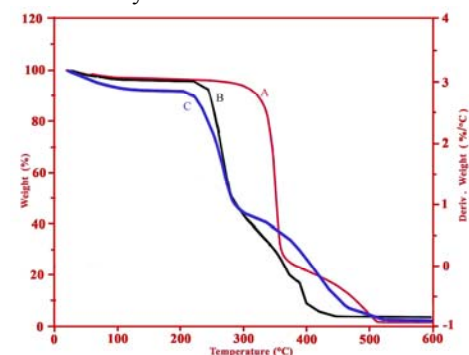

Figure 5: Combined curves of A: TGA spectra of UT cotton fabric; B: TGA spectra of FR cotton fabric treated by lithium bromide at optimum addition; C: TGA spectra of FR cotton fabric treated by lithium chloride at optimum addition

It is worth mentioning that •R is a less active radical than •H. It is also noticeable that halogenated flame-retardants absorb the required amounts of energy and the C-X (X =

halogen) bonds will break homolytically. The free halogen atoms generated by this process react with the polymer's hydrogen atoms, forming hydrogen halide molecules. These HX molecules also play an important role in hindering the chain reaction that occurs during the propagation of combustion or burning process. They may, for instance, deactivate or inhibit •OH radicals as follows:

$^{\cdot}OH + HBr \rightarrow H_2O + ^{\cdot}Br$

$^{\cdot}OH + HCl \rightarrow H_2O + ^{\cdot}Cl$
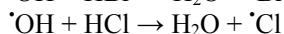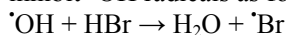
Then the newly formed free halogen radicals re-generate HX by capturing the free hydrogen radical present in the gaseous phase or by reacting with the polymer body:

$^{\cdot}H + ^{\cdot}X \rightarrow HX$

$RH + ^{\cdot}X \rightarrow HX + ^{\cdot}R$
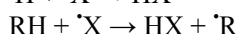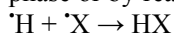
Various other reactions are proposed. Generally, the important effect is that the halogen atoms withdraw energy from the combustion-propagation region or from the burning zone so that the flame-retardancy is achieved.[5]

Thermal analysis and pyrolysis of cellulose

Thermal analysis was accomplished at a heating rate of 10 °C/min. The DTG and TGA of the cotton samples demonstrate that the pyrolysis of cellulose includes three stages: the initial stage, the main one and char formation/decomposition. The related temperature, speed and weight loss of every stage can be found from the TGA curves.

The TGA of pure cotton fabric (Fig. 2) shows three stages: in the initial stage, where the temperature range is below 300 °C, the most important changes occur in some physical properties, a slight weight loss being also recorded. Here, the damage to the polymer happens mostly in the amorphous region of cellulose. However, the main pyrolysis stage happens in the temperature range of 300-370 °C. In this stage, the weight loss is very fast and significant. Most pyrolysis products are considered to be generated in this stage. Glucose is one of the major products, together with all types of combustible vapors.[21]

Ultimately, above 370 °C, the dehydration and charring reactions tend to be completed. The thermograms illustrate that the flame-retarded cotton fabric treated with the optimum addition of lithium chloride underwent two mass losses: around 270 °C and 420 °C, respectively (Fig. 3). Note that

the corresponding decomposition temperature for the fabric treated with lithium bromide at its optimum range of flame-retardation zone is around 260 °C (Fig. 4).

The comparative TG curves illustrate that a significant mass loss happened rather smoothly below the degradation zone of pure cellulose (Fig. 5). TG/DTG data permit to deduce the catalytic dehydration of the substrate by the application of lithium bromide and/or lithium chloride, since the thermal degradation of cellulose treated by these salts occurred at a well blow temperature range as compared to the degradation range of untreated cotton fabric. Nevertheless, lithium bromide is more effective than lithium chloride, as only a minor treatment, with reaction concentration, is enough to gain the same efficiency in fire retardation.

The similarity of the major weight loss at these temperature shows that the action of the afore-mentioned salts is assigned *via* loosing of hydrogen–halides and water vapors in a punctual duration zone of cellulose thermal decomposition. Hence, the explanation for the flame retardancy of these salts by the Free-radical theory would be reasonable.[17] Moreover, the TGA results could also explain the Lewis acidic effects of these salts applied as flame-retardants. The plausible mechanism of flame-retardancy using these types of flame-retardants relies on the Chemical theory,[20] explaining the formation of solid carbon residue, *i.e.* generation of char rather than of volatile pyrolysis products when the polymer is subjected to thermal degradation. That is, decomposition of the cellulose substrate could be forced to form carbon residue (char) and water vapor *via* the catalytic dehydration process shown below:

$(C_6H_{10}O_5)_x \rightarrow 6xC + 5xH_2O.$
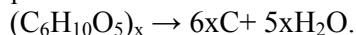
Ultimately, gases such as CO_2, H_2O, HBr and HCl, released when using these flame-retardants, may assist interruption of the burning process, i.e. the atmosphere in the vicinity of the inflamed cotton substrate is changed, dilution of the flammable vapors formed during combustion thus resulting. These gases may act as a blanket, preventing or making very difficult the access of air oxygen.[5] Therefore, the combination of fuel, oxygen and heat, *i.e.* of a fire triangle, to sustain the burning process, will be broken.[5]

CONCLUSIONS

A comparison between the efficiency of lithium bromide *versus* lithium chloride on the flame-retardancy imparted to the cotton fabric has been examined and commended *via* a vertical flammability tester, and also by thermogravimetric analysis of untreated and treated fabrics, at their optimum addition. Both salt-treated fabrics demonstrated a desirable flame-retardancy. However, lithium bromide appeared as much effective than lithium chloride, because a minor treatment with reaction concentration is needed for attaining the same performance of fire retardation. Their actions have been assigned to the liberation of the free halogen radicals in a punctual duration zone of cellulose thermal degradation. The hydrogen halides formed in the combustion zone of the cotton substrate act as a diluant of the flammable gases, or as a blanket, preventing the access of air oxygen and thus causing snuffing out of burning. Moreover, the acidic nature of the salts applied to the cotton fabric made it susceptible to form char and water vapor *via* catalytic dehydration during burning.

Ultimately, application of the vertical flammability tester evidenced the superiority of lithium bromide *versus* lithium chloride, in a 3.85/7.50 ratio, at optimum addition, for achieving the flame-retardancy of the cotton fabric. It should be noticed that the above-mentioned water-soluble salts could not be applied for the flame-retardancy of garments, however these results may provide some beneficial data and assessments to be put in practice for some other commercial purposes, such as in the dope of insulators, plastics and polymers.

REFERENCES

[1] P. Bhatt, Air Transfer Safety, 3710, (2000).
[2] H. Demir, E. Arkıs, D. Balköse and S. Ülku, *Polym. Degrad. Stab.*, **89**, 478 (2005).
[3] F. J .W. J. Labuschagne, W. W. Focke and J. C. Mentz, SA Patent No. 2001/4876, assigned to University of Pretoria, 2002.
[4] E. Kandare, G. Chigwada, D. Wang, C. A. Wilkie and J. M. Hossenlopp, *Polym. Degrad. Stab.*, **91**, 1209 (2006).
[5] M. Kesner and W. J. DeVos', *J. Chem. Educ.*, **78**, 41 (2001).
[6] J. Jang, H. Chung, M. Kim and H. Sung, *Polym. Test.*, **19**, 269 (2000).
[7] F. M. Farhan, S. M. Mostashari and G. Ghazi Moghaddam, *Int. J. Chem.*, **1**, 117 (1990).
[8] F. M. Farhan, S. M. Mostashari and G. Ghazi Moghaddam, *Int. J. Chem.*, **2**, 163 (1991).
[9] S. M. Mostashari, *Asian J. Chem.*, **17**, 434 (2005).
[10] S. M. Mostashari, *Int. J. Chem.*, **13**, 115 (2003).
[11] S. M. Mostashari and M. R. Babaei Chaijan, *Asian J. Chem.*, **17**, 1469 (2005).
[12] S. M. Mostashari and S. M. Golmirzadeh, *Asian J. Chem.*, **17**, 2007 (2005).
[13] S. M. Mostashari and A. Darsaraei, *Int. J. Chem.*, **15**, 89 (2005).
[14] S. M. Mostashari, M. A. Zanjanchi and O. Baghia, *Combustion, Explosion and Shock Waves*, **41,** 426 (2005).
[15] S. M. Mostashari and A. Farkhondeh, *Asian J. Chem.*, **17**, 2803 (2005).
[16] S. M. Mostashari and S. Baie, *Cellulose Chem. Technol.*, **41**, 341 (2007).
[17] S. M. Mostashari, M. A. Zanjanchi, H. F. Moafi, S. Z. Mostashari and M. R. Babaei Chaijan, *Polym.-Plast. Technol.*, **47**, 307 (2008).
[18] S. M. Mostashari and S. Z. Mostashari, *Polym.-Plast. Technol.*, **47**, 313 (2008).
[19] U. S. Department of Commerce Standard for Flammability of Children Sleepware (DOC.FF 3-71), Federal Register, **36**, July 19, 1971.
[20] R. W. Little, "Flame Proofing Textile Fabrics", American Chemical Society Monograph Series No. 104, Reinhold Publishing, New York, 1947.
[21] P. Zhu, S. Sui, B. Wang, K. Sun and G. Sun, *J. Anal. Appl. Pyrol.*, **71**, 645 (2004).