

# A COMPARISON BETWEEN ALKALINE EARTH METAL CHLORIDES AND THEIR CARBONATES AS FLAME-RETARDANTS FOR COTTON FABRICS

SEYED MOTERZA MOSTASHARI

*Faculty of Science, University of Gilan,  
P.O. Box 1914, Rasht, Iran*

Received April 14, 2008

The comparative effect of alkaline earth chlorides and/or carbonates on the flammability of a cotton fabric has been investigated. The vertical flame spread test evidenced that the optimum loading of both alkaline earth chlorides and/or carbonates increased with increasing their molecular weight, the explanation of this phenomenon being provided by the Free-Radical, Gas and Dust or Wall Effect theory. Moreover, the superiority of alkaline earth chlorides, with regard to their carbonates, on the flame-retardancy of cotton fabrics was verified.

**Keywords:** alkaline earth chlorides, alkaline earth carbonates, flame-retardancy, Free-Radical theory, Dust or Wall Effect theory

## INTRODUCTION

In recent years, several investigations have been devoted by the author to the efficiency of different inorganic materials as flame-retardants for cotton fabrics.<sup>1-19</sup> Fabric flammability has been studied by earlier described procedures. The studies evidenced the superiority of metals, with regard to their position in the periodic table, in imparting flame-retardancy to cotton fabric, *i.e.*, in lowering the ability of alkaline earth chlorides and/or carbonates, in correlation with their higher stability values. In fact, to gain the same performance of flame-retardancy by means of chlorides and/or carbonates from group II of elements, a harmonious deficiency, with regard to the position of alkaline earth metals in the periodic table, has been exemplified.

The present study compares the higher efficiency of selected alkaline earth metal chlorides, *versus* their carbonates, in imparting flame-retardancy to cotton fabric. Moreover, the correlated comparative curves illustrating the optimum percent quantities of the above-mentioned chemicals to achieve flame-retardancy for a cotton fabric *versus* the atomic weight of the metals have been

drawn,<sup>18,19</sup> so that their superiority should be visible. For a better explanation, data on the physico-chemical specifications of earth metal chlorides have been gathered and tabulated. Mention should be made of the fact that the experiments on flame-retardancy with beryllium and radium compounds were abandoned, due to the toxicity of beryllium dust which, in contact with the skin, causes dermatitis, while its dust or smoke inhalation causes a disease called berylliosis, quite similar to silicosis.<sup>20</sup> The application of radium compounds has not been accomplished, due to their scarcity and radioactivity.

## EXPERIMENTAL

All materials and procedures have been described elsewhere.<sup>1-19</sup> However, a detailed description of the flammability test is comprehensively provided below.

### *Flammability test*

A vertical flame spread test method for the estimation of fabric's combustibility – Mostashari's Flammability Tester (Fig. 1) – has been proposed. It is based on a rectangular aluminum frame cut on from one of its smaller

sides. The frame has inner grooves for inserting the fabric and five pairs of holes in each of its parallel legs, permitting to pin and fix the fabric inside it. The frame has two strips of 3 mm double sheet, cut 22.5 by 1.5 cm, perforated and welded at their right angles to a shorter 9 cm strip. Experimental conditions applied: average temperature – between  $20 \pm 2$  °C, relative humidity –  $65 \pm 2\%$ . Prior to the flammability test, the specimens were conditioned overnight. Each sample was pinned tightly to the 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. The ignition time was of 3 s. The procedure was applied to avoid the harsh circumstances of ignition. The accuracy of the burning time, determined with a stop-watch, was close to 0.1 s and char length was measured (in cm), for all fabrics. The flammability test was conducted in a put out fume cupboard, prior to the accomplishment of each experiment. Nevertheless, the exhaust ventilator was turned on for about 5 min, at the end of the burning. The above-mentioned method<sup>21</sup> was inspired by the procedure described in DOC FF 3-71.

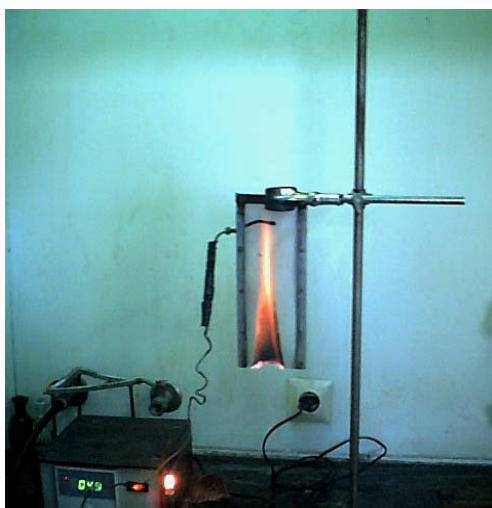


Figure 1: Mostashari's Flammability Tester with an inserted and pinned specimen in its internal splits, during the accomplishment of the flammability test

#### Graphical presentation

A Windows XP system with an Excel program was used, permitting the representation of the relative comparative curves.

The optimum added percent of the selected anhydrous alkaline earth chlorides and/or carbonates is illustrated in Table 1. Other tabulated data on the physico-chemical specifications have been taken over from different scientific sources.<sup>20,22,23</sup>

## RESULTS AND DISCUSSION

The data listed in Table 1 reflect the general trends concerning the relationship between the optimum percent of alkaline earth chlorides and/or carbonates present in dry specimens to impart flame-retardancy to cotton fabrics (woven, 200 g/m<sup>2</sup> with 20 yarns per 10 mm).

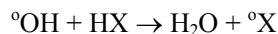
A reasonable downward increase can be observed for each series of chlorides and/or carbonates. Moreover, lower amounts of alkaline earth chlorides, with regard to their correlative carbonates, are needed to gain the same performance of flame-retardancy; such trends can be rationalized by their comparative correlative curves (Fig. 2). The superiority of chlorides with regard to their correlative carbonates could be referred to their mechanistic aspects. In fact, the halogen-containing compounds act as flame-retardants, which agrees with the Free-Radical theory,<sup>24,25</sup> according to which the mechanism manifested in the gas phase during burning might be involved, as due to the formation of high energy radicals, such as °H, °OH, °O, etc. These radicals can support combustion, so that their removal or conversion can assist the snuffing out of the flame. To achieve this goal, it would be helpful if these active radicals could be converted into less active ones.

Actually, suppression is believed to happen *via* halogen compounds, when they are applied as flame-retardants:

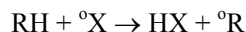
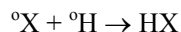


It should be noted that °R is a less active radical than °H.

HX also plays an important role in stopping the chain reaction developed during fire propagation or combustion, as its molecules may inhibit or deactivate the °OH radicals.<sup>24,25</sup>



The newly free halogen radicals regenerate HX, either by capturing the free hydrogen radicals present in the gaseous phase or by reacting with the substrate:



The significant overall effect is that the halogen atoms withdraw energy from the combustion-propagation zone or from the burning region, so that flame-retardancy is achieved.

When used as non-flammable gases, overall hydrogen halides form non-combustible protective layers interfering with the generation of inflammable volatiles in the combustion-propagation zone, thus achieving flame-retardancy. The action mode of alkaline earth carbonates is somewhat different from such an action, compared to that of chlorides.

It should be mentioned that both above-mentioned chemicals have an ionic nature, seen as increasing when their metal atom size increases. Meanwhile, they also show the tendency to form covalent compounds. In fact, alkaline earth metals give compounds with electrovalent and covalent nature.<sup>22</sup>

Correlated data on  $\Delta H_f^\circ$  ( $\text{kJ mol}^{-1}$ ), for the series:  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$ , show values of 100.6, 178.3, 234.6 and 269.3, respectively, whereas their  $\Delta G^\circ$  values ( $\text{kJ mol}^{-1}$ ) are of 48.3, 130.4, 183.8 and 218.1, respectively.<sup>26</sup> These figures agree<sup>20</sup> with their decomposition temperature values given in literature: 540, 900, 1290 and 1360 °C, respectively. In fact, the thermal stability of the carbonates increases with increasing the cation size.

All these observations illustrate that thermal stability increases downward with respect to the position of the metals in the periodic table, in the following order:  $\text{BaCO}_3 > \text{SrCO}_3 > \text{CaCO}_3 > \text{MgCO}_3$ , supporting the idea mentioned in literature, according to which “the thermal stability of the carbonates increases with increasing the cation size”.<sup>27</sup>

Therefore, these compounds remain intact<sup>28</sup> in the combustion zone of the cotton substrate, which is around 350 °C. Hence, higher amounts of chemicals will be required to achieve the same flame-retardancy performance.

Meanwhile, according to the Dust or Wall Effect theory, the flame-retardation effect of  $\text{BaCO}_3$  seems to be involved in the combustion zone of cellulose, as described in literature.<sup>29</sup> According to this theory, “if a high enough concentration of dust is present in the air, no flame can propagate”, as due to the absorption and dissipation of heat by inert dust, causing a decrease in temperature, named the Dust or Wall Effect.<sup>29</sup> The observed trends on the efficiency of correlative chlorides illustrate a similar capability to impart flame-retardancy. However, the data summarized in Table 1 reflect the general trends of the relationship between the optimum percent of anhydrous

alkaline earth metal chlorides necessary for achieving flame-retardation, and namely a reasonably increasing harmony as to the optimum addition, to retard the flame with increasing the molecular weight, could be verified. Similar expressions can be attained *via* their ionic nature with regard to their tendency towards a covalent character. The melting points in the series  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$  are as follows: 708, 772, 873 and 962 °C, respectively.<sup>26</sup> Indeed, their relatively low melting points may justify their tendency towards covalent characteristics,<sup>22</sup> as supported by the increase of the  $\Delta H_f^\circ$  ( $\text{kJ mol}^{-1}$ ) of these chlorides. The data characteristic of the series  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$  are the following: 642, 795, 828 and 860 ( $\text{kJ mol}^{-1}$ ), respectively.<sup>30</sup>

Since they become more and more ionic, the optimum percent of applied chlorides increases downward with respect to the position of their metals in the periodic table, for evidencing the same performance for flame-retardancy. These trends demonstrate the constantly increasing difficulties in releasing chlorine radicals to deactivate or convert the active radicals released during burning and illustrate a declining efficiency, as the metallic chlorides become more ionic. The tabulated data show the following order:  $\text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2 > \text{BaCl}_2$ .

Apparently, when metal chlorides become more ionic, they tend to act in favour of the Dust or Wall Effect theory. Note that a similar optimum percentage is needed for barium chloride as compared to barium carbonate, which shows the same increasing trend along with the molecular weight increment, indicating that the just mentioned chloride also complies with the Dust or Wall Effect theory on flame-retardancy.

## CONCLUSIONS

Although both alkaline earth metal chlorides and/or carbonates are efficient in retarding the flame, their flame-retarding efficiency seems to be determined by different factors, first of all by the relative ease of releasing halogen radicals, converting the atmosphere of the flame zone. However, alkaline earth chlorides do not follow a unique pathway to act as flame-retardants, that is their flame-retardancy trend diminishes with the increase in their molecular weight, which agrees with the explanation provided by the Free-Radical theory for light chlorides.

Table 1

A comparison between the efficiency of the selected alkaline earth metal chlorides and/or carbonates as flame-retardants for cotton fabric

Sample formula	Efficient additive % anhydrous dry salts	Efficient mole anhydrous salts	Efficient molar ratio chloride/carbonate, %	Atomic weight of metals, g/mol	Covalent radii of metals, Å	Molecular weight of salts, g/mol
MgCl <sub>2</sub>	4.30	0.045	<u>17.4</u>	24.31	1.36	95.218
MgCO <sub>3</sub>	21.23	0.251	100		1.36	84.32
CaCl <sub>2</sub>	5.60	0.050	<u>20</u>	40.08	1.74	110.986
CaCO <sub>3</sub>	24.06	0.240	100		1.74	100.08
SrCl <sub>2</sub>	26.20	0.165	<u>65.7</u>	87.62	1.91	158.326
SrCO <sub>3</sub>	37.20	0.251	100		1.91	147.63
BaCl <sub>2</sub>	51.20	0.245	<u>81</u>	137.34	1.98	208.248
BaCO <sub>3</sub>	53.22	0.269	100		1.98	197.35

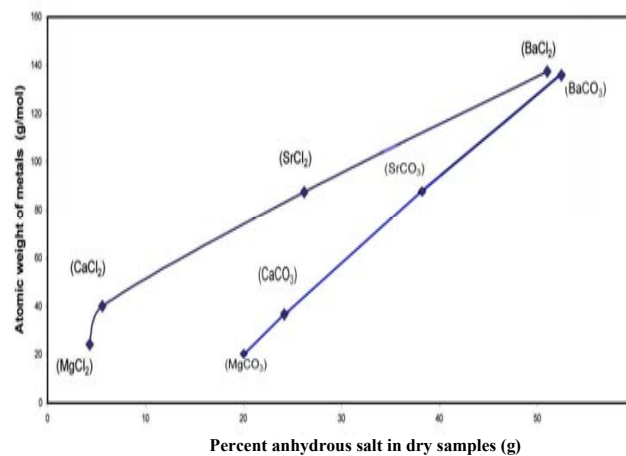


Figure 2: Relation between the atomic weight of the metals in some alkaline earth chlorides and/or carbonates and their optimum efficient percent of add-on values, corresponding to flame-retardancy

This trend seems to be correlated with the release of the halogen radicals, since these chlorides become more and more ionic and the generation of halogen radicals becomes more difficult. Therefore, the flame-retardancy of heavier chlorides could be explained by the Dust or Wall Effect Theory, *i.e.* the Free-Radical theory could not explain the flame-retardancy action of higher molecular weight alkaline earth metal chlorides. However, due to the higher thermal stability values of the alkaline earth metal carbonates, their flame-retardancy mode of action permits them to remain intact in the combustion zone of the cotton substrate, so that the higher stability values of these chemicals requires higher quantities to achieve flame-retardancy, hence it is likely that, when used as flame-retardants, they could act in compliance with the Dust or Wall Effect theory. Ultimately, the superiority of alkaline earth chlorides as compared to their carbonates as to the flame-retardancy effect on cotton fabrics could be demonstrated with the data here provided.

## REFERENCES

- <sup>1</sup> F. M. Farhan, S. M. Mostashari and G. Ghazi Moghaddam, *Int. J. Chem.*, **1**, 117 (1990).
- <sup>2</sup> F. M. Farhan, S. M. Mostashari and G. Ghazi Moghaddam, *Int. J. Chem.*, **2**, 163 (1991).
- <sup>3</sup> S. M. Mostashari, *Int. J. Chem.*, **13**, 115 (2003).
- <sup>4</sup> S. M. Mostashari, M. A. Zanjanchi and O. Baghi, *Combust. Explo. Shock*, **41**, 426 (2005).
- <sup>5</sup> S. M. Mostashari, *Asian J. Chem.*, **17**, 434 (2005).
- <sup>6</sup> S. M. Mostashari and M. R. Babaei Chaijan, *Asian J. Chem.*, **17**, 1469 (2005).
- <sup>7</sup> S. M. Mostashari and S. M. Golmirzadeh, *Asian J. Chem.*, **17**, 2007 (2005).
- <sup>8</sup> S. M. Mostashari and A. Darsaraei, *Int. J. Chem.*, **15**, 89 (2005).
- <sup>9</sup> S. M. Mostashari and A. Farkhondeh, *Asian J. Chem.*, **17**, 2803 (2005).
- <sup>10</sup> S. M. Mostashari, R. Amirrahmat and A. Farkhondeh, *Asian J. Chem.*, **18**, 2391 (2005).
- <sup>11</sup> S. Mostashari, *J. Appl. Fire Sci.*, **13**, 355 (2004-2005).
- <sup>12</sup> S. M. Mostashari, H. Haddadi and Z. Hashempoor, *Asian J. Chem.*, **18**, 2388 (2006).
- <sup>13</sup> S. M. Mostashari and O. Baghi, *J. Appl. Fire Sci.*, **12**, 203 (2003-2004).
- <sup>14</sup> S. M. Mostashari and S. Z. Mostashari, *J. Appl. Fire Sci.*, **13**, 325 (2004-2005).
- <sup>15</sup> S. M. Mostashari, Y. Kamali Nia and S. Baei, *Chinese J. Chem.*, **25**, 1 (2007).
- <sup>16</sup> S. M. Mostashari and Y. Kamali Nia, *J. Therm. Anal. Calorim.*, (accepted) (2007).
- <sup>17</sup> S. M. Mostashari and O. Baghi, *Cellulose Chem. Technol.*, **41**, 19 (2007).
- <sup>18</sup> S. M. Mostashari and S. Z. Mostashari, *J. Appl. Fire Sci.*, **14**, 13 (2005-2006).
- <sup>19</sup> S. M. Mostashari and S. Z. Mostashari, *Int. J. Polym. Mat.*, **56**, 641 (2007).
- <sup>20</sup> J. D. Lee, in "Concise Inorganic Chemistry", Chapman & Hall, London, 1991, pp. 147, 340, 351.
- <sup>21</sup> U. S. Department of Commerce – Standard for Flammability of Children's Sleepwear (DOC FF 3-71), Federal Register, **36**, No. 146, July 19 (1971).
- <sup>22</sup> A. K. De, in "A Textbook of Inorganic Chemistry", Wiley Eastern Ltd., New Delhi, 1983, p. 242.
- <sup>23</sup> N. N. Greenwood and A. Earnshaw, in "Chemistry of the Elements", Pergamon Press, Oxford, 1989, p. 122.
- <sup>24</sup> M. Kesner and W. de Vos, *J. Chem. Educ.*, **78**, 41 (2001).
- <sup>25</sup> A. Tohka and R. Zevenhoven, "Processing Wastes Derived Fuels Containing Brominated Flame-Retardants", Helsinki University of Technology, Dept. Mechanical Engineering, Epso P8-9 (2001).
- <sup>26</sup> K. N. Upadhyaya, in "A Textbook of Inorganic Chemistry", Vikas, New Delhi, 1998, p. 322.
- <sup>27</sup> R. C. Aggarwal, in "Modern Inorganic Chemistry", Kitab Mahal Allahabad, 1988, p. 387.
- <sup>28</sup> D. Price, A. R. Horrocks and M. Tunc, *Chem. Brit.*, **23**, 235 (1987).
- <sup>29</sup> Z. E. Jolles and G. I. Jolles, *Plast. Polym.*, **40**, 319 (1972).
- <sup>30</sup> C. E. Housecroft and A. G. Sharpe, in "Inorganic Chemistry", Pearson Education Ltd., Essex, 2001, p. 245.