

Overview of Flame Retardants Including Magnesium Hydroxide

Matthew D. Walter
Mark T. Wajer

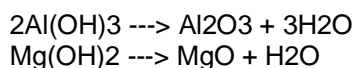
MARTIN MARIETTA MAGNESIA SPECIALTIES LLC
8140 Corporate Drive, Suite 220
Baltimore, MD 21236

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 1998¹. 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

ATH, Magnesium Hydroxide

Like ATH* (Al₂O₃·3H₂O), 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:



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." 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) and ATH.

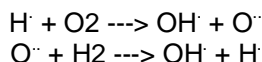
Phosphorous-Containing Flame Retardants

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

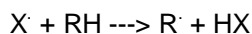
In the gas phase, a radical chain reaction occurs involving OH and H radicals formed by high energy decomposition of the plastic:



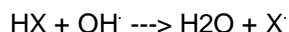
To remove these high-energy free radicals, the halogenated flame retardant first breaks down as shown:



The halogen radical reacts to form the hydrogen halide:



which in turn interferes with the radical chain mechanism:



The high energy H[·] and OH[·] radicals involved in combustion of the plastic are thus

removed by the flame retardant and replaced with lower energy X 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, LD50	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, LLC, 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, LLC 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. A summary 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 1¹⁷ 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 study¹⁸ 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 VO 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 LLC'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 properties¹⁹ shown in Table Three.

Smoke Emission Testing (ASTM E-662)

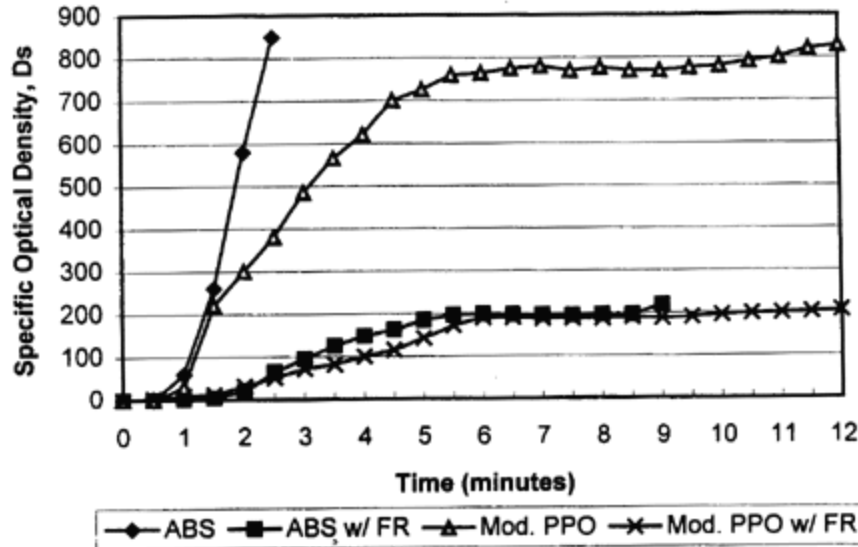


Figure 1 Specific Optical Density of Smoke Evolved from Various Plastics both with and without Magnesium Hydroxide (Loading: 40% by weight). (FR = Mg(OH)₂ Flame Retardant).

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 LLC 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. New work underway with metallocene catalyzed polymers indicates that coating of the magnesium hydroxide may be reduced or eliminated for various plastics.²⁰

Conclusions

Magnesium hydroxide acts as a flame retardant and smoke suppresser 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 name 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.

*Also known as aluminum hydroxide, Al(OH)₃

1. HAIRSTON, D.W., *Chemical Engineering*, 9 (1995), 65.
2. HORNSBY, P.R. and WATSON, C.L., *Polymer Degradation and Stability*, 30 (990), 74.
3. KIDDER, R.C., TROITZSCH, J.H., NAUMANN, E., and ROUX, H.J., From Course Work Materials in *New Developments and Future Trends in Europe and the United States for Fire Retardant Polymer Products*, (1989).
4. HASTIE, J.W., *High Temperature Vapors*, Academic Press, LLC, New York, 1975, p. 353.
5. WOOLEY, W.D. and FARDELL, P.J., *Fire Safety Journal*, 5 (1982), 29-48.
6. REINKE, R.E. and REINHARDT, C.F., *Modern Plastics*, 50 (1983), 94-98.
7. From *Industrial Minerals*, 336 (1995), 17.
8. GANN, R.G., from *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed., Volume 10, 935.
9. Material Safety Data Sheets from Ethyl Corporation for hexabromcyclododecane and dibromoneopentylglycol.
10. Material Safety Data Sheets from Velsicol Chemical Company for chlorendic anhydride and Occidental Chemical Corporation for bis(hexachlorocyclopentadieno)-cycloocta
11. *Sax's Dangerous Properties of Industrial Materials*, 8th Edition, R.J. Lewis, Sr., Vol. 111 (992), 2150.
12. From *Industrial Minerals*, 318 (1994), 23-45.
13. ZIEGAN, G. and HONGESBERG, H., from *Flame Retardants '92, 5th Conference*, 120-132.
14. HORNSBY, P.R., *Fire and Materials*, 18 (5), (1994), 269-276.
15. LEVESQUE, J.L. and HASTBAKA, M.A., from *RETEC Additive Approaches to Polymer Modification Conference Papers*, (9/1989), R89-190.
16. HORNSBY, P.R. and WATSON, C.L., *Polymer Degradation and Stability*, 30 (990) 73-87.
17. From Reference 14, p. 272.

18. From Reference 14, p. 275.
19. Taken from MagShield™ 98 Product Literature, Martin Marietta Magnesia Specialties, LLC
20. HUGGARD, M., *Flame Retardant Polyolefins: Impact and Flow Enhancement Using Metallocene Polymers*, Conference Proceedings (Additives for Metallocene Catalyzed Polymers, June 24-26, 1996), Intertech Conferences, 411 U.S. Route One, Portland, MA 04105, p. 9.

NOTICE The data and test results referred to herein are based on tests defined by flammability safety regulations and performed under laboratory conditions. This should not be construed as a representation or warranty of performance under actual fire conditions. The information contained herein is, to the best of our knowledge and belief, accurate. Any recommendations or suggestions made are without warranty or guarantee of results since conditions of use are beyond our control. Before using, the customer should determine the suitability of the product for the customer's intended application. We warrant only that this product will meet the specifications set forth herein. ANY OTHER REPRESENTATION OR WARRANTY, EITHER EXPRESS OR IMPLIED, IS SPECIFICALLY DISCLAIMED INCLUDING WARRANTIES OF FITNESS FOR A PARTICULAR PURPOSE AND MERCHANTABILITY. Our only obligation is to replace nonconforming product or to refund purchase price at our option. In no event shall we be liable in tort, contract or otherwise for any incidental or consequential damages.

MagShield is a trademark of
Martin Marietta Magnesia Specialties LLC