Strategies for the Stabilization of Thermoplastics Polyolefin Roofing Membranes

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Main business focuses are:

- **RUBBER**
- **PLASTICS**
- **PETROLEUM** Additives

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Main Plastics Business:

STABILIZATION SOLUTIONS

- Antioxidants
- Metal Deactivation
- UV Stabilizers
- Custom Blends

POLYMER MODIFIERS

REINFORCING AGENTS

Strategies for the Stabilization of Thermoplastics Polyolefin TPO Roofing Membranes

Agenda

- Background to TPO Roofing
- Polyolefin Auto-Oxidation and Stabilization
- Design of Experiments – TPO Roofing Stabilization

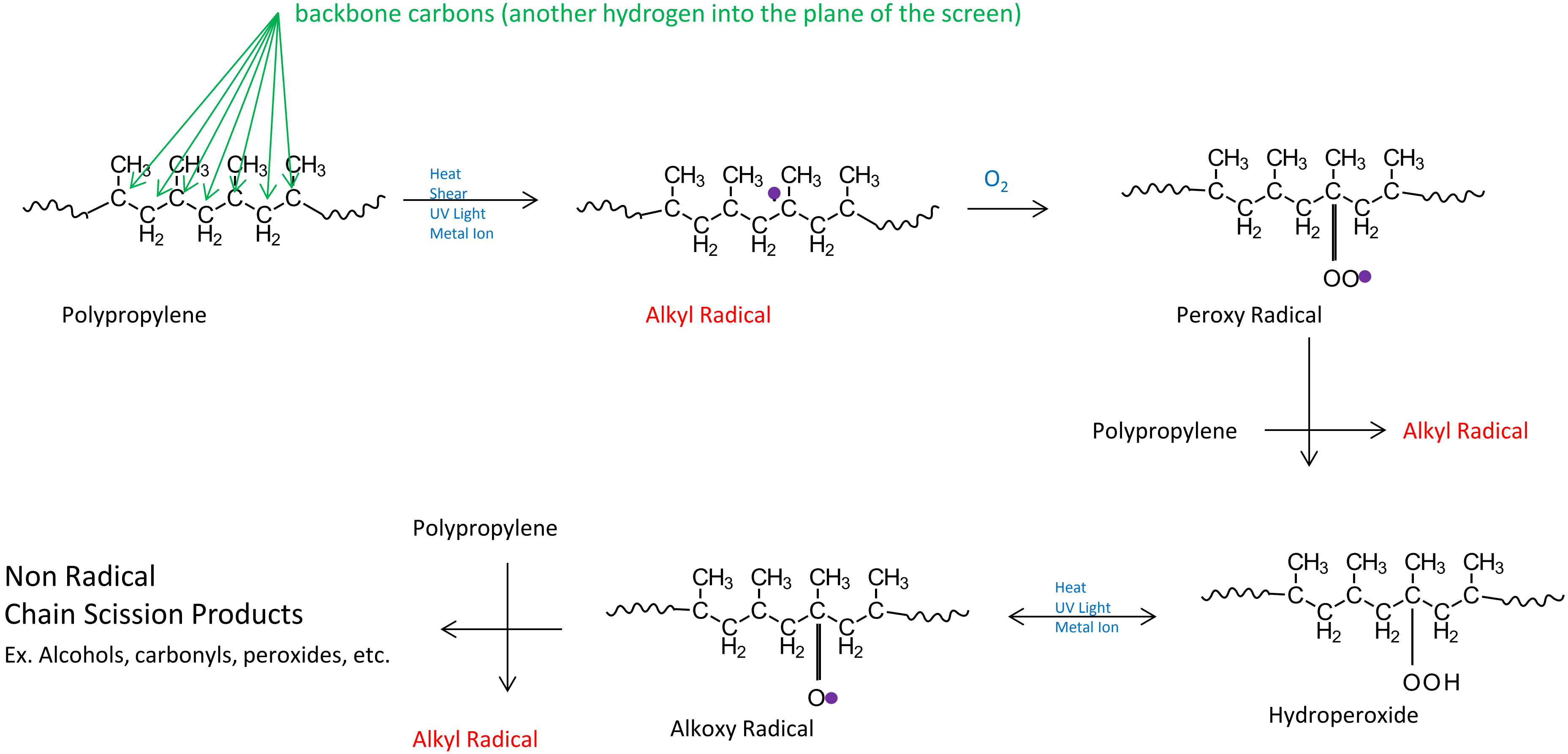
Background to TPO Roofing

Advantages of TPO Roofing

- Lightweight and easier to handle/install compare to other roofing materials
- Resistant to many chemicals
- Seams can be heat welded
- Good cold temperature flexibility
- No external plasticizers needed
- Economics

All good when this guy doesn't have to reinstall roofing for a long time!!!

Polyolefin Auto-Oxidation Chemistry Mechanism



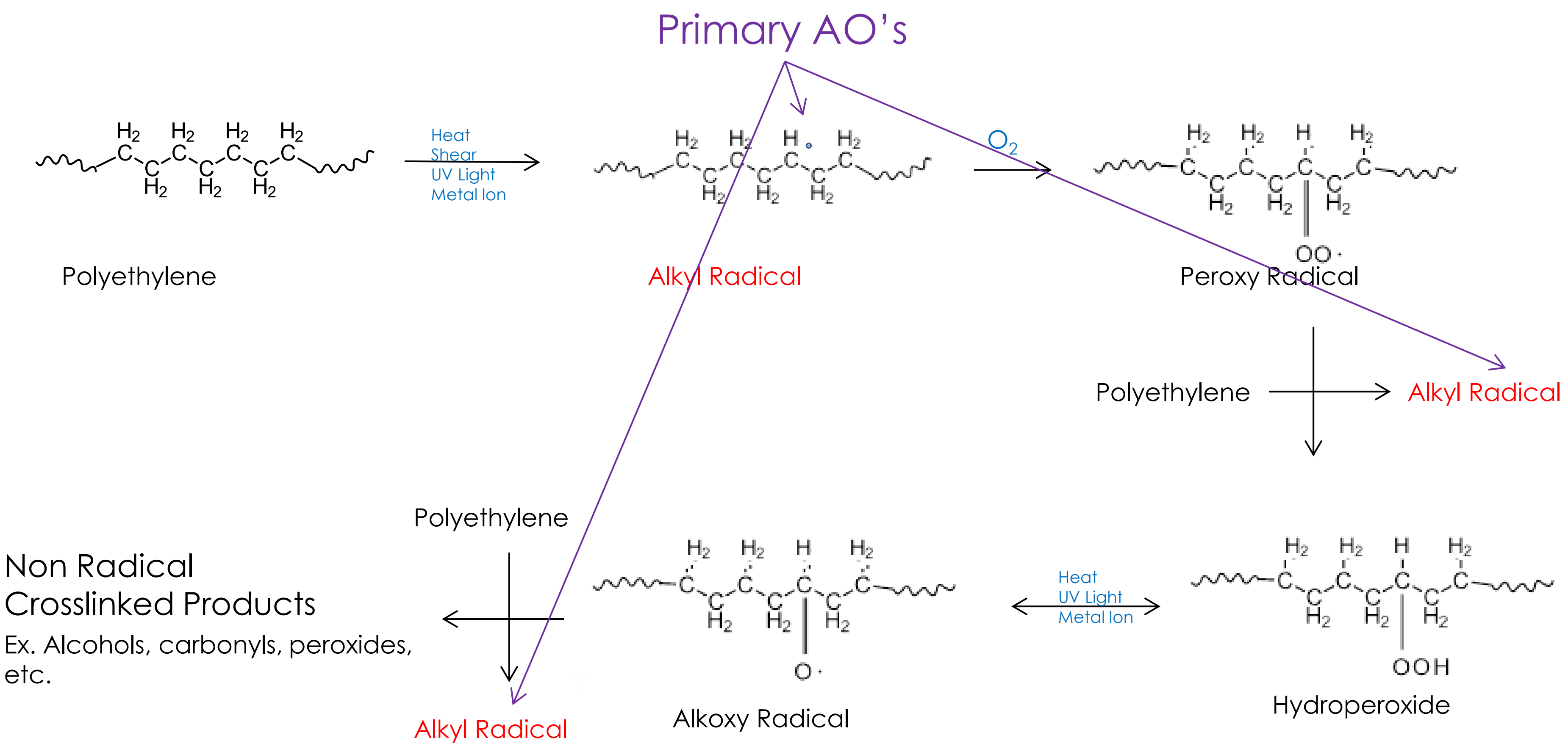
Polyolefin Auto-Oxidation Chemistry

Stabilization Additives

Primary AOs (Free Radical Scavengers)	**Secondary AOs** (Peroxide Decomposers)	**UV Stabilizers**
▪ Hindered Phenolics ▪ Diphenylamines ▪ Hydroquinolines	▪ Phosphites ▪ Thioesters ▪ Zinc 2-mercaptotoluimidazole (ZMTI) ▪ Co-synergists	▪ Hindered Amines ▪ UV Absorbers

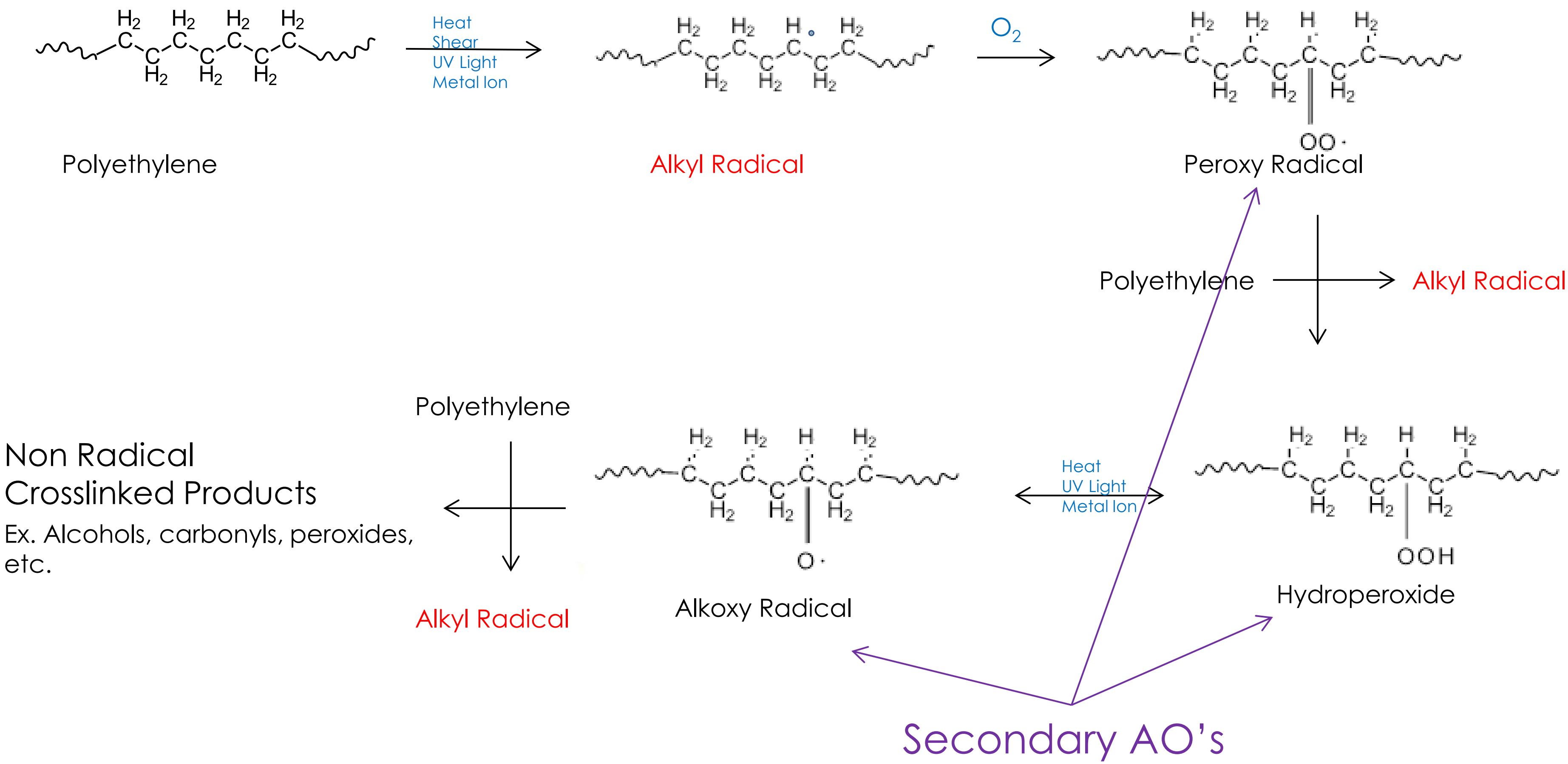
Polyethylene Auto-Oxidation Chemistry

Stabilization Additives



Polyethylene Auto-Oxidation Chemistry

Stabilization Additives

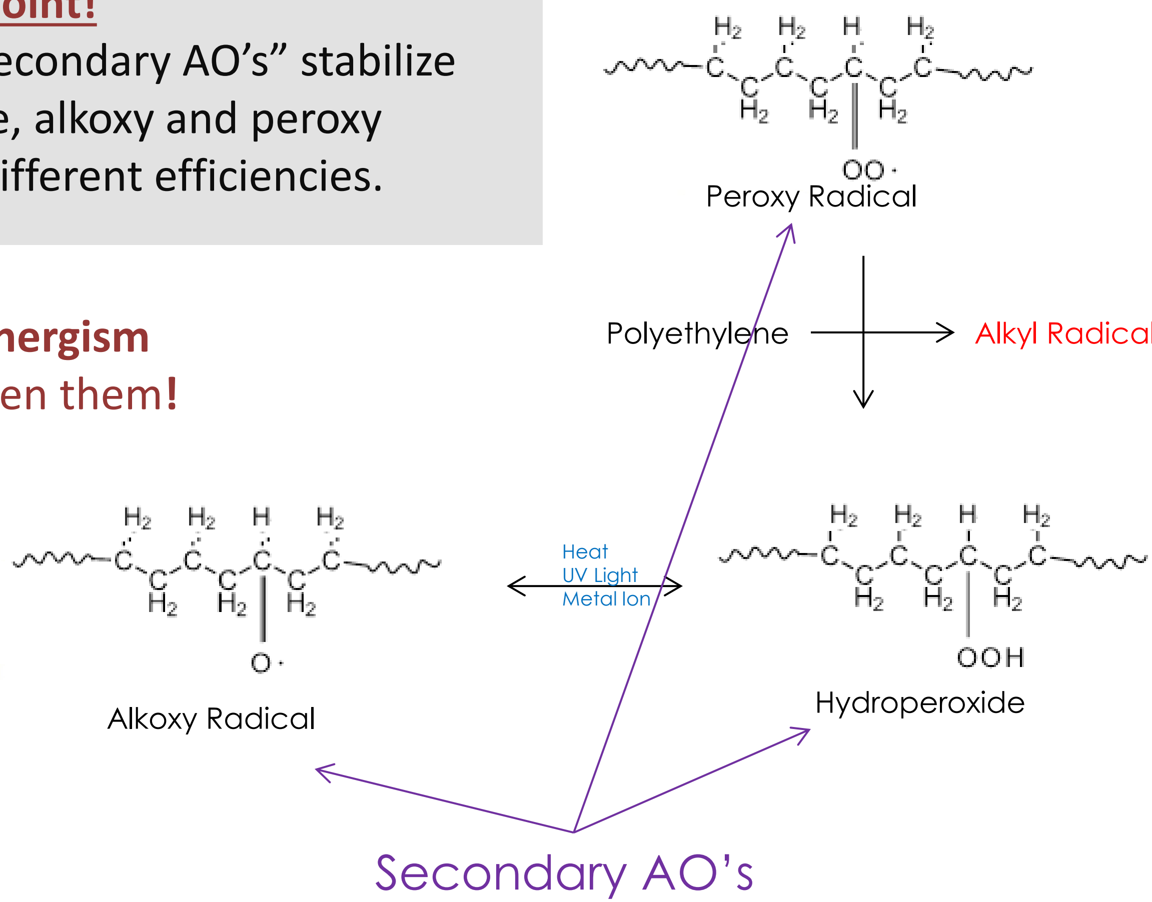


Polyethylene Auto-Oxidation Chemistry

Stabilization Additives

Important Point!
Different “Secondary AO’s” stabilize the peroxide, alkoxy and peroxy radicals to different efficiencies.

i.e. **Synergism** between them**!**



Stabilization
DOE Study

- Base Formulation
  - TPO/MgOH/TiO_2 65/30/5

TPO – *Lyondell CA10A* – supplied by Nexeo Solutions

MgOH – *MagShield S NB10* - supplied by Martin Marietta Magnesia Specialties

TiO_2 – *TiONA 696* – supplied by Cristal Global

Stabilization
DOE Study

- Base Formulation
  - TPO/MgOH/TiO_2 65/30/5

Constants:

- Hindered Phenolic AO
- HALS
- UVA
- Primary/Secondary will be held at a ratio of 1:1. (The combined total level will change, see below.)

Stabilization
DOE Study

Variables:

- HALS Level (Low 0.2 pph, High 0.5 pph)
- UVA Level (Low 0 pph, High 0.5 pph)
- Primary/Secondary Level (Low 0.2 pph, High 0.6 pph)
- Secondary AO type (three different types)

Stabilization
CTQs

- Physical tests after Exposure
  - Heat Aging: ASTM D6878: LTHA @ 116 °C for 224 days
    - Breaking strength, elongation, 90% Retained Value, others?
  - UV aging: ASTM D6878: Exposure 10,080 KJ/m^2/nm
    - Visual inspection for cracking crazing
  - Accelerated Heat Aging Test, LTHA @ 135°C until failure

Stabilization Study Status

- 116°C Oven
  - "**TPO + MgO + TiO_2**" samples showed serious cracking a 730 hours
  - "**TPO + MgO**" samples showed serious cracking at 1189 hours
  - All stabilized samples still good (currently 3000 hours)
- Weatherometer
  - At 844 KJ/m^2, "**TPO + MgO**" samples showed surface cracking, "**TPO**" samples showed slight cracking
  - At 1622 KJ/m^2, "**TPO + MgO + TiO_2**" samples are warped
  - All stabilized samples still good (currently 3500 KJ/m^2)

Stabilization Study Status

Accelerated Heat Aging (135°C)

By 102 hours "TPO + MgO + TiO_2" samples showed serious surface cracking

By 198 hours "TPO + MgO" samples showed serious surface cracking

By 865 hours half of "stabilized" samples showed serious surface cracking

- All with lower level of HALS

By 1200 hours all of the higher level HALS samples have showed surface cracking

DOE Results

135°C End-of-Life

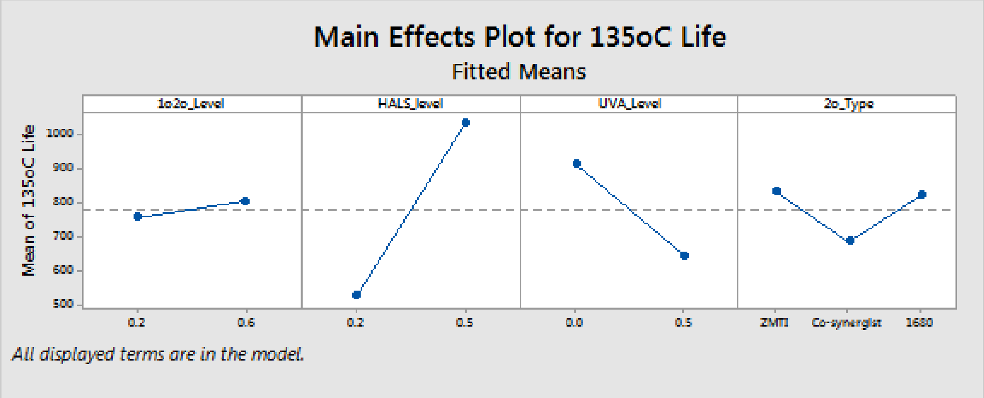
Error Model with 8 DF

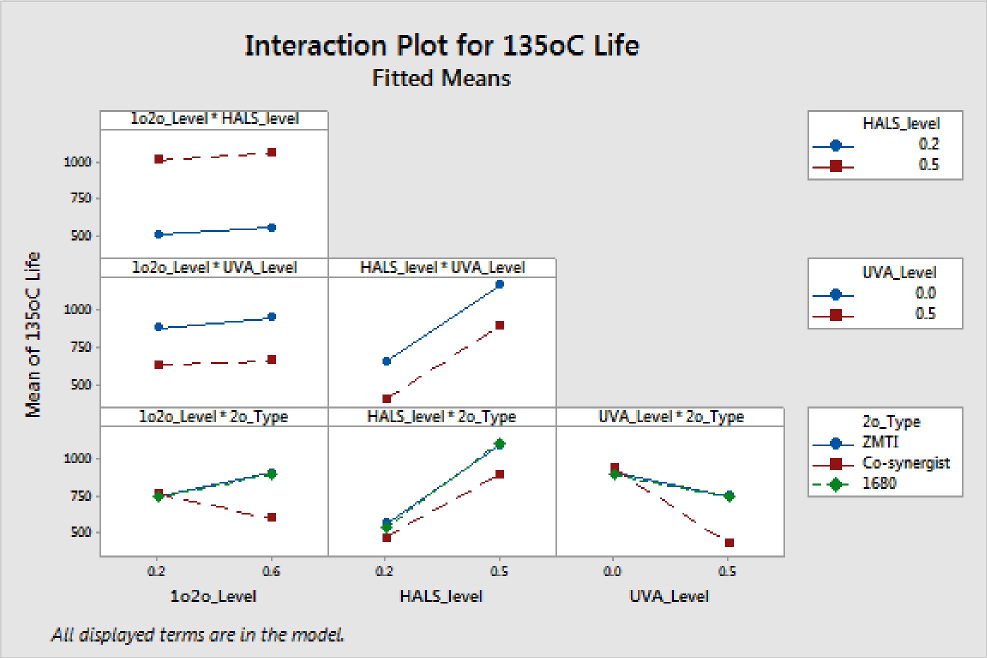
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	1671284	185698	28.77	0.000
Linear	5	1503571	300714	46.58	0.000
1o2o_Level	1	5373	5373	0.83	0.388
HALS_level	1	1041137	1041137	161.28	0.000
UVA_Level	1	300277	300277	46.52	0.000
2o_Type	2	68799	34400	5.33	0.034
2-Way Interactions	4	178614	44653	6.92	0.010
1o2o_Level*2o_Type	2	92984	46492	7.20	0.016
UVA_Level*2o_Type	2	101501	50751	7.86	0.013
Error	8	51644	6455		
Total	17	1722927			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
80.3459	97.00%	93.63%	74.14%

Main Effects plus Interactions





Conclusions

- HALS the "meat" of LTHA Stabilization
- UVA detriment to heat aging
- ZMTI as good as 1680
- Co-synergist interacted with UVA negatively

Next Steps

- Use two HALS at different MW's
- Look at higher levels of HALS
- Use two 2^{o} AOs for synergy
- Process stabilization

QUESTIONS?

Vanderbilt Laboratories