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Zinc compounds as flame retardants and smoke suppressants for rigid PVC

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The effect of the concentration of zinc hydroxy-stannate and zinc borate on the fire performance of rigid PVC formulations has been investigated. Fire testing was carried out using cone calorimetry as well as the limiting oxygen index (LOI) test. In addition, further testing was done to check that incorporation of the fire retardant additives did not have any detrimental effects on other properties of the formulated PVC, such as heat stability, colour or impact strength. The results demonstrated that zinc hydroxy-stannate is an excellent fire retardant and smoke suppressant at additions levels of 3 parts per hundred parts of PVC. Zinc borate did not have the excellent fire retardant properties of zinc hydroxy-stannate, but was found to be an efficient and cost-effective smoke suppressant, although the presence of free zinc oxide in the sample affected the thermal stability of the formulation.

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Keywords: Zinc compounds, flame retardants, smoke suppressants, rigid PVC

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INTRODUCTION

Due to its high chlorine content, PVC is inherently non-flammable: it will not continue to burn after removal of a source of ignition. Unplasticised PVC products (such as pipes, fittings, windows and cladding) are not found to contribute to fire propagation¹ and most rigid PVC formulations will pass most flame test specifications without the need for the incorporation of flame retardants. However, the higher the level of organic additive (e.g. processing aid and impact modifier) the less flame-resistant the formulation. There may be cases where flame retardants are needed in order to pass very severe fire regulations: such as the M1 classification of the French Building Standard using the Epiradiateur Radiation Test. Also, under the EU *Construction Products Directive*, there is a move to harmonise national fire legislation and testing.² The introduction of a new 'spread of flame' test or 'single burning item' (SBI) test may require some increase in the fire retardancy of current rigid PVC formulations.

PVC can generate high levels of black smoke when it is forced to burn. During the combustion of PVC, the polymer degrades to produce hydrogen chloride (HCl) and macromolecular polyene structures, which are further reduced to aromatic compounds and condense as tars.³ PVC smoke comprises a fog of HCl containing black particles that have volatilised from the aromatic condensed phase. Apart from the irritant effect of HCl

on the eyes and respiratory system, smoke can cause disorientation and hinder escape from the scene of the fire. It also impedes the entry of fire fighters. Hence, the reduction of smoke emissions is clearly desirable. Unlike flame retardancy, legislation on smoke evolution is still in its infancy, but it is receiving increasing attention. The new SBI test will monitor a range of parameters,² including the Smoke Growth Index (SMOGRA).

Although it does not burn, PVC is notorious for its poor thermal stability: at temperatures above 100°C, it begins to decompose, evolving HCl. Degradation is due to the progressive loss of HCl along the PVC chain, in what is described as an 'unzipping' reaction, leading to the formation of coloured and easily oxidisable conjugated polyene structures. As PVC is heated, it exhibits a characteristic series of colours (colourless → beige → yellow → orange → red → brown) which is typical of systems containing long conjugated polyene sequences. As heating is continued, further reactions occur, such as chain scission, which lead to degradation of mechanical properties.

Zinc carboxylates (e.g. zinc stearate) are widely used as heat stabilisers in PVC formulations.⁴ The stabilising action of zinc carboxylates is explained by the Frye-Horst mechanism,^{5,6} which proposes that stabilisation arises from esterifying displacement of labile chlorine atoms by the more stable carboxylate groups. Thus

progressive dehydrochlorination is prevented. There is, however, a major problem with the use of covalent metal carboxylates: the metal chlorides produced as a result of the substitution reaction will themselves cause further rapid degradation. Metal chlorides with Lewis acid character, such as ZnCl_2 and FeCl_3 , act as catalysts for alkylation reactions between PVC molecules and the polyene structures, also producing hydrogen chloride. Degradation proceeds rapidly and the PVC becomes a highly cross-linked carbonaceous char. Fortunately, it was discovered that alkaline earth carboxylates undergo ester exchange reactions with covalent metal chlorides, thus regenerating the covalent metal carboxylate. Unlike the covalent metal chlorides, alkaline earth chlorides do not promote dehydrochlorination.⁷ Hence the synergistic use of calcium and zinc fatty acid salts as thermal stabilisers in PVC formulations.

The detrimental effect of transition metal compounds on catalysing dehydrochlorination can be advantageous when it comes to retarding flame and smoke evolution. Transition metal compounds promote char formation in PVC and this is a mechanism for inhibiting fire and smoke propagation. Hence zinc compounds, notably borates and oxides, are used as flame retardants and smoke suppressants for PVC.^{8,9} A new addition to the market is zinc hydroxy-stannate.¹⁰

Zinc hydroxy-stannate was developed as a non-toxic alternative to the commonly used flame retardant, antimony trioxide, which has been classified as a category 3 carcinogenic substance. Although ZHS contains Sn, this is present in inorganic form and is biologically inert and, therefore, non-toxic. Organo-tin species, such as some of the short-chain dialkyl tin compounds used as PVC stabilisers, are toxic. The toxicity of the dialkyl tin decreases rapidly as the chain length of the alkyl group increases: hence, octyl tin compounds are approved for food packaging.

In a recent study¹¹ to assess the effectiveness of a number of fire retardant additives and fillers in rigid PVC formulations, it was found that zinc hydroxy-stannate, $\text{ZnSn}(\text{OH})_6$ (ZHS), had excellent fire retardant and smoke suppressant properties, and had no detrimental effect on important physical and mechanical properties. This product clearly has potential for use in rigid PVC. The work described in the current paper was undertaken to investigate the effect of the concentration of ZHS on fire performance.

In the same study,¹¹ it was also found that zinc borate, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3 \cdot 5\text{H}_2\text{O}$ (ZB), was a good smoke suppressant, but that its flame retardant properties were inferior to those of ZHS. In addition, the grade of zinc borate used gave a reduction in whiteness of the extruded product and, more importantly, a reduction in the Charpy impact strength of 7 kJ/m². However, because ZB looks promising as a smoke suppressant and is less than half the price of ZHS, it was decided to try using a finer grade of zinc borate (1 µm average particle size as opposed to 3 µm) to overcome the detrimental effect on mechanical properties. The effect of ZB concentration was also investigated in the new work programme and is reported below.

EXPERIMENTAL

Sample preparation

A standard PVC window recipe was used for these trials. The formulation was stabilised with dibasic lead phosphite and contained 4 phr (parts per hundred parts of polymer) of titanium dioxide pigment, 7 phr of acrylic impact modifier and 10 phr of calcium carbonate filler. The concentration of flame retardant (either ZHS or ZB) was increased from 1 to 5 phr in steps of 1 phr. About 20 kg of each formulation were prepared. The blends were mixed on a high-speed mixer at 120°C and cooled to 40°C.

Fire testing

Limiting oxygen index test

The limiting oxygen index (LOI) is the minimum oxygen concentration, in a variable oxygen/nitrogen atmosphere, that will just support combustion of a sample. The higher the measured value of LOI, the greater the fire retardancy. A value of LOI greater than 21 shows that the polymer does not ignite spontaneously in air. The LOI test is widely used for comparing the flammability of polymeric materials and is generally acknowledged to be useful for quality control purposes, although it does not purport to predict performance of a material in real fire conditions. The test conforms to ISO4589-2, BS2782 (Part 1, Method 141) and ASTM D2863.

Samples for LOI testing were cut from 3 mm thick extruded strip, which was produced on a Krauss-Maffei 2-25 KKL twin-screw extruder.

Cone calorimetry

Cone calorimetry is a very useful technique for laboratory-scale fire testing of polymeric materials. Results from this test have been shown to correlate well with data from full-scale fire tests. The test sample is irradiated by a conical heating element at a preset heat flux in the range 10–100 kW/m². The fire effluent is drawn off through a duct, where sensors are used to measure the rate of heat release and smoke production.¹² This test is cited in ISO 5660-1, BS476 (part 15) and ASTM E1354.

In the present study, the cone calorimeter heat flux was set at 50 kW/m², which relates to the more severe fire tests for building products. Two plaques of each formulation were tested. The important parameters used to assess fire performance are as follows:

Ignition time(s)

Time to ignition is the time taken for the whole surface of the sample to sustain burning. It is determined visually.

Peak rate of heat release (kW/m²)

This is the maximum value in the plot of heat release versus time. It indicates the intensity of the fire and how rapidly the fire will spread.

Table 1 Processing conditions to produce samples for impact testing

Die temperature	200°C
Adapter temperature	190°C
Zone 2 temperature	195°C
Zone 1 temperature	195°C
Screw temperature	160°C
Screw speed	45 rpm

Fire performance index ($s \cdot m^2/kW$)

The fire performance index is the ratio of the ignition time to the peak rate of heat release. It relates to the time to flashover in a full-scale fire.

Smoke

Smoke was assessed by two parameters: the average rate of smoke release during the first 3 min of burning ($m^2/s \cdot m$), and the total smoke generated during the test (m^2/m^2).

Samples for cone calorimetry were made by milling the PVC blends at 175°C on a twin-roll mill to produce crepes, which were pressed into plaques measuring 10 cm x 10 cm x 6 mm.

Impact testing

In order to produce samples for impact testing, the PVC blends were extruded on a Krauss-Maffei KMD 2-25 KKL twin-screw extruder using the processing conditions shown in Table 1. Extruded strips of width 30 mm and thickness 3 mm were produced and specimens cut from the extruded strips. Single-notch Charpy impact tests were carried out according to BS2782 Part 3 Method 359, as specified in BS7413.

Colour measurements

Colour measurements were carried out on extruded strips of material using a Dr Lange microcalorimeter. In this technique, reflected light from a xenon lamp is split into three components via an optical wave-guide and routed to three standard measurement filters. The colour of interest was the L^* value, which represents black to white (on a scale from 0 to 100).

Heat stability

Measurements of dynamic heat stability were carried out on a Brabender torque rheometer using a charge weight of blend of 35 g, a rotor speed of 60 rpm and a set temperature of 190°C. The time to degradation was recorded as the point at which the equilibrium torque started to rise, indicating that char formation and cross-linking were starting to take place.

RESULTS AND DISCUSSION**Fire testing***Limiting oxygen index test*

LOI test results are tabulated in Table 2 and plotted in Fig. 1. It is seen that even without the addition of flame retardants, the LOI value of 38.6 for the control sample shows that the rigid PVC window formulation has a good level of flame retardancy. Indeed, rigid PVC is regarded as flame retardant due to its high chlorine content of 57%.

From Fig. 1 it is seen that addition of both ZHS and ZB flame retardants cause an increase in LOI, although the increase is not directly proportional to the level added. In the previous study,¹¹ it was found that the standard deviation for the test (i.e. reproducibility of results including weighing out, mixing *etc.*) was 1.5. This means that the differences observed for the LOI values for ZHS and ZB are not statistically significant.

Cone calorimetry

Cone calorimetry results are tabulated in Table 2 and a discussion of the various fire performance parameters is given below.

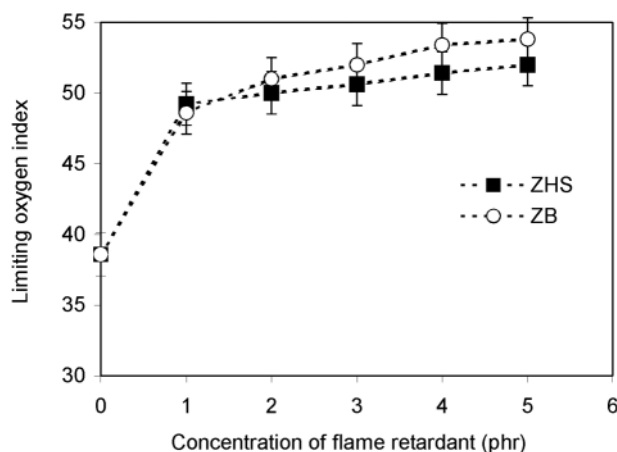
Time to ignition

PVC is a difficult material to ignite. In the case of the highly flame-retarded samples, it was difficult to get the samples to burn. Hence, the reproducibility of this test was not particularly good. The standard deviation for this test was found to be 40 s.

Values of ignition times in the cone calorimeter test for samples containing ZHS and ZB are compared in

Table 2 Results of fire testing

Flame retardant type & level	Limiting oxygen index ± 1.5	Ignition time (s) ± 40	Peak rate of heat release (kW/m^2) ± 10	Average rate of smoke release over 3 min ($m^2/s \cdot m$) ± 1	Total smoke generation (m^2/m^2) ± 350
0	38.6	34	229	16.60	6887.5
1 phr ZHS	49.2	85	146.15	6.61	4164.5
2 phr ZHS	50.0	87	126.4	5.82	3212.5
3 phr ZHS	50.6	390	121.65	4.10	2392
4 phr ZHS	51.4	406	95.85	3.69	1834.5
5 phr ZHS	52.0	367.5	105.04	3.14	1636
1 phr ZB	48.6	68	146.65	8.61	4130
2 phr ZB	51.2	68	140.95	5.61	2966
3 phr ZB	52.0	89.5	134.5	6.32	2987.5
4 phr ZB	53.4	107	110.1	6.08	2984
5 phr ZB	53.8	70	112.75	5.86	2959



1 Limiting oxygen index

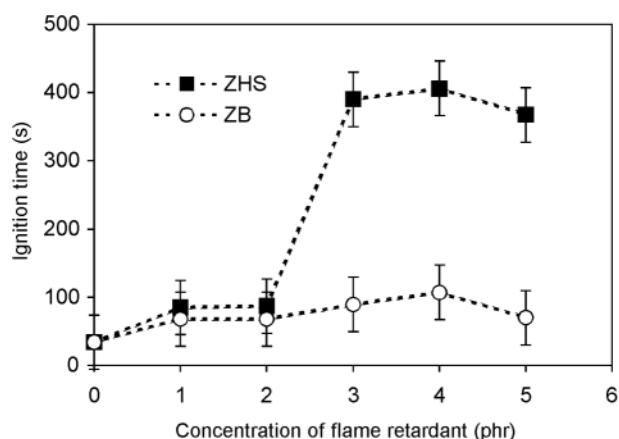
Fig. 2. The greater the value of time to ignition, the less the likelihood of the fire getting started. It is clear from the results in Fig. 2 that there is a discontinuity in the ignition times between 2 and 3 phr of ZHS, i.e. there is a sudden increase in time to ignition from 1.5 min up to 6.5 min, which is very significant. The same improvement was not found in the case of zinc borate, which confirms the superior fire performance of ZHS over ZB found in the previous study.¹¹

It is interesting to speculate why ZHS has superior performance over ZB in preventing ignition. Both are zinc compounds and promote cross-linking and char formation of PVC in a fire because of the Lewis acid effect of ZnCl_2 . However, the stannate ion is also thought to act in the vapour phase¹⁰ by a mechanism similar to that of antimony trioxide, for which both ZHS and zinc stannate are recommended as replacements. Antimony compounds have a specific synergy with halogen-containing materials. The synergistic mechanism is due to the formation of volatile antimony trihalide (SbCl_3) and oxyhalides (SbOCl , etc.), which increase the effectiveness of the halogen in quenching free radicals in the combustion process.¹³ Unlike antimony trioxide, zinc stannate and zinc hydroxy-stannate act in both the condensed and vapour phases and it is claimed that this unique dual phase action results in smoke suppression as well as flame retardancy.

Zinc borates act only in the condensed phase. In addition to the effect of Zn in catalysing the formation of a carbonaceous char in burning PVC, borate may act as a low melting glass that, together with mineral hydrates and metal oxides, provides a protective barrier to impede burning.⁹ The reason zinc borates do not retard the ignition of the fire appears to be because they do not act in the vapour phase and hence do not inhibit the flame chemistry.

Peak rate of heat release

The rate of heat release is a very important parameter because it indicates the intensity of the fire and hence



2 Ignition times

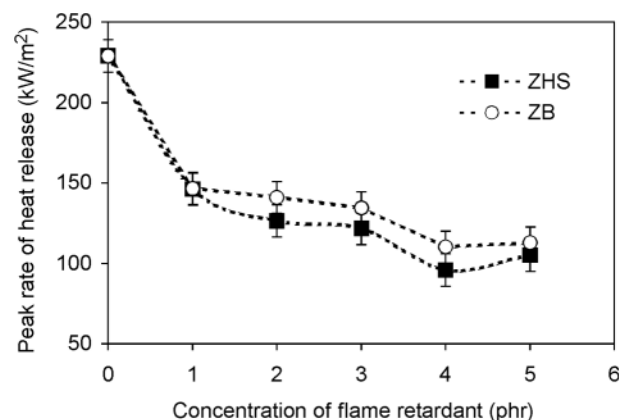
the survival time in the fire. Obviously, the lower the value of the peak rate of heat release the better. Data from the cone calorimeter are plotted in Fig. 3.

It is seen from Fig. 3 that the peak rate of heat release decreases with increasing concentration of both ZHS and ZB up to a level of 4 phr. In terms of the benefit observed, there is no point in adding more than 4 phr of either ZHS or ZB.

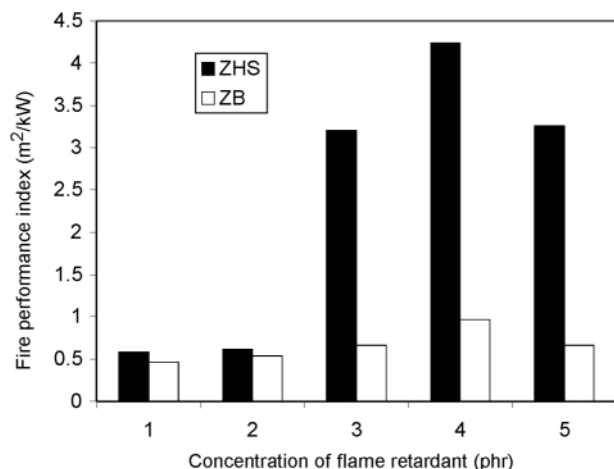
Fire performance index

The fire performance index (FPI) can be used to give an overall assessment of the fire performance of a material in the cone test. It is defined as the ratio of the ignition time to the peak heat release rate (in $\text{s.m}^2/\text{kW}$) and the higher the value of this parameter the better. The FPI is important because it has been shown to relate to the time to flashover, i.e. it indicates the time available to escape in a full-scale fire.¹⁴

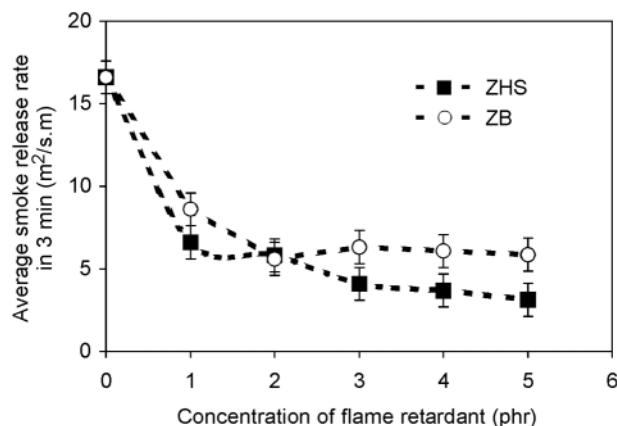
Values of fire performance index are plotted as a function of flame retardant concentration in Fig. 4. The discontinuity in performance between 2 and 3 phr of ZHS seen in the time to ignition data is also reflected in these data. The results indicate that 3 phr of ZHS is required to get excellent fire performance and that there is no benefit in adding more than 4 phr of ZHS. It is also



3 Peak rate of heat release



4 Fire performance index



5 Average rate of smoke release over 3 min

clear from the results that ZB does not confer the same improvements in fire performance as ZHS.

Average rate of smoke release over 3 min

Data for the average rate of smoke release over the first 3 min of burning are tabulated in Table 2 and plotted in Fig. 5. Obviously, the lower the value of this parameter the better. The average smoke release rate decreases with increasing concentration of ZHS up to an addition level of 3 phr; there was found to be no significant improvement at higher addition levels. Hence the optimum concentration of ZHS is 3 phr. In the case of ZB, the optimum addition level was found to be 2 phr: there was no improvement in average smoke rate at higher concentrations. The performance of ZB as a smoke suppressant is found to be inferior to that of ZHS at levels of 3 phr and above.

Total smoke

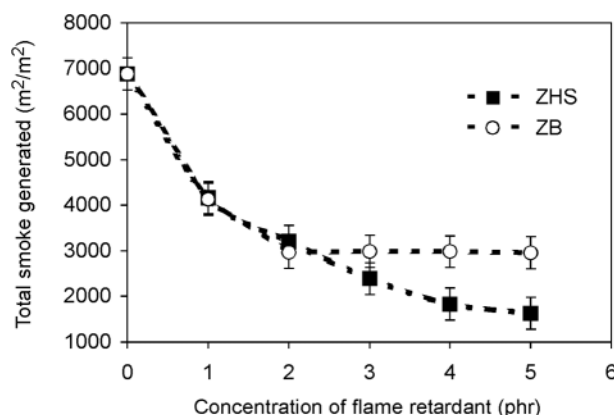
Values of the total smoke generated during each cone test are tabulated in Table 2 and plotted in Fig. 6. ZHS is a better smoke suppressant than ZB at addition levels in excess of 3 phr. The optimum addition level of ZHS is 4 phr. The optimum addition level of ZB is 2

phr: there is no further reduction in smoke evolution to be achieved by adding higher levels than this.

Impact testing

The Charpy impact test is a standard specified in BS2782 Part 3 for PVC-U window profiles. Charpy impact results are shown in Table 3. For each experimental run, 10 Charpy measurements were carried out. The values are an average of the 10 data points, except in cases where the failure mode was a mixture of ductile and brittle behaviour. In these cases, only the brittle values are considered. The number of ductile failures (hinge breaks) are also given in Table 3. These results show that mixed failure modes were found for samples containing 2, 3, 4 and 5 phr of ZHS, and 2 phr of ZB.

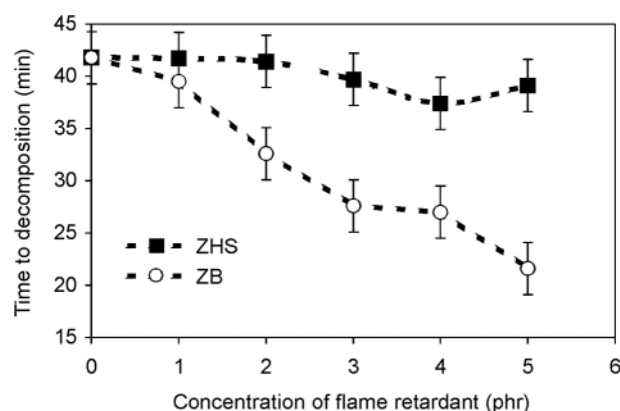
In BS2782, the Charpy test has a pass mark of 12.0 kJ/m². It can be seen that the samples containing 5 phr of ZB have failed the test. However, the finer grade of ZB used in the current study (1 µm average particle size) appears to give an improvement in Charpy behaviour over the coarser grade used in the previous study¹¹ (3 µm average particle size): the comparative values of impact strength for samples containing 5 phr of ZB are 10.96 ± 1.14 and 7.11 ± 0.55 , respectively.



6 Total smoke generated

Table 3 Results of mechanical and physical property tests

Sample Flame retardant level & type	Charpy test Impact strength (kJ/m²)	Charpy test Number of hinge breaks	Colour L* ± 0.71	Heat stability Time to decomposition (min) ± 2.5
0	13.02 ± 1.06	0	94.6	41.8
1 phr ZHS	12.52 ± 0.76	0	94.3	41.7
2 phr ZHS	14.50 ± 1.00	2	94.5	41.4
3 phr ZHS	13.16 ± 1.19	1	94.5	39.7
4 phr ZHS	14.34 ± 1.05	2	94.6	37.4
5 phr ZHS	14.14 ± 1.43	7	94.6	39.1
1 phr ZB	12.27 ± 0.85	0	94.5	39.5
2 phr ZB	12.72 ± 0.67	1	94.4	32.6
3 phr ZB	12.20 ± 0.73	0	94.5	27.6
4 phr ZB	12.71 ± 0.97	0	94.1	27.0
5 phr ZB	10.96 ± 1.14	0	94.2	21.6



7 Heat stability results

It is also seen from the data that addition of 2 or more phr of ZHS gives an improvement in impact performance. This positive effect of ZHS on impact behaviour was also noted in the previous trials.¹¹

Colour measurements

Colour measurements are given in Table 3. These are values of L^* , which represents black to white on a scale of 0–100. The data show that neither of the two flame retardants has a significant effect on colour.

Heat stability

Results from heat stability tests are tabulated in Table 3 and plotted in Fig. 7. These results indicate that ZHS does not cause a significant reduction in thermal stability of the PVC melt. However, the grade of ZB used in these trials does give rise to a significant drop in heat stability at an addition level of 2 phr and this deterioration increases with increasing concentration of ZB. This result would give cause for concern particularly when using higher levels of this flame retardant.

It should be noted that in the previous trial¹¹ there was no difference in the heat stability behaviour of formulations containing 5 phr of ZHS and 5 phr of ZB. The deterioration in heat stability behaviour caused by the current grade of ZB was thought to result from a difference in chemical composition compared with the previous grade – such as a quantity of free ZnO in the zinc borate. A sample was analysed by X-ray diffraction and it was indeed found that this grade of ZB contained a certain amount of free zinc oxide. Although ZnO is considered to be an effective smoke suppressant for PVC by catalysing the intermolecular cross-linking reactions,³ as discussed above, its detrimental effect in causing dehydrochlorination during processing renders it undesirable in rigid PVC formulations.

CONCLUSIONS

The results confirm that ZHS is an excellent flame retardant and smoke suppressant for rigid PVC

formulations. There was found to be a threshold addition level of 3 phr of ZHS, which gave a dramatic increase in the time to ignition. Hence, it is essential to add a minimum level of 3 phr of ZHS to realise its ignition prevention properties. Increasing the addition level from 3 to 4 phr did provide some extra benefits in terms of reduced rate of heat release and smoke generation. No benefit was seen in adding more than 4 phr of ZHS.

With regard to other properties, ZHS was found to give an improvement in Charpy impact performance; it did not affect the colour of the extruded profile and did not give a significant reduction in the thermal stability of the PVC melt.

ZB did not show the excellent fire retardant properties of ZHS. However, its smoke suppressant properties were nearly as good as those of ZHS, and it acted as an effective smoke suppressant at a level as low as 2 phr. In cases where fire performance is already adequate and it is required to improve smoke evolution, then ZB appears to be a cost-effective option.

The finer grade of ZB used in this study helped to overcome the problem of reduced impact performance found in the previous trial. However, the product was found to cause a deterioration in heat stability, which increased with increasing addition level. This did not occur with the grade of ZB used in the previous trial. Analysis of the product by X-ray diffraction showed that it contained a significant content of free zinc oxide, which would account for the observed reduction in heat stability. It is interesting to note that ZnO is effective in promoting char formation and may, therefore, be the reason for the very good smoke suppression properties found with this product. The optimum grade of ZB for use in rigid PVC formulations should have a fine particle size ($\sim 1 \mu\text{m}$) but without the free ZnO found in this particular case.

ACKNOWLEDGEMENTS

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