

# magnesium oxide's uses in rubber compounds

*The use of Magnesium Oxides in the Rubber Industry is very important to many halogenated and non-halogenated elastomers for numerous reasons. Also, Magnesium Oxides are available in many different grades with their corresponding properties. Choosing between these grades to perform a particular function can be difficult. With the basic understanding of these oxides' properties and performance characteristics, the compounder can confidently make the proper choice and even develop new solutions for challenging problems. The intent of this literature is to familiarize the reader with the different types, properties, grades/forms, functions, applications, and Magnesium Oxide's effects on the compound's processing properties.*

Magnesium Oxides (MgOs) have been utilized in the Rubber Industry for more than 100 years. Shortly after the discovery of sulfur vulcanization in 1839, MgO and other inorganic oxides proved to accelerate the slow cure rate of sulfur used alone. It was not until the early 1900s when organic accelerators were developed and replaced magnesium and other oxides as primary accelerators in curing systems. MgO consumption decreased until the early 1930s during the birth of a new synthetic elastomer which used this oxide extensively to stabilize and neutralize (acid scavenge) the compound – polychloroprene (CR). Even now, at the beginning of the next century, the primary use of MgO in the rubber industry is still in polychloroprene (CR) cure systems. Through the years, compounders realized the benefits of MgO in other elastomers such as: chlorosulfonated polyethylene (CSM), fluoroelastomer (FKM), halobutyl (CIIR, BIIR), hydrogenated NBR (HNBR), polyepichlorohydrin (ECO) among others. Let's first look at how rubber grade MgOs are produced and their properties.

## types

Early in the rubber industry only one type of MgO was available – *heavy* (due to its bulk density). This type was produced by thermally decomposing natural magnesites ( $MgCO_2$ ). The resultant grade was often impure, not very active and had a large particle size. With the development of CR, magnesia manufacturers produced a new, high purity, more active, smaller particle size MgO – *extra light*. This product was made by thermally decomposing basic magnesium carbonate ( $MgCO_3$ ). Still used today in pharmaceuticals and cosmetics, this MgO was replaced by a very active, smaller particle size MgO – *light or technical light*. Nearly all rubber compounders use this type of MgO. It is manufactured by thermally decomposing magnesium

hydroxide ( $\text{Mg}(\text{OH})_2$ ). Its bulk density is between that of heavy and extra light and has a very high activity and small particle size. These latter two properties – activity and particle size – are the most important properties of any MgO utilized in rubber compounding.

## properties

MgO's activity, surface area or surface activity is typically measured by one of two methods: BET (Brunauer, Emmett and Teller) or MAI (Morton Activity Index). BET and MAI measure the amount of nitrogen and iodine, respectively, adsorbed on the surface of a substance. The higher the BET or MAI value, the higher the activity and the more effective the MgO. Current MgOs' activities range from a MAI of 30 mg-I<sub>2</sub> per gram to 170 mg-I<sub>2</sub> per gram. A direct correlation can be calculated between MgOs' MAI and BET of the same type;  $\text{MAI} = 1.0894 (\text{BET} \#) + 5.23$ .

Measuring particle size, or more appropriately agglomerate size, is performed by X-ray sedigraph or SEM (scanning electron microscope). The smaller the agglomerate size, the better the dispersion in rubber and the more MgO particles per unit volume are available to perform their task.

Therefore, higher activity and smaller agglomerate size equates to increased MgO rubber performance and thus:

- more scorch safety – easier to handle stock
- better physical properties – higher quality compound
- more bin stability – longer lasting stock, less scrap

Other MgO properties are important such as bound water and dispersibility. Bound water, often measure by LOI (Loss On Ignition) testing, is a great quality control parameter and can indicate if the material has been overexposed to moisture and deactivated. Some test results suggest lower LOIs with high activity MgOs can outperform higher LOIs MgOs with equal surface activity.

Dispersibility is obviously important for any rubber chemical. For MgOs, the smaller the particle size (agglomerate size) the better, because more MgO per unit volume will be available to perform its function. Oil-dampened MgO products (granules or bars) are available to help insure the best dispersion possible. Also, these products, Akro-Mag<sup>®</sup> Bar – Green and Blue Label (bars, Akrochem) and Plastomag<sup>®</sup> (granules, Rohm & Haas Company), protect the MgO from moisture and carbon dioxide pickup.

Purity is not the same issue as in the past. With continuous improvements by the MgO manufacturers, higher purities are easily obtained with tight specifications. Particle size distribution can create a dispersion issue if the MgO contains a considerable amount of large particles. This concern is more common in coarse grades.

## grades/forms

MgOs are typically classified by activity (surface area). Elastomag<sup>®</sup> powders, produced by Rohm and Haas Company, are available as Elastomag 60, 100, 170, and 170 Special. The number in their name corresponds to their average MAI. Due to its low activity (MAI), Elastomag 60 is not used in rubber very often, except in fluoroelastomers. Elastomag 100 and 170 are the rubber workhorse grades with the Elastomag 170 being the premiere product. Elastomag 170 Special is typically used in rubber based adhesive formulations. Its average particle size is smaller than that of the Elastomag 170. Here are some typical properties of the Elastomag grades:

<i>Elastomag® Grade</i>	<i>60</i>	<i>100</i>	<i>170</i>	<i>170 Special</i>
Morton Activity Index (M.A.I.) mg I <sub>2</sub> /g	60	140	170	155
Assay, Volatile Free, as MgO%	99.0	98.0	99.0	98.0
Chloride, as Cl%	0.20	0.30	0.30	0.30
Calcium, as CaO%	1.20	1.20	1.20	1.50
Ignition Loss (L.O.I.)%	4.50	5.80	6.00	6.20
Specific Gravity	3.20	3.20	3.20	3.20
Passing 325 mesh%	100	100	100	100

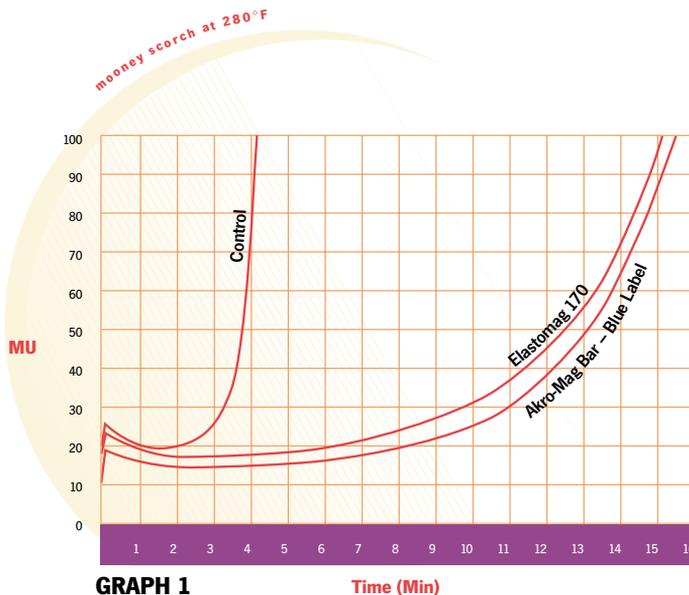
***Particle Size Distribution %***

20 microns or more	2.2	1.5	0.5	0.5
20 to 10 microns	2.3	3.0	0.5	0.5
10 to 5 microns	1.8	3.0	3.0	3.0
5 to 2.5 microns	23.7	20.0	21.0	8.0
2.5 to 1.25 microns	37.5	29.0	29.0	28.0
less than 1.25 microns	32.5	43.5	46.0	60.0

Other MgO forms are available as soft granules or bars. These products usually contain 35% - 60% naphthenic oil (65% - 40% active MgO). The oil serves three functions:

- protects the MgO from moisture and other chemicals – maintains activity
- increases dispersibility – delivers more MgO per unit volume
- easier to handle form – less dust, easy weigh-up

Although these oil-dampened products contain considerably less MgO, they are successfully used as a part-to-part replacement for the 100% active MgO powders. In fact, some compounders have experienced an increase in performance at a part-to-part substitution loading. The mooney scorch data below demonstrates the similar performance of a 55% active, oil-dampened MgO (Akro-Mag® Bar – Blue Label) and the powdered 100% active MgO (Elastomag 170) in a sulfur-modified CR test compound:



**GRAPH 1**

**Time (Min)**

Compound ID	Mooney-Initial lb-in	Mooney-Low lb-in	T <sub>S</sub> -5 min.sec	T <sub>S</sub> -10 min.sec
Control (No MgO)	25.74	20.60	3.00	3.34
Akro-Mag Bar – Blue Label	19.76	15.32	8.27	10.01
Elastomag 170	24.35	17.47	7.23	9.08

Sulfur-modified CR – 100.00 phr, zinc oxide – 5.00, stearic acid – 1.00, sulfur – 0.40, mag. oxide 4.00

From the data above, Akro-Mag Bar – Blue Label produces longer TS-5 and TS-10 values indicating an increase in scorch safety. The TS-5 is the time elapsed to raise the minimum viscosity 5 mooney units, i.e. the onset of cure. How could nearly half the amount of MgO at 2.2 phr perform similarly to 4.0 phr of the MgO powder? The answer for this is twofold: *the oil increases the dispersibility of the MgO and thus increases the concentration of MgO molecules per unit volume of rubber and the oil protects the MgO from any possible moisture pick-up which can deactivate a portion of the material.* From environmental and economical view points, oil-dampened MgO products are less dusty and typically cost less. Also, the Akro-Mag Bar product produces lower mooney values which will lead to improved processing for extruded and injection molded stocks.

Below is the rheometric data to the corresponding compounds above. Again, the same trend is achieved: increased scorch safety with the oil-dampened MgO.

Compound ID	Max. Torque lb-in	Min. Torque lb-in	T <sub>S</sub> -2 min.sec	T <sub>C</sub> -50 min.sec	T <sub>C</sub> -90 min.sec
Control (No MgO)	61.47	6.40	0.49	1.25	4.59
Akro-Mag Bar – Blue Label	76.86	5.10	1.50	3.38	7.07
Elastomag 170	79.65	5.54	1.42	3.29	7.30

## functions

### Acid Acceptor/Neutralizer:

The primary function of MgOs in CR and other halogenated elastomers (BIIR, CIIR, CPE, CSM, ECO, FKM), containing chlorine, bromine or fluorine, is to scavenge acidic byproducts (acid acceptor). These harmful byproducts are generated during processing, vulcanization and aging of rubber articles. Almost all CR compounds are vulcanized with zinc oxide and MgO with or without accelerators. During vulcanization and storage, chloride radicals and hydrogen chloride are created. These chloride-containing compounds can decompose the polymer chain and/or combine with zinc to produce zinc chloride. In turn, zinc chloride is a very strong accelerator during vulcanization and promotes scorchy (cures too fast for further processing) compounds. The MgO neutralizes the cure system and protects the polymer by reacting preferentially with the chloride and thus ridding the compound of polymer degradation or scorchy cures.

### Crosslinker/Cure Activator:

In addition to scavenging acidic byproducts, MgOs are also used as curing agents in CSM (Chlorosulfonated Polyethylene). In a chemical reaction with moisture, MgO crosslinks the hydrated chlorosulfonyl groups and forms ionic bonds. Excellent physical properties (except compression set) and colorability (v. lead

## FUNCTIONS: c o n t i n u e d

cures) can be obtained. Roofing and pond liner rubber articles are produced with this technology. In carboxylated nitrile compounds, MgOs are used as a curative forming ionic bonds at the reactive carboxylic acid (-COOH) site of the polymer. Studies suggest that lower activity MgO (Elastomag® 100) may be best suited for this application due to scorch concerns with metal oxides and XNBR. MgO is utilized in Echo S™ (Hercules), Accelerator 40B (amine) thiadiazole cures in CPE and ECO compounds as a basic metal cure activator. This vulcanizing system contributes very good heat resistance and compression set. In other halogenated elastomers, especially CR, MgO acts as a cure activator and increases the state of cure which leads to increased unaged and aged physical properties and fluid resistance.

### **Adhesive Component:**

MgOs are extensively used in CR contact adhesive compounds. They function as acid acceptors and react with phenolic resins to create resinates that have very good high temperature bond strength. In addition, MgOs of very small particle size, i.e. Elastomag 170 Special, discourage settling of the oxide and phasing of the adhesive compound.

### **Antidegradent:**

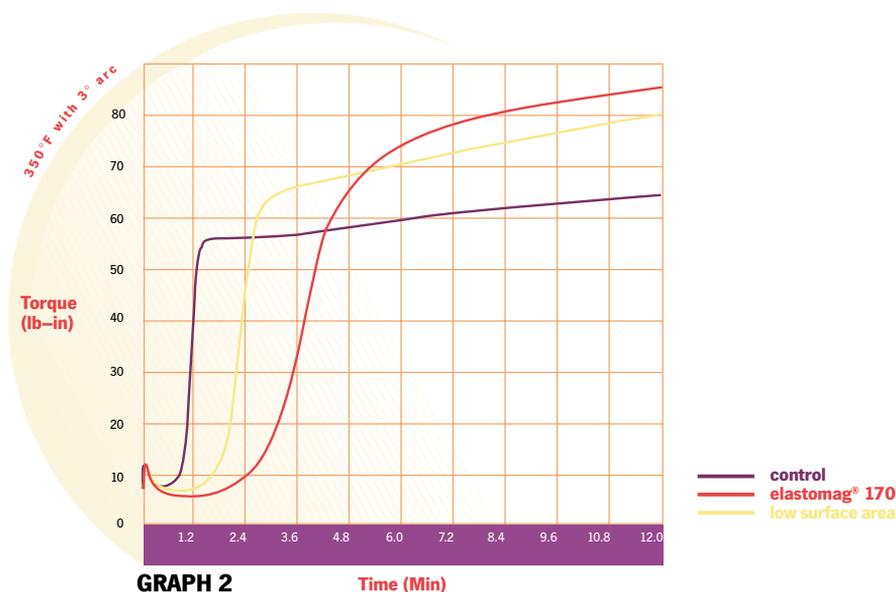
MgOs are often used as part of antidegradent packages for demanding applications in high performance polymers like HNBR. Studies have shown that MgO in combination with antioxidants greatly improves long term heat aged physical properties in both peroxide and sulfur-cured compounds. This technology has been recently utilized in EPDM compounds.

## applications/effects

### **Polychloroprene (CR):**

The largest volume use of MgO in the rubber industry is in CR compounds. As mentioned previously, the MgO scavenges chlorine containing byproducts which are detrimental to the rubber article. These byproducts are most harmful during processing.

The onset of cure or scorch time is the most noticeable processing property affected with the use of MgO. Typical tests such as rheometry (Ts2) and mooney scorch (Ts5) are used to measure scorch times. Most compounders prefer to use rheometry to measure scorch times. Ts2 is the time (in minutes) it takes a compound to raise its viscosity 2 mooney units from its minimum during cure, i.e. crosslinks are starting to form. In Graph 2 you can see the effect a low and high activity MgO can have in a sulfur-modified CR compound:



Compound ID	Max. Torque lb-in	Min. Torque lb-in	T <sub>S</sub> -2 min.sec	T <sub>C</sub> -50 min.sec	T <sub>C</sub> -90 min.sec	State-of-Cure lb-in
Control	64.30	6.99	0.41	1.07	5.12	59.18
Elastomag 170	85.52	5.08	1.59	3.51	6.53	80.44
Low Surf. Area MgO	80.16	6.12	1.22	2.20	7.11	74.04

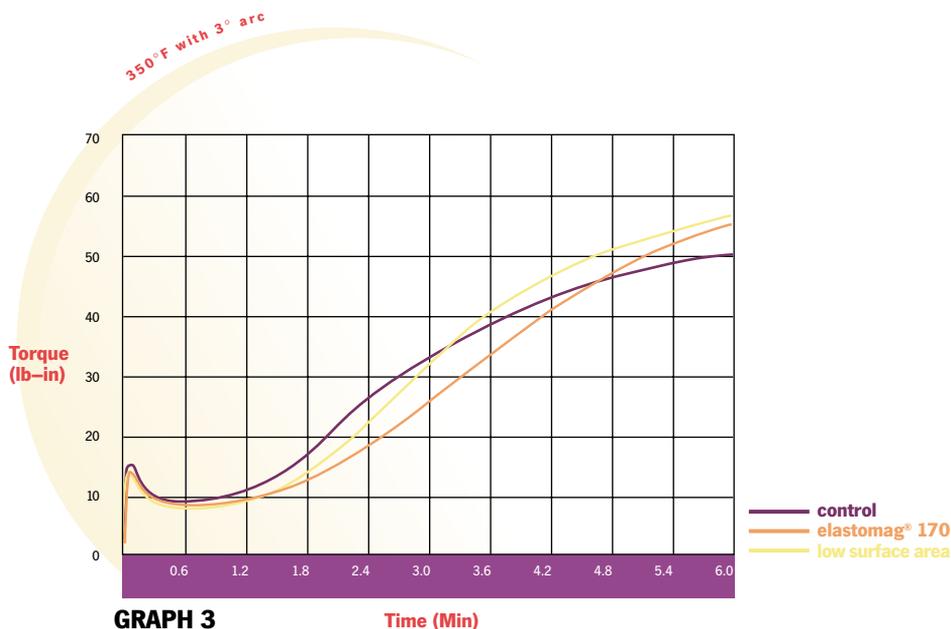
Sulfur-modified CR – 100.00 phr, zinc oxide – 5.00, stearic acid – 1.00, sulfur – 0.40, mag. oxide – 4.00

From this data, both MgO additions give more scorch time to the compound. But the higher surface activity MgO, Elastomag 170, increases the scorch time by 1 minute and 18 seconds, nearly 300% from the control, and an improvement of over 90% compared to the low surface area MgO. Obviously, this improvement can be very critical to the rubber compound. Additional scorch times lead to safer future processing and bin stability. Also, notice the increase in state-of-cure (max. torque – min. torque) due to the MgO additions. The Elastomag 170 produces a higher quality vulcanizate which has improved moduli, tensile strength, compression set resistance, rebound resilience, etc.; all the properties related to a higher state-of-cure. The same compound was aged in a warehouse during the summer months in Akron, Ohio and tested for Ts2s in an effort to evaluate their bin stabilities:

Compound ID	Initial T <sub>S</sub> -2 min.sec	30 Day T <sub>S</sub> -2 min.sec	60 Day T <sub>S</sub> -2 min.sec	90 Day T <sub>S</sub> -2 min.sec
Control	0.41	0.29	0.21	0.17
Elastomag 170	1.59	1.33	1.31	1.30
Low Surf. Area MgO	1.22	0.92	0.73	0.57

Again, the higher activity MgO extends the scorch time more than the lower activity product. This is important because a compound can be mixed and stored longer with the addition of a high quality MgO. If not, the compound may have to be scrapped.

The above data was accomplished with the use of a sulfur-modified CR compound. Interesting to note that a high quality, premium MgO is typically not necessary for a mercaptan-modified CR compound.



Compound ID	Max. Torque lb-in	Min. Torque lb-in	T <sub>S-2</sub> min.sec	T <sub>S-50</sub> min.sec	T <sub>S-90</sub> min.sec	State-of-Cure lb-in
Control	52.56	9.27	1.02	2.39	4.44	43.29
Elastomag 170	57.89	8.61	1.14	3.28	5.14	49.28
Low Surf. Area MgO	59.15	8.01	1.08	3.00	4.56	51.14

Mercaptan-modified CR - 100.00 phr, zinc oxide - 5.00, stearic acid - 1.00, ETU-22 PM(75) - 0.75, mag. oxide - 4.00

The data above shows marginal differences between T<sub>S2</sub> and State-of-Cure values of these mercaptan-modified CR formulations with the addition of high and low activity MgOs. The difference between sulfur- and mercaptan-modified CRs influencing scorch behavior is believed to be the influence of the additional, more liable and active chlorine compound (diallylic thiuram chlorine) generated by the sulfur-modified CR. The mercaptan-modified CR compound generates allylic chlorides, but not diallylic thiuram chlorides. The allylic chlorides still cause scorchiness, but not to the extent of the additional diallylic thiuram chlorine.

One caution: MgOs should not be part of the cure package if water resistance is a critical criteria because MgO will absorb copious amounts of water. Hysafe® (hydrotalcite – non-lead, JM Huber) or lead oxides should be used in these applications.

### Polychlorosulfonated Polyethylene (CSM):

In CSM, high activity (Elastomag 170) MgOs are used as acid acceptors and cross-linking agents. Because CSM contains chlorine, MgOs scavenge acid byproducts analogous to CR. As a cross-linking agent, MgOs are usually employed in non-black compounds due to its outstanding color stability. Typically 10 and 20 phr are used for peroxide and sulfur curing respectively. MgOs are also used as the sole curative in a reaction with moisture for very safe atmospheric cures in

## APPLICATIONS/EFFECTS: c o n t i n u e d

pond liners and single ply roofing membranes. The MgO reacts with the sulfonyl chloride group and water to produce ionic crosslinks within the polymer chains. This cure system produces products with excellent color stability and weather resistance. In black CSM compounds, MgOs are utilized in general purpose cure packages and sometimes in combination with lead oxide for heat resistance.

### Fluoroelastomers (FKM):

The uses of MgOs prove to be very interesting and essential in FKM compounding because with this polymer, the choice of high or lower activity MgO is critical. Also, MgOs have a dual function once again. They act as acid scavengers absorbing hydrogen fluoride and fluoride byproducts during cure and post curing. Also, MgO helps extract fluoride and hydrogen from the polymer to create unsaturation (double bonds) for additional crosslinking. Generally, low activity MgOs (Elastomag® 60) are added (15 phr) to diamine-cured FKMs. High activity MgOs (Elastomag 170) are used (3 phr) in bisphenol cures with the addition of calcium hydroxide (6 phr). As you would expect, the higher activity MgO is more efficient in absorbing and extracting fluoride and hydrogen molecules than the lower activity MgO and thus the choice for the bisphenol cures. But FKM diamine cures prefer lower activity MgOs (larger particle size) due to improved compression set resistance.

## handling

The handling and storage of MgOs is critical to the performance of the product. Water and carbon dioxide molecules (especially water) easily attached themselves to MgO molecules, which in turn bond to other MgO particles forming larger agglomerates. These agglomerates are very difficult to disperse properly without adequate shear. To alleviate this problem, MgO powders are usually packaged and shipped in bags that contain moisture and carbon dioxide barriers. Also, oil-dampened products like Akro-Mag Bars and Plastomag protect the MgO powder from moisture and carbon dioxide pick-up. Always remember that once the package is opened, make sure it is tightly resealed.

## conclusion

The use of magnesium oxides in rubber compounds is very important for many reasons. With the basic understanding of its functions, performance characteristics and available forms, a compounder can select the best suitable grade for his purpose. This literature focused on some basic processing effects when using magnesium oxides. In the future, look for an additional Solutions' insert discussing further influences of magnesium oxides used in rubber compounds



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