Mitsui Plastics Inc.

New Catalyst Neutralizer Polymer Protector Additive for Polyethylene

Presented to the 2019 SPE Polyolefins Conference, Houston, TX
History of acid scavengers in Polyolefins:

- First Generation 1955+: For over 60 years Metallic Stearates and oxides have been used in PE. Originally designed for 1-3\textsuperscript{rd} generation non-magnesium supported. Poor polyolefin oxidative stability requiring higher AO levels. Lewis Acid problem.

- Second Generation 1984+: Hydrotalcite used in PP and solution process LLDPE only. Improved oxidative stability. Color issues with certain catalysts and AO’s from high pH.

- Third Generation 2017+: Mitsui M-Series catalyst neutralizers and polymer protectors for 4\textsuperscript{th} - 6\textsuperscript{th} generation catalysts. Lower color improved and highest oxidative stability allowing AO reduction.
# Mitsui M-Series Catalyst Neutralizer
## Chemistry comparisons

<table>
<thead>
<tr>
<th>Mitsui Plastics Inc.</th>
<th>Metallic Stearates, Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various CAS numbers</td>
<td>FDA</td>
</tr>
<tr>
<td>Additive number:</td>
<td>3L</td>
</tr>
<tr>
<td>North America Supply</td>
<td>Developmental quantities</td>
</tr>
<tr>
<td>Particle size range in microns</td>
<td>0.5-0.8</td>
</tr>
<tr>
<td>Stoichiometry Formulation</td>
<td>Trade Secret</td>
</tr>
<tr>
<td>Acid mechanism:</td>
<td>Catalyst Neutralizer Polymer protector 4th, 5th 6th generation</td>
</tr>
<tr>
<td>Catalyst design:</td>
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</tbody>
</table>

- CaSt, ZnSt, ZnO
- USA, EU, Asia
- (C17H35COO)2 Ca (C17H35COO)2 Zn ZnO

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Catalyst neutralizer efficiency
Catalyst acid neutralizer efficiency

- **36.1 average efficiency**: 500 ppm to neutralize 35 ppm of acid
- **4.8:1 average efficiency**: 1000 ppm to neutralize 210 ppm of acid
- **10:1 average efficiency**: 700 ppm to neutralize 70 ppm acid

**Acid HCL ppm from TiCl4-MgCl2**

**Neutralizer ppm**

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Acid neutralized efficiency per similar volume

Correct neutralizer efficiency ppm neutralizer per 1 ppm acid

- High neutralizer efficiency
- PoorNeutralizer efficiency

- HT actual 35-3.4: 1
- CaSt theory 20:1 or
- Hydrotalcite Theory 10:1

ppm neutralizer per 1 ppm acid

- Catalyst efficiency

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Acid produced by polyolefin type
Mitsui neutralizer effective all catalysts and all densities

PPM of neutralizer per 1 ppm acid

- mLLDPE
- Polypropylene
- Hydrotalcite
- Polyethylene
- Metallic stearates
- Plastomers
- Metallic oxides
- Elastomers EPR, EBR, EOR, EPDM
- Metallic stearates, metallic hydroxides

Decreasing density

Correct efficiency factor ppm neutralizer/ppm acid
Incorrect 10:1 efficiency factor

Mitsui new neutralizer range

Catalyst efficiency

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M-Series catalyst neutralizer suggestions:

<table>
<thead>
<tr>
<th>Ziegler-Natta Catalyzed Polyolefins</th>
<th>SUGGESTIONS</th>
<th>ppm of acid from TiCl4</th>
<th>Commercial Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1g-cat/xxxxg Polyolefin</td>
<td>ppm Ti in polyolefin</td>
<td>phenolic AO ppm / phosphite AO ppm</td>
<td>Ppm of Mitsui M-Series</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ziegler-Natta Polyolefins</th>
<th>1gTiCl4 = 25.27% Ti</th>
<th>1gTiCl4 = 25.27% Ti</th>
<th>ppm of Mitsui M-Series</th>
<th>HCL = ppm Ti x (141.6/47.9 (ppm/mole))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1g-cat/50,500g 1kg-cat/50 tons PE</td>
<td>5 500/1000</td>
<td>600</td>
<td>35</td>
<td>0.934-0.920 LLDPE film grades</td>
</tr>
<tr>
<td>1g-cat/25,200g 1kg-cat/25.2 tons PE</td>
<td>10 375/750 =25% less AO</td>
<td>800</td>
<td>70</td>
<td>0.920-0.910 LLDPE film grades</td>
</tr>
<tr>
<td>1g-cat/12,600g 1kg-cat/12.6 tons PE</td>
<td>20-25 350/700 =30% less AO</td>
<td>1,000</td>
<td>140-175</td>
<td>0.880-0.909 Plastomers</td>
</tr>
<tr>
<td>1g-cat/8,400g 1kg-cat/8.4 tons PE</td>
<td>30 350/700 =30% less AO</td>
<td>1000</td>
<td>210</td>
<td>bi-modal HDPE (Mitsui CX).</td>
</tr>
</tbody>
</table>

- * ppm XRxl needed to neutralize catalyst acid, stabilized anti-oxidants and protect the polymer from degradation. 20x the HCL concentration.
- ** HCL from MgCl2 catalyst support which is 2.89 ppm HCL / 1 ppm Mg. So, 1 ppm Ti + 1 ppm Mg = 7 ppm HCL.
How does Mitsui’s M-Series neutralizer work?

- **Proprietary** blend designed for:
  - 4th – 6th generation TiCl4-MgCl2 catalysts.
  - polyolefin density ranges 0.640 – 0.965
- Color correction chemistry, Balanced pH and surface area = lowest color.
  - Performs excellent with antioxidants per pellet, LAB, YI.
- H/E lubricants reduces shear and heat stress
  - Improved polymer stability per FTIR
  - Improves antioxidant efficiency per OIT, HPLC
Polyethylene results

Mitsui ZRxL Development in HDPE pipe and LLDPE film resins
Problems with metallic stearates and oxides in Polyethylene

1. Acid scavenging chemistry:
   \[
   \text{CaSt} + 2\text{HCL} \rightarrow \text{CaCl}_2 + \text{Stearic acid}
   \]

2. \text{CaCl}_2 is a corrosive “Lewis acids” (ref.1)
   - Lewis acid examples: TiCl4, ZrCl4, ZnCl2, CaCl2, NaCl
   - Lewis acids destroy antioxidants and hindered amines (HALS).

3. \text{Stearic acid} has a 114°C flash point so carbonizes which forms black specs, die smoke and plate out.
Problems with metallic stearates and oxides at molders

- **Black specs**
  - Molded from 1st extruder pass of 0.906g/cc density LLDPE.
Polyethylene formulations

- **Bi-Modal HDPE**
  - 0.03 MI, **0.949 g/cc density**
  - Extrusion at 90 RPM, **Tm 190°C** *
  - Antioxidants: 500 ppm AO 1010 + 500 ppm AO 168
  - MPI 7L development vs Controls: CaSt, HT, HT-2

- **C6-LLDPE**
  - 0.50 MI, **0.917 g/cc density**
  - Extrusion at 90 RPM, **Tm 190°C** *
  - Antioxidants: 500 ppm AO 1010 + 500 ppm AO 168
  - MPI 3L development vs Controls: CaSt, ZnSt, ZnO, HT-2

- **C6-LLDPE**
  - 0.50 MI, **0.917 g/cc density**
  - Extrusion at 30 RPM, **Tm 250°C under N2** **
  - Antioxidants: 500 ppm AO 1010 +1,000 ppm AO 168
  - MPI 737P development vs HT, CaSt

New Fall 2018 developments with 25-30% AO reduction
Polyethylene formulations

- **C6-LLDPE**
  - 0.50 MI, 0.906 g/cc density
  - Extrusion at 30 RPM, \( \text{Tm} \, 250 \, ^\circ \text{C} \)
  - Antioxidants: 800 ppm AO 76 + 1400 ppm Weston 705T.
  - MPI 3L and 37L development vs CaSt

* Extruder details: 3/4in 20mm SSE with 33:1 L/D with 2 mixing zones \( Z_1 = 170 \, ^\circ \text{C}, Z_2 = 190 \, ^\circ \text{C}, Z_3 = 190 \, ^\circ \text{C} \), Die 190 C, screw RPM = 90

** Extruder details: 3/4in 20mm SSE with 33:1 L/D with 2 mixing zones
  - Die 250C, screw RPM = 30,
  - Rate 1.5-3.0 kg/hour.

Molding details: 30 Ton hydraulic injection press (SPEC capable, ASTM, ISO, test bars, 3"x3" GM texture Plaques, machined-in notched Izod bars.) 390/450/450 Deg. F, 2500psi
  - 30 seconds cooling time.
HDPE data:

Bimodal pipe grade 0.947 g/cc
Blow molding grade 0.950 g/cc

M-Series 7L development vs calcium stearate and Hydrotalcite
Extrusion at 90 RPM, Tm 190°
Antioxidants: 500 ppm AO 1010 + 500 ppm AO 168
M7L protects antioxidants

MPi 7L 32% less HDPE oxidation vs HT and 56% less than Calcium stearate

OIT @200c minutes

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M7L 31% - 80% more AO retained

1st vs 5th Extruder Pass 200c.

1st pass 7L retains 31% more AO vs CaSt

5th pass 7L 60% more 1010 retained vs CaSt

5th pass 7L 80% more 168 retained vs CaSt
M7L reduces extruder pressure in HDPE

ZR7L 20% lower extrusion pressure than HT and ZHT
M7L lowest color in Bi-modal HDPE pipe grade

Melt 190c

![Bar chart showing B color for different materials: Ctrl, AO, HT, HT-2, Cast, MPI 7L. Each material has three bars representing different values.]

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M7L 40-60% improvement in the quality of HDPE molded parts

% Standard Deviation from molding 10 HDPE parts

- AO only
- 500 ppm HT-2
- 1000 ppm CaSt
- 1000 ppm MPI 7L

TS % Std.Dev
1% Flex Mod % Std. Dev
M37L and M3L shows no color oxidation in HDPE

0.950g/cc HDPE pellet YI
SSE 1.25inch (32mm). 100 RPM at 550F (287c). 0 pass N2
800 ppm AO 1010 + 800 ppm AO 168 + below catalyst neutralizers
C6-LLDPE  0.917g/cc

MPI 7L and 37L development
vs CaSt, ZnSt, ZnO and Hydrotalcite

Extrusion at 90 RPM, Tm 190c

Antioxidants:  500 ppm AO 1010 + 500 ppm AO 168
M7L stable multi-pass MI
0.917 C6-LLDPE MI 190c/10kg

Increasing ppm of stearic acid + Lewis acid cracking the PE.
M3L and M7L low color LLDPE

YI from molded tensile bars 1st extruder pass, 3rd and 5th. 70c 6 week oven aging from 3rd pass.

Extruder details: 3/4in 20mm SSE 33:1 L/D
with Z1 =170 C, Z2 =190 C, Z3 =190 C, Die 190 C, screw RPM =90, Screw: mixing head

**Diagram:**
- MPI 3L 1000ppm
- MPI 7L 1000ppm
- ZnSt 1000ppm
- HT-2 500ppm
- CaSt 1000ppm
- ZnO 800ppm
- No AO
- AO Only 500-1010, 500-168

YI 1st pass
YI 3rd pass
YI 5th pass
YI 70c 6 wks 3rd pass

ZnO blue shade pigment color change is very high.
M3L 30% lower extruder pressure in LLDPE

Extruder pressure change
Z1 = 170 C, Z2 = 190 C, Z3 = 190 C, Die 190 C, screw RPM = 90, Screw: mixing head

NOTES: ZnO 1st extrusion black die drool and by 5th black powder residue
M3L and M7L 60-75% improvement in quality in LLDPE

Polymer Performance Quality Quotient = Higher number better quality
   HDPE 1% mod / Std. Dev
   LLDPE TS / Std. Dev

Red → Part to part Std. Dev. Lower number better quality
C6-LLDPE 0.917g/cc

New M-Series M737LP developments NOV 2018 vs calcium stearate and Hydrotalcite

1, 3, 5 Extrusion at 30 RPM, $T_m$ 250°C under N2
Antioxidants: 500 ppm AO 1010 +1,000 ppm AO 168
M737P no yellow 1-5 extruder passes

Pellet YI yellowness Index. AO only YI = 5.6

<table>
<thead>
<tr>
<th>Material</th>
<th>1st pass</th>
<th>3rd pass</th>
<th>5th pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSt 1000 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT-1 500 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M737LP 800 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M737LP 1000 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M737LP 800 ppm, 25% less AO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M737LP 1000 ppm, 30% less AO</td>
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</tbody>
</table>
M737P even with 30% less AO more stable than the Calcium Stearate Control

MFR 230c, 2.16kg  AO only 8.33g/10min.
M737P high oxidative stability even with 30% less antioxidants

OIT (oxygen induction time) 200°C in minutes

M737LP 45-145% increase in oxidative stability

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C6-LLDPE 0.906 g/cc
Mitsui’s M-Series M3L and M37L compared to Calcium Stearate
Extrusion at 30 RPM, Tm 250 c
Antioxidants: 800 ppm AO 76 + 1400 ppm Weston 705T.
M3L and M37L show improved MI stability in LLDPE plastomer

LLDPE 0.906g/cc MFR 230c/10kg vs 1,3,5 extrusions 246c

1200 ppm CaSt control
1000 ppm Mitsui 3L
1000 ppm Mitsui 37L

1,3,5 % change  1st pass  3rd pass  5th pass
Mitsui 3L and 37L show excellent low YI color in LLDPE plastomer.

LLDPE 0.906 YI E313; 1, 3, 5 extrusion passes 246c

- 1200 ppm CaSt control
- 1000 ppm Mitsui 3L
- 1000 ppm Mitsui 37L

1st pass, 3rd pass, 5th pass
## FTIR oxidation values vs YI raw data

### FTIR raw data

<table>
<thead>
<tr>
<th></th>
<th>M3L 1st</th>
<th>M3L 5th</th>
<th>M37L1st</th>
<th>M37L5th</th>
<th>CaSt 1st</th>
<th>CaSt 5th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corr Area</td>
<td>1/cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH2 group</td>
<td>720</td>
<td>2.319</td>
<td>2.865</td>
<td>4.223</td>
<td>1.28</td>
<td>3.71</td>
</tr>
<tr>
<td>CH2 group</td>
<td>730</td>
<td>1.246</td>
<td>1.085</td>
<td>1.124</td>
<td>1.953</td>
<td>1.354</td>
</tr>
<tr>
<td>C-C bond</td>
<td>1465</td>
<td>0.842</td>
<td>0.481</td>
<td>1.781</td>
<td>0.946</td>
<td>1.301</td>
</tr>
<tr>
<td>C=O</td>
<td>1720</td>
<td>0</td>
<td>0.062</td>
<td>0.137</td>
<td>0.277</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>1740</td>
<td>0</td>
<td>0.039</td>
<td>0.193</td>
<td>0.549</td>
<td>0.356</td>
</tr>
<tr>
<td>OH</td>
<td>3603</td>
<td>1.528</td>
<td>2.013</td>
<td>1.306</td>
<td>3.468</td>
<td>1.883</td>
</tr>
</tbody>
</table>

### Carbonyl Index (area) vs. YI

![Graph showing FTIR oxidation values vs YI](image)

The correlation equation is:

\[ y = 7.7803x - 7.11 \]

\[ R^2 = 0.9267 \]

### Ratio C=C/C2

| 1740/730 | 0.035945 | 0.171708 | 0.281106 | 0.262925 | 2.654676 |

### Ratio C=O/C2

| 1720/730 | 0 | 0 | 0.031746 | 0.101182 | 1.992806 |

### Pellet YI

-8.97, -5.35, -9.34, -4.78, -6.12, 8.33
M Series no PE oxidation and lowest color. CaSt high oxidation even with low color.
M-Series recycle improvements + odor reduction

- **Performance:**
  1. 45-145% increased time to oxidize. (DSC OIT oxygen induction time at 200c.)
  2. Antioxidant is preserved per LC analysis:
     - 30% increase 1\textsuperscript{st} extruder pass
     - 60-80% increase 5\textsuperscript{th} extruder pass
  3. Average 50-90% less degradation - per FTIR. (C=O carbonyl @1720-1740-cm / C2 % @ 730-cm)

- **Value:** average 50-90% increase in recyclability and odor reduction due to antioxidant preservation and reduced polymer oxidation.
Mitsui Plastics Inc. M-Series for Polyethylene

Summary

- Market:
  - Effective in all 4th – 6th generation ZN catalysts.
  - Replace 800 -1,000 ppm metallic stearate or metallic oxide with equal ppm of M-Series.

- Improved Quality:
  - 45-145 % increased time to oxidize. (OIT DSC oxygen induction time at 200c.)
  - 30% increase in antioxidant retention - per HPLC 1st extruder pass. 60-80% by 5th pass.
  - 40-50% reduction in film gels – per customer
  - Average 50-90% less degradation - per FTIR. (C=O carbonyl @1720-1740-cm / C2 % 730-cm)

- Improved: Performance:
  - 20-30% reduction in extruder pressure. Possible, lower melt fracture.
  - 40-60% increase in LLDPE tensile strength and HDPE Flex. Mod.
  - 40-75 % reduction in part to part Std. Dev.

- Savings + improved quality and performance – up to $500,000 / each 1B lbs.
M-Series powder and pellet forms

Made in Germany (pellets in mm)

Made in USA
For further information and samples:
Reference:

- Please contact:
  - Don Beuke – Mitsui Plastics Inc.
  - 918-914-2947
  - D.Beuke@mitsui.com

- REF 1. Mechanism of Lewis Acid Metallic stearates and oxides
  - ZnCl₂ CaCl₂ are Lewis acids because it can accept an electron pair from a Lewis base like OH- Tert-butyl phenolic antioxidant.
  - A Lewis acid is a molecule that can accept an electron pair and a Lewis base is a molecule that can donate and electron pair. When a Lewis base combines with a Lewis acid an adduct is formed with a coordinate covalent bond.
  - i.e. CaCl₂ + 2 (OH- T-butyl phenol) →Ca(OH)₂ + 2Cl +2 H₂O → 4HCL + O₂
Thank you

SPE Polyolefins Conference – Dr. Thoi Ho Additives Chair.
Our polyolefin customers – you know who you are!
Mitsui Plastics Inc. USA – financial support (many RINGI’s)
Amazing plastics laboratories: Nobukatsu Shigi – Japan, Dr. Amit Dharia – USA,
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