POLYOLEFIN ADDITIVES 2018 Conference – Cologne (Germany)

Selecting metal soaps for optimum acid scavenging performance in polyolefin

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Peter Greven GmbH & Co. KG

1. Introduction Peter Greven
2. Metal soaps
   - Production methods and their influence on the application as acid scavenger
   - Starting materials and their influence
3. Market trends and resulting selection of the raw materials
   - Tallow based versus vegetable based metal soaps
4. Conclusions

Introduction Peter Greven – Fact Sheet

Family owned company founded in 1923.

Leading producer of oleo-chemicals with more than 90 years of experience.

Product portfolio including metallic and alkaline soaps, esters and dispersions.

Four production sites spread among three continents.

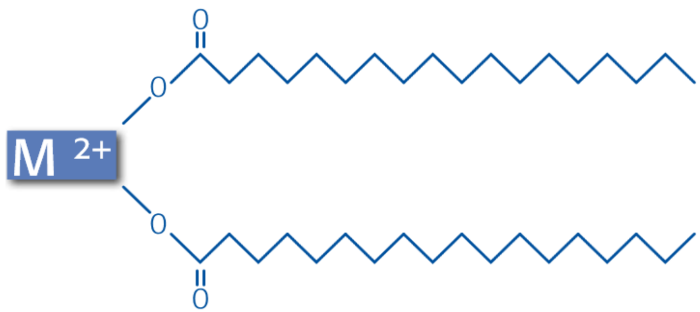
Development of customer specific solutions as core competence.

High importance of of sustainable business management.

Introduction Peter Greven – Well Positioned Globally

Peter Greven supplies customers in more than 85 countries!

Metal soaps – general information



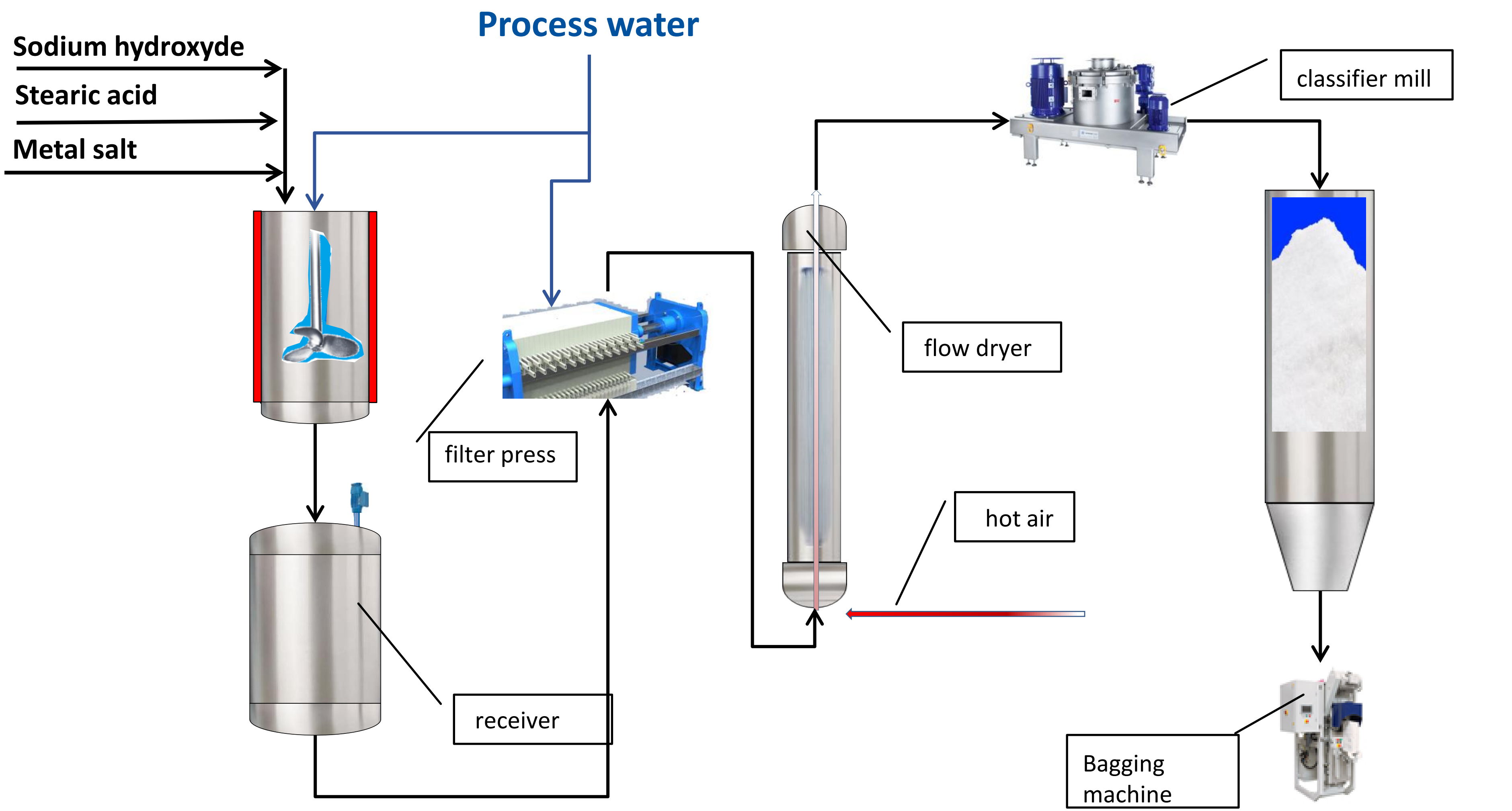
Inorganic part

- Calcium / Zinc
- Influence on
  - Melting point
  - Solubility / compatibility
- General influence on
  - Stabilisation
  - Melt viscosity

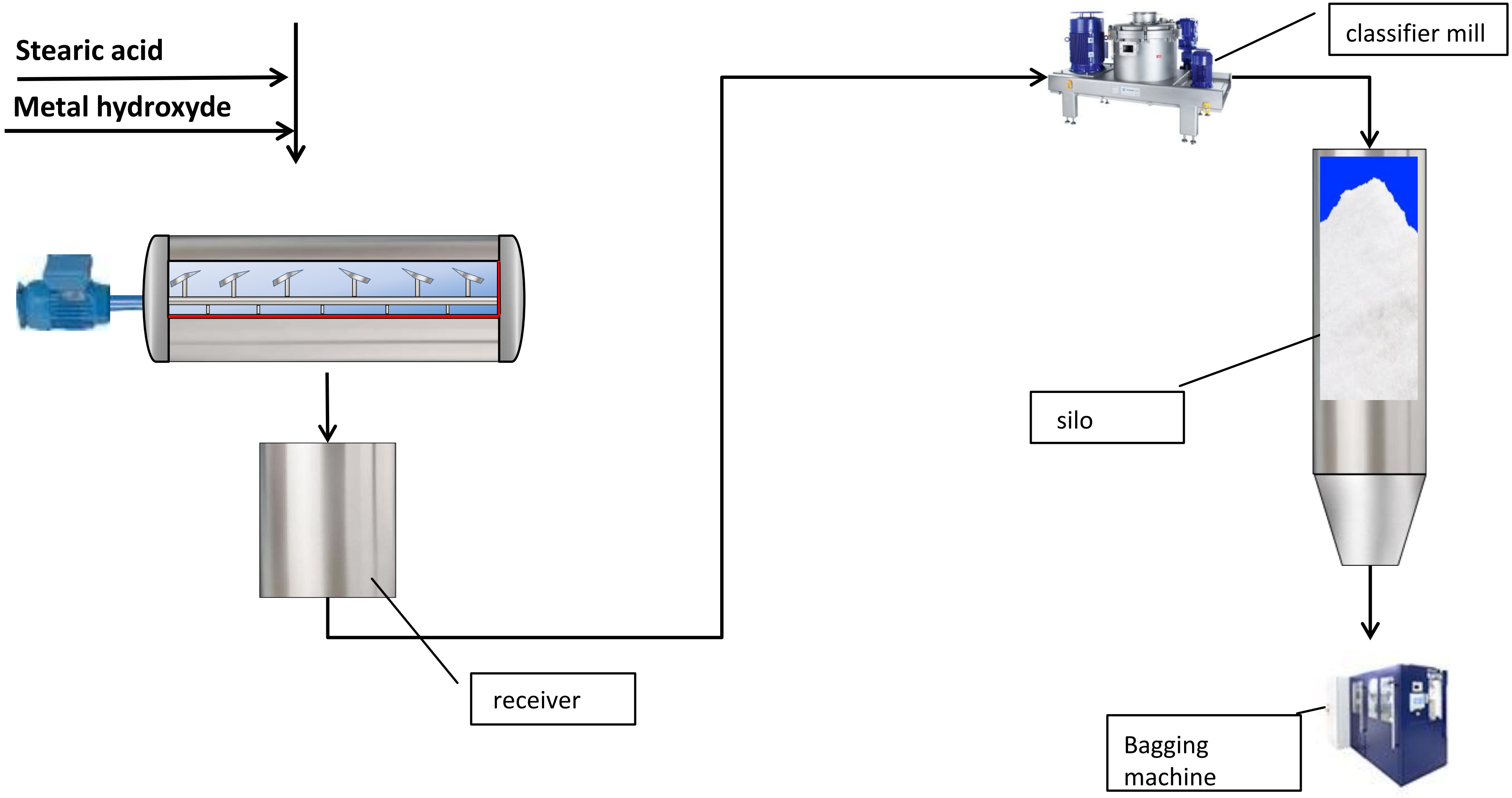
Organic part

- Fatty acids of different chain length and functional groups
- Influence on
  - Melting point
  - Solubility / compatibility
- General influence on
  - Lubricant properties
  - Thermal stability

Metal soaps – production methods – precipitation process



Metal soaps – production methods – direct process

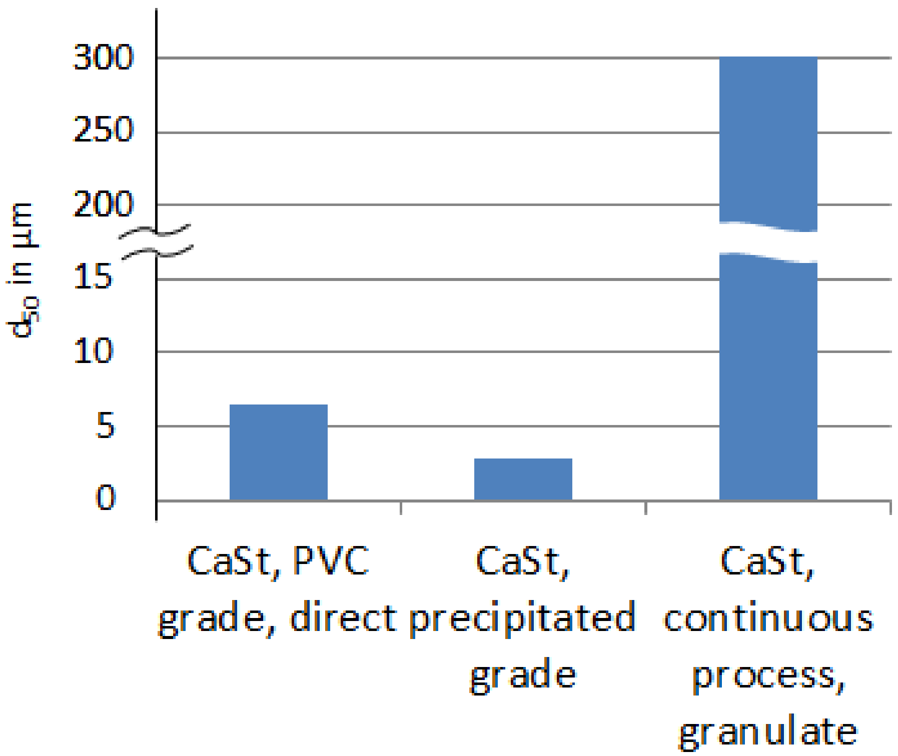


PETER GREVEN
Your partner for oleochemicals

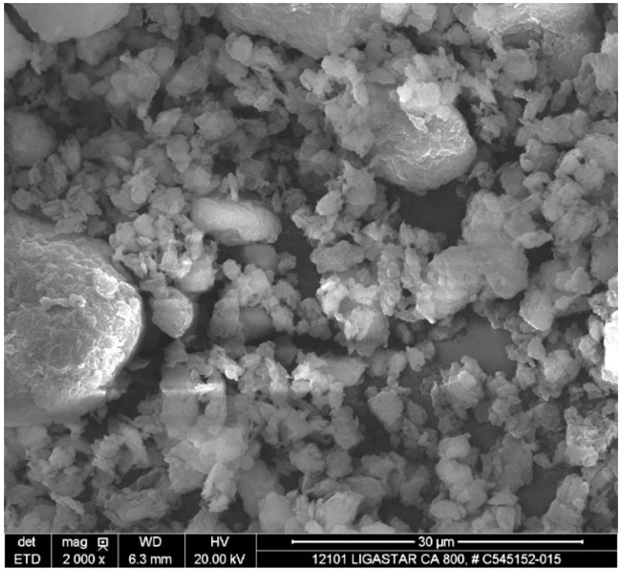
Metal soaps - different properties due to the production methods

	Precipitation process	Direct process	Melting process	COAD® process
Description	Two reaction steps: 1. Production of a soap 2. Precipitation of the metallic soap by adding the metal base	Metallic based 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 & 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	• Very suitable for the production of granules

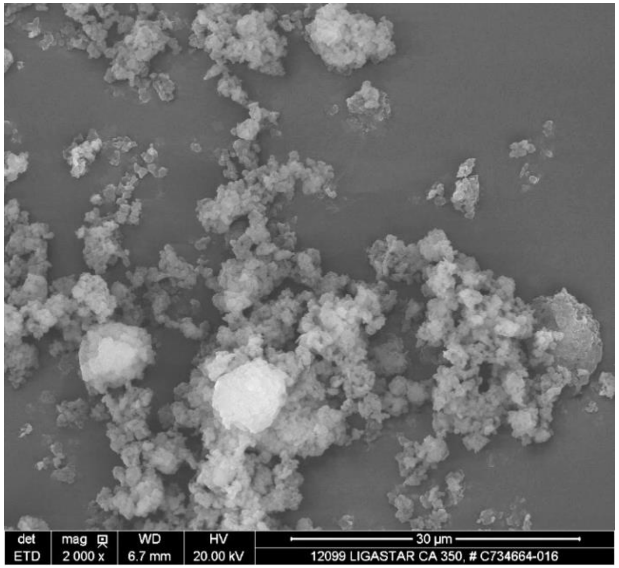
Metal soaps - different properties due to the production methods



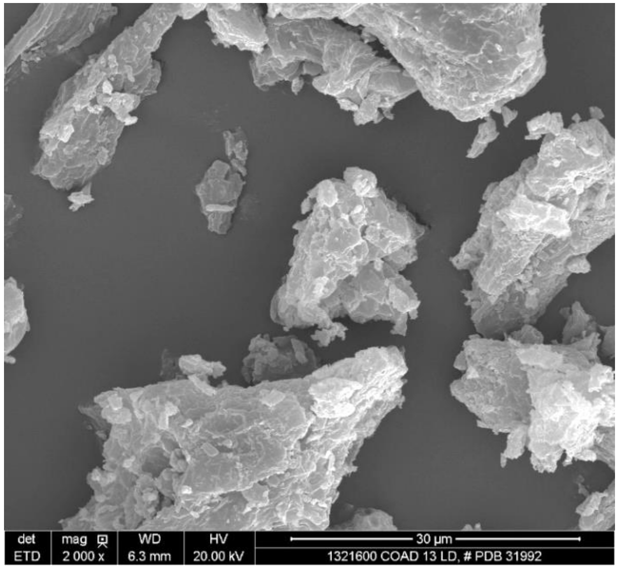
Metal soaps - different properties due to the production methods



CaSt, PVC grade, direct



CaSt, precipitated grade

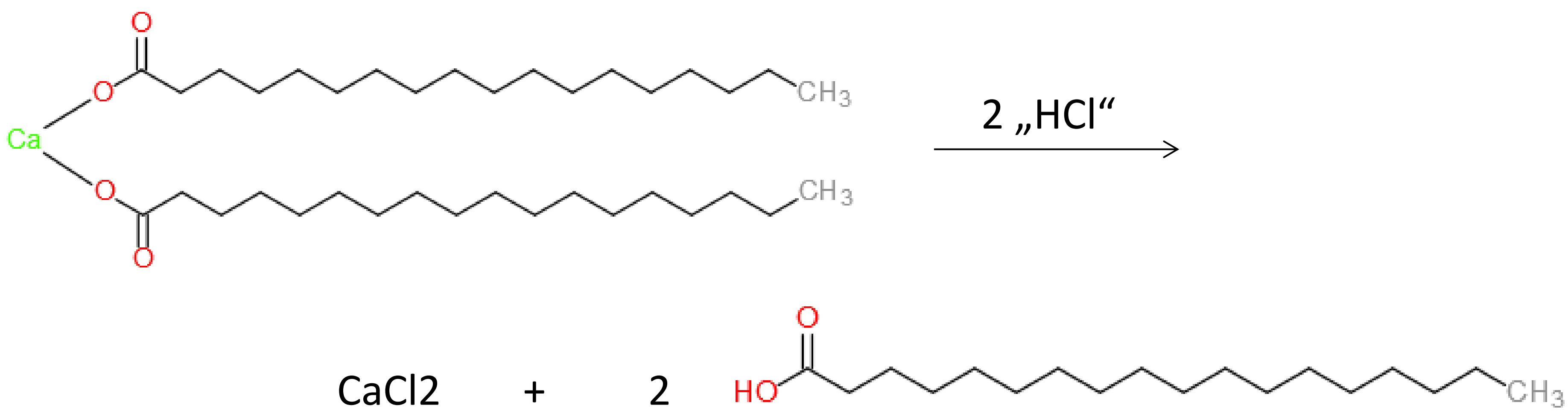


CaSt, continuous process, granulate

- Direct grade: “round“ particles
- Precipitated grade: fine particle, high specific surface, rough surface => formation of agglomerates
- Continuous process, granulate: bigger particles, very compact, layers

Metal soaps - Influence on their application as acid scavenger

- Theoretical aspects:
  - Catalyst residues may be present in Polyolefins
  - Such residues may contain chlorides => hydrochloric acid formation
  - Metal soaps act as acid scavenger in order to prevent corrosion (e.g.)



Metal soaps - Influence on their application as acid scavenger

- Corrosion tests:
  - Metal plates (S235JRC+C) were put into PP and placed in an oven for 3 h at 240 °C
  - After cooling the plates were removed from the PP and were hanged in a desiccator for 6 days.
  - Conditions in the desiccator: 21 °C; 91 % rel. humidity

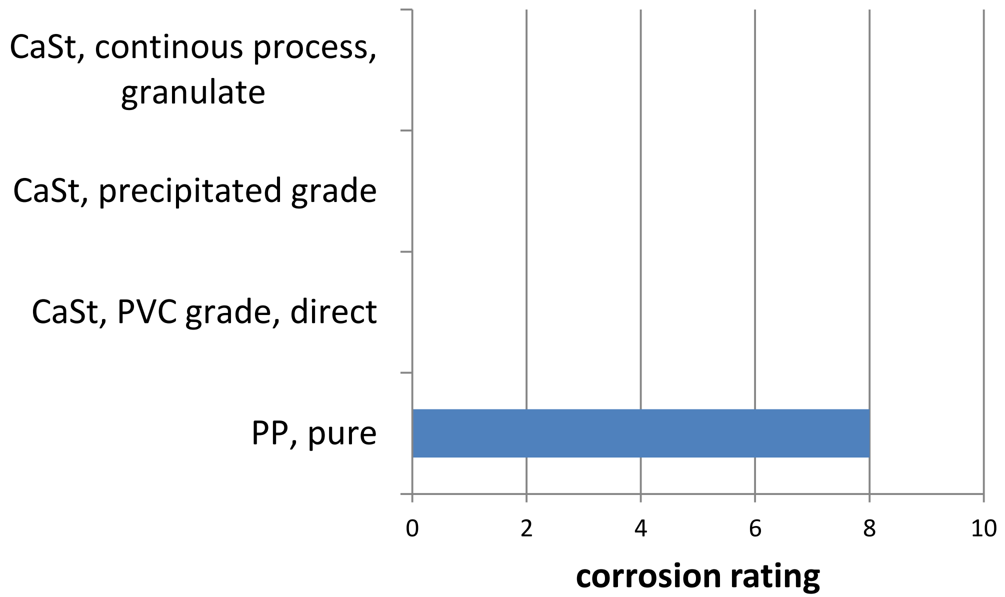
PP, pure

PP + 500 ppm CaSt

Ranking:
0: no corrosion
1: corrosion nearly not visible
2: very weak corrosion
3: weak corrosion
4: corrosion
5: …
6: …
7: …
8: surface nearly complete corroded

Metal soaps - Influence on their application as acid scavenger

- Corrosion tests:



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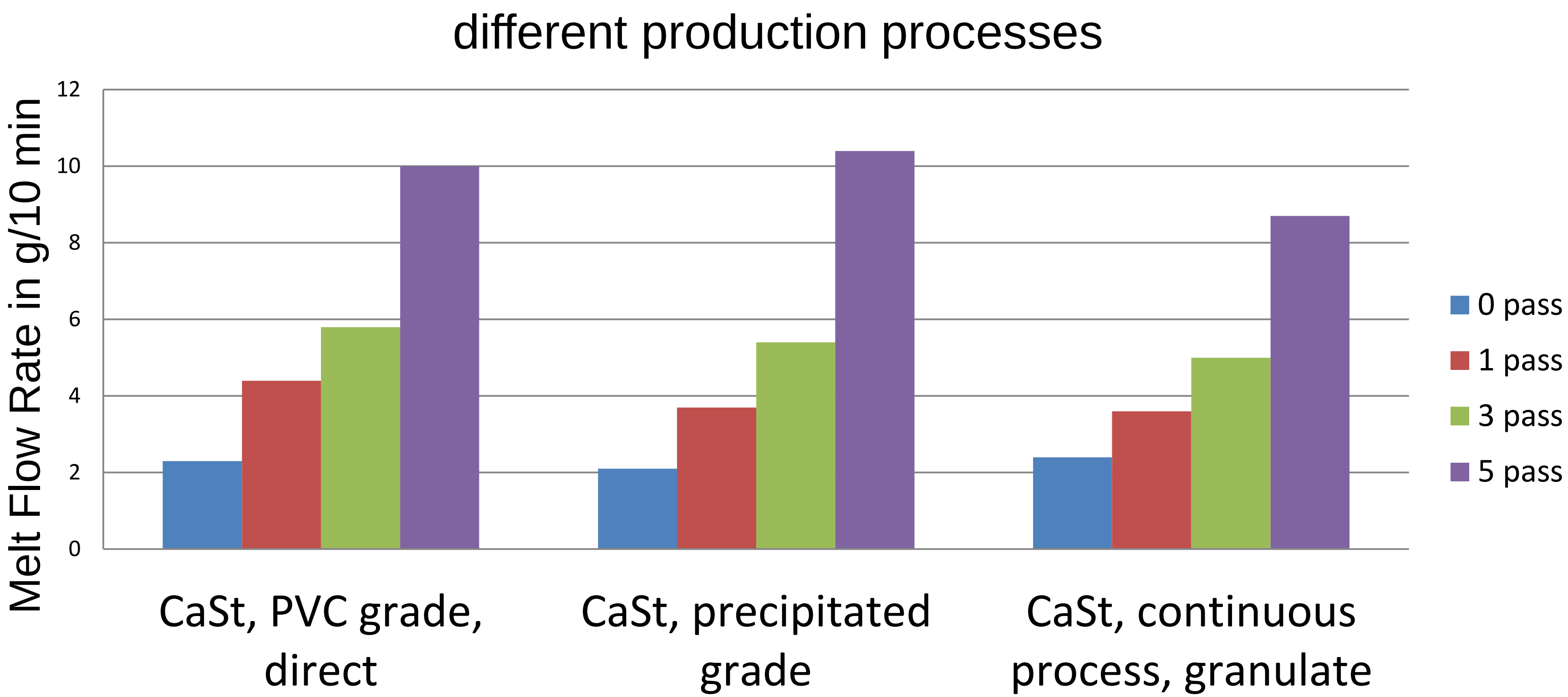
Metal soaps - Influence on their application as acid scavenger

- Test conditions:

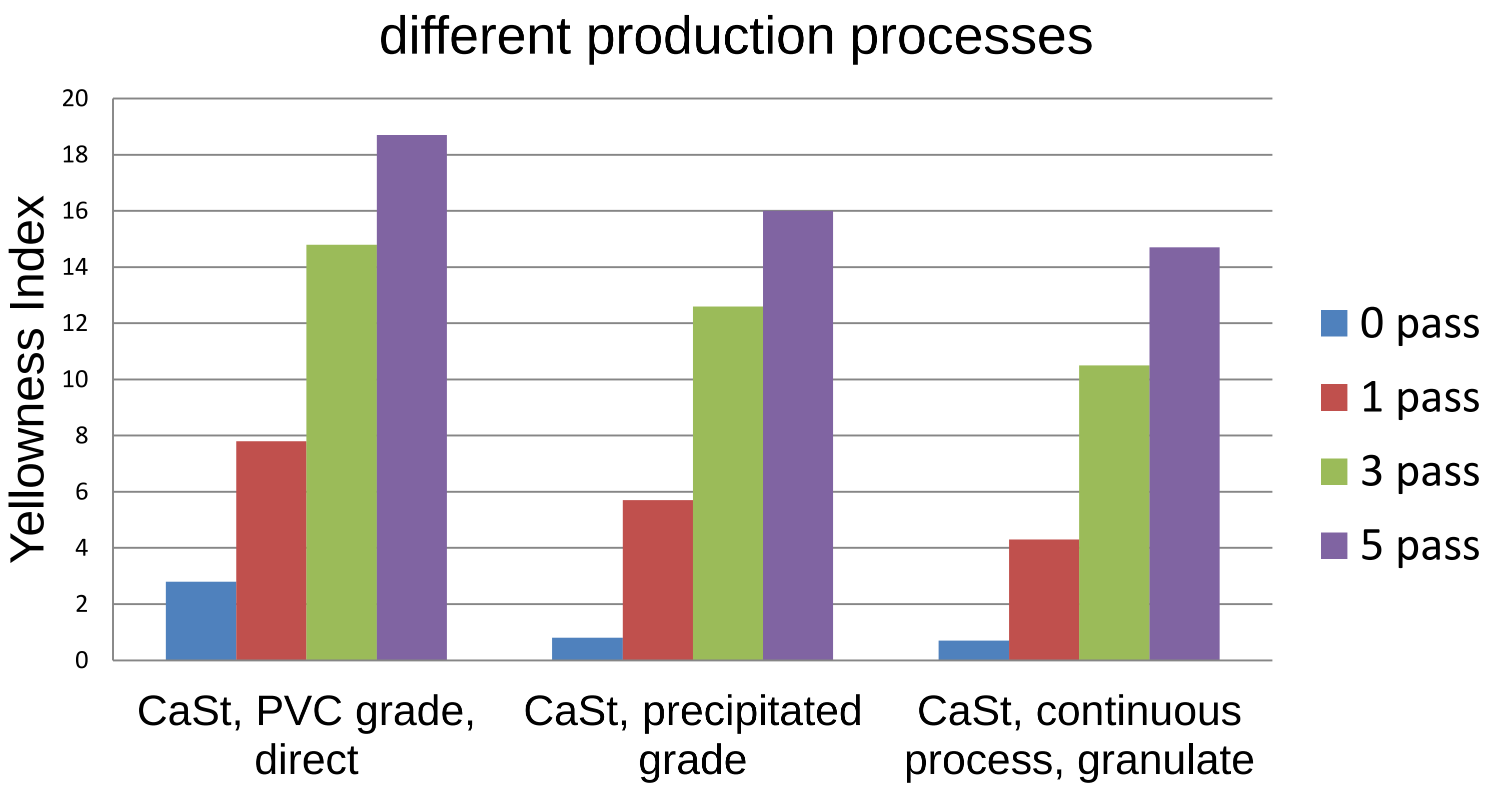
- Polymer: Unstabilised Spheripol PP-H, MFI 2
- 1500 ppm AO B215 (1:2 of 1010 / 168)
- 500 ppm Calcium Stearate
- Multiple extrusions on a PRISM 16 twin-screw extruder / L/D 25
- Atmosphere: Air
- Temperature: 260 °C
- Speed: 500 rpm

Metal soaps - Influence on their application as acid scavenger



- No significant difference between direct grade and precipitated grade.
- Calcium Stearate from the COAD process shows the lowest influence on MFR

Metal soaps - Influence on their application as acid scavenger



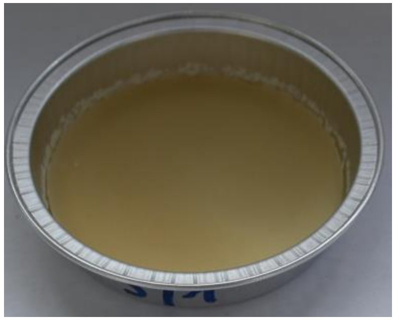
- Addition of 500 ppm CaSt, precipitated grade or continuous grade results in a low initial colour
- After 5 extrusion the sample with the continuous grade CaSt shows the lowest increase of the Yellowness Index

Metal soaps - Influence on their application as acid scavenger

- Thermal stability of the calcium stearates (samples were heated at 180 °C for 1 h under air

CaSt, PVC grade, direct

CaSt, precipitated grade

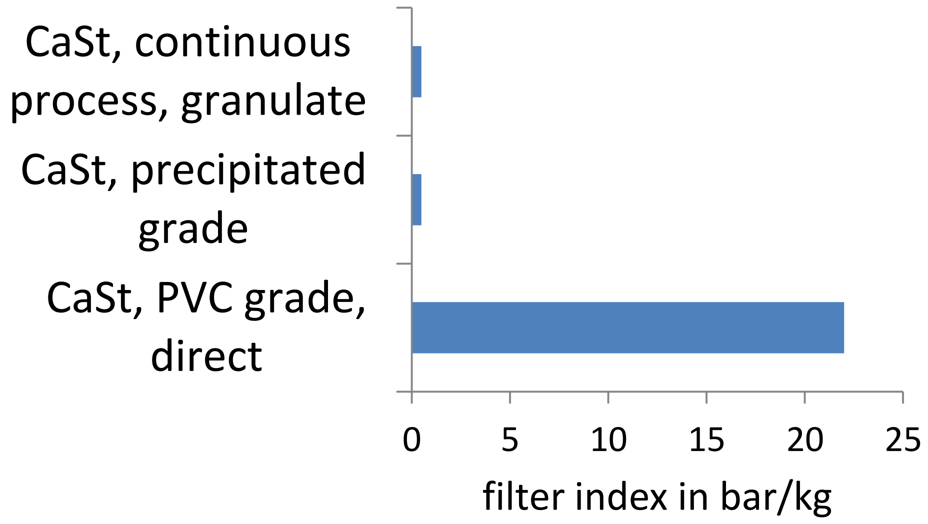


CaSt, continuous process, granulate

- Thermal stability of the Calcium stearate is dependant on the production process
- But has no significant influence on the YI

Metal soaps - Influence on their application as acid scavenger

- Specific purity-grade is required in special extrusion and molding applications
- The filter index (ISO 23900-5) is a criteria to select the suitable Calcium Stearates
- Filter pressure is defined as the increase of pressure per kg sample



- PVC grade is not suitable for Polyolefin
- The other CaSt yield good FI, independent from the production process

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   - **Starting materials and their influence**
3. Market trends and resulting selection of the raw materials
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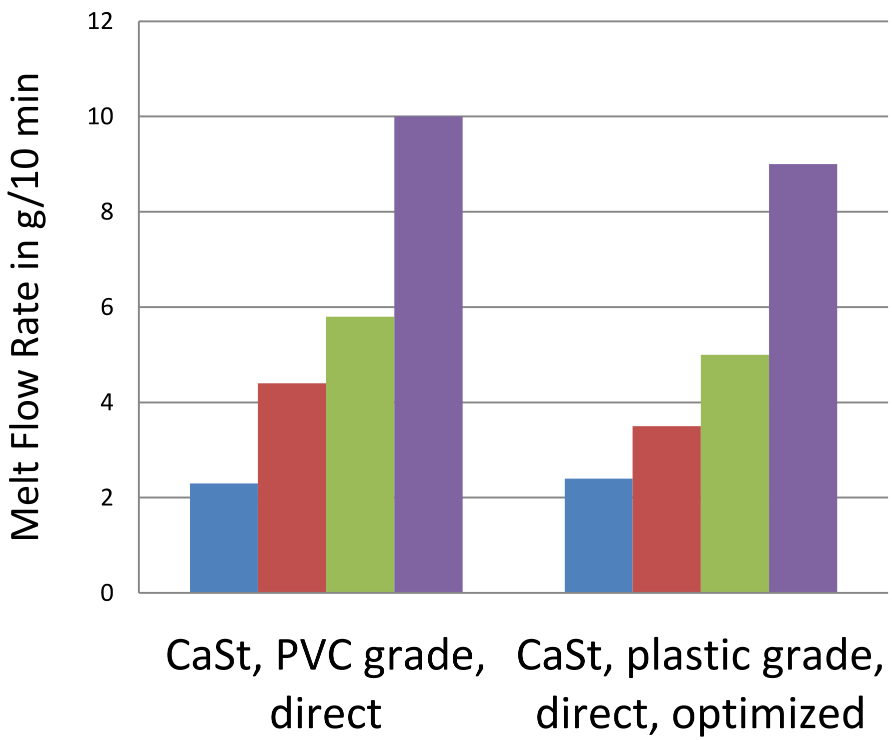
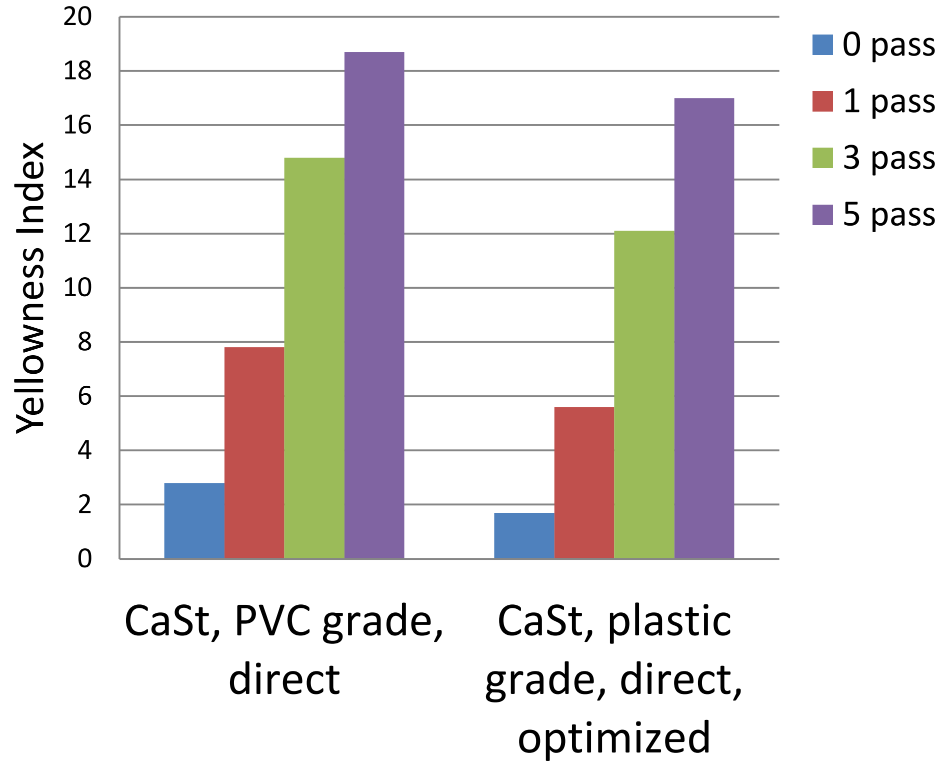
Metal soaps - Starting materials and their influence

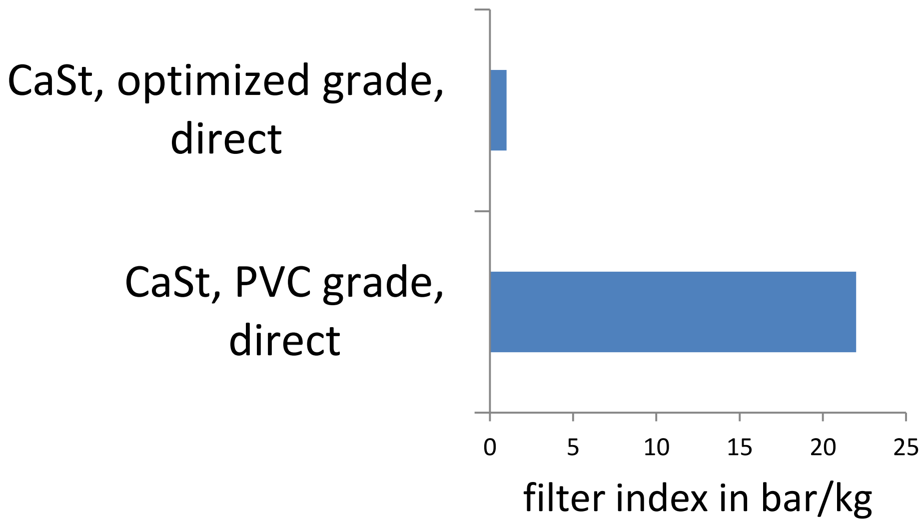
- Inorganic part
  - Variation of the inorganic raw material

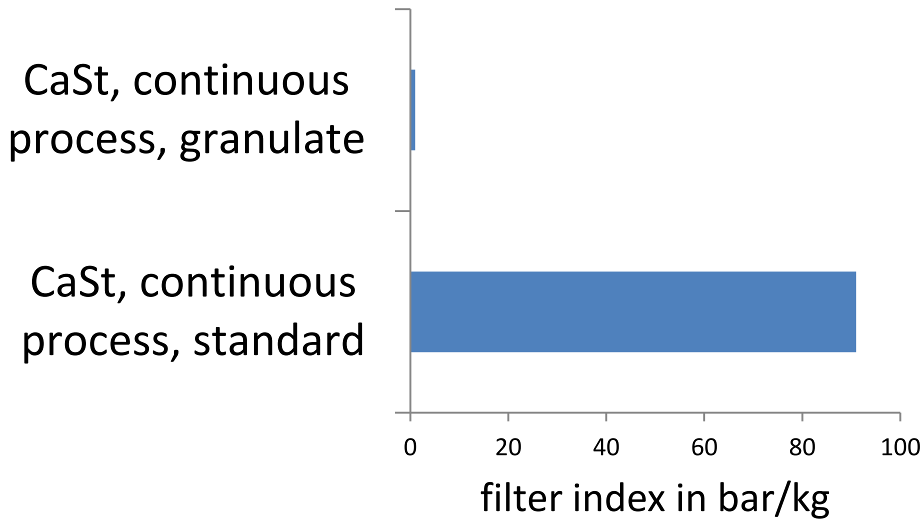




Metal soaps - Starting materials and their influence

Filter index:

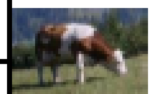
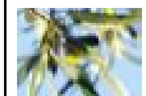




- Inorganic part
  - The choice of the $Ca(OH)_2$ is significant for the properties of Calcium Stearate and its application in Polyolefin

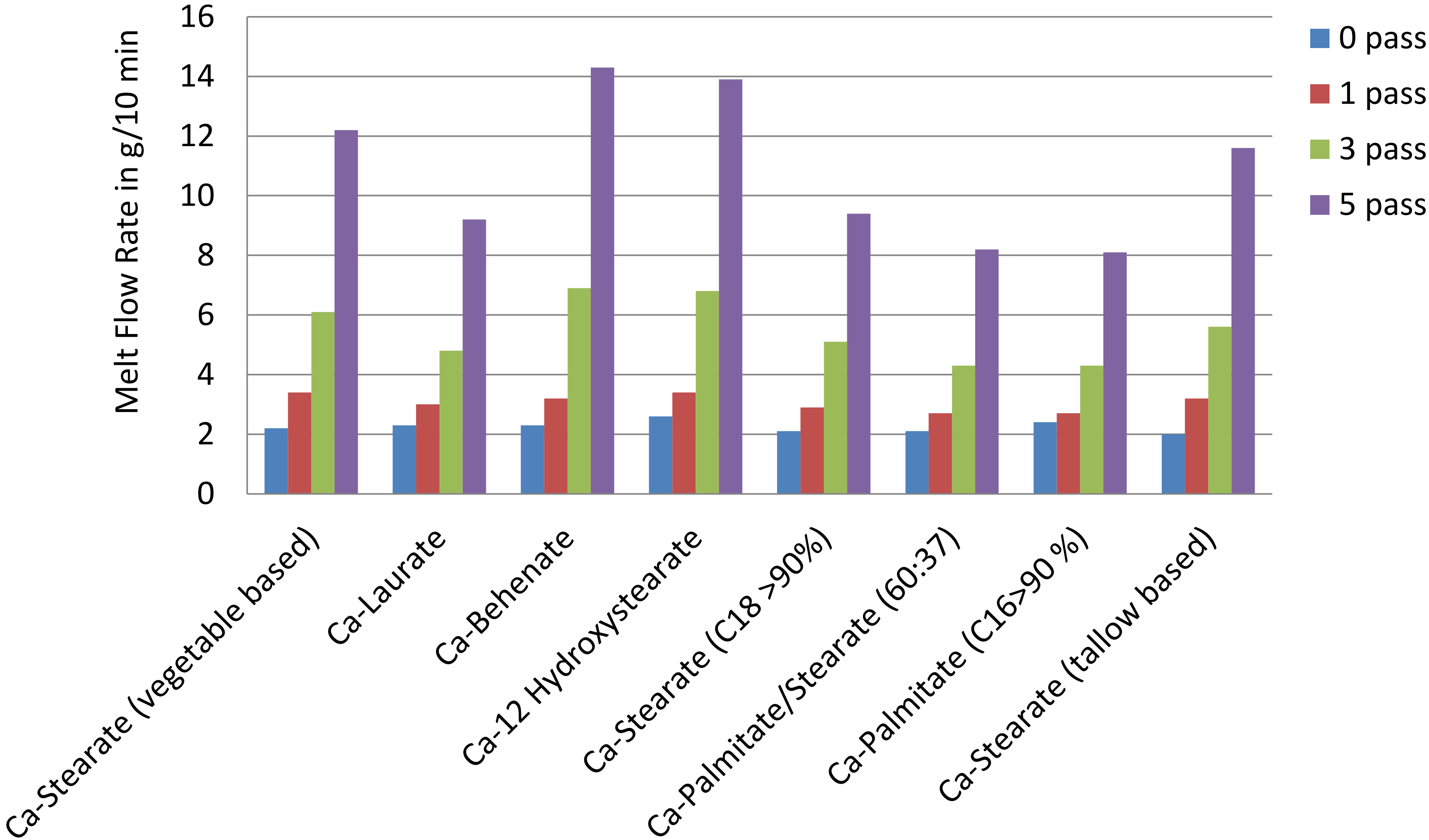
Metal soaps - Starting materials and their influence

Organic part

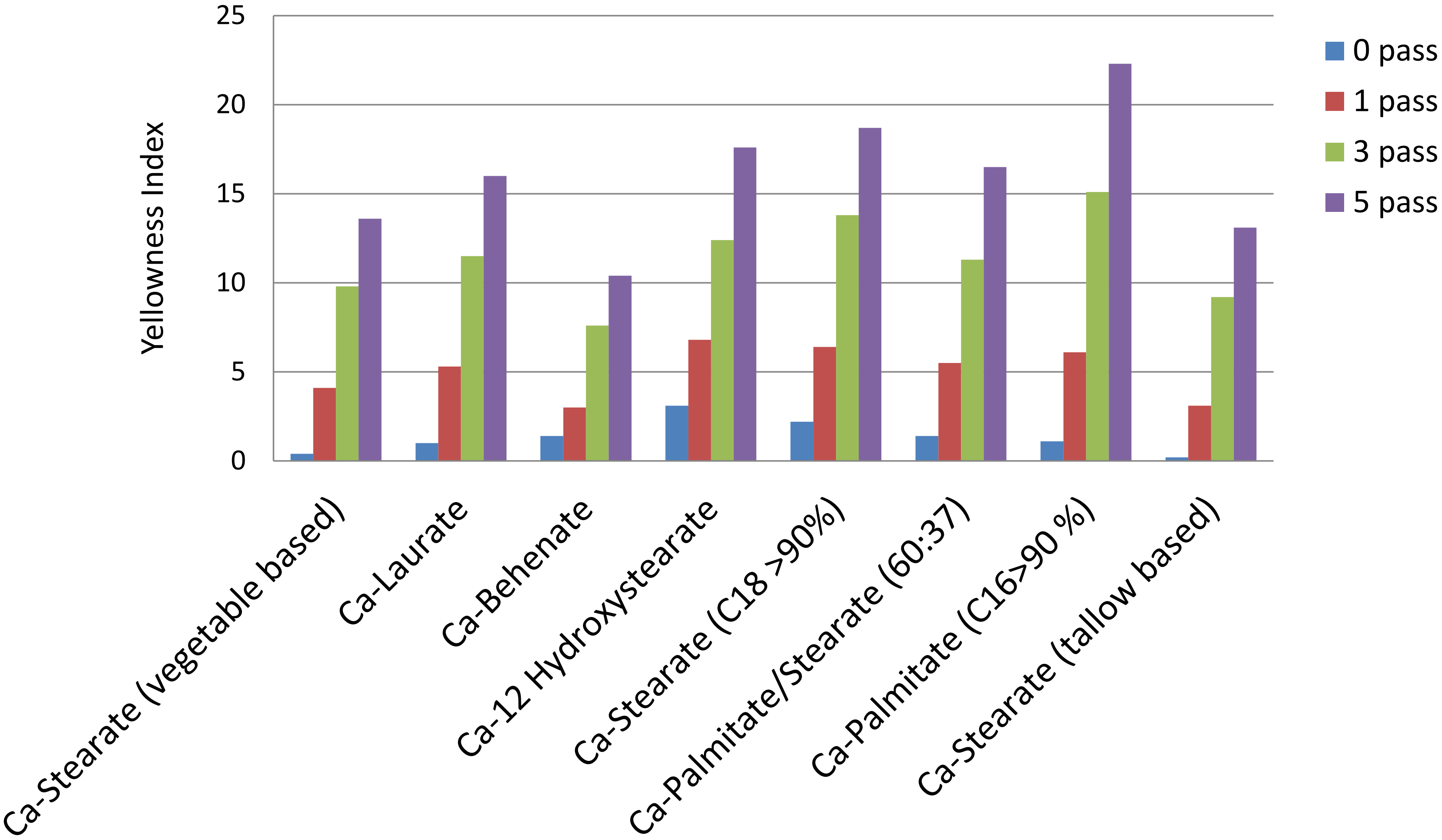
fatty acids [%]	tallow	palm oil	palm kernel oil	cocos oil	olivene oil	rapeseed oil	sunflower oil
							
saturated							
C6				< 0,7			
C8			4,00	4,6 - 10			
C10			5,00	5,0 - 8,0			
C12	0 - 0,5	0 - 0,5	50,00	45,1 - 53,2			0 - 0,1
C14	2,0 - 6,0	0,5 - 2,0	15,00	16,8 - 21,0	0 - 0,5		0 - 0,2
C16	20,0 - 30,0	39,9 - 47,5		7,5 - 10,2	7,5 - 20,0	1,0 - 3,0	5,0 - 7,6
C17	0,5 - 2,0	0 - 0,2			0 - 0,3		0 - 0,2
C18	15,0 - 30,0	3,5 - 6,0		2,0 - 4,0	0,5 - 5,0	1,0 - 3,0	2,7 - 6,5
C20	0 - 0,5	0 - 1,0		0,2 - 0,5	0 - 0,6		0,1 - 0,5
C22	0 - 0,1	0 - 0,2			0 - 0,2	35,0 - 64,0	0,3 - 1,5
unsaturated							
C16 *		0 - 0,6		-	0,3 - 3,5		0 - 0,3
C17 *	0 - 1				0 - 0,3		0 - 0,1
C18*	30,0 - 45,0	36,0 - 44,0	15,00	5,0 - 10,0	55,0 - 83,0	13,0 - 38,0	14,0 - 39,4
C 18 **	1,0 - 6,0	9,0 - 12,0	2,00	1,0 - 2,5	3,5 - 21,0	10,0 - 22,0	48,3 - 74,0
C18 ***	0 - 1,5	0 - 0,5		0 - 0,2	0 - 1,0	2,0 - 10,0	0 - 0,3

- Main important starting materials for the production of technical fatty acids
- However, they are not used with the original C-chain distribution

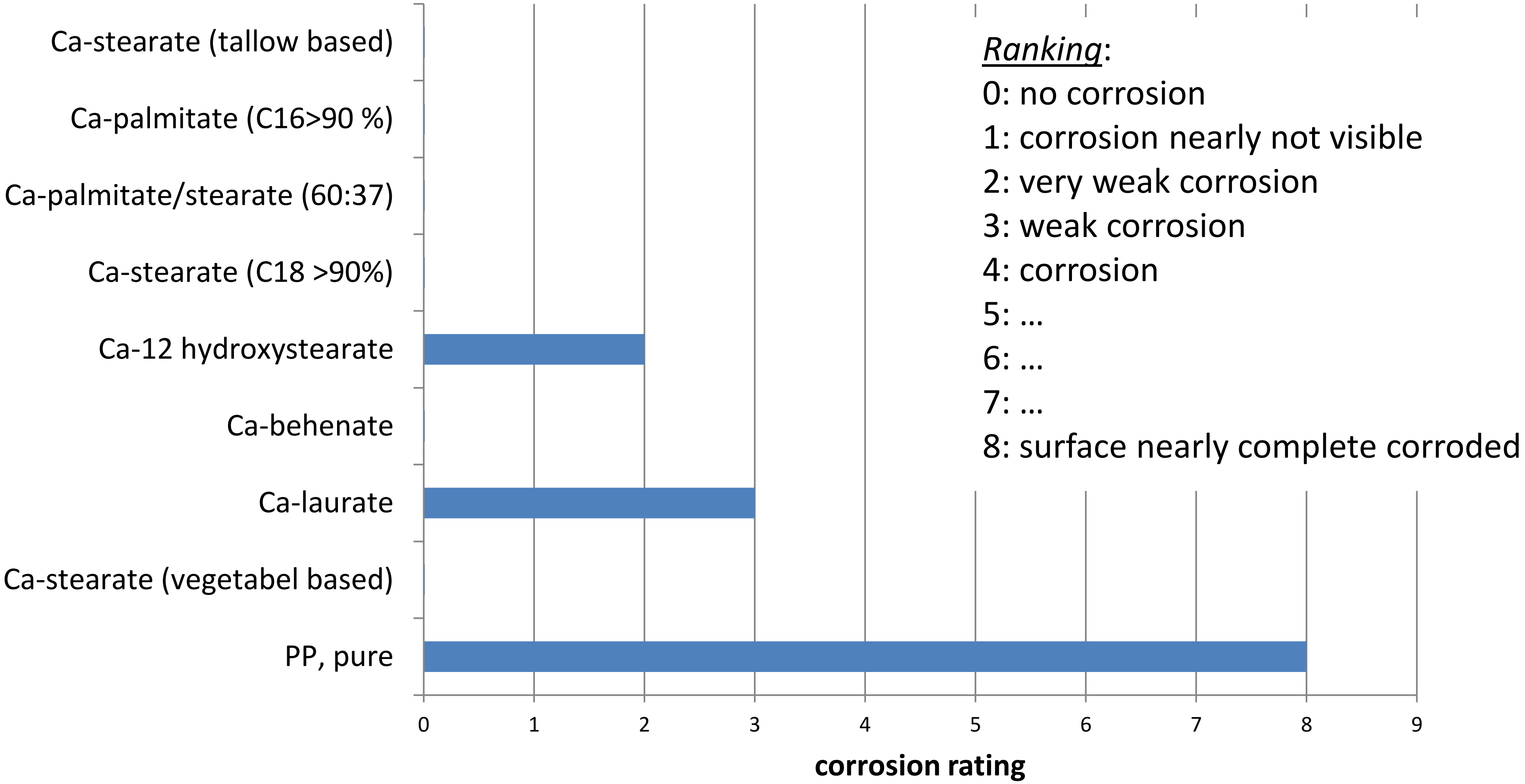
Metal soaps - Starting materials and their influence



Metal soaps - Starting materials and their influence



Metal soaps - Starting materials and their influence



- Weak corrosion if Ca-12 hydroxystearate or Ca-laurate are added
- No corrosion by using the other Ca-soaps

Metal soaps - Starting materials and their influence

- Regarding the MFR the C-chain length C16 seems to be an optimum, but shows the highest increase of the YI
- Calcium Behenate has a lubricating effect due to its higher unpolar part in the fatty acid chain
- By using Calcium Laurate or Calcium Hydroxystearate as acid scavenger weak corrosion was observable.
- The „technical“ Calcium Stearates show an increase in the MFR but the Yellowness Index is less influenced compared to the other calcium soaps.
- The choice of the calcium soap has an influence on MFR, YI and corrosion - but based on the results there is no need to use an other calcium soap as acid scavenger than Calcium Stearate.

Market trends and resulting selection of the raw materials

- In the case of Calcium Stearate two different main sources are possible:

Tallow based

- TSE
- Are not world wide accepted

↓

- Tallow is available in many countries

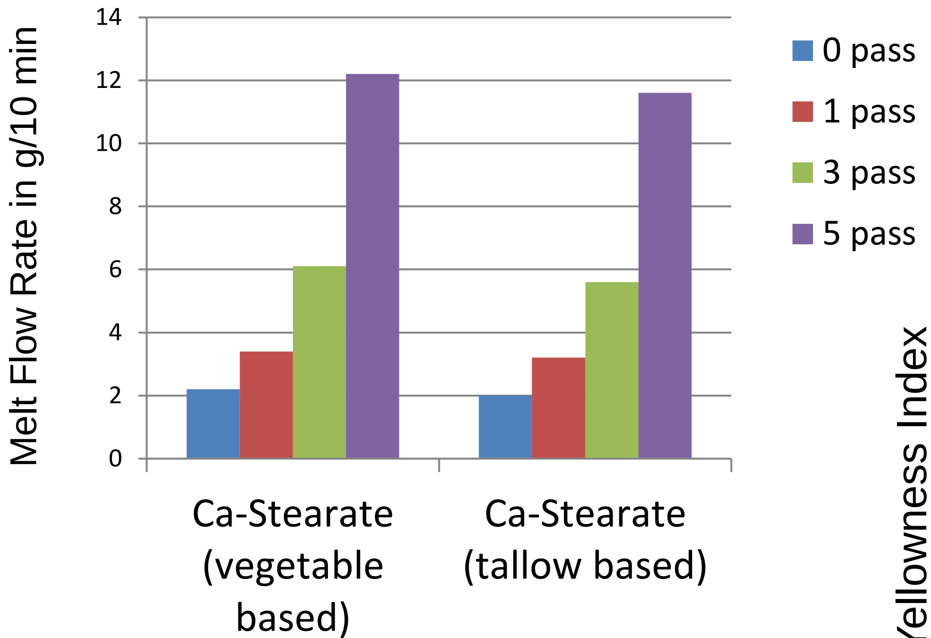
vegetable / palm oil based

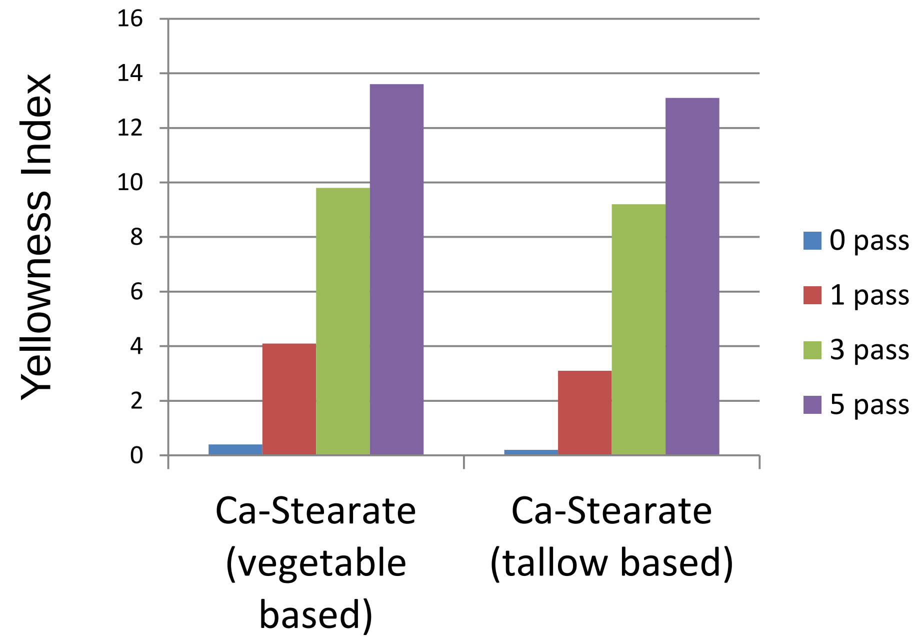
- GMO
- sustainability

↓

- Certified raw materials are available, e.g. RSPO certified

Market trends and resulting selection of the raw materials

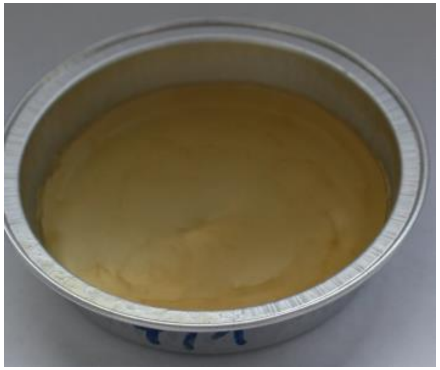




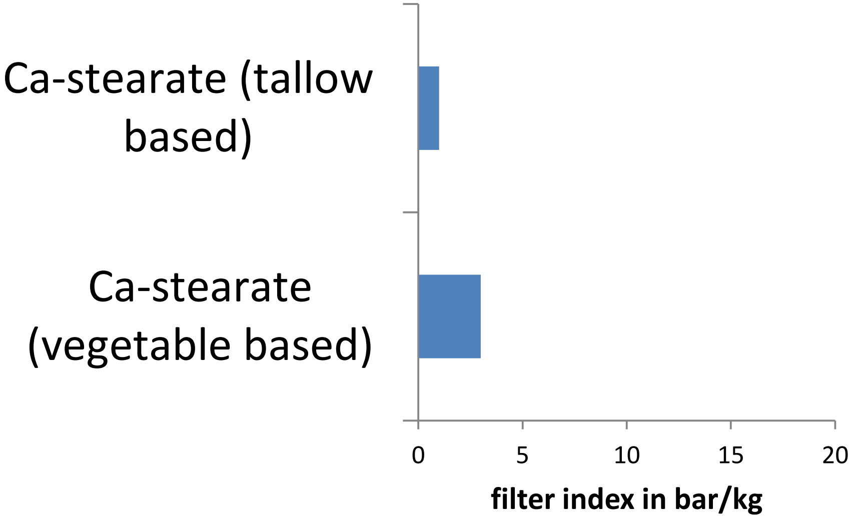
- No differences between vegetable based Calcium Stearate and tallow based Calcium Stearate

Market trends and resulting selection of the raw materials

CaSt, vegetable based



CaSt, tallow based



- The filter index is good independent on the raw material source.
- The thermal stability is also comparable.
- Corrosion test: no corrosion observable

Summary / Conclusion 1

- The use of stearates from various manufacturing processes has historical reasons
  - In the past Calcium Stearates with good filter indices were only achieved via the precipitation process.
  - Beside the very low filter indices, the thermal stability of this Calcium Stearate grade is excellent.
  - Precipitation process is more complex and more expensive compared to the other processes.

⇨ In the last years the direct process was further developed

Summary / Conclusion 2

- Further development of the direct process
  - The direct process was optimized and Calcium Stearates with improved flowability and very good filter indices could be achieved.
  - This Calcium Stearates can be applied as acid scavenger in Polyolefin.
  - The optimizing is based on the choice of the raw materials and the improvement of the process parameters

- Nowadays dust reduced acid scavengers are requested (occupational health and safety)
  - Using the COAD process a dust reduced, easy to dose Calcium Stearate with excellent filter indices can be achieved.

Summary / Conclusion 3

- Variation of the organic part
  - Considering the C-chain length, Calcium Palmitate shows a minor effect on the MFR, however a strong effect on the YI
  - Calcium Behenate shows a lubricating effect and at the same time the lowest increase of YI
  - Due to the availability of technical stearic acid Calcium Stearate was the first choice for producing acid scavengers in the past.
  - Based on the results Calcium Stearate is still the best choice (performance like and also economical like)
  - Tallow or vegetable based Calcium Stearate could be applied likewise

Thank you very much for your attention