

Compounding metal hydrate flame retardants

Magnesium hydroxide and ATH flame retardants require much higher loadings than halogen-based flame retardants. Jim and Ann Innes of Flame Retardants Associates, Inc. review various flame retardant standards and the amount of metal hydrate needed in specific polymer systems. In addition, changes in compounding techniques and formulation technology are needed to incorporate these flame retardant types into useable products, as well as the use of processing aids and modification of the metal hydrate flame retardant. Martin Marietta Magnesia Specialties has launched extensive research programmes to combine magnesium hydroxide flame retardants into polymers. Jim and Ann Innes present some of the recent results produced.

Formulation and compounding

There are several helpful rules for formulation and compounding when working with metal hydrate flame retardants. The first rule is to build a formulation based on the known characteristics of the metal hydrate. It is critical to remember the flame retardant and filler characteristics to be imparted to the system by the metal hydrate component. The formulation should be developed using basic principles of polymer formulation. For example, do not expect to use the same base resin or the same processing aids that are used

with halogen flame retardant systems. In other words, avoid formulating by simple substitution of a metal hydrate for a halogen compound in a flame retardant formulation. This almost never works. In addition, the resin previously used to produce non-flame retardant products will most likely not be appropriate for a metal hydrate flame retardant product.

Knowing what flame retardant standard is required and confirming the appropriateness of that standard for the application is paramount to successful formulating. This second rule also applies to metal hydrate systems. Frequently a customer specifies UL94 V-0 because this is

a familiar standard, which is easy to understand and execute. However, the application may actually require more or less severe flame retardant performance. The application may be entirely unrelated to the UL94 test standard. Examples of common building products specifications are listed in Table 1, which are not related in any way to UL94.

Another rule for compounding metal hydrate systems is to understand fully the mechanisms by which metal hydrate flame retardants operate (see box). These mechanisms are distinctly different from those of halogen flame retardants. The differences will affect the end product in a fire scenario. These differences must be considered during the development of the polymer formulation and in the overall product design.

Metal hydrate effects on the base resin

Metal hydrate flame retardants affect the polymer matrix in many ways. First, consider melt flow index or MFI. G.

Table 1: Common building specifications

Building specification	Title/description
ASTM E84	Standard test method for surface burning characteristics of building materials
ASTM E108	Standard test methods for fire tests of roof coverings
ASTM E162	Standard test method for surface flammability of materials using a radiant heat source

Kirschbaum's 1994 research¹ illustrates the effects of fill level on MFI and on tensile strength in polypropylene resin. Melt flow is significantly reduced with increasing fill level. Tensile strength is also affected, but not by nearly as much (see Table 2). The data are also shown in Figure 1, which shows the effect of filling on this 7 MFI resin. The curve changes significantly as the fill amount exceeds 45%. At the 45% fill level, the curve indicates that the polymer matrix cannot accept any additional filling. Past this fill loading the curve indicates degradation of the polymer backbone. There is subsequent loss of physical properties.

Similar fill effects in another resin were found by Atofina². Table 3 presents the findings in ethylene butyl acrylate copolymer with magnesium hydroxide and calcium carbonate fillers. In this instance the drop in MFI is again dramatic. In this case common extrusion or injection moulding grades of polymer are not indicated. A much higher MFI base resin is required for a successful formulation.

These fill effects are also apparent in research on magnesium hydroxide in EVA conducted by Martin Marietta Magnesia Specialties, a US-based supplier of magnesium hydroxide flame retardant compounds. The data are shown in Figure 2. Compounds were prepared on a roll mill using three 28% vinyl acetate EVA resins with melt flows of 3.8, 40.5 and 140. Various loadings of magnesium hydroxide with 2% calcium stearate were compounded and the resultant melt flows were determined. At 65% loading, the 40.5 MFI resin decreased to 3.2 MFI, while the 3.8 MFI resin decreased to 0.47. The graph only shows the final compound melt flow for the 140 MFI resin, which decreased to 17.8 MFI.

From this work it is apparent that starting with a higher melt flow base resin is critical to success in producing a 65% magnesium

Flame retardance through metal hydrates

Metal hydrate compounds provide effective flame retardance by several routes. First, they dilute the amount of fuel available to sustain combustion during a fire. They contain a significant amount of bound water (31% in the case of magnesium hydroxide) which is released at high temperatures (beginning at 330°C for magnesium hydroxide) providing a blanket effect which limits the oxygen available for combustion. Metal hydrates also absorb heat from the combustion zone, which reduces the prospect of continued burning. They produce a char during burning that results in further flame retardant protection and less smoke generation. Magnesium hydroxide also generates a magnesium oxide coating during combustion, which deflects the flame's heat away from the polymer or fuel source. Halogen flame retardants operate quite differently in the vapour phase of the burning process, primarily trapping free radicals generated in the flame front. To do this most halogen flame retardants need the help of a synergist such as antimony oxide.

Table 2: Magnesium hydroxide fill level effects in polypropylene

% Mg(OH) ₂	MFI	Tensile Strength (MPA)
0	7.0	23.0
35	5.4	24.9
40	4.0	24.7
45	2.2	24.3
50	1.2	23.0
55	0.8	22.5
60	0.2	21.8
65	0.1	20.0

Table 3: Filler effect on MFI of ethylene butyl acrylate copolymer

Initial MFI	Filler	Loading (%)	Compounded MFI
320	None	0	320
320	Mg(OH) ₂	60	30
320	Mg(OH) ₂	68	4
320	CaCO ₃	72	11
40	None	0	40
40	Mg(OH) ₂	60	5
40	Mg(OH) ₂	68	0.7
40	CaCO ₃	72	2

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hydroxide compound. Figure 3 shows oxygen index (O.I.) data for the various loadings of magnesium hydroxide in the 40 MFI EVA resin. There is a significant change from 24.3 O.I. at 50% loading to 40 O.I. at 65% loading. This effect is consistent across the various melt flow grades of EVA used in this investigation.

Processing aids

Processing aids also affect polymer systems that incorporate metal hydrate

flame retardants. An extensive programme to define these effects has been launched by Martin Marietta. The goal is to understand how best to combine process additives and magnesium hydroxide metal hydrate flame retardants into polymers. Polypropylene was chosen as the base resin for this work.

Formulation components included polypropylene resin (Basell Profax 6231, Homopolymer 20 MFI), magnesium hydroxide and stabilizer (Ciba Specialty

Chemicals' PolyAd Stabilizer MM1252-25 containing Irganox 1010, DLTDP, phosphite). These components were combined in a 40:60:1 parts ratio. Preparation of experimental compounds was done using a Haake Rheocord 90 fitted with a 300 cc mixing bowl and Banbury type rotors and a 3.4 batch factor. The mixer temperature was 200°C and the mixing speed was 60 rpm. The torque data reported is at elapsed time where the peak torque (filler additions) is t (time) = 0. The results of evaluations on various magnesium hydroxide materials are shown in Table 4.

The torque data was analyzed and several conclusions drawn. First, fatty acid coatings are more effective than silane coatings as processing aids in polypropylene formulations. Second, increasing amounts of metal stearate coatings provide processing benefits. Finally, the mix of reacted stearate and addition of calcium stearate to the formulation is as effective as all other stearate coatings. Selected data are presented in bar graph format in Figure 4 to illustrate the results shown in Table 4.

The amount of work received by the polymer and the resulting polymer degradation caused by the work are directly related to the torque reduction. The polymer degradation occurs in the first stages of compounding, which is best demonstrated by the rheometry curves shown in Figure 5 (Torque units are in milligrams). The incorporation of processing aids significantly reduces the work input. In turn this reduces the polymer degradation. All formulations show a leveling off of work input after the initial peak in work.

Physical testing of Haake samples is considered inconclusive because such samples are usually compression moulded. Therefore, further trials were run in a Leistritz 40 mm twin screw extruder. Extrusion temperature at the die was 220°C.

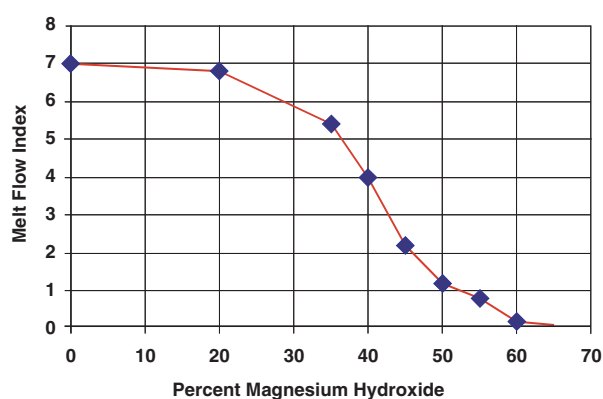


Figure 1: Magnesium hydroxide fill level effect on melt flow in polyolefin resin.

Table 4: Magnesium hydroxides - torque analyses

Magnesium hydroxide Type and coating	Torque at t minutes from peak (mg)				
	t0	t1	t2	t4	t6
Standard precipitated	7667	2617	2333	1983	1867
Ultrafine precipitated	6383	2367	2017	1917	1783
Ultrafine 1% amino silane	7167	2267	2083	1883	1733
Ultrafine 0.5% vinyl silane	6867	2267	1967	1733	1700
Standard 0.5% magnesium stearate	7000	2450	2117	1833	1750
Standard 1% magnesium stearate	5433	2017	1867	1667	1533
Ultrafine 1% magnesium stearate	6300	1917	1700	1500	1417
Special precipitated proprietary coat	3083	1417	1200	1100	1000
Special precipitate fatty acid coat	4133	2000	1583	1450	1400
Standard 1.5% magnesium stearate	5883	2350	2017	1833	1700
Standard 2% magnesium stearate	2867	1933	1633	1500	1433
Standard 3% magnesium stearate	3667	2067	1750	1633	1517
Standard 1% mag. stear./2% Ca stear.	3267	1767	1617	1500	1417

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The basic formulation included 39% Basell Profax 6231 (Homopolymer 20 MFI), 1% Stabilizer (Ciba Specialty Chemicals' PolyAd MM 1252-25 containing Irganox 1010, DLTDP, Phosphite) and 60% magnesium hydroxide with various coatings. The results are shown in Table 5.

No unusual results were observed in these trials on different coatings and coating methods. As might be expected, with increasing stearate content the final compound became less stiff and processing became easier.

Additional fillers

Some applications require greater fire retardant performance. Flame retardant performance can be increased by the incorporation of clay or talc in polyethylene formulations. Martin Marietta's programme included modifying the experimental formulations to provide this improved performance. Initial trials were done using talc as an additional filler. The results are shown in Table 6.

Each of these formulations contained 2% calcium stearate and 1% stabilizer package as in previous formulations. The UL94 V-0 3.2mm rating improved to UL94 V-0 1.6mm with the reduction of the magnesium hydroxide content from 65% to 60% and with the addition of talc at 5%. A reduction to 52% magnesium hydroxide with a 10% talc addition resulted in a return to UL94 V-0 at 3.2mm and UL94 V-2 at 1.6mm.

The incorporation of 5% talc into these formulations significantly increased the flame retardant performance. Incorporation of 10% talc with 52% magnesium hydroxide resulted in flame retardant performance equivalent to that of the 60% magnesium hydroxide formulation. More confirming work now needs to be done.

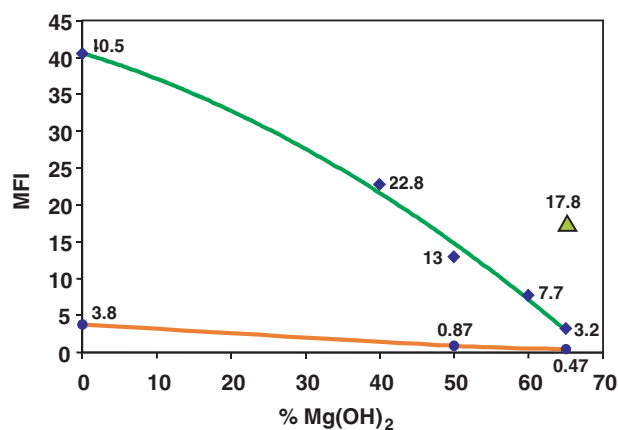


Figure 2: Melt flow versus magnesium hydroxide loading in three different MFI EVA resins.

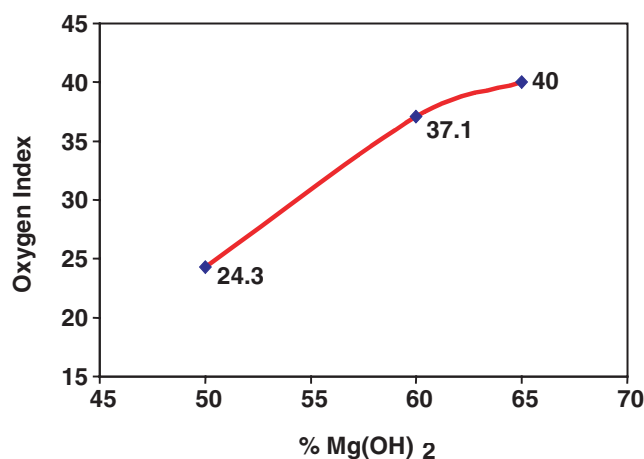


Figure 3: Oxygen Index versus percentage magnesium hydroxide in EVA.

Table 5: Twin screw magnesium hydroxide coatings analyses

Property	Uncoated	1% stearate	2% stearate	Silane
Flammability UL94 3.2mm	V-1	V-0	V-0	V-0
Flammability UL94 1.6mm	V-2	V-2	V-2	V-2
Flexural Modulus	659	583	572	645
Izod Impact	0.19	0.17	0.18	0.05
Tensile Strength Yield	2980	3100	3141	3080
Tensile Strength Break	2550	3100	3140	3080
Yield Elongation	0.7	0.6	0.5	0.6
Young's Modulus	886	961	1090	897
MFI	4.5	3.5	11.8	4.8

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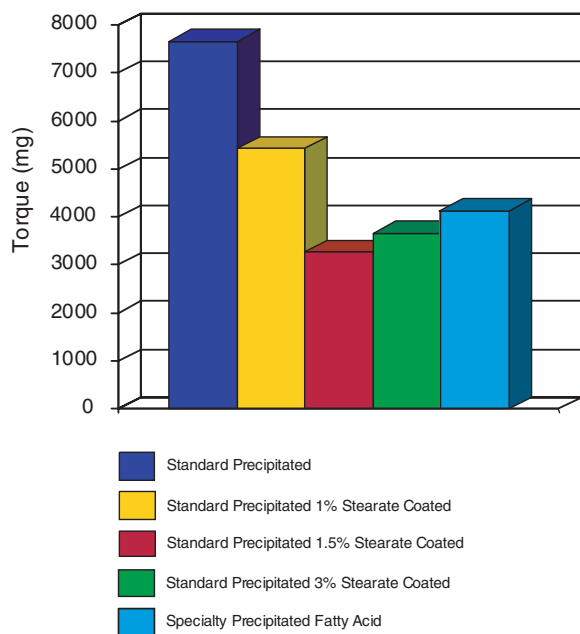


Figure 4: Torque data for selected magnesium hydroxide products.

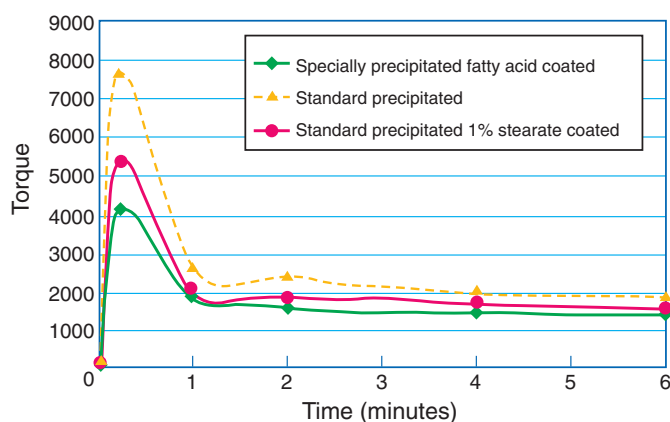


Figure 5: Rheometry curves.

Table 6: Flame retardance of talc modified formulations

Talc amount	Mg(OH) ₂ (%)	Flammability	
None	65	V-0 3.2mm	V-2 1.6mm
None	60	V-0 3.2mm	V-2 1.6mm
5%	60	V-0 3.2mm	V-0 1.6mm
10%	52	V-0 3.2mm	V-2 1.6mm

Conclusions

Several general rules of formulating and compounding should be observed when attempting to formulate metal hydrate flame retardant systems. These rules will be helpful in achieving optimal flame retardancy and requisite physical properties for the application. An understanding of metal hydrate flame retardant mechanisms is mandatory and a thorough knowledge of the effects of fillers on resin properties is also critical. Compared to halogen flame retardants, metal hydrates have significantly different effects on the polymer matrix. Additional fillers when used in the metal hydrate formulation can also impact flame retardancy and processing aids can affect the ease of compounding. All such effects must be fully considered in developing successful metal hydrate formulations. Metal hydrates alone or in combination with other fillers can provide an economic alternative to meeting the flame retardant and physical property requirements for many diverse applications.

References

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