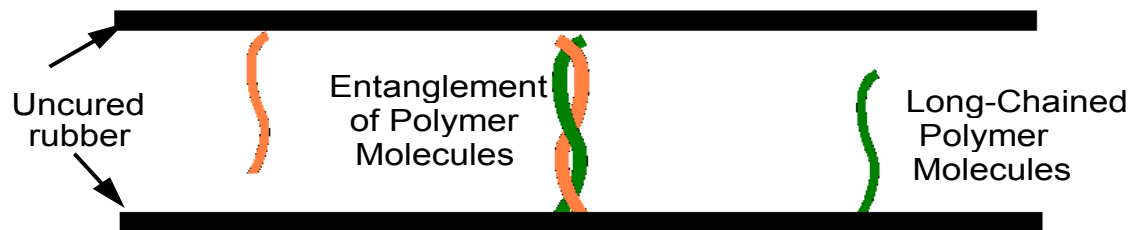


## Anti-Tacks

Why are anti-tacks necessary? Uncured rubber does not have great adhesive characteristics compared to other substrates but does like to stick to itself. This property is called tack. Freshly mixed rubber is especially tacky. Figure 1 illustrates the theory of tack for uncured rubber.



*Fig. 1. The theory of tack and cohesion of uncured rubber*

The theory states that long-chained polymer molecules project in a helical fashion from the surface of fresh rubber. The helical structures tend to unravel and project more when rubber has just been mixed. When two similar uncured rubber surfaces come into contact with each other, these long-chained polymer molecules can become entangled and thus create cohesion between the two substrates. The helical structures will revert back to a tighter coil after a period of time, causing a stronger cohesion bond. As viscosity of the uncured compound is lowered and temperature rises, tack increases.

If rubber could be mixed, milled and then cured without ever coming into contact with itself, anti-tacks would not be necessary. Due to space limitations and logistics, this is not practical in the rubber industry. To utilize their space and time effectively, rubber companies stack (i.e., wig-wag) or place rubber on pallets or bins. It is thus essential to have a barrier coating to prevent the sticking of slabs or pellets of uncured rubber.

### What is an Anti-tack?

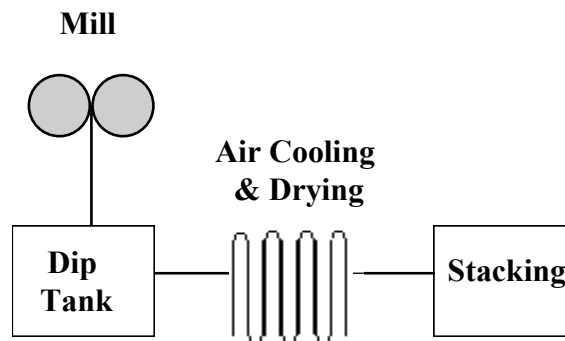
An anti-tack is a material or compound applied to the surface of uncured rubber that allows for release or separation after storage.

## History

Anti-tacks evolved much like other products in the chemical industry. As little documentation exists about the evolution of anti-tacks, actual dates of their development are not readily available. Anti-tack development followed the progress and changes in the rubber industry. It was also pushed by the improvements in quality standards, health standards, cost effectiveness and environmental controls that all rubber companies have experienced over time.

Fillers such as talc, mica, clay and calcium carbonate were used as dusting agents to prevent rubber from sticking. These materials were used for years and are still used extensively today as neat materials and as components of anti-tack formulas. Zinc and calcium stearates were used as partitioning agents in limited applications because of their higher cost.

Formulated anti-tacks were first created when the production of rubber compounds dramatically increased due to improvements in rubber mixing equipment. The increased production meant that rubber had to be cooled quickly before it could be stacked. Water dip tanks were installed next to mills so the rubber could be cooled. After being dipped or sprayed with water, the rubber was hung on racks to be dried. The drying and cooling effect was enhanced by fans blowing air across the surface of the rubber. The cooling tank became an ideal spot to coat the uncured rubber. Figure 2 is a diagram of a typical set-up for dipping uncured rubber.



**Fig. 2.** Schematic of a typical set-up for dipping, cooling, drying and stacking uncured rubber

The early anti-tacks probably contained high levels of various fillers and were augmented with “soaps” to help coat the rubber. Soon, rubber companies became more sophisticated and started formulating their own anti-tack compounds. Each rubber company developed anti-tacks suited to their particular needs, thus resulting in the proprietary nature of these formulas.

Suppliers to the rubber industry saw an opportunity to manufacture anti-tack coatings or dips, and rubber manufacturers were ready to be supplied with these products. There were several benefits to purchasing pre-mixed anti-tacks from outside suppliers, as follows:

- 1) Convenience - Plants could reduce inventories and reduce personnel requirements to prepare slab dips.
- 2) Efficiency - The rubber chemist could focus on rubber-related problem solving and formulation.
- 3) Anti-tacks supplied from outside vendors could work on a wide range of elastomers, eliminating the need for several in-house formulas.
- 4) Quality - Pre-mixed anti-tacks, which only require mixing with water to the correct solids level, reduce variation in the slab dip, thereby improving overall coating performance and quality.

Currently, there are a few rubber companies still making their own anti-tack dips, but the majority are buying compounded dips. The types of anti-tacks available and their development will be discussed next.

## **Anti-tack Products**

There are three classes of anti-tacks and coatings available today.

- Non-pigmented, non-water dispersible
- Non-pigmented, water dispersible
- Pigmented, water dispersible

Non-pigmented anti-tacks are used whenever the compound will not be re-milled or re-mixed prior to molding. If any pigment were present, the final rubber product would contain surface defects. This occurs because pigment on the surface was not incorporated into the rubber compound before molding. Non-pigmented anti-tacks either melt into the rubber product being molded or do not cause surface defects if left on the surface of the uncured rubber.

Pigmented anti-tacks, which are generally more cost effective, can be used whenever the compound will be re-milled or re-mixed before molding. Re-mixing the rubber compound incorporates the surface coating into the rubber mass.

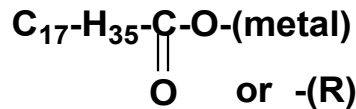
## **Non-Water Dispersible, Metallic Stearates**

Metallic stearates have a long history of use in the rubber industry as release agents. They have primarily been 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 in their dry neat state, dispersed in water and alcohol and formulated with surfactants that provide a wettable grade. These various forms will be discussed in terms of their function and use in a rubber manufacturing facility.

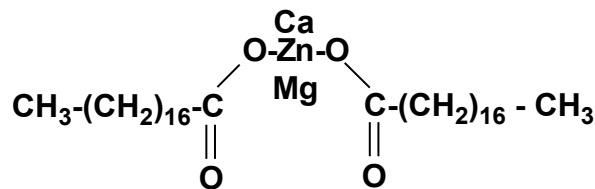
Metallic stearates have long been used as release coatings for uncured rubber. Typically, they are zinc, calcium and magnesium stearate. Zinc stearate has been the most commonly used to date, but government environmental regulations have limited its use and control its working range. This has caused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

A stearate is generally thought of as a salt. This salt (or soap) of a stearic acid is formed by replacing the carboxylic hydrogen with a metal to yield a salt (see Figure 3).



*Fig. 3. Carboxylic hydrogen replaced.*

The combination of the metallics zinc, calcium and magnesium would therefore yield a stearate, as seen in Figure 4 below:



*Fig. 4. Chemical structure of metallic stearates Ca, Zn and Mg*

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

The physical properties of these three stearates are all fairly similar. 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 appears in Table I.

**TABLE I**

Product	Melting Point, °C
Zinc Stearate	120
Magnesium Stearate	140
Calcium Stearate	160

The melting point is a deciding factor in the decision about what product to use on the surface of the uncured rubber. When the rubber compounder is used to make 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 melting point of zinc stearate, this has typically not been a problem. Zinc stearate will melt during molding and will 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 those of the common elastomers. Table II compares the solubility parameters of these stearates to those of elastomers. This data provides a better understanding of why metallic stearates have excellent compatibility with most elastomers.

**TABLE II**

<b><u>Stearates</u></b>	<b>Solubility Parameter <math>\delta</math> [(MPa)<sup>1/2</sup>]</b>
Zinc Stearate	
Magnesium Stearate	18
Calcium Stearate	
<b><u>Elastomer</u></b>	
Natural Rubber	
SBR	
Polyisoprene	
Polybutadiene	16–20
CPE	
Acrylic	
Chlorosulfonated PE	
CR	

### **Commercial Stearic Acid**

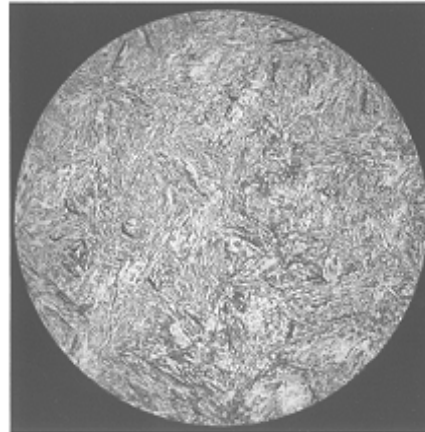
The commercial grades of metallic stearates are not pure, as the soap is made from commercial stearic acid (generally produced from tallow) that contains 30–60 percent palmitic acid.

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 with a waxy feel.

Commercial 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 5 and 6*). Likewise, they can vary from hard and brittle substances to quite soft and crumbly ones.



**Fig. 5** 40x magnification of a macrocrystalline stearic acid under polarized light.



**Fig. 6** 40x magnification of microcrystalline stearic acid under polarized light.

## Macrocrystalline Stearic Acids

Macrocrystalline stearic acids are those that fall in the ratio of 45:55 stearic to palmitic on a weight basis. When first manufactured commercially, they were physically produced by pressing the mixed fatty acids derived from animal tallow. The liquid oleic acid was squeezed out of the crystalline mass of solid acids by hydraulic pressure; the greater number of pressings, the less oleic acid 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 the increased removal of oleic acid. The resulting solid acid mixture became the standard commercial type stearic acid and contained the typical stearic:palmitic acid ratio of 45:55. The physical characteristics of stearic and palmitic acids are given in Table III.

**TABLE III**
**Physical Contents of Pure Solid Fatty Acids**

<b>Fatty Acid</b>	<b>Formula</b>	<b>Molecular Weight</b>	<b>M.P. °C</b>	<b>Boiling Point at 16 mm, °C</b>
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 85–90 percent solid acid in which the stearic:palmitic ratio of 45:55 prevails. The remaining 10–15 percent consists of the unsaturated oleic and linoleic liquid acids. Double-pressed acids are purer and more refined. As a result, lesser quantities of oleic are present, usually a maximum of five percent with only trace quantities of linoleic acid. These solid acids are white and rather hard, waxy, crystalline materials. Triple-pressed acids 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 a stearic acid content above the macrocrystalline range, that is, containing more than 50 percent stearic acid, are generally referred to as high-stearic types. When the stearic:palmitic ratio is between 50:50 and 90:10, the acids are very tough, hard microcrystalline solids. As the stearic acid content increases, the crystalline structure becomes much finer and the materials become softer.

**Economics and Performance**

The choice of stearic acid in making 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 acids and those containing up to 70 percent stearic acid. Stearic acids with ratios above 70 percent would probably not be economically feasible. The processes used to create high stearic contents are more extensive and increase the cost of 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, as 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 melting point allows these materials to be used in several applications. A typical industrial rubber goods manufacturer could have several processes that require uncured rubber be prevented from sticking. Following are some of the common processes that would use metallic stearates:

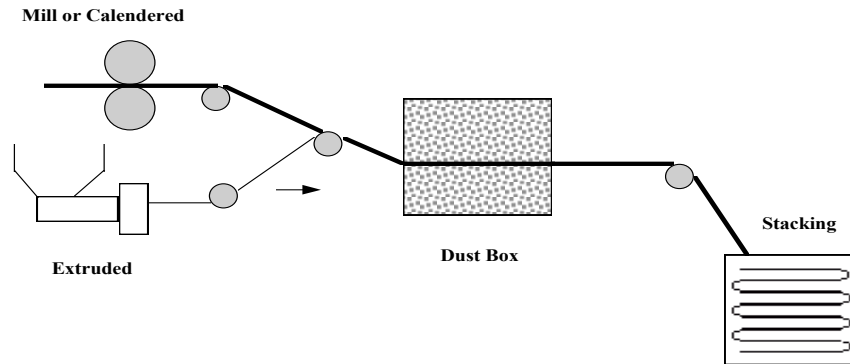
- *Slabs*
- *Pellets*
- *Extrusions*
  - *Hoses*
  - *Profiles*
  - *Strips for injection molding*
- *Transfer molding*
- *Compression molding preforms*

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 metallic stearates are used are listed below.

- Uncured rubber needs to have 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, that is, compression and transfer molding. This process requires that the release agent have no pigments or fillers.

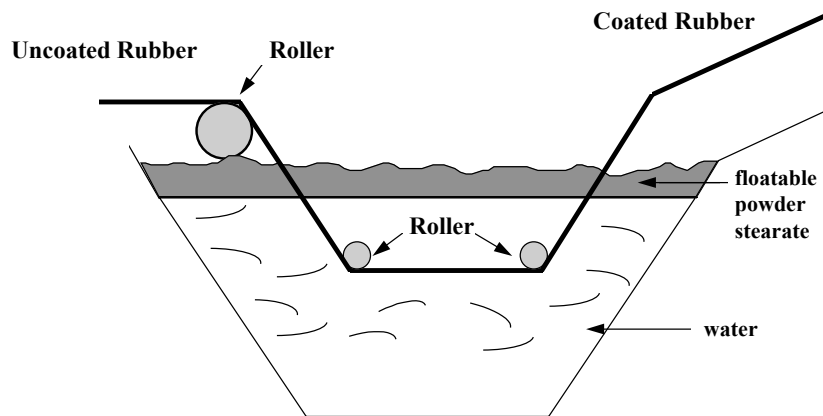
Metallic stearates can be applied to rubber several ways and in different forms. In the powdered neat states, stearates are applied or dusted onto the surface of the rubber by passing the rubber through a trough or box containing the stearate. This process is somewhat crude and dusty but is effective in applying the lubricant to the surface of the uncured rubber. Figure 7 illustrates this process.





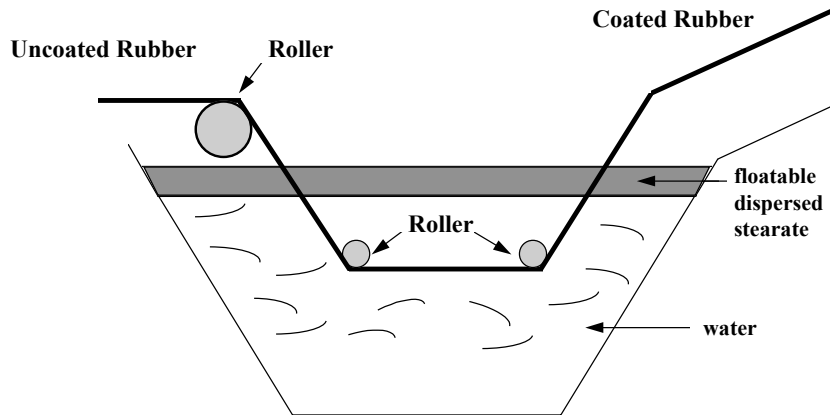
**Fig. 7. Dust box**

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 allows the powder to remain on the surface and not to be “wetted” out. Again, this process is effective but causes a great deal of dusting and thus many housekeeping problems. *Figure 8* is a graphic illustration of this process.



**Fig. 8. Floatable powder stearate**

For water-cooled systems, stearates are normally provided in 20–30 percent active pastes. These pastes are usually a combination of stearate, water and a small quantity of alcohol. These formulations allow stearates to be added to the dip tanks directly, or they can be premixed in tanks that 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 advantage of using this type of material is that the stearate is still floatable and can be used in water-cooled take-off units. Figure 9 shows how these products would appear in a slab dip tank.



**Fig. 9. Floatable stearate dispersion**

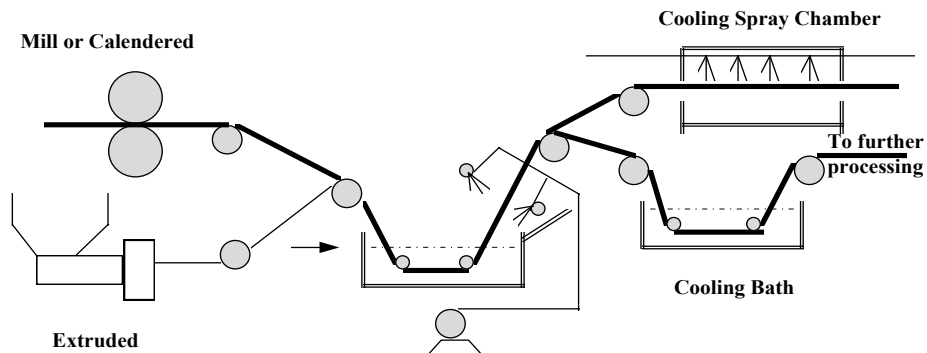
The floatable stearate dispersions can be modified such that the dustiness associated with them will be minimized. The hydrophobic nature of metallic stearates is particularly important because this property allows for the cooling of rubber with water. Several rubber companies use water or refrigerated water to remove as much heat as possible 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, as follows:

- Added to the water-cooling tank
- Applied after the water-cooling tank
- Applied and then passed through a water cooling tank or sprayed with water

All these processes can be accomplished because the metallic stearates are water-repellent and will not wash off. Figure 10 shows the various configurations of a water-cooled process that would apply metallic stearates.

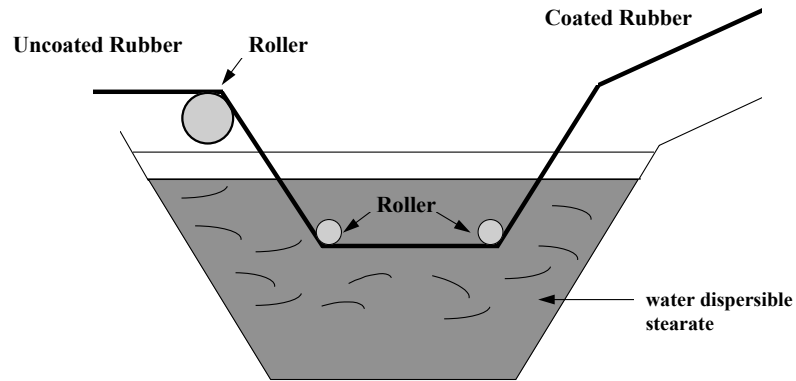
## Water Cooled

(External Release Coating)

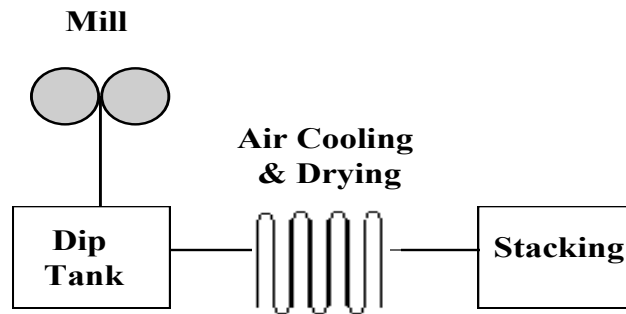


**Fig. 10. Water-cooled application**

The metallic stearates are available in water-dispersible forms. These products are normally 30–50 percent active and have surfactant packages that allow for dispersibility throughout a dip tank (see Figure 11). These products will require mixing in the dip tank to prevent settling. The dispersible products are used on air-cooled lines (see Figure 12.)



**Fig. 11. Water-dispersible stearates**



**Fig. 12.** Air cooling

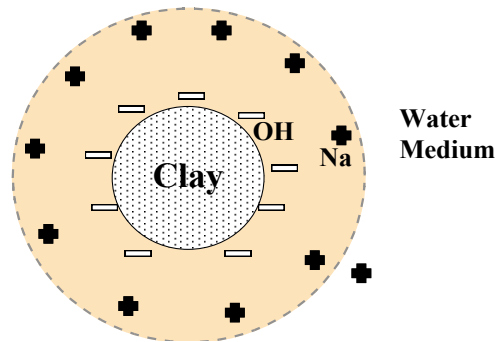
The surfactant package used in these products would cause the stearate to be washed off if used in a water-cooled system. Water-dispersible products can be used for all the applications previously mentioned in this paper.

## Environmental

The U.S. 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 issue. The key to this is that calcium stearate requires either higher curing temperatures or longer molding time to ensure solubilization into the elastomer.

## Pigmented Slurries

The greatest portion of most slurry anti-tack dips is filler. The fillers used include clay, calcium carbonate, talc and mica. The majority of slurries use a large amount of clay. Clay minerals have a unique set of physical and chemical properties that make them an excellent base for anti-tacks. The particle size, surface morphology and surface reactivity of clays play a role in their use in slurry dips. Clays also have colloidal properties that can be utilized to formulate excellent anti-tacks. When clays are dispersed in water, they form colloidal particles. Figure 13 illustrates a typical clay particle dispersed in water. The clay particle carries a negative charge, and the positive charges surrounding the particle are the result of cations hydrolyzed from the clay particle.



**Fig. 13.** Clay colloidal micelle

The chemical properties of clay enable the dip chemist to use many organic compounds that could interact with the clay and produce an effective rubber release coating. The organic compounds that interact with clay are very important in promoting the wetting and release properties. Surfactants are normally used to provide these properties. The surfactant systems are designed to give maximum wetting capability and not cause foaming in the dip tanks. In addition, the surfactants must be resistant to absorption by the uncured rubber compounds.

### Physical Form

Pigmented slurry anti-tacks are normally formulated as 50 percent active solids in an aqueous medium. Slurry anti-tack dips are normally used at 6–8 percent solids. This level may have to be increased during the summer months when sticking is especially bothersome.

### Drawbacks

Because slurry anti-tacks are 50 percent water, freight costs include the cost of shipping water. Other problems such as dusting, settling and foaming may occur occasionally. Last, slurry dips can freeze in winter.

### Dry Powder Pigmented

Dry powder pigmented anti-tack dips represent the latest in dip developments. These products were formulated mainly to replace slurry dips. Dry powder anti-tacks were initially formulated with clays as their main filler component. Recent developments include calcium carbonate as filler. Clays are used for many of the same reasons stated earlier. The chemical properties of clay can be utilized in dry powder form the same as they are in slurry form.

Dry powder anti-tack dips are formulated very carefully to maximize wetting and release characteristics. Obviously, these dips contain highly effective surfactant systems. They also contain additives that provide other necessary performance properties.

Calcium carbonate dry powder anti-tacks are based on similar chemistry but depend more on the surfactant systems for their performance properties. Calcium

carbonate dips have been gaining popularity over clay-based dips, particularly at tire and rubber companies. In comparing the structures of clay and calcium carbonate, the ragged rock-like structure of calcium carbonate may provide advantages in adhesive applications. The flat, planar surface of clay could contribute to adhesive failure. Further testing is under way to better understand the differences in adhesion.

## **Physical Form**

The dry powder dips, packaged in 50-lb. bags, not only save the rubber customer money on freight but are also twice as effective. Dry powder dips are designed to work between two percent and four percent solids. Since their introduction, they have been highly successful in replacing slurry dips. Dry powder dips are more convenient and safer to use in a plant than 55-gallon drums. In addition, bags can be completely emptied, saving material costs, and easily disposed of, while 55-gallon drums require special treatment and handling.

## **Drawbacks**

Dry powder dips provide many benefits compared to other slab dips, but they do not work in every situation. Because they are used at low levels, the amount of coating on the surface of the rubber may not provide adequate release, especially on cold flow compounds. The wetting properties can be marginal on certain elastomers, such as ethylene propylene diene monomers (EPDM). Furthermore, like many other slab dips, dry powder slab dips can cause foaming in highly agitated systems.

Clay-based dips can affect the physical properties of rubber and have been found to be detrimental to tear resistance and wire cord adhesion. Calcium carbonate-based dips do not affect the physical properties to the same extent.

## **Liquid Lubricants**

Liquid lubricants comprise a wide range of formulated and synthesized compounds. These materials are used in many rubber release applications, such as anti-tacks, hose lubricants, mandrel lubes and release agents for preform and extruded profiles.

Liquid lubricants used as anti-tacks are chemically classified as fatty acid soaps. These soaps have excellent wetting and release characteristics but have a tendency to be high foamers. Because these materials do not contain fillers, the fatty acid soap acts as the partitioning agent between two rubber slabs. Liquid lubricants generally are soft, pliable compounds after drying on the rubber surface, which makes them ideal for cold-flow compounds.

These materials are mostly used in applications needing non-pigmentation. Liquid lubes are used mainly on uncured rubber compounds that will be subsequently molded and cured without further mixing. They are used like metallic stearates in the sense that they do not cause surface defects and are visible upon non-molding or other vulcanization techniques.

**Physical Form**

Liquid lubricants typically are 20–30 percent water-based liquids sold in 55-gallon drums.

**Drawbacks**

Liquid lubricants are not commonly used in dip operations. Some of their problems stem from foaming and providing too much lubricity. The lubricity can cause rubber to slip off pallets and conveyor belts during cold-feed extrusion. In addition, liquid lubricants do not allow the rubber to “grab on” the processing equipment like pigmented dips.

**RELEASE AGENT APPLICATION GUIDELINE**

	FLOATABLE, NON-PIGMENTED				WATER DISPERSIBLE, NON-PIGMENTED						WATER DISPERSIBLE, PIGMENTED	
	ZINC STEARATE	CALCIUM STEARATE	ZINC STEARATE LOW DUST	CALCIUM STEARATE, LOW DUST	WETTABLE STEARATE	WETTABLE CALCIUM STEARATE	FATTY SOAP, 30%	EMULSIFIED WAX	POTASSIUM STEARATE, 20%	CLAY-BASED SLURRIES	DRY POWDER DIPS	
<b>EXTERNAL RELEASE FOR:</b>												
Slab Stocks	•	•	•	•	•	•				•	•	
Extrudates	•	•	•	•	•	•	•	•	•			
Pre-forms	•	•	•	•	•	•	•	•	•			
Molded Goods	•	•	•	•	•	•	•	•	•			
Air-cooled systems					•	•	•	•	•	•	•	
Water-cooled systems	•	•	•	•								
<b>AGITATION REQUIRED (Premix tank and dip tank)</b>												
- Standard (lightning mixer)					•	•			•	•	•	
- Minimal (recirc)							•	•				
<b>Recommended % solids level*</b>	3-10	3-10	3-10	3-10	3-10	3-10	3-5	3-5	3-5	6-10	6-10	

\*Solids level dependent on individual operating conditions

## Powder Liquid Dispersions

Rubber compounding ingredients vary from ultra-high viscosity elastomers to water-thin liquids with a myriad of powders, resins, accelerators, etc. and with varying degrees of dispersibility. The mixing of all these ingredients together requires specific procedures and mixing conditions, such as temperature, time, speed of rotors, etc. To ensure quality, many raw materials are modified for enhanced dispersion.

High viscosity liquids and resins, as well as high loading of low viscosity esters and oils, lend themselves to be dispersed on dry carriers and then to be added to an internal mixer or two-roll mill. In general, these products are dispersions of liquids and semi-solids onto highly absorbent carriers. The advantage of using these products include:

- Elimination of the handling problems associated with high viscosity liquids and semi-solids by converting them to powder
- Elimination of the need for heated inventory storage of high viscosity liquids or non-pouring liquids
- Reduction in batch preparation time
- Reduction in equipment clean up time
- Improvement in batch incorporation time and raw material dispersion
- Reduction in the amount of costly materials wasted when viscous liquids or semi-solids cling to the walls and bottoms of drum packages
- Improvement in package disposability by using fiber drums or paper bags as standard packages

These benefits can increase productivity and improve profitability. The percent active or the amount of liquid that is absorbed is typically 72 percent. Following is a list of the materials that can be converted to powders:

- Monomeric/polymeric ester plasticizers
- Liquid polymers: nitrile, epichlorohydrin and polybutene
- Process oils
- Coumarone-indene resins
- Pine tars
- Petrolatums
- Co-agents (monomers)
- Peptizers
- Chlorinated paraffins
- Accelerators
- Antioxidants
- Process aids
- Catalysts

Essentially, any product that can be heated to a liquid state is a candidate for converting to a powder concentrate. Many of these products can be pre-weighed and put into low melt bags.



	Powder Concentrate DBEEA	Neat DBEEA
<b><u>Mooney Viscosity at 121°C</u></b>		
Minimum Viscosity	30	27
t5, min	11.8	10.4
t10, min	14.3	11.9
<b><u>Rheometer at 170°C</u></b>		
t'c(90), min	4.6	4.5
<b><u>Original Physicals</u></b>		
Mod. at 300 % Elong., MPa	5.9	5.9
Tensile Ultimate, MPa	12.1	11.7
psi	1750	1700
Elongation at Break, %	600	570
Hardness, Duro A, pts.	61	59
Specific Gravity	1.219	1.202
Tear Strength, ppi	230	318
Low Temperature Imp't, C	-42	-42
<b><u>Air Oven Aging, 70 h at 125°C</u></b>		
Elongation Change, %	-37	-37
Weight Change, %	-3.9	-4.3
<b><u>ASTM 1 Oil, 70 h at 125°C</u></b>		
Elongation Change, %	-35	-35
Volume Change, %	-11	-10
<b><u>ASTM 3 Oil, 70 h at 125°C</u></b>		
Elongation Change, %	-20	-19
Volume, Change	2.4	2.5
<b><u>Distilled Water, 70 h at 100°C</u></b>		
Elongation at Break, %	-13	-16
<b><u>Volume Change, %</u></b>		
70 h	4.6	3.2
10 d	6.9	3.0
24 d	7.7	1.4
42 d	9	2.6