STRONG BASE CATALYSED INTUMESCENT FLAME RETARDANTS

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1. INTRODUCTION

Intumescent flame retardants form a foamed-char barrier layer when exposed to a flame [1,2]. Conventional systems are based on the acid catalysed dehydration of carbonifics such as dipentaerythritol. Metal oxides also have utility as catalytic flame retardants [3]. For example, both antimony and tin have been used to impart flame resistance to cellulosics without any assistance from halogen compounds [4]. Apparently they alter the condensed phase thermal degradation pathways in such a way that more non-volatile char and less flammable gases are generated [5]. Recently it was discovered that potassium carbonate enhances the charring of polymers containing pentaerythritol-silica combinations as flame retardant [6].

2. EXPERIMENTAL

Potassium bitartrate and pentaerythritol mixtures were ground together using a mortar and pestle until the blends appeared homogeneous. Thermogravimetric (TG) and differential scanning calorimetric (DSC) data were obtained in an air atmosphere using a Netzsch STA 409 simultaneous TG/DSC instrument.

Tablets with a diameter of 13mm and a thickness of 5 mm were used for pyrolysis experiments. They were obtained using a Lepton® die with a hydraulic press providing a compression force of 10 tons. The tendency of the mixtures to char and intumesce was evaluated by placing the pressed tablets in stainless steel crucibles and exposing them to an oven temperature of 500 °C for a few minutes.

3. RESULTS AND DISCUSSION

Tang and Neill [7] found that even low levels of potassium bicarbonate modify pyrolysis kinetics of α-cellulose to yield more char. This suggests that the potassium carbonate effect observed by Gilman et al. [6] may also be related to strong base catalysis of char forming reactions. Since high water solubility poses a disadvantage we searched for insoluble potassium salts. Potassium bitartrate was chosen as it has the added advantage of combining the interacting alcohol functional groups in the same molecule. Potassium bitartrate indeed shows considerable charring and foaming when exposed to an open flame. The TGA/DSC scan in Fig. 1 shows that it is stable up to 250°C. An endothermic decomposition ($\Delta H \approx 0{,}4$ MJ/kg), evolving CO_2 and steam occurs between 250 and 300°C and yields 48% char, 77% of which represents potassium carbonate. The downward slope of the TG trace suggests that the carbon in the char slowly oxidises at higher temperatures.

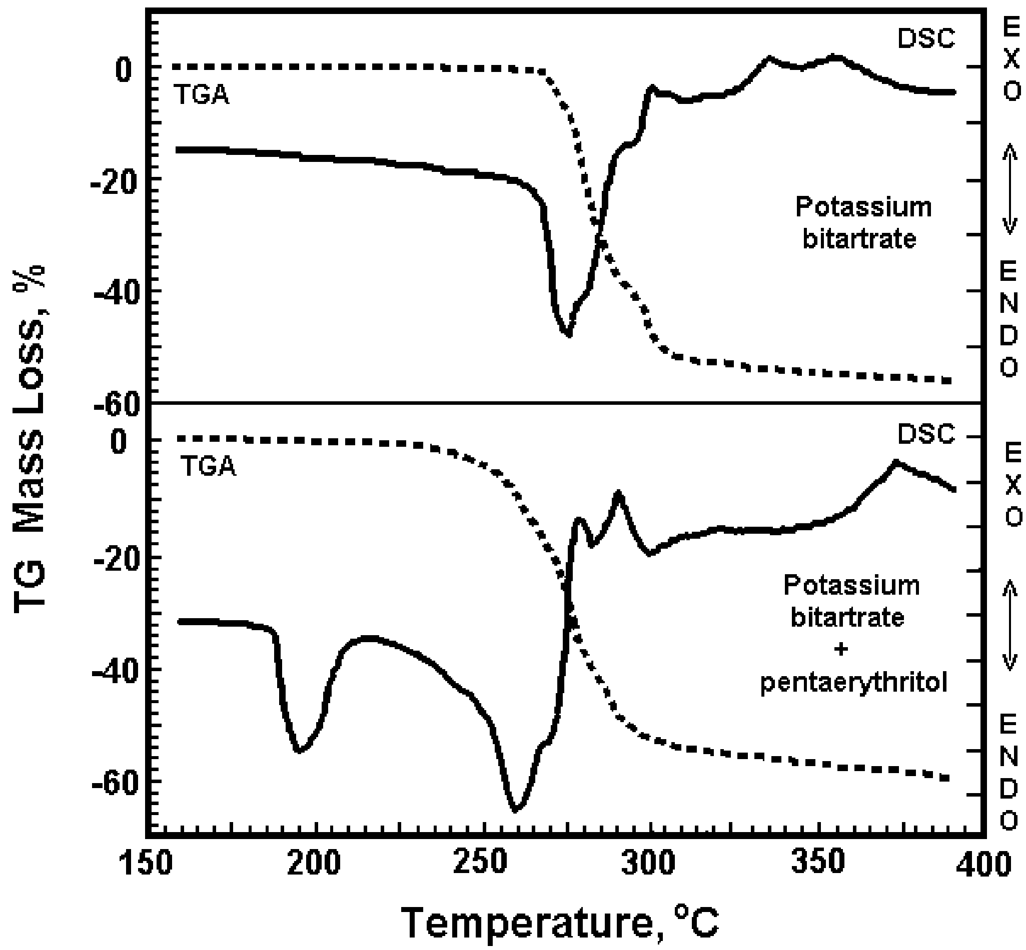

Fig. 1: DSC/TG Traces for Potassium Bitartrate and its 2:1 Mixture with Pentaerythritol. Scan rate: 10°C/min.

Combinations of potassium bitartrate and pentaerythritol show improved performance. Fig. 2 shows the effect of blend composition on the char yield and apparent foam height. A 2:1 ratio of bitartrate to pentaerythritol is close to optimal. Fig. 1 shows the TG/DSC scan and Figure 3 illustrates the char structure obtained when pyrolysing this combination. The coarse cell structure of the foam-char requires further improvement.

Unfortunately, when exposed to a flame, the residual char ablates via a “glowing combustion” mode. Phosphoric acid derived chars do not show this deficiency. Patai et al. [8] found that strong bases show high catalytic activity in the thermal oxidation of carbon. The catalyst efficiency decreases in the order [9,10]:

alkali metals > alkali earth metals > group IIIA - IVA elements

This implies that the potassium residues are responsible for catalysing the thermal oxidation of the residual char. Preliminary results confirm that other, less basic metals, such as aluminium, still show the charring effect but with much reduced oxidation activity.

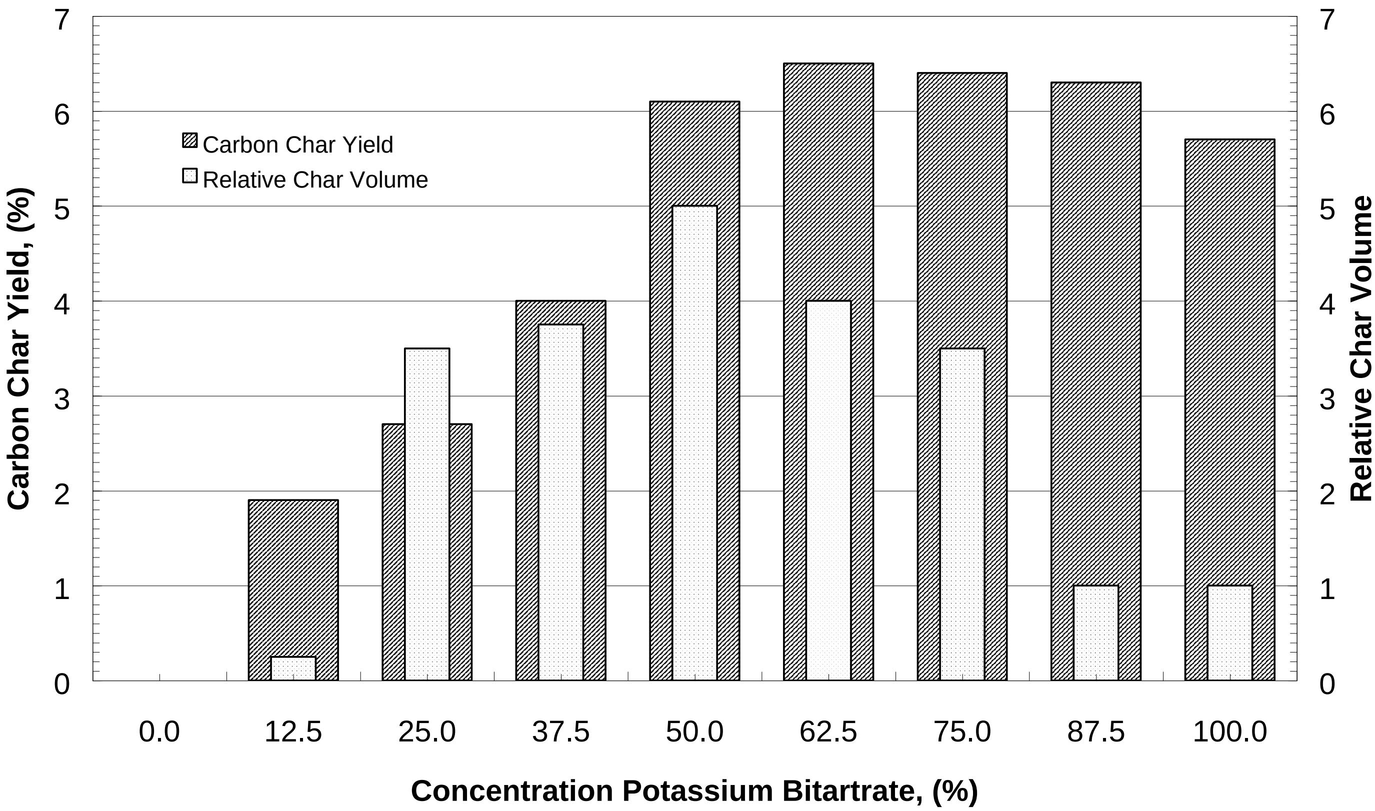

Fig. 2: Oven Pyrolysis of Potassium Bitartrate-Pentaeryhtritol Blends

Fig. 3: Intumescence of a 2:1 Mixture of Potassium Bitartrate and Pentaerythritol following Exposure of a Pressed Pellet to an Oven Temperature of 500°C for a few Minutes.

4. CONCLUSIONS AND RECOMMENDATIONS

Potassium bitartrate is a flame retardant candidate showing intrinsic intumescence on heating. It combines the alcohol and “latent base” functionalities in the same molecule. Combinations with pentaerythritol show improved performance with respect to char yield and char volume. Base catalysis is an attractive alternative to conventional acid catalysed intumescent flame retardant systems as it could help to alleviate corrosion problems during polymer processing. Unfortunately, strongly basic residues also catalyse the oxidative destruction of the char-foam at high temperatures. Further work is required to overcome this “glowing combustion” effect and to improve the char-foam cell structure.

5. REFERENCES

1. H.L. VANDERSALL, *J. Fire Flamm.* **2** (1971) 97.
2. G. CAMINO, L. COSTA and G. MARTINASSO, *Pol. Degrad. Stab.* **23** (1989) 359.
3. C.F. CULLIS and M. HIRSCHLER, *Eur. Polym. J.* **20** (1984) 53.
4. J.E. RAMABOTTOM, "Fire-proofing of Fabrics", (His Majesties Stationary Office, London, England, 1947).
5. W.L. WILLS, US Patent 2 607 729, August 19, 1952.
6. J. W. GILMAN et al., *Polymer Preprints*, **38** (1) (1997) 802.
7. W.K. TANG and W. K. NEILL, *J. Pol. Sci.* **C** (2) (1964) 65.
8. S. PATAI, L. RAJBENBACH AND E. HOFFMANN, *J. Applied. Chem.* **2** (1952) 306, 311.
9. J.F. RAKSZAWSKI and W.E. PARKER, *Carbon* **2** (1964) 53.
10. J.T. GALLAGHER and H. HARKER, *Carbon* **2** (1964) 163.