

## The effect of magnesium hydroxide/ zinc borate and magnesium hydroxide/ melamine flame retardant synergies on polypropylene

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### -----ABSTRACT-----

The effects of combination of two flame retardant systems on flammability properties of polypropylene were tested. The polypropylene samples (200g by weight) were prepared using 20% mixture of magnesium hydroxide/ zinc borate and magnesium hydroxide/ melamine flame retardant systems. The flammability properties were assessed as a function of ignition time (otherwise known as the glow time) and Flame Propagation Rate (FPR). The results obtained from the magnesium hydroxide/zinc borate systems showed a decrease in the flame propagation rate when compared with the polypropylene sample prepared using magnesium hydroxide as the only flame retardant system, although there is no significant change in the glow time. Magnesium hydroxide/melamine flame retardant synergy showed an appreciable increase in the glow time and also decreased the flame propagation rate of the polypropylene sample; it therefore gave a better flame retardant synergy than magnesium hydroxide/ zinc borate system.

**Key words:** magnesium hydroxide, zinc borate, melamine, synergy, ignition time, flame propagation rate.

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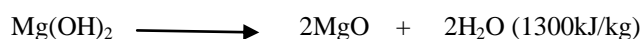
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### I. INTRODUCTION

The general use of polypropylene in our everyday life is driven by their remarkable combination of properties, low weight and ease of processing. However, because of the chemical nature of polymers which is made up of carbon and hydrogen, they are highly combustible. Both natural and synthetic polymers can ignite on exposure to heat. This ignition occurs spontaneously or results from external source such as spark or flame. If the heat evolved by the flame is sufficient to keep the decomposition rate of the polymer above that required to maintain the evolved combustibles within the flammability limits, then a self sustaining combustion cycle will be established (Troitzch, 1990).

Safety requirement are currently becoming more and more drastic in terms of polymers reaction to fire and their resistance performance. Therefore, to provide additional support from fire and to increase escape time when fire occurs, method to enhance flame retardant properties of consumer goods have been obtained (Laoutide, et al 2008). These efforts include the development of flame retardant systems, these systems are intended to inhibit or stop combustion process. They can either act physically (by cooling, formation of protective layer or fuel dilution) or chemically (reaction in the condensed or gas phase). Flame retardant systems interfere with various processes involved in polymer combustion, which is; heating, pyrolysis, ignition and propagation of thermal decomposition (Troitzsc, 1990; Horrocks and Price, 2001).

Persisting question about health hazards of conventional flame retardants in recent years, have built a driving force for the introduction of plastic composites combining excellent fire performance with low smoke generation and low combustion gas toxicity as well as corrosivity (The Plastic and Rubber Institute; 1992). The usage of magnesium hydroxide, zinc borate and melamine in thermoplastic elastomers and thermoplastic is one of the favoured alternatives to flame retardants releasing toxic and/or corrosive gases during smoldering and fire. The endothermic degradation of magnesium hydroxide occurs at a higher temperature (>300C), which is interestingly with respect to the extrusion and injection moulding processes of some polymers. The flame retardant action of magnesium hydroxide is very effective up to 400°C. Beyond this temperature, exothermic character of degradation predominates.



The water released from the reaction above dilutes the combustible gas mixture, which limits the concentration of reagents and the possibility of ignition (Delfosse, 1989).

In order to achieve high fire performance levels, it is necessary to develop a flame retardant system based on a combination of different flame retardant agents. The concept of synergism is used to optimize flame retardant formulations and enhance the performance of mixtures of two or more additives. Synergism is achieved when the performance level due to a mixture of additives  $xA + yB$  ( $x+y=1$ ) for a given property (P) is greater than that predicted for the linear combination ( $xP_A + yP_B$ ) of the single effect of each additive  $P_A$  and  $P_B$  (Laoutide, 2008). Hence, the introduction of zinc borate and melamine flame retardants agents separately into magnesium hydroxide flame retardant in a polypropylene sample which is the purpose of this research.

Zinc borate such as  $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$  are the most frequently used flame retardants. They take the appearance of non-hygroscopic white, semi-crystalline powder ranging from 1.5 to 15 $\mu$ m. Their endothermic decomposition (503kJ/Kg) between 290°C and 450°C liberates water, boric acid and boron oxide ( $B_2O_3$ ), although some grades do not hydrate due to the absence of hydroxyl groups. The  $B_2O_3$  formed softens at 350°C and flows above 500°C leading to formation of vitreous layer. The water liberated from dehydration processes of hydroxyl groups may represent up to 14% of water release depending on grades (Meller, 1952; John, 1992). The flame retardants action mainly originates from the interaction of  $Zn^{2+}$  ions with certain flame retardants to make them more effective and from the ability of the borate moiety to create a glassy layer on the surface of burning polymer material. Consequently, zinc borate show complex modes of action with other polymer additives.

Melamine is a thermally stable crystalline product whose structure is the 1-3-5-triazine ring 2,4,6-triamino-1,3,5-triazine. It is characterized by a melting point as high as 345°C that contains 67wt% Nitrogen atoms. Melamine sublimates at about 350°C, upon sublimation; a significant amount of energy is absorbed decreasing the temperature. At high temperature, melamine decomposes with the elimination of ammonia, which dilutes oxygen and combustibles gases and leads to the formation of thermally stables condensate known as melam, melem and melon (Coata et.al. 1990). These reactions are known to compete with melamine volatilization and are more pronounced if melamine volatilization is impeded, e.g. by the formation of a protective layer. The formation of melam, melem and melon generates residues in the condensed phase and results in endothermal processes, also effective for flame retardancy. Melamine combines the advantages of low cost, halogen free and offering excellent ignition resistance. Melamine retards flame propagation and has a good performance with regard to corrosion, smoke formation and the relatively low toxicity of the combustion gases.

## **II. MATERIALS AND METHOD**

### **2.1 MATERIALS**

Polypropylene was obtained from CEEPLAST Industry Limited, Adaelu Street, Osisioma Industrial Layout, Aba, Abia State, Nigeria. Melamine powder was gotten from Polymer and Textile Engineering Laboratory, Federal University of Technology Owerri, Nigeria.

### **2.2 PREPARATION OF ZINC BORATE**

The zinc borate used was synthesized in the Polymer and Textile Engineering Laboratory, Federal University of Technology Owerri, Nigeria.

#### **2.2.1 MATERIALS USED**

Sulphuric acid, zinc oxide, sodium tetraborate pentahydrate, methanol and distilled water.

#### **2.2.2 APPARATUS**

Beaker, stirrer, retort stand, thermometer and Bunsen burners

#### **2.2.3 METHOD OF PREPARATION**

The zinc borate was prepared as specified by Nelson P. (Nei et. al. 1972). To 773.4g of water in a reaction flask was added 154.2g of 96%  $H_2SO_4$  and 122.8g  $ZnO$  to give zinc sulphate solution. To this stirred solution at 100°C was added 432g of sodium tetraborate pentahydrate and 17.6g of zinc oxide. The resultant reaction was stirred at 95°C for 5.5hrs. The reaction was cooled and the crystalline product separated by filtration washed with water and methanol and air dried to give 3.8g of zinc borate having the following analysis. 37.85%  $ZnO$ , 47.65%  $B_2O_3$  and 14.5%  $H_2O$ . This corresponds to the formula  $2.04ZnO \cdot 0.3B_2O_3 \cdot 3.5H_2O$ .

### **2.3 PREPARATION OF POLYPROPYLENE SAMPLES**

The powdered flame retardant mixture as shown in the tables was introduced into the polypropylene resin and mixed. The sample was moulded using injection moulding machine at CEEPLAST Industry Limited, Adaelu Street, Osisioma Industrial Layout, Aba, Abia State, Nigeria. The flame retardant polypropylene sample produced has a net weight of 200g with polypropylene resin constituting 90% (i.e. 180g) and the flame retardant synergy making up the remaining 10% (i.e. 20g).

**TABLE 2.0 Sample formulations for magnesium hydroxide/zinc borate**

SAMPLES	POLYPROPYLENE (g)	MAGNESIUM HYDROXIDE (g)	ZINC BORATE (g)
CONTROL SAMPLE	200	0	0
M/Z1	180	20	0
M/Z2	180	15	5
M/Z3	180	10	10

**TABLE 2.1 Sample formulations for magnesium hydroxide/melamine**

SAMPLES	POLYPROPYLENE (g)	MAGNESIUM HYDROXIDE (g)	MELAMINE (g)
CONTROL SAMPLE	200	0	0
M/MM1	180	20	0
M/MM2	180	15	5
M/MM3	180	10	10

**2.4 FLAMMABILITY TESTS**

The flammability test which include the flame ignition time (otherwise known as glow time) and flame propagation rate were carried out using the Underwriters Laboratory (UL) Vertical Test Method. This was done in the Polymer and Textile Engineering Laboratory, Federal University of Technology Owerri, Imo State Nigeria. This is a very important test for plastic and is usually recommended for polypropylene.

**2.4.1 IGNITION TIME TEST**

**2.4.1.1 MATERIALS**

Control sample, flame retardant samples

**2.4.1.2 APPARATUS**

Retort stand, metric rule, stop watch, gas cylinder and Bunsen burner

**2.4.1.3 METHOD**

The sample was clamped according to UL94 HB at constant distance of 5cm between the lower tip of the sample and the flame source from the Bunsen burner. The glow time was recorded as a visually perceptible sparking flame appeared on the sample.

**2.4.2 FLAME PROPAGATION RATE**

The materials and the apparatus were as used in ignition time test

**2.4.2.1 METHOD**

The rate of spread of fire is recorded as the flame propagation rate. Test samples were marked X<sub>1</sub>, X<sub>2</sub> and X<sub>3</sub>, X<sub>1</sub> is a distance of 2.5cm from the end, X<sub>2</sub> is a distance of 3cm from the X<sub>1</sub> mark while X<sub>3</sub> is another distance from X<sub>2</sub> mark. The sample was clamped at a constant distant distance of 5cm between the lower tip and the heat source. The flame propagation time (FTP) was recorded as the time between an initial supply of flame and the combustion of the X marks. Flame propagation rate is the ratio of the distance from the sample end (X) and the flame propagation time.

$$FPR = X/FPT \dots\dots\dots equ. 2.0$$

Where X = X<sub>1</sub> + X<sub>2</sub> + X<sub>3</sub> = 8.5cm

**III. RESULTS AND DISCUSSIONS**

Table 3.0 showed that the addition of 20g magnesium hydroxide to the test sample increased the glow time from 13secs to 21secs. The magnesium hydroxide /zinc borate synergy did not have significant effect on the glow time of the test sample compared to using magnesium hydroxide alone. This is because both magnesium hydroxide and zinc borate have comparable endothermic degradation temperatures of 300°C and 290°C respectively (Meller, 1952; John, 1992). The addition of 5g of zinc borate showed a reduction in the glow time by 2secs while the 10g of zinc borate maintained the glow time at 21secs (see fig 3.0).

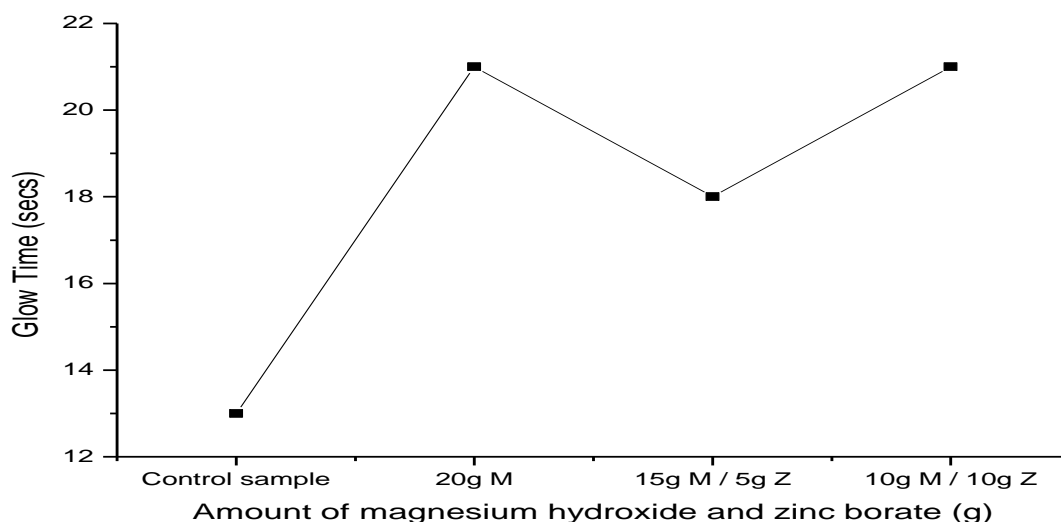
From table 3.1, it was observed that the magnesium hydroxide/melamine flame retardant synergy improved the fire resistance of the polypropylene sample. The glow time increased from 21secs to 26secs. This is as a result of higher endothermic degradation temperature of 345°C characteristics of melamine (see fig 3.1).

In table 3.2, the addition of zinc borate to the magnesium hydroxide flame retardant reduced the flame propagation rate of the propylene sample from 0.0370cm/s to 0.0291cm/s. This reduction in the burning rate is as a result of the water of hydration present in the chemical structure of zinc borate. During burning the water is released to extinguish the fire through cooling (see fig. 3.2).

In table 3.3, the result obtained showed that magnesium hydroxide/melamine synergy decreased the flame propagation rate from 0.0370cm/s to 0.0226cm/s. Melamine is known to act by a combination of effects: in contact with heat they decompose, acting as a heat sink, and release inert nitrogen gases which dilute the oxygen and flammable gases. They also chemically and physically (char formation) inhibit burning, and contribute to intumescent coating formation (blows char into a protective foam which prevents dripping). Hence, the reduction in burning rate as obtained in the fig 3.3 above.

**Table 3.0: Glow time test results for magnesium hydroxide and zinc borate**

Sample	Distance from flame	Amount of Mg(OH) <sub>2</sub>	Amount of zinc borate	Glow Time (sec.)
Control Sample	5	0	0	13
M/Z1	5	20	0	21
M/Z2	5	15	5	18
M/Z3	5	10	10	21



**Fig 3.0: Glow Time vs Flame Retardant System: magnesium hydroxide and zinc borate**

**Table 3.1: Glow time test results for magnesium hydroxide and melamine**

Sample	Distance from flame	Amount of Mg(OH) <sub>2</sub>	Amount of melamine	Glow Time (sec.)
Control Sample	5	0	0	13
M/MM1	5	20	0	21
M/MM2	5	15	5	22
M/MM3	5	10	10	26

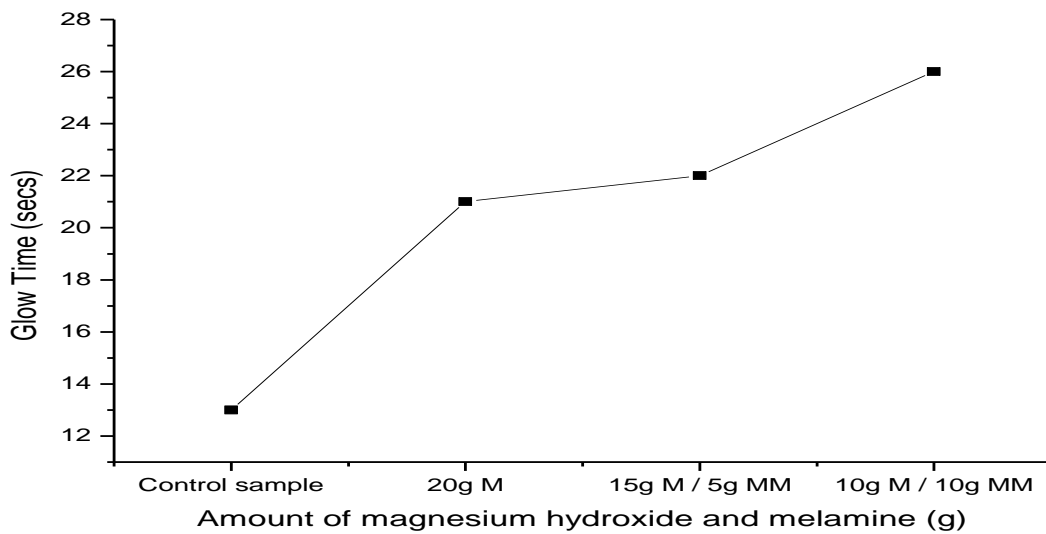


Fig 3.1: Glow Time vs Flame Retardant System: magnesium hydroxide and melamine

Table 3.2: Flame Propagation Rate of sample with magnesium hydroxide and zinc borate

Sample	Distance from flame (cm)	Amount of Mg(OH) <sub>2</sub>	Amount of zinc borate	Time of Burning (secs)			Total Time of Burning of 8cm	Flame Propagation Rate (cm/s)
				2.5cm mark	3cm from 2.5cm	2 <sup>nd</sup> 3cm mark		
Control Sample	5	0	0	89	70	57	216	0.0370
M/Z1	5	20	0	112	75	65	252	0.0317
M/Z2	5	15	5	116	76	61	253	0.0316
M/Z3	5	10	10	128	84	63	275	0.0291

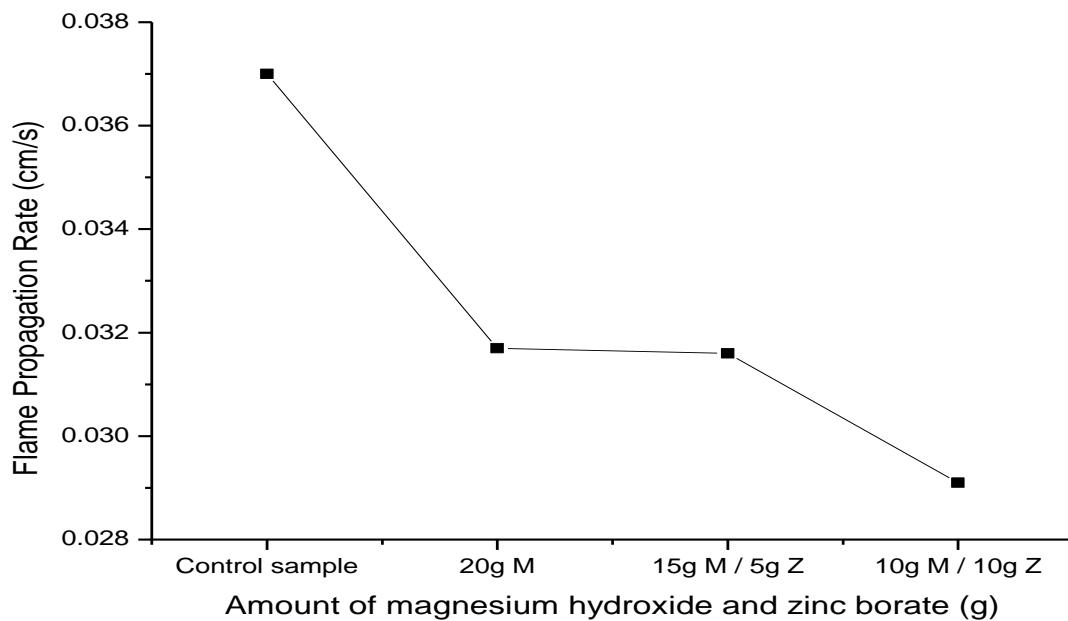


Fig 3.2: FPR vs Flame Retardant System: magnesium hydroxide and zinc borate

Table 3.3 Rate of burning of sample with magnesium hydroxide and melamine

Sample	Distance from flame (cm)	Amount of Mg(OH) <sub>2</sub>	Amount of melamine	Rate			Total rate of burning of 8cm	Flame Propagation Rate (cm/s)
				2.5cm mark	3cm from 2.5cm	2 <sup>nd</sup> 3cm mark		
Control Sample	5	0	0	89	70	57	216	0.0370
M/MMI	5	20	0	112	75	65	252	0.0317
M/MM2	5	15	5	131	87	67	285	0.0281
M/MM3	5	10	10	160	118	76	354	0.0226

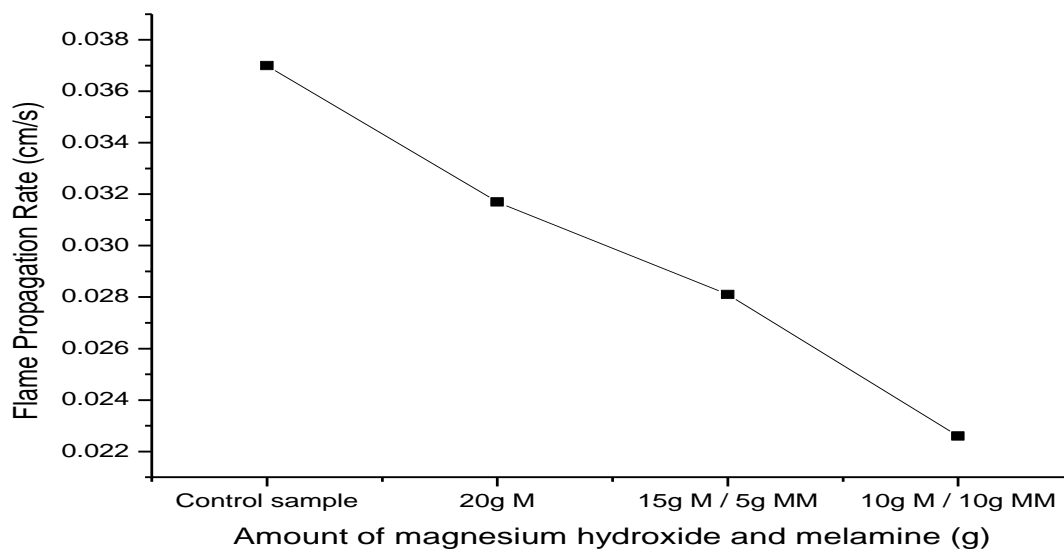


Fig 3.3: FPR vs Flame Retardant System: magnesium hydroxide and melamine

#### IV. CONCLUSION

The test results showed that combination of different flame retardant systems are more effective than using only one flame retardant. Both the magnesium hydroxide/zinc borate and magnesium hydroxide/melamine flame retardant synergies offered improved resistance to fire. The combination of magnesium hydroxide and melamine gave a higher resistance to fire than magnesium hydroxide/zinc borate synergy, both in the flame ignition time and flame propagation rate. This is because melamine has a higher endothermic degradation temperature of 345°C compared to zinc borate that has 290°C.

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