




ADVANCED MATERIALS

# **Martinal® ALUMINUM HYDROXIDE** **Magnifin® MAGNESIUM HYDROXIDE**

Halogen-Free Fire Retardants  
for the Cable Industry

A collection of various colored electrical cables (yellow, blue, green, red, white) with their outer insulation removed, showing the internal copper conductors. The cables are arranged in a fan-like pattern, fanning out from the bottom left towards the top right. The background is a solid light blue.

Safe, sustainable and efficient  
flame retardants and smoke  
suppressants to reach the most  
stringent cable requirements

# Martinal® Aluminum Hydroxide + Magnifin® Magnesium Hydroxide

Martinal® aluminum hydroxide (ATH) and Magnifin® magnesium hydroxide (MDH) are halogen-free fire retardant additives that have proven themselves over time as dependable stalwarts that have met and exceeded the demanding requirements of compounders and producers. The environmentally-friendly Martinal and Magnifin products are non-corrosive, inert and without effect of pigmentation smoke suppressors. Martinal® and Magnifin® flame retardants are available in various grades, tailor-made precisely to the specific properties of major plastic systems meeting the most stringent requirements of the wire & cable industry.

Precipitated Martinal® ATH and Magnifin® MDH are used most commonly in different polymeric backbones for cable compounds. The high purity Martinal® and Magnifin® grades are designed for use in plastics and rubber, but can also be used in other applications. Table 1 shows the major physical properties of Martinal® ATH.

| Martinal® ATH Physical Data |                        |
|-----------------------------|------------------------|
| Al(OH) <sub>3</sub>         | Approximately 99.6%    |
| Minor Impurities            | Na <sub>2</sub> O      |
| Loss on Ignition (1200°C)   | Approximately 34.5%    |
| Crystal Structure           | Hydrargillite          |
| Mohs Hardness               | 2,5 - 3,0              |
| Refractive Index            | 1,58                   |
| Specific Heat               | 1,19 J/g·K at 295 K    |
| Density                     | 2,42 g/cm <sup>3</sup> |
| Solubility in Water         | Almost Insoluble       |

TABLE 1

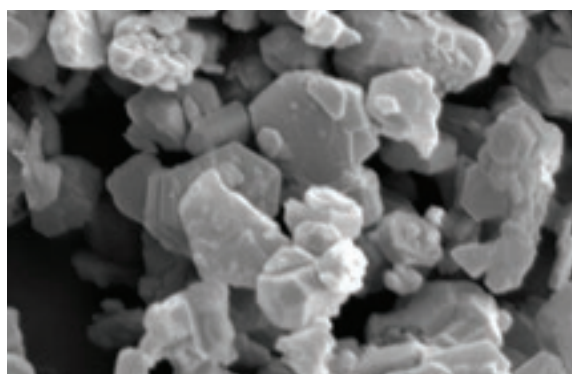


Figure 1: SEM image of Martinal® OL-104 LEO shows the hexagonal platelet structure of the crystals

Martinal and Magnifin products are available in various particle sizes and specific surface areas. Table 2 below shows the particle size distribution for the standard Martinal grades.

| Martinal® ATH Particle Size Distribution |           |  |                         |
|--|-----------|--|-------------------------|
| Martinal ATH Grades                      | D50/μm    | BET Specific Surface Area/m <sup>2</sup> | Oil absorption/mL/100 g |
| ON-320                                   | 15 - 25   | 1  | 20 - 30                 |
| ON-313 S                                 | 11 - 15   | 1,5                                      | 20 - 30                 |
| ON-310 S                                 | 8 - 11    | 2,5                                      | 20 - 30                 |
| OL-104 LEO                               | 1,8 - 2,1 | 4  | 27 - 32                 |
| OL-107 LEO                               | 1,6 - 1,9 | 7  | 28 - 33                 |
| OL-111 LE                                | 0,9 - 1,4 | 11                                       | 50 - 65                 |

TABLE 2

A number of coated grades are available that can help meet various wire and cable product requirements. The Martinal® product range includes de-agglomerated and fine precipitated grades. The final two digits in the product name describe the specific surface area (BET) expressed in m<sup>2</sup>/g. An overview of the Martinal® fine precipitated, uncoated and coated grades with end-use recommendations are provided in table 3.

| Martinal ATH Fine Grades        | Product Description               | Recommendations for Use/Special Properties  |
|---------------------------------|-----------------------------------|---|
| OL-104 LEO, OL-107 LEO          | Uncoated, Standard Grades         | Multipurpose grades for PE copolymers, rubber, TPE, PVC                               |
| OL-111 LE                       | Uncoated, High Surface Area Grade | Special grade for elastomers with stringent tensile strength requirements             |
| OL-104 ZO, OL-107 ZO, OL-104 RO | Vinyl Silane Coated Grades        | Mainly for cross-linked PE copolymers and silicon rubber                              |
| OL-104 C, OL-107 C              | Fatty Acid Coated Grades          | Mainly for PVC-P and PVC-U  |
| OL-104 IO, OL-107 IO            | Amino Silane Coated Grades        | Mainly for thermoplastic polar PE copolymers  |
| OL-104 GO                       | Proprietary Coated Grades         | Thermoplastic or cross-linked systems with stringent elongation at break requirements |

TABLE 3

Martinal® LEO grades have extremely low electrolyte content and therefore are the ideal choice for use in insulation compounds. Of course, they can also be utilized in sheathing compounds. In addition to their outstanding electrical properties, the Martinal® LEO products exhibit high thermal stability, outstanding compounding performance and good flowability.

Martinal® OL-111 LE has a high surface area which makes it a perfect fit for elastomer based applications, which require high tensile strength, such as conveyor belts and profiles.

The vinyl silane coated grades are suited for grafted and cross-linked EVA and rubber formulations. In addition to wire and cable applications, these grades are used as reinforcing additives in silicone rubber for high voltage insulators, in which the ATH provides improved arc tracking resistance.

Fatty acid treated grades, which include Martinal OL-104 C and Martinal OL-107 C, are predominately used in plasticized and rigid PVC.

The amino silane surface treatment makes ATH suitable for thermoplastic polar polymers like EVA and EEA and helps to improve the mechanical properties.

Martinal OL-104 GO has a proprietary surface coating and is designed for applications that require higher elongation at break in both thermoplastic and in cross-linked systems.

Magnifin® magnesium hydroxide [Mg(OH)<sub>2</sub>] is a high purity synthetic magnesium hydroxide. A patented manufacturing process is employed to produce a uniform fine particle size and a regular crystal structure. Magnifin® MDH is recommended in applications where the processing temperature exceeds the decomposition temperature of aluminum hydroxide, i.e., above 200°C. Table 4 lists the typical physical properties of Magnifin products.

Like Martinal® ATH, the fine precipitated Magnifin® MDH grades are available in different

| Magnifin® MDH Physical Data |                       |
|-----------------------------|-----------------------|
| Mg(OH) <sub>2</sub>         | > 99.8%               |
| Mohs Hardness               | 2,5                   |
| Refractive Index            | 1,56 - 1,58           |
| Density                     | 2,4 g/cm <sup>3</sup> |
| Surface Moisture            | ≤ 0,3 %               |
| Oxides                      | ≤ 0,2%                |

TABLE 4

| Magnifin® MDH Particle Size Distribution |           |  |
|--|-----------|--|
| Magnifin Grades                          | D50/μm    | BET Specific Surface Area/m <sup>2</sup> |
| H-5                                      | 1,6 - 2,0 | ca. 5                                    |
| H-7                                      | 0,9 - 1,3 | ca. 7                                    |
| H-10                                     | 0,8 - 1,1 | ca. 10                                   |

TABLE 5

particle size distributions, specific surface areas and coating systems. Table 5 shows the particle size distributions of the standard grades. The final two digits in the product name describe the specific surface area (BET) expressed in m<sup>2</sup>/g.

Table 6 below gives an overview of the uncoated and coated Magnifin® grades with some typical application recommendations.

| Magnifin MDH Grades                              | Description                | Recommendations for Use/Special Properties   |
|--|----------------------------|--|
| H-5, H-7, H-10                                   | Uncoated, Standard Grades  | Multipurpose grades for PE copolymers, rubber, TPE, PVC                                    |
| H-5 A, H-10 A                                    | Vinyl Silane Coated Grades | Mainly for cross-linked PE copolymers and silicone rubber                                  |
| H-7 C, H-7 C3                                    | Fatty Acid Coated Grades   | Mainly for PVC-P and PVC-U   |
| H-5 IV, H-10 IV                                  | Amino Silane Coated Grades | Mainly for thermoplastic polar PE copolymers   |
| H-5 GV, H-5 HV, H-5 MV, H-10 MV, H-5 TV, H-10 TV | Proprietary Coated Grades  | Thermoplastic or cross-linked systems with stringent elongation at break requirements, TPU |

TABLE 6

# Martinal® Aluminum Hydroxide + Magnifin® Magnesium Hydroxide

## FLAME RETARDANT EFFECT OF MARTINAL® ATH AND MAGNIFIN® MDH

The flame retardant effect of Martinal® ATH and Magnifin® MDH is based on their endothermic decomposition into aluminum or magnesium oxide respectively and water – all of which are entirely innocuous, non-corrosive substances.

The endothermic reaction absorbs considerable amounts of heat during combustion of the polymeric material. With Martinal® ATH, the reaction results in a total heat consumption of 1051 J/g  $\text{Al}(\text{OH})_3$ .



For Magnifin® MDH, the corresponding reaction results in a total heat of combustion of 1316 J/g  $\text{Mg}(\text{OH})_2$ .



The polymer is thus protected against rapid decomposition, the formation of flammable by-products is retarded, and the water vapor produced displaces the oxygen and works like an inert gas. A protective layer made up of aluminum or magnesium oxide and the products of carbonization form on the surface of the polymer, further hindering combustion. This protective layer also reduces smoke density by adsorbing soot particles.

The thermal stability of Magnifin® MDH is considerably higher than that of Martinal® ATH. Martinal® ATH starts to release water at about 200°C. Magnifin® MDH remains stable up to about 320°C (figure 1). The degree of flame retardancy attainable with Martinal® ATH and Magnifin® MDH strongly depends on the filler loading of the compound. All common processing techniques can be used, although the

processing temperature should only briefly exceed 200°C when using aluminum hydroxide, as this is the temperature at which dehydration begins (figures 1 and 2).



Picture 2

One way to evaluate flame retardant efficiency is to burn flame retarded compounds in the cone calorimeter (picture 2). 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 calorimeter measures the oxygen consumption and calculates the heat release rate. Usually, the heat release rate is shown as a function of time.

Thermal Stability of Aluminum Trihydrate (ATH) and Magnesium Hydroxide (MDH)

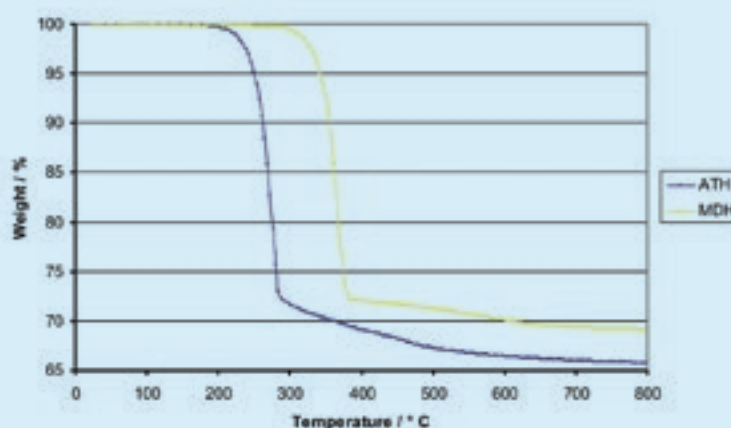


FIGURE 1

ATH - Water Release at Constant Temperature

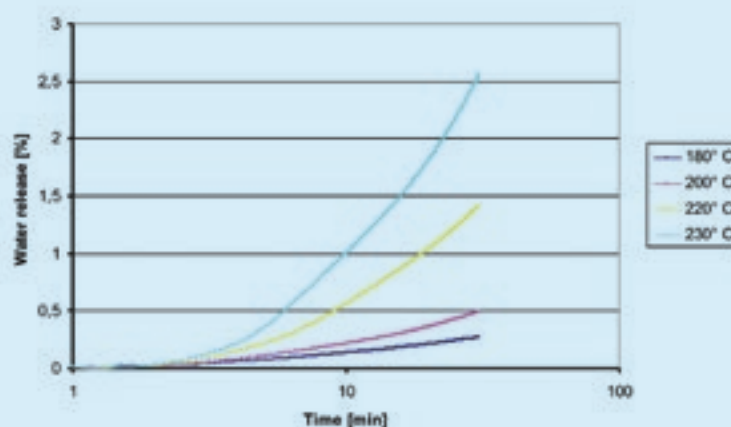


FIGURE 2



The curves (figures 3 & 4) from cone calorimeter measurements indicate the high correlation of loading with the heat release rate.

Two things are important for fire resistance. First, reduce the heat release rate and secondly, delay the time to ignition as much as possible. The heat release rate is indicated along the y axis while the time to ignition is plotted along the x axis. At a heat flux of 35 kW/m<sup>2</sup> the unfilled polymer starts to burn after ca. 80 seconds and reaches a maximum heat release rate of more than 550 kW/m<sup>2</sup>. The addition of ATH and MDH helps to reduce the heat release rate significantly; the time to ignition is delayed 120–160 seconds.

### CABLE COMPOUNDS

Due to the large number of end-use applications, each cable construction needs to meet specific test requirements. The polymers used in wire and cable can be classified roughly into thermoplastics, thermoplastic elastomers and cross-linked elastomers. The choice of the polymer and flame retardant system depends on the physical and chemical properties defined in the cable standard. Because of the wide variety of different polymer based compounds, a detailed description of polymers used for specific applications would be outside of the scope of this brochure.

Therefore, we must first explain the basic relationships between the characteristics of Martinal® ATH and Magnifin® MDH on the one hand and the characteristics of compounds on the other using simple test formulations. We then present reference formulations for some common cable materials with Martinal® and Magnifin® flame retardants.

It should be noted that the mixing process (e.g., using a Buss kneader, twin-screw extruder or internal mixer) and the method of preparation of the test specimens (e.g., by extrusion, compression and injection molding) have an impact on the test results. Furthermore, mechanical properties measured on extruded cable generally differ significantly from laboratory test samples.

The heat release rate formulation provided is for guidance only. It is up to the user to optimize the formulation to meet specific application requirements. Test results were measured on laboratory equipment.

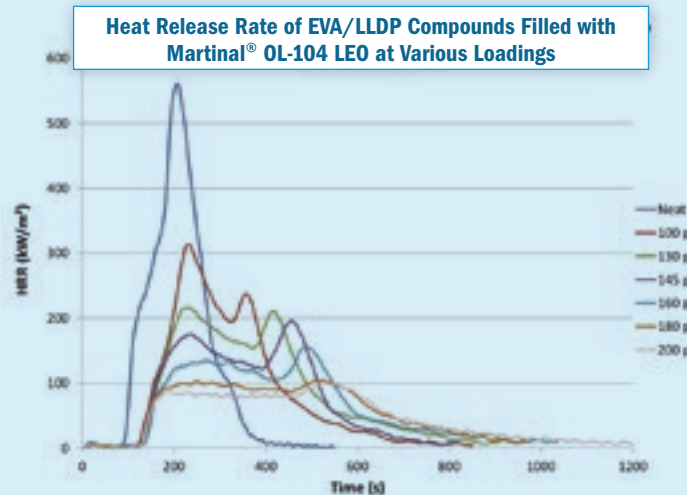


FIGURE 3

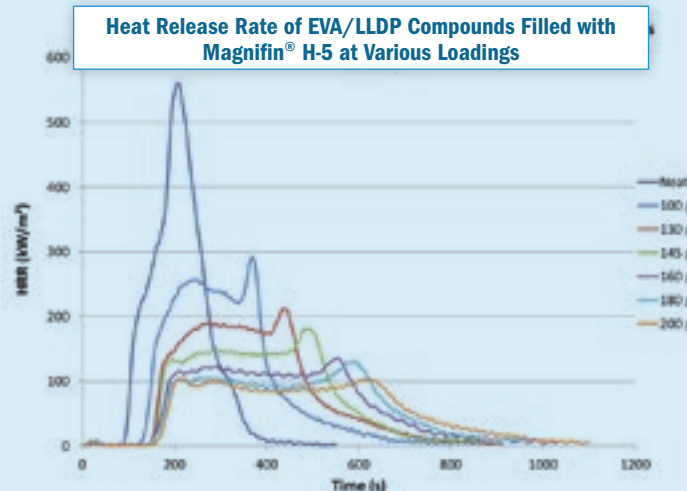


FIGURE 4

# Martinal® Aluminum Hydroxide + Magnifin® Magnesium Hydroxide

## THERMOPLASTIC SYSTEMS PE AND PE-COPOLYMERS

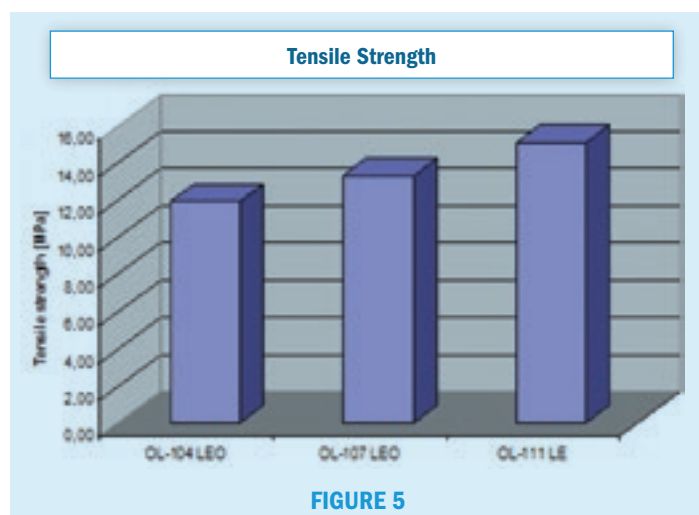
### ETHYLENE VINYL ACETATE (EVA) COPOLYMER TEST FORMULATION FOR ATH & MDH

Copolymers of ethylene with vinyl acetate (VA) are common polymers in the cable industry. Typical VA contents of the copolymers varies between 12 and 70%. Copolymers with high VA content (>40%) behave similarly to rubber and therefore need to be cured or cross-linked.

The higher the VA content, the higher the limiting oxygen index (LOI) in Martinal® ATH or Magnifin® MDH filled compounds. The oxygen index according to ASTM D-2863 is the minimum quantity of oxygen in an oxygen/nitrogen atmosphere necessary to burn for three minutes.

The synergism between the VA group and the hydroxide is even stronger for Magnifin® ATH than for Martinal® MDH.

Basic test data such as mechanical, rheological and electrical properties after water aging as well as flame retardancy can be derived from the test formulation in table 7, where maleic anhydride grafted polymers are used as compatibilizers. The mean specific BET surface area of the flame retardant grades Martinal® OL-104 LEO, OL-107 LEO and OL-111 LE is 4, 7 and 11 m<sup>2</sup>/g, respectively.



| EVA/LLDPE Test Formulation for ATH |                 |                |
|------------------------------------|-----------------|----------------|
| Components                         |                 | Quantity (phr) |
| Escorene™ UL 00328                 | EVA             | 67             |
| Escorene™ LL 1001 XV               | LLDPE           | 17             |
| Mah Gr Polymers                    | Coupling Agent  | 16             |
| ATH                                | Flame Retardant | 160            |
| Ethanox® 310                       | Antioxidant     | 0,75           |

| EVA/LLDPE Test Formulation for MDH |                 |                |
|------------------------------------|-----------------|----------------|
| Components                         |                 | Quantity (phr) |
| Escorene UL 00328                  | EVA             | 69             |
| Escorene LL 1001 XV                | LLDPE           | 19             |
| Mah Gr Polymers                    | Coupling Agent  | 12             |
| MDH                                | Flame Retardant | 150            |
| Ethanox 310                        | Antioxidant     | 0,75           |

**TABLE 7**

*Escorene™ is a registered trademark of ExxonMobil.*

*Ethanox® is a registered trademark of SI Group.*

For the Magnifin® grades H-5, H-7 and H-10 mean BET area is 5, 7 and 10 m<sup>2</sup>/g.

According to figure 5, higher tensile strength can be achieved by using finer grades of Martinal® ATH or Magnifin® MDH. This is primarily due to the reinforcing effect of the higher surface area additives.

Table 8 on the following page shows typical data such as melt-flow, LOI value (sample size 3 mm x 6 mm) and volume resistivity after seven days in water at 70°C for different specific surface areas of Martinal® ATH and Magnifin® MDH in the above test formulation. Furthermore, results from cone calorimeter measurements are indicated.

According to table 8, a higher specific surface results in a higher viscosity of the compound, whereas the LOI increases slightly. Also the cone calorimeter behavior is improved for products having higher specific surface area.

| Product Grade        | Tensile Strength | Elongation at Break | Melt Flow Index 150/21.6 | Oxygen Index 3 x 6mm <sup>2</sup> | Volume Resistivity after Seven Days at 70°C in Water | Cone Data @ 35 kW/m <sup>2</sup> , Sample Size 100 x 100 x 3mm Time to Ignition | Peak Heat Release Rate | MAHRE                | FIGRA                |
|----------------------|------------------|---------------------|--------------------------|-----------------------------------|--|---|------------------------|----------------------|----------------------|
|                      | [MPa]            | [%]                 | [g/10 min]               | [% O <sub>2</sub> ]               | [ohm x cm]   | [s]   | [kW/m <sup>2</sup> ]   | [kW/m <sup>2</sup> ] | [kW/m <sup>2</sup> ] |
| Martinal® OL-104 LEO | 11,9             | 226                 | 5,6                      | 35,1                              | 1,0 x 10 <sup>13</sup>                               | 126   | 132                    | 71                   | 0,5                  |
| Martinal® OL-107 LEO | 13,3             | 209                 | 5                        | 37,3                              | 1,0 x 10 <sup>13</sup>                               | 135   | 121                    | 67                   | 0,4                  |
| Martinal® OL-111 LE  | 15,1             | 185                 | 0,9                      | 39,2                              | 3,0 x 10 <sup>12</sup>                               | 152   | 93                     | 58                   | 0,4                  |
| Magnifin® H-5        | 14               | 179                 | 3,3                      | 30,5                              | 5,2 x 10 <sup>13</sup>                               | 191   | 99                     | 57                   | 0,4                  |
| Magnifin® H-10       | 15               | 190                 | 0,8                      | 32,2                              | 1,5 x 10 <sup>14</sup>                               |   |                        |                      |                      |

TABLE 8

The behavior of Magnifin® MDH as a function of the specific surface area is similar to Martinal® ATH (see table 8).

Special surface coatings were developed both for Martinal® ATH and Magnifin® MDH (tables 3 and 6). This makes, for example, the addition of silane for amino silane coated grade Magnifin® H-5 IV unnecessary (table 10), which simplifies the step and improves final product consistency.

The characteristics of the coated grade Magnifin® H-5 MV and H-10 MV are particularly notable. In the test formulation presented here, we achieve elongation at break rates of about 700%, very good electrical properties and an improved melt flow (table 10).

Other suitable coupling agents to improve polymer

| EVA/LLDPE Test Formulation for Coated MDH |                 |                |
|---|-----------------|----------------|
| Components                                |                 | Quantity (phr) |
| Escorene UL 00328                         | EVA             | 75             |
| Escorene LL 1001 XV                       | LLDPE           | 25             |
| Coated Magnifin MDH                       | Flame Retardant | 150            |
| Ethanox 310                               | Antioxidant     | 0,75           |

TABLE 9

interaction are, in addition to amino silanes, grafted polymers like maleic acid modified EVA or PE. Also vinyl silane/peroxide systems are suitable, as long as the amount of peroxide used is low enough to keep the compound thermoplastic.

| Product Grade     | Tensile Strength | Elongation at Break | Melt Flow Index 150/21.6 | Oxygen Index 3 x 6mm <sup>2</sup> | Volume Resistivity after Seven Days at 70°C in Water |
|-------------------|------------------|---------------------|--------------------------|-----------------------------------|--|
|                   | [MPa]            | [%]                 | [g/10 min]               | [% O <sub>2</sub> ]               | [ohm x cm]   |
| Magnifin® H-5     | 9,6              | 87                  | 3,7                      | 30,7                              | 2,9 x 10 <sup>11</sup>                               |
| Magnifin® H-5 IV  | 11,2             | 153                 | 3,6                      | 35,5                              | 4,7 x 10 <sup>11</sup>                               |
| Magnifin® H-10 IV | 12,9             | 157                 | 1,6                      | 34,3                              | 6,1 x 10 <sup>13</sup>                               |
| Magnifin® H-5 MV  | 7,0              | 772                 | 21,2                     | 28,9                              | 2,2 x 10 <sup>14</sup>                               |
| Magnifin® H-10 MV | 6,3              | 717                 | 14,9                     | 35,0                              | 2,2 x 10 <sup>14</sup>                               |

TABLE 10

# Martinal® Aluminum Hydroxide + Magnifin® Magnesium Hydroxide

## REFERENCE FORMULATION FOR CABLES

### THERMOPLASTIC EVA COMPOUNDS

Table 11 shows typical reference formulations for thermoplastic cable compounds with Martinal® ATH. Magnifin® MDH is suitable in cases where process temperatures are higher than 200°C. These formulations can be used to develop compounds to meet more stringent product standards. If UV-protection is needed or if the insulation is in contact with copper, the stabilization package needs to be changed accordingly.

| Thermoplastic EVA Reference Formulation  |                | Quantity (phr) |               |
|--|----------------|----------------|---------------|
| Components                               |                | Formulation 1  | Formulation 2 |
| Escorene UL 00328                        | EVA            | 67             | 67            |
| Escorene LL 1001 XV                      | LLDPE          | 17             | 17            |
| Fusabond® 226 D                          | Coupling Agent | 8              | 8             |
| Lotader® 3210                            | Coupling Agent | 8              | 8             |
| Martinal OL-104 LEO                      | ATH            | 160            |               |
| Martinal OL-107 LEO                      | ATH            |                | 160           |
| Ethanox 310                              | Antioxidant    | 0,75           | 0,75          |
| Ethaphos® 368                            | Antioxidant    | 0,25           | 0,25          |
| Typical Values                           |                |                |               |
| MFI (g/10 min)                           | 150°C/21.6 kg  | 5,5            | 4,9           |
| Tensile Atrngth (MPa)                    |                | 12,5           | 13,9          |
| Elongation at Break (%)                  |                | 210            | 195           |
| After Seven Days at 70°C Water Immersion |                |                |               |
| Tensile Strength (MPa)                   |                | 11,5           | 12,5          |
| Elongation at Break (%)                  |                | 225            | 192           |

TABLE 11

Fusabond® is a registered trademark of DuPont.  
Lotader® is a registered trademark of Arkema.  
Ethaphos® is a registered trademark of SI Group.

### POLYPROPYLENE (PP) COMPOUNDS

Due to the higher compounding and processing temperatures for PP, the special proprietary coated grades Magnifin® H-5 GV, H-5 HV, H-5 MV and H-10 MV are recommended.

Table 12 gives some indication for a PP compound flame retarded with coated Magnifin® MDH. With that specific kind of surface treatment, high levels of elongation at break and melt flow can be achieved. Furthermore, the impact strength is positively impacted. According to the cone calorimeter results, there is only a minor difference of the fire retardancy due to the surface treatment.

| Polypropylene Reference Formulation              |                       | Quantity (phr)         |                        |
|--|-----------------------|------------------------|------------------------|
| Components                                       |                       | Formulation 1          | Formulation 2          |
| Moplen® RP-210G                                  | PP                    | 100                    | 100                    |
| Magnifin H-5 MV                                  | MDH                   | 185,7                  |                        |
| Magnifin H-5 GV                                  | MDH                   |                        | 185,7                  |
| Typical Values                                   |                       |                        |                        |
| MFI [g/10 min]                                   | 230°C / 5 kg          | 7.7                    | 8.1                    |
| E-Modulus [MPa]                                  | Tear                  | 2791                   | 2886                   |
| Tensile Strength [MPa]                           |                       | 14,8                   | 15,1                   |
| Elongation at Break [%]                          |                       | 348                    | 282                    |
| LOI [% O <sub>2</sub> ]                          | 3 x 6 mm <sup>2</sup> | 30,2                   | 29,0                   |
| After Seven Days at 70°C Water Immersion         |                       |                        |                        |
| Volume Resistivity [ohm x cm]                    |                       | 5,6 x 10 <sup>14</sup> | 5,0 x 10 <sup>14</sup> |
| Water Pick-Up [%]                                |                       | 0,14                   | 0,09                   |
| Cone Data @ 35 kW/m <sup>2</sup> 100 x 100 x 3mm |                       |                        |                        |
| Time to Ignition [s]                             |                       | 82                     | 85                     |
| Peak Heat Release Rate [kW/m <sup>2</sup> ]      |                       | 175                    | 200                    |
| MAHRE [kW/m <sup>2</sup> ]                       |                       | 113                    | 117                    |
| FIGRA [kW/m <sup>2</sup> ]                       |                       | 1,2                    | 1,5                    |

TABLE 12

Moplen® is a registered trademark of Lyondellbasell.



## POLYVINYL CHLORIDE (PVC) COMPOUNDS

In most applications, it is preferable to have a PVC cable insulation compound with a limiting oxygen index (LOI) of at least 26% O<sub>2</sub>. Formulations 1 to 3 in table 13 have a LOI value of between 26 and 27%. Higher LOI values are possible by adding phosphate or brominated plasticizer Sb<sub>2</sub>O<sub>3</sub>. Martinal® ATH and Magnifin® MDH have the additional advantage of significantly reducing smoke (figures 6, 7, 9, 10 and 12). The addition of zinc borate can further reduce smoke formation.

Coated ATH and MDH grades improve oil absorption, rheology and the physical properties. For PVC, the following Martinal® and Magnifin® grades are recommended:

OL-104 C, OL-107 C, OL-104 ZO, OL-107 ZO, OL-104 GO, H-7 C, H-7 C3, H-5 A, H-10 A, H-5 MV, H-10 MV.

The addition of about 3-6 phr of zinc borate can be helpful in reducing dripping, smoke formation and helps passing higher flame test standards such as DIN 4102 (EN 13501).

| PVC Wire & Cable Formulations with Higher LOI            |                       | Quantity (phr) |               |               |
|--|-----------------------|----------------|---------------|---------------|
| Components   |                       | Formulation 1  | Formulation 2 | Formulation 3 |
| PVC K-Value 70   | PVC                   | 100            | 100           | 100           |
| Palatinol® DIDP  | Phthalate Plasticizer | 55             | 55            | 55            |
| Baeropan® MC KA 83-5                                     | Lead-Free Stabilizer  | 2,7            | 2,7           | 2,7           |
| Martinal OL-104 LEO                                      | ATH                   | 100            | 50            | 45            |
| Zinborel® Fine   | Zinc Borate           |                |               | 5             |
| CaCO <sub>3</sub>  | Chalk                 |                | 10            | 10            |
| Typical Values   |                       |                |               |               |
| Tensile Strength [MPa]                                   |                       | 16,1           | 16,0          | 16,1          |
| Elongation at Break [%]                                  |                       | 341            | 348           | 341           |
| LOI [% O <sub>2</sub> ]                                  | 3 x 6 mm <sup>2</sup> | 27,0           | 26,0          | 26,7          |
| UL94   | 3 mm                  | V-0            | V-0           | V-0           |
| Smoke Density ASTM E662 (Non-Flaming Modus)              |                       |                |               |               |
| DS Maximum   |                       | 477            | 496           | 344           |
| DS 3 Minimum   |                       | 42             | 46            | 53            |
| Smoke Density ASTM E662 (Flaming Modus)                  |                       |                |               |               |
| DS Maximum   |                       | 501            | 436           | 446           |
| DS 3 Minimum   |                       | 293            | 273           | 273           |
| Cone Data @ 50 kW/m <sup>2</sup> 100 x 100 x 3mm         |                       |                |               |               |
| Time to Ignition [s]                                     |                       | 19             | 17            | 18            |
| Peak Heat Release Rate [kW/m <sup>2</sup> ]              |                       | 116            | 148           | 145           |
| MAHRE [kW/m <sup>2</sup> ]                               |                       | 93             | 107           | 113           |
| Total Smoke Production [m <sup>2</sup> /m <sup>2</sup> ] |                       | 2986           | 2809          | 2772          |
| Maximum Smoke Value [m <sup>2</sup> /g]                  |                       | 10             | 11            | 11            |

TABLE 13

Palatinol® is a registered trademark of BASF. Baeropan® is a registered trademark of Baerlocher. Zinborel® is a registered trademark of Societa Chimica Larderello.

# Martinal® Aluminum Hydroxide + Magnifin® Magnesium Hydroxide

## CROSS-LINKED (XL) SYSTEMS WITH PE AND PE-COPOLYMERS

Because of increased demand for cables having a higher temperature resistance (used for photovoltaic, automotive and railroad applications), cross-linking is gaining importance. Peroxide curing and electron beam usage have some disadvantages such as temperature limitations during compounding to avoid premature decomposition of the peroxide and higher costs for e-beam application. The silane cross-linking could be another interesting route to XL cables.

Compounds flame retarded with Martinal® ATH or Magnifin® MDH can be cross-linked using all common procedures (i.e., peroxide, silane or radiation cross-linking). In the following section, we present reference formulations for peroxide cross-linking.

## PEROXIDE CROSS-LINKED PE AND EVA FORMULATIONS

As indicated in table 14, Martinal® OL-104 LEO and OL-107 LEO ATH can be used to obtain high levels of tensile strength while maintaining sufficient elongation at break. Besides good mechanical properties, these formulations are appropriate to meet the demand for outstanding electrical properties because of the low electrolyte content of Martinal® ATH and the nonpolarity of the PE.

| Cross-Linked PE Formulation      |              | Quantity (phr) |               |
|----------------------------------|--------------|----------------|---------------|
| Components                       |              | Formulation 1  | Formulation 2 |
| Engage™ 8003                     | PE           | 50             | 50            |
| Exact™ 8230                      | PE           | 50             | 50            |
| Martinal OL-104 LEO              | ATH          | 180            |               |
| Martinal OL-107 LEO              | ATH          |                | 180           |
| Irganox® PS 802                  | Antioxidant  | 2              | 2             |
| Ethinox 310                      | Antioxidant  | 1,5            | 1,5           |
| Dynasylan® 6498                  | Vinyl Silane | 1,8            | 1,8           |
| Perkadox® 14/40 B-GR             | Peroxide     | 5              | 5             |
| A-C 617A                         | PE Wax       | 2              | 2             |
| Typical Values                   |              |                |               |
| Tensile Strength (MPa)           |              | 15,7           | 18,2          |
| Elongation at Break (%)          |              | 255            | 178           |
| After 14 Days at 121°C Air Aging |              |                |               |
| Tensile Strength (MPa)           |              | 15,5           | 19,9          |
| Elongation at Break (%)          |              | 205            | 187           |

TABLE 14

Engage™ is a registered trademark of Dow.  
Exact™ is a registered trademark of ExxonMobil.  
Irganox® is a registered trademark of Ciba Specialty Chemicals.  
Dynasylan® is a registered trademark of Evonik.  
Perkadox® is a registered trademark of AkzoNobel.

An example of a polar cross-linked formulation is indicated in table 15. Because of the higher VA content of the polymer in use the resistance to oil aging is considerable. It's like in the unpolar XL recipe which contains PE Martinal® OL-107 LEO ATH, which results in higher tensile strength than the standard Martinal grade because of the higher specific surface area.

| Cross-linked EVA formulation     |              | Quantity (phr) |               |
|----------------------------------|--------------|----------------|---------------|
| Components                       |              | Formulation 1  | Formulation 2 |
| Levapren® 500 HV                 | EVA 50% VA   | 67             | 67            |
| Martinal OL-104 LEO              | ATH          | 180            |               |
| Martinal OL-107 LEO              | ATH          |                | 180           |
| Rhenogran® PCD-50/EVA            | Antioxidant  | 3              | 3             |
| Rhenofit® DDA                    | Antioxidant  | 1,5            | 1,5           |
| Dynasylan 6498                   | Vinyl silane | 1,8            | 1,8           |
| Rhenofit TRIM/S                  | Activator    | 0,7            | 0,7           |
| Perkadox 14/40 B-GR              | Peroxide     | 6              | 6             |
| Edenol® 888                      | Plasticizer  | 3              | 3             |
| Typical Values                   |              |                |               |
| Tensile Strength (MPa)           |              | 11,0           | 13,9          |
| Elongation at Break (%)          |              | 190            | 164           |
| After 14 Days at 121°C Air Aging |              |                |               |
| Tensile Strength (MPa)           |              | 11,7           | 14,3          |
| Elongation at Break (%)          |              | 192            | 175           |

TABLE 15

Levapren® is a registered trademark of Arlanxco Performance Elastomers.  
Rhenogran® and Rhenofit® are registered trademarks of Lanxess.  
Edenol® is a registered trademark of Emery Oleochemicals.

## SILANE CROSS-LINKED PE AND EVA FORMULATIONS

The compounding process is typically divided into three separate steps: compounding, extrusion and cross-linking. The initial step is to graft the vinyl silane to the polymer(s) of the formulation and to add the halogen-free flame retardant (one or two step compounding process). Extrusion of the cable together with the cross-linking catalyst is the second step. Finally, the last part is the cross-linking via hydrolysis of the silane alkoxy groups supported through a catalyst usually obtained directly after the extrusion in a water bath/sauna.

To achieve silane cross-linking, different processes can be used. Typically, in a first compounding step, the vinyl silane is grafted to the polymer. The flame retardant is added in a second compounding step. More demanding but interesting because of the lower compounding capacity used is the one step compounding process.

Here grafting and adding of the filler takes place in parallel. Good results could be obtained using a Buss Kneader with L/D of 22. Table 16 shows results obtained with a silane cross-linked formulation.

| Silane Cross-Linked EVA Formulation   |                 | Quantity (phr) |               |
|---|-----------------|----------------|---------------|
| Components  |                 | Formulation 1  | Formulation 2 |
| Escorene UL 00328   | EVA             | 75             | 75            |
| Escorene LL 1001 XV   | LLDPE           | 25             | 25            |
| Martinal OL-104 LEO   | ATH             | 160            |               |
| Martinal OL-107 LEO   | ATH             |                | 160           |
| Vinyl Silane/Peroxide Mix   | Grafting System | 1,44           | 1,44          |
| Antioxidants Mix  | Stabilizers     | 3              | 3             |
| <b>Properties after Cross-Linking (+2.5% DBTDL in EVA 0.2%) after Four Hours at 95°C - Extruded Tapes 2mm Thickness</b> |                 |                |               |
| Tensile Strength (MPa)  |                 | ca. 12,5       | ca. 13        |
| Elongation at Break (%)   |                 | ca. 210        | ca. 170       |
| <b>Cone Data @ 35 kW/m<sup>2</sup> 100 x 100 x 3mm</b>  |                 |                |               |
| Time to Ignition [s]  |                 | 113            |               |
| Peak Heat Release Rate [kW/m <sup>2</sup> ]   |                 | 134            |               |
| MAHRE [kW/m <sup>2</sup> ]  |                 | 86             |               |
| FIGRA [kW/m <sup>2</sup> ]  |                 | 0,6            |               |

TABLE 16

## EPDM COMPOUNDS

For EPDM and EPM elastomers, Martinal® ATH and Magnifin® MDH are suitable flame retardants. These elastomers can accept higher filler loadings with

| Cross-Linked EPDM Formulation |                       |                |
|-------------------------------|-----------------------|----------------|
| Components                    |                       | Quantity (phr) |
| Vistalon™ 2504N               | EPDM 50/50            | 100            |
| Magnifin H-5                  | MDH                   | 80 - 100       |
| Calcined Kaolin               | Silicate              | 70 - 90        |
| Micronized CaCO <sub>3</sub>  | Chalk                 | 15 - 25        |
| Vulkanox® ZMB2/C5             | Antioxidant           | 1,2            |
| Dynasylan 6498                | Vinyl Silane          | 1,2            |
| Rhenofit TAC/S                | Activator             | 1              |
| Perkadox 14/40 B-GR           | Peroxide              | 7              |
| ZnO RS                        | Curing Promotor       | 5              |
| Tudalen® B 8013               | Plasticizer           | 3              |
| Stearic acid                  | Lubricant             | 2              |
| A-C 617A                      | PE Wax                | 4              |
| <b>Total Values:</b>          |                       |                |
| LOI (% O <sub>2</sub> )       | 3 x 6 mm <sup>2</sup> | 40             |

TABLE 18

Vistalon™ is a registered trademark of ExxonMobil.  
Vulkanox® is a registered trademark of Lanxess.  
Tudalen® is a registered trademark of Klaus Dahleke KG.

minimum effect on mechanical properties. Tables 17 and 18 show typical EPDM reference compounds for sheathing and insulation applications.

| PVC Wire & Cable Formulations with Higher LOI          |                       | Quantity (phr)         |                        |                        |                        |
|--|-----------------------|------------------------|------------------------|------------------------|------------------------|
| Components   |                       | Formulation 1          | Formulation 2          | Formulation 3          | Formulation 4          |
| Buna EP G 2470 LM P                                    | EPDM Rubber           | 100                    | 100                    | 100                    | 100                    |
| Martinal OL-104 LEO                                    | ATH                   | 170                    |                        |                        |                        |
| Martinal OL-107 LEO                                    | ATH                   |                        | 170                    |                        |                        |
| Magnifin H-5   | MDH                   |                        |                        | 170                    |                        |
| Magnifin H-10  | MDH                   |                        |                        |                        | 170                    |
| Vulkanox HS/LG   | Antioxidant           | 1,5                    | 1,5                    | 1,5                    | 1,5                    |
| Vulkanox ZMB2/C5                                       | Antioxidant           | 1                      | 1                      | 1                      | 1                      |
| Dynasylan 6498   | Vinyl Silane          | 1,7                    | 1,7                    | 1,7                    | 1,7                    |
| Rhenofit TAC/S   | Activator             | 1                      | 1                      | 1                      | 1                      |
| Perkadox 14/40 B-GR                                    | Peroxide              | 5                      | 5                      | 5                      | 5                      |
| ZnO RS   | Curing Promotor       | 5                      | 5                      | 5                      | 5                      |
| Tudalen B 8013   | Plasticizer           | 10                     | 10                     | 10                     | 10                     |
| A-C 617A   | PE Wax                | 10                     | 10                     | 10                     | 10                     |
| <b>Typical Values</b>                                  |                       |                        |                        |                        |                        |
| Tensile Strength [MPa]                                 |                       | 10,7                   | 13,2                   | 11,5                   | 13,1                   |
| Elongation at Break [%]                                |                       | 237                    | 185                    | 177                    | 185                    |
| LOI [% O <sub>2</sub> ]                                | 3 x 6 mm <sup>2</sup> | 25,2                   | 24,9                   | 31,0                   | 27,0                   |
| <b>After Seven Days at 70°C Water Immersion</b>        |                       |                        |                        |                        |                        |
| Volume Resistivity [ohm x cm]                          |                       | 5,3 x 10 <sup>14</sup> | 2,5 x 10 <sup>13</sup> | 1,2 x 10 <sup>12</sup> | 2,5 x 10 <sup>13</sup> |
| <b>Cone Data @ 35 kW/m<sup>2</sup> 100 x 100 x 3mm</b> |                       |                        |                        |                        |                        |
| Time to Ignition [s]                                   |                       | 200                    | 181                    | 185                    | 173                    |
| Peak Heat Release Rate [kW/m <sup>2</sup> ]            |                       | 285                    | 326                    | 234                    | 182                    |
| MAHRE [kW/m <sup>2</sup> ]                             |                       | 101                    | 105                    | 105                    | 88                     |
| FIGRA [kW/m <sup>2</sup> ]                             |                       | 0,7                    | 0,8                    | 0,8                    | 0,7                    |

TABLE 17

An EPDM-based bedding compound with high level of fire resistance (LOI >50% O<sub>2</sub>) is shown in table 19.

| EPDM Formulation for Bedding |             |                |
|------------------------------|-------------|----------------|
| Components                   |             | Quantity (phr) |
| Vistalon 5601                | EPDM        | 60             |
| Escorene UL 02020            | EVA         | 40             |
| Martinal ON-313 S/ON-320     | ATH         | 350 - 400      |
| Vulkanox HS/LG               | Antioxidant | 1              |

TABLE 19

# Martinal® Aluminum Hydroxide + Magnifin® Magnesium Hydroxide

## SMOKE REDUCING EFFECT OF MARTINAL® ATH AND MAGNIFIN® MDH FLAME RETARDANTS

The production of smoke during the combustion of plastic samples can be measured in the NBS smoke chamber according to ASTM E662. Although a real fire scenario cannot be simulated in the NBS chamber because of the great number of possible parameters that influence burning and smoke propagation, an assessment of smoke generation of various formulations under identical boundary conditions is possible.

The ASTM-standard requires measurements in both the non-flaming mode (i.e., the sample, mounted in a vertical position, is subjected only to a heat radiant source) and the flaming mode (i.e., with additional flaming on the bottom of the sample). The resulting smoke reduces the intensity of a light beam that crosses the chamber vertically. The light signal detected by a photo-multiplier allows the calculation of the so-called optical density. A high level of optical density in the chamber indicates a high smoke level. Because the amount of smoke depends on sample thickness, the latter was kept constant at 2mm in all subsequent measurements.

ASTM E662 smoke formation can also be measured with the cone calorimeter. The burnt gases are conveyed through a pipe system in which the smoke density is measured via attenuation of a laser light beam. Maximum smoke production can be determined and the smoke production rate can be monitored.

Table 20 shows an EVA/LLDPE-based test formulation with Martinal® ATH or Magnifin® MDH utilized as the additive and a loading level of 160 phr (61.5 wt.-%).

| EVA/LLDPE Test Formulation |                 |                |
|----------------------------|-----------------|----------------|
| Components                 |                 | Quantity (phr) |
| Escorene UL 00328          | EVA             | 67             |
| Escorene LL 1001 XV        | LLDPE           | 17             |
| MAH gr Polymers            | Coupling Agent  | 16             |
| ATH or MDH                 | Flame Retardant | 160            |
| Ethanox 310                | Antioxidant     | 0,75           |

TABLE 20

Figures 6 and 7 compares the total and maximum smoke production for Martinal® ATH and Magnifin® MDH compounds obtained from cone calorimeter measurements at a heat flux of 35 kW/m<sup>2</sup>. Test

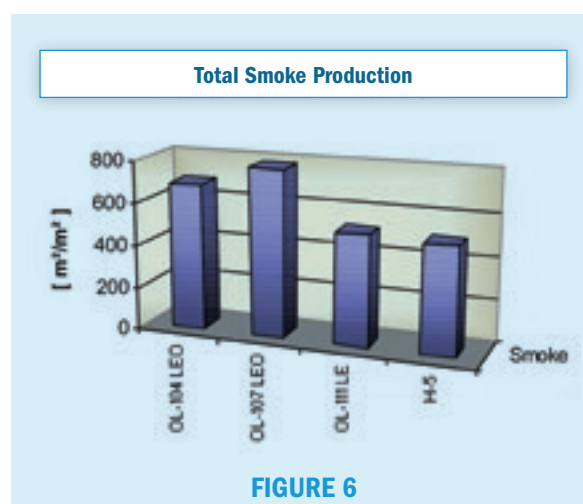


FIGURE 6

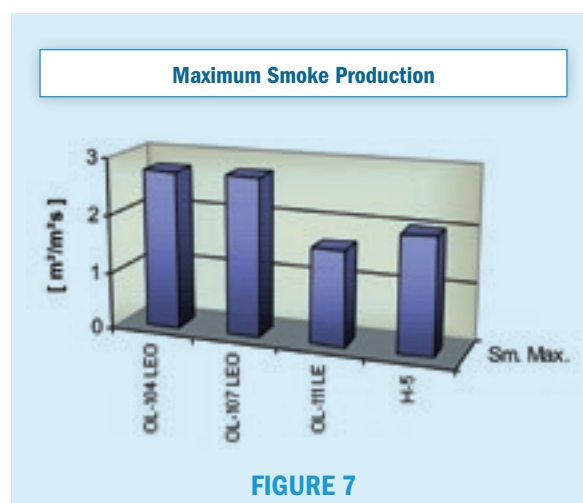


FIGURE 7

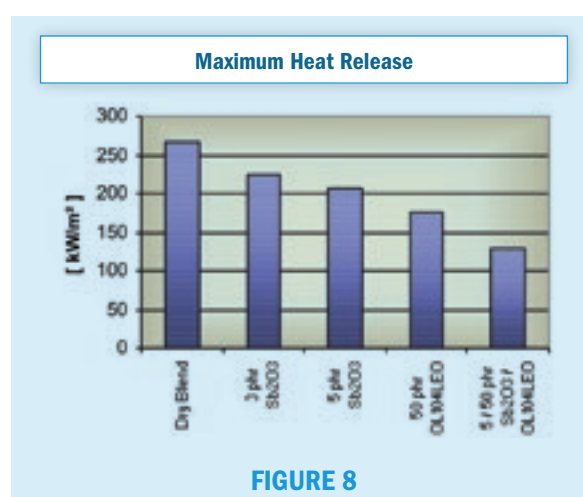


FIGURE 8

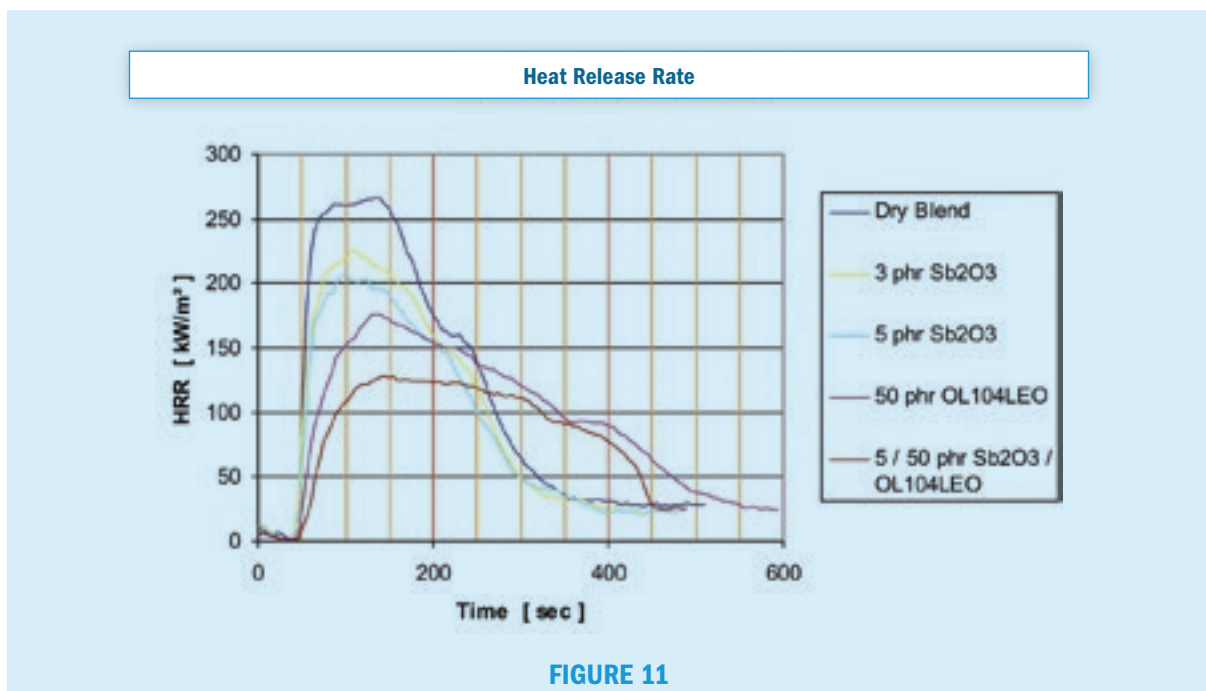
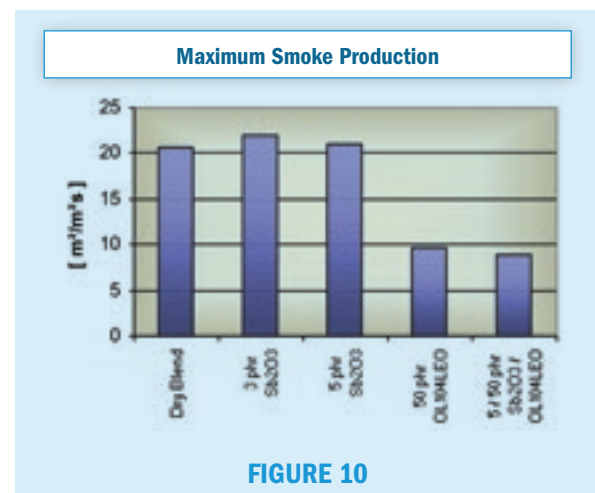
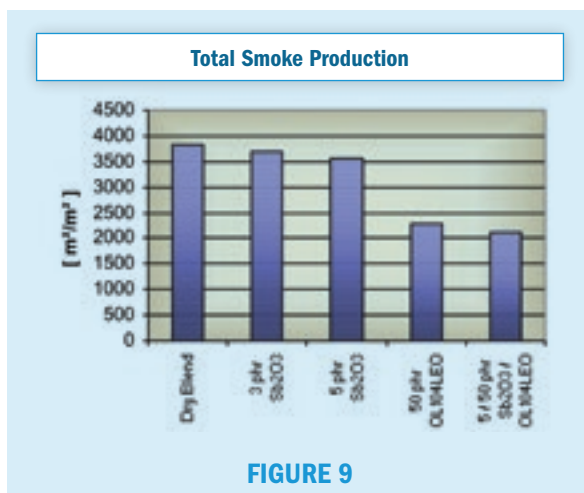


results show that Magnifin® H-5 and Martinal® OL-111 LE filled compounds result in slightly lower smoke than Martinal® OL-104 LEO/OL-107 LEO filled compounds. Loading is 61.5 wt.-% in EVA/LLDPE, at a sample size of 100 x 100 x 3mm, and a heat flux of 35 kW/m<sup>2</sup>.

Figure 8 on the preceding page shows the maximum heat release rate of PVC-P compounds filled with different flame retardants at 35 kW/m<sup>2</sup>.

Figures 9 & 10 below indicate the total and maximum smoke production rate of PVC-P compounds filled with different flame retardants at 35 kW/m<sup>2</sup>.

Figure 11 highlights the heat release rate of PVC-P compounds filled with different flame retardants at 35 kW/m<sup>2</sup>.



# Martinal® Aluminum Hydroxide + Magnifin® Magnesium Hydroxide

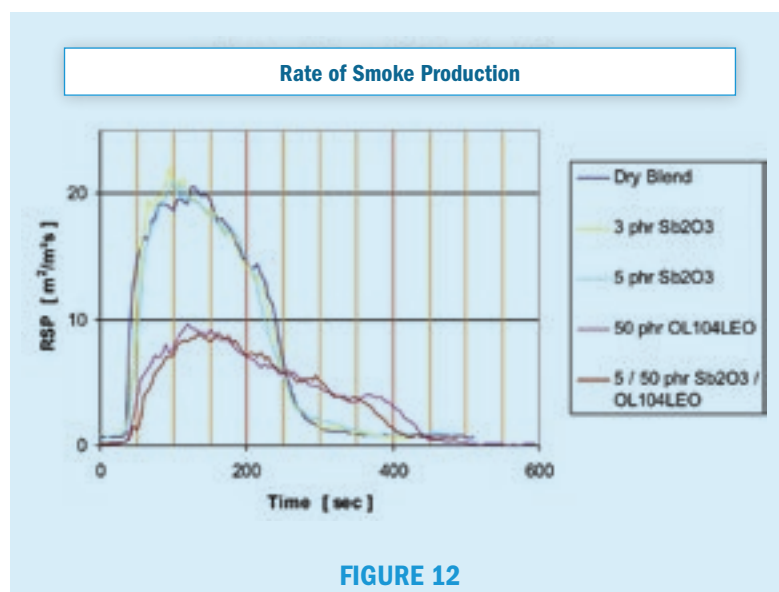


FIGURE 12

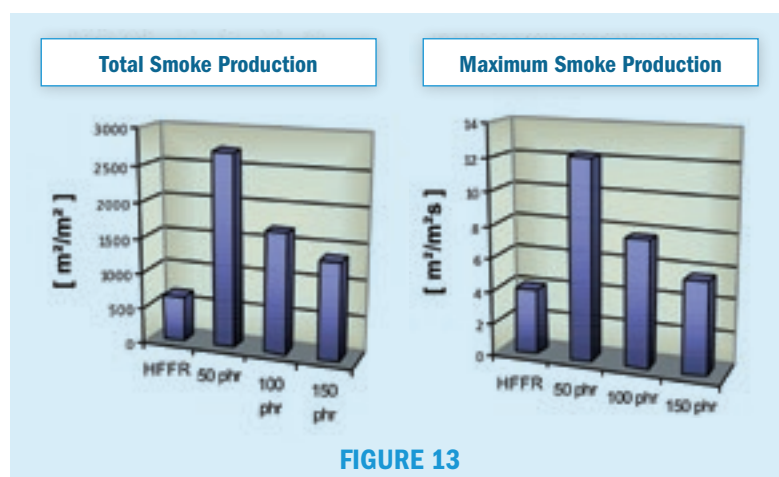


FIGURE 13

Table 21 below shows a PVC-P formulation with antimony trioxide and aluminum hydroxide as a flame retardant. Measurements in the cone calorimeter at a heat flux of 35 kW/m² (sample size 100 x 100 x 3mm) show the impact of the different flame retardants on heat release rate and smoke

| Plasticized PVC Test Formulation |                                |                |
|----------------------------------|--------------------------------|----------------|
| Components                       |                                | Quantity (phr) |
| SH-7020                          | PVC K 70                       | 100            |
| DIDP                             | Plasticizer                    | 55             |
| Naftosafe® PKX 2208/1            | Stabilizer                     | 4,5            |
| Omya EXH 1                       | CaCO <sub>3</sub>              | 10             |
| White Star                       | Sb <sub>2</sub> O <sub>3</sub> | 0/3/5          |
| Martinal OL-104 LEO              | ATH                            | 50             |

TABLE 21

formation. Compared to the PVC-P compound without a flame retardant ("dry blend"), any flame retardant reduces the maximum heat release rate (figure 4, page 5). The lowest value can be obtained through the combination of 5 phr antimony trioxide and 50 phr Martinal® OL-104 LEO ATH. The lowest total and maximum smoke production is achieved when using 50 phr Martinal ATH as single FR or when combining 5 phr antimony trioxide and 50 phr Martinal OL-104 LEO (figures 9 & 10, page 13). The heat release rate curves of the different compounds as a function of the test time are shown in figure 11 on the preceding page. The rate of smoke production over the burning time is depicted in figure 12 at right.

Table 22 below shows a plasticized PVC (PVC-P) test formulation using Martinal® ATH at various loadings that were measured in the cone calorimeter regarding smoke formation.

From figure 13 at right one can clearly see that a higher amount of aluminum hydroxide in PVC leads to a lower smoke formation. But even at 150 phr, PVC still generates more smoke than halogen-free flame retarded compounds. HFFR reference is based on 160 phr Martinal® OL-104 LEO in EVA 328/LLDPE/MAH gr measured @ 35 kW/m² heat flux.

| Plasticized PVC Test Formulation |                   |                |
|----------------------------------|-------------------|----------------|
| Components                       |                   | Quantity (phr) |
| SH-7020                          | PVC K 70          | 100            |
| DIDP                             | Plasticizer       | 55             |
| Naftosafe PKX 2208/1             | Stabilizer        | 4,5            |
| Omya EXH 1                       | CaCO <sub>3</sub> | 10             |
| Martinal OL-104 LEO              | ATH               | 50/100/150     |

TABLE 22

### COMPOUNDING OF HIGHLY FILLED SYSTEMS

Homogeneous and agglomerate-free incorporation of Martinal® ATH and Magnifin® MDH into the polymer matrix are important to achieve a good balance of flame resistance and physical and electrical properties in the final product. The choice of the correct polymer, the halogen-free flame retardant and the compounding process are also important factors that influence product properties. Suitable equipment for producing highly filled compounds include the Buss kneader, twin-screw extruder, Farrel continuous mixer and internal mixer. To achieve optimum dispersion and uniformity, the Buss kneader, a co-rotating twin-screw extruder, or the Farrel continuous mixer are preferred. In order to achieve consistent product quality, the following guidelines are recommended:

#### BUSS KNEADER:

- Two or preferably three feeding ports with gravimetric feeding. We recommend adding the polymer to the first feeding port together with approximately 50% of the total flame retardant material and the remaining flame retardant material into the second feeding port.
- L/D ratio of 15.
- Presence of a ventilation opening, preferably a vacuum degassing facility.
- Precise temperature control.

#### TWIN-SCREW EXTRUDER:

- Co-rotating.
- L/D ratio of at least 32.
- Two, even three feeding ports with gravimetric forced feeding. The entire polymer is preferably fed into the first port. In the second port, preferably a side feeder, all of the flame retardant can be added. For very high

fire retardant loadings, it may be necessary to add a part of the flame retardant together with the polymer.

- Precise temperature control.
- Several openings for venting as well as a vacuum degassing unit.

Suitable temperature control and an optimized screw configuration are essential for optimum properties in both mixing equipment options. Please contact us, we will be glad to assist you!

Coated products may behave differently than the uncoated grades. Especially in internal mixers, this can lead to problems if processing parameters are not appropriately adjusted.

In this case, a laboratory internal mixer (GK 1.5E) was used to produce PP compounds (65 wt. % filler loading) with uncoated Magnifin® H-5 and coated Magnifin® H-5 GV MDH. While the power draw on the motor with the uncoated Magnifin® H-5 is typical, the coated product results in a “slide through” effect, with greatly reduces power draw (and thus lower shear and heat generation). In extreme cases, the PP did not melt. In this case, an adjustment of the processing parameters becomes necessary (e.g., rotor speed, upside-down mixing, batch size, etc.).

Figure 14 shows power consumption of the kneader and discharge extruder of a 46mm Buss kneader during compounding of Martinal® OL-104 LEO ATH in EVA/LLDPE (loading 61.5%). Because of the improved compounding behavior, the power consumption as well as the variation of the power consumption is reduced. This enables a higher throughput of the compounding process without the risk of blocking the equipment due to strong power consumption peaks. Furthermore, there is potential to reduce the total power consumption and thus the possibility to decrease energy expenditures.

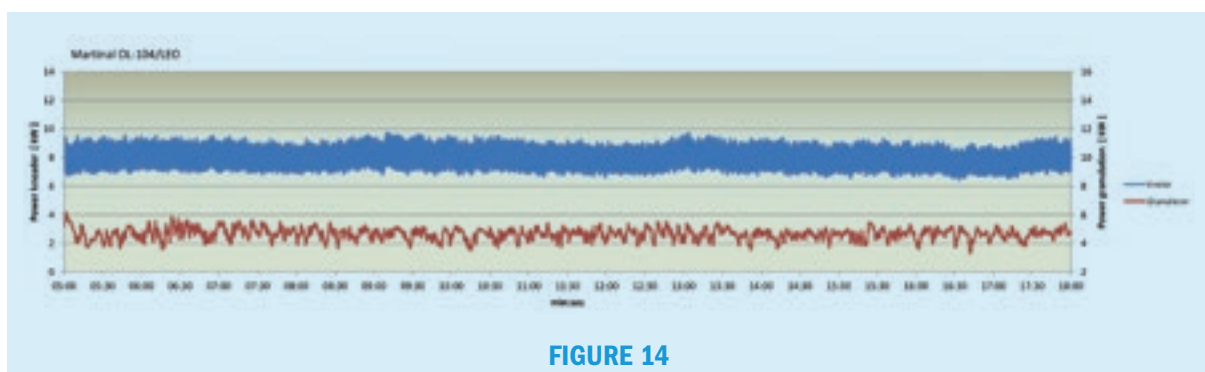


FIGURE 14

# 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

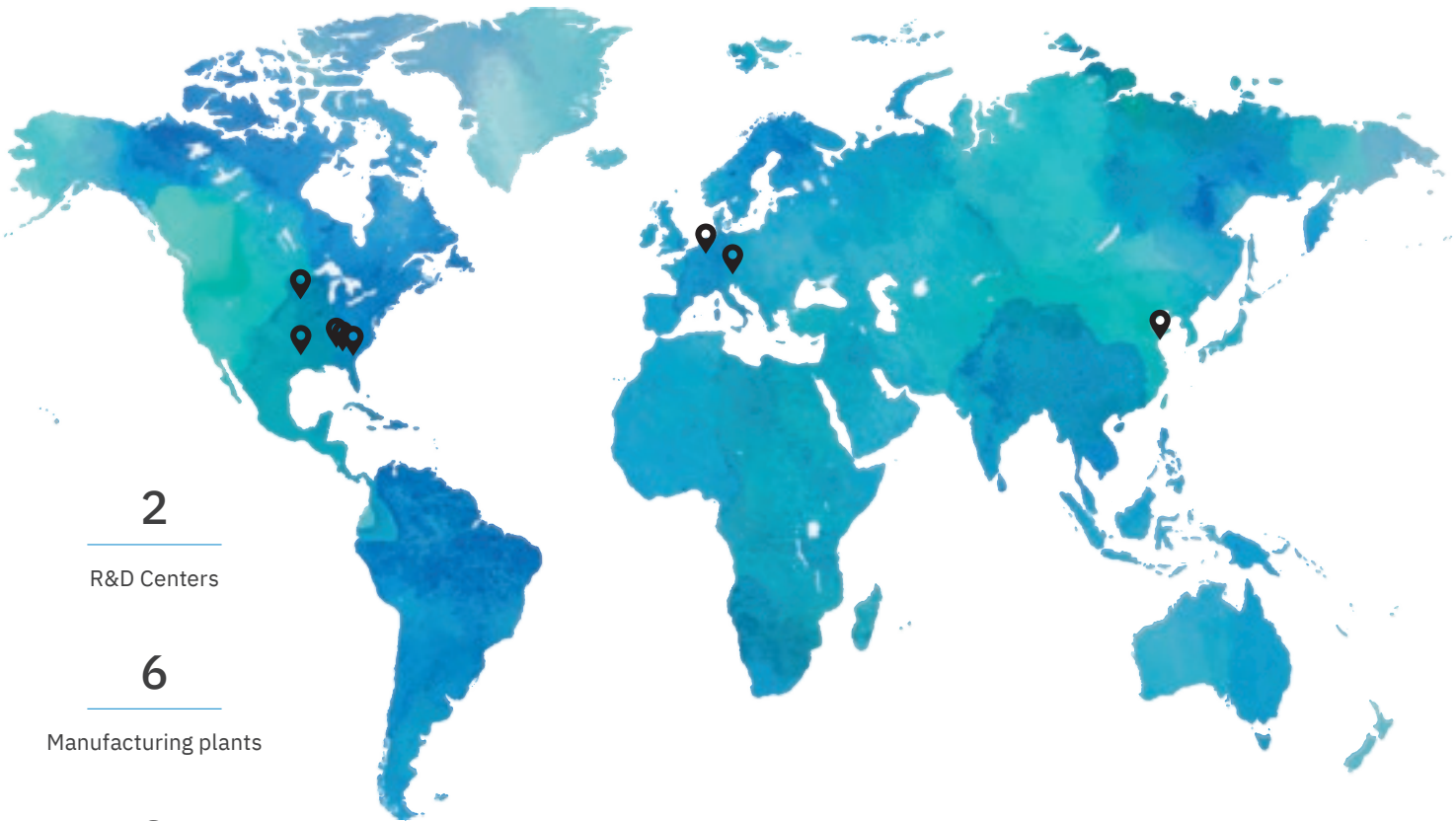
Fairmount, GA  
Atlanta, GA  
Kennesaw, GA  
Marblehead, IL  
Bauxite, AR

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Bergheim, Germany  
Breitenau, Austria

## Asia Pacific

Qingdao, China



2

R&D Centers

6

Manufacturing plants

3

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