Zinc stannates as alternative synergists in selected flame retardant systems

A R Horrocks, G Smart, D Price and B Kandola

Centre for Materials Research and Innovation
University of Bolton, Deane Road
Bolton, BL3 5AB, UK

ABSTRACT

Zinc stannates, including zinc hydroxystannate, are used components within synergistic fire retardant systems usually in conjunction with halogenated species in a number of polymers. Their behaviour is similar to antimony III oxide (ATO) in that they enhance the effectiveness of the halogenated and, principally brominated retardant (Br-FR), present. Unlike antimony III oxide, they are non-toxic but are specific in their synergistic activity. Furthermore, they are effective smoke suppressants.

This paper reviews the published literature with regard to this synergistic specificity as well as the role of zinc stannates as synergists and smoke suppressants in halogenated polymers exemplified by poly(vinyl chloride), polyolefins exemplified by polypropylene, polyamides, acrylonitrile-butadiene-styrene and polyester and epoxy resins.

KEYWORDS: Zinc stannate, zinc hydroxystannate, antimony III oxide, poly(vinyl chloride), polypropylene, polyamide, acrylonitrile-butadiene-styrene, polyester, epoxy, flame retardancy, smoke suppressant

1. INTRODUCTION

Zinc hydroxystannate (ZHS) and zinc stannate (ZS) are each used as a component within synergistic fire retardant systems usually in conjunction with halogenated species. They are generally assumed to behave in a manner similar to antimony III oxide (ATO) in that they enhance the effectiveness of the halogenated and principally brominated retardant (Hal-FR) present. In addition, they have added performance effects that are not exhibited by ATO, namely smoke suppression activity, reduction of carbon monoxide formation and promotion of char formation. Both ZHS and ZS are used successfully in applications involving key polymers like PVC, polyamide and unsaturated polyester.

ZHS and ZS are related compounds that are chemically similar and are genuine mixed oxides where the zinc and tin atoms are built into a crystal lattice rather than a simple oxide.
blend. It is the chemical arrangement of the zinc and the tin within the crystal structure which gives these materials their fire protection performance.

ZHS contains hydroxyl groups that are driven off by heat (180°C) in the initial stages of a fire cooling the flames and slowing the combustion reaction. The use of these two materials is defined by this physical characteristic in that:

- ZHS is recommended for use in formulations that are processed below 180°C.
- ZS is stable at up to 400°C and is recommended for use over all temperature ranges.

Both ZS and ZHS are marketed as being so-called “environmentally friendly”, cost-effective, non-toxic replacements for ATO. The properties of commercially available ZHS and ZS are listed in Table 1.

As Flamtard H and S, zinc hydroxystannate and zinc stannate respectively were first developed as antimony III oxide (ATO) synergist replacements for use in PVC cables during the late 1980s by William Blythe Ltd and Alcan [1]. It was shown that both could be introduced into halo-polymers at levels of 1-15 phr and would demonstrate significant advantages in smoke reduction relative to ATO-containing formulations while producing similar levels of flame retardancy. For instance at 10 phr levels in a flexible cable formulation, early results showed that for ATO, ZS and ZHS gave respective LOI values of 30.5, 29 and 28.5 vol%. Smoke emissions were in the decreasing order ATO > ZS > ZHS and CO emissions were in the similarly decreasing order ATO >> ZHS > ZS. At the same time Cusack reviewed the use of tin-containing species as potential flame retardants and reported the effects of introducing both zinc stannates into a variety of halo-polymers including flexible and rigid PVC and polychloroprene [2]. In rigid PVC, for instance, inclusion of 5 phr of ZHS and ZS in rigid PVC increased the polymer LOI from 46.5 to 65.6 and 59.3 vol% respectively with 37 and 41% reductions in smoke with respect to the pure polymer. In addition, he reported results that demonstrated that both stannates functioned as synergists when present with halo-containing species present in other polymers such as alkyd resins and polyesters, outperforming ATO in most instances.

Unlike antimony III oxide, these stannates are non-toxic but they are specific in that ZS or ZHS/Hal-FR interactions depend on the brominated (halogenated) species and probably on the polymer matrix within which they are present. Limited formal literature exists on the use and FR behaviour of ZHS and so most information is often of a proprietary nature.
With the concerns regarding the use of certain brominated flame retardants in use, which in some cases have led to bans coupled with toxicological issues regarding antimony III oxide (ATO), there are significant opportunities for ZHS as an ATO replacement which together with selected Br-FRs of low environmental hazard may be fashioned for use in selected polymers and products.

Unlike ATO, which shows no FR activity when used alone, unless present in a halogenated polymer like PVC, both ZHS and ZS can be used alone in non-halogenated polymeric systems as char-promoters and smoke suppressants.

This paper reviews the current position of ZHS and ZS in particular as synergists in flame retardant formulations for specific polymers of current commercial interest - namely poly(vinyl chloride), polypropylene, aliphatic polyamides, acrylonitrile-butadiene-styrene copolymers and polyester and epoxy resins. While not covering all polymeric systems, we consider the review covers a significant fraction of the literature regarding the roles and effects of ZHS and ZS. In so doing it will provide a comprehensive overview of the present importance and potential of these agents.

2. GENERAL FLAME RETARDANT ACTIVITY

As recent brief overviews have shown [3, 4, 5] in many highly flammable, fusible polymers, the relatively inexpensive aluminium and magnesium hydroxides are often used in combination with brominated FR systems in order to achieve high levels of flame retardancy. The use of ZHS- or ZS-coated alumina trihydrate (ATH) or magnesium hydroxide (MH) makes lower loadings of these latter feasible without compromising flame retardancy or smoke suppression. and can be used with brominated polyester, polypropylene, flexible PVC, EVA and polyamide. Formulations with the coated ATH or MH often have increased LOI values with lower levels of fillers. The increase in LOI is usually polymer-dependent with some formulations realising better results than others. For example, Cusack et al [3] show that using 20phr filler alone in flexible PVC promotes an increase in LOI from 27 vol% for uncoated ATH to 37 vol% for samples containing ZHS-coated ATH. The increase was not as large for MH but the LOI still increased from 27 for uncoated sample to 33 vol% for the coated sample. Similar increases were also observed in brominated
polypropylene and polyester although are not as great. It appears that 20phr of coated filler gives the same LOI result as 40phr of uncoated filler.

Smoke suppression properties of MH are improved at all levels by the addition of ZHS but when used with ATH, it is only at lower levels that an improvement is seen. The coated fillers comprised 10 wt% ZHS and 90 wt% ATH and MH and 10 wt% ZS on 90 wt% MH [3]. The fire retardant properties are dependent on a relatively high chlorine/tin ratio which is achievable with PVC, but other polymers will need a brominated compound incorporated in the formulation to achieve the necessary ratio and aliphatic or alicyclic agents may be more effective than aromatic bromo-compounds.

The use of ultrafine powders with a typical particle size of 0.1-0.4 μm to coat the flame retardant improves the dispersion of the fillers in the polymer matrix. Commercial grades of ZHS/ZS typically have a particle size d_50 of 1.4 – 2.2 μm [4] whereas conventional solid flame retardants have particle sizes often in the range 20-50 μm, unless of the microfine variety, where in the case of ATH and zinc borate, for example, median diameters below 10 μm are available. Thus surface coating by ZHS or ZS is feasible. Furthermore, FR additives or fillers are normally used at quite high levels such as 50-60 phr, to confer flame retardancy which does have an impact on rheology and other properties, therefore any modification that can result in lower filler levels is to be welcomed [5]. ZHS starts to convert to ZS and water above 180°C so while useful for PVC and polypropylene would not be suitable for polymers with a high processing temperature. However, it is reported be stable at processing temperatures as high as 210°C [1].

Brown et al have studied the effects of particle size and distribution on rheology in ZS/ATH and ZS/MH formulations [6] with subsequent work undertaken on the surface properties of ZS [7]. Surface atomic compositions determined by XPS (see Fig. 1) for both ZS and ZS deviate from their theoretical values and these are considered to be a consequence of processing and production variables such as reagent levels used, pH, washing methods and also subsequent drying/thermal treatments. These workers also show that slow roasting of ZHS to ZS, that elemental ratios may change and that the product has superior flame retardancy and smoke suppressing properties compared to mixtures of ZS and ZHS. For example, in PVC while cone calorimetrically determined peak heat release rate values (at 40 kW/m² heat flux) for ZHS, roasted ZHS and ZS each present at about 5 wt% of 87, 78 and
122 kW/m\(^2\) respectively, smoke release values (as specific extinction area) were 229, 157 and 297 m\(^2\)kg\(^{-1}\). They conclude that some of these differences are a consequence of their relative surface areas, their elemental surface compositions and their related abilities to capture free radicals during the burning process.

3. ZINC HYDROXYSTANNATE AND ZINC STANNATE ACTIVITIES IN SPECIFIC POLYMERS

3.1 Poly(vinyl Chloride), PVC: Although, unmodified PVC is self-extinguishing, organic plasticisers are added which usually reduce the LOI significantly. While two of the earliest patents claim the use of ZS and ZHS as either conferring flame retardancy [8] or, more unusually, heat stabilisation [9] respectively in PVC specifically and chloropolymers generally, it is in the area of flame retardancy that most interest lies. It is typically used either as a complete [10] or partial replacement [11] for antimony III oxide. In the latter situation, Daniels [12] claims that Sb\(_2\)O\(_3\) levels should not be greater than 1.5 wt% for optimum effect.

Zinc stannates are effective when combined with other potential synergists and when used in both flexible and rigid PVC formulations both ZS and ZHS combined with zinc borate give good fire retardancy [10, 11, 13, 14, 15]. Results from Shen are shown in Figure 2 [16] for Firebrake ZB® which has the formula 2ZnO.3B\(_2\)O\(_3\).3.5H\(_2\)O and which interacts synergistically with antimony III oxide. Normally the latter shows a maximum effectiveness as a flame retardant in flexible PVC at 8-10 phr and the addition of zinc borate extends its performance in terms of oxygen index by at least an additional 2 LOI units.

As previously mentioned and referred to [3], zinc hydroxystannate (ZHS) when used with or to coat magnesium hydroxide (MH) or ATH is effective as a flame retardant and smoke suppressant as also claimed in a recent patent for use in PVC cable formulations [17]. The originally published work by Cusack and Hornsby [3] demonstrated that zinc hydroxystannate when coated on to either ATH or MH increased the limiting oxygen index of flexible PVC samples synergistically with respect to when each hydroxide filler was present alone. This effect is seen qualitatively in Figure 3 where ZHS-coated ATH and MH increases in LOI value with respect to the presence of hydroxide only per unit mass of filler and where ZHS coatings are 10 wt% with respect to total filler. Thus effective ZHS
concentrations range from 1 to 5 phr. Unfortunately, the LOI results for comparable mixtures of each uncoated hydroxide containing equivalent amounts of ZHS or ATO are not available for direct comparison with these coated values. However, notwithstanding this omission, Figure 3 shows that for ZHS-coated ATH, 50 phr increases the LOI by 20 units compared with only 7 units by 50 phr ATH alone. Earlier work by Cusack [2] reports that for flexible PVC having LOI=28.5 vol%, addition of 7phr ZS and ZHS respectively raises LOI values to 36.0 and 35.0 vol%, namely 7.5 and 6.5 units. Thus the separate LOI components arising from ATH and ZHS alone give a total of about 13.5 vol%, far less than the combined ZHS/ATH (at 50 phr) LOI contribution of 20 vol%. This, therefore, provides a more quantitative measure of the claimed synergy in ZHS-coated hydroxide formulations in PVC.

Cusack, Hornsby *et al* subsequently investigated the possible effects of MH particles before and after coating with ZHS having different morphologies [16, 19]. The uncoated MH shows aggregation of small crystallites which have a large surface area, but coating the MH gives rise to large particles with different surface features. There is evidence to show that the coating remains on the filler surface even after melt processing and that the improvement in fire retardant properties is attributed to better dispersion of tin compounds in the polymer matrix. LOI is seen to increase with zinc borate added to the formulation. While these coating effects have been qualitatively studied, there has been no reported work that attempts to quantitatively determine whether ZHS (or ZS): ATH (or MH) particle diameter ratios may be optimised to maximise flame retardant effects.

A more recent publication [20] shows that ZHS-coated (at about 10 wt%) CaCO₃ and ZS-coated CaCO₃ as treatment for semi-rigid PVC promotes a significant improvement in LOI from a value of 28.5 vol% for a PVC/plasticiser/CaCO₃ only formulation to as high as 36.5 vol% for both ZS- or ZHS-coated modifications. These results are plotted in Figure 4 from the published data [20] and because the addition of up to 3 wt% alone of either ZHS or ZS (equivalent to the approximate respective contents in the coated samples) generates maximum LOI values of 32.5 and 33.5 vol% respectively, the stannate-coated samples show synergistic effects. The anaerobic char yields increased from 21.9 wt% to above 50 wt% for the highest concentration (30phr) ZS-coated CaCO₃ variant with the claim that the increased char compactness in which tin and zinc play an important part, is the cause of the increased flame retardancy.
Typical rigid, unplasticised PVC formulations for use in windows give LOI values as high as 38.6 vol% or so without the use of any flame retardants but including ZHS in the formulation can increase the LOI to 52.0 vol% dependent on ZHS levels used [21] demonstrating the effectiveness of synergistic activity in these systems. Use of ZHS in such formulations is dependent on processing temperature which may be greater than 180°C in the case of heavily filled formulations such as those used in structural applications.

In plasticised PVC it is reported that the ZHS/ATH combination also reduces smoke production when compared with systems containing just ATH [8]. If a further reduction in smoke is required then using ZHS/MH is considered appropriate although again, optimal ratios have not been reported. It is well known that HCl evolved during thermal decomposition of PVC reduces flammability but contributes greatly to the level of smoke produced. MH, which is more basic, is more effective at neutralizing HCl and hence smoke than ATH [18].

Thermoanalytical and other evidence has suggested that both ZS and ZHS work in the condensed and vapour phases [2], which is thought to be the reason for the combined effects of improved flame retardancy and smoke suppression. In chlorine-containing polymers generally, presence of tin compounds is associated with increased char and reduced volatile formation and this is considered to be a part reason for smoke and CO reductions. The optimum level of ZHS for smoke suppression is about 4phr, which it is claimed reduces total smoke generated by 70% [21]. There is also evidence of volatilisation of tin and to a lesser extent zinc as halide and oxyhalide species which then function in the gas phase in manners similar to antimony III oxide-derived halides and oxyhalides [22].

3.2 Polypropylene, PP: There appear to be three significant patents in this area [23, 24, 25]. Yukihiko et al [23] report that the effect of ZS in cable sheathing made from ethylene-ethyl acrylate containing a metal hydroxide flame retardant. The addition of 3 parts by weight of ZS allowed a 23% reduction in the level of the metal hydroxide to give the same level of flame retardance using LOI and UL-94 as tests. In the patent of O’Brien [24], claims are made for an insulating material for cables comprising a blend of polyolefins and flame retardant mixture of halogenated flame retardant, non- halogenated flame retardant and flame retardant intumescent. The non-halogen flame retardant can be selected from zinc borate, ATH, MH, ZS, etc., but the patent gives no details of flame tests.
Bromine-containing PP containing 15 wt% by of bromine (a ethane bis-1,2 (pentabromophenyl)) with a LOI=22.3 vol% used with ZS-coated MH present at up to 65 phr generated only small improvements in LOI raising the value by about 2.5 units to a maximum value of 24.9 vol%, which could be attributed to inability of PP to form a char [3]. Interestingly, the recent patent by Bromine Compound Ltd., [23] claims flame retardant polyolefin compositions for use as fibres and injection/extruded moulded articles comprising tris(bromoneopentyl) phosphate, a free radical source and an additional flame retarding compound including zinc and tin compounds as being effective. No examples are given, however.

3.3 Aliphatic polyamides, notably PA6 & PA 66: The higher temperatures of processing polyamides such as nylon 6, 11 and 6.6 require the use of zinc stannate as a possible synergist because of its superior melt stability above 200°C. The role of zinc stannates in halogen-containing polyamides (nylon 6.6) was demonstrated by Chaplin [13] and Markezich and Mundhenke [26] who showed that zinc stannate could be used as a synergist in combination with zinc borate and halogenated flame retardants based on both chlorine and bromine. While synergism with both brominated and chlorinated fire retardants is claimed for a number of zinc additives including ZS there was no attempt to identify its specific role or efficiency although the various systems tested permits a reduction in the overall quantity of flame retardant used without synergist to achieve the same performance. The 1994 patent of Chaplin [13] describes the successful flame retarding of nylon 6.6 with a mixture of zinc stannate (2wt%) and borate (4wt%) together with Dechlorane Plus (12 wt%) to yield a UL94 V-0 rating. The four more recently cited patents for zinc salts in polyamide [27, 29, 29, 30] in this area are less definitive in that two [27, 28] used either a vulcanizable mixture of silicones or glass as fillers to impart some flame retardancy with zinc borate used as a secondary additive, at levels of 0.1 – 5% by weight for improved flame retardancy. The claim is made that average polymer burn time reduces from 11 to 1 s for the sample containing zinc borate and a mixture of silicones [27]. Hironaka claims that the zinc stannates may be used as ATO or sodium antimonate replacements in polyamides but cites no specific examples [29]. However, Hideaki et al [30] claim that a moulded polyamide containing an aromatic ring-containing bromine compound with bromine content of 40-50% and zinc stannate as a flame retardant synergist included in the formulation will provide
acceptable levels of flame retardancy yielding UL94 V-0 ratings for some formulations. The preferred bromine compound is brominated polystyrene.

Generally ATO cannot be used as a synergist because it catalyses polyamide decomposition leading to the formation of gaseous ammonia which forms bubbles in moulded and extruded products and the end products of the decomposition reaction promotes discoloration. However, while sodium antimonate has been claimed to be of use in aromatic polyamide systems [31], Hideaki et al [30] indicate that poor thermal stability and discoloration are evident when present with a brominated flame retardant in aliphatic and aliphatic-aromatic polyamides used in moulding materials. In contrast, ZS used on its own improves the heat resistance of the polyamide but not enough to impart flame retardance on the moulded polymer. In the presence of brominated retardants such as brominated polystyrene, high levels of flame retardancy are accompanied by acceptable levels of colour [30].

3.4 Acrylonitrile-butadiene-styrene copolymers (ABS): Jung et al [32] report that polycarbonate (PC)/ABS blends containing huntite-hydromagnetite (basic magnesium carbonate) and triphenyl phosphate (TPP) as flame retardants had an improved LOI when ZS was included in the formulation which suggests it is acting as a synergist in this flame retardant system. As TPP was introduced into a PC-ABS resin containing 25 phr huntite-hydromagnite and 2.5 phr ZHS, LOI values increased from 28.1 vol% for 0 phr TPP through 29.4 at 10 phr TPP to 31.6 vol% at 20 phr TPP. This is a particularly interesting observation in that this claimed synergism did not occur in the presence of a halogenated flame retardant and so the possibility of phosphorus-stannate synergism is established. Petsom et al [33] show that both ZHS and ZS when used alone in ABS offer little or no flame retardant properties (see Table 2), but as expected, act as synergists when used in combination with the halogen-containing flame retardants 1,2-bis(tribromophenoxy)ethane (BTBPE) and chlorinated polyethylene (CPE). Normally between 10-20 wt% of antimony oxide would be used to flame retard ABS together with 5-35 wt% of a brominated compound. For the brominated flame retardant in the presence of a zinc stannate or zinc hydroxystannate, the selected data presented in Table 2 shows the optimum stannate formulation LOI value to be about 24±0.1 vol% with the following samples achieving this value: 4-6 wt% ZHS or ZS and 20-23 wt% BTBPE. These were inferior to the formulations in which ZHS or ZS is replaced by an equal quantity of antimony III oxide. The formulation comprising 6wt% ATO and 23 wt% BTBPE yields an LOI value of 29.0 vol%. Thus in ABS ZHS and ZS are less
effective than ATO-containing systems on a weight-for-weight basis, which perhaps illustrates the greater specificity of ZS and ZHS to certain halogen-containing retardants and possibly polymer types. However, high values of LOI may be obtained with zinc hydroxystannate if an addition halogen flame retardant such as CPE is present as well and the maximum value obtained occurred with co-addition of up to 5 wt% CPE to give LOI = 29.6 vol% for ABS containing 6 wt% ZHS, 20 wt% BTBPE and 5 wt% CPE.

3.5 Epoxy resins: Nothing of substance has been reported in the literature of any research on ZHS or ZS as a flame retardant component with epoxy resins. However, the HALFREE project funded through the Sustainable Technologies Initiative and undertaken at ITRI has resulted in the production of a halogen-free inorganic flame retardant for use in the electronics industry [34]. Here ultrafine particles of tin-based fire retardants are coated on to lower cost fillers such as ATH and MH. This is still at laboratory scale and needs to be scaled up, but very encouraging results show that when compounded with epoxy these products outperform conventional bromine containing materials at a lower cost. The epoxy resins selected are those used to make printed circuit board and encapsulating membranes for semiconductors. Results show that heat is released more slowly and emissions of smoke and CO₂ are reduced. It has been impossible to obtain specific data because of confidentiality agreements, however.

3.6 Polyester resins: All relevant published sources have referred to polyester thermoset resins which need to have either a brominated or chlorinated additive included for the ZHS, used as an inorganic synergist, to work successfully. Cusack et al report that for ZHS and ZS, the higher the halogen: tin ratio the better is the fire retardancy, whereas ATO is deactivated at elevated halogen to Sb molar ratios with the optimum ratio being 3 : 1 [35]. Furthermore, the degree of dispersion and the surface areas of the flame retardant agents present determined their overall efficiency. Subsequent work [36] showed that ZHS at levels <5phr is generally an effective synergist to be used as a substitute for ATO but only in certain systems. In a later paper, these same workers reported that ZHS is as effective as ATO in the alicyclic chlorinated and the aromatic brominated systems [37]. Six halogenated flame retardants representing each organic type (aliphatic, alicyclic and aromatic) and both chlorinated and brominated types were used with four inorganic synergists including ZHS and ATO. A degree of synergism was also observed between ZHS and iron III oxide with increased char formation being apparent although colouration was a problem with some
formulations. By recording the changes in LOI and percentage reductions in peak heat release (PHRR) and smoke parameter derived from cone calorimetry at 50 kW/m² for the series of flame retardants each present at 20 phr along which each synergist at 4 phr generates, the differences in synergising ability of zinc hydroxystannate and antimony III oxide may be observed in Figure 5. The differences in respective LOI value-enhancing effects by each synergist are expressed as (ΔLOIZHS- ΔLOIATO) and values are largely negative indicating that antimony III oxide is a superior synergist, especially with decabromodiphenyl oxide(or ether), DBDPO. ZHS is seen to be slightly superior for hexabromocyclododecane, HBCD. The relative effects of each synergist in reducing the PHRR values with respective to flame retardant alone again show variable results with ZHS generally showing greater reductions for four of the retardants. When reductions in smoke parameter are considered, ZHS shows greater reductions than ATO for Dechorane Plus, HBCD and DBDPO while the converse is seen for Cereclor 70, tetrachlorophthalic anhydride and dibromoneopentyl glycol. Based on all the results, the authors recommended use of ZHS with chlorinated paraffins, tetrachlorophthalic anhydride (TCPA), chlorendic anhydride, dibromoneopentyl glycol (DBNPG) or hexabromocyclododecane (HCB), but not with Dechlorane Plus, tetrabromophthalic anhydride (TBPA) or decabromodiphenyl oxide (DBDPO).

Generally, smoke reduction can be difficult to quantify at times as it is dependent on compound and halogenated additive. Earlier work by Cusack et al [38, 39] suggested that 2 wt% ZHS is more effective at reducing smoke obscuration (measured by cone calorimeter at 50kW/m² incident flux as smoke parameter) by promoting a 73% reduction compared with 45% for 2 wt% ATO in a chlorinated (as chlorendic anhydride) system with respect to the resin only value. Respective reductions are 42% and 12% in a brominated (as dibromoneopentyl glycol) system. However, their later work outlined previously and illustrated in Figure 5 [37] showed that such a simple differentiation is not generally valid. However, the importance of fillers such as alumina, whether hydrated or anhydrous, is also an important factor. In polyester resins containing DBNPG, ATO or Sb₂O₃ increase smoke emission from unfilled and alumina-filled resins, while ZHS or ZnSn(OH)₆ significantly reduce both the rate of production, and the maximum level, of smoke generated from these materials [40]. The generally superior smoke suppressing quality of ZHS in the presence of DBNPG alone was previously demonstrated (see Figure 5) [37].
With regard to mechanisms operating, formulations containing ZHS plus brominated flame retardant or low levels (10 wt%) of chlorinated flame retardant give larger char yields, by as much as four times the respective yields of the halogenated FR alone. At higher levels (20 wt%) of chlorinated flame retardant, there is no increase in the char yield with the addition of ZHS, which is thought to be because the very high halogen:tin ratio favours formation and volatilisation of metal halides causing ZHS to function almost entirely in the vapour phase, although thermoanalytical studies indicate some condensed phase activity [37, 39]. It is likely that increases in char-forming ability may be related to reduced smoke formation, although this may be dependent upon tin:halogen ratios, of course. The effect of ZHS on the amount of CO and CO₂ evolved is questionable with very varied results although the above mentioned DBNPG/anhydrous Al₂O₃ system shows markedly reduced CO emissions. Zinc borate was also tried as a co-additive with ZHS but the performance was poor [37] unlike the synergistic activity seen in PVC [16].

Kicko-Walczak has published a number of papers [41, 42] under the ecological heading with regard to improved environmental sustainability of flame retardant polyester resins containing styrene and bromine or chlorine in the chain plus a smoke suppressant and in which addition ZHS/Al(OH)₃ and ZS/Mg(OH)₂ combinations confer non-flammability as opposed to the slower burning resins containing ZS/Sb₂O₃ formulations. Subsequent work [43, 44] reported the mechanistic studies of action of zinc stannates, identifying with ZHS a multi-stage degradation step. The first step occurs up to 200°C when the resin decomposes to release phthalic anhydride and styrene. This is followed by a second stage over the range 240-340°C and represents the interaction of the bromine moiety with ZHS, which on decomposing to ZS, then generates the volatile tin bromides, SnBrₓ where x = 2 or 4:

\[
Y–\text{CH}_2\text{-Br} + [\text{ZnSn(OH)}_6 \rightarrow \text{ZnSnO}_3 + \text{H}_2\text{O}] \rightarrow \text{Zn}_2\text{SnO}_6 + \text{SnBr}_x
\]

The third stage occurs over the range 340-420°C during which the final char structure is formed and the vapour phase flame retardant reactions take place. The released tin bromides are considered to be hydrolysed in the flame to tin II oxide and hydrogen bromide, the latter then inhibiting flame reactions:

\[
\text{SnBr}_2 + \text{H}_2\text{O} \rightarrow \text{SnO} + 2\text{HBr}
\]
Evidence also exists that tin II and IV oxides may also function in the gas phase and inhibit flame reactions via H⁺ scavenging [40]:

\[
\begin{align*}
\text{SnO} + \text{H}^+ & \rightarrow \text{SnOH}, \\
\text{SnOH}^- + \text{H}^+ & \rightarrow \text{SnO} + \text{H}_2, \\
\text{SnO}_2 + \text{H}_2 & \rightarrow \text{SnO} + \text{H}_2\text{O}
\end{align*}
\]

At higher temperatures the char is oxidised. Overall generation of CO₂ is reduced with ZHS as a synergist [36, 43]. While these reactions are supported by the earlier observations of Cusack et al [37] that as indicated by char analysis of burnt Cereclor 70/ZHS-containing polyester, 99 wt% of the tin has volatilised along with 60-90 wt% of the original zinc content, none of these mechanisms, however, attempt to explain the origins of increased char formation.

Finally, the effectiveness of zinc stannates as synergists in polyester resins generally is demonstrated by an International Tin Research Institute (ITRI) technical publication [45] and the quite recent application of experimental design methods by Hernangil et al [46] to define optimised formulations with respect to optimising flame retardancy, smoke suppression and retention of mechanical properties.

4. EFFECT OF NANOCLASTS

Recent work undertaken at ITRI [47] has shown that combining a nanoclay with the conventional filler, ATH, in a flame retardant system for polymers produces a more coherent char than either additive alone. Substitution of 10% ATH with nanoclay is beneficial in improving LOI (25.1-27.4), time-to-ignition (TTI) (56-66s) and a reduction in average and peak heat release rates. The addition of ZHS into the system further improves the results with ZHS/ATH/nanoclay system at 100phr having lower peak and average heat release rates than ATH at 150phr.

In other polymers such as ethylene-vinyl acetate copolymers, combinations of ZHS and nanoclays have been studied by Cross et al [48, 49, 50] who found that in an otherwise halogen-free system, incorporation of ZHS greatly enhances the performance of an ATH/nano-clay synergistic fire-retardant system formulation. Here, for example, the cone
calorimetrically-determined peak heat release rate (PHRR) of pure EVA is reduced from 1400 to about 450 kW/m² following the inclusion of 100 phr ATH. Replacement of 10 phr ATH by 10 phr ZHS produced a further reduction in PHRR to just above 400 kW/m². Addition of a nanoclay (81 phr ATH, 10 phr nanoclay, 9 phr ZHS) produced yet a further reduction in PHRR to just below 250 kWm². By coating the ZHS with nanoclay (90 phr ATH, 10 wt% ZHS coated with nanoclay at 10 phr) generated a similar PHRR value just below 300 kW/m². Similar reductions have been reported for similar combinations with magnesium hydroxide with PHRR values <100 kW/m² being recorded for EVA filled with 100 phr MH and 10 wt% ZHS coated with nanoclay in a 90/10 mass proportion. These results allow marked reductions to be made in overall filler levels while maintaining the desired levels of flame-retardant and smoke-suppressant properties and suggest that the use of nanoclays in conjunction with zinc stannates has potential across a number of different polymeric and flame retardant systems.

Very recent work in our own laboratories has assessed the role of nanoclays in a number of halogen-free flame retardant formulations present in polyester resins based on zinc borate and stannate as smoke suppressants and ammonium polyphosphate as the condensed phase flame retardant [51]. Formulations were based on those in Table 4.

The fire performance was studied by cone calorimetry under 50 kW/m² incident flux and smoke evolution was determined by this, smoke density and tube furnace methods. The cone calorimetry results are shown in Table 5 where TTI is the time to ignite, PHRR is peak heat release, FIGRA is the fire growth index (FIGRA=PHRR/TTI) and SEA is the average specific smoke extinction area. These results show that while the addition of either ZS or ZHS increase PHRR values of resin-APP formulations, they have a superior smoke suppressing effect when compared with the resin-APP-zinc borate formulation. Addition of the nanoclay, a montmorillonite modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium methyl sulphate (Cloisite 25A, Southern Clay Inc), while PHRR values tend to be reduced, smoke values as SEA are slightly increased for all smoke suppressants. However, this parameter is mass dependent and does not take into account the rate at which smoke is produced which is why the pure resin appears to have the lowest smoke-generating property; hence it does not represent a true indicator of smoke generation. This is overcome by defining the smoke parameter, SP, as the product of SEA and PHRR and this is claimed to be more indicative of smoke obscuration in a real fire [37, 51] (see also Figure 5). SP values are included in Table 5. These values show that now the resin has a
much higher smoke producing tendency than all additive-containing formulations and that ZB and ZS in particular have smoke suppressing activities. However, the addition of nanoclay generally increases SP values for all additive-containing formulations.

Cone calorimetry represents burning in a well-ventilated fire while most fires occur in poorly ventilated conditions, which usually exacerbate smoke generation. Use of a smoke chamber typified by ISO 5659 is often made for commercial smoke testing and this represents burning within a less-well-ventilated condition. Results of optical density, $D_s$, determined under 50kW/m$^2$ heat flux for selected samples are listed in Table 5 although and unfortunately, no data for the APP/zinc stannate/Cl 25A formulations is available. However, these results do suggest that the addition of a clay suppresses further smoke generated when zinc borate is present and this could indicate a similar behaviour in zinc stannate-containing formulations.

5. MECHANISMS OF ACTION

It is well known that ATO works as a synergistic flame retardant in the vapour phase by interfering with the free radical reactions of the combustion process [22] whereas it is suggested by thermal analysis and other techniques that ZHS works both in the condensed and the vapour phases, as previously stated [2, 37, 39]. Generally an ideal mole ratio Sn:halogen = 1:4 is considered to be the optimal ratio [2], although Cusack et al. [37] suggest that mole ratios as high as 14:1 for halogen: (Sn + Zn) may be effective, the mechanisms proposed by Kicko-Walczak [44] for ZHS in bromine-containing unsaturated polyesters discussed above (section 3.6) probably apply generally to other polymers. This multi-stage retardant activity was noted earlier by Andre et al. [39], for both ZHS and ZS in polyester resins containing either chlorine- or bromine-containing species, although no reactions are given. They noted also that ZHS alters both the initial and oxidative resin decomposition stages with the low temperature (<190$^\circ$C) weight losses increasing following its addition, possibly via dehydration to ZS. However, the overall thermogravimetric analytically determined weight losses of the later pyrolysis reactions ($\leq$400$^\circ$C) are reduced and hence char residues increased following the addition of ZHS (see Table 3). While chars may contain zinc and tin, hence explaining some of the observed char residual increase, elemental analysis has indicated that significant amounts zinc and tin are also volatilised which indicates vapour phase action [32, 36] identified above. Table 3 shows also that
increased char parallels smoke reduction following ZHS addition suggesting a relationship. The mechanism by which smoke suppression works can be explained by a two-stage process. The initial stage is char promotion leading to reduction in the supply of flammable volatiles as evidenced by results in Table 3 with a second stage of gas phase oxidation of the soot and aromatic tars produced during polymer pyrolysis [39].

6. CONCLUSIONS

There is no doubt that zinc stannates may be used as synergists with halogenated flame retardants and halogen-containing polymers as partial or complete substitutes for antimony III oxide. While this review has focused on a number of polymers in which interest in such substitution has been considerable, it is evident from the cited publications and others that they are effective in other polymers such as ethylene-vinyl acetate (EVA) copolymers [5, 19, 48]. This is not surprising, since interest in these as alternatives to PVC for use in cables has been considerable in recent years.

In conclusion it is evident that the zinc stannates exhibit the following features listed below.

- They can act as non-toxic replacements for antimony III oxide, either partially or wholly, behaving as synergists with halogen-containing flame retardants and halogen-containing polymers, although their activities appear to be more dependent upon the exact chemical characteristics of the halogen flame retardant.
- Their activity, like that of ATO, is primarily in the vapour phase but additionally there is condensed phase activity in certain formulations and polymers.
- They act as effective smoke suppressants (and because of their fire retardant properties when employed in association with ATO/halogen-based flame retardant formulations to provide smoke suppression, also permit a reduction in ATO use)
- There is some evidence that they can synergise some phosphorus-based/polymer flame retardant systems [32].
- Development work has shown that ZHS may be precipitated as crystallites on the surface of other solid particulate flame retardants such as magnesium and aluminium hydroxides to produce a coated material of enhanced efficacy.
- In the presence of metal hydroxides such as ATH, recent evidence suggests that they can improve or even synergise ATH/nanoclay formulations in polymers like EVA.
Choice of whether to use ZHS or ZS will depend on the thermal stability requirements during processing coupled with related processing factors and cost. ZHS may be used in polymeric formulations that are heated up to 180°C while ZS may be used at all processing temperatures up to 400°C.

ACKNOWLEDGEMENTS: The authors wish to acknowledge the financial assistance from William Blythe Ltd., UK in undertaking this review.

REFERENCES

16 Shen K.K (2006). overview of flame retardancy and smoke suppression of flexible PVC. In proceedings SPE Vinyltech Conference in Atlanta, October 18, 2006


45 Anon, ‘Zinc stannates in polyester resins’, *International Tin Research Institute*, Technical Bulletin No.3


<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conference ANTEC Conference Proceedings*. <strong>3</strong>: 3850-3853</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Tables

**Table 1:** Properties of commercial grades of zinc stannates [1].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Properties</th>
</tr>
</thead>
</table>
| Zinc hydroxystannate (ZHS), ZnSn(OH)$_6$ | White powder  
% Tin 41.0 – 43.0  
% Zinc 22.0 – 23.5  
% Moisture 0.7 max  
Average particle size (d50) 1.4 – 2.2. microns  
Conductivity, micro siemens 800 max  
ppm Chloride: 2000 max  
Whiteness, Wi 81 min  
Nom Surface area: 4.5 m$^2$/g  
Change of Chemical Form > 180°C |
| Zinc stannate (ZS), ZnSnO$_3$ | White powder  
% Tin 53.0 – 56.  
% Zinc 26.2 – 27.5  
% Moisture 0.5 max  
Average particle size (d50) 1.4 – 2.2. microns  
Conductivity, micro siemens 800 max  
ppm Chloride: 2000 max  
Whiteness, Wi 62 min  
Nom Surface area: 3.3 m$^2$/g  
Phase change > 600°C |
Table 2: Selected LOI results of ABS containing 1,2-bis(tribromophenoxy)ethane (BTBPE) in combination with synergists ATO, ZS or ZS [33]

<table>
<thead>
<tr>
<th>BTBPE, wt%</th>
<th>Synergist, wt%</th>
<th>LOI, vol%</th>
<th>ΔLOI, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>17.9</td>
<td>-</td>
</tr>
<tr>
<td>ZHS</td>
<td>2</td>
<td>18.0</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>18.2</td>
<td>0.3</td>
</tr>
<tr>
<td>ZS</td>
<td>2</td>
<td>17.9</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>18.2</td>
<td>0.3</td>
</tr>
<tr>
<td>ATO</td>
<td>2</td>
<td>18.9</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>19.1</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>19.4</td>
<td>1.5</td>
</tr>
<tr>
<td>20</td>
<td>ZHS</td>
<td>23.8</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>24.0</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>23.5</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>23.9</td>
<td>6.0</td>
</tr>
<tr>
<td>ATO</td>
<td>4</td>
<td>26.5</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>27.8</td>
<td>9.9</td>
</tr>
<tr>
<td>23</td>
<td>ZHS</td>
<td>24.0</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>24.1</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>23.9</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>24.0</td>
<td>6.1</td>
</tr>
<tr>
<td>ATO</td>
<td>4</td>
<td>27.9</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>29.0</td>
<td>11.1</td>
</tr>
</tbody>
</table>
Table 3: Char residues determined by TGA/DTG/DTA in air of polyester resins in the presence of chlorinated polyethylene (Cereclor 70) and decabromodiphenyl oxide (DBPDO) and zinc hydroxystannate [39]

<table>
<thead>
<tr>
<th>Halogen additive</th>
<th>Zinc hydroxystannate</th>
<th>Char residue, 400°C, wt%</th>
<th>Smoke reduction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Cl as C70</td>
<td>-</td>
<td>15.2</td>
<td>-</td>
</tr>
<tr>
<td>20% Cl as C70</td>
<td>5 phr</td>
<td>16.3</td>
<td>37</td>
</tr>
<tr>
<td>10% Br as DBPDO</td>
<td>-</td>
<td>22.6</td>
<td>-</td>
</tr>
<tr>
<td>20% Br as DBDPO</td>
<td>5 phr</td>
<td>29.7</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>5 phr</td>
<td>27.0</td>
<td>19</td>
</tr>
</tbody>
</table>
Table 4: General formulations for polyester resin, flame retardant (FR), smoke suppressant (SS) and nanoclay [51]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resin, phr</th>
<th>Flame Retardant, phr</th>
<th>Smoke Suppressant, phr</th>
<th>Nanoclay, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Res</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Res/FR</td>
<td>83</td>
<td>17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Res/FR/SS</td>
<td>83</td>
<td>8.5</td>
<td>8.5</td>
<td>-</td>
</tr>
<tr>
<td>Res/FR/SS/Clay</td>
<td>79</td>
<td>8.5</td>
<td>8.5</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 5: Cone calorimetric data (at 50 kW/m\(^2\) heat flux) from formulations of ammonium polyphosphate (APP), smoke suppressant and nanoclay (Cloisite 25) present in polyester resin [51]

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI (s)</th>
<th>PHRR (kW/m(^2))</th>
<th>FIGRA (kW/s)</th>
<th>Avg. SEA m(^2)/kg</th>
<th>Smoke parameter, SP (MW/kg)</th>
<th>Ds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Res</td>
<td>34</td>
<td>1153</td>
<td>11.5</td>
<td>580</td>
<td>665</td>
<td>1320</td>
</tr>
<tr>
<td>Res/APP</td>
<td>31</td>
<td>456</td>
<td>5.0</td>
<td>939</td>
<td>432</td>
<td>422</td>
</tr>
<tr>
<td>Res/APP/ZB</td>
<td>37</td>
<td>404</td>
<td>2.3</td>
<td>864</td>
<td>358</td>
<td>525</td>
</tr>
<tr>
<td>Res/APP/ZS</td>
<td>28</td>
<td>578</td>
<td>6.4</td>
<td>526</td>
<td>308</td>
<td>582</td>
</tr>
<tr>
<td>Res/APP/ZHS</td>
<td>35</td>
<td>615</td>
<td>4.9</td>
<td>754</td>
<td>472</td>
<td>460</td>
</tr>
<tr>
<td>Res/APP/ Cl 25A</td>
<td>34</td>
<td>453</td>
<td>5.0</td>
<td>966</td>
<td>439</td>
<td></td>
</tr>
<tr>
<td>Res/APP/ZB/ Cl 25A</td>
<td>35</td>
<td>531</td>
<td>4.6</td>
<td>897</td>
<td>476</td>
<td>444</td>
</tr>
<tr>
<td>Res/APP/ZS/ Cl 25A</td>
<td>35</td>
<td>586</td>
<td>6.5</td>
<td>767</td>
<td>468</td>
<td></td>
</tr>
<tr>
<td>Res/APP/ZHS/Cl25A</td>
<td>38</td>
<td>521</td>
<td>4.3</td>
<td>852</td>
<td>444</td>
<td></td>
</tr>
</tbody>
</table>
Figures

![Graph showing atomic percentages for Zinc stannate and zinc hydroxystannate](image)

**Figure 1:** Atomic percentages (as mole %) for Zinc stannate and zinc hydroxystannate [7]
Figure 2. Oxygen index values of PVC formulations containing zinc borate (Firebrake ZB®) as co-synergist; dioctyl phthalate (DOP) is the plasticiser. Source: Rio Tinto Mines/U.S. Borax [16]
Figure 3. Limiting oxygen index values of zinc hydroxystannate-coated alumina trihydrate and magnesium hydroxide fillers in flexible PVC containing 35 phr dioctyl phthalate as plasticiser [3]
Figure 4. The LOI of semi-rigid PVC containing zinc hydroxy and zinc stannate coated calcium carbonate filler [20]
Figure 5: Comparison of the burning properties as the difference in elevation of LOI (ΔLOI_{ZHS} - ΔLOI_{ATO}), in percentage reduction of peak heat release rate (ΔPHRR_{ZHS} - ΔPHRR_{ATO}) and percentage reduction in smoke parameter (ΔSmoke_{ZHS} - ΔSmoke_{ATO}) of zinc hydroxystannate (ZHS) and antimony III oxide (ATO) in polyester resins containing halogenated additives; TCPA – tetrachlorophthalic anhydride, DBNPG – dibromoneopentyl glycol, HBCD – hexabromocyclododecane, DBDPO- decabromodiphenyl oxide (or ether) [37]