Overview of Flame Retardants Including Magnesium Hydroxide

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There are many classes of compounds which are useful as flame retardants. Inorganic minerals, organo-phosphates, and halogenated compounds are all commonly used for their ability to inhibit combustion and smoke generation in plastics and other materials. In 1993, United States industries consumed 810 million pounds of flame retardant additives, and demand is projected to be over one billion pounds in 1998[1]. While currently a small part of this large market, Magnesium Hydroxide is attracting attention because of its performance, price, low corrosiveness, and low toxicity. The current market for magnesium hydroxide in flame retardants is about ten million pounds per year, with the potential to surpass thirty million pounds per year in the near future.

Basic Fundamentals of Various Flame Retardants

Alumina Tri-Hydrate (ATH) and Magnesium Hydroxide

Like ATH ($Al_2O_3 \cdot 3H_2O$), magnesium hydroxide ($Mg(OH)_2$), is an acid- and halogen-free flame retardant for various plastics. Both hydroxides decompose endothermically when heated according to the reactions:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

The gaseous water phase is believed to envelop the flame, thereby excluding oxygen and diluting flammable gases.[2] Similar to the function of char formed by phosphorous-containing flame retardants, a heat insulating material may form on the surface of the plastic in contact with the flame, reducing the flow of potentially flammable decomposition products to the gas phase where combustion occurs.[2] In both of the reactions, the decomposition products are non-toxic and the mineral phases, especially MgO, are alkaline, reducing the likelihood of acidic, corrosive gases exiting the plastic.

The physical and chemical properties of magnesium hydroxide and ATH are shown in Table One. Magnesium hydroxide has a 100°C higher decomposition temperature than ATH, allowing a higher processing temperature in compounding and extruding the plastic. Also, magnesium hydroxide adsorbs more energy during the decomposition process.

Table One: Comparison of Properties of $Mg(OH)_2$ and ATH

	$Mg(OH)_2$	ATH
Bound Water, %	31.0	34.6
Specific Gravity	2.36	2.42
Mohs Hardness	2.5	3.0
Refractive Index	1.56-1.58	1.57
Initial Decomposition Temperature	330°C	230°C
Enthalpy of Decomposition	328 cal/g	280 cal/g

Table One: *Comparison of Properties of $Mg(OH)_2$ and ATH.*

Phosphorous-Containing Flame Retardants

Phosphorous-containing flame retardants mainly influence flame retardancy in the condensed phase. They are particularly effective in materials having a high oxygen content, such as cellulose and some oxygen-containing plastics. The basic flame retarding mechanism involves thermal conversion of the phosphorous-containing flame retardant to phosphoric acid in the condensed phase of the plastic. The phosphoric acid extracts water from the burning plastic, causing it to char. The char insulates the plastic from flame and heat, preventing volatile, combustible gases from exiting the bulk.[3] Since phosphoric acid is formed in the burning plastic, there is increased likelihood that the smoke will be corrosive. Halogenated organophosphates are sometimes used as a flame retardant.[3] The halogens, as will be shown in the next section, interfere with the radical chain reaction, while the phosphorous forms a char.

Halogenated Flame Retardants

Halogenated flame retardants are organo-halides selected to vaporize in a similar temperature range as that of the plastic resin. Once in the gas phase, the halogen, typically chlorine or bromine, decreases the concentration of high energy free radicals that are involved in the combustion process.[3] Eliminating these free radicals reduces flame intensity, decreases the amount of heat transferred to the plastic, consequently slowing or eliminating the burning of the plastic. A mechanism for this action has been proposed as follows:[3]

In the gas phase, a radical chain reaction occurs involving OH and H radicals formed by high energy decomposition of the plastic:

$$H^{\cdot} + O_2 \rightarrow OH^{\cdot} + O^{\cdot\cdot}$$

$$O^{\cdot\cdot} + H_2 \rightarrow OH^{\cdot} + H^{\cdot}$$

To remove these high-energy free radicals, the halogenated flame retardant first breaks down as shown:

$$RX \rightarrow R^{\cdot} + X^{\cdot} \qquad \text{where X is either Cl or Br.}$$

The halogen radical reacts to form the hydrogen halide:

$$X^{\cdot} + RH \rightarrow R^{\cdot} + HX$$

which in turn interferes with the radical chain mechanism:

$$HX + H^{\cdot} \rightarrow H_2 + X^{\cdot}$$

$$HX + OH^{\cdot} \rightarrow H_2O + X^{\cdot}$$

The high energy $H^{\cdot}$ and $OH^{\cdot}$ radicals involved in combustion of the plastic are thus removed by the flame retardant and replaced with lower energy $X^{\cdot}$ radicals. These radicals react with the plastic hydrocarbons to produce the hydrogen halide, regenerating the flame retardant.

Since halogenated flame retardants are regenerative, much lower loadings (typically ~10% by weight) are required compared to ATH or magnesium hydroxide (typically ~50% by weight). Brominated flame retardants are typically more effective than those utilizing chlorine because of a narrower vaporization temperature leading to higher concentration of the flame retardant in the flame zone.[3] Synergistic agents, such as antimony oxides, further increase the effectiveness of both brominated and chlorinated flame retardants by enabling the halogen to stay in the flame zone for longer periods.[4]

While halogenated flame retardants and halogen-antimony combinations provide better flame retardance in most systems, use of these compounds has given rise to some concern.[5,6] In particular, much attention has been focused on the corrosiveness and toxicity of smoke and other emission products generated during the combustion of plastics utilizing these materials. In recent years there has been much speculation that legislation will arise restricting the use of these compounds as flame retardants. Some brominated flame retardant producers have voluntarily agreed to put restrictions on production, export, and import of their products in European countries in advance of such legislation.[7] In contrast to the potentially hazardous halogenated flame retardants, magnesium hydroxide is considered a nuisance dust and is not volatilized during combustion of the plastic. Table Two shows toxicity data for brominated and chlorinated compounds.

Additionally, as landfill space declines, or becomes unpopular, incineration and recycling of used plastics will become more widespread. Plastics formulated with halogenated flame retardants pose problems for incinerators in design, operation and maintenance, as well as a danger to public health from the incineration product gases.[8]

Table Two: Range of Toxicity Values for Flame Retardant Types		
Compound Class	Toxicity, LD_{50}	Reference Number
Brominated, (inhalation)	2.49-200 mg/L	[9]
Chlorinated, (inhalation)	2.25-203 mg/L	[10]
Magnesium Hydroxide, (inhalation)	None published, $Mg(OH)_2$ is considered a nuisance dust	[11]

Table Two: *Toxicity Values for Flame Retardant Types*

Use of Magnesium Hydroxide as a Flame Retardant in Plastics

There are many producers of magnesium hydroxide for flame retardants.[12] Martin Marietta Magnesia Specialties, Inc., the Solem Division of J.M. Huber, and Morton International are the larger domestic producers with Dead Sea Periclase (Israel), Kyowa (Japan), and Magnifin (Austria) being some of the foreign producers. Grades of magnesium hydroxide range from coated, micronized powders (for higher end, higher loading applications) to uncoated magnesium hydroxide as a direct replacement for ATH. Kyowa and Magnifin specialize in the more expensive coated, high-end grades of magnesium hydroxide while Martin Marietta Magnesia Specialties, Inc. produces MagShield® S in uncoated form as a direct ATH replacement.

Several studies[13,14,15,16] illustrating the effectiveness of magnesium hydroxide as a flame retardant in plastics have been performed. These have concluded that magnesium hydroxide is effective at reducing smoke emissions from burning plastics. Summaries of the more important factors determining the performance of magnesium hydroxide as a flame retardant follow:

1) The endothermic decomposition commencing at about 330°C for magnesium hydroxide (versus about 230°C for ATH) withdraws heat from the substrate, slowing the rate of thermal degradation of the plastic.

2) The release of water vapor upon decomposition of magnesium hydroxide dilutes the fuel supply present in the gas phase.

3) The relatively high heat capacities of both magnesium hydroxide and the decomposition products formed upon decomposition of magnesium hydroxide reduce the thermal energy available to degrade the plastic.

4) The decomposition products provide increased insulation of the plastic from the heat source through char formation.

5) The high filler content usually associated with magnesium hydroxide- treated plastics acts as a solid phase diluent.

Figure 1[17] shows typical results of smoke emission testing (ASTM E662, under flaming conditions) on various plastics with and without 40% by weight of magnesium hydroxide. The magnesium hydroxide in this study significantly lowers the overall level of smoke produced.

Furthermore, the use of magnesium hydroxide causes a considerable delay in the onset of smoke evolution and markedly slows the rate of smoke release. Clearly, these factors have major implications in real life.

Another study[18] showed the results of UL 94 testing (Ignitability of Plastics by a Small Flame, or Vertical Burn Test) where polyamide and polypropylene plastics were compounded with $Mg(OH)_2$ at 60% by weight loading. These compositions attained a V(O) classification representing a high resistance to ignition, according to the UL 94 test.

For a flame retardant to be useful in compounded plastics, it must not degrade the physical properties of the plastic. In a typical flexible wire PVC formulation, Martin Marietta Magnesia Specialties Inc.'s MagShield® S was found to slightly improve the physical properties of the PVC formulation compared to ATH and a competing, higher grade magnesium hydroxide. The compounded PVC utilized a 30 PHR loading of each flame retardant and resulted in a plastic with the properties[19] shown in Table Three.

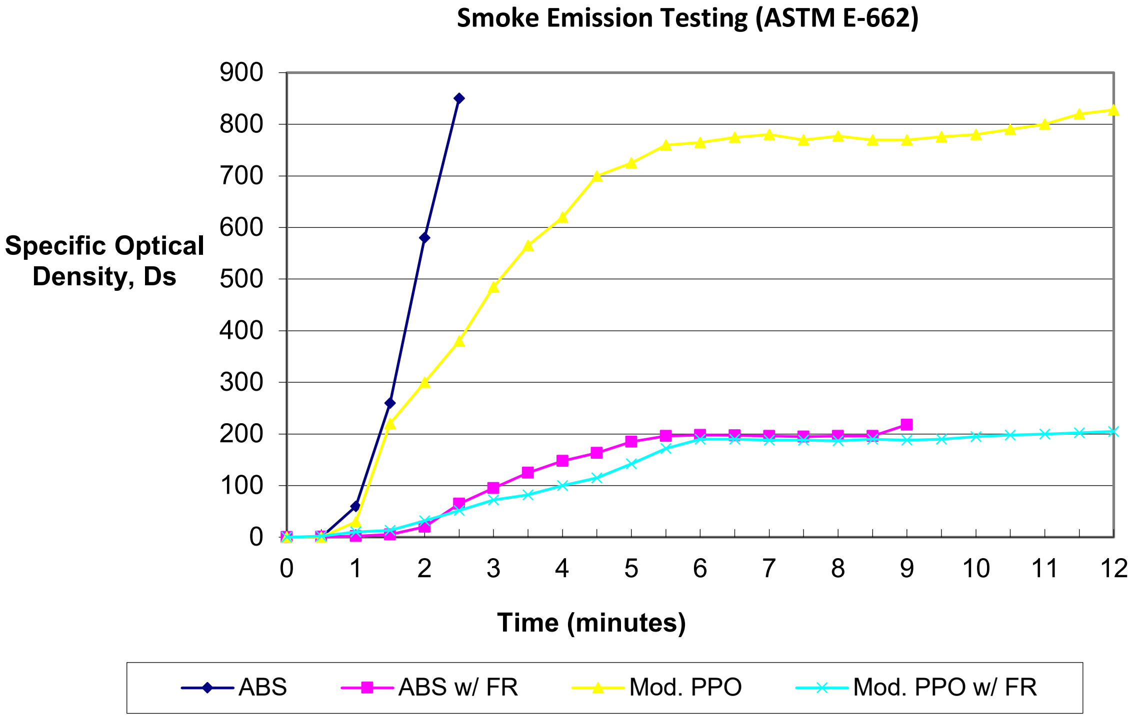


Figure 1 *Specific Optical Density of Smoke Evolved from Various Plastics both with and without Magnesium Hydroxide (Loading: 40% by weight). (FR = $Mg(OH)_2$ Flame Retardant).*

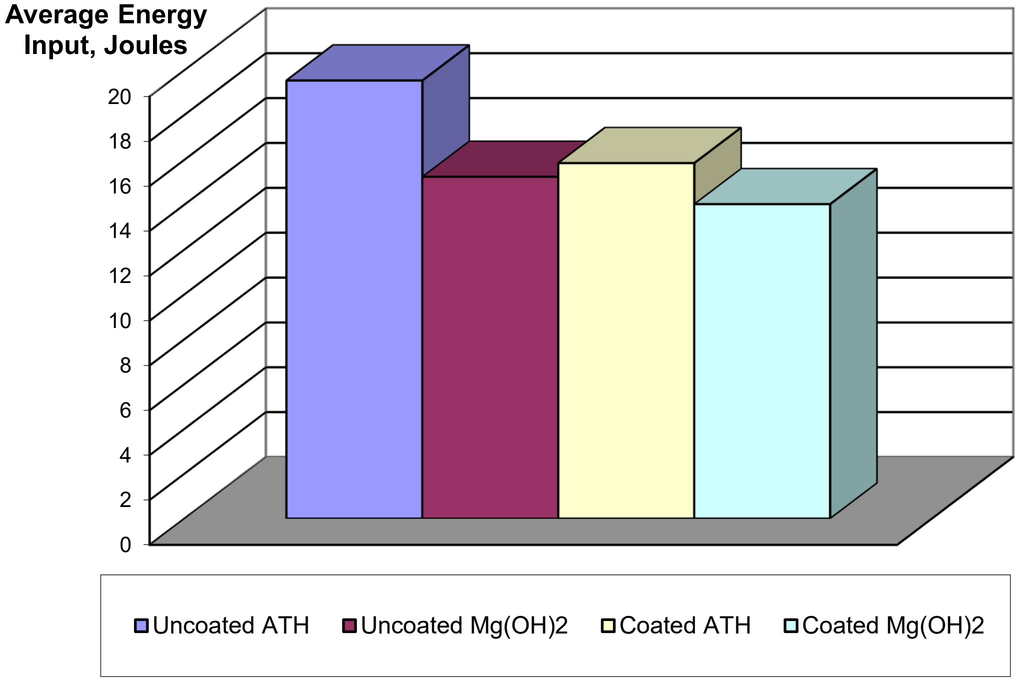
Table Three: Physical Properties of a Typical Flexible Wire and Cable PVC Formulation with Magnesium Hydroxide and ATH

	MagShield® S	ATH	Competitive $Mg(OH)_2$
Elongation, %	139	118	136
Tensile Breaking Strength, psi	2610	2365	2499
Tensile Modulus, psi	20330	19173	20116
Melt Flow Index, (g/10 min)	0.90	0.43	1.00

Table Three: *Data from Martin Marietta Magnesia Specialties Inc. testing*

Plastics requiring higher loadings, such as polypropylene and polyamides, typically require the use of specialty magnesium hydroxide grades having fatty acid coatings or specific physical properties. The special properties of these materials allow for high loadings with little to no degradation of the physical properties of the plastic. A recent study was undertaken to evaluate the amount of work required to compound metal hydrates into polypropylene. By measuring the average energy input required to mix the PP/FR compositions, an idea of the relative "processibility" of the FR may be generated. In the present work, a Brabender Plasticorder was used to measure the energy input requirements of 50% FR/50% PP compositions. The results are shown graphically in Figure 2.

Figure 2: Average Energy Input by Flame Retardant Type



It is notable that ATH required either a Stearate or Silane treatment to be compounded as easily as did the uncoated $Mg(OH)_2$ samples. Further reductions in the energy requirements for $Mg(OH)_2$ were realized with either Silane or Stearate surface treatments. Additional improvements in processibility for certain polymers has been demonstrated with metallocene catalyzed polymers which may lessen or eliminate the need for special surface treatments of metal hydrate additive.[20]

Conclusions

Magnesium hydroxide acts as a flame retardant and smoke suppressor in plastics mainly by withdrawing heat from the plastic during its decomposition into magnesium oxide and water. The water vapor that is generated dilutes the fuel supply to the flame. Decomposition products insulate the plastic from heat and produce char that impedes the flow of potentially flammable gases to the flame.

Increasing legislation and concern about the use and recyclability of halogenated flame retardants make magnesium hydroxide more attractive to plastics producers. Magnesium hydroxide offers flame retardance and smoke suppression from a substance that is acid- and halogen-free and has low toxicity values. In most cases, with proper selection of the grade of magnesium hydroxide, no compromise need be made for physical properties and flame retardancy of the plastic. For high-loading applications where the use of high-end or coated magnesium hydroxide is dictated, legislation maybe the dominant driving force for specifying magnesium hydroxide as opposed to halogenated flame retardants. The more economical route for lower loading applications may be the use of lower-priced grades of magnesium hydroxides such as MagShield® S.

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