

PETER GREVEN Your partner for plastic additives





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LIGASTAR® Metallic Soaps LIGALUB® Ester Lubricants LIGASTAB® Metallic Soaps & Preblends

Sustainability is an important aspect of our corporate philosophy. As a middle-sized, family owned company we have produced additives based on renewable raw materials ever since and provide long-term experience with raw materials and production technologies. On this basis, we regularly develop new products and customer-specific solutions for a variety of applications. Plastics is one of our most important industries. The application possibilities of our products are as diverse as the sector itself. Thanks to our application related know-how we developed a tailored product portfolio which offers sustainable solutions for all different types of plastics.





METALLIC SOAPS Technical introduction

Metallic soaps are salts of fatty acids, especially of stearic acid. They are often referred to as all-round talents as they can be used in many different applications and offer several advantages.

Advantages:

- Excellent lubricating properties
- Good stabilizing properties
- Good gelling properties
- Very good release properties
- Outstanding hydrophobing properties

There are four important technological processes for the production of the metallic soaps:

Production processes of metallic soaps									
	Indirect conversion	Direct conversion	Melting process	COAD [®] process					
Description	Two reaction steps 1. step: Production of a soap 2. step: Precipitation of the metallic soap by adding the metal base	Metal base powders are added to the fatty acid. Reaction temperature is below the melting point of the metallic soap.	Metallic components are added to the liquid fatty acid. Reaction temperature is above the melting point of the metallic soap.	During this continuous process stearic acid is processed with a metallic base. The reaction is similar to direct conversion.					
Properties	 very high degree of fineness high specific surface area low bulk density neutral pH-value high salinity 	 lower degree of fineness good flowability higher bulk density pH-value > 7 low salinity 	 dust free good flowability high bulk density clear melt low salinity 	 · dust free · good flowability · neutral pH-value · low salinity 					

ESTERS Technical introduction

Esters comprise a group of chemical compounds that are formed through the reaction of an acid (e.g. stearic acid, oleic acid) and an alcohol (e.g. glycerin, pentaerythritol).

Esters are – like metallic soaps – essential additives in the plastics industry. Their effects and properties are based on the different characteristics of the functional groups and non-polar components as well as their ratios.

Esters with short-chain hydrocarbon chains, such as diethyl adipate, exhibit solvent properties. The extension of the hydrocarbon chains results in waxy products. One example is stearyl stearate, which is used as a lubricant in the plastics industry. The influence of polar groups is significantly pronounced if polyols are used for the production of esters. In this way the behaviour of lubricants in PVC or ABS can be controlled. Polar esters are more compatible and act as internal lubricants, for example glycerol monostearate. If the polarity is reduced, products with a more external lubricant effect are obtained.

The ratio of the polar proportion and non-polar hydrocarbon chains also leads to surfactant-like properties. This effect is exploited in many cases. Esters, such as glycerol monooleate or PEG 400 monooleate, are used as antifogging agents in PVC. Glycerol monostearate is used as an antistatic agent for polyolefins or to stabilize the foam structure of EPS.





PVC – METALLIC SOAPS

PVC (polyvinyl chloride) is one of the oldest and most commonly used plastics. PVC is durable and light, exhibits a low permeability, is fire resistant and offers good insulation properties. In addition, PVC rarely absorbs water and is stable towards acids, alkalis, alcohols, oil and gasoline.

PVC is difficult to convert and processing additives are needed to improve the melt viscosity and the flow properties of PVC. Furthermore stabilizers are needed for the processing of PVC. Peter Greven has been producing and developing metallic soaps, preblends and lubricants that are used in the PVC industry for many decades.

Metallic soaps in PVC

Metallic soaps are among the most important additives for PVC because they offer excellent stabilizing and also very good lubricating properties.







particle size

FINE

COARSE



PVC – METALLIC SOAPS

Evaluation of metallic soaps in Ca/Zn PVC profile formulations



The shorter the chain length, the faster the gelation.

Fig. 7: Variation of Ca/Zn formulations								
Variation in formulation	CA 12 OXY 0.5 phr ZN 101/6 1.5 phr	CA 12 OXY 0.7 phr ZN 101/6 1.3 phr	CA 12 OXY 1 phr ZN 101/6 1 phr	CA 12 OXY 1.3 phr ZN 101/6 0.7 phr	CA 12 OXY 1.5 phr ZN 101/6 0.5 phr			
Ca/Zn	0.2	0.32	0.6	1.12	1.8			
Mass T°C at die entrance (°C)	178	179	179	180	181			
Pressure 18 D (Bar)	8	12	23	25	20			
Pressure 22 D (Bar)	63	69	80	88	90			
Pressure 25 D (Bar)	130	132	141	147	151			
Torque (Nm)	84	93	109	117	118			
Output (Kg/h)	3.52	3.30	3.18	3.04	2.755			
YI	18.4	20.4	23.4	27.6	31.1			
DHC (min)	33	35	41	47	46			

By increasing the calcium ratio, a faster gelation is realized and then pressure, torque and mass temperature increases – the yellowness index increases and the thermal stability is extended.



Product portfolio of metallic soaps for PVC

Product	Description	Metal content (%)	Humidity (%)	FFA (%)	Sieve residue (%)	Melting point (°C)
LIGASTAR CA 600	Calcium salt of stearic acid	7.0-7.7	max. 3.0	max. 1	> 45 µm max.3	140-160
LIGASTAR CA 600 G2	Calcium salt of stearic acid	7.0-7.9	max. 3.0	max. 1	-	145-160
LIGASTAR CA 12 OXY	Calcium salt of hydroxy stearic acid	6.5-7.1	max. 3.0	max. 1	-	140-147
LIGASTAB CAL	Calcium salt of lauric acid	8.6-10.0	max. 3.0	max. 1	-	-
LIGASTAR ZN 101/6	Zinc salt of stearic acid	10.5-11.3	max. 0.5	max. 1	> 45 µm max. 2	118-122
LIGASTAR ZN 101/6 FG	Zinc salt of stearic acid	10.5-11.3	max. 0.5	max. 1	> 1000 µm max. 1	118-122
LIGASTAR ZN 104 FG	Zinc salt of stearic acid	10.5-11.3	max. 0.5	max. 1	> 1000 µm max. 1	118-122
LIGASTAB ZN 108 FG	Zinc salt of short chain fatty acids	16.0-19.0	max. 1.0	max. 2	> 1000 µm max. 1	max. 140
LIGASTAB ZN 108 S	Zinc salt of short chain fatty acids	16.0-19.0	max. 1.0	max. 2	-	max. 140
LIGASTAB ZNL	Zinc salt of lauric acid	13.0-15.0	max. 0.5	max. 1	-	-
LIGASTAR MG 700	Magnesium salt of stearic acid	4.1-5.0	max. 6.0	max. 2	-	145-160



PVC – PREBLENDS

LIGASTAB PREBLENDS offer the following advantages:

- The products are dust free and offer very good free-flowing properties
- Due to the high bulk density the processability is more efficient
- · Formulations are simplified
- · Mixing times are reduced
- Due to the dust free properties the products are excellent from a safety point of view

There are many different variations of these preblends, for example:

LIGASTAB CZ 21

This preblend is a mixture of calcium and zinc soaps of selected fatty acids. In addition to the usage in stabilizer systems, the product is also characterized through its outstanding compatibility with PVC.

LIGASTAB CZ 30

This dust free preblend is a mixture of calcium and zinc soaps of stearic acids and is used in stabilizer systems for PVC. Due to the special production process the mixture is very homogeneous; there is no risk of separation.

Due to the complex combination of calcium/zinc stabilizers a preblend of calcium and zinc soaps is an advantage in the melting process. Benefits of these combination products are the homogeneity of the mixture and the dust free properties. Furthermore work has shown that the decreasing of the melting range is the essential advantage of the preblends compared to the single calcium and zinc soaps. The different melting ranges are shown in the following graph (fig. 8): The melting range of LIGASTAB CZ 30 is around 100 °C. By looking at the single components the melting point of zinc stearate as well as the melting point (transformation into a 2-D-crystal lattice) of calcium stearate is around 120 °C.

Therefore a decrease in the melting range of around 20 °C is observed.

The same result is also observed for LIGASTAB CZ 21: the melting range is decreased by around 20 °C as well.

This decreased melting range results in lower mixing times and a reduction of the processing temperature. Therefore, the production process is improved.



PVC – LUBRICANTS

Lubricants are, just like stabilizers, essential additives for PVC production. Internal and external lubricants are distinguished which results in the following characteristics:

Internal lubricants

- · Improved compatibility due to polar groups in the C chain
- · No formation of single lubricant phases
- · Decrease the softening temperature of PVC
- · Acts as macromolecular binder

External lubricants

- · Low compatibility with PVC
- · Reduction of adhesion of hot plastics with other material surfaces
- · Act as release agent without degradation on plate-out properties

The selection of the right lubricant for the PVC formulation is very important. In particular the gelation time plays an important role, thus selected lubricants and their gelation times are shown in figure 9:



Product portfolio of ester lubricants for PVC incl. applications

		Physical form	AV	SV	OHV	Melting range	Fune	ction			
									Profiles,		
Chemical Type	Product	solid/liquid	(mg KOH/g)	(mg KOH/g)	(mg KOH/g)	(C°)	internal	external	sheetes	Pipes	
Fatty Acids	LIGALUB SH	solid	195-205	198-208	-	55-64		**	•	•	
	LIGALUB FSO	solid	172-185	180-192	min. 150	71-80		*	•	•	
	LIGALUB 9 GE-H	solid	max. 5.0	175-185	min. 155	84-88	****		•	•	
	LIGALUB 10 GE	liquid	max. 1.0	160-170	-	-	****				
Glycerol Esters	LIGALUB 11 GE	solid	max. 1.0	160-175	-	54-65	****		•		
	LIGALUB 12 GE	liquid	max. 1.0	176-184	-	-	****		•		
	LIGALUB GT	solid	max. 2.0	195-205	-	57-65	*	***	•	•	
	LIGALUB 36 FE	solid	max. 2.0	100-115	-	50-60	**	***	•	•	
Alcohol Esters	LIGALUB 80 MEG	solid	max. 2.0	-	max. 14	65-75	****	*	•	•	
	LIGALUB 81 MEG	solid	max. 3.0	-	max. 14	60-80	****	*	•	•	
	LIGALUB 45 ITD	liquid	max. 1.0	110-120	max. 15	-	****		•		
Polyol Esters	LIGALUB 55 PE	solid	max. 2.0	165-180	105-135	49-56	***	**	•	•	
	LIGALUB 70 KE	solid	max. 15.0	270-280	-	50-60	*	****	•		
Complex Esters	LIGALUB 71 KE	liquid	max. 3.0	250-260	-	-	**	***			
	LIGALUB 74 KE	solid	max. 12.0	245-260	-	77-85	**	***	•	•	
Blends	LIGALUB 78 KE	solid	max. 12.0	-	-	100-120	*	***	•	•	
	LIGALUB 121 KE	solid	max. 1.5	120-150	-	60-72	**	**	•	•	



PVC-U				PV	C-P			Stabilizer	
Injection moulding	Bottle	Film	Extrusion	Calender	Injection moulding	Plastisol	Calcium/Zinc	Tin	Barium/Zinc
	•	•		•			•	•	•
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	•	•	•		•	•	•	•	•
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PVC – ANTI-FOGGING ADDITIVES

Anti-fogging Additives

In the food packaging and agricultural sector anti-fogging additives are added to plastic foils in order to prevent the formation of condensation drops. Without additives being added, the surface can steam up with water vapour. For this reason the content of the package, especially cooled food products, would not be clearly visible. Additionally, arising water drops restrict the light transmission, which can for example be a problem within agricultural sector as the plant growth could be retarded.

Product portfolio of anti-fogging additives

Product	Description	AV (mg KOH/g)	OHV (mg KOH/g)	CP (°C)
LIGALUB PEG 400 MO	Polyol ester	< 2.0	~ 90	< 0
LIGALUB PEG 400 ML	Polyol ester	< 2.0	~100	< 10
LIGALUB AF 40	Combination product	< 1.5	~ 150	< 0
LIGALUB AF 42	Combination product	< 1.5	260-290	< 3

Effectiveness of anti-fogging additives

In a first step, the anti-fogging additives migrate to the surface and act like surface active agent, which means the surface tension is reduced and as a consequence the water drops will spread into one steady film of water which is transparent. Our product portfolio includes polyol esters as well as combination products. During the usage of LIGALUB AF 40 and LIGALUB AF 42 the focus is on good short term results (fig. 10) as well as on excellent long term results (fig.11).



These results show that our anti-fogging additives migrate to the surface but won't be washed out over time, neither in short-nor long-term monitoring.

POLYOLEFINS

Besides PVC, polyolefins are one of the most important plastics. Due to their good chemical consistency and electrical insulation characteristics polyolefins are used in many different applications, like for example films (for packaging), household goods, transport containers, sheets, pipes and fibers.

As PVC, polyolefins belong to the thermoplastics which can be processed in specific temperature ranges. However, they are easier to process than PVC as they offer a very good thermal stability with absence of oxygen. Due to the catalysts used metallic soaps are necessary as additional additives.

Metallic soaps in polyolefins

For the stability of polyolefins, antioxidants are predominantly used. However, most catalysts used for the production of polyolefins contain chloride and there is a risk of hydrochloric acid formation during processing which can affect performance and easily corrode processing tools. To avoid this 0.05 to 0.20 % calcium or zinc stearate are added to the formulation. Calcium stearate is particularly suitable as it has a higher chemical affinity to chloride. Figure 12 shows the function of metallic soaps as acid scavenger. Metal plates were immersed into PP melt for a defined time. Without an acid scavenger the metal plate (S235JRC+C) corrodes within 6 days at room temperature and with a relative humidity of 90 %. Only 500 ppm calcium stearate is enough to stop the process of corrosion.

Metallic soaps from different production processes will have different physical characteristics, but all can be used for polyolefin production. In that application it may be preferred to use a 'powder' stearate for the ease of dispersion, but it may be desirable to use a 'granulate/ dust free' grade for easier and cleaner material handling. Depending on the production process, stearates do not only vary in terms of grain size but also grain structure.

Within COAD[®] process (continuous) we receive layered particles resulting in faster distribution and enhanced solubility of the calcium stearate. This is particularly advantageous for applications where filter index is important.



PP without calcium stearate PP with 500 ppm calcium stearate

Fig. 12: Function as acid scavenger



Fig. 13: Comparison of grain structures





Precipitated process

Direct process

Filter index

Beside the classic metallic soap parameters such as low moisture, free fatty acid and low calcium content the filter index plays an important role for some applications: during production of polyolefine fibers, the increase in pressure during processing must not be too high to prevent loss of production. Therefore the included calcium stearate must be optimized to such an extent that the filter index is very low.



As you can see from figure 14 calcium stearates from precipitated process as well as from COAD process offer good filter index results. Prerequisite for those results are further parameters that have to be considered during production.



Continuous process

Due to globalization and raw material availability it is important to have the possibility of using stearic acid from both, vegetable and tallow base. However, the choice of raw material should not have any influence on the products' properties. To evaluate the influence of the raw material base we performed multiple extrusion tests



The test results are shown in figure 15 and 16. They outline that stearates based on vegetable raw materials offer results comparable with tallow based products.







Product portfolio of metallic soaps for polyolefin industry

Product	Description	Metal content (%)	Humidity (%)	FFA (%)	Sieve residue (%)	Melting point (°C)
LIGASTAR CA 350	Calcium salt of stearic acid	6.3-7.0	max. 3.5	max. 0.8	> 71 µm max. 2	140-160
LIGASTAR CA 350 FT*	Calcium salt of stearic acid	6.3-7.0	max. 3.5	max. 0.8	>71 µm max. 1	140-160
LIGASTAR CA 800	Calcium salt of stearic acid	6.5-6.9	max. 3.0	max. 0.8	> 71 µm max. 2	140-160
LIGASTAR CA 860*	Calcium salt of stearic acid	6.5-6.9	max. 3.0	max. 0.8	> 71 µm max. 2	140-160
LIGASTAR CA 860 G2 FT*	Calcium salt of stearic acid	6.6-7.3	max 3.5	max. 0.8	n.a.	140-160
LIGASTAR ZN 101/6*	Zinc salt of stearic acid	10.5-11.3	max. 0.5	max. 1.0	> 45 µm max. 2	118-122
LIGASTAR ZN 101 CG	Zinc salt of stearic acid	10.5-11.0	max. 0.5	max. 1.0	>71 µm max. 1	118-123

* The product is also available as vegetable and RSPO Mass Balance certified grade.

Esters and fatty acids in polyolefins

In most cases polyolefin can be processed without the use of additional lubricants as the applied stearates offer a lubrication effect. However, for some applications the use of lubricants is beneficial. The products LIGALUB 11 GE-V, LIGALUB 11 GE/50-V and LIGALUB 11 GE/90-V are preferred as antistatic agents.

Product portfolio of esters and fatty acids for polyolefin industry

Product	Description	AV (mgKOH/g)	SV (mgKOH/g)	Melting point (°C)
LIGALUB SH	Special fatty acid	195-205	198-208	55-64
LIGALUB 9 GE-H	Glycerol ester	max. 5	175-185	84-88
LIGALUB 11 GE	Glycerol ester	max. 1	160-175	54-65
LIGALUB 11 GE-V	Glycerol ester	max. 1	160-175	54-65
LIGALUB 11 GE/50-V	Glycerol ester	max. 5	-	57-65
LIGALUB 11 GE/90-V	Glycerol ester	max. 5	-	60-70
LIGALUB 55 PE	Polyol ester	max. 2	165-180	49-56
LIGALUB 70 KE	Complex ester	max. 3	250-260	50-60
LIGALUB 71 KE	Liquid complex ester	max. 15	270-280	-
LIGALUB 78 KE	Blend	max. 12	-	100-120



SMC/BMC

Fibre-reinforced plastics (SMC, BMC)

Fibre-reinforced plastics are moulding compounds which consist of unsaturated urea, melanin or phenolic resin. In addition mineral fillers, fibre glass as well as some processing aids and additives are included. A distinction is made between SMC (sheet moulding compound) or BMC (bulk moulding compound) depending on the manufacturing process.

During processing of the moulding compound the resin is hardened. SMC/BMC is, for example, used for electronic components or vehicle

construction. Metallic soaps (mainly zinc and calcium stearate) are used as separating agents for the forming process. Zinc stearate is often preferred due to its low melting point.

During the pressing of the mass, stearates migrate to the surface and result in a very good release effect without influencing the surface quality. Precipitated stearates are very suitable here as they offer a very good pre-distribution and a high specific surface area.

Product	Description	Metal content (%)	Humidity (%)	FFA (%)	Sieve residue (%)	Melting point (°C)
LIGASTAR ZN 101 CG	Zinc salt of stearic acid	10.5-11.0	max. 0.5	max. 1.0	> 71 µm max. 1.0	118-123
LIGASTAR ZN 101/7	Zinc salt of stearic acid	10.5-11.3	max. 0.5	max. 1.0	>45 µm max. 2 .0	118-122
LIGASTAB ZN 70	Zinc salt of stearic acid	10.4-11.2	max. 0.5	max. 1.5	> 150 µm max. 0.2	118-126
LIGASTAR CA 350	Calcium salt of stearic acid	6.3-7.0	max. 3.5	max. 0.8	> 71 µm max. 2.0	140-160
LIGASTAR CA PSE/S2	Calcium salt of stearic acid	7.0-7.7	max. 3.0	max. 1.0	> 45 µm max. 3.0	140-160

Product	Description	AV (mg KOH/g)	SV (mg KOH/g)	OHV (mg KOH/g)	Melting point (°C)
LIGALUB SH	Special fatty acid	195-205	198-208	-	55-64
LIGALUB SR	Special fatty acid	194-212	-	-	57-64

For the choice of the right stearate it has to be considered that there might be an influence on the viscosity of the mass. The viscosity decreases with higher particle size (see fig. 17).



However, the dosage of stearates with smaller particle size is lower, therefore an opposite effect can be observed.



ENGINEERING PLASTICS

Engineering plastics represent a group of thermoplastics, which differ from standard plastics in mechanical and technical characteristics or chemical stability. Especially efficient polymers are listed together in the subgroup of "high performance polymers". In many cases the mechanical properties are optimized by the addition of glass fibres. Representatives of engineering plastics are for example:

Polystyrene (PS/EPS)

This is a thermoplastic polymer that becomes soft while heating and is converted to semi-finished products like films or transparency films as well as a large range of finished products. Polystyrene has a comparatively good thermal stability and mostly gets along without stabilizers. This is not the case for co-polymers, therefore the use of antioxidants is required. The use of olechemical additives is limited to the range of lubricants and mould release agents, which have to be added to the plastic mainly to guarantee an optimal processability. The influences of lubricants are similar to those seen with PVC.

Acrylonitrile-butadiene-styrene-copolymer (ABS)

This is a non-transparent thermoplastic polymer material made from the monomers acrylonitrile, 1,3 butadiene and styrene. Strong and enduring, even under low temperatures, it offers a high resistance against heat and chemicals and it is easy to process.

Polycarbonate (PC)

The term polycarbonate describes a polymer which is put together out of many identical unities of bisphenol A connected through carbonate compounds in its basic structure. Polycarbonate is moulded in the desired form by melting or under pressure into a form or matrix.

Polyethylene terephthalate (PET) / polybutylene terephthalate (PBT):

PET and PBT also belong to the polyesters. They are characterized by their breaking strength and high temperature resistance. Pentaerythritol esters can be used as processing aids. As PET and PBT are often used for applications with food contact, the additives also need to be approved accordingly. We have a food contact notification of the FDA (FCN 001963) at our disposal for our saturated pentaerythritol esters.

Polyamide (PA)

Polyamides are macromolecules where monomers are interlinked by amide bonds or peptide formation. Natural polyamides are peptides or proteins like hair, wool, silk and egg albumen. Synthetically produced, long-chain aliphatic polyamides are also called nylon after the first pure synthetic fibre, which was brought to market by Du Pont in 1939.

Polymethylmethacrylate (PMMA)

PMMA is a synthetic, glass-like thermoplastic material and arises as the result of polymerization of monomeric methacrylic acid methyl ester.



Product portfolio for engineering plastics

Product	PS/EPS	ABS	PC	PET/PBT	PA	PMMA
LIGASTAR CA 600			Ö		Ö	Ŭ
LIGASTAR ZN 101/6	Ö	Ö	Ö		Ö	Ö
LIGASTAR ZN 104 FG	Ö	Ö	Ö		Ö	Ö
LIGASTAR MG 700	Ö					
LIGASTAR AL D2	Ö	i i i i i i i i i i i i i i i i i i i	Ö		Ö	Ŭ
LIGASTAR AL TR			Ö		Ö	Ŭ
LIGASTAR NA R/D			Ö		Ö	Ö
LIGASTAR KA M	Ö					Ö
LIGALUB SH	Ö					Ö
LIGALUB FSO	Ö	Ö			i i i i i i i i i i i i i i i i i i i	Ö
LIGALUB 9 GE-H					i i i i i i i i i i i i i i i i i i i	Ö
LIGALUB GT		i i i i i i i i i i i i i i i i i i i				
LIGALUB 11 GE	Ö					
LIGALUB 11 GE-V	Ö					
LIGALUB 11 GE/50-V	Ö	i i i i i i i i i i i i i i i i i i i				
LIGALUB 11 GE/90-V	-ÖF		Ö			Ö
LIGALUB 36 FE	Ű		Ö			Ö
LIGALUB 50 PE	Ö		Ö	Ö	Ö	
LIGALUB 55 PE		Ö	Ö	Ö	Ö	Ö
LIGALUB 70 KE	Ö	Ö	Ö	Ö	Ö	
LIGALUB 71 KE		Ö		Ö	Ö	
LIGALUB 78 KE		Ö			Ö	



Peter Greven GmbH & Co. KG Peter-Greven-Straße 20–30 · 53902 Bad Muenstereifel, Germany Phone +49 2253 313 -0 · Fax +49 2253 313 -134 eMail sales@peter-greven.com · www.peter-greven.com