

## EFFECT OF AMMONIUM PHOSPHATES ON THE FLAMMABILITY PROPERTIES OF HIGH-IMPACT POLYSTYRENE (HIPS)

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### ABSTRACT

125  $\mu\text{m}$ -thick pure (additive-free) high-impact polystyrene film was prepared by compression moulding technique. 7.5 % (w/w) of three ammonium phosphates ( $(\text{NH}_4)_3\text{PO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$ ) were added, singly and in combination, to the pure polystyrene granules to produce 125  $\mu\text{m}$ -thick films by the same method. Burning time, flame spread, limiting oxygen index, ignition time, and after-glow time of the eight samples (additive-free/control and filled) were determined to evaluate the efficiency of the three fillers in the fireproofing and/or flammability of the high-impact polystyrene plastic film. From the results, burning time, limiting oxygen index, ignition response index and after-glow time of the filled samples were found to be higher than the control/unfilled polystyrene sample. However, flame spread of the filled samples was found to be lower than that of the control sample. The efficiency of the fillers in fireproofing the polystyrene film was found to follow the order:  $(\text{NH}_4)_3\text{PO}_4 > \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4$ . Additivity effect was observed when the fillers are added in pairs with the fireproofing efficiency following the order:  $(\text{NH}_4)_3\text{PO}_4 + \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_3\text{PO}_4 + (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{H}_2\text{PO}_4$ . Antagonism was, however, observed in fireproofing efficiency when all the three fillers are present in the polystyrene film. The fireproofing efficiency of the ammonium salts is attributed to the quantity and the ease with which ammonia gas ( $\text{NH}_3$ ) is released when the filled polystyrene films are heated.

**Keywords:** Ammonia, combustion, flame, plastics, styrene

### INTRODUCTION

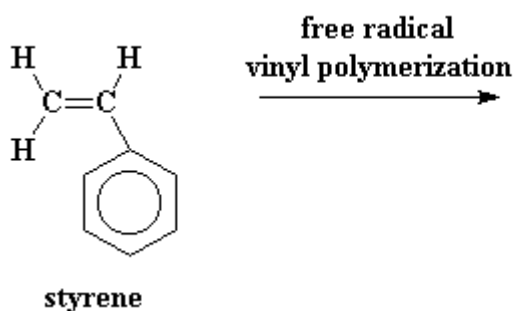
Today, plastics are being designed to meet ever exacting and specific needs. They have usurped many functions of materials traditionally used by man (metals, glass, ceramics, etc) and are influencing our lives in a way that no one would have thought possible a century ago. Lehn (2002) has reported that plastics, in their applications, must satisfy a number of criteria, including resistance to burning. Most plastics contain additives incorporated into

their formulations to modify some properties that allow them to effectively fulfill their intended use (Mihai *et al*, 2007).

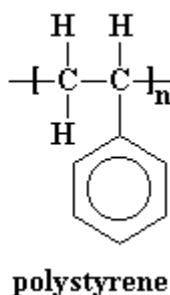
Flammability of materials, especially hydrocarbon polymers, is an important parameter that has been, and still is, an active area of research (Armstrong, 2005). Although to varying degrees, it was reported that all synthetic hydrocarbon polymers are susceptible to burning during their manufacture and subsequent use (McCrum *et al*,

1997).

Polystyrene (IUPAC: poly(1-phenylethane-1,2-diyl)), sometimes abbreviated PS, is a hydrocarbon



polymer produced by free radical vinyl polymerization, from the monomer, styrene (Painter and Coleman, 1999):



Polystyrene is one of the most widely used commodity thermoplastics and accounts for about 25 % of the total plastics used in packaging. It is an inexpensive hard plastic that is substantially used in critical construction, electrical and transport applications in which prevention of ignition and/or spread of flame is mandatory (Sperling, 2006). Polystyrene is classified according to DIN4102 as a "B3" product, meaning highly flammable or "easily ignited" (Varatharajan and Williams, 2000). Consequently, flame retardants are added to its products in the inner surface of engine compartments and underside of vehicle bonnets to protect them from direct flaming (Rubinstein and Colby, 2006).

In this study, three ammonium phosphates ((NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) are incorporated into high-impact polystyrene, singly and in combination, and their flammability properties studied in comparison to the pure/unfilled (control) sample.

## MATERIALS AND METHODS

**Materials:** Commercial high-impact polystyrene granules (Polystyrol) were obtained from Fluka Chemie GmbH, Switzerland, and the three ammonium phosphates ((NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) used in formulating the films were all analytical-reagent grade obtained from Hoescht Chemicals, AG, Germany.

**Sample Preparation:** The formulations from which the samples are prepared are shown in Table 1. 125 μm-thick film of pure (additive-free) Polystyrol is prepared by compression moulding technique in a 12.20 X 1.22 X 0.13 cm mould for 5 minutes at a pressure of 4.72Pa using a Tetrahedron Automatic Press. The above procedure is repeated by adding 7.5 % w/w of the three fillers ((NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>), singly, in pairs and all the three fillers combined, to the pure Polystyrol granules.

**Table 1: Amounts of the components (% w/w) used in preparation of the sample film formulations.**

Component	Amount (% w/w)							
	100	92.5	92.5	92.5	92.5	92.5	92.5	92.5
PS	100	92.5	92.5	92.5	92.5	92.5	92.5	92.5
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	0	7.5	0	0	0	0	0	0
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0	0	7.5	0	0	0	0	0
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	0	0	0	7.5	0	0	0	0
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> + (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0	0	0	0	7.5	0	0	0
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> + NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	0	0	0	0	0	7.5	0	0
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	0	0	0	0	0	0	7.5	0
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> + (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	0	0	0	0	0	0	0	7.5
Sample Code	A	B	C	D	E	F	G	H

**Burning Time:** Bunsen-burner flame is applied to the bottom of each sample in a vertical position and the time taken for the sample to burn 7.5 cm mark is noted according to ASTM D 568 (Anon, 2008). The procedure is repeated three times and the average value reported as each sample's burning time.

**Flame Spread:** Each sample is supported on a 45-Degree Incline and ignited with a flame from a hypodermic needle and burning allowed on both sides of each sample. The time taken for the burning-through of each sample is noted according to ASTM D 1433 (Anon, 2008). The procedure is repeated three times and the average value reported as each sample's flame spread.

**Limiting Oxygen Index (LOI):** Each sample is mounted vertically and ignited at the top with a Bunsen-burner flame. The concentration of oxygen in the atmosphere flowing past each sample is lowered to the minimal and the amount that supports combustion for each sample is noted according to ASTM D 2863 (Anon, 2008). The procedure is repeated three times and the average value reported as each sample's LOI.

**Ignition Time/Ignition Response Index (IRI):** A Bunsen-burner flame is applied to the lower edge of each sample in a vertical position and the

time of flame impingement that causes the sample to ignite is recorded according to ASTM D 3713 (Anon, 2008). The procedure is repeated three times and the average value reported as each sample's response to flame impingement (Ignition Time).

**After-Glow Time:** 2.5 cm Bunsen-burner flame is applied to the lower edge of each sample in a vertical position. The flame is removed and the time taken for the burning sample to extinguish is noted according to ASTM D 3801 (Anon, 2008). The procedure is repeated three times and the average value reported as each sample's after-glow time.

## RESULTS AND DISCUSSION

The results of the study are shown in Tables 2 and 3. Table 2 shows the burning time, flame spread and after-glow time of the eight sample films used in the study. From Table 2, it can be seen that all the three fillers are capable of inducing self-extinguishing property in the high-impact polystyrene in the amount of the fillers added (7.5 % w/w).

**Table 2: The burning time, flame spread and after-glow time of the eight sample films studied.**

Sample Code	Burning Time (s)	Flame Spread (s)	After-Glow Time (s)
A	57	43	35
B	41	24	18
C	46	30	24
D	43	27	21
E	27	19	13
F	23	17	11
G	32	21	15
H	52	36	29

Comparing the burning time of the filled sample films, the film containing all the three fillers has the longest combustion time of 52 seconds. It is second to only the control sample (A), which has burning time of 57 seconds. The burning times of the sample films singly filled with the three ammonium salts (samples B, C and D) are higher than those samples containing pairs of the three ammonium salts (samples E, F and G). The order of susceptibility of the samples to burning follows the order  $F > E > G > B > D > C > H$

> A. It can also be observed, from Table 2, that presence of the fillers decreases the time taken for the 7.5 cm sample films to burn.

Similar trends of susceptibility of the samples to both flame spread and after-glow time were found. These results imply that, although to varying extents, all the three ammonium salts (singly and/or in combination) have reduced the burning time of the pure high-impact polystyrene polymer.

**Table 3: The limiting oxygen index (LOI) and Ignition Time/Ignition Response Index (IRI) of the eight sample films.**

Sample Code	Limiting Oxygen Index	Ignition Time (s)
A	18.75	32
B	38.97	15
C	31.57	21
D	35.64	18
E	46.12	11
F	51.05	9
G	41.23	12
H	19.35	26

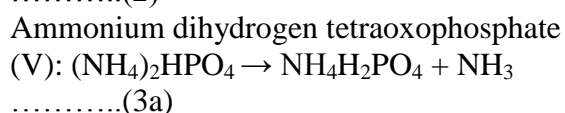
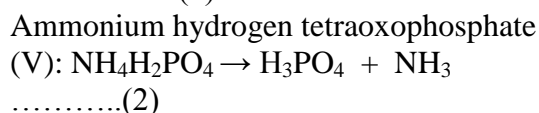
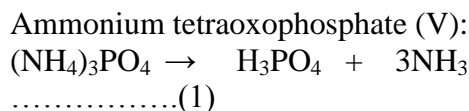
Table 3 presents the results of the limiting oxygen index and the ignition index of the sample films. From the Table, It can be seen that the LOI of the control sample (A) is only 18.75. It can also be observed that the filled samples have higher limiting oxygen indices, although to different degrees, than the control sample. This implies that the filled samples need larger amount of oxygen to burn than the control sample. The order of limiting oxygen

index (LOI) follows:  $A < H < C < D < B < G < E < F$ . The LOI values of all the samples further indicate that only samples A and H are flammable, as their LOI values  $< 21$ . This is, as reported earlier, due to the fact that any material whose LOI value  $\leq 21$  is considered flammable (Hwan-Man *et al*, 2003).

The values of ignition time, from Table 3, can be seen to follow an opposite trend to that of the LOI, with the order of ignition

time being:  $F < E < G < B < D < C < H < A$ .

The results obtained can be ascribed to the equations for the combustion of the three ammonium phosphates are shown in Scheme 1 below:



Scheme 1: Equations for the combustion of the three ammonium phosphates used in filling the high-impact polystyrene film.

Ammonium phosphates thermally decompose into tetraoxophosphate (V) acid ( $\text{H}_3\text{PO}_4$ ) and ammonia ( $\text{NH}_3$ ). The ammonia produced is reported to act as a strong base in the condensed phases (solid and liquid) and as a diluent in the gas phase (Allcock *et al*, 2003). Since ammonia does not support combustion, it shields the high-impact polystyrene films from being accessed by air, slows the flame propagation, narrows the flammability limits and cools the already burning material.

From Scheme 1, it can be observed that the efficiency of the ammonium phosphate salts is  $(\text{NH}_4)_3\text{PO}_4 > \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4$ . This is because, as can be seen from equation 1,  $(\text{NH}_4)_3\text{PO}_4$  decomposes to yield three molecules of ammonia ( $\text{NH}_3$ ). It is followed, as can be seen from equation 2, by  $\text{NH}_4\text{H}_2\text{PO}_4$ , which decomposes to yield one molecule of ammonia ( $\text{NH}_3$ ). That  $\text{NH}_4\text{H}_2\text{PO}_4$  is more efficient than  $(\text{NH}_4)_2\text{HPO}_4$  can be seen from equations 3a and 3b. Although ammonia ( $\text{NH}_3$ ) is produced in equation 3a, this is in addition to  $\text{NH}_4\text{H}_2\text{PO}_4$ , without the formation of  $\text{H}_3\text{PO}_4$ . It is only if  $\text{NH}_4\text{H}_2\text{PO}_4$  decomposes, in equation 3b, that  $\text{H}_3\text{PO}_4$  is produced.

## CONCLUSION

All the three ammonium salts, singly and in combination, were found to markedly improve flammability of the high-impact polystyrene polymer. The overall fireproofing efficiency of the eight sample films was found to follow the order:  $F > E > G > B > D > C > H > A$  or  $(\text{NH}_4)_3\text{PO}_4 + \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_3\text{PO}_4 + (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_3\text{PO}_4 > \text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_3\text{PO}_4 + (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{H}_2\text{PO}_4 > \text{PS}$ . Consequently, their use, in place of the very expensive oxides of antimony, bismuth and molybdenum and toxic halogenated hydrocarbons, in fireproofing polystyrene plastics is highly recommended.

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