

# Synergistic Benefits of Metal Hydroxides and Zinc Borate in Flame Retardant Wire and Cable Performance Compounds

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## Abstract

This paper discusses the use of metal hydroxides such as magnesium hydroxide or alumina trihydrate with zinc borate for formulating high-performance wire and cable compounds, including the polyolefin compounds for data cable jacketing and automotive wire applications. Results of extensive fire performance investigations using UL 94 and cone calorimetry are discussed in order to determine the optimal ratio of borate to metal hydroxide for a given base polymer and compound application. Compound performance tradeoffs associated with using the MDH and borate fire retardant combination are investigated. Enhanced compound performance using the unique MDH particles, such as Vertex™ 100, in combination with Firebreak® ZB-Fine zinc borate is illustrated.

## Introduction

Demand growth for halogen-free, low-smoke flame retardant wire and cable products has continued to drive compound design and engineering using certain cost-performance effective flame retardant additives. This has led to continuous research effort to methodically examine some of the commercially available non-halogen fire retardant systems. A new magnesium hydroxide product called Vertex 100 has been developed by J. M. Huber Corporation to offer a set of compound performance benefits such as enhanced fire property at attractive cost. Vertex 100 is characterized by its uniquely engineered particle morphology that forms the key material attributes to enable the significant improvement in compound performance.

Metal hydroxides such as alumina trihydrate (ATH) and magnesium hydroxide (MDH) provide good flame

and smoke properties when used at high loading levels (typically 50-60 % by weight for polyolefin-based systems). At these levels, there can be performance tradeoffs such as reduced physical/mechanical properties and processing rheological performance. Zinc borate such as the *Firebreak*® products is a boron-based flame retardant that can function as an effective charring promoter as well as a smoke suppressant. Adding borates to a metal hydroxide containing compound can result in synergistic performance benefits, notably in the compound fire performance and rheological properties.

The  $B_2O_3$  released from decomposition of the borate promotes formation of a ceramic layer, along with MDH or ATH. In addition, as with the metal hydroxides, certain zinc borates also give off water when decomposed, diluting the combustible gases and suppressing smoke. Earlier literature reports suggest that the interaction of metal hydroxide with borate can lead to a hard residue with porous structure which functions also as a thermal insulator or barrier protecting the polymer. Such strong chars can prevent the volatile gases from reaching a combustible ambience.

While the metal hydroxide-borate flame retardant system can be used for a broad range of polymers, this study focuses on the synergistic performance of this FR system in an EVA polymer compound system.

## Materials and Testing

All MDH and zinc borate materials used in this study are commercial products, listed in Table 1a and Table 1b. A wire and cable compound system based on an EVA polymer was used. The EVA resin has

28% VA content unless otherwise noted and a moderate molecular weight. The compound also contains a polymeric compatibilizer as well as several functional additives. Test compounds were prepared in a Brabender mixer followed by two-roll milling of the mixture to achieve increased compound homogeneity. All material testing were performed according to ASTM and UL procedures.

**Table 1a. Particle characteristics of MDH studied**

Material ID	Product	Average Particle Size (microns)	Surface Area ( $\text{m}^2/\text{g}$ )
MDH-1	Vertex 100*	0.8	14
MDH-2	Zerogen 50*	1	7
MDH-3	Comp A**	1.1	7

\* Products of J. M. Huber Corporation

\*\* Comparative MDH product available commercially

Vertex™ is a trademark of J. M. Huber Corporation.

Zerogen® is a registered trademark of J. M. Huber Corporation.

**Table 1b. Zinc borate materials studied**

Product	Chemical formula	Average Particle Size (microns)
Firebrake® ZB	$2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3.5\text{H}_2\text{O}$	9
Firebrake® ZB-Fine	$2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3.5\text{H}_2\text{O}$	2
Firebrake® 415	$4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$	5

Firebrake® is a registered trademark of Luzenac/Borax.

Cone calorimetry testing was performed per ASTM E-1354, tested on compression molded plaques with thickness of 0.125", using 50kW/M<sup>2</sup> heat flux. UL 94 vertical burn testing was done with 1/16" thickness plaques.

## Results and Discussion

For many flame retardant compounds used for wire and cable applications that use the metal hydroxide as the main flame retardant, the high loading levels of metal hydroxide call for consideration of using the MDH that has been surface modified to help achieve enhanced dispersion of MDH in the polymer. Different silanes have been used to modify the surface of MDH for this purpose. The silicon-

functional side of the silane molecule undergoes hydrolysis on MDH surface, with hydrolyzed silane molecules reacting and interacting with the MDH surface. The organic-functional end of the silane molecule dictates how the surface treated MDH interacts with the polymer.

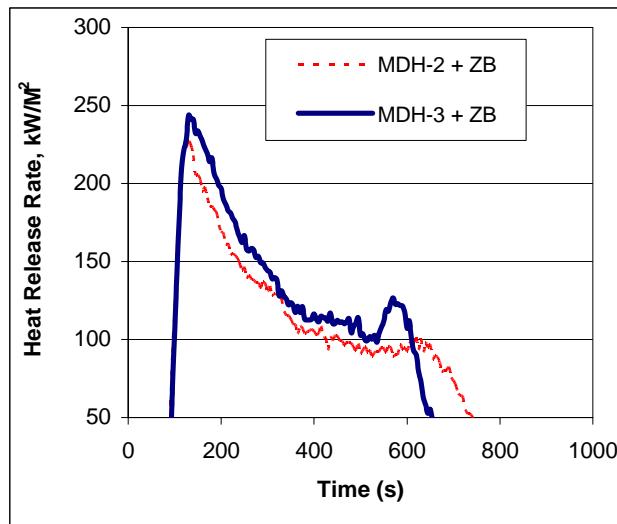


Fig. 1a. Effect of MDH surface treatment; Heat release data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1.)

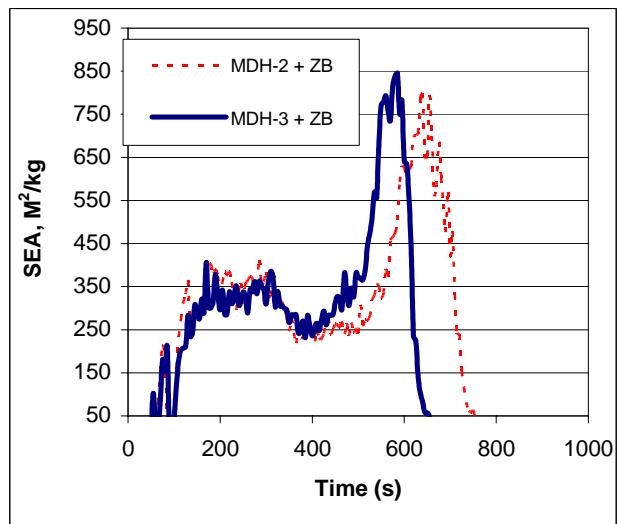


Fig. 1b. Effect of MDH surface treatment; Smoke generation data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1.)

Vinylsilane and aminosilane are two of those silanes that can improve coupling of MDH to polyolefin resins such as EVA. An MDH treated with vinyl silane (MDH-2) and an MDH treated with aminosilane (MDH-3) were compared first to determine which of

the two would provide better fire performance for the polymer system studied. The results from cone calorimetry testing are shown in Figures 1a and 1b for heat release and smoke production, respectively.

Based on the cone data, the vinylsilane-treated MDH appears to have slightly better fire performance of the two. Limiting Oxygen Index testing showed that the compound made with the vinylsilane-treated MDH having a higher LOI value of 38% vs. 35% for the compound made with the aminosilane-treated MDH. The rest of studies presented here were based on use of the vinylsilane-treated MDH.

Three zinc borate products listed in Table 1b were compared for their synergistic effect with MDH in fire performance, measured by the cone calorimetry. Our objective was to see that, for a specific MDH-filled EVA compound system, which zinc borate would provide the best overall fire performance. We were also interested in determining the possible property and performance gaps in the material attributes other than fire performance, among these different zinc borates, using a vinylsilane-treated MDH.

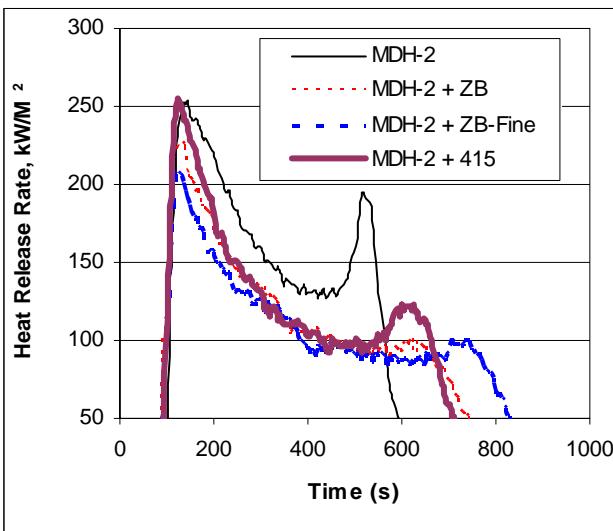


Fig. 2a. Heat release data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1 when the borate is used. 415 denotes Firebreak 415. MDH-2 was treated with vinylsilane.)

Figures 2a and 2b show the heat release and smoke production measurements on the compounds made with and without zinc borate. Two observations are made from these results. First, replacing 20% of MDH with zinc borate showed improvement in heat reduction and smoke suppression, and this is true for all three borates investigated. This is indicated by

reduced and deferred heat release and deferred smoke generation when a zinc borate was added. The changes in heat and smoke dynamic profiles suggest a performance benefit by using a combination of MDH and borate in improving the compound fire performance.

Secondly, Firebreak ZB and particularly Firebreak ZB-Fine appear to be more effective than Firebreak 415 in imparting the FR synergy. This is attributed to the presence of higher  $B_2O_3$  content in ZB and ZB-Fine than in 415. Between ZB and ZB-Fine, the latter also seems to be more effective of the two.

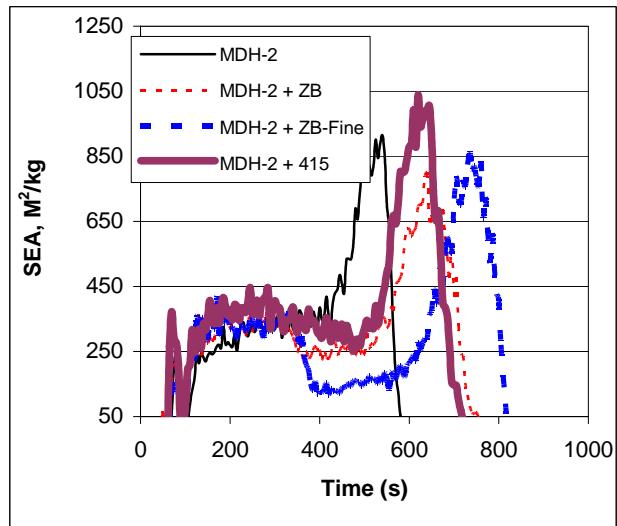


Fig. 2b. Smoke generation data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1 when the borate is used. 415 denotes Firebreak 415. MDH-2 was treated with vinylsilane.)

It should be pointed out that, by keeping the total FR loading level unchanged, the use of an MDH-borate combination would not affect negatively other compound properties, such as mechanical property or processing rheology. This will be discussed in a later section.

The synergistic benefits in compound fire performance with the MDH-borate system was also confirmed on another MHD material (MDH-1 or Vertex 100) that has different morphological characteristics than MDH-2 and MDH-3. This is illustrated by the comparative cone testing results shown in Figures 3a and 3b.

MDH-1 or Vertex 100 is a new product of J. M. Huber Corporation which has been engineered to provide attractive cost-performance benefits for non-halogen, low-smoke wire and cable applications. One quick

and clear observation of Figures 3a and 3b is that adding zinc borate to the Vertex 100-filled EVA compound can reduce heat release magnitude while pushing back the secondary heat release peak. The same is also true for the smoke suppression shown by Figure 3b.

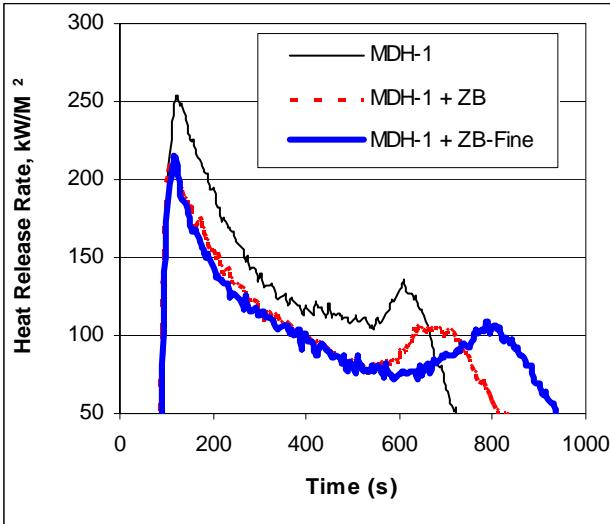


Fig. 3a. Effect of adding zinc borate to MDH-1 filled EVA compound, Heat release data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1 when the borate is used. MDH-1 was treated with vinylsilane.)

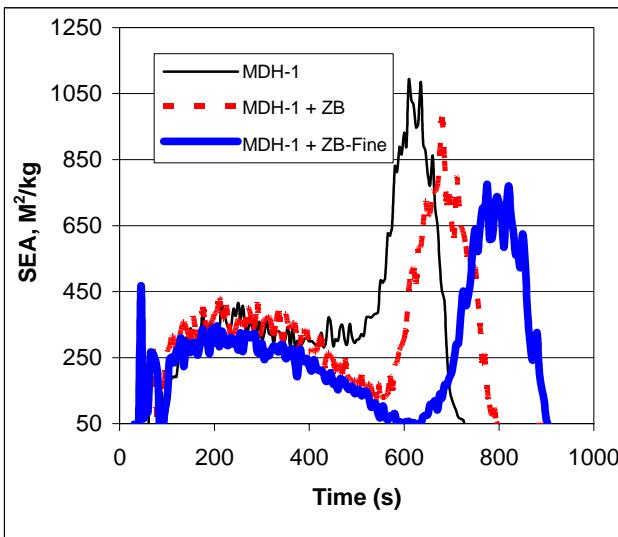


Fig. 3b. Effect of adding zinc borate to MDH-1 filled EVA compound, Smoke generation data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1 when the borate is used. MDH-1 was treated with vinylsilane.)

By comparing borate ZB and ZB-fine as an FR synergist with Vertex 100, one observes that ZB-Fine

is more effective in delaying the secondary peak of heat release and smoke production for the compound. This synergy between Vertex 100 and borates is consistent with what was observed in other premium but more expensive grades of commercial MDH grades such as MDH-2 and MDH-3 listed in Table 1a.

Given its unique morphological features of particles, Vertex 100 has been shown to be more effective in reducing compound heat and smoke when burned as compared to other premium MDH grades such as MDH-2 and MDH-3 that have been traditionally used in formulating low-smoke wire and cable compounds.

Figures 4a and 4b demonstrate such enhancements in fire performance that can be expected from Vertex 100 or MDH-1. In these two figures, Vertex 100 clearly shows more favorable dynamic profiles of flame and smoke. Also evidently, substitution of a small portion of Vertex 100 with Firebreak ZB-Fine while keeping the total FR loading unchanged, one is able to further enhance the compound fire performance as shown.

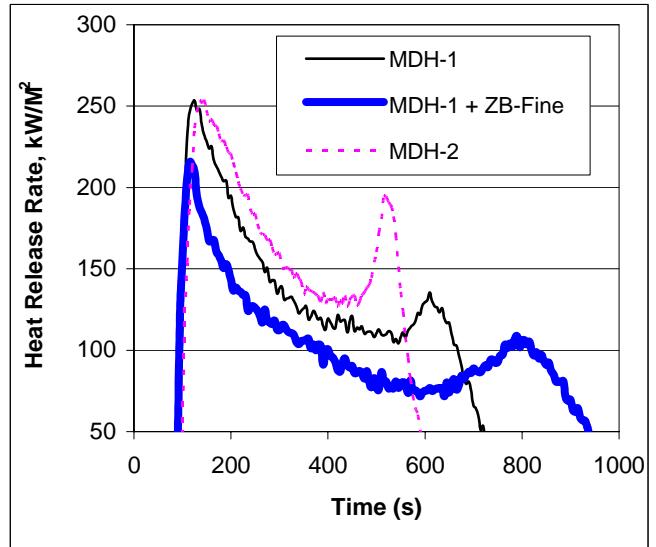


Fig. 4a. Fire performance comparison of MDH-1, heat release data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1 when the borate is used. MDH-1 and MDH-2 were treated with vinylsilane.)

Additional formulations were also made with varying ratios of borate to MDH in order to study their fire retarding synergism, both effectiveness and efficiency. These results are shown in Table 2 and Table 3. In Table 2, fire testing results are shown for three compounds made with same total loading level

of flame retardants (MDH + borate) but with varying ratios of MDH to borate.

It appears that there may be an optimal ratio of MDH to borate between 5 and 12 that provides best overall fire performance. While all three ratios of MDH to borate resulted in V0 and comparable oxygen index values, it is clear that there are finite fire performance differences among them based on the cone measurements. Literature references have also indicated that borate used at 5-10% by weight of total composition may provide an effective and maximized synergism with MDH.

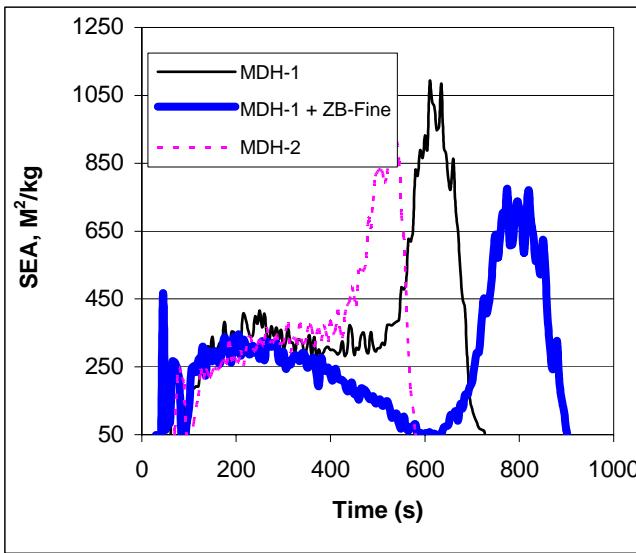


Fig. 4b. Fire performance comparison of MDH-1, Smoke generation data by cone calorimetry. (Total FR in EVA is 60 wt%, ratio of MDH to borate is 5:1 when the borate is used. MDH-1 and MDH-2 were treated with vinylsilane.)

**Table 2. Effect of MDH to borate ratio on FR performance (total FR loading ~ 65%, Firebreak ZB-Fine used)**

Ratio of MDH to borate	Time to ignition, s	Peak HHR, kW/m²	Ave. SEA, M²/kg	UL 94	LOI
11.8	68	61	84	V0	40
5.4	64	163	60	V0	39
3.2	60	168	87	V0	38

A closer look into the heat release profiles for the compounds with three different ratios of MDH to borate given in Table 2 results in the comparison shown in Figure 5. The highest MDH to borate ratio of 11.8 had produced the slowest heat release, while the lowest ratio of MDH to borate at 3.2 yielded an

added secondary heat release peak not observed with the two higher ratios of MDH to borate.

Using the ratio of 5:1 for MDH to borate, we also studied the effect of various total FR loading level in the compound. The results are shown in Table 3. It is clear that compound fire performance began to suffer when the total FR loading level falls below 60%. Therefore, it is important to determine the proper total loading level of FR additives in a commercial low-smoke compound to assure that compound fire performance is met.

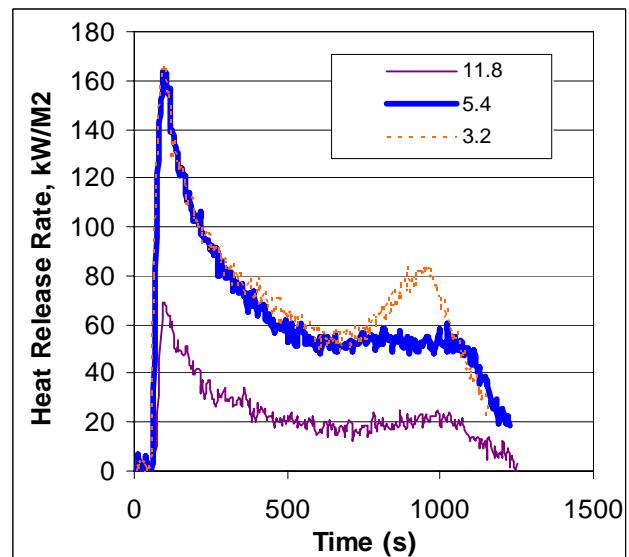


Fig. 5. Effect of MDH to borate ratio on heat release. The legends denote the ratio of MDH to borate. (Total FR in EVA is 65 wt%, 3 ratios of MDH to borate are shown, MDH-1 used were treated with vinylsilane.)

As indicated in the introduction, use of metal hydroxide flame retardants to make wire and cable compounds causes concerns for reducing mechanical properties relative to some of the halogen-based compounds. Given the fire performance synergy between MDH and borate as illustrated earlier, we also investigated the effect of adding zinc borate to an MDH-filled compound on the compound mechanical property. Table 4 gives such results comparing the surface-modified MDH with unmodified MDH.

As shown, substituting a portion of MDH with zinc borate does not markedly shift the compound mechanical property when using the borate at low levels (e.g., <10%) for the systems studied. One important observation can be made from the Table 4 data. There can be certain performance tradeoffs when using certain surface-treated MDH in a given

polymer system. Here as shown by Table 4, while there is a significant improvement in fire performance indicated by UL 94 results when using the silane-treated MDH, there is also a reduction in compound tensile strength going from untreated MDH to treated MDH.

**Table 3. Effect of total FR loading (Firebrake ZB-Fine+MDH-1) on fire performance (MDH to borate ratio ~ 5:1)**

Total FR, wt%	Time to ignition, s	Peak HHR, kW/m <sup>2</sup>	Ave. SEA, M <sup>2</sup> /kg	UL 94	LOI
64	64	163	60	V0	39
60	64	216	255	fail	37
48	57	377	439	fail	29

Therefore, selection of the surface treatment type as well as use of the treated MDH is dependent on the optimal compound performance balance in meeting the requirements.

**Table 4. Effect of borate on EVA compound mechanical properties (total % of MDH-1 + Firebrake ZB-Fine = 65%)**

	Untreated MDH-1			Vinylsilane-treated MDH-1		
	Zn Borate, wt%	0	5	10	0	5
Tensile Strength,	1544	1531	1499	1385	1306	1266
Elongation at break, %	95	102	105	106	115	140
UL-94	Fail	Fail	Fail	V-0	V-0	V-0

One other compound performance consideration is its processability as it can affect the extrusion process and extrusion throughput. Figure 6 compares Brabender rheometer results of three MDH-filled EVA compounds, with or without zinc borate. For the compound system studied, replacing MDH with borate actually resulted in more favorable processing rheology, i.e., lowered compound viscosity. This may be attributed to the formation of a more desirable particle packing between MDH and zinc borate particles when being inter-dispersed in the polymer. The synergistic effect for the EVA compound performance by using Vertex 100 and Firebrake ZB-Fine is evident in both fire performance and processing benefit.

This processing benefit resulting from using the MDH-borate system can enable use of the high

molecular weight polymers to help offset the possible mechanical property tradeoffs, such as tensile strength as discussed in Table 4. This also illustrates the opportunity for engineering and optimizing a flame retardant compound by selectively using proper flame retardants and polymers. It is worth pointing out that such gains in compound processing by using a borate and an MDH may not be universally always present or available with other non-selective combination of MDH and borate.

Figure 6 also shows the lowering of compounding viscosity when using the surface-treated MDH vs. the untreated MDH. A similar reduction was also observed with the 10% loading level of the borate in the MDH-filled EVA. Referred back to the data given in Table 4, one notices that the compound performance benefits with use of the treated MDH can be multi-dimensional.

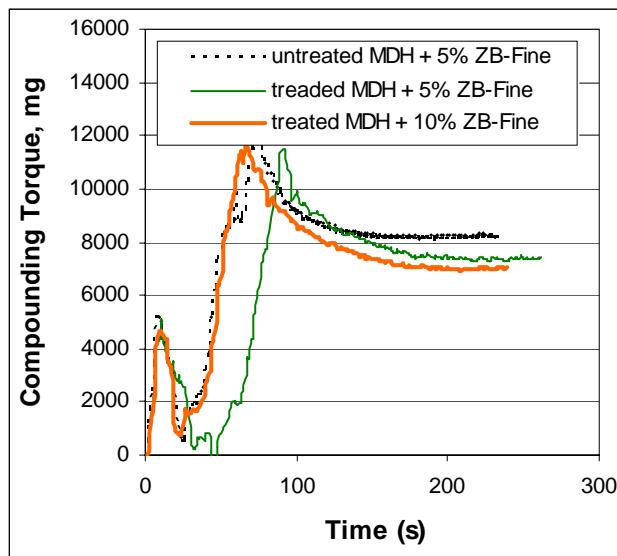


Fig. 6. Effect of adding borate on compounding rheology (Total FR in EVA is 65 wt%, with MDH-1 treated with vinyl silane.)

The similar synergistic benefit in fire performance as seen with the MDH/zinc borate system can also be observed with the ATH/borate system. Figure 7 shows the effect of adding Firebrake ZB-Fine to an ultrafine particle size ATH in a comparable EVA compound system. It is clear that replacing 5 % of ATH with the borate reduces the heat production.

It is interesting to note, however, that the degree of heat reduction seen here with the ATH/borate combination is not as significant as observed when the same level of zinc borate is added to an MDH-

filled compound. This may be attributed to the fact that ZnO tends to form a harder char with MgO than with Al<sub>2</sub>O<sub>3</sub>, the latter two metal oxides formed as a result of thermal decomposition of the respective metal hydroxide.

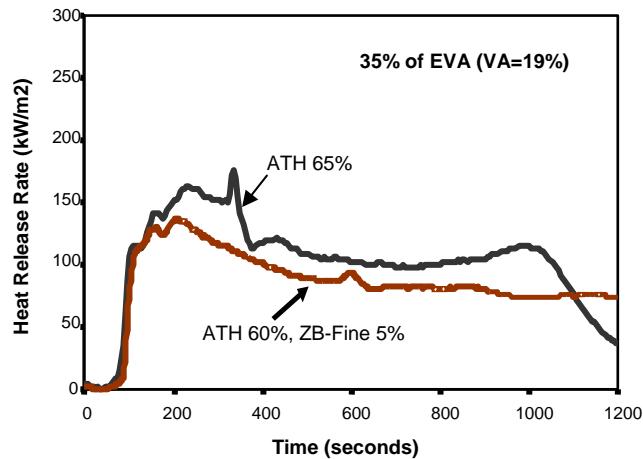


Fig. 7. Effect of adding zinc borate to an ATH-filled EVA on fire performance shown by cone calorimetry heat release (Total FR in EVA is 65 wt%, with an untreated ATH)

## Conclusions

This work studied the performance synergism between magnesium hydroxide and zinc borate when used to make flame retardant compounds for wire and cable applications. For the polyolefin compound system investigated, addition of a zinc borate to a polymer filled with an MDH can result in significant performance synergies or enhancements, including fire performance and compound processing benefits. When used in conjunction with metal hydroxides, Firebreak zinc borates can further reduce rate of heat release, smoke evolution, and promote the formation of a strong char/ceramic residue.

This study shows that there is an optimum ratio of MDH to borate when using both together for a maximized performance balance. For the EVA compound system investigated, this optimal ratio was found to be between 5 and 10. Increased usage of the borate could result in higher compound cost with limited additional gains in the performance benefit.

Three different zinc borate products were studied in three different MDH materials. The fine particle size borate, Firebreak ZB-Fine is found to impart a best fire performance synergy with MDH. Vertex 100, a new MDH product by J. M. Huber Corporation, shows better overall fire performance, both with and without

addition of a borate, as compared to two other commercial MDH materials that are characterized by different particle morphology from that of Vertex 100. The combination of Vertex 100 and Firebreak ZB-Fine appears to result in best overall performance improvement for the EVA compound used, in compound fire property and processing behavior.

The performance gain resulting from a special combination of MDH and borate allows for use of high molecular weight polymer to help minimize any possible reduction in compound mechanical properties that may be related to the high loading level of the FR additives.

Use of the surface-modified MDH can also bring about compound performance benefit such as enhanced fire performance and processing. It was also observed that zinc borate can improve processing rheology. Care must be exercised, however, in selecting the right surface treatment type for a given polymer to achieve this added performance benefit.

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