Molybdate/Borate Complexes for Enhanced Cable Compound Fire Performance

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Abstract

Demand for low smoke wire and cable compounds including low smoke zero halogen (LSZH) compounds has been steadily growing. Such compounds often contain special additives promoting char formation thus lowering amount of smoke generated when burned. Molybdenum compounds (molybdenum oxide, ammonium octamolybdate, zinc molybdate, etc.) are widely used in flexible PVC-based wire and cable formulations as FR synergists and smoke suppressants. It was also recently demonstrated that zinc molybdate can promote char formation in certain EVA compound systems. Precipitation of molybdates onto the surface of inert minerals can significantly increase active surface area resulting in enhanced FR efficacy. Further improvement of FR performance can be achieved by precipitation of a molybdate phase on the surface of a select group of flame retardant materials such as metal hydroxides. This paper discusses the fire performance of a molybdate/borate complex consisting of a zinc molybdate shell and a zinc borate core, in two cable compound systems – flexible PVC and EVA. The effect of zinc molybdate/borate complex structure and composition on FR efficacy is discussed.

Keywords: Low-Smoke, Cable Compounds, Flexible PVC, EVA, Magnesium Hydroxide, Aluminum Hydroxide, Zinc Molybdate, Zinc Borate, Char Formation.

1. Introduction

The development of polymer compounds for wire and cable applications is a challenge that must address demanding specifications and regulations with well defined end-use requirements. For some applications, the National Fire Protection Association (NFPA) has established particularly rigorous flame and smoke standards. For example, plenum rated communication cable must pass NFPA 262, the Steiner Tunnel Test. To qualify for use, flame spread must not exceed 5 feet. In addition, peak smoke must not exceed 0.5 units and the average smoke throughout the test must be below 0.15 units.

Because PVC is an inherently flame retardant polymer, it remains a material of choice in many wire and cable applications. However, PVC, particularly when flame retarded with antimony oxide, is known to generate high levels of smoke during combustion. Also new directives such as the construction products directive (CPD) in Europe appear to promote the use of more environmentally friendly zero-halogen wire and cable materials.

The trend toward low smoke zero halogen (LSZH) materials is expected to continue in the coming years and in recent years a number of new wire and cable formulations have emerged. Ethylene vinyl acetate copolymer (EVA) is commonly used in wire and cable because of its chemical and physical properties. Similarly, polyolefins can offer desirable properties for wire and cable insulation. However, to meet fire retardant standards, effective environmentally friendly FR additives are needed. Metal hydroxides such as aluminum trihydrate (ATH) and magnesium dihydroxide (MDH) are widely used and provide fire performance by heat reduction and smoke suppression. However loading levels of greater than 60% are often required to achieve necessary FR performance leading to deterioration of mechanical properties and high processing viscosity that can diminish compounding or extrusion efficiency. In some cases, loading requirements of metal hydroxides can be lowered by controlled particle size or surface modification. From a practical standpoint, some optimized balance among FR properties, mechanical properties, processing characteristics and compound cost is desired.

One approach to improving FR performance and physical properties in metal hydroxide filled LSZH compounds is with co-additives. Metal molybdates are environmentally friendly char forming catalysts that have been used for years in low-smoke PVC and other polymer systems. It was also recently demonstrated that zinc molybdate can promote char formation in certain EVA compound systems [1]. Despite recent advancements, the search for improved FR co-additives and FR synergies continues to generate interest in the wire and cable industry.

In this work we report on the development of a new engineered flame retardant/smoke suppressant technology based on the surface treatment of zinc borate with zinc molybdate. In flexible PVC, this zinc borate/molybdate complex provides smoke suppression superior to that of a physical blend of the two components [2]. This material also provides FR and smoke suppression in LSZH systems. In EVA compound, the combination of zinc borate and zinc molybdate results in a significant reduction in the rate of heat release as determined by cone calorimetry.
2. Materials

All work was conducted using Vertex 100 magnesium hydroxide (1.5 microns median particle size, and surface area of 14 m²/g) and Micral 9400 precipitated ATH (1.0 microns median particle size, and surface area of 5 m²/g), both products manufactured by J.M. Huber Corporation.

Kemgard 911C is a zinc molybdate/talc complex manufactured by J.M. Huber Corporation. Kemgard smoke suppressants are produced by a proprietary process that results in a high surface area molybdate precipitated onto an inorganic core.

Zinc molybdate/zinc borate complexes were produced by a proprietary precipitation process that results in a high surface area zinc molybdate precipitated onto a zinc borate core [2]. Three samples of zinc molybdate/zinc borate complexes with different zinc molybdate content were prepared (Table 1). Specific surface area of zinc molybdate component was calculated using BET surface area of core zinc borate material, BET surface area of test materials and composition (Table 1).

Table 1: Calculated specific surface area of zinc molybdate component in zinc molybdate/zinc borate complexes.

<table>
<thead>
<tr>
<th>Description</th>
<th>BET surface area (measured), m²/g</th>
<th>Zinc Molybdate specific surface area (calculated), m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc borate core</td>
<td>2.9</td>
<td>n/a</td>
</tr>
<tr>
<td>10% zinc molybdate</td>
<td>5.5</td>
<td>28</td>
</tr>
<tr>
<td>17.4 % zinc molybdate</td>
<td>5.3</td>
<td>16.3</td>
</tr>
<tr>
<td>24.8% zinc molybdate</td>
<td>6.3</td>
<td>16.3</td>
</tr>
</tbody>
</table>

High surface area of zinc molybdate component is a result of the deposition of the zinc molybdate onto the zinc borate particle surface.

An SEM image of the zinc molybdate treated zinc borate is shown in Figure 1. The zinc molybdate is found as very small platelets that decorate the surface of the larger zinc borate particle.

3. Experimental Procedures

Polymer compounding was conducted using a Brabender lab mixer, followed by sheeting out on a two-roll mill. Test specimens were then compression molded. Two different wire and cable formulations were used – flexible PVC and EVA. The PVC resin used in this work was Oxyvinsyl 240F, a K70 PVC resin commonly used in wire and cable applications. Also chosen for this work was DuPont’s Elvax 265, a 28% VA content EVA copolymer specifically designed for polyolefin industrial applications. Details of formulations are presented in the Result and Discussion section below.

Figure 1. SEM Image of zinc molybdate/zinc borate complex.

FR testing of polymer compounds were performed according to the following ASTM procedures:

- ASTM E1354; Cone Calorimeter, 50kW/m²
- ASTM E662; NBS Smoke Chamber, measured in flaming mode
- UL 94; Vertical Burn Test, 1/16” thickness

Pyrolysis Combustion Flow Calorimeter (PCFC) testing was conducted according to ASTM D7309. This method, developed by Lyon, Walters and coworkers at the Federal Aviation Administration Laboratory [3] is a microscale test that determines heat release rates as a function of temperature. The total heat release (THR) is the integral of the heat release rate/time curve.

4. Results and Discussion

4.1 Performance of zincborate/zinc molybdate complexes in flexible PVC [2]

A model flexible PVC formula (Table 2) was used to compare the zinc molybdate/zinc borate complexes prepared according to [2] with a physical blend of zinc borate and zinc molybdate. Also included in the study was Kemgard 911C, a zinc molybdate treated talc. All three of these materials contained the same level of zinc molybdate. In the control formula Micral 9400 precipitated ATH was added at 50phr. The three test systems were done at 5, 10 and 15 phr. ATH levels were adjusted to maintain a fixed total filler level.

The data in Figure 2 shows the 4 minute NBS smoke (Flaming Mode) for the 3 molybdate containing systems (17.4% zinc molybdate) at the three loading levels. The data demonstrates that Kemgard 911C, the zinc molybdate treated zinc borate and the physical blend of zinc molybdate and zinc borate do lower the smoke generation and that the effectiveness of these is dependent
on use level. Identical behavior is observed with the maximum smoke density, as shown in Figure 3.

**Table 2: Flexible PVC formulation used in this study.**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>PHR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC Resin (K70)</td>
<td>100</td>
</tr>
<tr>
<td>DOP Plasticizer</td>
<td>Varies</td>
</tr>
<tr>
<td>Antimony Oxide</td>
<td>3</td>
</tr>
<tr>
<td>Aluminum Hydroxide</td>
<td>50</td>
</tr>
<tr>
<td>Thermal Stabilizer</td>
<td>3</td>
</tr>
<tr>
<td>Zinc Molybdate /Zinc Borate Complex</td>
<td>Varies</td>
</tr>
</tbody>
</table>

Comparing the results with Kemgard 911C and the zinc molybdate treated zinc borate demonstrates that selection of the inorganic substrate does influence the efficiency of smoke suppression. This is not an unexpected result since it is known that zinc borate can promote char formation in PVC and that talc is largely inert. The more surprising result is that the effectiveness of the zinc molybdate treated zinc borate was much greater than that of a physical blend with the same chemical composition. This is true at all use levels and all times.

A synergy in smoke suppression between zinc borate and molybdates in flexible PVC has been reported previously [4]. The results here further suggest that the synergy can be enhanced when the molybdate is precipitated onto a zinc borate core.

Zinc compounds (zinc borate, zinc molybdate) are known to promote the dehydrochlorination of PVC that initiates chemical crosslinking. On the other hand, molybdenum compounds are known to promote char formation and this char accounts for smoke suppression performance. Mechanistically, molybdates have been shown to react with the HCl produced by the pyrolysis of PVC to form MoOₓClₓ, a potent Lewis acid. This can then promote crosslinking in a number of ways [5-7]. The most likely mechanism is the Friedel-Crafts alkylation of alkene linkages that are formed during PVC thermolysis (eq 1) [5-7].

\[ \text{CH}=\text{CHCHCl} + \text{CH}=\text{CHCH}=\text{CH} \rightarrow \text{CH}=\text{CHCH} \overset{\text{Lewis acid}}{\text{CH}} + \text{HCl} \]  \( \text{eq 1} \)

It can be seen in both Figure 2 and Figure 3 that the smoke density development in the sample containing 5 phr of the zinc molybdate treated zinc borate was comparable to that of the sample containing 15 phr of the physical blend. This is a remarkable result and suggests a far more efficient use of the zinc molybdate chemistry due to its much higher specific surface area compared to bulk zinc molybdate (5-8 m²/g).

4.2 Performance of zincborate/zinc molybdate complexes in EVA

Molybdates have been used as a flame retardant/smoke suppressant for many years in halogen containing systems, especially in rigid and flexible PVC. More recently use of molybdates in some halogen-free systems has been reported. [1, 8]. It was demonstrated [1], that zinc molybdate can promote char formation in EVA formulation containing magnesium hydroxide (Figures 4A and 4B).

Replacement of part of Vertex 100 magnesium hydroxide with zinc molybdate (4:1 ratio) led to significant reduction of heat release rate and delay of secondary heat release peak as shown on Figure 4A.
Partial replacement of magnesium hydroxide with zinc molybdate also leads to a delay of the secondary smoke peak formation, although the total amount of smoke increases (Figure 4B).

![Figure 4A. Cone Calorimeter Curves (Rate of Heat Release) for EVA Containing Magnesium Hydroxide and Magnesium Hydroxide/Zinc Molybdate blend 4:1 ratio. Total loading level 64% [1].](image)

Use of zinc molybdate/zinc borate complex instead of pure zinc borate leads to a further reduction of the heat release rate as well as an additional delay in secondary heat release peak formation indicating more efficient char formation (Figure 5A).

![Figure 4B. Cone Calorimeter Curves (Specific Extinction Area) for EVA Containing Magnesium Hydroxide and Magnesium Hydroxide/Zinc Molybdate blend 4:1 ratio. Total loading level 64% [1].](image)

Similar effects of zinc borate and zinc molybdate/zinc borate complex were observed in smoke generation measured by cone calorimetry (Figure 5B).

The mechanism of char formation promotion by zinc molybdate in EVA is believed to be similar to that in PVC and based on Friedel-Craft alkylation alkene linkages formed during EVA decomposition:

$$\text{O} = \text{C} - \text{CH}_3$$

$$\text{O} - \text{CH} = \text{CH} \_ \_ \_ \_ \_ \text{z} \_ \text{CH} = \text{CH} - \text{CH} = \text{CH} + \text{CH}_2\text{COOH}$$

$$\text{z} = \text{Lewis Acid (Mo}^{6+} \text{surface)}$$

Use of pure zinc molybdate in wire and cable formulations is impractical because of unfavorable economics. We have recently shown [1] that Kemgard MZM, a zinc molybdate modified magnesium hydroxide, also promotes char formation and can be effectively used as a flame retardant in EVA wire and cable applications.

In this work, FR performance of zinc molybdate modified zinc borate was investigated using a model EVA based formulation shown in Table 3.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA Copolymer (28% VA)</td>
<td>29.1</td>
</tr>
<tr>
<td>Magnesium Hydroxide</td>
<td>Varies</td>
</tr>
<tr>
<td>Zinc Borate</td>
<td>Varies</td>
</tr>
<tr>
<td>Zinc Molybdate-Zinc Borate Complex</td>
<td>Varies</td>
</tr>
<tr>
<td>Polymeric Compatibilizer</td>
<td>6.0</td>
</tr>
<tr>
<td>Processing Aid</td>
<td>0.7</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Char formation synergy between zinc molybdate and zinc borate in zinc molybdate/borate complex is confirmed by Pyrolysis Combustion Flow Calorimeter (Figure 6). Partial replacement of magnesium hydroxide with zinc borate (5:1 ratio) leads to a small increase of the peak heat release temperature indicating formation of a stronger, more thermally stable char.

At the same time, partial replacement of magnesium hydroxide with zinc molybdate/borate complex (at the same 5:1 ratio) leads not only to the increase of peak heat release temperature, but also to significant reduction of total heat released (area under the curve). This is an indication of the reduced amount of volatile
combustible ingredients forming during char thermal decomposition.

Figure 5A. Cone Calorimeter Curves (Rate of Heat Release) for EVA Containing Magnesium Hydroxide, Zinc Borate and Zinc Molybdate-Zinc Borate Complex (24.8% zinc molybdate).

Figure 5B. Cone Calorimeter Curves (Rate of Smoke Production) for EVA Containing Magnesium Hydroxide, Zinc Borate and Zinc Molybdate-Zinc Borate Complex (24.8% zinc molybdate).

In this paper, we also observed failure of EVA compound containing 64% of magnesium hydroxide, but UL94 performance was improved to V-1 ($t_1 + t_2 = 42$ sec) when MDH was partially replaced with zinc borate (Figure 7).

Figure 6. PCFC of Elvax 265 EVA Containing Magnesium Hydroxide, Zinc Borate and Zinc Molybdate-Zinc Borate Complex (17.4% zinc molybdate).

Figure 7. UL94 Vertical Burn (1/16") of Elvax 265 EVA Containing Magnesium Hydroxide and Zinc Compounds (10:1) ratio. Total loading level 64%.

Increase of zinc molybdate content in zinc molybdate complex leads to significant improvement of UL-94 performance. At 24.5% zinc molybdate level, the compound achieves the UL-94 V0 rating. This data presents additional evidence of FR synergy existing between zinc molybdate and zinc borate in EVA.

NBS Smoke density results for the EVA compounds containing 64% total filler are shown in Figure 8. We have previously shown [1] that magnesium hydroxide was a very effective smoke
suppressant in EVA and replacement of any part of MDH with zinc molybdate led to an increase of smoke density.

![Figure 8. NBS Smoke Density for EVA containing 64% FR additive at varying MDH/Zinc Compound Ratios](image)

On the contrary, partial replacement of magnesium hydroxide with zinc borate leads to significant reduction of maximum corrected smoke density (Figure 8). If magnesium hydroxide is partially replaced with zinc molybdate/zinc borate complex, reduction of maximum corrected smoke density is even more significant. Zinc molybdate content in zinc molybdate/zinc borate complex does not seem to play significant role in 10-24% range.

5. Conclusions

Polymer compound for wire and cable applications face increasingly rigorous flame and smoke standards. At the same time, the industry is moving away from some traditional FR additives that may pose health or environmental concerns. As a result there is a growing need for efficient, environmentally friendly FR materials.

Previous work indicated an FR synergy between zinc borate and molybdates. In this paper we reported on the development of a new FR additive based on the precipitation of a high surface area zinc molybdate onto the surface of a zinc borate core. The resulting structure enhances the borate/molybdate synergy and provides FR and smoke suppression in several different polymer systems.

In flexible PVC, the zinc molybdate treated zinc borate proved to be a very effective smoke suppressant. Significantly, the performance was far greater than that of a physical blend with the same chemical composition. This can be attributed to the unique physical structure where small platelets of zinc molybdate decorate the surface of the larger zinc borate particle.

Both zinc borate and zinc molybdate are known to be effective flame retardants in EVA, especially when used in combination with metal hydroxides. Presumably both contribute to flame retardancy by promoting char formation, although the mechanisms may differ. In this work we demonstrated that a zinc molybdate/zinc borate complex outperforms pure zinc borate in MDH filled EVA. This is due to a synergy between the two zinc compounds as well as more efficient use of the molybdate surface because of high surface area.

The zinc molybdate content in the zinc molybdate/zinc borate complex also affects FR efficiency of this material. Higher zinc molybdate content leads to better compound performance in UL94 vertical burn test and also lowers the amount of smoke generated.

The combination of zinc molybdate and zinc borate in a single, high surface area composite appears to provide outstanding FR and smoke suppression performance in both PVC and EVA. Future work will expand into other polymer systems such as polyethylene, polypropylene and polyolefin elastomers (e.g. ethylene octene copolymer).

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7. References


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