



PETER GREVEN Your partner for plastic additives

P E T E R 
GREVEN
Your partner for oleochemicals

The background of the page is a composite image. The top left shows a microscopic view of a plant cell with a green cytoplasm and a brown nucleus. The bottom left shows a close-up of a green leaf with a large, clear dew drop. A blue curved shape separates the top left from the rest of the page.

PETER GREVEN Your partner for plastic additives

LIGASTAR®

Metallic Soaps

LIGALUB®

Ester Lubricants

LIGASTAB® Metallic Soaps & Preblends

Sustainability and the demand for renewable raw materials are becoming more and more important in many areas. Peter Greven as a middle-sized family owned company has always produced additives based on renewable raw materials and can look back to a long experience with these raw materials and associated production technologies. This is the basis for the continuous development of new products and customized solutions for various applications.

The plastic industry offers numerous possibilities for the use of our products and is therefore one of our most important divisions.

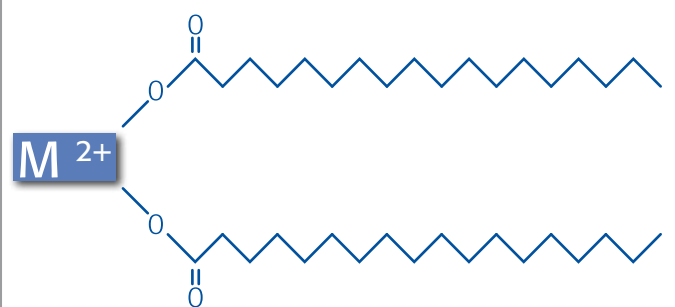


METALLIC SOAPS Technical introduction

Metallic soaps are salts of fatty acids, especially of stearic acid. Often metallic soaps are called all-round talents as they can be used in many different applications and offer several advantages:

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

Fig. 1: Composition and structure of Metallic Soaps



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

Production process of metallic soaps

	Indirect conversion (wet process)	Direct conversion (semi-wet process)	Melting 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
Properties & Advantages	· 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 melting · low salinity



ESTERS Technical introduction

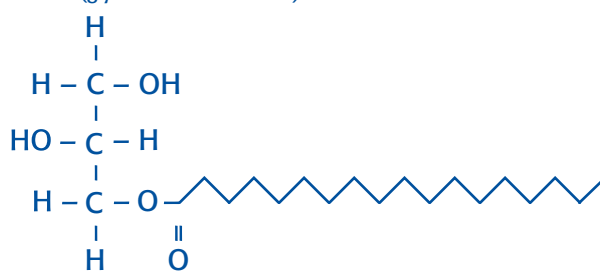
Esters comprise a group of chemical compounds that are formed through the reaction of an acid (e.g. stearic acid, oleic acid) and an alcohol (e.g. glycerin, pentaerythritol).

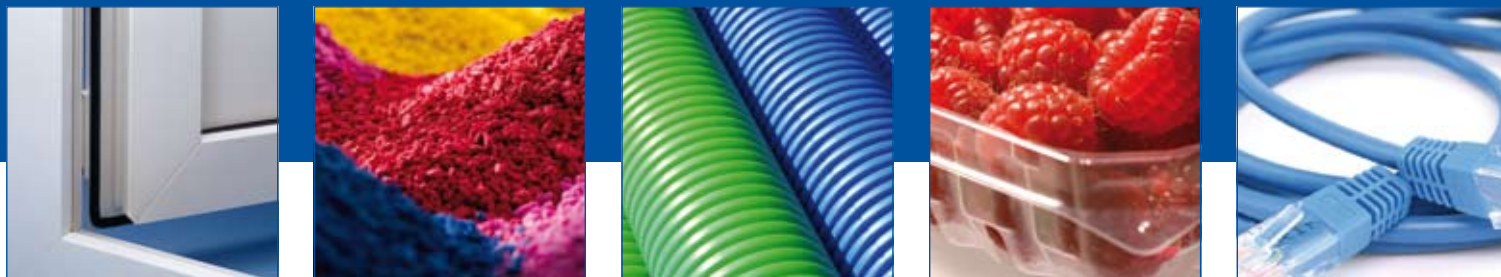
Esters are – like metallic soaps – essential additives in the plastics industry. Their effects and properties are based upon the different characteristics of the functional groups and non-polar parts as well as their ratios.

Esters with short-chain hydrocarbon chains exhibit solvent properties, like diethyl adipate for example. The extension of the hydrocarbon chains results in waxy products. One example is stearyl stearate, which is used as 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 glycerin 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 glycerin monooleate or PEG 400 monooleate are used as antifogging agents in PVC. Glycerin monostearate is used as antistatic agent for polyolefins or in stabilizing the foam structure of EPS.

Fig. 2: Composition and structure of an ester
(glycerol monostearate)





1. PVC a) 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 acid, alkali, alcohol, oil and petrol.

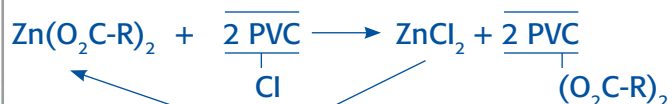
PVC is difficult to convert and processing additives are needed to improve the melting viscosity and the flow property of PVC. Furthermore stabilizers are needed for the processing of PVC. Peter Greven has been producing and developing metallic soaps, lubricants and preblends that are used in the PVC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

1. a) 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. The reaction process of PVC stabilization is shown in the following figure:

Fig. 3: Reaction process of PVC stabilization

Zinc salt acts as primary PVC stabilizer (substitution of labile chlorine atoms)



Resulting ZnCl_2 is a Lewis acid and accelerates the PVC degradation.
Ca/Zn synergy is coming from the zinc regeneration through calcium salt.



Calcium salt is able to catch HCl and resulting CaCl_2 is neutral towards PVC degradation

For the selection of the right metallic soap the particle size is of great importance. Therefore, Peter Greven offers a broad portfolio of different metallic soaps.

Figure 4 and 5 present some products in relation to the degree of fineness:

Fig. 4: Different calcium stearate types with particle size

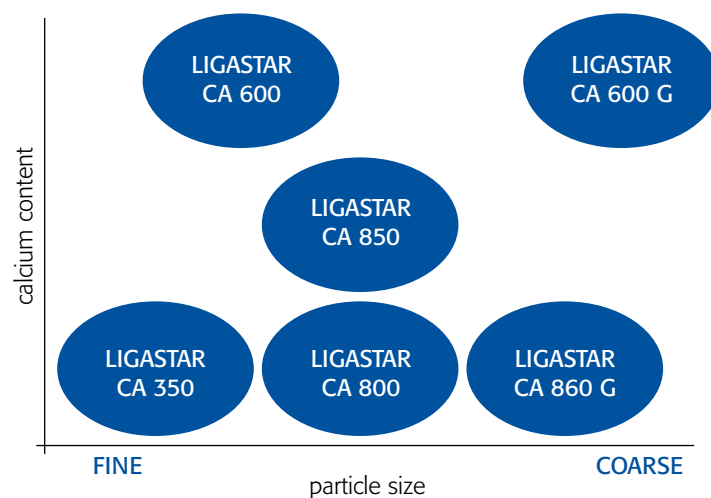
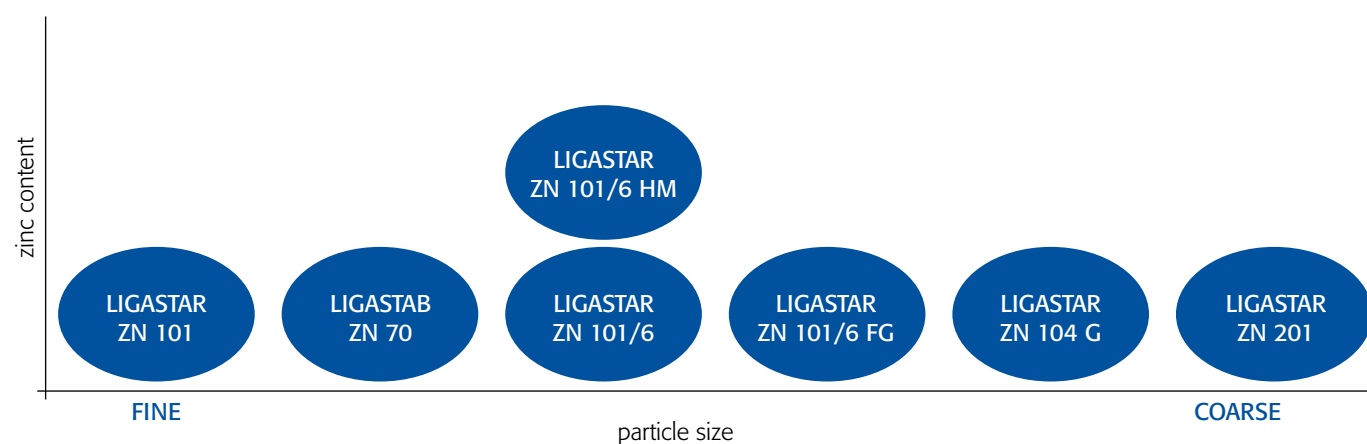


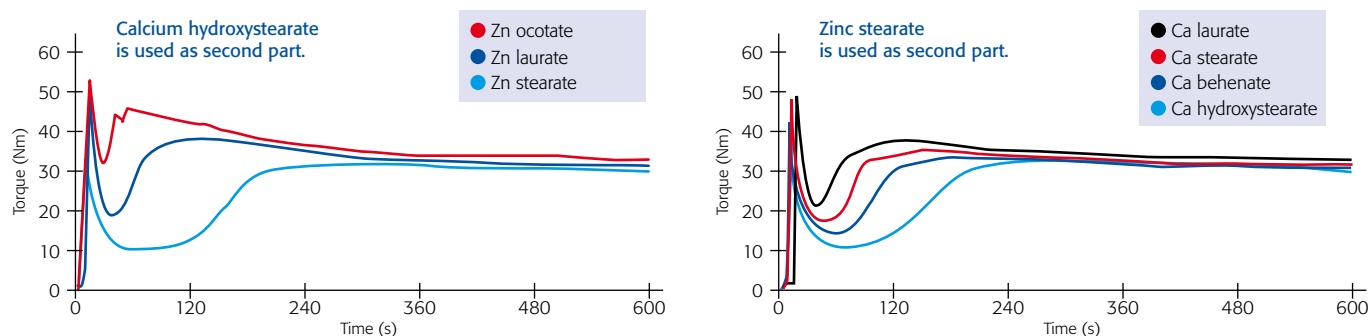
Fig. 5: Different zinc stearate types with particle size



1. PVC a) METALLIC SOAPS

Evaluation of metallic soaps in Ca/Zn PVC profile formulations

Fig. 6: Influence of fatty acid chains on gelation



The shorter the chain length, the faster the gelation.

Fig. 7: Variation of Ca/Zn formulations

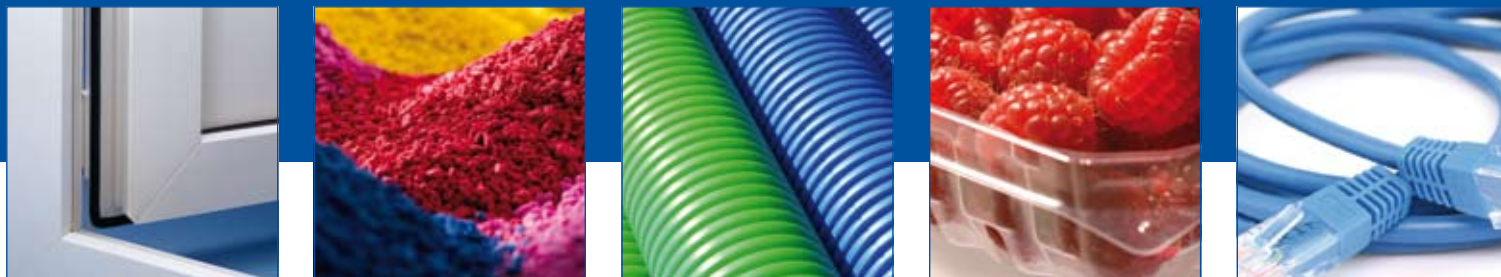
Variation in formulation	CA 12 OXY 0,5 phr ZN 101/6 1,5 phr	CA 12 OXY 0,7 phr ZN 101/6 1,3 phr	CA 12 OXY 1 phr ZN 101/6 1 phr	CA 12 OXY 1,3 phr ZN 101/6 0,7 phr	CA 12 OXY 1,5 phr ZN 101/6 0,5 phr
Ca/Zn	0,2	0,32	0,6	1,12	1,8
Mass T°C at die entrance (°C)	178	179	179	180	181
Pressure 18 D (Bar)	8	12	23	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	< 3	max. 1	> 45 µm max.3	150-160
LIGASTAR CA 600 G	Calcium salt of stearic acid	7,0-7,9	< 3	max. 1	-	145-160
LIGASTAR CA 12 OXY	Calcium salt of hydroxy stearic acid	6,5-7,1	< 3	max. 1	-	140-147
LIGASTAB CAL	Calcium salt of lauric acid	8,6-10,0	< 3	max. 1	-	-
LIGASTAR ZN 101/6	Zinc salt of stearic acid	10,5-11,3	< 0,5	max. 1	> 45 µm max. 2	118-122
LIGASTAR ZN 101/6 FG	Zinc salt of stearic acid	10,5-11,3	< 0,5	max. 1	> 1000 µm max. 1	118-122
LIGASTAR ZN 104 G	Zinc salt of stearic acid	10,5-11,3	< 0,5	max. 1	> 1000 µm max. 1	118-122
LIGASTAB ZN 108	Zinc salt of short chain fatty acids	16,0-19,0	< 1	max. 2	> 45 µm max. 5	max. 140
LIGASTAB ZN 108 FG	Zinc salt of short chain fatty acids	16,0-19,0	< 1	max. 2	> 1000 µm max. 1	max. 140
LIGASTAB ZN 108 S	Zinc salt of short chain fatty acids	16,0-19,0	< 1	max. 2	-	max. 140
LIGASTAB ZNL	Zinc salt of lauric acid	13,0-15,0	< 0,5	max. 1	-	-
LIGASTAR MG 700	Magnesium salt of stearic acid	4,1-5,0	< 6	max. 2	-	145-160
LIGASTAB BA 610	Barium salt of stearic acid	18,8-20,9	< 1	max. 1	> 150 µm max. 1	-



1. PVC b) 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

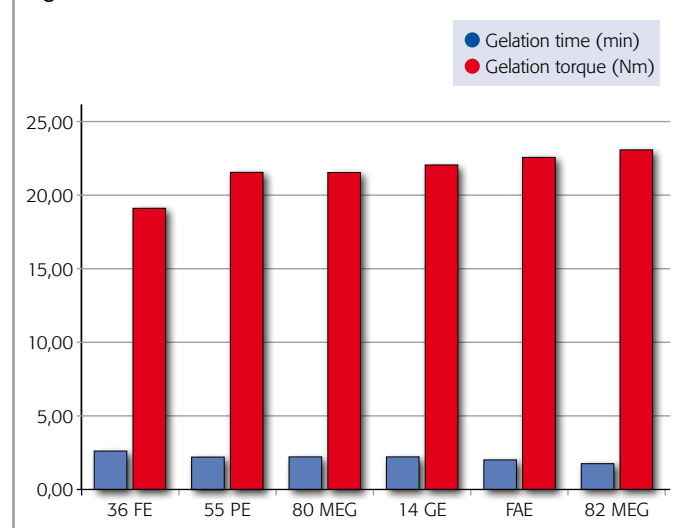
- Improved compatibility due to polar groups in the C-chain
- No formation of single lubricant phases
- Decrease the softening temperature of PVC
- Acts as macromolecular binder

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 8:

Fig. 8: Gelation behaviour of selected ester lubricants

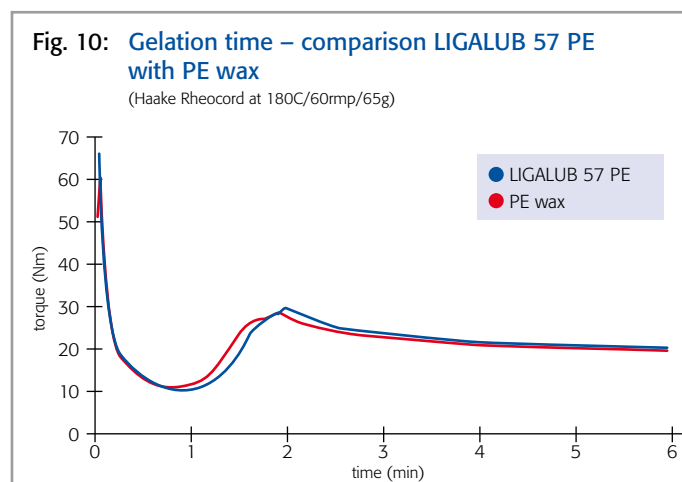
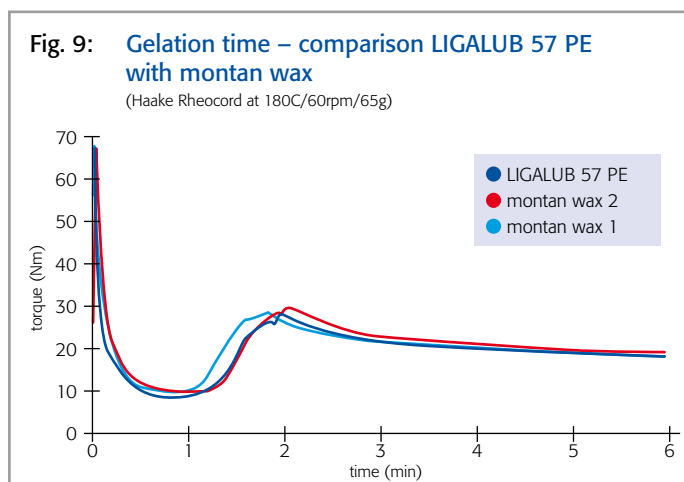


Beside the lubricants shown in figure 8 a further lubricant is highlighted:

LIGALUB 57 PE is an external lubricant for the processing of unplasticized PVC, e.g. for the production of pipes and profiles. It improves the surface gloss and the finish. **LIGALUB 57 PE** shows a very good compatibility in PVC due to polar groups and so shows a low tendency

for plate out. Moreover it offers very high external lubrication effects. By using this ester lubricant, the dosage of other typical external lubricants such as montan or PE waxes can be reduced.

Figure 9 compares **LIGALUB 57 PE** to montan wax and figure 10 shows **LIGALUB 57 PE** in comparison to PE wax.



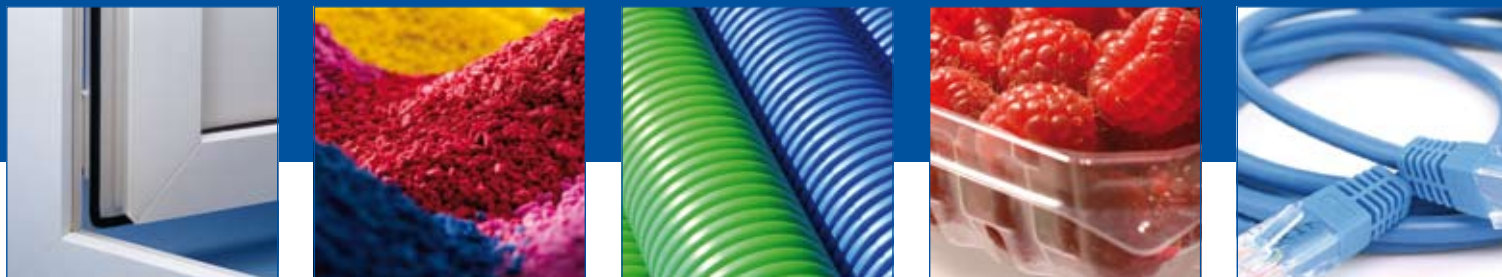
1. PVC b) LUBRICANTS

Product portfolio of ester lubricants for PVC incl. Applications

Chemical Type	Product	Physical form	AV	SV	OHV	Melting range	Function		Profiles, Sheets	Pipes	
		solid/liquid	(mg KOH/g)	(mg KOH/g)	(mg KOH/g)	(C°)	internal	external			
Fatty Acid	LIGALUB SH	solid	195-205	198-208	-	55-64		**	•	•	
	LIGALUB FSO	solid	172-185	180-192	min. 150	71-80		*	•	•	
Glycerol Esters	LIGALUB 9 GE-H	solid	max. 5	175-185	min. 155	84-88	****		•	•	
	LIGALUB 10 GE	liquid	max. 1	160-170	-	-	****				
	LIGALUB 11 GE	solid	max. 1	160-175	-	54-65	****		•		
	LIGALUB 12 GE	liquid	max. 1	176-184	-	-	****		◦		
	LIGALUB 14 GE	solid	max. 2	180-190	-	53-58	*****		•	•	
	LIGALUB GT	solid	max. 2	195-205	-	57-65	*	***	•	•	
Alcohol Esters	LIGALUB 36 FE	solid	max. 2	100-115	-	50-60	**	***	•	•	
	LIGALUB 37 FE	solid	max. 2	93-105	-	60-73	*	****	•		
	LIGALUB FAE	solid	max. 2	164-176	-	40-45	*****		•	•	
	LIGALUB 80 MEG	solid	max. 2	-	max. 14	65-75	****	*	•	•	
	LIGALUB 45 ITD	liquid	max. 1	110-120	max. 15	-	****		•		
Polyol Esters	LIGALUB 55 PE	solid	max. 2	165-180	105-135	49-56	***	**	•	•	
	LIGALUB 57 PE	solid	max. 3	-	max. 15	63-70		*****	•	•	
Complex Esters	LIGALUB 70 KE	solid	max. 15	270-280	-	50-60	*	****	•		
	LIGALUB 71 KE	liquid	max. 3	250-260	-	-	**	***			
	LIGALUB 74 KE	solid	max. 12	245-260	-	77-85	**	***	•	•	
Blend	LIGALUB 78 KE	solid	max. 12	-	-	100-120	*	***	•	•	
	LIGALUB 121 KE	solid	max. 1,5	120-150	-	60-72			•	•	



PVC-U				PVC-P				Stabilizer			
	Injection Moulding	Bottle	Film	Extrusion	Calender	Injection Moulding	Plastisol	Calcium/Zinc	Lead	Tin	Barium/Zinc
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1. PVC _c) PREBLEND S

LIGASTAB PREBLEND S 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

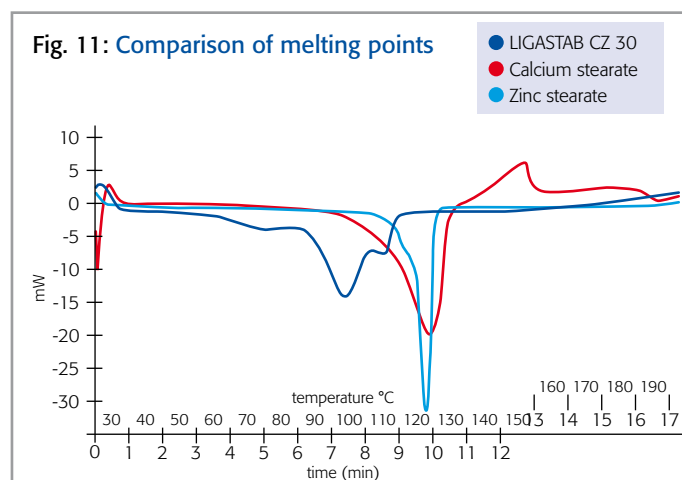
This flaked preblend is a mixture of calcium and zinc soaps of selected fatty acids. It is used in stabilizing systems for PVC and offers very good compatibility in PVC.

LIGASTAB CZ 30

This dust free preblend is a mixture of calcium and zinc soaps of stearic acids and is used in stabilizing 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 in comparison to lead stabilizers a preblend of calcium and zinc soaps in the melt process is an advantage. 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. 11):



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.

2. SMC/BMC

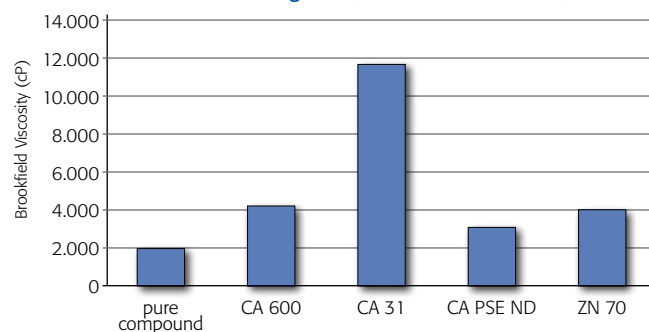
Fibre-reinforced plastics (SMC, BMC)

Fibre-reinforced plastics are moulding compounds which consist of unsaturated urea, melanin or phenolic resin. In addition mineral fillers, fibre glass some processing aids and additives are included. One differentiates 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 processing. Often zinc stearate is 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.

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

Fig. 12: Brookfield viscosity before and after addition of different release agents (concentration 1,23 wt%)



Product	Description	Metal content (%)	Humidity (%)	FFA (%)	Sieve residue (%)	Melting point (°C)
LIGASTAR ZN 101 CG	Zinc salt of stearic acid	10,5-11,0	< 0,5	max. 1	> 71 µm max. 1	118-123
LIGASTAR ZN 101/7	Zinc salt of stearic acid	10,5-11,3	< 0,5	max. 1	> 45 µm max. 2	118-122
LIGASTAB ZN 70	Zinc salt of stearic acid	10,4-11,2	< 0,5	max. 1,5	> 150 µm max. 0,2	118-126
LIGASTAR CA 350	Calcium salt of stearic acid	6,3-7,0	< 3,5	max. 0,8	> 71 µm max. 2	150-160
LIGASTAR CA 600	Calcium salt of stearic acid	7,0-7,7	< 3,0	max. 1	> 45 µm max. 3	150-160
LIGASTAR CA 850	Calcium salt of stearic acid	6,8-7,5	< 3,0	max. 1	> 71 µm max. 1	145-160

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

3. POLYOLEFINS

Next to PVC the Polyolefins constitute one of most important plastics today. Due to their good chemical consistency and electrical insulation characteristics polyolefins are used in many different applications. Some of their main fields of applications are films (for packaging), household goods, transport containers, sheets, pipes and fibers.

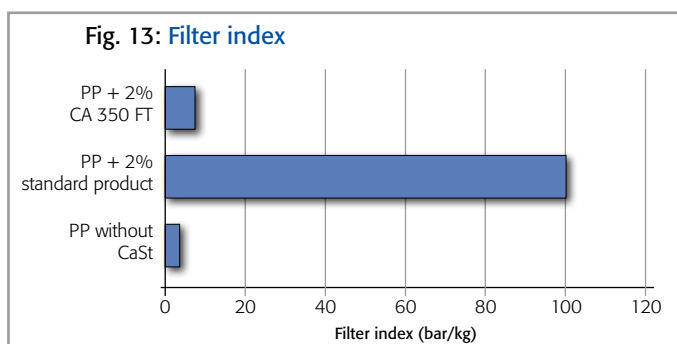
As with PVC, Polyolefins belong to the thermoplastics which can be processed in specific temperature ranges. However they are easier to process than PVC, as they offer a very good thermal stability with absence of oxygen. Due to the catalysts used metallic soaps are used as additional additives.

Metallic soaps in polyolefins

For the stabilization of polyolefins predominantly antioxidants are used. However, most catalysts 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 0,2% calcium or zinc stearate are added to the formulation. Calcium stearate is especially suitable as it has a higher chemical affinity to chloride.

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 polypropylene 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. The following graph (fig. 13) shows the filter indices of different calcium stearates.





Product portfolio of metallic soaps for polyolefin industry

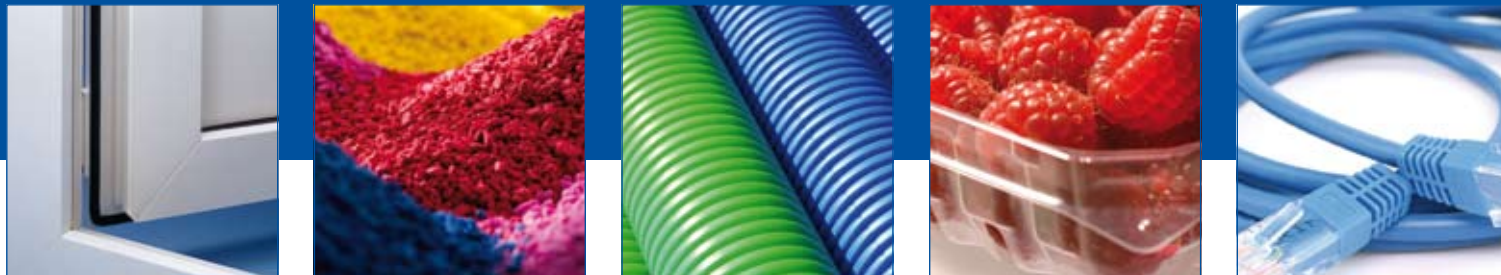
Product	Description	Metal content (%)	Humidity (%)	FFA (%)	Sieve residue (%)	Melting point (°C)
LIGASTAR CA 350	Calcium salt of stearic acid	6,3-7,0	< 3,5	max. 0,8	> 71 µm max. 2	150-160
LIGASTAR CA 350 FT	Calcium salt of stearic acid	6,3-7,0	< 3,5	max. 0,8	> 71 µm max. 1	150-160
LIGASTAR CA 800 / CA 860	Calcium salt of stearic acid	6,5-6,9	< 3,0	max. 0,8	> 71 µm max. 2	145-160
LIGA CALCIUM STEARATE CPR-2-V	Calcium salt of stearic acid	6,7-7,5	< 3,0	max. 0,5	325 mesh max. 1	140-150
LIGA CALCIUM STEARATE CPR-5	Calcium salt of stearic acid	6,4-7,2	< 3,0	max. 0,5	325 mesh max. 1	140-150
LIGASTAR ZN 101/6	Zinc salt of stearic acid	10,5-11,3	< 0,5	max. 1	> 45 µm max. 2	118-122
LIGASTAR ZN 101 CG	Zinc salt of stearic acid	10,5-11,0	< 0,5	max. 1	> 71 µm max. 1	118-123
LIGA ZINKSTEARAT ZPR-2-V	Zinc salt of stearic acid	10,4-11,2	< 1,0	max. 1,5	200 mesh max. 1	115-125

Lubricants 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/50** and **LIGALUB 11 GE/90** are preferred as antistatic agents.

Product portfolio of lubricants for polyolefin industry

Product	Description	AV [mgKOH/g]	SV [mgKOH/g]	OHV [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	min. 155	84-88
LIGALUB 11 GE	Glycerol ester	max. 1	160-175	-	54-65
LIGALUB 11 GE/50	Glycerol ester	max. 5	-	-	57-65
LIGALUB 11 GE/90	Glycerol ester	max. 5	-	-	60-70
LIGALUB 55 PE	Polyol ester	max. 2	165-180	105-135	49-56
LIGALUB 70 KE	Complex ester	max. 15	270-280	-	50-60
LIGALUB 71 KE	Complex ester	max. 3	250-260	-	-
LIGALUB 78 KE	Blend	max. 12	-	-	100-120



4. ENGINEERING PLASTICS (high-performance plastics)

Engineering plastics represent a group of thermoplastic, which differ in mechanical and technical characteristics or chemical stability from standard plastics. 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 (poly) 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.

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 the application in engineering plastics

Product	PS/EPS	ABS	PC	PA	PMMA
LIGASTAR CA 600					
LIGASTAR CA 850					
LIGASTAR ZN 101/6					
LIGASTAR ZN 104 G					
LIGASTAR MG 700					
LIGASTAR AL D2					
LIGASTAR AL TR					
LIGASTAR NA R/D					
LIGASTAR KA M					
LIGALUB SH					
LIGALUB FSO					
LIGALUB 9 GE-H					
LIGALUB GT					
LIGALUB 11 GE					
LIGALUB 11 GE/50					
LIGALUB 11 GE/90					
LIGALUB 36 FE					
LIGALUB 37 FE					
LIGALUB 50 PE					
LIGALUB 55 PE					
LIGALUB 70 KE					
LIGALUB 71 KE					
LIGALUB 78 KE					



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