# 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 1-3rd 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 4th -6th generation catalysts. Lower color improved and highest oxidative stability allowing AO reduction.

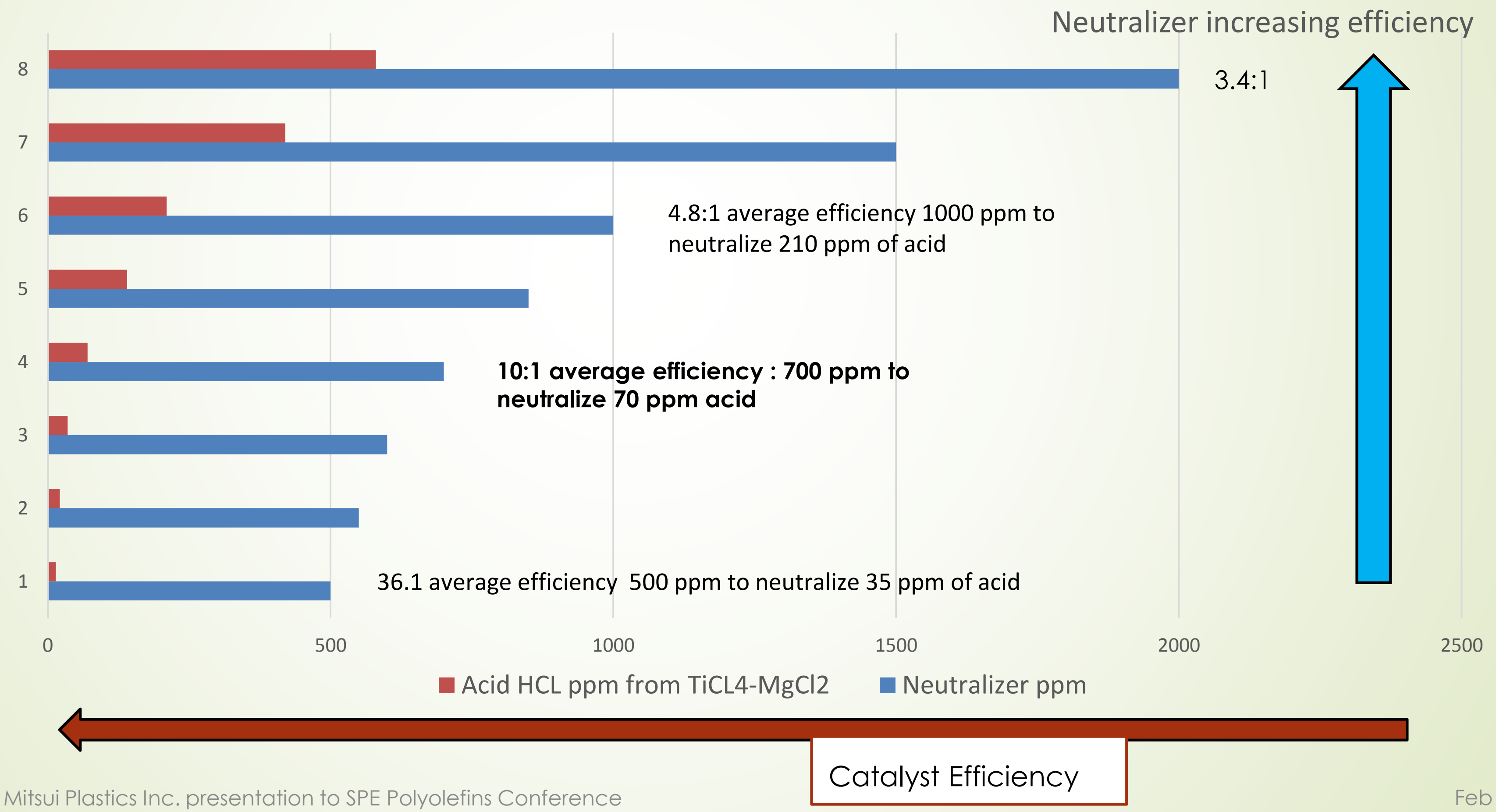
# Mitsui M-Series Catalyst Neutralizer Chemistry comparisons

| Mitsui Plastics Inc. | | | | | Metallic Stearates, Oxides |
|---|---|---|---|---|---|
| Various CAS numbers | | | FDA | EU 10/2011 listed | |
| Additive number: | 3L | 7L | 37L | 70P, 737LP | CaSt, ZnSt, ZnO |
| North America Supply | Developmental quantities | Developmental quantities | Developmental quantities | Developmental quantities | USA, EU, Asia |
| Particle size range in microns | 0.5-0.8 | 0.5-0.8 | 0.5-0.8 | 0.5-0.8 | 10-35 |
| Stoichiometry Formulation | Trade Secret | Trade Secret | Trade Secret | Trade Secret | $(C_{17}H_{35}COO)_2Ca$<br>$(C_{17}H_{35}COO)_2Zn$<br>ZnO |
| Acid mechanism:<br><br>Catalyst design: | Catalyst Neutralizer Polymer protector<br>4th , 5th 6th generation | Catalyst Neutralizer Polymer protector<br>4th , 5th 6th generation | Catalyst Neutralizer Polymer protector<br>4th , 5th 6th generation | Catalyst Neutralizer Polymer protector<br>4th , 5th 6th generation | Acid Scavenger<br><br>1st and 2nd generaton |

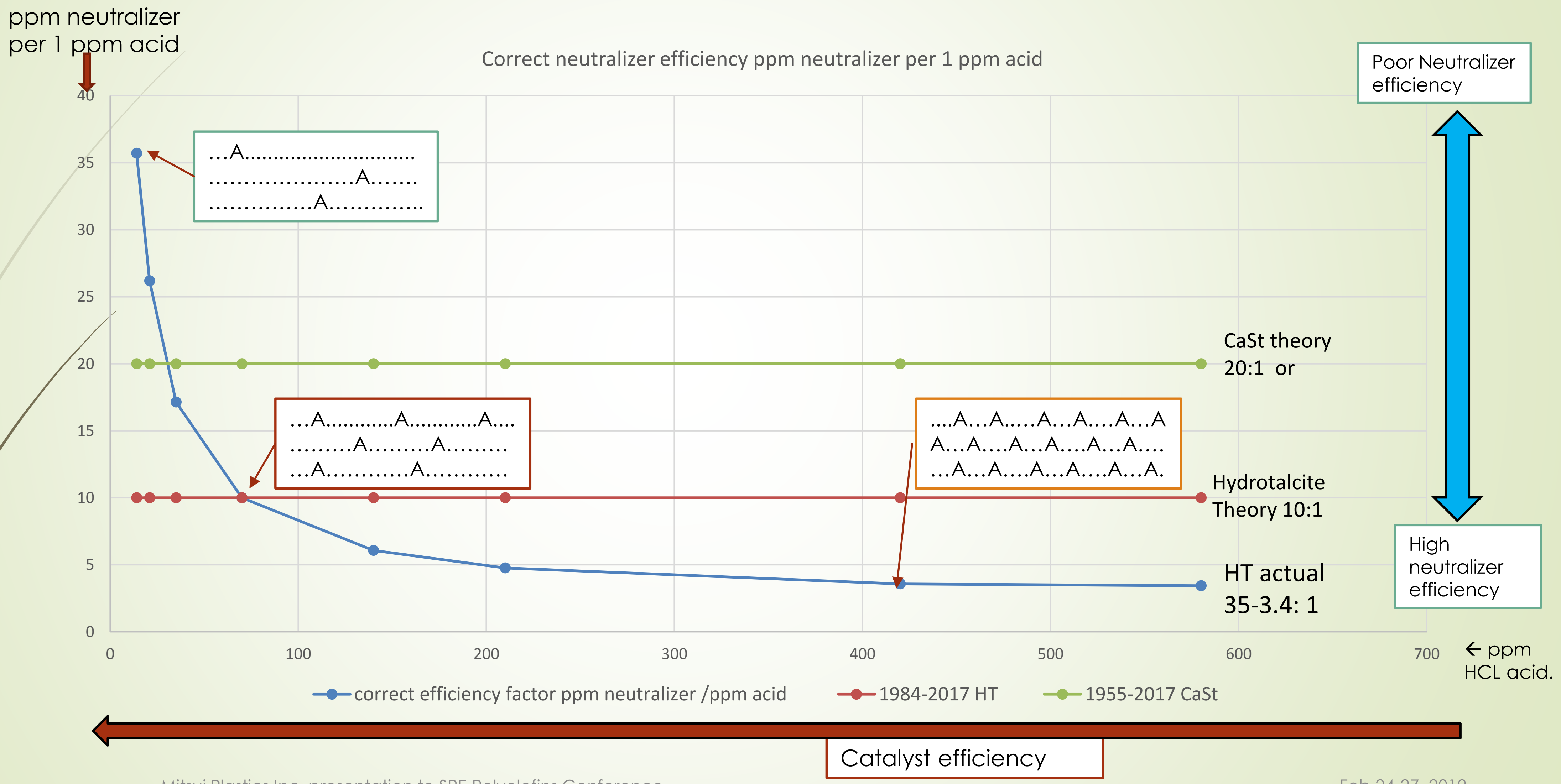
# Mitsui Plastics

## catalyst neutralizer efficiency

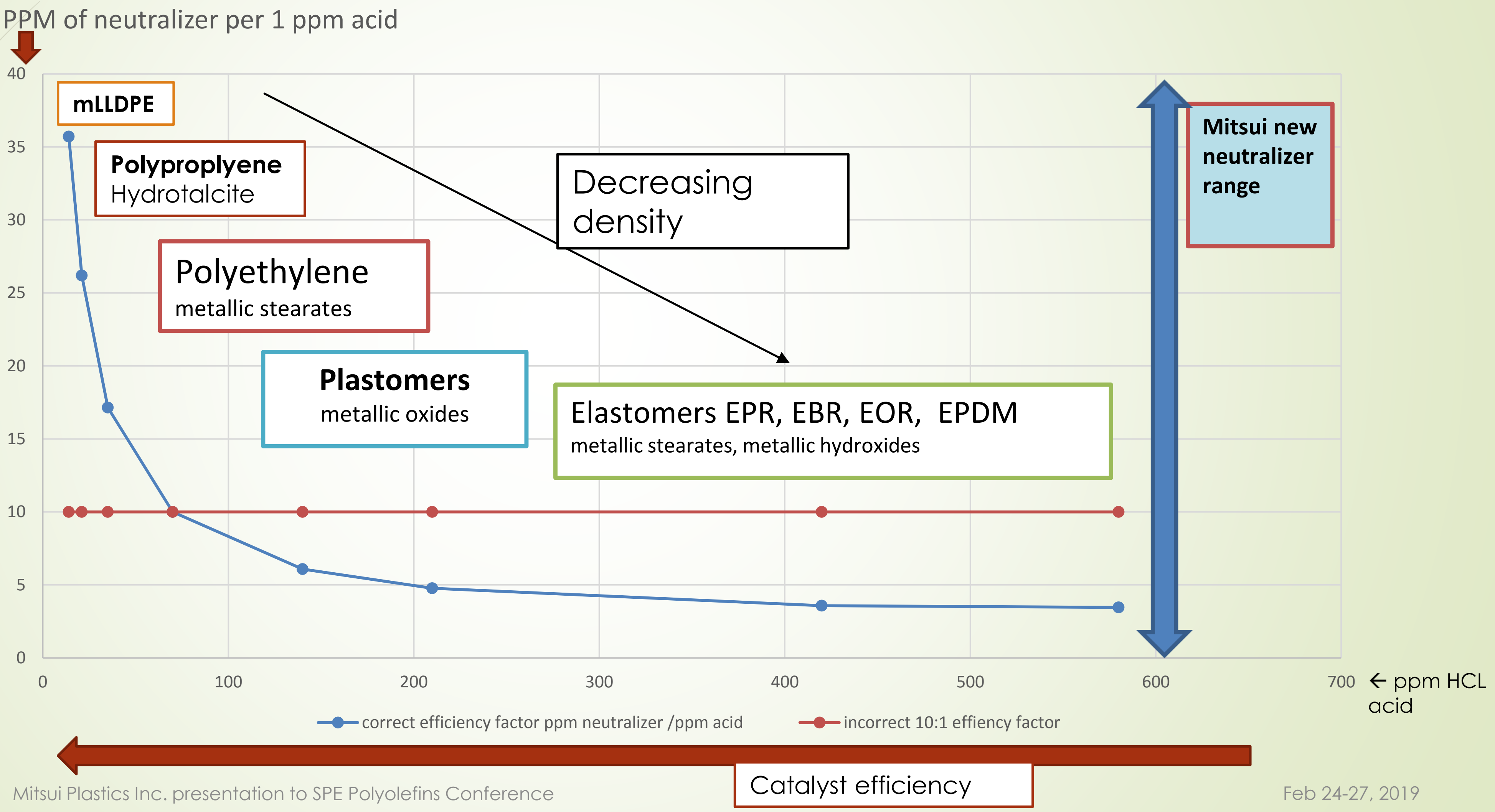
# Catalyst acid neutralizer efficiency



# Acid neutralized efficiency per similar volume



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



# M-Series catalyst neutralizer suggestions:

| | | | SUGGESTIONS | | ppm of acid from TiCl4 | Commercial Examples |
|---|---|---|---|---|---|---|
| **Ziegler-Natta Catalyzed Polyolefins** | g-cat/xxxxg Polyolefin | ppm Ti in polyolefin<br>1gTiCl4 = 25.27% Ti | phenolic AO ppm / phosphite AO ppm | Ppm of Mitsui M-Series | HCL = ppm Ti x (141.6/47.9 (ppm/mole)<br>**1 ppm Ti = 4 ppm HCL**<br>**1 ppm Mg = 3ppm HCL****  | |
| **Polyethylene** | 1g-cat/50,500g<br>1kg-cat/50 tons PE | 5 | 500/1000 | 600 | **35** | 0.934-0.920LLDPE film grades |
| | 1g-cat/25,200g<br>1kg-cat/25.2 tons PE | 10 | 375/750<br>=25% less AO | 800 | **70** | 0.920-0.910 LLDPE film grades |
| | 1g-cat/12,600g<br>1kg-cat/12.6 tons PE | 20-25 | 350/700<br>=30% less AO | 1,000 | **140-175** | 0.880-0.909 Plastomers<br>Bi-modal HDPE pipe and film grades |
| | 1g-cat/8,400g<br>1kg-cat/8.4 tons PE | 30 | 350/700<br>=30% less AO | 1000 | **210** | bi-modal HDPE (Mitsui CX). |

Increasing catalyst Efficiency

- * ppm XRxL needed to neutralize catalyst acid, stabilized anti-oxidants and protect the polymer from degredation. **20x the HCL concentration.**
- ** HCL from MgCL2 catalyst support which is 2.89 ppm HCL / 1ppm Mg. So, **1ppm Ti + 1 ppm Mg = 7 ppm HCL.**

# How does Mitsui's M-Series neutralizer work?

- **Proprietary** blend designed for:
  - 4th – 6th generation $TiCl_4$-$MgCl_2$ 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

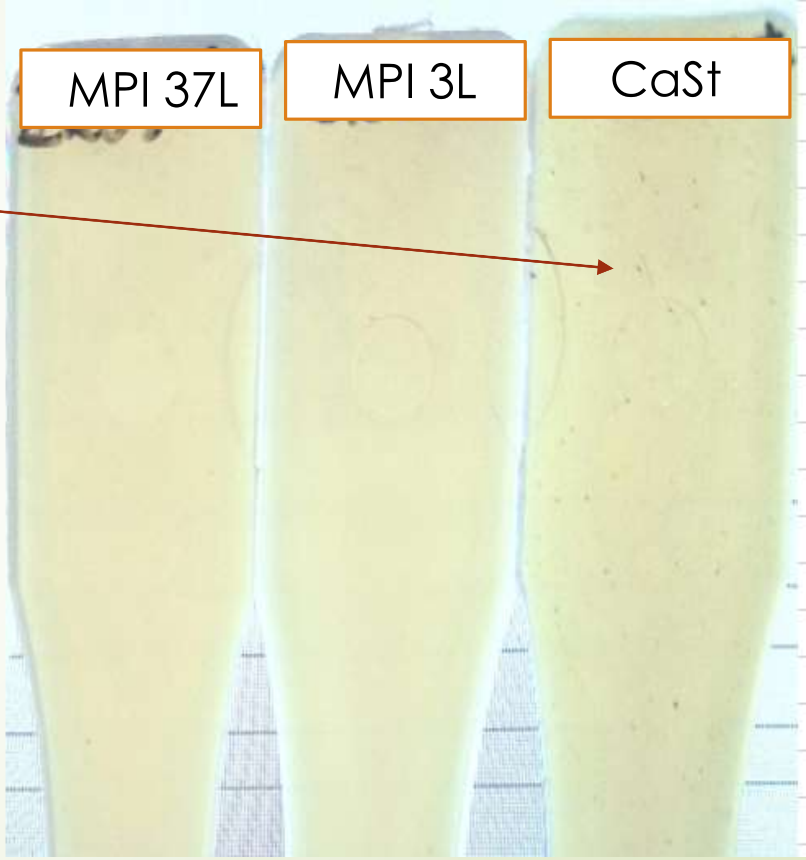

1. Acid scavenging chemistry:

   CaSt + 2HCL → CaCl2 + Stearic acid

2. CaCl2 is a corrosive "Lewis acids" (ref.1)
   - Lewis acid examples : TiCl4, ZrCl4, ZnCl2, CaCl2, NaCl
   - Lewis acids destroy antioxidants and hindered amines (HALS).
3. Stearic acid has a 114c 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 190c ***
  - 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 190c ***
  - 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 250c 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, **Tm 250 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 Z1 =170 C, Z2 =190 C, Z3 =190 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



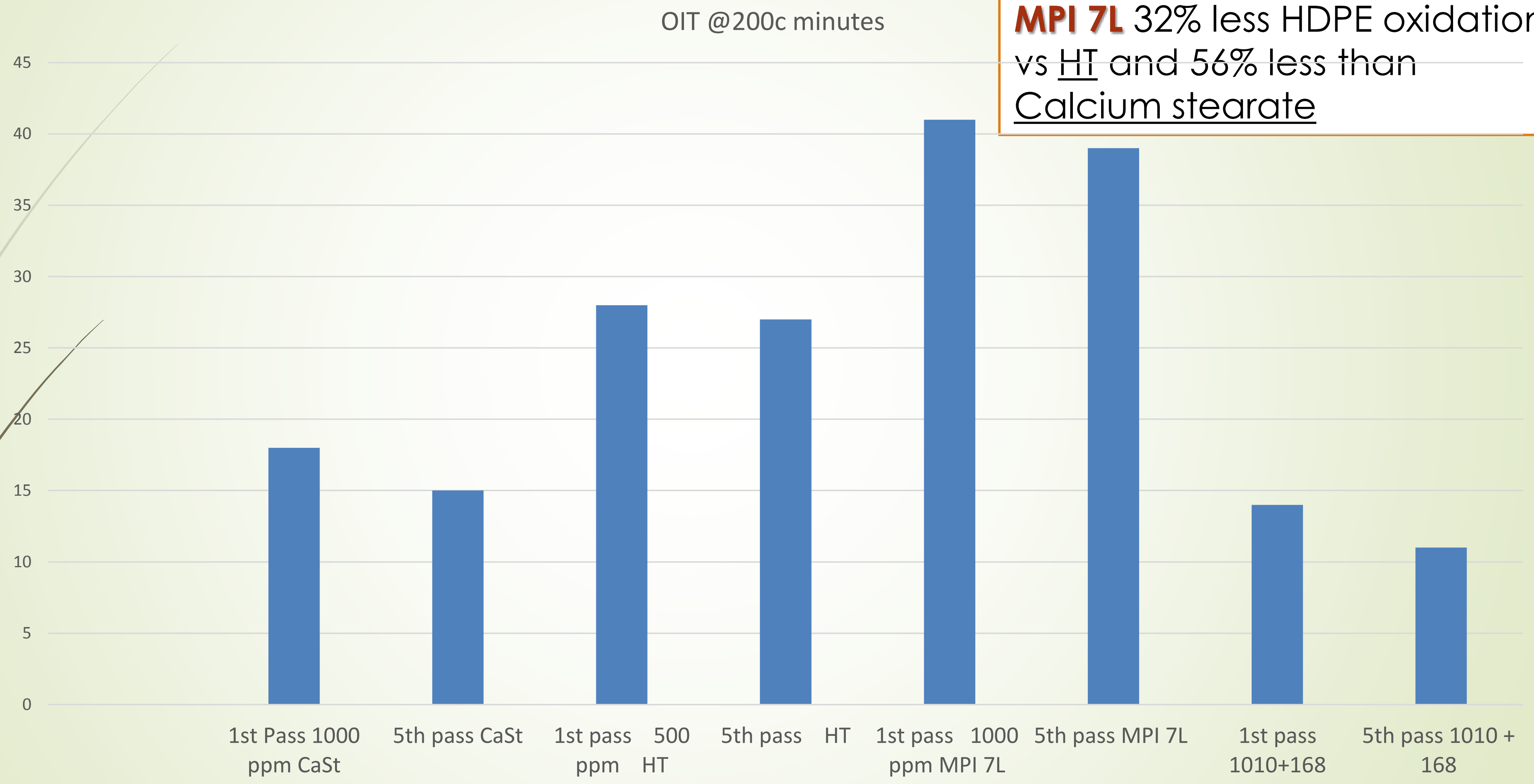
M-Series 7L  development vs calcium stearate and Hydrotalcite

Extrusion at 90 RPM, **Tm 190c**

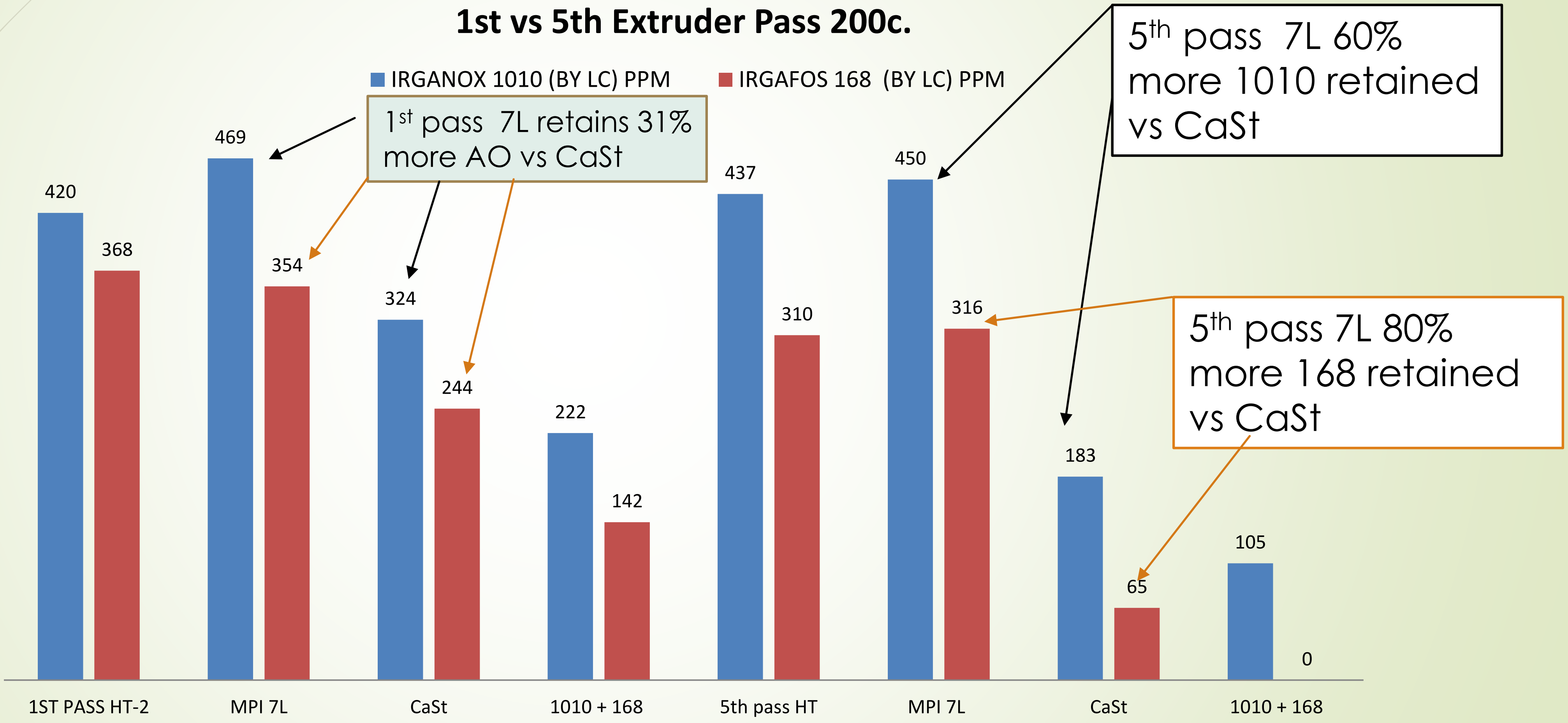
Antioxidants:  500 ppm AO 1010 + 500 ppm AO 168

# M7L protects antioxidants

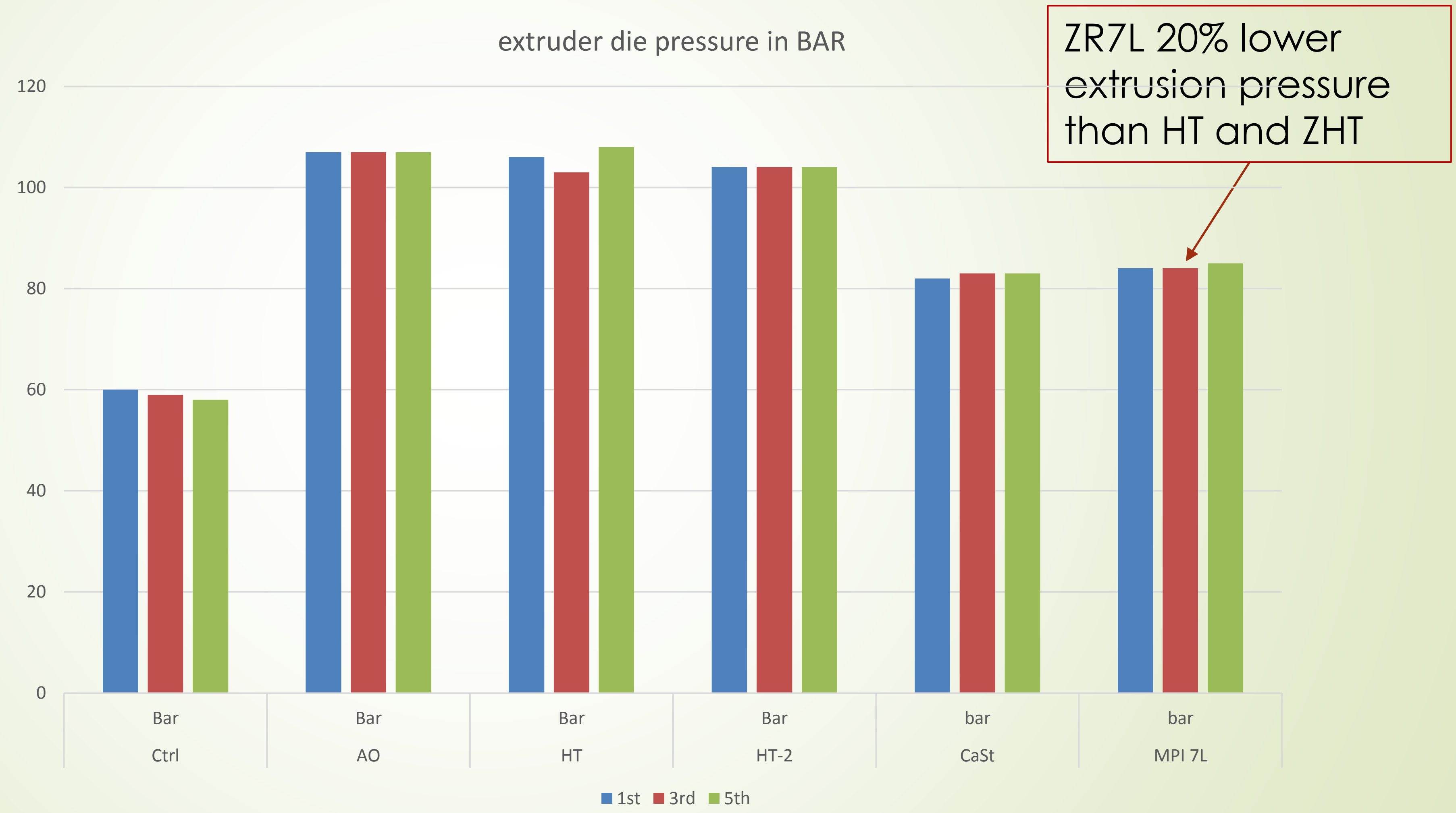
**MPI 7L** 32% less HDPE oxidation vs HT and 56% less than Calcium stearate



# M7L 31% - 80% more AO retained

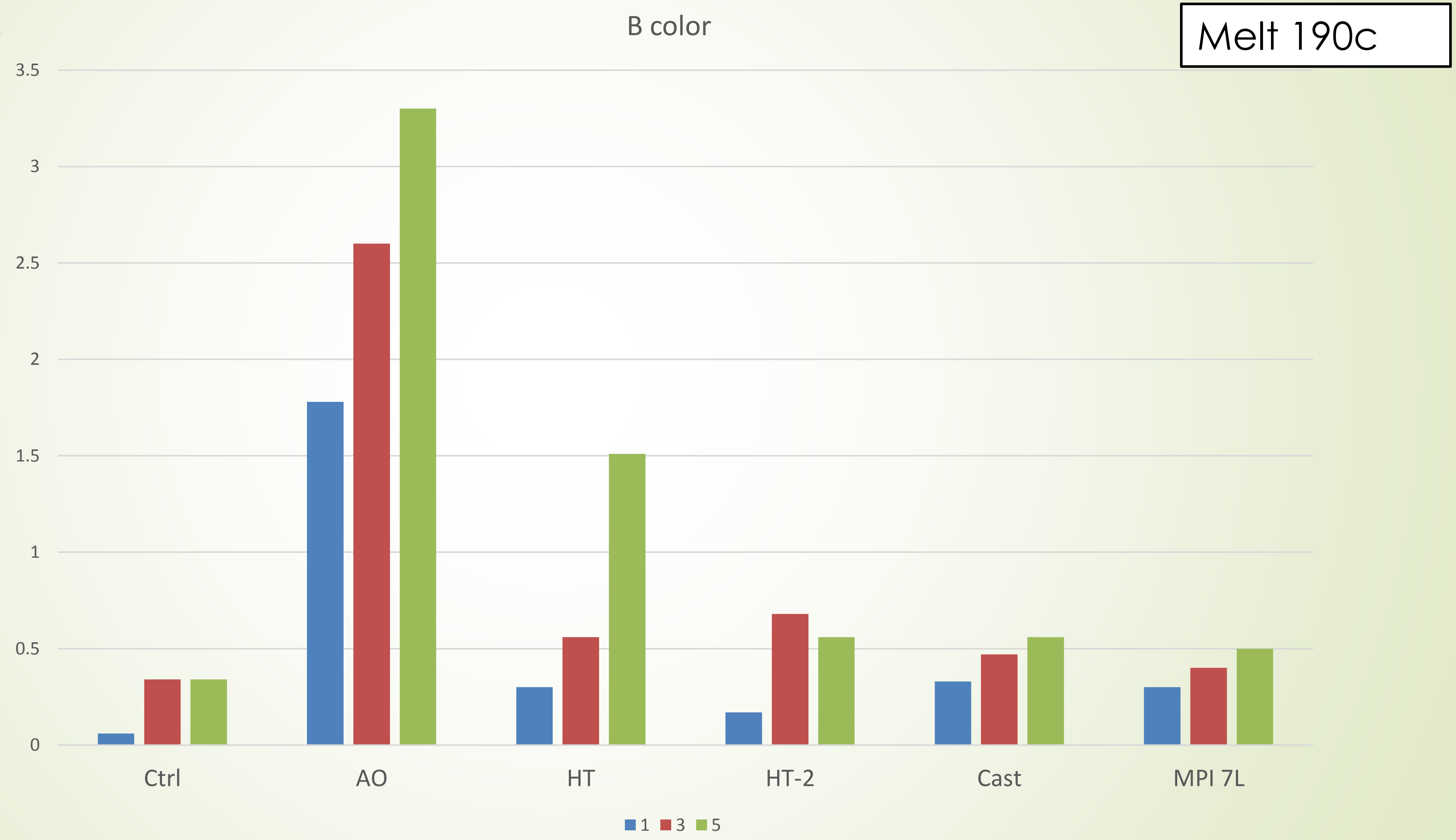


# M7L reduces extruder pressure in HDPE

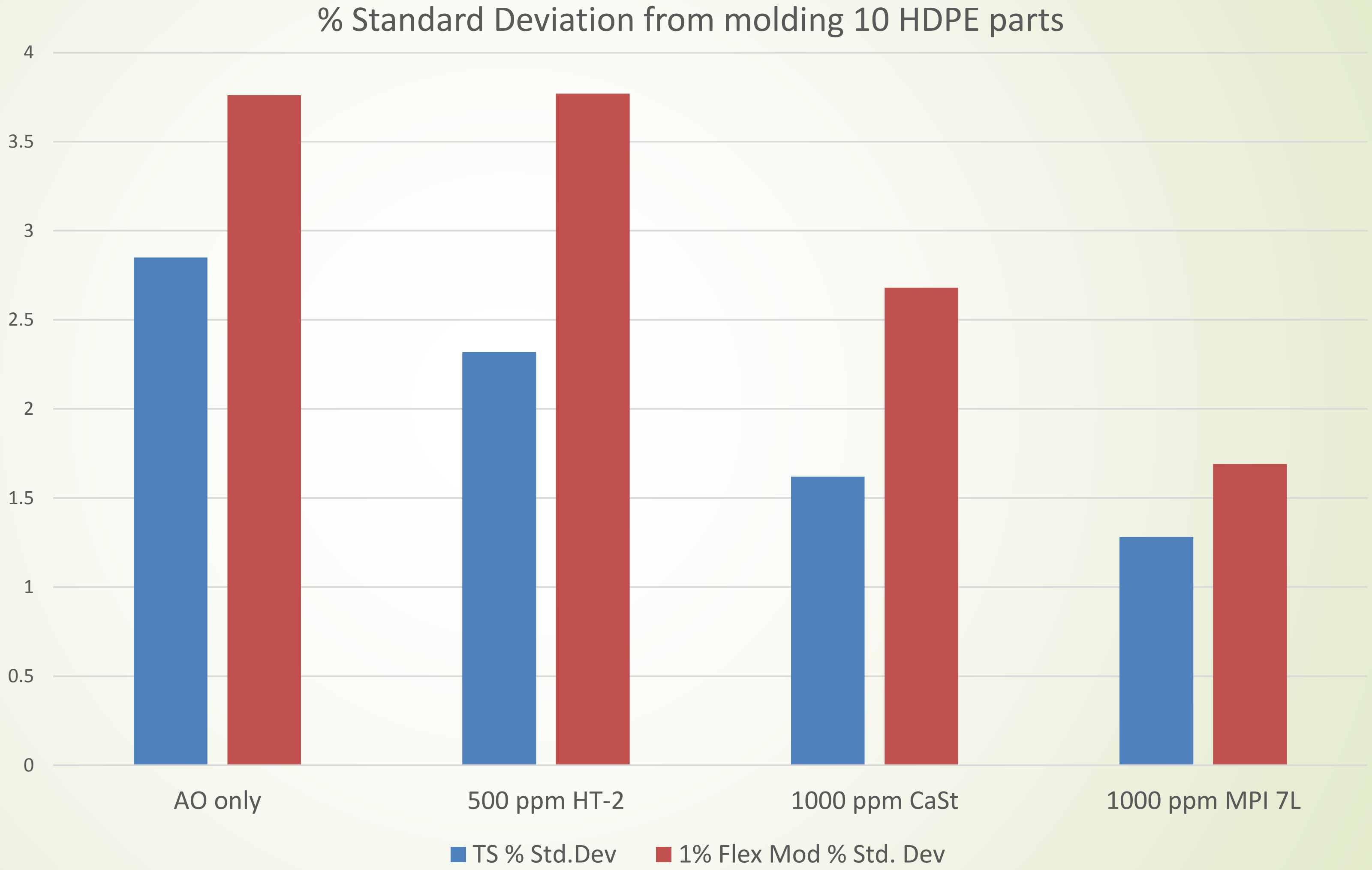


# M7L lowest color in Bi-modal HDPE pipe grade



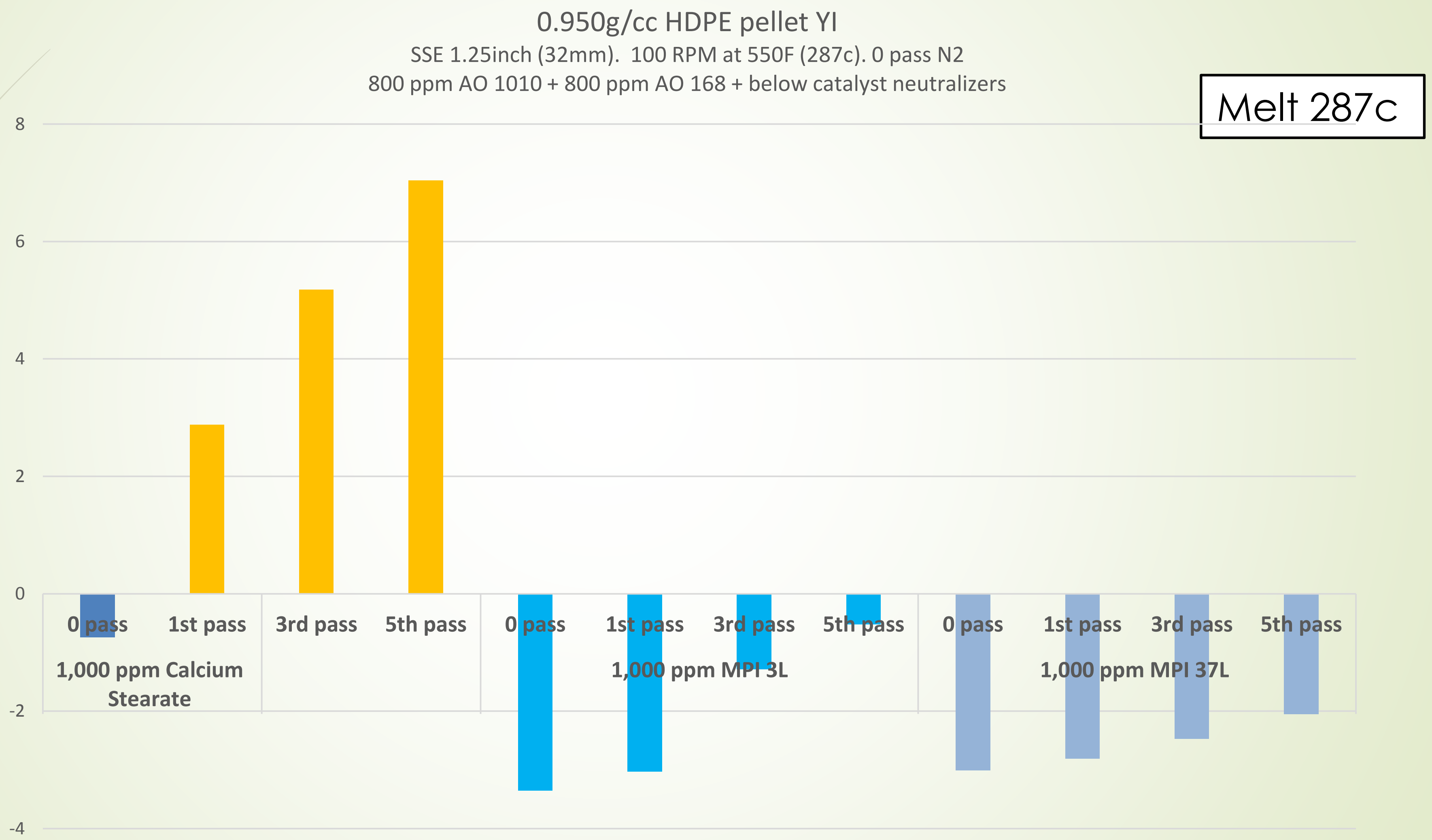


# M7L 40-60% improvement in the quality of HDPE molded parts



# M37L and M3L shows no color oxidation in HDPE





# C6-LLDPE 0.917g/cc

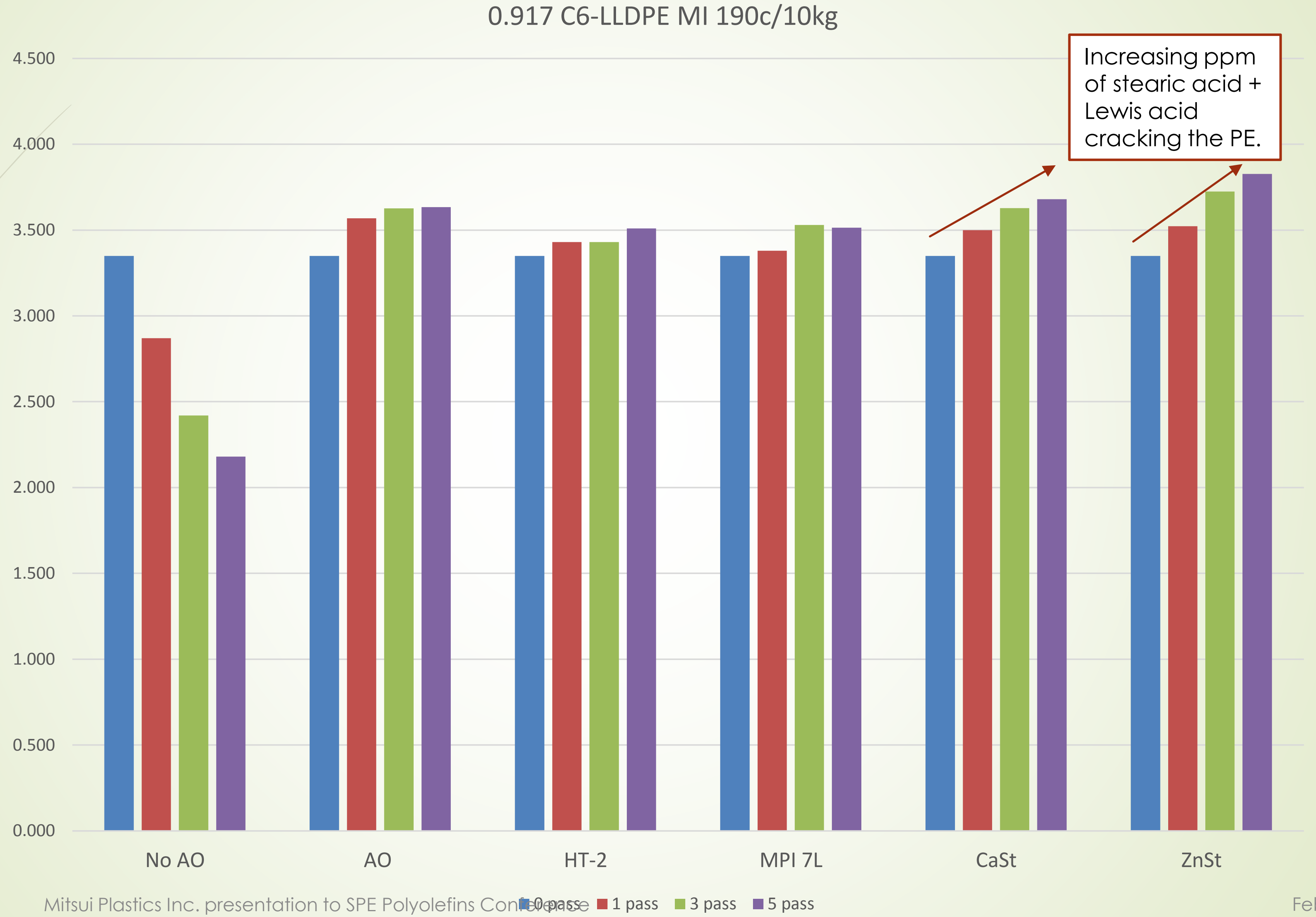
MPI 7L and 37L development

vs CaSt, ZnSt, ZnO and Hydrotalcite

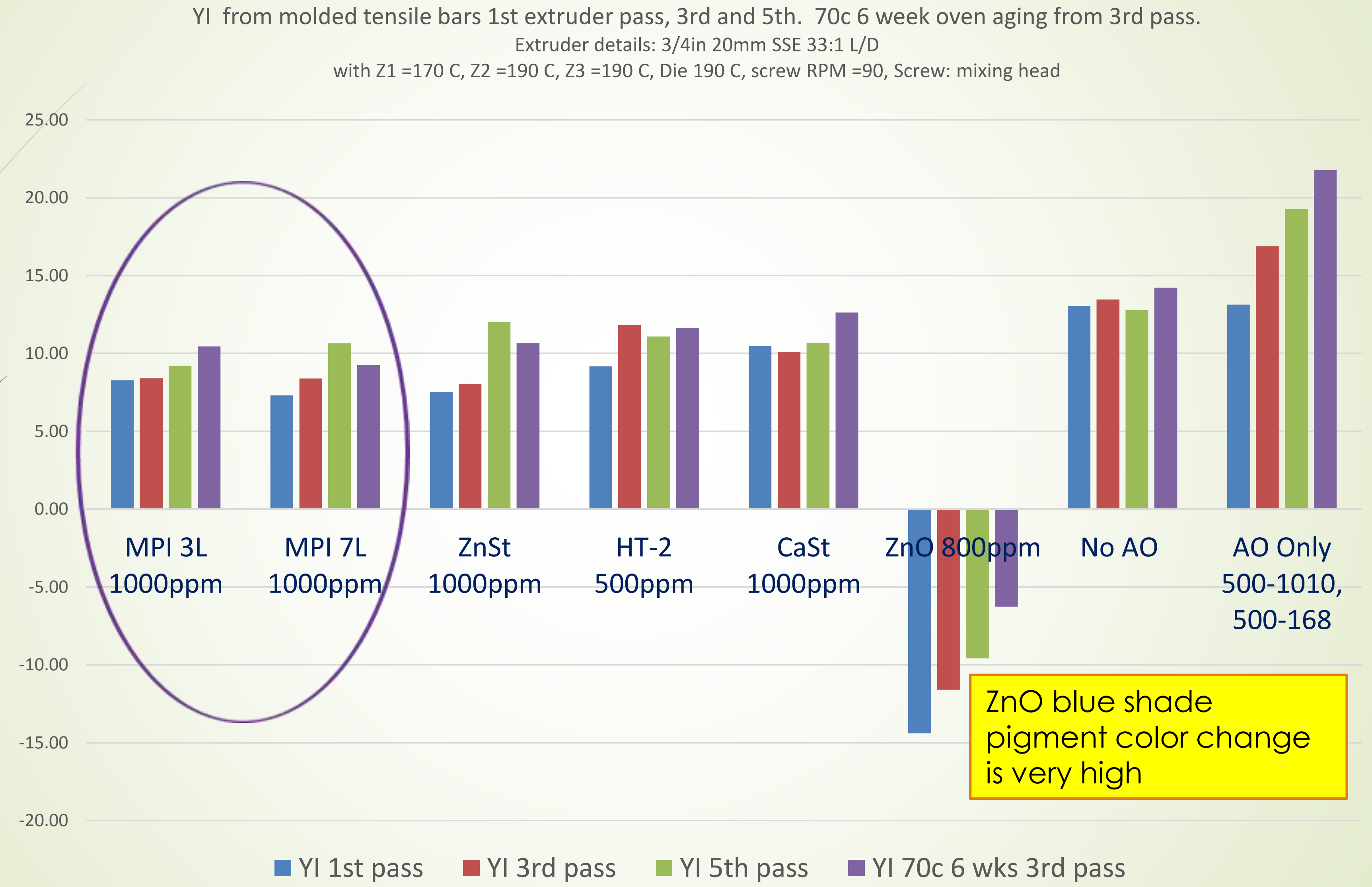
Extrusion at 90 RPM, **Tm 190c**

Antioxidants: 500 ppm AO 1010 + 500 ppm AO 168

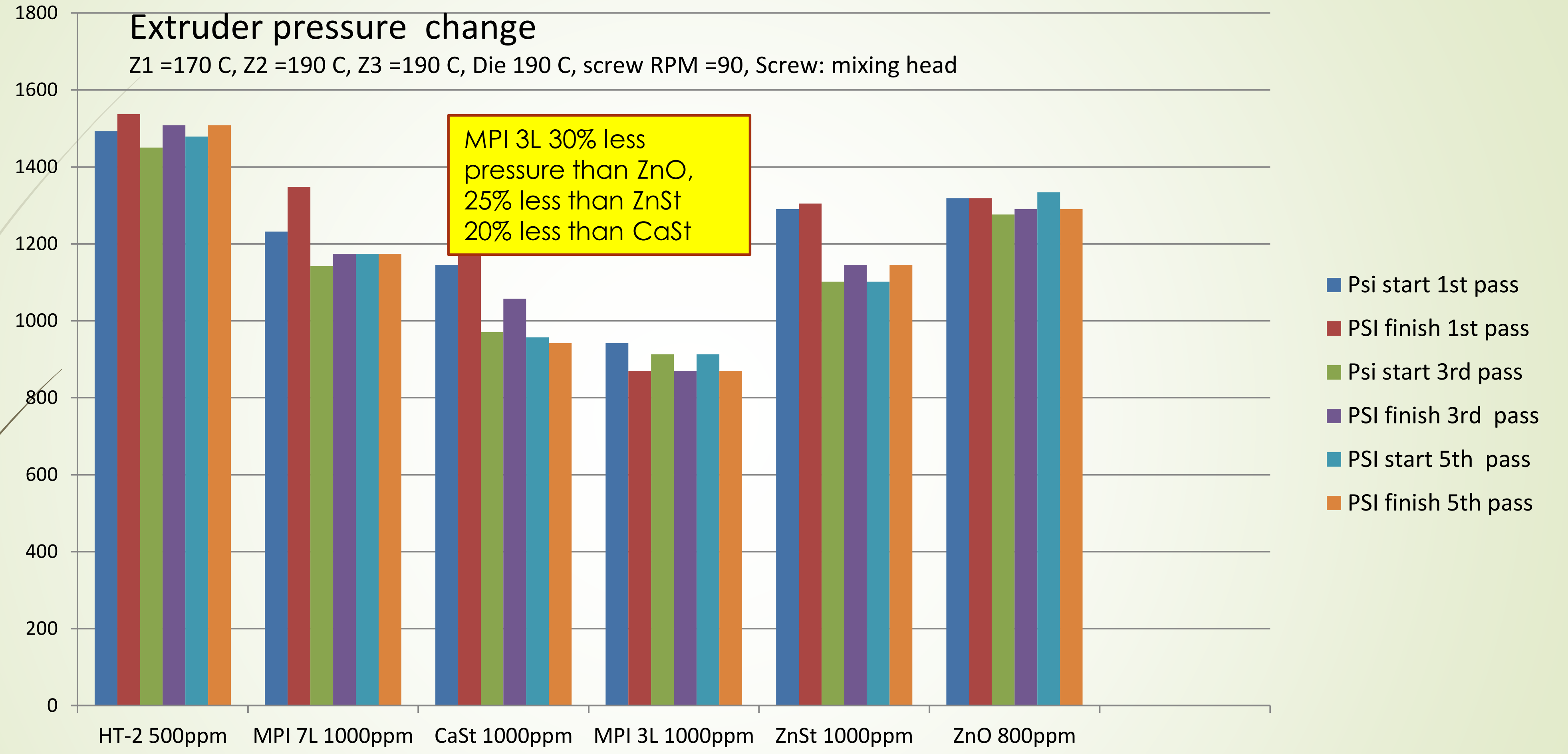
# M7L stable multi-pass MI



# M3L and M7L low color LLDPE



# M3L 30% lower extruder pressure in LLDPE

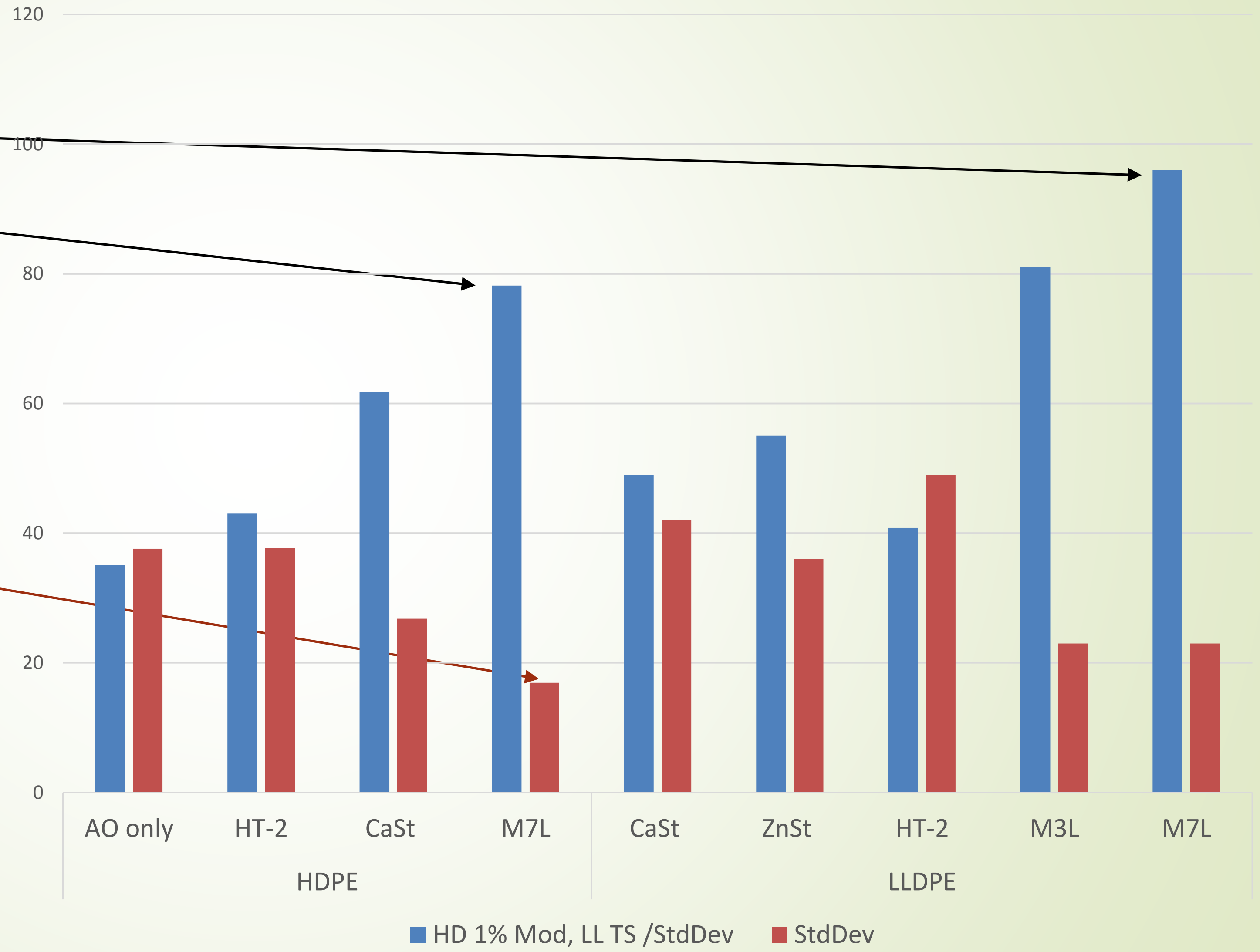



NOTES: ZnO 1st extrusion black die drool and by 5th black powder residue

# 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



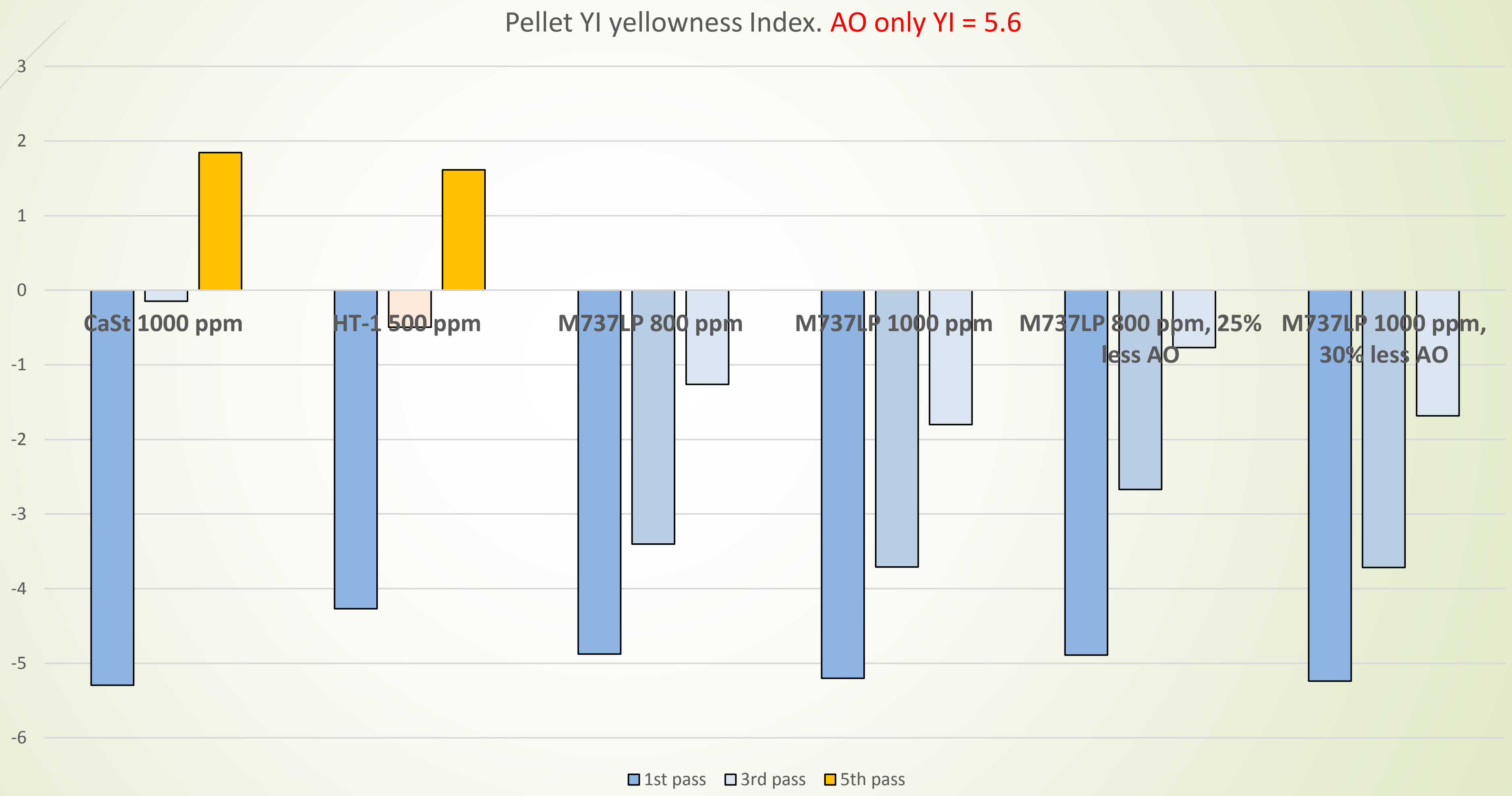
# C6-LLDPE 0.917g/cc

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

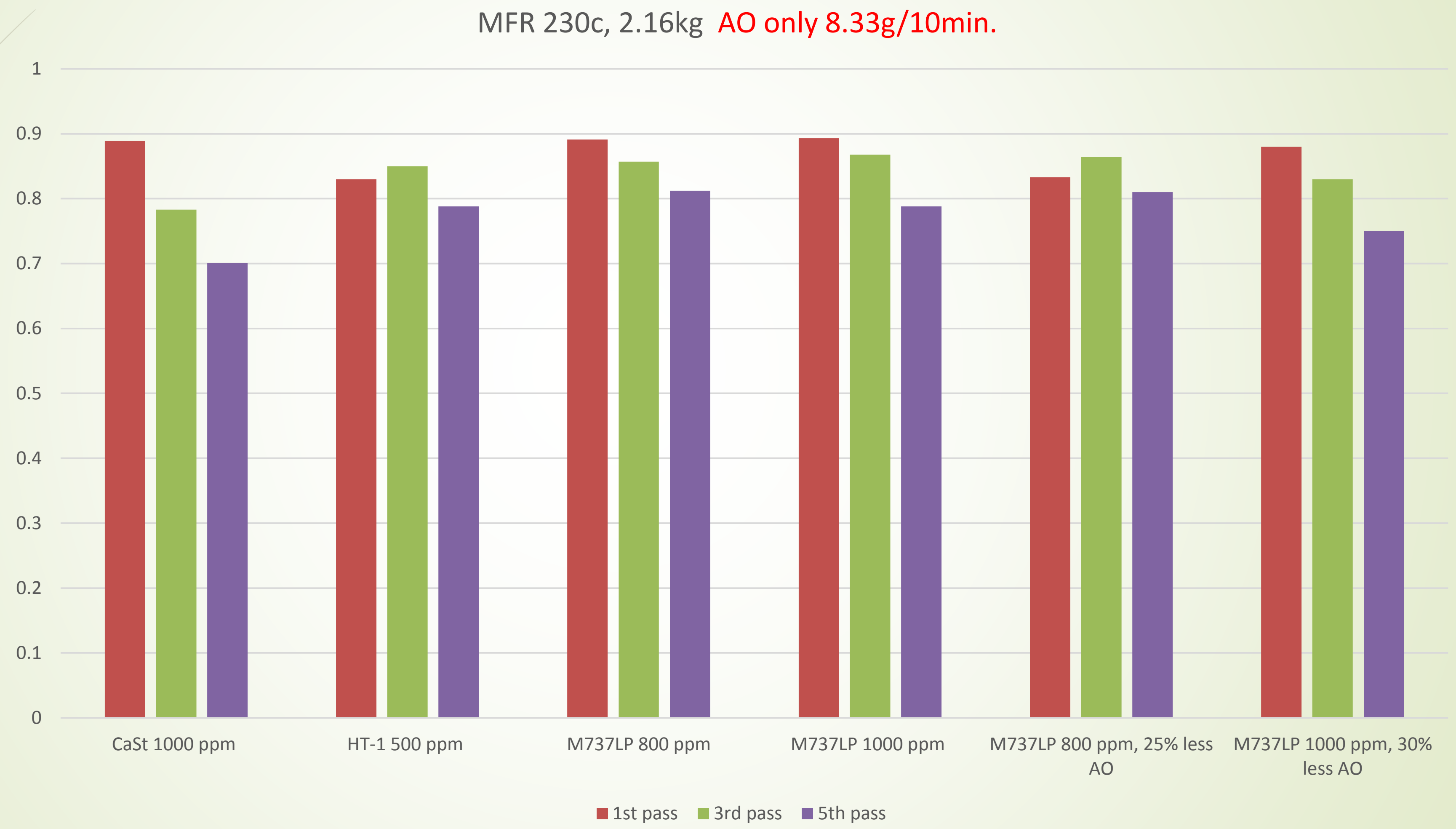
1, 3, 5 Extrusion at 30 RPM, **Tm 250c under N2**

Antioxidants: 500 ppm AO 1010 +1,000 ppm AO 168

# M737P no yellow 1-5 extruder passes

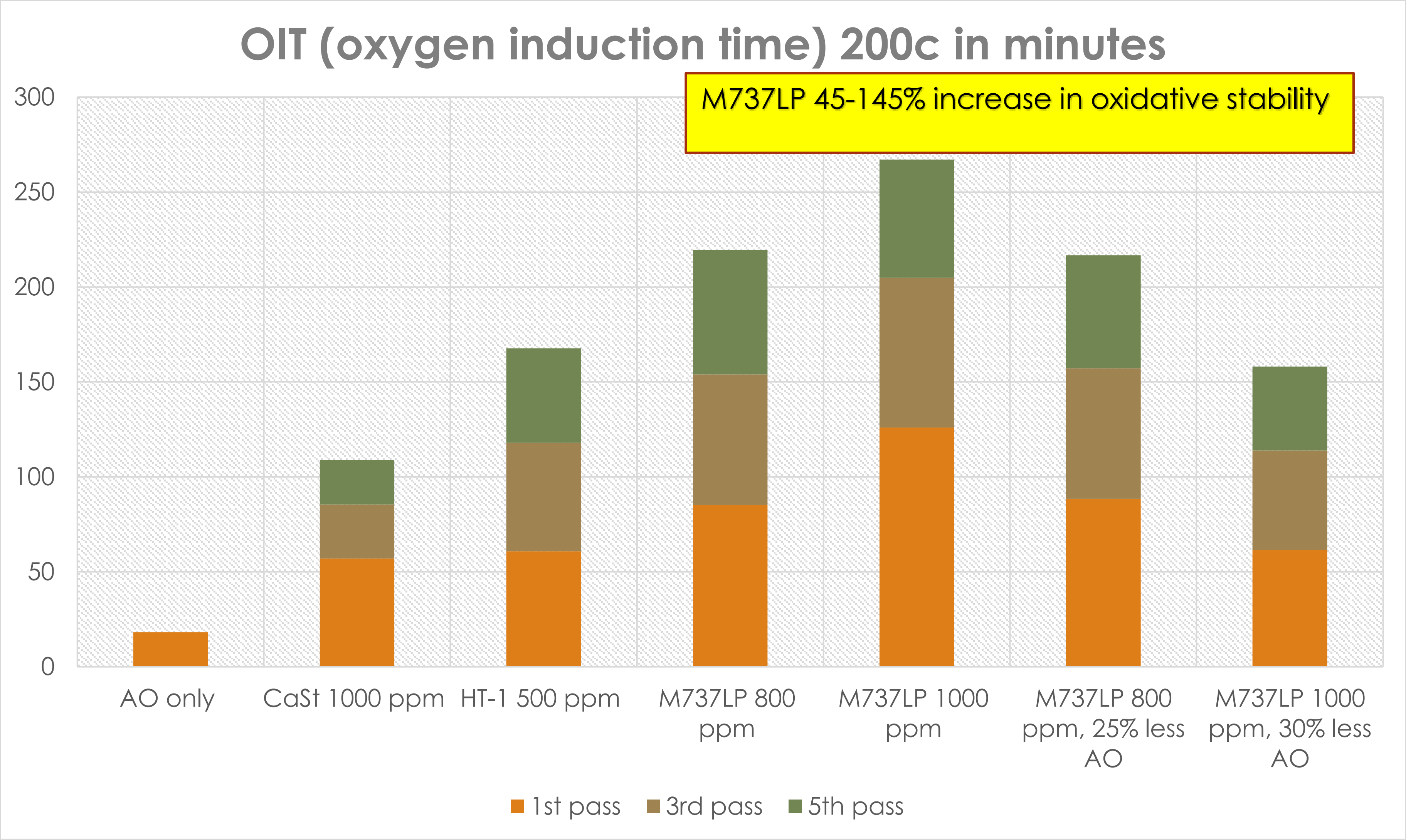


# M737P even with 30% less AO more stable than the Calcium Stearate Control



# M737P high oxidative stability even with 30% less antioxidants





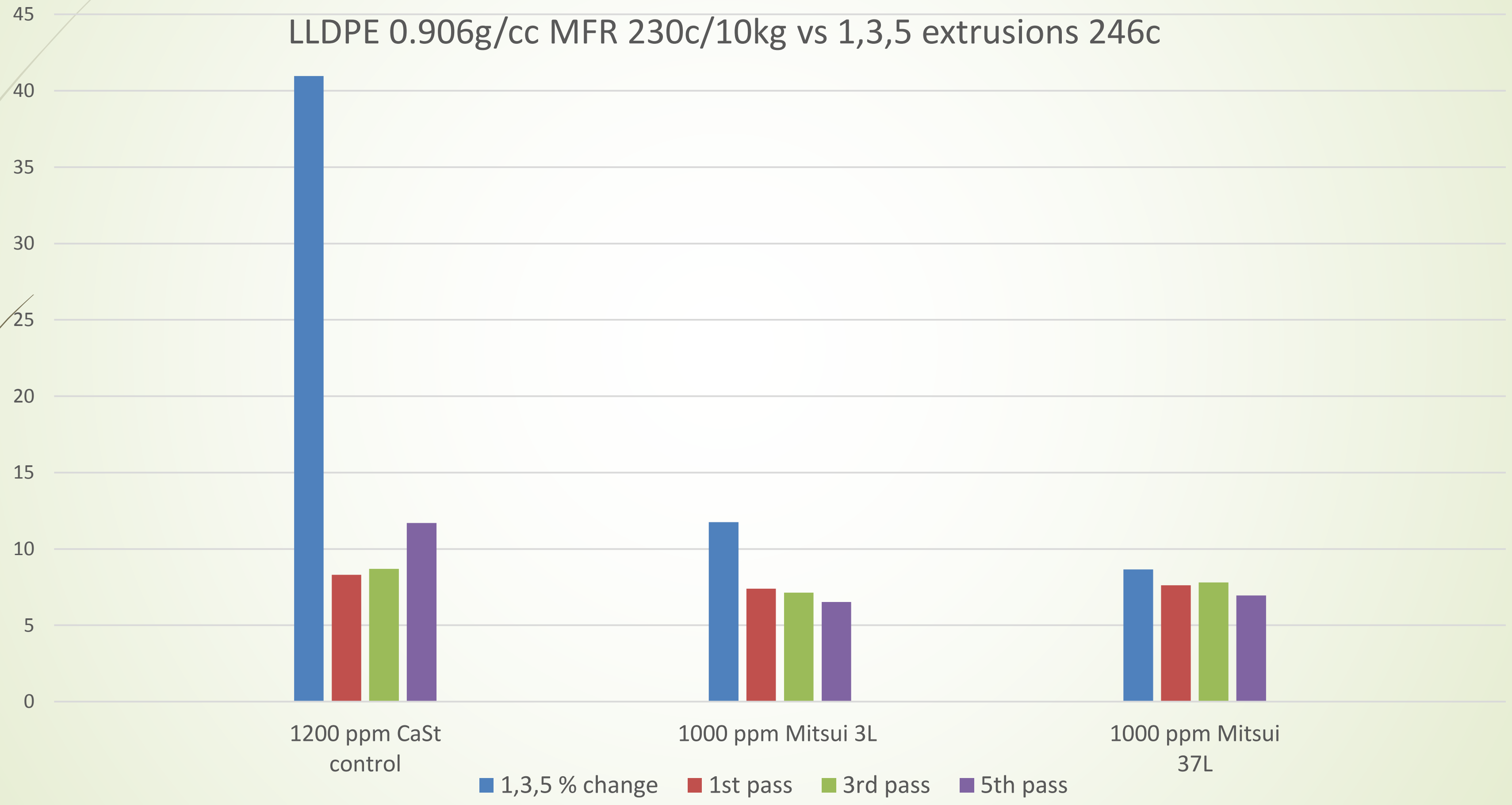
# C6-LLDPE 0.906 g/cc

Mitsui's M-Series M3L and M37L compared to Calcium Stearate

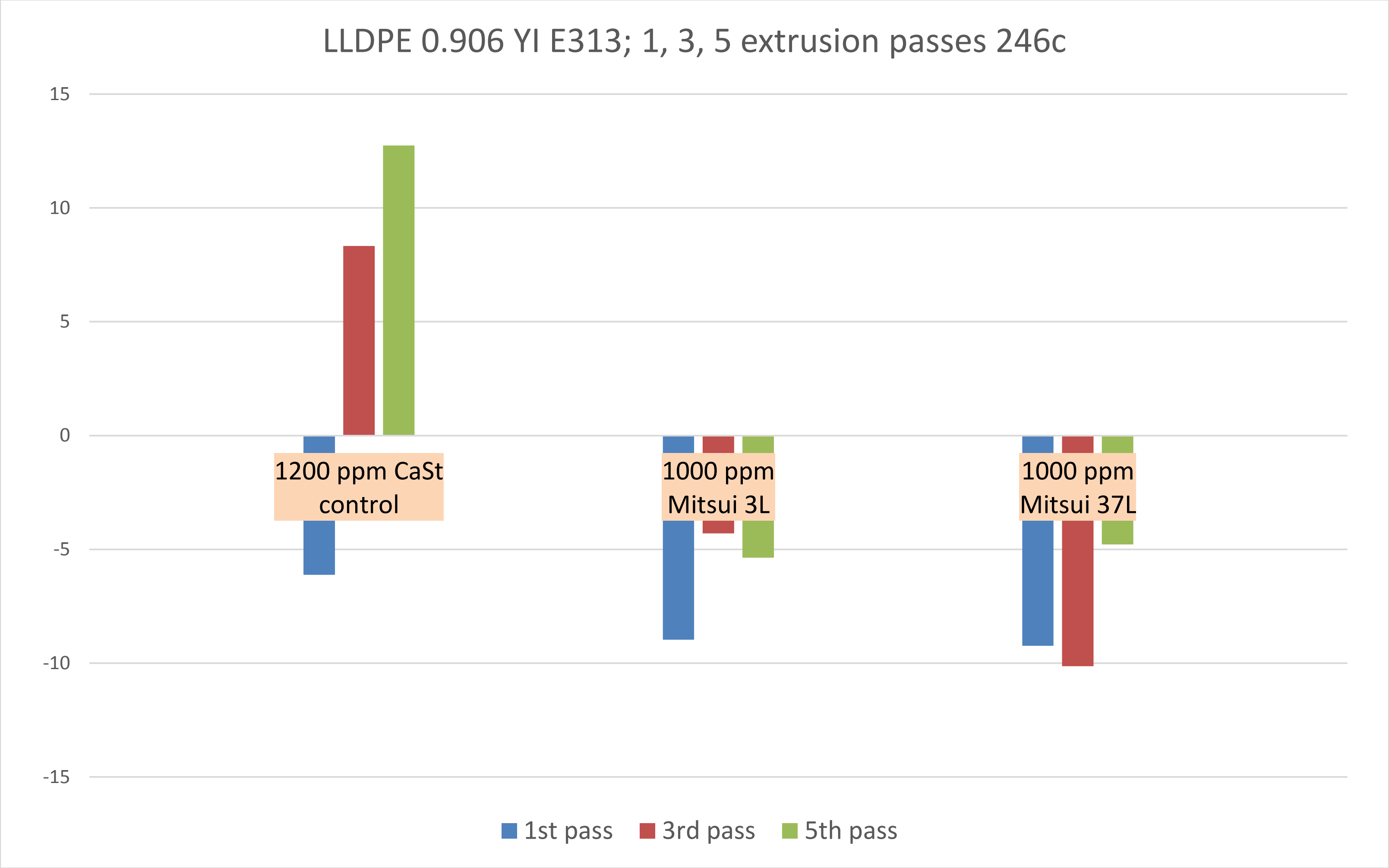
Extrusion at 30 RPM, **Tm 250 c**

Antioxidants: 800 ppm AO 76 + 1400 ppm Weston 705T.

# M3L and M37L show improved MI stability in LLDPE plastomer

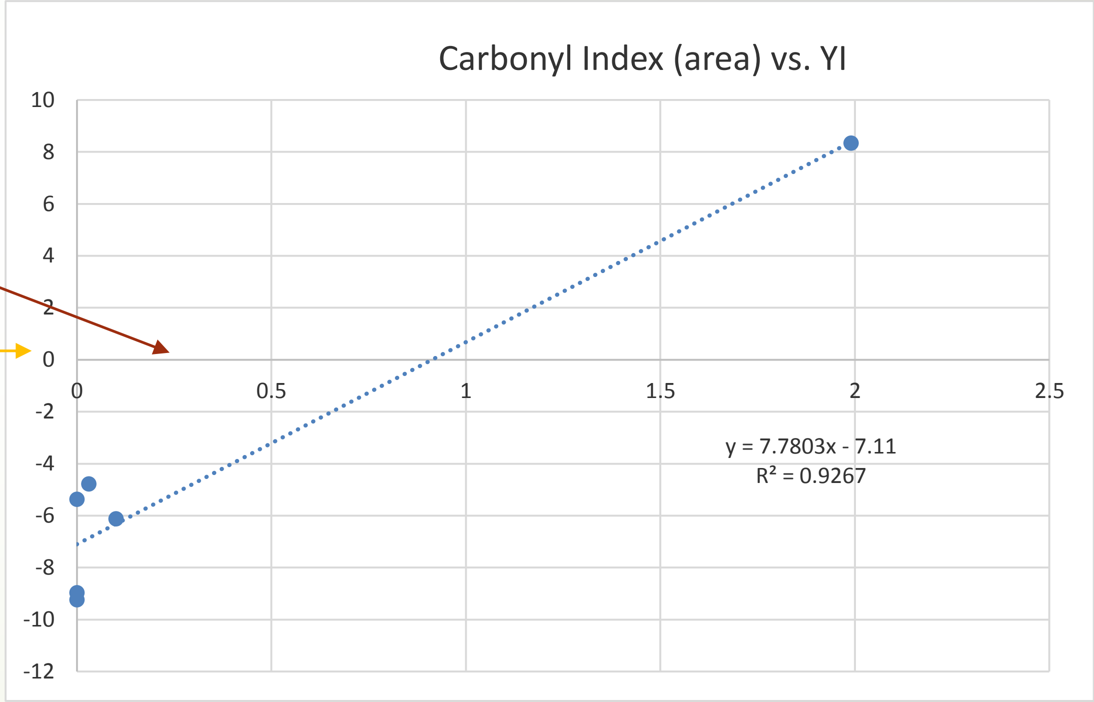


# Mitsui 3L and 37L show excellent low YI color in LLDPE plastomer

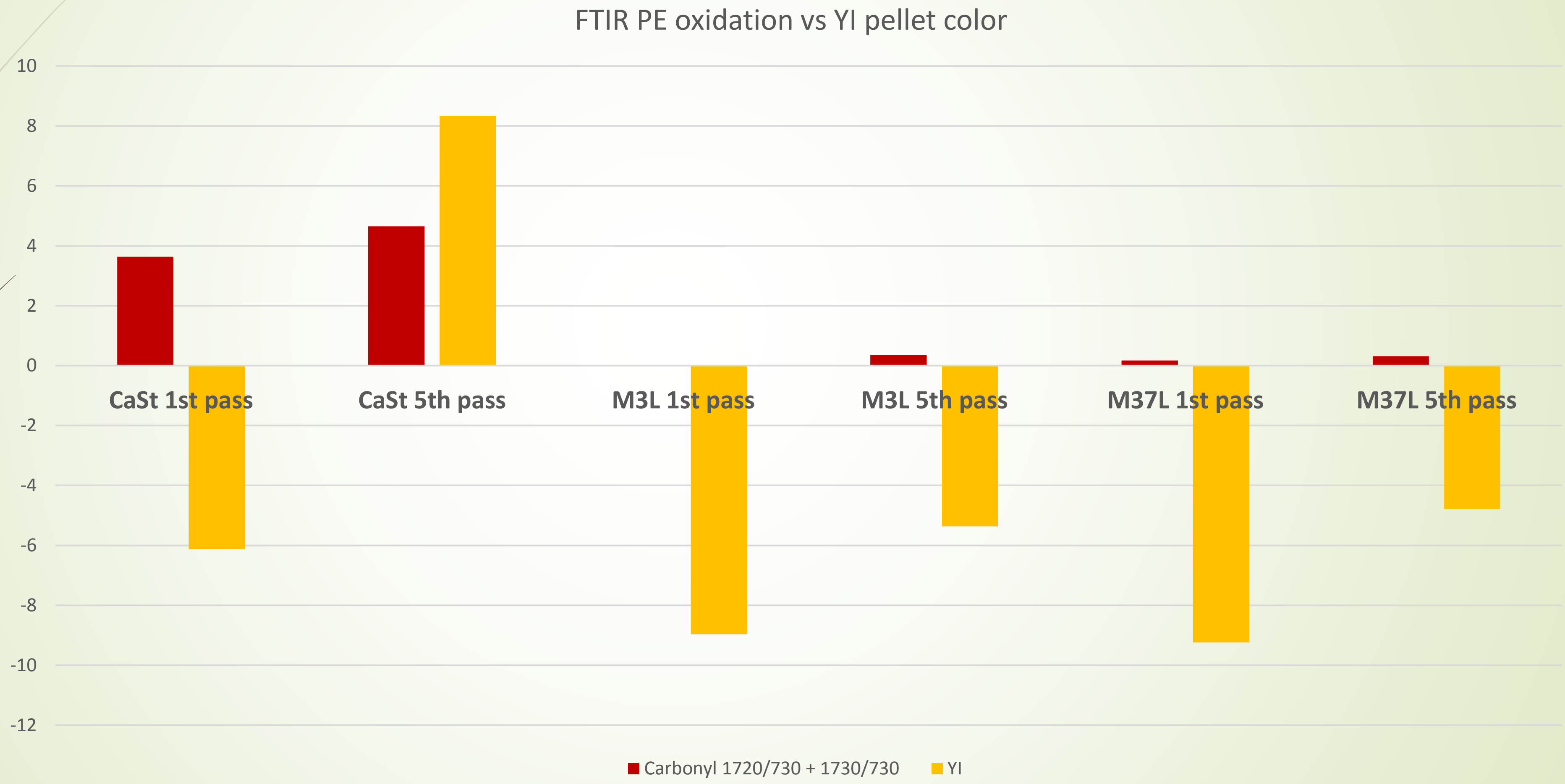


# FTIR oxidation values vs YI raw data

| FTIR raw data | | M3L 1st | M3L 5th | M37L1st | M37L5th | CaSt 1st | CaSt 5th |
|---|---|---|---|---|---|---|---|
| | | Corr Area | | | | | |
| | 1/cm | | | | | | |
| CH2 group | 720 | 2.319 | 2.865 | 4.223 | 1.28 | 3.71 | 3.627 |
| CH2 group | 730 | 1.246 | 1.085 | 1.124 | 1.953 | 1.354 | 0.139 |
| C-C bond | 1465 | | 0.842 | 0.481 | 1.781 | 0.946 | 1.301 |
| C=O | 1720 | | | | 0.062 | 0.137 | 0.277 |
| C=O | 1740 | 0 | 0.039 | 0.193 | 0.549 | 0.356 | 0.369 |
| OH | 3603 | 1.528 | 2.013 | 1.306 | 3.468 | 1.883 | 1.505 |
| Ratio C=C/C2 | 1740/730 | 0 | 0.035945 | 0.171708 | 0.281106 | 0.262925 | 2.654676 |
| Ratio C=O/C2 | 1720/730 | 0 | 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 1st extruder pass
     - 60-80% increase 5th 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 degredation - 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. $CaCl_2$ + 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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