

Metallic Stearates: A Review Of Their Function And Use As Release Agents For Rubber Compounds

ABSTRACT

Metallic stearates have a long history of use in the rubber industry as release agents. They have been primarily used to keep uncured rubber from sticking to itself. Metallic stearates have also been used as mold release agents for cured rubber. The applications of these products are numerous and many rubber companies have found unique ways to utilize their physical and chemical properties. In this paper we will discuss these products in detail, including the following: chemistry, physical properties, compatibility with elastomers, environmental concerns, and their function as release agents for rubber.

Metallic stearates can be supplied in various forms such as their dry neat state, dispersed in water and alcohol, and formulated with surfactants that provide a wettable grade. These various forms will be discussed as to their function and use in a rubber manufacturing facility.

INTRODUCTION

Metallic stearates have long been used as release coatings for uncured rubber. Typically, they are zinc, calcium and magnesium stearate. Zinc stearate has been the most commonly used one to date, but government environmental regulations have limited its use and control its working range. This has caused greater interest in the calcium stearate by the rubber companies. There is also increased interest in the magnesium stearate as well.

Stearates, in general, are thought of as a salt. This salt, or soap of a stearic acid is formed by replacing the carboxylic hydrogen by a metal to yield a salt (see *Figure 1*).

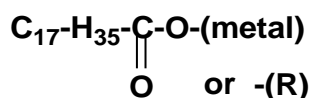


Fig. 1. Carboxylic hydrogen replaced

The combination of the metallics, zinc, calcium and magnesium would, therefore, yield a stearate formula as seen in *Figure 2* below:

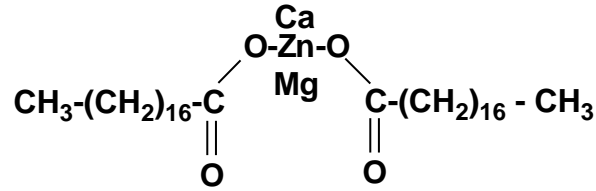


Fig. 2. *Chemical Structure of Metallic Stearates
Ca, Zn, and Mg Stearate*

These metallic stearates are insoluble in water and, therefore, act as a water repellent. This will be an important issue later in application technology.

The physical properties are all fairly similar between all three stearates. The most significant property difference as it relates to the rubber release agents is their melting points. A list of the common stearates and their melting points are shown in TABLE I.

TABLE I

<u>Product</u>	<u>Melt Point, °C</u>
Zinc Stearate	120
Magnesium Stearate	140
Calcium Stearate	160

The melt point plays a deciding factor in the decision of which kind of product to use on the surface of the uncured rubber. When the rubber compounder is making stock for compression, transfer molding, hoses or extruded profiles, the molding or cure temperature and time duration will limit what can be used on the surface of the compound. With the low melt point of zinc stearate, this has typically not been a problem. The zinc stearate will melt during molding and be absorbed into the compound without leaving discoloration or defects on the surface of the final molded rubber part.

The chemical structure of metallic stearates consists of a very long stable hydrocarbon chain. The long-chain hydrocarbon structure is insoluble in water and, thus, provides the hydrophobic nature of metallic stearates. The solubility parameter values of these stearates are low, and are similar to the common elastomers. TABLE II compares solubility parameters of these stearates to elastomers. This data provides a better understanding on why metallic stearates have excellent compatibility in most elastomers.

TABLE II

<u>Stearates</u>	Solubility Parameter <u>δ [(MPa)^{1/2}]</u>
Zinc Stearate	
Magnesium Stearate	18
Calcium Stearate	
 <u>Elastomer</u>	
Natural Rubber	
SBR	
Polyisoprene	
Polybutadiene	16 - 20
CPE	
Acrylic	
Chlorosulfonated PE	
CR	

Commercial Stearic Acid -

The commercial grades of metallic stearates are not pure, since the soap is made from commercial stearic acid (generally produced from tallow) which contains 30-60% palmitic acid. Stearic acids are straight-chained saturated, monobasic acids found abundantly in animal fats and in varying degrees in cottonseed, corn, soya, coco and palm oils. In their pure state, these acids are solid crystalline, opaque white materials having a waxy feel.

Commercially, stearic acid has other minor fatty acid constituents such as myristic and oleic acids. Depending on the proportion of various acids present, their physical structure can range from *macrocrystalline* to *microcrystalline* (see *Figures 3 and 4*). Likewise, they can vary from hard and brittle substances to quite soft and crumbly.



Fig. 3 40x magnification of a macro-crystalline stearic acid under polarized light.

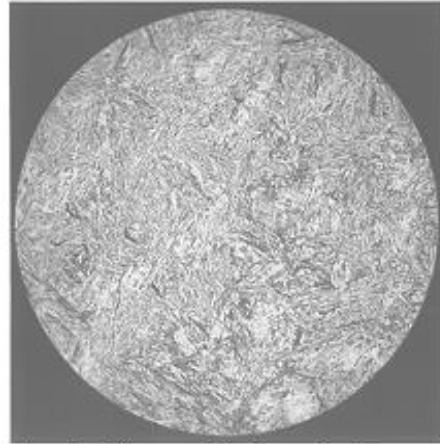


Fig. 4 40x magnification of micro-crystalline stearic acid under polarized light.

Macrocrystalline Stearic Acids -

Macrocrystalline stearic acids are those which fall in the ratio of 45:55 stearic to palmitic on a weight basis. When first manufactured commercially, they were produced physically by pressing the mixed fatty acids derived from animal tallow. The liquid oleic acid was squeezed out of crystalline mass of solid acids by hydraulic pressure. The greater number of pressings, the less oleic remained in the solid portion.

This procedure led to the commonly accepted designation for different grades of stearic acid--single, double and triple-pressed. These designations indicate increasing purity as measured by additional removal of oleic acid. The resulting solid acid mixture became the standard commercial type stearic acid and contained the typical stearic:palmitic acids ratio of 45:55. The physical characteristics of stearic and palmitic are given in TABLE III.

TABLE III

Physical Contents of Pure Solid Fatty Acids

<u>Fatty Acid</u>	<u>Formula</u>	<u>Molecular Weight</u>	<u>M.P. °C</u>	<u>Boiling Point @ 16mm, °C</u>
Stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	284	69.6	240
Palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	256	62.9	222
Myristic	$\text{CH}_2(\text{CH}_2)_{12}\text{COOH}$	228	54.4	202

Single-pressed products typically contain from 85-90% solid acid in which the stearic:palmitic ratio of 45:55 prevails. The remaining 10-15% are the unsaturated liquid acids, oleic and linoleic. Double-pressed acids are purer and more refined. As a result, lesser quantities of oleic are present, usually a maximum of 5% with only trace quantities of linoleic acid. These solid acids are white and rather hard, waxy, crystalline materials.

Triple-pressed types are the highest quality macrocrystalline stearic acids available and contain practically no unsaturated acids. In the molten state, they are extremely stable and virtually colorless and odor-free.

High Stearic Acids -

Mixtures with stearic acid content above the macrocrystalline range, i.e. containing more than 50% stearic acid, are generally referred to as high-stearic types. For stearic:palmitic ratios between 50:50 and 90:10 such acids are hard, very tough, microcrystalline solids. As the stearic acid content increases the crystalline structure becomes much finer and the materials possess softer consistencies.

Economics and Performance

The choice of stearic acid used to make metallic stearates will obviously be governed by end-use applications and cost. The stearates used in the rubber industry typically would be manufactured from the triple-pressed stearic to those made from high stearic acids containing up to 70% stearic. Stearic acids with ratios above 70% would probably not be economically possible. The processes used to create high stearic content are more extensive and add cost to the end product. Metallic stearates used in premix tanks and slab dip tanks are made from stearic acids that have a very low unsaturated fatty acid content to help prevent rancidity. In the case of zinc stearates, this is not a problem since zinc compounds will kill bacteria and mold. This particular function of zinc stearate will be discussed in detail later in this paper.

Applications

Metallic stearates provide some unique properties that make them ideal rubber release agents. The combination of lubricity, hydrophobicity and melt point allow these materials to be used in several applications. A typical industrial rubber goods manufacturer could have several processes that require uncured rubber be kept from sticking. Following are some of the common processes that would use metallic stearates.

slabs
pellets
extrusions
 – *hoses*
 – *profiles*
 – *strips for injection molding*
transfer molding
compression molding preforms

Metallic stearates are used for several reasons. Each rubber company has different requirements and may require various rubber release agents depending on their process or compound needs. The most common reasons why metallic stearates are used are listed below:

- uncured rubber needs heat removed quickly, to prevent scorching, thus, the rubber needs to be water-cooled before stacking or storage
- uncured rubber will be molded with minimal or no post milling or mixing, i.e. compression and transfer molding. This process requires that the release agent have no pigments or fillers

Metallic stearates can be applied to rubber several ways and in different forms. In the powdered neat states, stearates are applied or dusted onto the surface of the rubber by passing the rubber through a trough or box containing the stearate. This process is somewhat crude and dusty, but is effective in applying the lubricant to the surface of the uncured rubber. *Figure 5* illustrates this process:

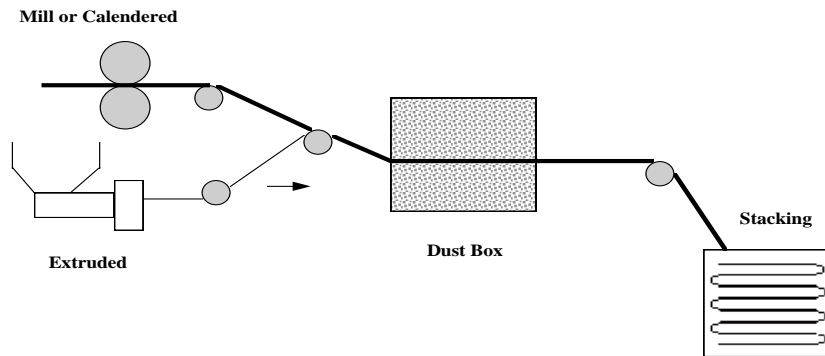


Fig. 5. *Dust Box*

Another way in which the powdered stearates are applied is in water-cooled systems. The stearate is simply added and floated on the surface of the dip tank. The hydrophobic nature of metallic stearates allow for the powder to remain on the surface and not be “wetted” out. Again, this process is effective, but does cause a great deal of dusting, thus, many housekeeping problems. *Figure 6* provides a graphic illustration of this process.

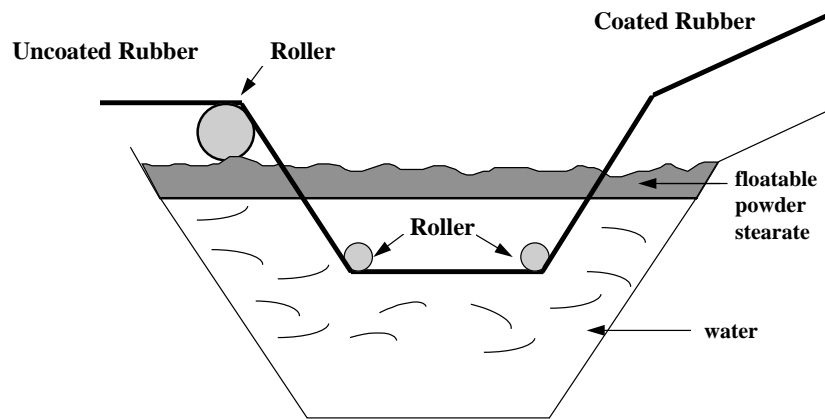


Fig. 6. *Floatable Powder Stearate*

For water-cooled systems, stearates are normally provided in 20-30% active pastes. These pastes are usually a combination of stearate, water and a small quantity of alcohol. These formulations allow for stearates to be added to the dip tanks directly or can be premixed in tanks which provide a more thorough dispersion. Most suppliers of these stearate dips recommend that the stearate paste be premixed before adding to the dip tank. The advantages of using this type of material is that the stearate is still floatable and can be used in water-cooled take-off units. *Figure 7* shows how these products would appear in a slab dip tank.

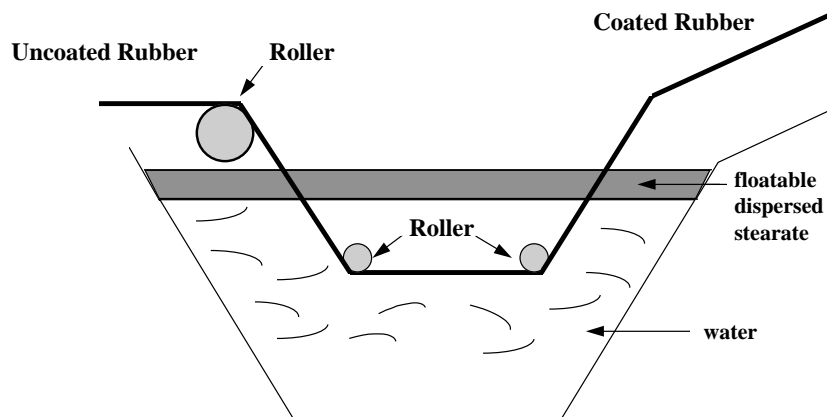


Fig. 7. *Floatable Stearate Dispersion*

The floatable stearate dispersions can be modified such that the dustiness associated with them will be minimized.

The hydrophobic nature of metallic stearates is especially important because this property allows for the cooling of rubber by water. Several rubber companies use water

or refrigerated water to remove as much heat from the uncured rubber before storage. This helps prevent scorching of these compounds before they are cured. Metallic stearates can be applied in several ways in a water-cooling process:

- stearates are added to the water-cooling tank
- are applied after the water-cooling tank
- applied and then passed through a water cooling tank or sprayed by water

All these processes can be accomplished because the metallic stearates are water-repellent and will not wash off. *Figure 8* shows the various configurations of a water-cooled process that would apply metallic stearates.

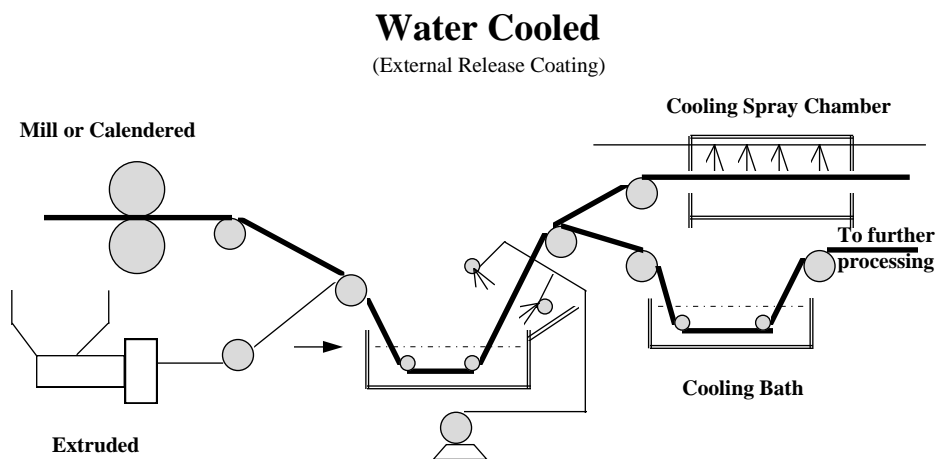


Fig. 8. Water-cooled Application

The metallic stearates are available in water-dispersible forms. These products are normally 30-50% active and have surfactant packages that allow for dispersibility throughout a dip tank (see *Figure 9*). These products will require mixing in the dip tank to prevent settling. The dispersible products are used on air-cooled lines (see *Figure 10*.)

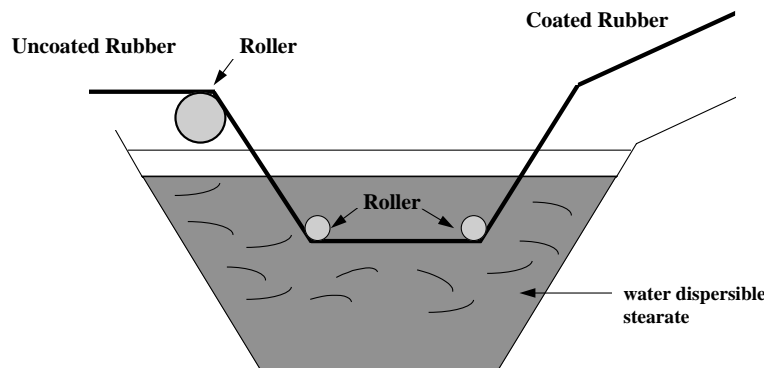


Fig. 9. Water-Dispersible Stearates

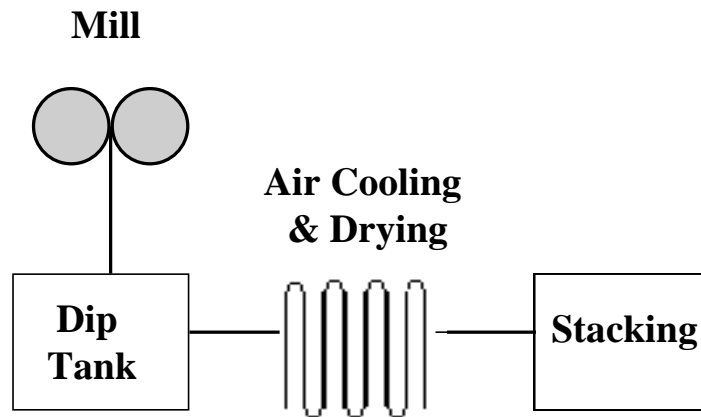


Fig. 10. Air cooling

The surfactant package used in these products would make stearate the wash off if used in a water-cooled system. Water dispersible products can be used for all the applications previously mentioned in this paper.

Environmental

The Environmental Protection Agency has placed limits on the amount of zinc content in water effluent. The limit in most areas of the U.S. is 50 pphr. Zinc compounds can kill the bacteria essential for the breakdown of organic matter in waste treatment facilities. Zinc stearate can be a problem and many companies have adopted calcium stearate products to solve this problem. The key to this is calcium stearate requires either higher curing temperatures or longer molding time to insure solubilization into the elastomer.

SUMMARY

Metallic stearates can be used in several operations in a rubber company to provide release. The physical properties of lubricity, hydrophobicity, compatibility and melt point are all important in providing the necessary performance required of a rubber release agent. The versatility of how they can be applied and formulated are the reasons why many rubber manufacturers still choose metallic stearates.

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