The Perception of Metallic Stearates as Acid Acceptors

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Metallic Stearates
Past and Present

• The use of metallic stearates in polyolefins is derived from their earlier use in PVC and PVC research which gave only a general understanding of their function and behavior in polyolefins.

• Today the wide range of applications and quality in polyolefins continues to complicate our understanding as it relates to stabilization of the matrix.
Metallic Stearates
In Polyolefins Today

- Calcium Stearate
- Zinc Stearate
- Sodium Stearate
- Lithium Stearate
- Magnesium stearate
- Manganese Stearate
- Cobalt Stearate
- Cerium Stearate
- Aluminum Stearate
- Potassium Stearate
- Copper Stearate
- Ferric Stearate
- Nickel Stearate
Classical Uses of Metallic Stearates

- Internal & External Lubricant
- Mold Release
- Rheological Control (Flow)
- Color Control
- Dispersing Aid (Pigments/Fillers)
- Stabilization
- Buffer/Acid Acceptor
Typical Problems Associated With Metallic Stearates

- Plate-out
- Window Fogging
- Corrosion
- Discoloration
- Odor and Taste
- Antagonisms with Stabilizers
- Filterability
- Die-Drool and Smoking at the die
- De-Nucleant
Definition of a Good Acid Scavenger

- Corrosion Protection
- Little or no Plate-out
- Minimal water carry over
- Minimal water bath scum.
- Low water content
- Low static charge
- Low migration, blooming
- Little window fogging
- Low discoloration initial and post fabrication.
- Non-toxic, low price
- Low void generation
- Thermally stable
- Transformation products minimal
Typical Distribution of Fatty Acid in Sodium Stearates

- Caprate 0.50%
- Laurate 2.5%
- Palmitate 28-57%
- Stearate 28-68%
- Myristic 3-5%
- Pentadecanoic up to 0.50%
- Margaric Acid up to 2%
- Oleic acid up to 0.50%
- Arachidic and Behenic acid 30-40%
- Lauric Acid up to 0.50%
Typical Distribution of Fatty Acid in Calcium Stearates

- Myristic (C14) 2 - 5%  
  M.P. ~ 54 °C
- Pentadecylic (C15) up to 1%  
  M.P. ~ 53 °C
- Palmitic (C16) 28 - 50%  
  M.P. ~ 63 °C
- Margaric (C17) sat. up to 2%  
  M.P. ~ 61 °C
- Stearic (C18) 46-67%  
  M.P. ~ 70 °C
Impurities in Metallic Stearates

- Transition metals of iron, nickel, copper and strontium.
- Contamination from manufacturing including filter media.
- Phenolic antioxidant and their oxidized transformation by-products.
- Phosphorus and silica.
- Metallic oxides
Without question or thought an acid acceptor like a metallic stearate is added either because it was used previously, historically, or for good measure.

The weighed variable given in any system is typically minimal.

However, it is more important than most give it credit.
Rapid Changes in Polyolefin Catalyst Chemistry

- We have evolved from First and Second Slurry Catalyst systems in the 1960-1970’s to Third and Fourth and Fifth Generation supported gas phase catalysts in the production of polypropylene.

- Selectivity control agents, supports and control agents all complicate the issues of stabilization.
First In - First Out
No Time to Study Variables

Rapid Changes in catalyst development always exceeds the ability of Product Development to tailor, study the affects of catalyst change on a final commercial product.

Each change requires a proper study of long term effects but commercialization trumps science in corporations.
Separation of PP Powder from diluent and unreacted Monomer
Neutralization and Alcohol Recovery
Slurry Wash Water & Acidic Cat.
SECOND GENERATION CATALYST TECHNOLOGY

Titanium chloride catalyst residues in the (+3) oxidation state are believed to be the principal forms existing in second generation polypropylene catalyst (slurry technology). These compounds are very unstable and react vigorously with air or moisture.

Residues in the (+4) oxidation state are also unstable and reactive but are believed to exist in smaller quantities in second generation polypropylene.

\[
\text{TiCl}_3 + \text{IPA} \rightarrow [\text{Ti(IPA)}_5 \text{Cl}]_2 \text{Cl} \text{(Blue Ti:Complex)}
\]

\[
\text{Water} [\text{Ti(IPA)}_5 \text{Cl}]_2 \text{Cl} \rightarrow [\text{Ti(H}_2\text{O)}_6 \text{Cl}]_3 \text{Cl} \text{ ( + 3 State)}
\]

\[
\text{3230-260C} [\text{Ti(H}_2\text{O)}_6 \text{Cl}]_3 \rightarrow \text{TiO}_2 + \text{HCl}
\]

Also in theory oxidation of titanium chloride can produce: \( \text{TiOCl}_2, \text{TiO}_2^3; \text{TiCl}_4 \)

Excessive Oxygen: \( \text{TiCl}_3 \xrightarrow{O_2} \text{TiOCl}_2 \xrightarrow{O_2} \text{TiO}_2 + \text{TiCl}_4 \)
Catalyst Killing Agents

Best: IPA when used with HCl

Less Effective: Methyl, ethyl, n-propyl, m-butyl and s-butyl in the presence of HCl

■ Best solvent reduces Al and Ti levels but has no particular advantage in regard to polymer acidity or chloride removal.

■ Keeping the system acidic prevents Ti and Al hydrolysis with residual water in the decomposition alcohol. Without HCl levels of Al and Ti catalyst residue would not be reduced in the finished polymer.

Hydrocarbon Slurry Treatment

100: 1 (min. ratio)

IPA/HCl ▶ lower Ti/Al residuals

HCl  1st Step

ROH  2nd Step  Friedel Craft Type Reactions to give oily products

■ (Alkyl sulfonic acids >> aromatic sulfonic acids)

\[ \text{H}_2\text{SO}_4 \xrightarrow{\text{methanol}} \text{Al/Cl} \]  No Affect on Ti

Sulfonic/Sulfuric - Methanol ▶ Al/Cl/Ti  (Cheaper System)

■ Sulfur removal limited utility of this approach. Also, poor melt color stability results. Water wash and basic wash would reduce levels of sulfur.
Two Step Deashing
Catalyst Decomposition and Removal

Catalyst Removal

Decomposed catalyst residues can be readily extracted from the bulk hydrocarbon phase by contacting the process slurry with water. Typical reaction believed to take place during the washing operation.

\[
\text{Ti (ROH)}_4 \text{Cl}_3 + 6\text{H}_2\text{O} \rightarrow \text{Ti (H}_2\text{O)}_6 \text{Cl}_3 + 4\text{ROH}
\]

\[
\text{EtAlCl} - \text{OR} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{HCl} + \text{ROH} + \text{C}_2\text{H}_6
\]

\[
\text{AlCl} - (\text{OR})_2 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{HCl} + 2\text{ROH}
\]

\[
\text{AlCl}_3 : \text{ROH} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{HCl} + \text{ROH}
\]
INTERACTIONS BETWEEN CATALYST RESIDUES

\[ \text{DLTDP} + [\text{Ti (IPA)}_5\text{Cl}]\text{Cl}_2 \xrightarrow{250 \degree C, 15 \text{ min.}} \text{Mono or Di-Chelated Complex (Dark Yellow)} \]

Based on Infrared Analysis the most conceivable complex formed would contain a nine-membered chelate ring.

\[
\begin{align*}
\text{R} & = (\text{CH}_2)_{11}\text{CH}_3 \\
\text{CH}_2 & \quad \text{CH} = \text{C} \quad \text{--OR} \\
\text{S} & \quad \text{O} \\
\text{Ti} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH} = \text{C} \quad \text{--OR} \\
\text{RO} & \quad \text{C} = \text{CH} - \text{CH}_2 \\
\text{O} & \quad \text{O} \\
\text{Ti} & \quad \text{S} \\
\end{align*}
\]
Supported Catalyst Structures Today For Polypropylene
Typical Crystallite of High Yield Catalyst
High Activity Catalyst Residuals

- Major Active Species include Lewis Acids of Magnesium, Aluminum.
- Residual Titanium and chloride levels low
- Dimers and Trimers (Low Mw oligomers).
- Selectivity Control agents
Major Concerns Today From Catalyst in Polypropylene

- Catalyst residues affect stabilizers dramatically by dealkylation of the tertiary butyl groups of primary antioxidants and causing secondary antioxidant to rapidly degrade forming black specks.
- Major problems with L.T.H.A and discoloration (initial and long term).
Calcium stearate reacts with the catalyst residues in polyolefins to form calcium chloride and/or stearic acid and aluminum stearate. Aluminum stearate subsequently decomposing during polymer processing to give stearic acid which is responsible for plate out, smoke at the extruder die, etc.

Conclusions clearly recommend that propylene be deashed as throughly as possible to remove the troublesome aluminum and that the chlorides should be flashed rather than neutralized in slurry. Following these recommendations will allow lower usage of metallic stearate, reduce water content of the polymers, give better corrosivity, less plate out and less smoking at the die.
Historically Proposed Mechanism of Neutralization

\[ 2\text{HCl} + [\text{CH}_3 (\text{CH}_2)_{16} \text{COO}]_2 \text{Ca} \rightarrow \text{CaCl}_2 + 2 \text{CH}_3 (\text{CH}_2)_{16} \text{COOH} \]

* Problem w/Hypothesis - Stearic acid always found in "plate-out" but only traces found in virgin polymer powder direct from the plant.

Currently Proposed Mechanism of Neutralization

Complex hydroxylated (or isopropoxyxylated) chlorinated aluminum species formed during the decomposition, react with calcium stearate in slurry surge to give calcium chloride and aluminum stearate.

\[ 2 \text{[Al(IPA)Cl}_5] \text{Cl}_2 + 3 \text{Ca} [00\text{C(CH}_2)_2]_{16} \text{CH}_3]_2 \rightarrow \]

\[ 2 \text{Al}[\text{OOC(CH}_2)_{16} \text{CH}_3]_3 + 3 \text{CaCl}_2 + 10 \text{IPA} \]

Aluminum Stearate \[ \triangle \rightarrow \] Stearic Acid

\[ 250^\circ - 325^\circ \text{C} \]
\[ (480^\circ - 615^\circ \text{F}) \]

(Intermolecular cross-linked form) \[ 6.33 \mu \]

\[ \rightarrow \] Intramolecular Bonded Form
\[ 6.33 \mu \]
Free Fatty Acid in Polypropylene

Stearic acid exists as the monomer in molten polypropylene. In this state, the acid provides active hydroxyl and carbonyl groups that then are available for the formation of stable complexes with additives which contain proton donors or acceptors.

PP acts as a inert solvent and does not react with the acid. Stearic acid will react readily with aluminum and magnesium species in the molten polymer.
Hygroscopic Nature Of Metallic Stearates

<table>
<thead>
<tr>
<th>Metallic Stearate</th>
<th>Moisture Content</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td></td>
<td>Conditioned $^1$</td>
</tr>
<tr>
<td>Zinc</td>
<td>60</td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>Calcium</td>
<td>299</td>
<td></td>
<td>509</td>
</tr>
<tr>
<td>Potassium</td>
<td>61</td>
<td></td>
<td>283</td>
</tr>
<tr>
<td>Aluminum</td>
<td>279</td>
<td></td>
<td>412</td>
</tr>
</tbody>
</table>

$^1$ 48 hours at 88% relative humidity at room temperature
EFFECT OF SELECTIVE METALLIC STEARATES ON CORROSIVITY OF POLYOLEFINS

<table>
<thead>
<tr>
<th>Acid Acceptor (0.10%)</th>
<th>Water Content (ppm)</th>
<th>Corrosivity **</th>
<th>LTHA 150 C ***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Stearate</td>
<td>264</td>
<td>C+, B-</td>
<td>56</td>
</tr>
<tr>
<td>Sodium Stearate</td>
<td>233</td>
<td>A</td>
<td>60</td>
</tr>
<tr>
<td>Potassium Stearate</td>
<td>177</td>
<td>B</td>
<td>57</td>
</tr>
<tr>
<td>Zinc Stearate</td>
<td>167</td>
<td>C+</td>
<td>40</td>
</tr>
</tbody>
</table>

* Ten mil compression molded plaques, 7 days at 88% R.H at 73F.

** Stainless steel immersion in molded polymer 8 hours.

*** Ten mil plaques compression molded and trimmed of flash, days to failure by decomposition.
EFFECT OF METAL STEARATE ANTACID COMPOSITION ON THE MELT STABILISATION PERFORMANCE OF HINDERED PHENOLIC/PHOSPHITE COMBINATIONS IN LLDPE

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Metal stearates such as calcium and zinc stearates are widely used as antacid agents (i.e., acid scavengers) in stabiliser packages for polyethylenes. This study investigates the effect of both the origin of the stearine blend (i.e., vegetable or animal) and metal ion (i.e., Ca\textsuperscript{2+} or Zn\textsuperscript{2+}) used in the formation of the metal stearate on the melt stabilisation performance of combinations of hindered phenolic (Irganox 1010 (I1010)) and Phosphite (Irgafos 168 (I168)) antioxidants in an LLDPE.

A multiple pass extrusion experiment was carried out at a melt temperature of 200 °C and melt stabilisation performance was monitored by melt flow rate measurements. The level of stabiliser consumption was measured after each extruder pass via HPLC analysis of solvent extracts. Although antagonism was observed with all formulations containing metal stearates, a noticeably greater detrimental effect was apparent with metal stearates based on the vegetable derived stearine blend. The more subtle effect of the metal ion was superimposed on the latter trend and it was apparent that Zn\textsuperscript{2+} had a greater detrimental effect than Ca\textsuperscript{2+}. Addition of metal stearates increased the consumption of both I1010 and I168, however, metal stearates based on the vegetable derived stearine blend gave rise to the highest stabiliser consumption.

Investigation of this seemingly surprising difference in performance stimulated analysis of the metal stearates themselves; hydroperoxide levels and other relevant data that may afford further insight into this effect will be presented.
Mono- and Di-Stearate Levels

Research into the manufacturing and process control of all types of metallic stearates produced past and present has shown that levels of mono stearate and di-stearate and fatty acid distribution of raw materials alters the chemistry and performance of each stearate.

Metal contamination from the raw materials also affects stability and long term durability of the plastic. Complex metallic phenolates cause major filterability problems in textile fibers spinning.
Influence of Zinc MonoStearate Levels On Melt Viscosity of Third Generation Polypropylene Homopolymer

Formulation:
B-Blend 0.10%
(1:2 Blend)
ZnSt2 0.10%

Melt Flow (230 C)

Multiple Passes at 260 C

- 10.8% MonoStearate
- 38.6% MonoStearate
- 65.4% MonoStearate
- 93.2% MonoStearate
Melt Flow Y.I.

1000 ppm Acid Acceptor added

- Calcium Stearate
- Sodium Stearate
- Zinc Stearate
- Hydrotalcite

* Polypropylene 2.5 MF nominal powder, 500 ppm phenolic AO, 700 ppm secondary phosphorus.
Oven Stability of Compression Molded 10 Mil Polypropylene Films

Thermo-Oxidative Stability at 150 C (Days to Failure)

Formulation:
B-Blends at 0.1%
10 mil Films

Metals: Al 75 ppm
Ti <1 ppm
Mg 3 ppm
Cl- 20 ppm

1st Pass-Pwdr-Pellet
2nd Pass-Pellet-Pellet
at 260 C.

Calcium Stearate (0.10% wt.)

B-Blend (1:1) 1st Pass
B-Blend (1:1) 2nd Pass
B-Blend (1:2) 1st Pass
B-Blend (1:2) 2nd Pass
LTHA.97
Oven Stability of Compression Molded 10 Mil Polypropylene Films

Thermo-Oxidative Stability at 150°C 20 (Days to Failure)

Formulation:
B-Blends at 0.1%
10 mil Films
Non-Deashed PP
Metals: Al 66 ppm
Cl 30 ppm
Ti <1 ppm
Mg 3 ppm

Calcium Stearate (0.10% wt.)

B-Blend (1:1)
1st Pass

B-Blend (1:2)
1st Pass

1st Pass-Pwd-Pellet
Percent Retention of Tenacity
(4.0 inches/min.)

Formulation:
B-Blend 0.10%
CaSt2 0.10%
0.10% HALS

Xenon Arc WOM (Hours)

- 17.7% MonoStearate
- 44.5% MonoStearate
- 71.7% MonoStearate
- 100% MonoStearate

MONO.UV
Influence of Calcium Monostearate on Recrystallization of PP

![Graph showing the effect of Calcium Monostearate on DSC (Peak) for different pH levels and blend percentages. The x-axis represents Calcium Monostearate (%) with values 71.7, 44.5, and 17.7, and the y-axis represents DSC (Peak) values from 110 to 124.]

- 0.1% B-blend
- 0.1% MST

- pH 11.9
- pH 10.66
- pH 9.85
Influence of Zinc Monostearate on Recrystallization of PP

DSC (Peak)

0.1% B-Blend
0.10% MST

Zinc Monostearate (%)

0.1% B-Blend
0.10% MST

No AO/MST
0.10% MST

pH 6.59
pH 6.56
pH 6.47
Hindered Amines
Metallic Stearates and Free Fatty Acids

**Stain of Injection mold by Salt**

1. by N-H HALS
   
   ADK STAB LA-77  
   (Sanol LS770)
   
   +  
   
   Stearic acid
   
   (R = C\textsubscript{17}H\textsubscript{35})
   
   easy
   
   Stain of injection mold

2. by N-Me HALS
   
   +  
   
   Stearic acid
   
   (R = C\textsubscript{17}H\textsubscript{35})
Metallic Stearates
Control Over Discoloration

• Metallic Stearates can only control color of a polyolefin matrix if the system is in balance.

• Exceeding the buffer balance of pH and free acidity towards the basic side will increase color.

• Types of primary antioxidants and levels determine the degree of interaction between metallic stearates.
BHT or Ionol

Irganox 1010
Goodrite 3114 or Irganox 3114

Irganox 1076
Long Term Storage of Polyolefin
Typical Yellowing
<table>
<thead>
<tr>
<th>IONOG CP, %w</th>
<th>VIRGIN</th>
<th>1ST PASS</th>
<th>2ND PASS</th>
<th>3RD PASS</th>
<th>4TH PASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 %w</td>
<td>8.4</td>
<td>22.6</td>
<td>33.3</td>
<td>37.3</td>
<td>51.5</td>
</tr>
<tr>
<td>0.10 %w</td>
<td>8.4</td>
<td>14.4</td>
<td>32.3</td>
<td>34.0</td>
<td>35.9</td>
</tr>
<tr>
<td>0.25 %w</td>
<td>7.8</td>
<td>10.2</td>
<td>16.2</td>
<td>20.7</td>
<td>25.9</td>
</tr>
</tbody>
</table>

COLOR DEVELOPMENT DURING PROCESSING

FARREL INJECTION MOLDER 550 °F
Influence of Trace Aluminum in Low Density Polyethylene

Discoloration From The Reactivity of Hydroxy Substituted Benzophenone with Trace Aluminum
Antagonism

A + B = C
Transformation of Phenolic Antioxidants

Base Catalyzed Oxidation Transformation By-Products of Primary Phenolic Antioxidants

BHEB  BHT,1076;1010
Stages of Base Catalyzed Oxidation of Irganox 1076
Yellow--Orange---Pink
New Generation Polypropylene
Versus Old Slurry Methods

The old perceptions of how metallic stearates work are no longer realistic.

The new catalysts have higher activities and higher yields and are more active due to the finishing steps in manufacturing.

De-ashing steps vary dramatically at manufacturers and catalysts are still active when the additives are integrated in the resin process.

Alternative acid acceptors are clearly warranted
Alternate Acid Buffers/Acceptors in Polyolefins Today

- Metallic oxides of calcium, zinc, magnesium.
- Amides
- Lactones
- Epoxy resins
- Silicates and zeolitic structures
- Hydrotalcites
- Metallic Lactates
- Metallic stearoyl lactylates
- Metallic pelargonates
- Metallic behenates
Conclusions

• Metallic Stearates today are challenged significantly by alternative and more selective and effective acid acceptors.

• All metallic stearates vary in quality and type. Not all manufacturers provide the same product. Care in selection today is more important than 20 years ago.

• Consistent performance requires consistent product all the time.