



## **Magnesium oxide: A Forgotten Specialty Chemical**

*By Marcelo Fraga de Sousa\**

Buckman, Sumaré, SP - Brazil

### **ABSTRACT**

The use of magnesium oxide basifying agents in the leather tanning process is a worldwide industry practice. The role of this product during basification and its importance at the end of chrome tanning are well known. But, important features of magnesium oxide (MgO) and the processes used to manufacture this compound are not that well understood by the tanning industry. In recent years MgO based basifying agents have been treated by some as a "commodity chemical" and important technical features of this compound have been neglected. As a consequence, the professional tanning industry has lost some control over the quality of basification, placing at risk the integrity of the process and the wetblue produced. Magnesium oxide characteristics, such as size distribution and surface area of particles, are important in determining the reactivity of the product and therefore highly relevant to basification. The main objective of this article is to provide information to professional tanners to assist them in optimizing control over this part of the tanning process. This paper aims to provide information relevant to the production of MgO, its purification and control of quality, and application of MgO in basification. In addition to size distribution and average surface area of particles, other aspects and features of MgO that impact the quality of processing along with the storage of wet blue leather and its interaction with other important chemical auxiliaries in the wet process will be discussed.

*Key Words: Magnesium oxide, MgO, basification, tanning, leather, wetblue*

### **INTRODUCTION**

During the traditional process of chrome tanning, the carboxyl groups in collagen are protonated by the acids used in pickling. This protonation neutralizes the ionic charge of the carboxyl and reduces its affinity for chromium allowing penetration of the tanning agent through the pelt cross-section. After the diffusion of chromium, the carboxyl groups are ionized again to ensure that the tanning agent reacts with as many carboxylic groups as possible. This ionization is carried out by increasing the pH of the float during the basification process.

The main sources of carboxyl groups in collagen are the side chains of the amino acids aspartic acid and glutamic acid, and the carboxylic endings of the molecule. Each of

these carboxyl groups has a specific ionization potential and ionization occurs when the pH of the micro-environment is raised above the corresponding pKa value.

Table 1 - Reference values of pKa for collagen carboxyl groups<sup>1</sup>.

Source of carboxyl	Structural formula	Typical pKa *
Terminal Carboxylic	R – COOH	3,1
Aspartic acid	NH <sub>2</sub> -CH(CH <sub>2</sub> -COOH)-COOH	3,9
Glutamic acid	NH <sub>2</sub> -CH(CH <sub>2</sub> -CH <sub>2</sub> -COOH)- COOH	4,3

\*Values at 25 °C for the isolated amino acid. Source: J.T. Edsall e J. Wyman. *Biophysical Chemistry* (Academic Press, 1958), chapter.8.

In the micro-environment of the pickled pelt, the pKa values may change due to the ionic strength of the medium and the interaction between amino acids side chains. Regardless of the factors involved in determining the pKa value, in a traditional process of tanning (pickling with sulfuric acid and formic), it is necessary to add an alkali to ionize the carboxyl group. Basifying agents (alkali) generates OH<sup>-</sup> ions in water, either by ionization or dissociation, depending on the type of agent used. These ions react with H<sup>+</sup> (or H<sub>3</sub>O<sup>+</sup>) in the medium causing a rise in pH to values near the pKa of the carboxyl groups in collagen resulting in ionization. The collagen carboxyl groups are then available for linking to chromium and this leads to the stabilization of the protein and it's processing into tanned leather. Without the use of an alkali agent, the time required for completion of the tanning reaction would be high, making the process impractical. Different types of products can be used as basifying agents, namely: soda ash, sodium bicarbonate, sodium formate, magnesium oxide. In the last 15-20 years magnesium oxide has acquired a prominent position as a basifying agent, being the most widely used for chrome tanned cattle hides today. Many reasons have led to this choice, including:

- Availability of MgO around the world
- Ease of pH control during basification
- Chemical compatibility with other products used in tanning
- Low risk to operators and the environment

### MAGNESIUM OXIDE

MgO is an oxide of alkaline reaction, i.e., generates the dissociated OH<sup>-</sup> ions in water.



The speed at which this dissociation occurs is the main technical characteristic of MgO that is of interest to the tanner. If the dissociation is rapid, the MgO is considered highly reactive, if the dissociation is slow, it will be of low reactivity. For traditional chrome tanning, low magnesium oxide reactivity is the most widely used. The reactivity of MgO is a result of three factors: chemical composition (purity), particle size distribution, and surface area. Each of these parameters will be discussed in detail.

Magnesium oxide for industrial use is obtained from two main sources: mineral (mines) and water (sea, salt lakes, groundwater salines, etc). Depending on its origin, treatment of the oxide can vary, but the final features are defined by the same operations regardless of the origin. This means that the reactivity of MgO does not depend on the source of production, but from the operations used in refining the product.

#### **NATURAL SOURCES OF MgO**

In 2005, approximately 88% of MgO produced worldwide was mined and extracted from magnesium-rich rocks<sup>2,3</sup>. Among these the main source is the magnesite ( $\text{MgCO}_3$ ). Other sources include minor minerals such as dolomite ( $\text{Ca.Mg}(\text{CO}_3)_2$ ), brucite ( $\text{Mg}(\text{OH})_2$ ), hydro-magnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) and olivine ( $(\text{Fe,Mg})_2\text{SiO}_4$ ). The remaining 12% were produced from water sources: oceans, salt lakes, groundwater salines. In these latter sources of magnesium oxide, the most common form of the salt is carnallite ( $\text{K,MgCl}_3 \cdot 6\text{H}_2\text{O}$ ).

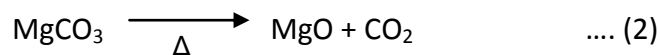
Commercial magnesium oxide is made three ways: calcined (caustic), "dead-burned", and fused. Each of these forms has different physical and chemical properties determined mainly by the temperature of calcination (burning) and the types and concentrations of impurities in the final product. The calcined product produced at temperatures below 900 °C, has particles with high surface area ( $> 25 \text{ m}^2/\text{g}$ ) and reacts rapidly with dilute acid in water. Magnesium oxide "dead-burned" is formed at temperatures above 1200 °C, has a particle surface area lower than the calcined ( $< 20 \text{ m}^2/\text{g}$ ) and is less reactive chemically. The fused MgO is formed at temperatures of about 2800 °C and is even less reactive than the "dead-burned" product.

About 85% of magnesium oxide produced worldwide (2005) is of low reactivity, "dead-burned" or fused, and only 15% is calcined<sup>2,3</sup>. This preference is due to the fact that the main use of MgO is in the manufacture of refractory products (especially for the steel industry) and this industry needs products of very low reactivity.

### MgO PRODUCTION FROM MINERAL SOURCE

The theoretical concentration of MgO in magnesite rock, the main commercial source of the oxide is 47%. This mineral is found in two forms in nature: crystalline and crypto-crystalline. In the first, the content of impurities is higher and the color of the magnesite varies from white to dark brown. The main contaminating element is iron, as Fe<sup>++</sup> ion, replacing Ca<sup>++</sup> and Mg<sup>++</sup>. Crypto-crystalline magnesite is usually found in association with serpentine (magnesium silicate) and in relatively pure deposits, usually white. Most of the impurities found in crypto-crystalline magnesite can be removed using conventional physical techniques of purification without chemical processing.

MgO production from mineral sources is a process composed of several stages: extraction, physical processing and chemical processing. The physical process is intended to concentrate, purify and define the final characteristics of MgO. The main operations involved in this stage are: sieving and rough grinding, calcination (burning), hydro-cyclone, flotation, magnetic separation of elements, color grading, purification, grinding and final sieving. Normally the concentration and purification steps are done after calcination, since this stage dramatically reduces the volume of material to be treated (loss of CO<sub>2</sub>):

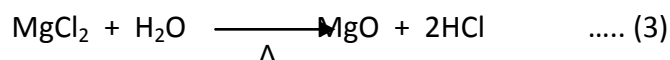


*Thermal decomposition of magnesite to MgO (calcination)*

Chemical processing will not be discussed in this paper, since it is used only for the production of oxides for special applications (i.e. purity > 99% MgO).

### PRODUCTION OF MgO FROM AQUATIC SOURCES

Despite being a simple operation, the high energy costs involved in the production of MgO from saline water sources, results in the final product being more expensive than MgO from mineral origin. In the production of MgO from marine sources (less concentrated), the magnesium salt is precipitated as hydroxide, purified using dolomite and then burned. This process involves usually two stages of calcination and purification and requires a higher level of purification of inputs, mainly dolomite. Processing either on the basis of salt lakes or other water sources that are more concentrated in magnesium salts (such as the Dead Sea) two routes can be followed: selective precipitation of Mg(OH)<sub>2</sub> and further processing (similar to the sea route) or recovery and direct thermal decomposition of MgCl<sub>2</sub>. In this type of processing, the main problem is the high content of boron commonly found in saline lakes.



In both routes, the concentration and purification steps, calcination, grinding and final sieving are also used as in processing from mineral sources.

### **CHARACTERISTICS OF MgO**

The main characteristics of magnesium oxide of interest to the tanning process are: chemical composition (purity) and reactivity.

#### Chemical Composition:

To meet the purity levels required for use in tanning, the purification steps are relatively simple. Levels of MgO >95% are easily obtained. Even in magnesium oxide of 94% purity, some components cannot be totally eliminated due to economic constraints and technical challenges. These remain in the final product as impurities.

The main impurities in technical grade MgO are oxides of Ca, Fe, Si, Al, Mn and B. These elements are present in the natural sources of the raw material, whether in the form of salts or oxides of Mg. Of these elements Ca, Fe and Si are the most important in terms of concentration in the final product, especially calcium. In the case of MgO produced from salt lakes, Boron is the most difficult element to remove.

Magnesium compounds found in nature are almost always associated with calcium compounds. Compared to the other elements, the similarity between these compounds makes the removal of calcium more difficult during the purification of MgO. Thus in a purified magnesium oxide the level of Ca can vary from 0.5% to 3% (expressed as CaO) depending on the source of extraction and processing route. Although the CaO present in the basifying agent does not interfere with the tanning process, it is possible that high levels of this element can result in higher residual CaO in the wet blue leather. A simple analysis of the basifying agent can remove doubts about the source of CaO in the wet blue and avoid unnecessary problems.

Iron oxides are a common mineral in MgO and can vary from 0.1% to 5% in the final product. The magnesium oxide used in the tanning industry contains an average of 0.5% Fe<sub>2</sub>O<sub>3</sub>, which is a fairly low and inert component in the tanning process (compared to CaO), but even at low concentrations (0.2%) the Fe<sub>2</sub>O<sub>3</sub> is sufficient to turn the MgO a beige / brown color. Magnesium oxide from water origin usually contains no Fe oxides (in most cases), which leads to a whiter color. This difference in the whiteness has led to the belief that the purity of MgO is associated with its color. This is a misconception and it is not uncommon to see a "white" MgO of 94% purity and MgO that is "beige" in color with purity above 97%. An important observation in the case of Fe is the fact that in some MgO basifying agents it is possible to find residues of iron, even magnetic "filings" that can come in contact with equipment during processing. These impurities, unlike Fe

oxides originating from the raw material, are not inert and can react chemically with other compounds used in tanning.

Silicates are another chemically inert element found in basifying agents, but if present in high concentrations can cause damage through abrasion. Silicates in basifying agents are usually found in concentrations ranging from 0.1% to 2% as  $\text{SiO}_2$ .

#### Reactivity:

The reactivity of magnesium oxide depends on the purity, but is defined primarily by two parameters: the porosity and particle size distribution.

Porosity can be expressed as the average surface area of particles (also expressed as bulk density) and is defined and controlled during the material burning process. Calcination can be done in two stages, especially in the case of MgO of marine origin. During calcinations magnesium carbonate (mineral source), magnesium hydroxide (marine source) and magnesium chloride (salt lakes) are transformed into magnesium oxide. During calcination  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are expelled from the material, leaving interstitial spaces (pores) in the final structure of the MgO. The higher the temperature and the higher the calcination time employed, the lower the proportion of interstitial spaces in the final oxide. This is essential in defining the type of MgO obtained and its application: the higher the proportion of those spaces (pores) on the oxide mass, the greater the surface area of particles and the final reactivity of MgO. By contrast, particles with less surface area (oxides less porous, less dense), have lower reactivity. Thus:

- High temperature calcination = Low Reactivity
- Low temperature calcination = High Reactivity

Calcination temperatures below  $1000\text{ }^\circ\text{C}$  produce MgO with high surface area ( $>25\text{ m}^2/\text{g}$ ) and low reactivity. This type of MgO is normally used for agricultural, pharmaceutical, waste treatment, production of adhesives, etc. and is called ashes. Calcination temperatures above  $1200\text{ }^\circ\text{C}$  result in MgO particles of small surface area ( $<20\text{ m}^2/\text{g}$ ) and low reactivity. These are the types of magnesium oxide normally used as basifying agents and are called "dead-burned." Even higher temperatures ( $2800\text{ }^\circ\text{C}$ ) result in virtually inert products, they are called fused MgO and are used in the refractory industry.

The particle size distribution is defined during milling and the final product sieving. This is usually the last stage of processing and contributes to the final reactivity of MgO. The operations involved are simple and easy to control, but the choice of the type of mill to be used (depending on the final application of MgO) and mesh sieve sizes used may require special control. When considering basifying agent application, the ideal balance between surface area (porosity) and particle size distribution cannot be predicted theoretically. Adjusting these characteristics to achieve the desired reactivity is an iterative process that will result in ideal ranges or levels for each parameter. It is highly

recommended that the process of determining these ideal ranges is carried out as a interface project, evaluating the results of changing the parameters on drum application.

### **THE BASIFYING AGENT MgO**

Basifying agents based on magnesium oxide should not be considered a “commodity”. Despite small differences in chemical composition observed between commercial versions, different levels of reactivity found in this product make it a specialty. This means that specific care is needed to control the quality to ensure consistent product performance in the tannery.

#### Control of purity:

This is the easiest parameter to be monitored and specified. Variations in the concentration of MgO and even impurities (CaO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> or others) are generally too small to make an impact in the tanning process. Still, it is important to know the composition of the product and to create a history of application to avoid unwanted surprises, especially with regard to CaO and SiO<sub>2</sub>. In terms of concentration of MgO, values between 94% and 99% are normally found in basifying agents used in the tanning industry and this variation in the content of MgO does not usually result in significant changes to the values of the basification pH curve.

It is worth mentioning here that we are just referencing "pure" basifying agents, i.e. where the magnesium oxide is the only active component. There are "complexed" or "masked" basifying agents in the market. The salts present in these compositions include organic acids that complex or mask the properties of metals (like chromium). These basifying agents are typically used in processes that seek to further deplete chromium in the final tanning liquor. While the ability to raise the pH and the reactivity of the product is provided only for the MgO present, the masking salts/acids interfere in the kinetics of the reaction of chromium with the carboxyl groups. This masking effect reduces the reactivity of chromium with the carboxyl groups and allows the pH to be raised to higher values than normal during the basification. Thus, more carboxylic groups are ionized resulting in more possible points for bonding of chromium and increased fixation in the leather. This reduces the concentration of chromium in the final tanning liquor.

#### Control of Reactivity:

This is the most difficult and important parameter to be monitored and specified for a pure basifying agent. Reactivity is mainly a function of the surface area of MgO particles and size distribution of the product and monitoring in the tannery environment becomes a little more complicated. This increases the importance of information provided by the

basifying agent supplier. The tannery can develop practical methods for Quality Control on laboratory scale that simulates the behavior of the basifying agent during the tanning process. If the method is well structured, reliable, and practical, you can create a database of reactivity and monitor the basifying behavior of products and even compare the performance of products from different origins.

#### Process Control:

Even though the magnesium oxide characteristics are well defined and specified in terms of chemical composition, surface area and particle size distribution, behavior during basification is greatly influenced by other process factors. The rate of heating, the acid reserve in the medium (float) and hides, the chromium offer during tanning, float volume, and running time are all determinants of the basification pH curve and indicators for process control.

When the magnesium oxide used in tanning is of low reactivity ("dead-burned"), dissociation of the product in water, even in acid medium, is slow and only occurs fully with rising temperature. At temperatures below 30 °C the dissociation of MgO is slow, so the basification process may not be completed in a suitable time frame, so it is important to gradually heat the tanning liquor to temperatures above 48 °C. The acidic reserve present in the float and leather from the pickling stage, determines the dose of MgO needed. Although a stoichiometric estimate is not commonly used because of the difficulty in determining values necessary for the calculation (water volume, thermal equilibrium conditions, concentrations of common ions, number of carboxylic groups, etc.), an increase in acidic reserve should be accompanied by an increased dose of MgO. The proportion of MgO/acids must be determined empirically and it commonly varies from one tannery to another, even in small proportions due to the peculiarity of the process and equipment. As the main objective of MgO is to provide OH<sup>-</sup> ions to accelerate the reaction of chromium with collagen carboxyl groups, and whereas the chromium salt used is an acidic reaction, it is a logical observation that increasing the supply of chromium should be accompanied by an increase in the dose of MgO.

#### **FINAL CONSIDERATIONS**

In summary, magnesium oxide is a simple chemical but complex material. Different types of processing, sources of production, and end-use requirements result in products with very different physical characteristics, although chemically very similar. From the standpoint of chrome tanning, the main type of MgO used is the low reactive version and reactivity is the main feature to be monitored in quality control. Reactivity, in this case is determined by chemical composition, surface area, and particle size distribution of the product. The latter two parameters are crucial. Quantitative analysis and monitoring of



these parameters is difficult in the tannery environment, and therefore should be measured and reported by the supplier of basifying agents. However, the tanning industry will benefit from methodologies, semi quantitative or qualitative, that help monitor the reactivity of basifying and predict behavior during basification. This is very useful to optimize the process and compare and control basifying agents from different sources.

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