Baerlocher Additives

Metallic Stearates

we add character to plastics

BÆRLOCHER

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The Baerlocher Group of Companies is one of the world's leading suppliers of additives for the plastics industry with a strong focus on PVC. Baerlocher has extensive technology and market know-how drawn from more than 190 years of company history.

Additives play a crucial role in determining processing properties as well as product quality and character. Baerlocher offers a broad range of additives for polymers suitable for various industries.

Baerlocher is your global partner for Ca-based solutions and metal soaps.

By developing and supplying innovative additives, Baerlocher enables the plastics industry worldwide to manufacture high-quality and sustainable products.

www.baerlocher.com

Global presence and more than 1200 employees worldwide make sure that we are always close to the customer. Future-oriented, we are continuously investing in research and development. Our innovative power results from the creativity of our in-house scientists and technical experts. Baerlocher has R & D facilities in Germany (Munich-Unterschleissheim), France (Marseille), Italy (Lodi), the United States (Dover, Cincinnati) and India (Dewas).

Environmentally sound production processes as well as the safety and protection of people and environment are key corporate goals. As a globally active group of companies we are aware of our responsibility, regardless of time or place. We are committed to the principles of "Responsible Care": Our quality management is certified to ISO 9001 and our environmental management system to ISO 14001, encouraging our employees to work together in a responsible way. This policy will not least benefit our customers.

Baerlocher products

BAEROPAN
BAEROSTAB
BAEROPOL
BAEROLUB
BAEROPHOB
BAEROCID
BAEROCIN
CEASIT
ZINCUM

BÆRLOCHER

Introduction

Metallic stearates are compounds of long-chain fatty acids with metals of different valencies. The most important metallic stearates, in terms of quantity, are the metallic stearates of aluminium, calcium, magnesium and zinc.
The main advantage is their manifold range of use.
The most important ones are: lubricating properties, separating properties, water repellence, gelling capacity, stabilising effect, foam inhibition, acid scavenger.
Baerlocher metallic stearates are available in different product forms: as fine powders with a large surface, as prills, as flakes, as pastilles, as AV-granules, as rodlike-granules.

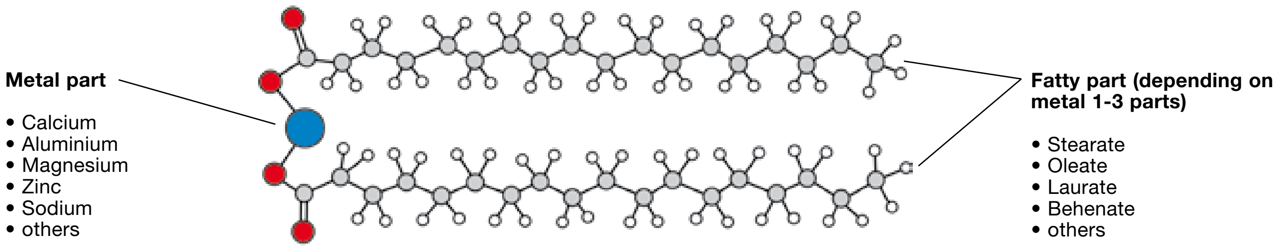
Baerlocher SPA-additives

- **highest quality**
- **variety of physical forms**
- **top performance**
- **cost effective**
- **globally available**

Contents

Metallic Stearates

Metallic stearates are compounds of long-chain fatty acids with metals of different valencies; some metallic stearates are not soluble in water, whereas other stearates, i.e. compounds of long-chain fatty acids with alkaline metals or ammonia are soluble in water. The most important metallic stearates, in terms of number of applications and quantities produced, are the metallic stearates of calcium, zinc, magnesium and aluminium.



Stearates of greatest commercial importance are produced from the commercial fatty acids derived from natural sources, with the predominance of those being sources containing mostly stearic acid and palmitic acids. Due to the OH-group present in the fatty acid molecule, 12-hydroxystearates are usually more soluble in polar solvents and their melting point is higher than the metal salts of mixtures of predominantly stearic and palmitic acids.

Owing to the shorter chain length of the fatty acid, the properties of laurates are greatly influenced by the respective metal base. The basic properties of metallic stearates such as water repellence and gelation are maintained, whilst lubricating and separating properties are already significantly reduced. As a consequence of the double bond present in the fatty acid, oleates have a lower melting point than the corresponding stearates.
Their solubility is usually slightly improved.

Among the many interesting properties of metallic stearates, the most important are:

• lubricating properties
• separating properties
• water repellence
• gelling capacity
• stabilising effect
• foam inhibition

Contrary to most other lubricants and release agents, metallic stearates are characterised by their relatively high melting point. Therefore, metallic stearates in the form of a fine dry powder can act as a dry lubricant (like graphite) when used in this solid powder form. In most cases, the hydrophobic nature of metallic stearates is highly desirable.

Lubrication and release properties, as well as water repellency, are characteristics of all metallic stearates. The special effects of these properties are determined by the cation, the chain length of the fatty acid and certain other properties of the respective metallic stearate (e.g. the water of crystallisation content).

The gelling properties of the aluminium stearates are particularly effective, however, satisfactory gelation depends on the type of stearate (mono-, di- or tribasic stearate), its polarity and the viscosity and solvent properties of the liquid component.

Calcium stearate, magnesium stearate and zinc stearate have stabilising and processing aid effects in a wide range of thermoplastics. Aluminium and magnesium stearates are used as foam inhibitors for various suspensions.

Interchangeable silos as environmentally friendly packaging

state-of-the-art production line

Applications in the plastics industry

Metallic stearates, which have been used primarily as acid scavengers, lubricants and release agents by the plastics industry, are becoming increasingly important in melt processing. In addition to optimising production, the use of metallic stearates allows the processor to produce finished articles with smoother surfaces and lower friction.

Metallic stearates are mainly produced from organic raw materials. Therefore, they tend to degrade to some degree when exposed to excessively high temperatures, resulting in discolouration. Baerlocher has developed a range of thermostable metallic stearates, which are highly resistant to discolouration when used in transparent or brightly coloured thermoplastics even at high processing temperatures

Main fields of plastics applications

Metallic Stearate	PE	PP	PS	ABS	PA	PVC	SMC/BMC
Calcium	●	●	●	●	●	●	●
Zinc	●		●		●	●	●
Ca/Zn	●					●	
Magnesium				●	●		
Aluminium					●		●

Applications in the pharmaceutical and cosmetics industry

Due to their outstanding lubrication and release properties, their thixotropic effect and their capacity for gelation, metallic stearates are used by the pharmaceutical and cosmetics industry. Their lubricating and release properties are utilised during dragée preparation and tablet pressing, whilst their gelation capacities assist in the production of creams and ointments. The hydrophobic properties of metallic stearates prevent pharmaceutical and cosmetic products in powder form from absorbing water and thus from forming agglomerates.

Additionally, metallic stearates are used in shampoos, eyeliners, lipsticks, sun protective lotions, medicated ointments, body and foot powders, etc. Although metallic stearates are added to these articles in relatively low dosages ranging from 0.05 to 1 %, significant volumes of metallic stearates are required for this application in Europe alone.

Further industrial applications

Metallic stearates prevent solid washing powders and detergents from water absorption. They are also used as anti-caking agents and mould release agents. In the textile industry, metallic stearates are applied for dry impregnation and as antistatic agents. The printing ink industry utilises metallic stearates as swelling and suspension aids for other additives such as pigments. They are also employed as lubricants and release agents for pastels and as matting agents for gravure inks. They are added to cements and fillers on account of their excellent oil binding properties. During the production of waxes and the processing of liquid wax compounds, they act as suspension agents and increase water repellency. They are added as anti-caking agents to different types of fillers and very hygroscopic salts and also in order to improve water resistance. The metal-processing industry uses metallic stearates as lubricants, release agents and dry-film lubricants.

Fields of application

Building Industry	Hydrophobic agents
Lacquer Industry	Matting agents and abrasives
Lubricant Industry	Thixotropic agents for the production of lubricants and greases
Rubber Industry	Mold release agents – Anti-tack agents
Paper Industry	Coating agents
Metal Industry	Lubricants for powder metallurgy, wire drawing and tubing
Pharmaceutical and Cosmetics Industry	Mold release agents for tabletting

Although we are familiar with many of the traditional metallic stearates applications, we often receive inquires about special applications. It is not always possible to comply with these highly specialised requests by offering standard products. We are therefore often asked to develop and produce special product types. For example: we may be asked to improve the free-flowing properties without changing granule size and structure, whilst maintaining surface properties and mean particle size; our customers may ask for particularly thermostable metallic stearates. For certain applications, e.g. the water repellent finishing of concrete, metallic stearates must be completely free from salt without losing their hydrophobic properties.

Heavy metal content and contamination must be reduced as much as possible. Customers may ask for metallic stearates with a specific pH-value, alkalinity or content of fatty acid. Odour and taste must often meet special requirements. Baerlocher has always been open to these requests (and welcomes any future challenges) and in most cases has been able to produce a metallic stearate corresponding to the special requirements of our customers. Baerlocher GmbH was the first company in Europe to produce metallic stearates on an industrial scale and our extensive experience in the manufacture, the applications and the development of our special stearates is always at the service of our customers.

Baerlocher has been the leader in producing metallic stearates in different product forms for the benefit of our broad customer base. Therefore, we are in a position to offer the appropriate product in the appropriate product form for almost any application.

The variety of product forms is as follows:
- Fine powders with a high surface area
- Coarse powders
- Prills
- Flakes
- Pastilles
- AV-granules
- Rod-shaped pellets

In addition to flexibility of producing many physical forms, most of our products are also offered as derivatives of either animal or vegetable based fatty acids.

Variety of physical forms

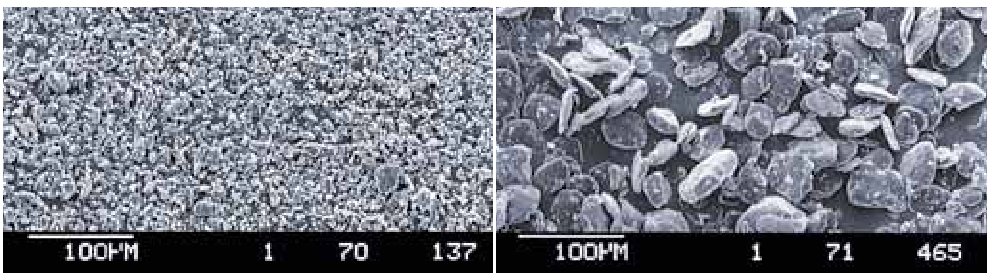
The Baerlocher group uses four different methods for the production of metallic stearates, with each method imparting its own specific properties to the final product:

1. Precipitation (or double-decomposition) reaction

The fatty acid is first saponified in relatively large volume of heated water with an equimolar to a slight excess quantity of a strong alkali solution (sodium hydroxide, caustic potash solution, ammonia). The resulting alkali stearate is soluble in water (pict. 1). Particle size, surface area and particle morphology or shape are influenced by the concentration of reactants and precipitation rates. In general, the higher the dilution of the saponified fatty acid, the smaller the particles and the larger the surface will be. These properties determine the bulk (apparent) density, which is typically low for precipitated metallic stearates. The desired water-insoluble metallic stearate is subsequently produced by adding a metal salt solution (e.g. calcium chloride solution, aluminium sulphate solution). The reaction follows the formula (pict. 2).
The water-soluble salts such as sodium chloride or sodium sulphate, generated as by-products of the precipitation reaction, must be removed from the metallic stearate by filtration and washing. Finally, the resulting wet cake must be dried and the product deagglomerated or milled. This double-decomposition reaction typically produces very light, fine powders with a large surface area and a more platelet morphology. These types of metallic stearates are used in applications requiring fine particle size and high surface area for the best lubrication and release properties and where special emphasis is placed on good hydrophobic properties.

$C_{17}H_{35}COOH$	+	NaOH	➔	$C_{17}H_{35}COO^{-}Na^{+}$	+	H_2O	Pict. 1
stearic acid	+	sodium hydroxide	➔	sodium stearate	+	water	

$2\ C_{17}H_{35}COO^{-}Na^{+}$	+	$M^{2+}2X^{-}$	➔	$(C_{17}H_{35}COO^{-})_2M^{2+}$	+	$2Na^{+}X^{-}$	Pict. 2
sodium stearate	+	metal salt solution	➔	metal stearate	+	water soluble salt	
M = Zn^{2+}, Ca^{2+} or similar;	X = Cl^{-}, 1/2 SO_4^{2-} or similar						



left: Zincum SW derived from the AV-process

right: Ceasit POE derived from direct reaction

2. Direct reaction

The reaction between stearic acid and metal oxide, hydroxide or carbonate takes place at an elevated temperature in a large excess of water. The reaction illustrates that there are no by-products (pict. 3).
Particle size, and thus particle surface and bulk weight are influenced by the relation of stearic acid to water. The higher the dilution, the smaller the particles and the larger the surface will be. The metallic stearates produced by direct reaction are also relatively fine powders with a high degree of purity, being free of water-soluble salts. Not all metallic stearates can be effectively produced by this method, due to low reactivity of certain metal oxides, hydroxides or carbonates. The reaction can be run effectively at atmospheric pressure, but an advantage of this method is that it can also be run under pressure and at higher temperatures (>100 °C) to produce certain types of metallic stearates, which cannot normally be obtained under atmospheric conditions by the direct reaction process. In most cases, the product must be filtered and dried to the final desired moisture content.
Direct reaction in water generally produces a more rounded, agglomerated particle, with higher bulk density than precipitated stearates.

2 $C_{17}H_{35}COOH$	+	$Ca(OH)_2$	➔	$(C_{17}H_{35}COO^-)_2Ca^{2+} \cdot H_2O$	+	H_2O	Pict. 3
stearic acid	+	calcium hydroxide	➔	calcium stearate	+	water	

3. Fusion process

During the fusion process, metal oxides or hydroxides and stearic acid are heated under pressure with continual stirring beyond the melting point of the metallic stearate product. As the melting point of most metallic stearates is higher than 100 °C, the water resulting from the reaction escapes as steam. Therefore, a drying step is unnecessary. A variety of physical forms can be produced from this process, depending on the melting range of the final product. For relatively low or sharp melting metallic stearates, all forms (pastilles, prills, flakes and powder) are generally feasible. A very high degree of purity is achievable with the fusion process (pict. 4).

2 $C_{17}H_{35}COOH$	+	ZnO	➔	$(C_{17}H_{35}COO^-)_2Zn^{2+}$	+	H_2O	Pict. 4
stearic acid	+	zinc oxide	➔	zinc stearate	+	water	

4. AV process

Baerlocher's AV process is a combination of the direct reaction and fusion processes. Metal oxides or hydroxides are heated according to a patented method with a fatty acid and a small quantity of water in a pressurised reactor, with the final temperature corresponding more or less to the melting point of the soap. The added water and the water resulting from the reaction are removed under reduced pressure at the end of the reaction cycle.
The AV process allows the very efficient production of a variety of stoichiometries, including very pure products. AV technology is generally used to produce metallic stearates in free-flowing granule or powder forms (pict. 5).

2 $C_{17}H_{35}COOH$	+	$Mg(OH)_2$	➔	$(C_{17}H_{35}COO^-)_2Mg^{2+} \cdot H_2O$	+	H_2O	Pict. 5
stearic acid	+	magnesium hydroxide	➔	magnesium stearate	+	water	

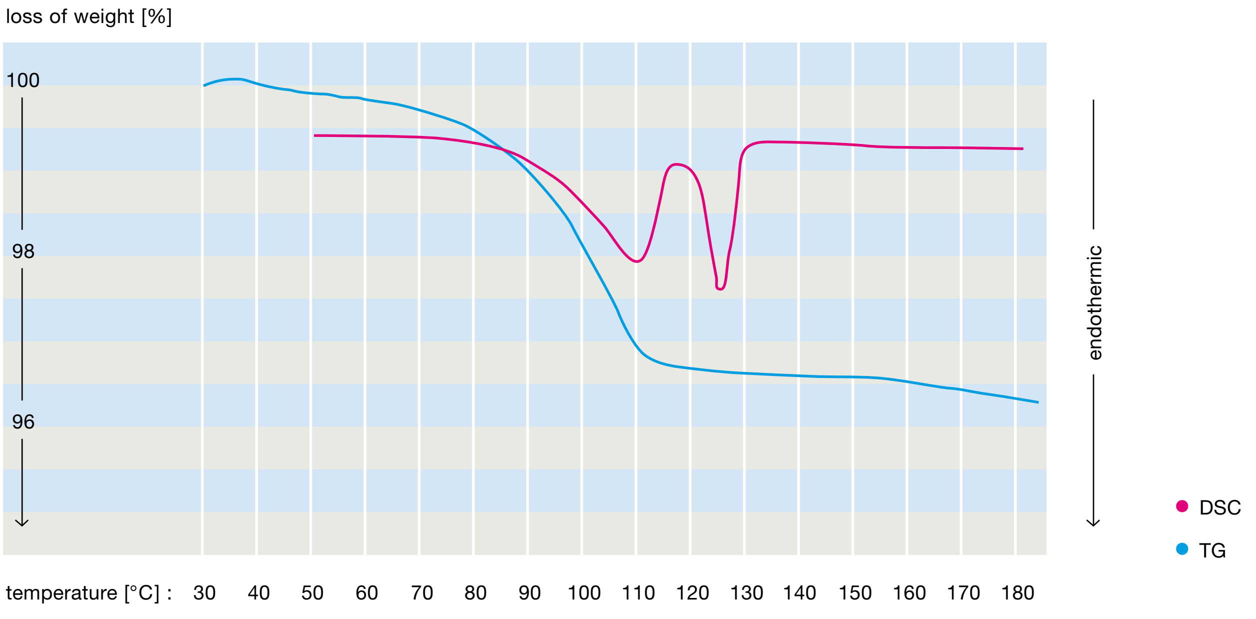
Calcium Stearates

Calcium stearates, which are recognized as physiologically safe, have become increasingly important in the last few years. They are insoluble in most solvents. They dissolve only slightly when heated in aromatic compounds, chlorinated hydrocarbons or vegetable and mineral oils and waxes. Calcium stearates are mainly used as lubricants, mold release agents and acid scavengers by the plastics industry. The pharmaceutical and cosmetics industry uses calcium stearate as an anti-caking additive for powders and granules and as an excipient for pressing tablets. The building industry uses it as hydrophobic agent for inhibiting moisture absorption and preservation of building materials and construction.

Behaviour of calcium stearate on heating

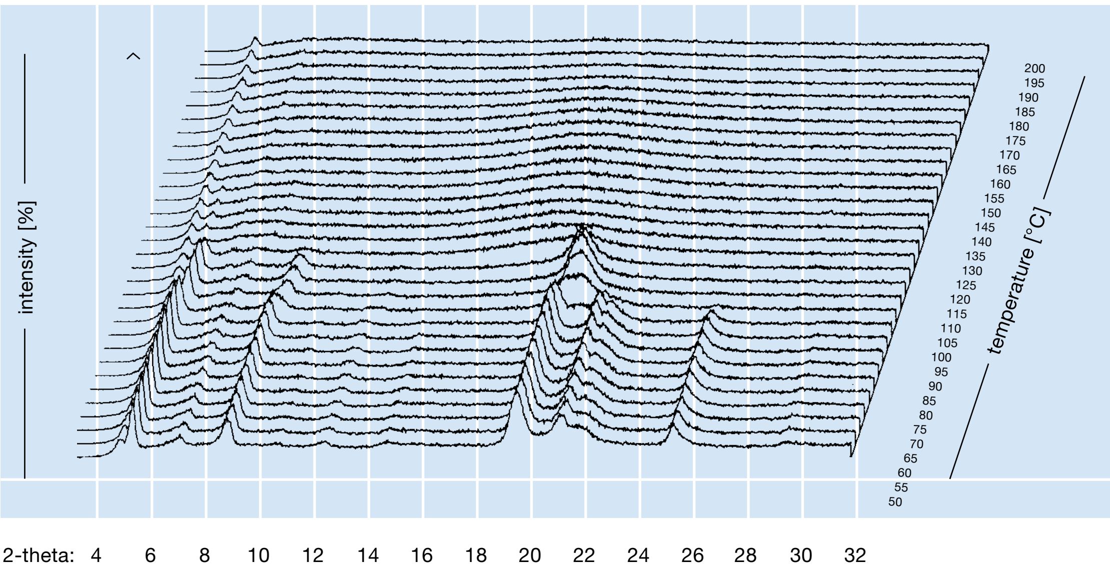
Calcium stearate shows some interesting effects when heated. It dehydrates and starts to soften at temperatures between 120 °C and 130 °C and takes a viscous consistency at approx. 160 °C. This state lasts whilst the material is heated occurring some slight discolouration. The thermogravimetric diagram (TG) shows that calcium stearate loses about 3 % of its weight at approx. 100 °C. This weight loss corresponds to one mole water of crystallisation, which is split off at this temperature. A differential scanning calorimetry-measurement (DSC) indicates this separation of water crystallisation by an endothermic peak. The temperature-dependent X-ray diffraction diagram demonstrates that the crystalline structure of calcium stearate changes as a consequence of the separation of water crystallisation.

TG and DSC measurement of calcium stearate



As the temperature increases, there is a second endothermic peak at approx. 125 °C, which correlates with the collapse of the crystal lattice. The TG diagram shows that the weight does not change. After the crystal lattice has collapsed, i.e. above 125 °C, there is still a very broad peak to be seen between approx. 15° and 25° on the 2-theta-scale in the X-ray diffraction diagram.
This peak is no longer derived from a crystalline substance and indicates that calcium stearate is not a classical melt, but rather an amorphous structure existing between the individual molecules, with only a short range order like in the case of glass for example. This explains the high viscosity of the calcium stearate “melt”.

Temperature depending X-ray diffraction of calcium stearate



Heat stability of calcium stearates

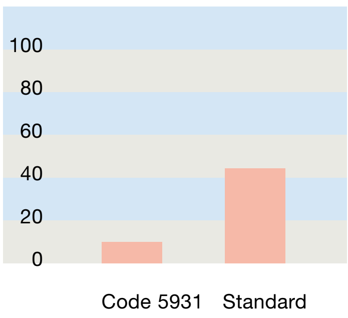
If calcium stearates are used in transparent or lightly pigmented thermoplastics and thermosetting plastics, it is very important that there is no undesirable discolouration at normal processing temperatures. With Ceasit AV, Ceasit SW/F, Ceasit PC and Ceasit POE, Baerlocher is in a position to offer some particularly thermostable calcium stearates.

Calcium stearate for PE and PP film and fibre applications

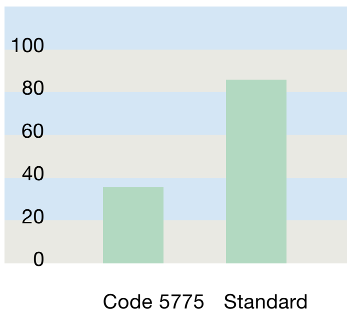
Specific calcium stearate grades, designed with high purity and low filtration index, are especially suited for use as acid scavengers/lubricants in polyethylene and polypropylene film and fibre applications where very fine extruder screen packs are used. A low filtration index is related to minimizing the back-pressure build-up on extruder screen-packs, resulting in the minimum number of screen-pack changes and maximum output of the extruder.

Back-pressure build-up of calcium stearates on extruder screen-packs

Powders



Granules



High quality calcium stearate can be used to produce PE / PP film and fibres

Zinc Stearates

Zinc stearates are insoluble in polar solvents, but more soluble in aromatic compounds and chlorinated hydrocarbons when heated. Their main application areas are the plastics and rubber industries where they are used as release agents and lubricants which can be easily incorporated. The outstanding clarity and heat stability properties of our crystal clear zinc stearate grades make them particularly suitable for impact and crystal grade polystyrene and other clear polymers. Zinc stearate functions as an acid scavenger and processing aid in certain polyolefin applications.

The paint and coatings industry uses our zinc stearates for pigment suspension and to improve grindability and matting. The building industry uses powdered, precipitated zinc stearates as hydrophobic agents for plasters.

Zinc stearate Code 8512
Clear melting – clear soluble

Precipitated Zincum 5 is used as hydrophobic agent in mortar and plasters

Magnesium Stearates

Like calcium stearates, magnesium stearates are almost insoluble in normal solvents. They are able to hold considerable quantities of water and take on a creamy consistency. Magnesium stearates are therefore used to improve the retention of creams and semi-rigid wax articles as well as to produce waxes.
Since they are recognized as physiologically safe, they are used by the cosmetics and pharmaceutical industry. Magnesium stearates improve the free-flowing properties and are added as anti-caking agents to powders.
One of the principle uses of magnesium stearate is as a tablet excipient in pharmaceutical dosage forms.
Thermostable magnesium stearates are used as lubricants and release agents for the processing of thermoplastics and thermosets.

Aluminium Stearates

Aluminium stearates are produced by the precipitation process only. There are three possible combinations of aluminium with fatty acids:

The ratio of aluminium to fatty acid does not necessarily correspond to the stoichiometric values. Any ratio is possible between the extremes 1:1 and 1:3. Therefore there are many varieties of aluminium stearates, generically referred to as aluminium mono-, di- or tri-stearate, whose properties differ from one another in respect to physical properties such as melting point, free fatty acid and particularly the gelling properties. Oils with a low viscosity are best thickened by aluminium tri- and di-stearates, whilst very viscous oils form stiffer gel when combined with aluminium di- or mono-stearates.

The dropping point of aluminium greases usually range from 110 °C to 120 °C, but we are in a position to offer special stearates whose dropping point exceed 200 °C. All aluminium greases are highly hydrophobic and are characterised by outstanding transparency and good adhesion to metallic surfaces.
Due to their excellent water repellency, aluminium stearates are used in coatings and building industry materials as water repellent ingredients.
Aluminium mono-, di- and tri-stearates are insoluble in water, lower alcohols, esters and ketones. In benzenes, aromatic compounds and halogenated hydrocarbons as well as in natural and mineral oils, they dissolve to a gel when heated.

Aluminium mono stearates	Aluminium di stearates	Aluminium tri stearates
Al – OH Al – OH Al – fatty acid	Al – OH Al – fatty acid Al – fatty acid	Al – fatty acid Al – fatty acid Al – fatty acid

Alkali Stearates

Lithium stearates

Hydrophilic lithium stearates distinguish themselves by their excellent swelling properties. Different compositions of fatty acids are available in our product range. Depending on the product type properties like dropping point temperatures of greases containing lithium stearates are much higher than those of aluminium stearates.

Lithium stearates are widely used to thicken natural as well as synthetic oils and help to increase the melting point and flexibility of micro-crystalline waxes and paraffins. They are also used during the production of light weight metal mouldings. The advantage of lithium stearates with long fatty acid chain lengths is the minimal residue after thermal treatment.

Sodium stearates and Sodium Oleates

Sodium stearates and oleates are produced by direct reaction according to a Baerlocher patented process. Possible applications of these products are e.g. swelling of alcohols, lubrication and nucleating during the processing of thermoplastics.

Sodium oleates are mainly used as hydrophobic agents for building plasters, where homogenous dispersion is easily obtained due to its solubility in water. The alkaline components of the plaster and the sodium stearate forms a calcium stearate which is also finely dispersed, thus imparting high water-repellency properties to the plaste.

we add character to plastics

Reach out for the Future: **www.baerlocher.com**

Please download the following brochures from our webpage:

Baerlocher Additives for PVC

- Extrusion and Injection Moulding
- Cables and Wires
- Calendered Films and Sheets
- Lead Stabilizers
- Lubricants
- Organotin Stabilizers
- Plastisol
- Sheets and Foamed Profiles

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