Further Developments on metal soaps as processing promoter for the rubber industry

By Michael E. Wolers, K.P.Ho, Mike Trowman

Performance Additives Sdn.Bhd; Subang Jaya; Selangor Darul Ehsan, Malaysia

Abstract

Metal soaps have been for a long time the key product for the improvement of processability in tyre compounding.
Originating from the 'classic' zinc- and calcium stearate, modifications of the fatty acid base were made to reduce melting points and improve polymer compatibility.

The resulting products were mostly zinc based, since calcium soaps tended to be less compatible and showed detrimental effects on the cross linking density.

This paper is going to address recent changes and modification concerning the metal base of these materials to improve effectiveness and, consequently, enable the compounder to use lower dosage levels.
We are also going to discuss the often confusing number of products in the market and the reasons behind it.

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Introduction

Metal soaps as processing promoter have been mentioned in the literature as early as in the late forties/early fifties[1]

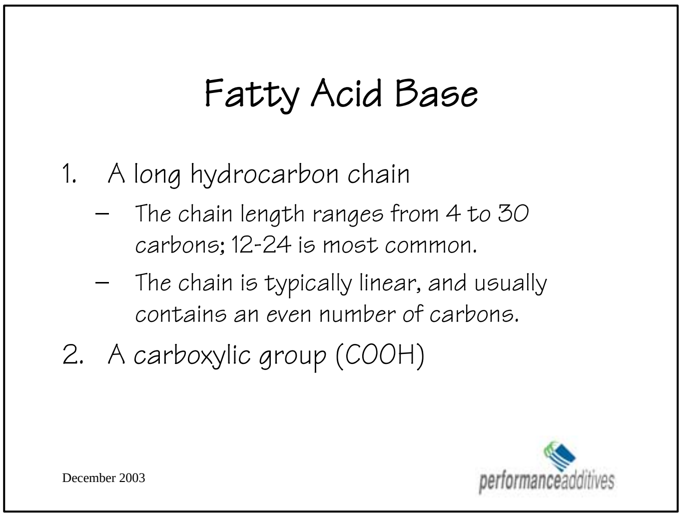
In those days, metal soaps usually meant zinc soaps and/or calcium soaps.

This paper is going to address the advances in development that happened in recent years to metal soaps.

Metal Soaps

Zinc soaps were mainly adopted as replacements for chemical peptizer because they were found to remain effective as viscosity reducers in natural rubber when carbon black was present which removed the necessity for a “premastication” step and they did not reduce the rubber’s molecular weight, thus giving high tensile and tear properties. B.Crowther in1989[2] first published the theory of emulsifier lubrication.

In general, metal soap based processing promoters are based on fatty acids. These fatty acids are mostly naturally occurring and can be animal- or vegetable based. The make up is typically of a hydrocarbon chain and a carboxylic group.



Slide 1

They can have somewhere between 4 and 30 C- atoms; 12 –24 C chains are commonly used. Chain length, saturation and linearity affect the melting point of the final product.

Fatty Acids (linear)

- Lauric Acid $C_{12}H_{24}O_2$ sat.
- Myristic Acid $C_{14}H_{28}O_2$ sat.
- Palmitic Acid $C_{16}H_{32}O_2$ sat.
- Oleic acid $C_{18}H_{34}O_2$ unsat..
- Stearic Acid $C_{18}H_{36}O_2$ sat.

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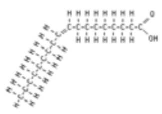
Slide 2

Other variations are caused by the degrees of unsaturation, which affects the compatibility in rubber.

Typical fatty acid structure



Oleic acid, a monounsaturated fatty acid. Note that the double bond is *cis*; this is the common natural configuration.

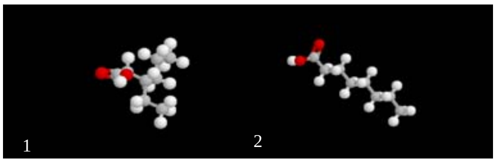
Stearic acid, a saturated fatty acid

December 2003

Slide 3

Fatty Acids (branched)

1. 2-Ethylhexanoic Acid $C_8H_{16}O_2$
2. Octanoic Acid $C_8H_{16}O_2$



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Slide 4

Simple saponification of saturated or unsaturated fatty acids by zinc or calcium produces a wide range of process additives:

Saponification Example

$$2R-\overset{O}{\overset{\|}{C}}-OH + ZnO \;\; - \;\; (R-\overset{O}{\overset{\|}{C}}-O)_2Zn + H_2O$$

Route A

$$2R-\overset{O}{\overset{\|}{C}}-O^{-}Na^{+} + ZnCl_2 \;\; - \;\; (R-\overset{O}{\overset{\|}{C}}-O)_2Zn + 2NaCl$$

Route **B**

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Slide 5

In order for fatty acid based metal soaps to work, certain surfactant properties are necessary. This can be achieved by choosing the right fatty acid type, which has a strong effect on the resulting soap properties.

Fatty Acid type	Soap Properties
Carbon chain length	
Less than C 10	Too short to form micelles
Higher than C 10	Form micelles-surfactants
Chain length mixtures	
Monodisperse	Crystalline,high melt point, poor dispersion,can bloom!
Polydisperse	Amorphous,low melt point, easy disperse, hardly bloom !
Polarity: High	Better reactivity w/silicas
Low	More internal lubrication
Branching: If present	Reduces crystallinity, lowers Melt point,soluble(No bloom)

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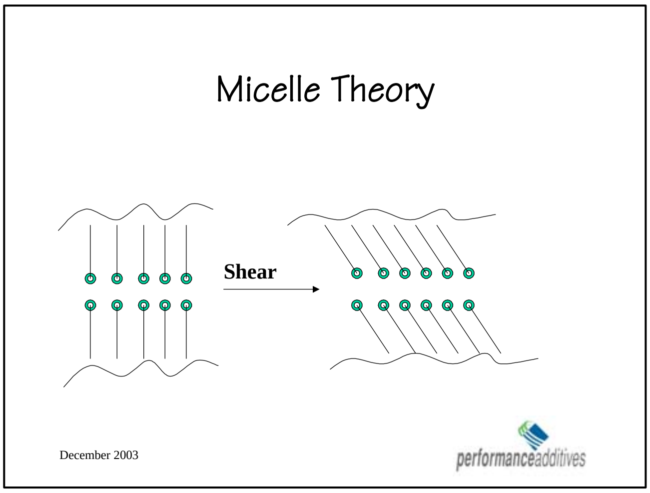
Slide 6

Crowther[2] theorized that, since metal soaps exhibit surfactant behavior, they form lamellar micelles in rubber which act as strong lubricants between the high molecular weight chains when subjected to high shear forces:



Slide 7

He also demonstrated that in natural rubber simple zinc soaps provide lower viscosity; less reversion; lower heat buildup; higher heat resistance and higher tensile and tear properties than mastication with or without chemical peptizer.
Since all these property improvements are desirable in tires and particularly in natural rubber treads, zinc soaps became widely used.

However with certain specific cure systems, cure rate is slowed, so in these cases removal of 1-2phr stearic acid corrects the situation.

Unfortunately, these effects are not as pronounced in synthetic rubber so, as synthetic rubber became more widely used in radial passenger treads and sidewalls and more recently, vinyl polybutadiene; solution vinyl styrene polybutadiene and Neodymium catalyzed polybutadiene in combination with special silica and very fine carbon blacks, the need for improved process additives, particularly those based on zinc soaps was clear.
Examination of chemical and physical "cause and effects" quickly shows the most positive directions for improvement and eliminates impractical approaches:

Development Approaches

- Traditional: Fatty acid C_{14}- C_{18} unsaturated
- Higher C # or saturated : high melting point- impractical
- Branching : disrupts crystallinity, lowers melt point;more soluble and stronger cure activation- good potential

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Slide 8

Development Approaches

- Aryl groups : more polarity, chance of bloom, potential.
- Substitution of zinc by potassium : Higher melting point, less divalency and more polarity- good potential, particularly with high silica compounds !
- Use of Calcium as readily available metal base

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Slide 9

Branched salts gave the promised improvements, but only in natural rubber. They also required a second synthesis step using additional chemicals, which increased cost and produced liquids, all being unacceptable for radial passenger tires. The introduction of aryl groups also produced materials with great potential, but again while effects in natural rubber were very strong they were not nearly as positive in synthetics however they have found wide use for new and retreaded truck tires [3].

This only left the replacement of part of the zinc by potassium. Stone and Koss [4] showed that such a material gave significantly reduced mixing torque and time; improved dispersion; and improved dynamic properties with synthetics. This was confirmed with particular attention paid to extrusion property improvements in both black and silica compounds by Steger et al [5, 6].
During evaluations for more efficient mixing cycles of silica / silane treads it was found that the silanisation reaction should be complete before the addition of the zinc / potassium soap.

Now a few words about what is available in the market.

There are a vast and often confusing number of products available. To give an idea of what is out there; here are some generic comparison data on zinc soaps:

Brand A:	Zn %	fatty acid base	filler	droppt.°C
Zinc soap 1:	10.5	unsaturated	0	100
Zinc soap 2:	8.5	unsaturated	11.5	85
Zinc soap 3:	9.0	unsaturated, blend w./ester		100
Zinc soap 4:	23	branched	0	liquid
Zinc soap 5:	16	aromatic/aliphatic		115
Brand B:				
Zinc soap 1:	13	un-/saturated	0	100
Zinc soap 2:	9.0	un-/saturated	15	100
Zinc soap 3:	10	un-/saturated, blend w/paraffin		97
Zinc soap 4:	10	same as above		97
Zinc soap 5:	13	un-/saturated	0	83

Slide 10

I could continue that list with more suppliers but that would more or less repeat it!

A pure zinc soap based on saturated/unsaturated linear fatty acids should contain between 12.0 and 13.0% Zinc.

Higher numbers indicate a different acid base (branched, aromatic), as shown at Manufacturer A; # 4 and # 5.

Lower numbers are blended or diluted with something else; either for technical reasons, - as an ester/soap or zinc/potassium soap blend-, or simply to cheapen the product, like blends with paraffinic wax and/or fillers (clay; $CaCO_3$).
In products with exactly the same analytical data, the differences are usually in the degree of purity of the fatty acid, thus resulting in lower cost (and a bad smell, sometimes).

Future Outlook:

With Zinc coming more and more under fire by regulators as a potentially hazardous metal, everybody involved is working on replacing or at least reducing the amount of zinc in rubber compounds.

Of course, the zinc- and zinc/potassium soap we discussed here are very small contributors compared to the necessary 2 – 5 phr of zinc oxide we have to use to activate our cure systems. However, as a responsible company, this would not be the right way to approach it.

Performance Additives has commercialized products with reduced zinc content, where potassium or esters in part overtake the function of the zinc. At the same time, higher efficiency of the additive helps to reduce zinc even further.

As an example, 4 phr of standard zinc soap contribute 0.52 phr of zinc to the compound; the same amount of zinc/potassium soap reduces it to 0.34 phr.
As proven by experience, the higher effect of the Zn/K soap can reduce the dosage level by 50%, which, in the end, will result in only 0.17 phr of zinc, or 1/3 of the original level.

Our latest development, **ULTRA-FLOW™ 800**, is an absolutely zinc-free alternative product which shows similar characteristics in compound mixing and processing as traditional zinc soaps, including excellent compatibility with almost every standard polymer.

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