



## ADVANCED MATERIALS

# Halogen-Free Fire Retardants and Smoke Suppressants **in Composite Applications**



Reducing resin consumption  
and adding safety for  
thermoset composite  
applications



# Safe. Sustainable. Efficient.

**When things heat up** and you need advanced fire retardant performance for molding compounds, turn to the exclusive halogen-free Alumina Trihydrate (ATH) grades from Huber Engineered Materials. Our products allow for standard and higher loadings while offering the latest developments in low viscosity technology – thus providing increased fire retardance, low formation of smoke and toxic gases and no corrosivity while lowering formulation costs and reducing the need for halogens. Our MoldX® optimized ATH, Martinal® ATH and SB ATH products help to

achieve and pass the most stringent fire testing standards including EN 45545, EN 13501-2, UNECE R118, UL 94 V-0, IMO Res.A.653(16), AC 25.853-1, Gost 12.104, ASTM E84, ASTM E662, and ASTM E162 among others. Typical applications requiring fire retardance include Sheet Molding Compounds (SMC), Bulk Molding Compounds (BMC), pultrusion, lamination, RTM, spray-up and vacuum infusion.



## Major Points of Learning:

**Page 2** | Why Use Alumina Trihydrate (ATH) as a Fire Retardant and Smoke Suppressant

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## Fabrication Technique and Huber's Recommended ATH Grades

### SMC, BMC, LAMINATION AND SPRAY-UP



### PULTRUSION, RTM AND VACUUM MOLDING



Key Martinal®,  
MoldX® and SB ATH  
Product Benefits:

- Halogen-free
- Flame retardance and smoke suppression in molded parts
- Reduced flame spread
- Increased ATH loading levels
- Lower viscosity formulations
- Better glass wet-out
- Lower pull forces
- Maximum efficiency

# Why Use Alumina Trihydrate (ATH) as a Fire Retardant and Smoke Suppressant?

The world's most widely used flame retardant chemistry is Alumina Trihydrate, also known as Aluminum Hydroxide or ATH.

**Here's how ATH works:** At approximately 428°F (220°C), the three water molecules in ATH are released in an endothermic reaction.



*Starting @200°C Consuming 280 cal/g*

The heat energy from the flaming plastic is absorbed, and the released water molecules quench the surface of the surrounding materials, thus providing flame retardance and smoke suppression (refer to the illustration at left). It is an environmentally-friendly reaction with no toxic emissions.

ATH is not only more economical than halogenated compounds, it is also much safer. Composites containing chlorinated or brominated fire retardants emit hydrogen chloride (HCl) gas or hydrogen bromide (HBr) when burned. These substances are toxic to the skin, eyes and lungs.

Lastly, ATH is inert and compatible with all composite resin types. Although resins used in composites are organic, they do not have the same degree of flammability. The resins below are listed in order of decreasing flammability.



Acrylic

Polyurethane

Polyester

Vinyl Ester

Epoxy

Phenolic

MOST FLAMMABLE

LEAST FLAMMABLE



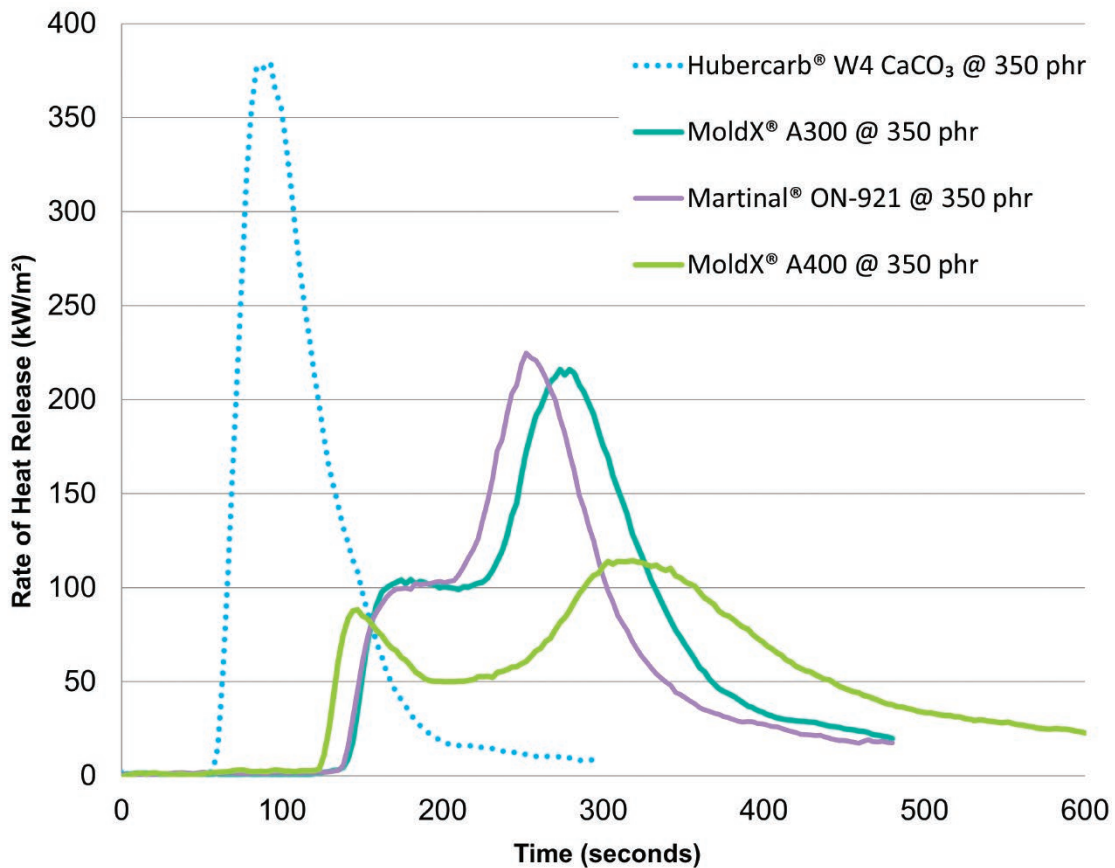
## Fire Retardance of ATH vs. Calcium Carbonate

The Rate of Heat Release (RHR) graph below compares the fire retardance of both MoldX® and Martinal® ATH grades and calcium carbonate.

For composite applications not requiring fire retardance, calcium carbonate is often used as it is widely available and economical. Although calcium carbonate does not burn, it is not a fire retardant. Thus, it does nothing to prevent the resin from burning. Therefore, there is only a small delay in the time to ignition and high flammability. The composites containing ATH have longer time to ignition and much lower flammability.

As mentioned on the next page, ATH loading level is a key determinant of fire retardance and smoke suppression, as shown below where MoldX® A110 and Martinal® ON-921 impart virtually the same fire retardance performance. MoldX® A400 offers superior fire retardance and smoke suppression, and this unique product is introduced in detail on page 12.

ASTM E1354 Cone Calorimeter Rate of Heat Release @ 50kW/m<sup>2</sup>



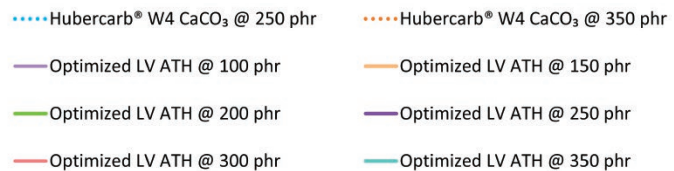
# ATH and Fire Retardance

Fire retardance can be measured in several ways. The Cone Calorimeter is one method that gives reliable information including the Rate of Heat Release (RHR) and Smoke Generation. The curves in the two graphs below were generated using a Cone Calorimeter.

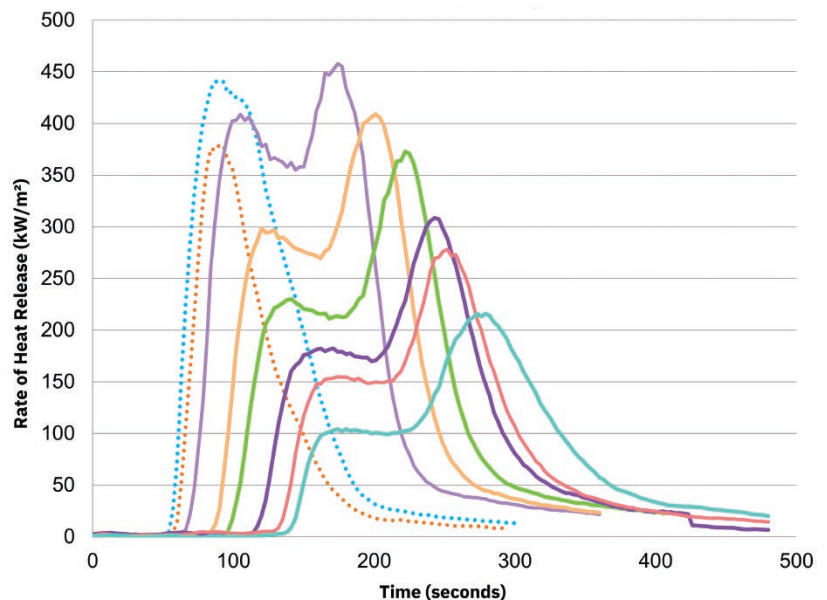
There is a direct correlation between the amount of ATH in the formula and the RHR and smoke generation when all other variables are held constant. The upper graph makes this obvious. Higher levels of ATH in the formulation lead to longer times-to-ignition and lower heat release rates and lower smoke generation. Note that the formulation without ATH (blue line, containing 250 phr of calcium carbonate) has the fastest ignition time. Not only is ATH the most economical fire retardant, it also functions as a smoke suppressant. The correlation between ATH loading and smoke production is also very strong as you see in the Smoke Reduction Rate chart below.

When viewing these two graphs, some might express curiosity about having a 300 phr loading while still maintaining a reasonable viscosity. Viscosity vs. loading will depend on many variables including:

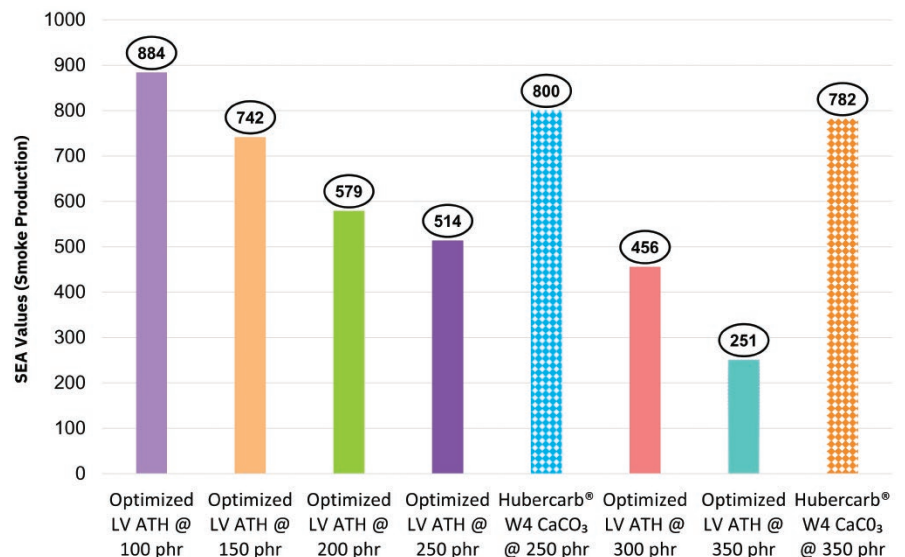
- Fabrication process
- Fiberglass content
- Resin type
- ATH selection
- Loading level (shown later)



ASTM E1354 Cone Calorimeter Rate of Heat Release @ 50kW/m<sup>2</sup>



ASTM E1354 Cone Calorimeter (SEA) Average Smoke Generation Values



Specific Extinction Area (SEA) is the ratio of smoke production to specimen mass loss (m<sup>2</sup>/kg) averaged over the test duration.

# How to Impart Fire Retardance and Smoke Suppression in SMC, BMC, Lamination and Spray-Up Applications

Thermoset composite processes, such as the ones at right, require viscosity low enough to achieve good mold-flow.

- Bulk Molding Compounds (BMC)
- Lamination
- Cured-In-Place-Pipe
- Sheet Molding Compounds (SMC)
- Spray Up
- Tooling Applications
- Resin Transfer Molding
- Hand Lay-Up
- Wet Mat

Since resins are flammable, a significant quantity of ATH may be needed, depending on the fire retardance performance criteria. For moderate fire retardance performance, economical grades at loadings such as 50 to 100 phr may be sufficient.

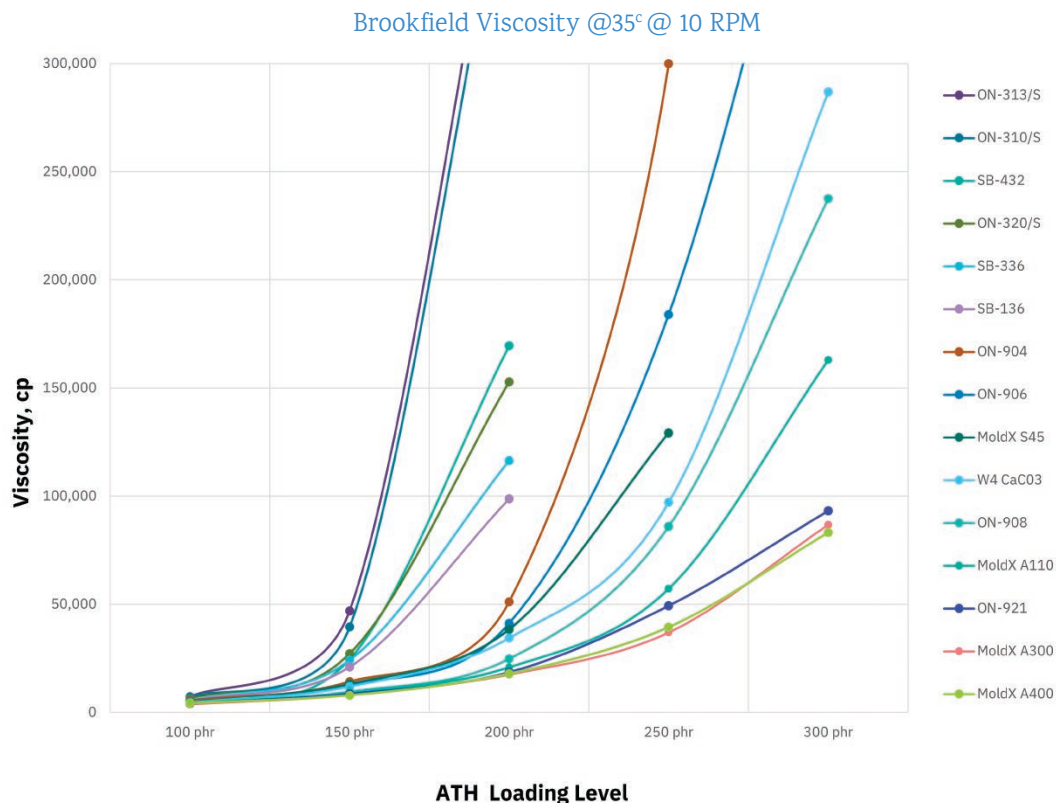
Huber's Martinal® ON-310S, Martinal® ON-320, SB-336 or SB-432 have been reliably used for decades either as the sole halogen-free fire retardant additive or in blends with different fire retardant chemistries. We recommend these grades for applications which require moderate performance and cost efficiency.

However, when trying to reduce or eliminate halogens and still meet stringent fire retardance performance criteria, the viscosity profile of the above economical grades may not allow the loading necessary. Therefore, Huber recommends our optimized ATH products to meet these more demanding requirements. **W**

At low loadings, there is little difference in viscosity among all the ATH grades. However, at high loadings, the viscosity differences are substantial. Only optimized ATH grades can achieve workable viscosities when loaded above 150 phr, and the difference in viscosity among the optimized grades is only seen at loadings greater than 200 phr.

**THE GRAPH BELOW SHOWS VISCOSITIES OF HUBER ATH PRODUCTS IN THE SAME FORMULATION AT FIVE DIFFERENT LOADING LEVELS BASED ON 100 PHR OF THIS SIMPLE MASTERBATCH:**

PHR	INGREDIENT
95	Aropol® MR 14029 Polyester Resin
5	Styrene
100	Masterbatch





# Why Huber?

Choosing the right additives and ingredients requires the formulator to balance mechanical properties, viscosity, cost, fire retardance and smoke generation. We invite you to take advantage of Huber's comprehensive array of offerings and our unique technical ability to create customized application solutions to meet your most demanding situations.

## ATH SELECTION DEPENDS ON YOUR PROCESS

Huber has the experience to help you choose the right ATH product for your process.

For some fabrication methods, such as SMC, BMC and continuous lamination, it is critical to maintain low viscosity while imparting fire retardance. Huber designed optimized ATH products to allow formulators to use up to 300 phr ATH and still have good mold flow. Since ATH acts as both a fire retardant and smoke suppressant, halogen-containing fire retardants can be reduced or eliminated.

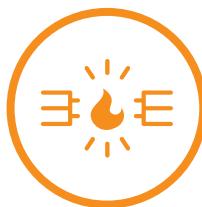
In other processes such as pultrusion, resin transfer molding and vacuum infusion, low viscosity is also desirable, but it is most important to reduce the force at which the compound is infused into the fiberglass. The data on page 15 shows how different ATH products impact the pull forces for pultrusion applications.



Broad product line with production in both Europe and North America



Global sales force ready to assist with formulating



Strong technical expertise in Huber's modern technical service labs in both Europe and North America which includes comprehensive fire testing capabilities



Unparalleled customer service



Reliable source of supply

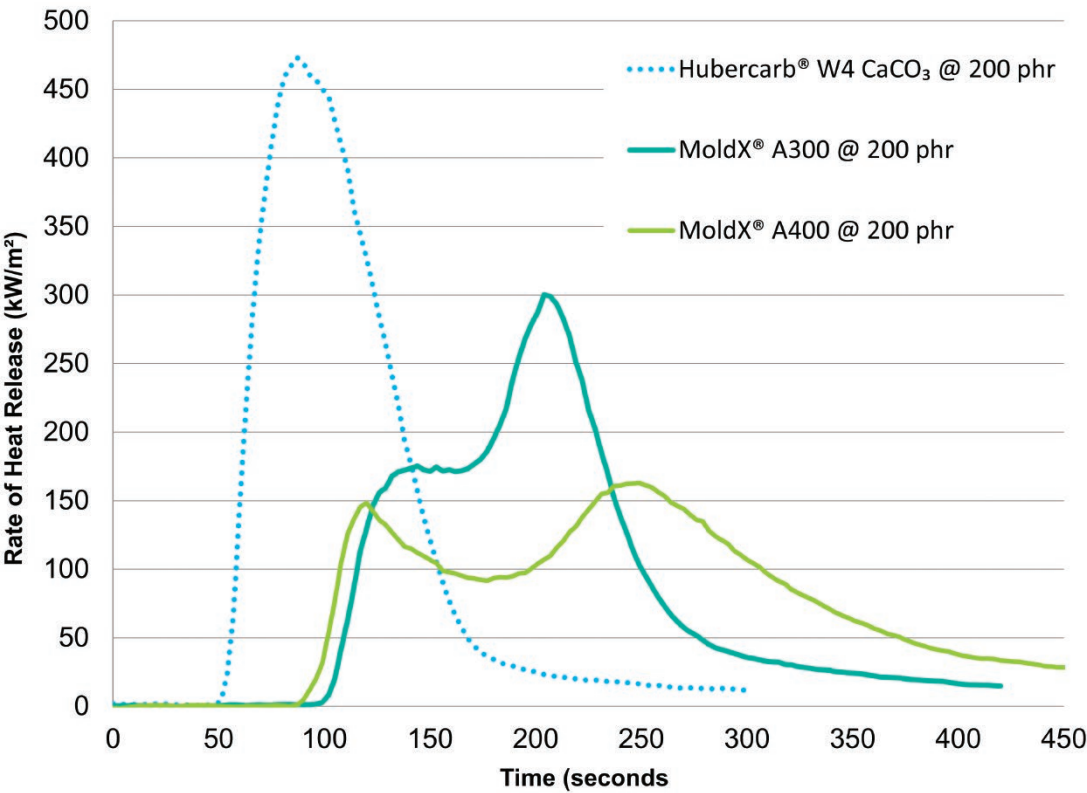
The table references key products sold by Huber into the composites market.  
The 200 phr viscosity measurements are from the SMC formulation below the table.

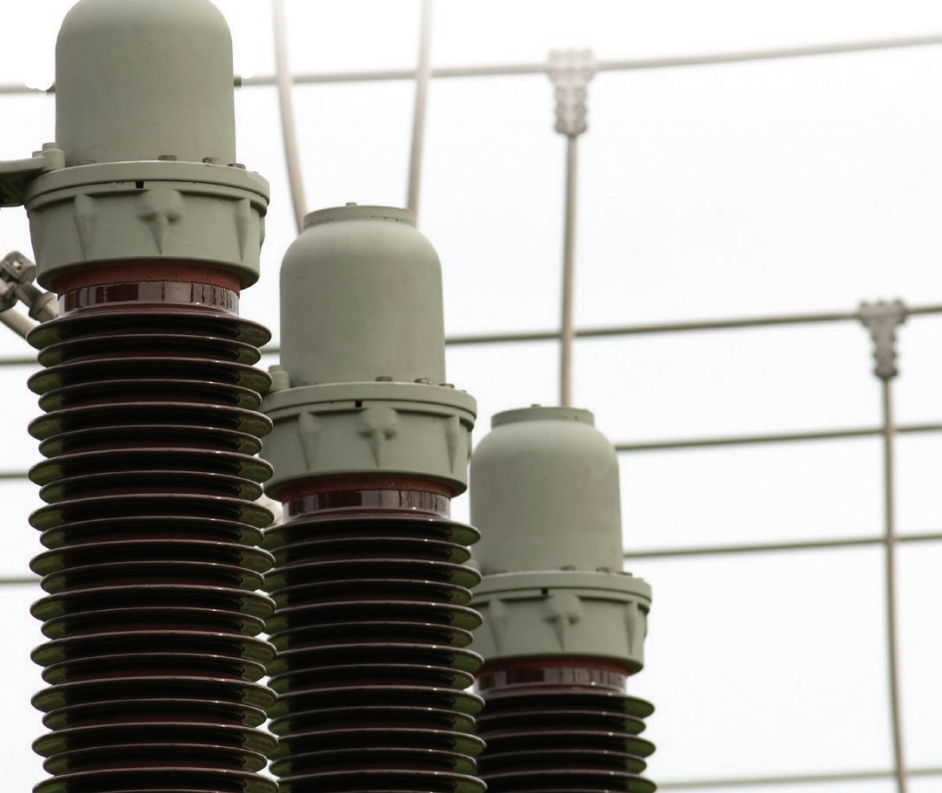
	STANDARD GROUND ATH GRADES				OPTIMIZED ATH GRADES							FOR PULTRUSION AND INFUSION	
	MARTINAL® ON-313 S	MARTINAL® ON-320	SB-336	SB-136	MARTINAL® ON-906	MOLDX® S45	MARTINAL® ON-908	MOLDX® A110	MARTINAL® ON-921	MOLDX® A400	MOLDX® A300	MOLDX® P18	MOLDX® P12
ATH CONTENT	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%	99.6%
D50 (MICRONS)	13	20	15	18	6	10	8	10	12	10	10	5	4
WHITENESS COLOR	White	White	Off White	Off White	White	Off White	White	Off White	White	Grey	Off White	Off White	Off White
150 PHR VISCOSITY IN SMC FORMULATION	44,000	20,000	18,000	17,000	21,300	15,000						1,800	1,300
200 PHR VISCOSITY IN SMC FORMULATION							31,840	19,040	16,800	14,040	13,740		

THE SMC MASTERBATCH FOR  
THE CURVES BELOW:

PHR	INGREDIENT
65	Polylite® 31608-00 Polyester Resin
25	Polylite® 31701-35 Polystyrene Resin
10	Styrene
1.25	Norox® 500-75OMS Initiator
5	Zinc Stearate

SMC Compounds Rate of Heat Release @ 50 kW/m²





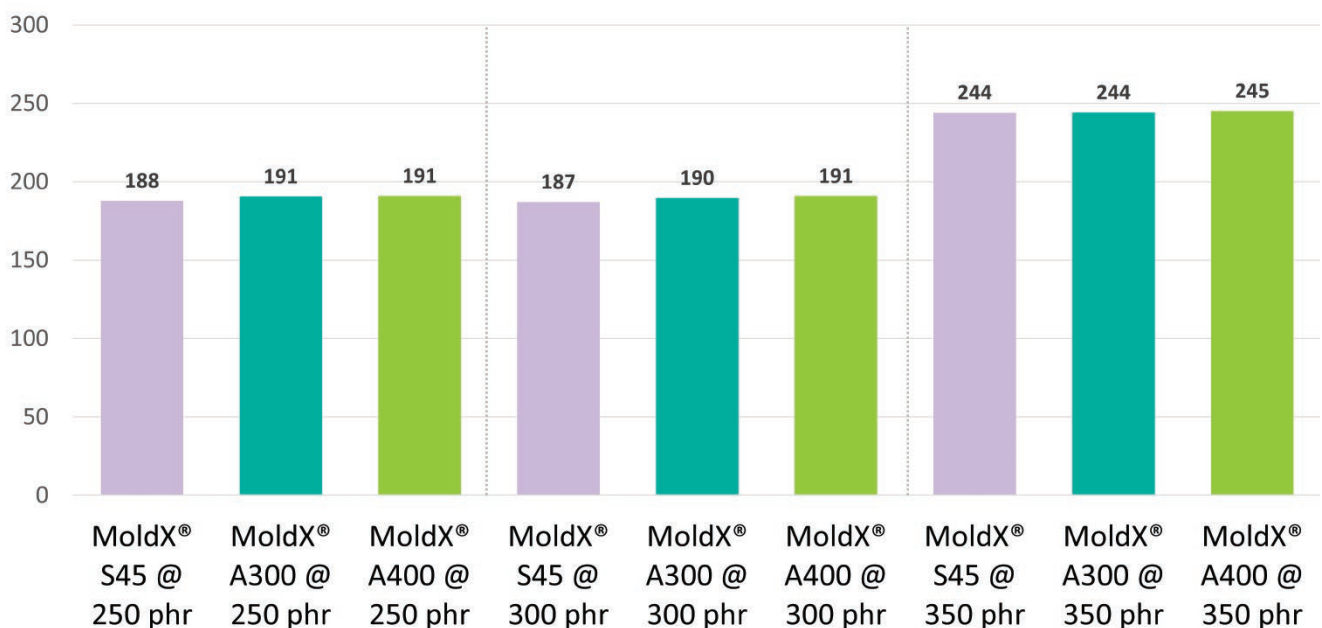
## Importance of Arc Track Resistance in Composites



Arc Track resistance is commonly requested for composites. Arc resistance is a measure of the time required to make an insulating surface conductive under a high voltage / low current arc in carefully controlled laboratory conditions. Stated another way, it is the ability of the composite to resist the action of a high voltage electrical arc. The higher the number, the more insulating the compound is.

The chart below shows how the use of ATH provides excellent arc track resistance between 150 and 300 phr, and there is a step-change improvement when ATH content is 350 phr. The choice of ATH is not a determining factor in arc track resistance.

ASTM D-495 Arc Track Resistance (seconds)

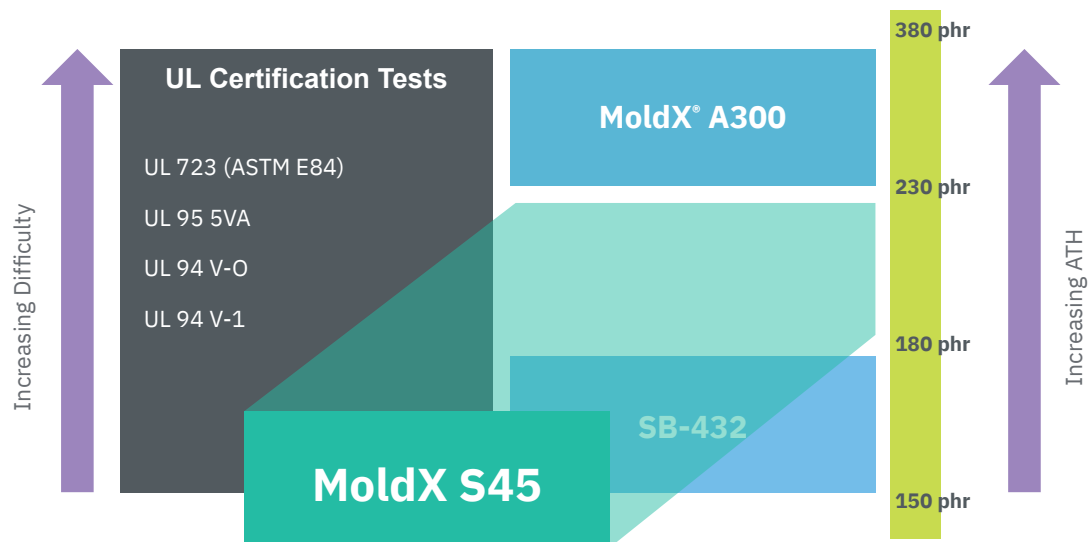


# MoldX® S45 Optimized ATH

For SMC, BMC, Hand Lay-Up and Polyurethane Applications

MoldX® S45 optimized ATH is a halogen-free fire retardant product designed for fiberglass reinforced polyester applications such as SMC, BMC and laminating. The MoldX® S45 grade is engineered to allow higher loadings (180 to 230 phr) versus competitive ATH products and offers excellent processing.

MoldX® S45 Optimal Loading Level: Between 180 and 230 phr



Huber's modern Cone Calorimeter in Fairmount, Georgia (US) measures rate of heat release and smoke generation.

# Introducing **MoldX® A300 and A400 Optimized ATH** for Your Most Stringent Applications

The charts on the following page compare the curves of formulations containing calcium carbonate, MoldX® A300\* optimized ATH, Martinal® ON-921\* ATH and MoldX® A400\* optimized ATH at 350 phr.

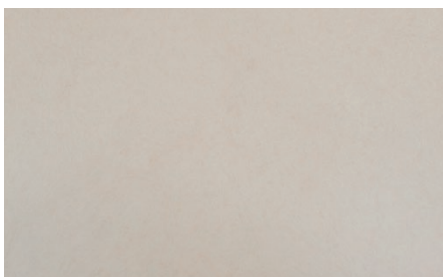
MoldX® A400 optimized ATH is recommended for applications requiring ASTM E-84 Class A Certification and when fire retardant performance standards are the most rigorous and color sensitivity is not an issue.

Compared with calcium carbonate, MoldX® A300 and Martinal® ON-921 offer significant improvement in fire retardance at the same loading, but MoldX A400 provides substantially more improvement, in both flame retardance and smoke reduction.

## MoldX® A300 and A400 Color Comparison

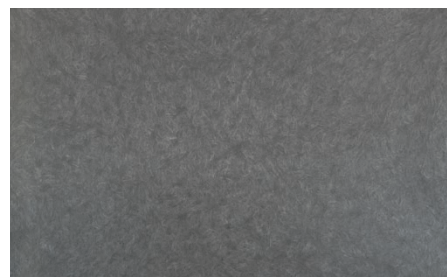
①

**MoldX®A300 @300 phr**



②

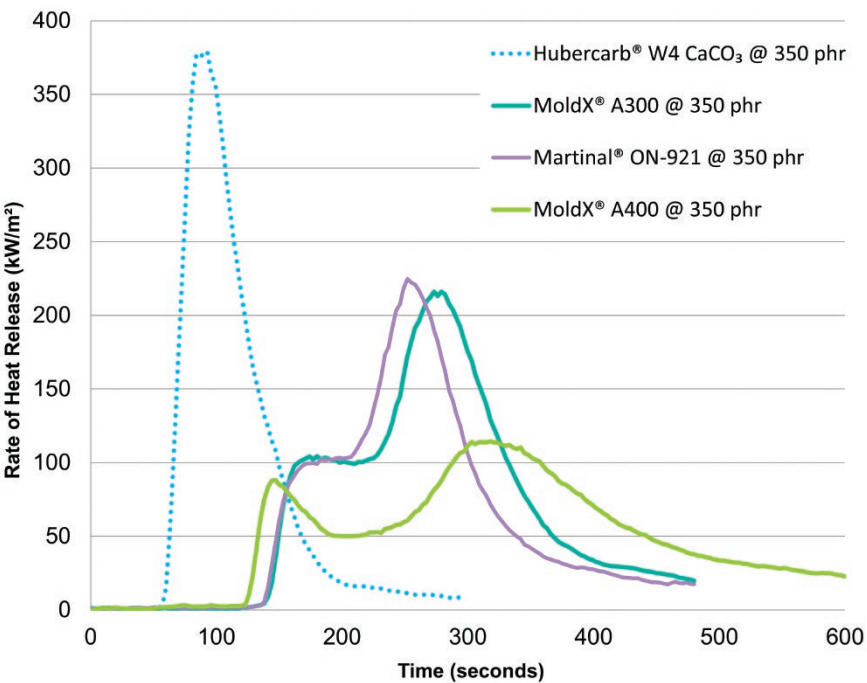
**MoldX® A400 @300 phr**



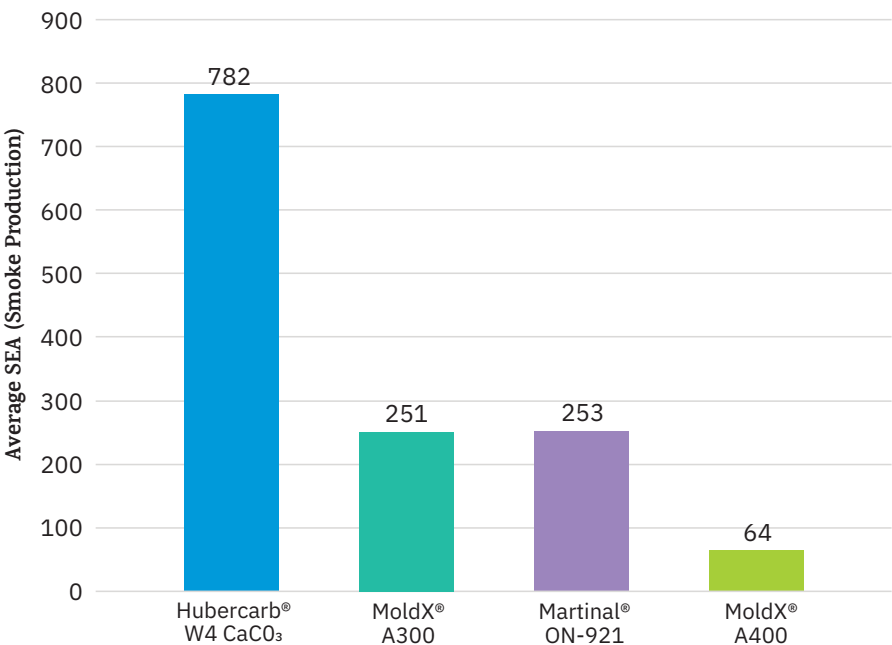
MoldX A300 has superior color characteristics versus MoldX A400.  
*The panel thickness for the images above is 100 mils. Resin used is unsaturated polyester.*

# Rate of Heat Release in BMC Compounds at 350 phr

ASTM E1354 Cone Calorimeter Rate of Heat Release @ 50kW/m<sup>2</sup>



ASTM E1354 Cone Calorimeter Rate of Smoke Production



A key tool utilized to evaluate flame retardant efficiency is the Cone Calorimeter. The sample of the compound is exposed to heat radiation and starts to burn at a time depending on the composition of the compound. The Cone measures oxygen consumption and calculates the heat release and smoke production rate, which is usually shown as a function of time. The graphs above and on the preceding page show how increased loadings of Huber’s Martinal® and MoldX® ATH products result in a substantial decreased heat release rate and decreased smoke generation. You can see MoldX® A400 optimized ATH outperforms exceptionally well in the critical areas of flammability and smoke suppression.



## How to Impart **Fire Retardance** and **Smoke Suppression** in Pultrusion, Resin Transfer Molding, Vacuum Bag Molding and Resin Infusion Applications

Like the applications featured earlier, high loadings and low viscosity are desirable for pultrusion, RTM, vacuum bag molding and resin infusion. However, there is an additional need in these applications, and that is the desire to minimize the forces necessary to move the liquid resin / ATH / fiberglass compound through the die.

SB-432 ATH and Martinal ON-310 S ATH are recommended when the ATH loading is below 60 phr and glass content is <60%. However, when more ATH is needed to meet a fire retardant specification, these products may not be ideal, as the pull forces will increase and cause problems during manufacturing.

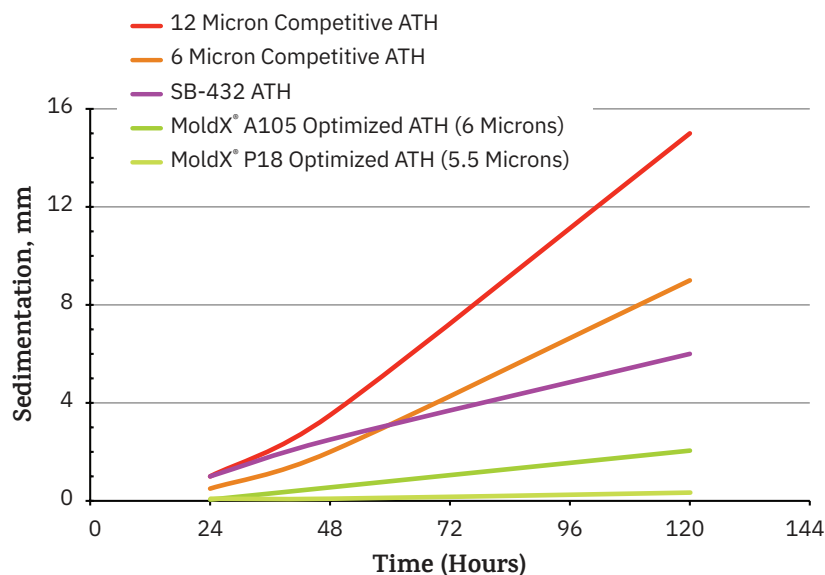
Customers producing by these processes are seeking:

- Reliable up-time (No fiberglass breakages)
- Constant line speed
- Minimized sedimentation

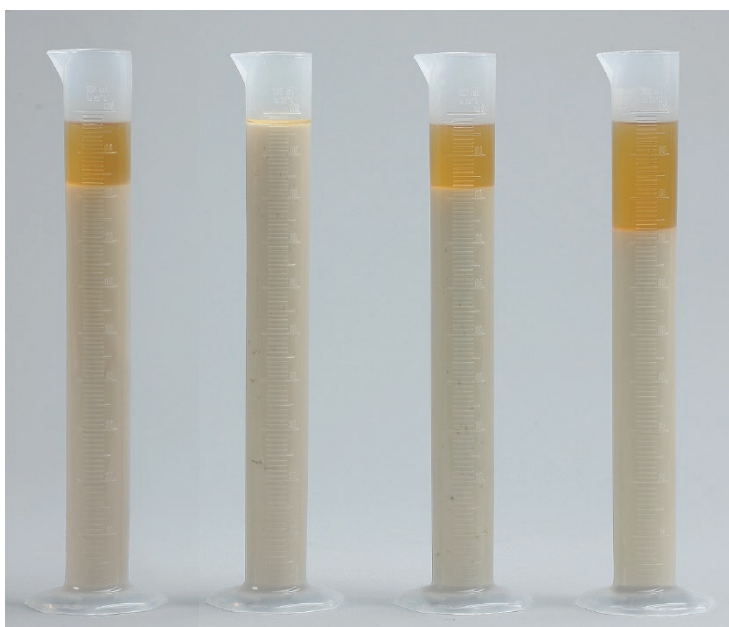
MoldX® P18 and MoldX® S45 optimized ATH were developed specifically to enable high ATH loadings while minimizing pull forces. It may not impart the lowest viscosity, but that is not as critical. The lack of coarse particles in MoldX® P18 and MoldX® S45 results in lower sedimentation, reliable production and faster line speeds. MoldX® P18 optimized ATH is engineered specifically for pultrusion, resin infusion and vacuum bag molding applications. The product's narrow particle size distribution gives superb processing performance with fiberglass content greater than 60% by weight.

### A Technical Showcase Featuring MoldX® P18 Optimized ATH

ATH Settling Behavior in Modar® Fire-Retardant Resin 875 at 25°C



## 100 phr ATH in Modar® Fire-Retardant Resin 875 stored at room temperature after five days



MOLDX® P18  
OPTIMIZED ATH  
(5.5 MICRONS)

6 MICRON  
COMPETITIVE ATH  
PRODUCT

12 MICRON  
COMPETITIVE ATH  
PRODUCT

## MoldX® P18 ATH

Means Lower Pull Forces and Reduced Sedimentation

FORMULATION INGREDIENTS	FORUMULATION I	FORMULATION II	FORMULATION III
ISOPHTHALIC POLYESTER RESIN	100	100	100
COMPETITIVE ATH – 2 MICRONS	100	-	-
COMPETITIVE ATH – 6.5 MICRONS	-	100	-
MOLDX® P18 OPTIMIZED ATH	-	-	100
FIBERGLASS (WEIGHT %)	62%	62%	62%
PERFORMANCE COMPARISON			
VISCOSITY @ 25°C #6 SPINDLE 10 RPM	2,890	2,490	1,630
PULL FORCE (POUNDS)	1,130	6.634	930

# Our global footprint

The Huber Advanced Materials (HAM) SBU is a specialty chemicals business with a global, leading position in the development and production of halogen-free fire retardant solutions, smoke suppressants and specialty aluminas touching lives and enhancing safety for millions of people around the world.

## Americas

Fairmount, GA  
Atlanta, GA  
Kennesaw, GA  
Marblehead, IL  
Bauxite, AR

## Europe

Bergheim, Germany  
Breitenau, Austria

## Asia Pacific

Qingdao, China



2

R&D Centers

6

Manufacturing plants

3

Customer Care  
Centers



**Huber Advanced Materials  
Martinswerk GmbH**

+49 2271 9020  
info@martinswerk.com  
www.martinswerk.com

**Europe, Middle East, Africa & India**

**Huber Advanced Materials**

+1 866 564 8237  
hubermaterials@huber.com  
www.hubermaterials.com

**Americas**

**Huber Advanced Materials HEM  
(Qingdao) Co. Ltd.**

+86 532 58792008  
hubermaterials@huber.com  
www.hubermaterials.com

**Asia Pacific**