Thermo-Oxidative Stability of Black Pigmented Polyolefins at Elevated Temperatures

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Highlights of The Presentation

- A solution to extended long term thermo-oxidative stability of black pigmented polyolefins is now commercially possible. Both 150 C oven stability and O.I.T at 190 C compliment each other.
- No compromise in Jetness or UV performance. No need for dyes !

Market Analysis of Black Pigmented Polypropylene

- In 2001 there were approximately 260 million pounds of filled PP used in automotive under the hood applications in North America.
- Air intake 14%, Battery Cases 27%, Housing/Covers 29%, Fan Shrouds and Blades 11% and other shields 12%.

Market Analysis - Continued

- Space restrictions under the hood are raising the standards for thermo-oxidative stability at 150C and 190 C O.I.T testing by Ford.
- Ford requires 1,000 hours at 150C with 75% retention of physical properties and O.I.T.testing at 190C. GM setting standards of 336 hours oxidative stability or 1,000 hrs 140C.

Long Term Specifications By Detroit Automotive

- The common belief perpetuated by the plastic industry from years of unsuccessful research or lack of research has reduced the expectations by Detroit and others for enhanced thermo-oxidative stability at elevated temperatures. Downsizing and reduced R&D have compounded this perception.

Black Pigmentation Requirements

- The level of carbon black is usually just enough to give a uniform color. It is not added for UV stabilization. Loading levels range from 0.25% to 1.00% by weight. This range of loading equates to between 650 thousand to 2.6 million pounds of carbon black. Actual consumption is estimated at 1.5 million pounds. Problems with recycled resins.

Testing Relationships and Predictions

- Testing at 150 C for 1,000 hours equates to over 10 years of performance in under-the-hood applications. Actual testing of parts from 10 year old cars found that the mechanical properties were still adequate.
- Today over 3,000 hrs is possible !

Testing Relationships and Predictions

- Oxygen Induction Time is used to compliment oven aging tests. Shorter testing times result with smaller sample weights. The method is reportedly less reproducible to oven testing and due to greater extrapolation less correlation between it and actual in-use performance is reported.

Fact or Fiction

- Mediocre performance in filled and non-filled polyolefins drives the market requirements and so does UV stability of polyolefins. Once a technology breaches mediocre performance new standards are established which sets new bench marks for the industry regardless of paradigms.

Needs & Wants in the Industry Today for Black Pigmented PP

- The need to extend thermo-oxidative stability of black pigmented polyolefins and its UL rating does exist. Ford announced new protocols two years ago at ACS San Diego,California. The question of weather the industry is ready for this technology will be decided in the market.

Old and New Black Pigmented Polypropylene

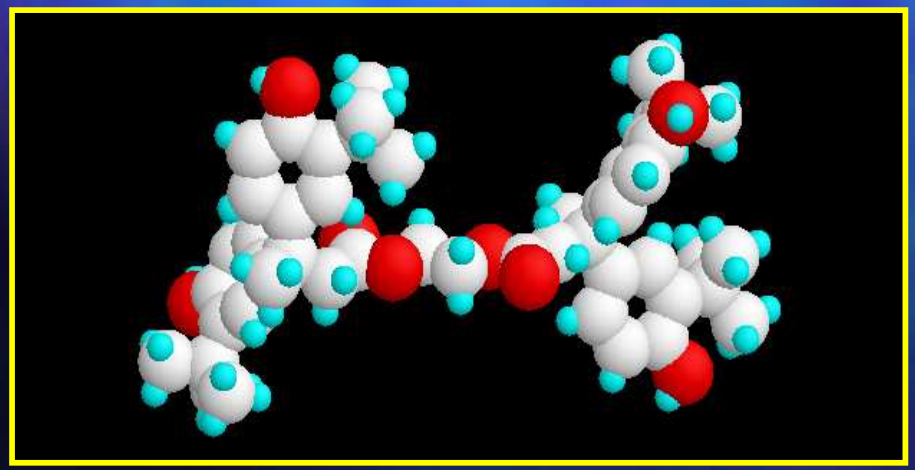
1.0% Final Black Pigment

Experimental Design

- Melt Compounding of Polypropylene Homopolymer with Black Colorants with conventional primary and secondary antioxidants with and without co-additives. Acid Acceptors common to all formulations. Pellets injection molded into 95 mil chips for L.T.H.A at 150 C in a circulating air oven and O.I.T testing of pellets and molded chips.

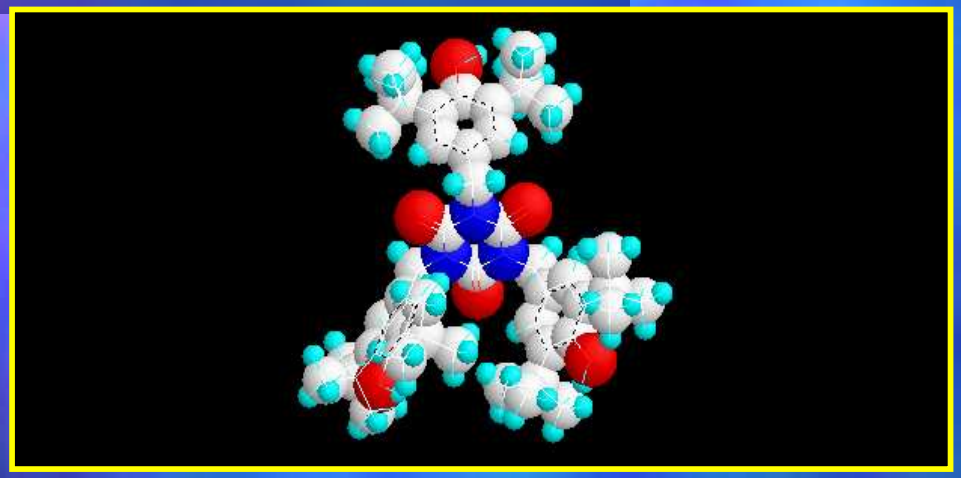
Additives Used In the Study

Antioxidant - AO-1

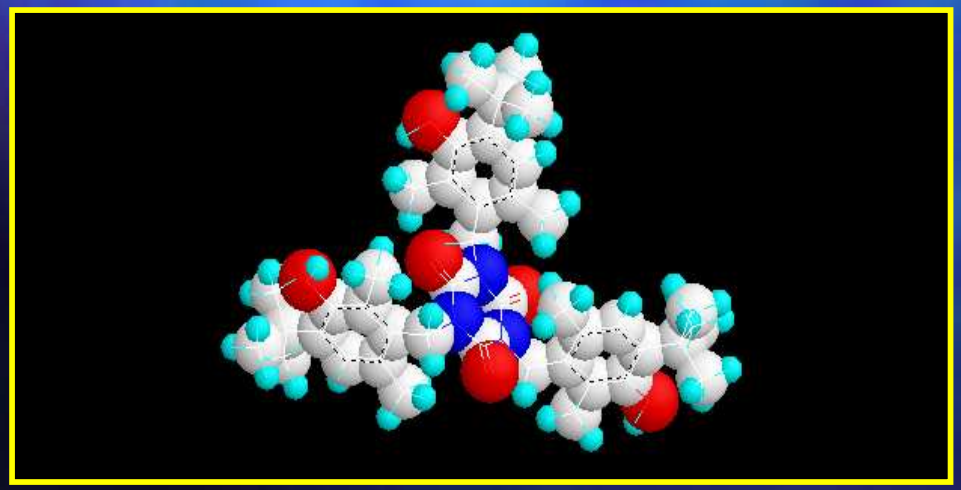


Antioxidant - AO-2

Additives Used in the Study

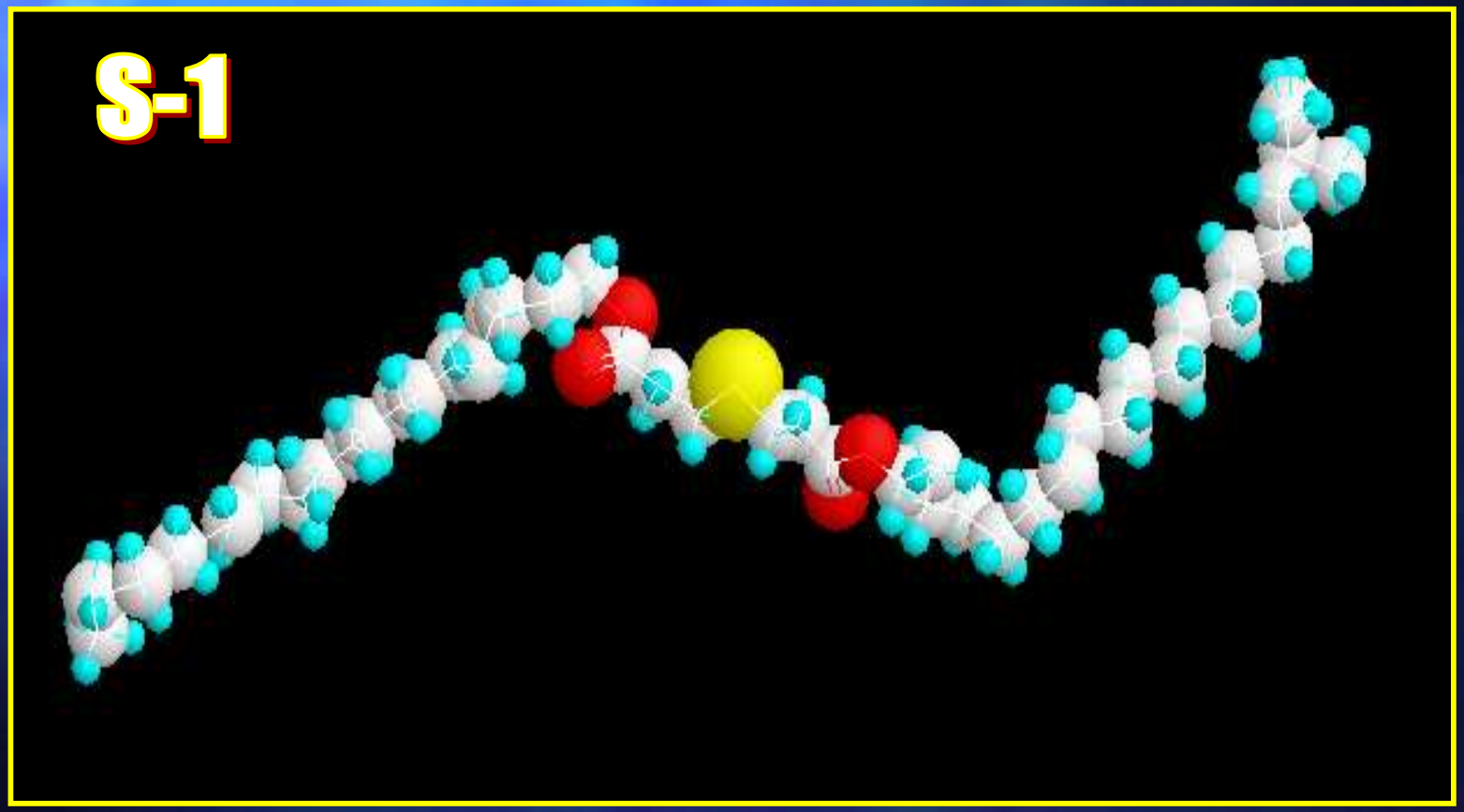


Antioxidant - AO-3

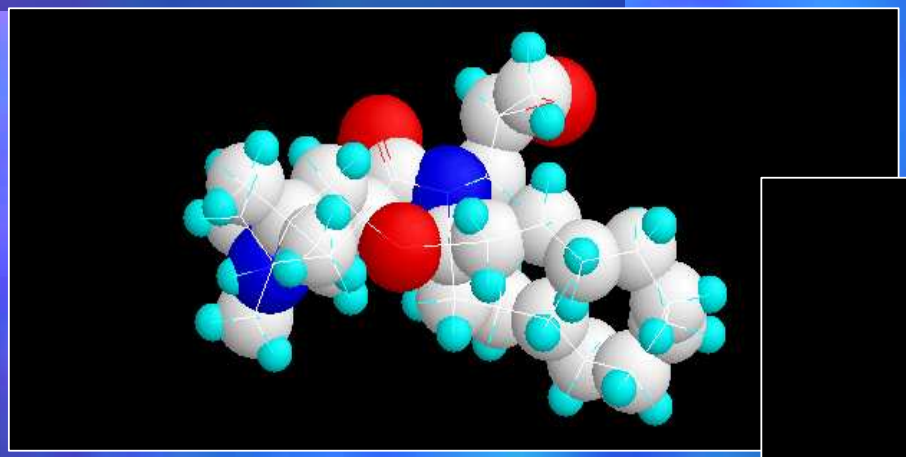


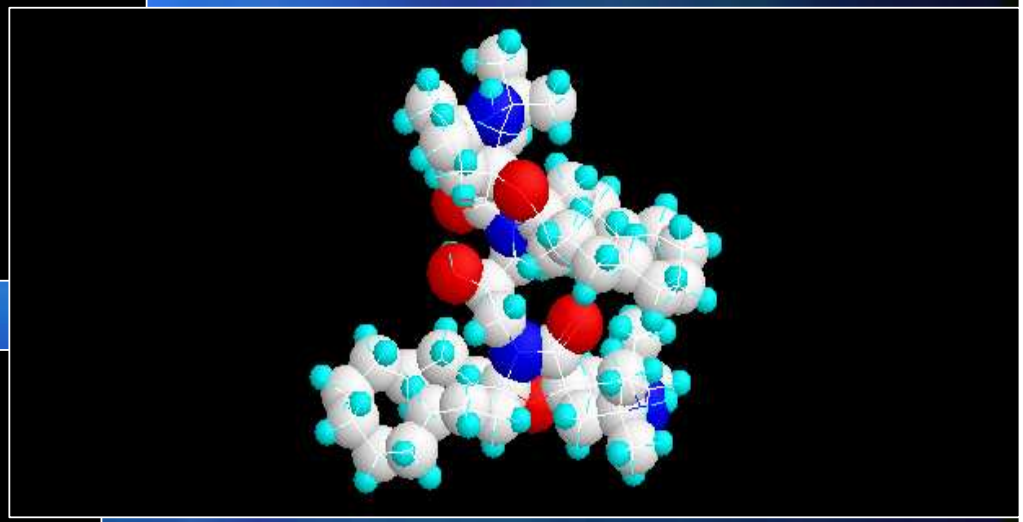
Antioxidant - AO-4

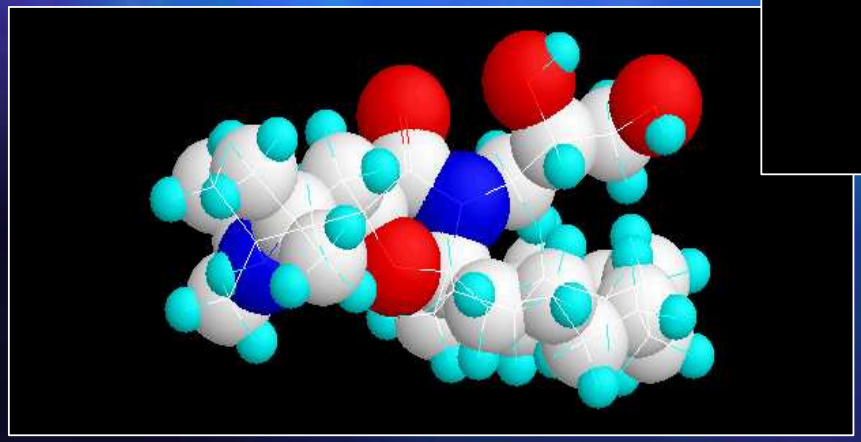
Esters of Propionic Acid Used in The Study



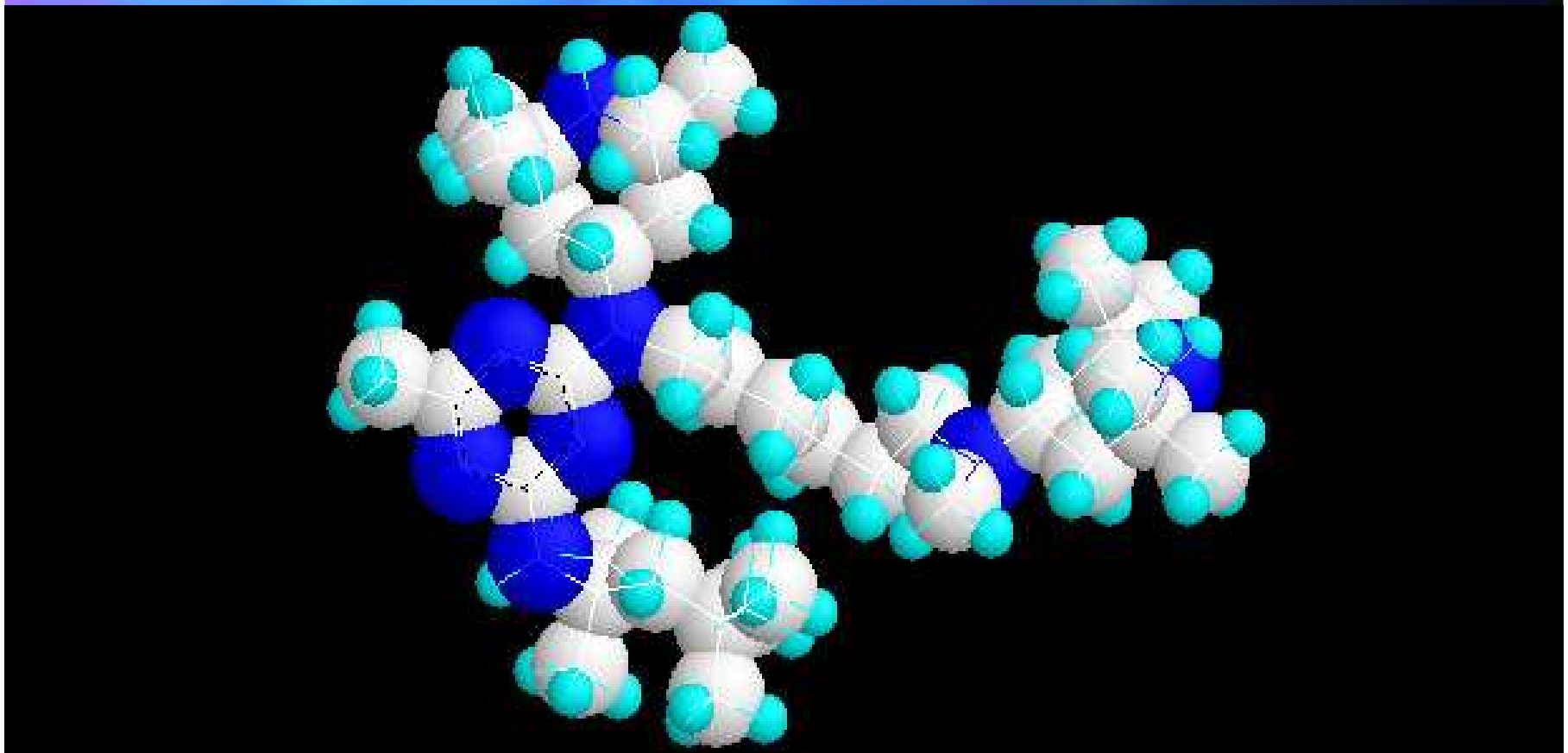
Catalysts Used in the Study



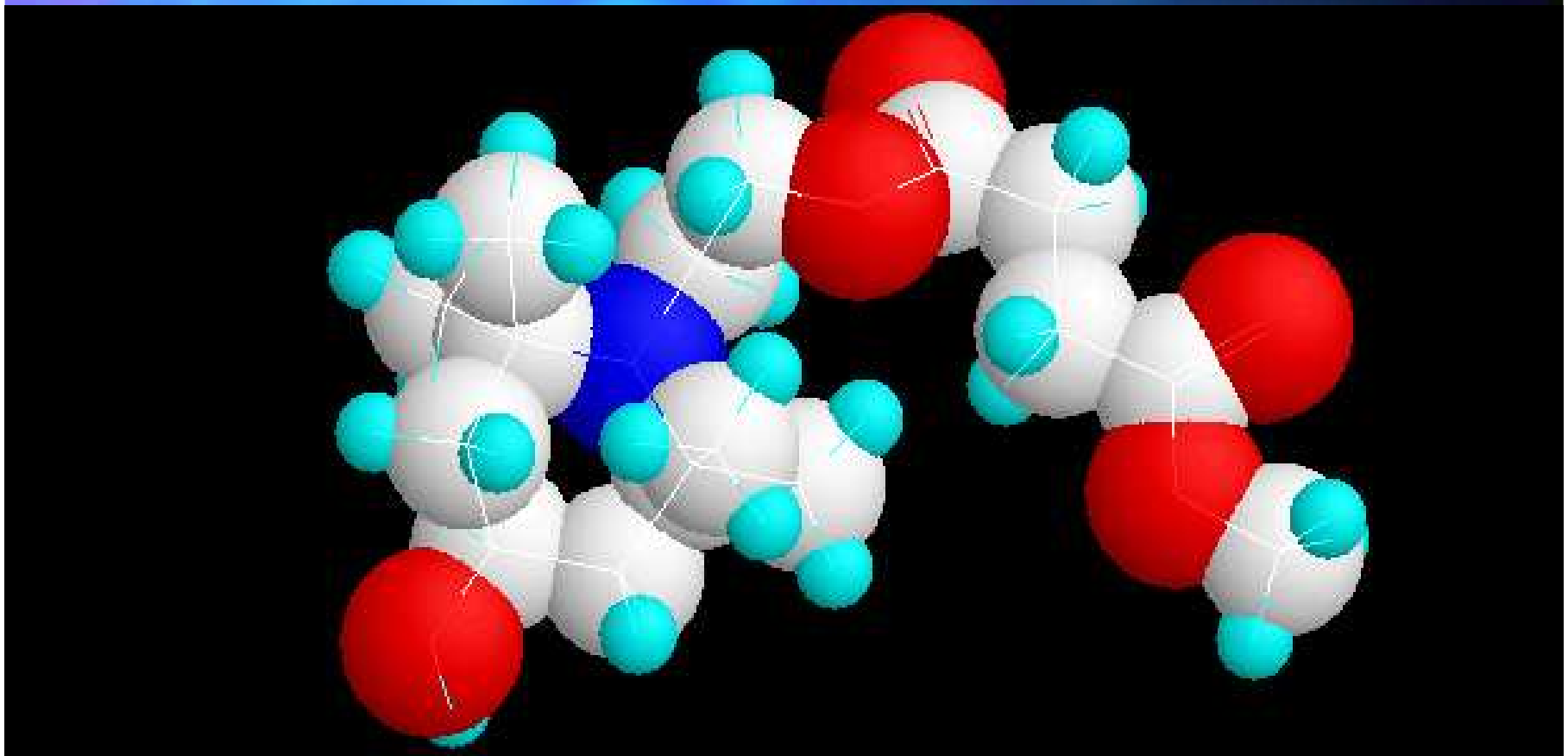




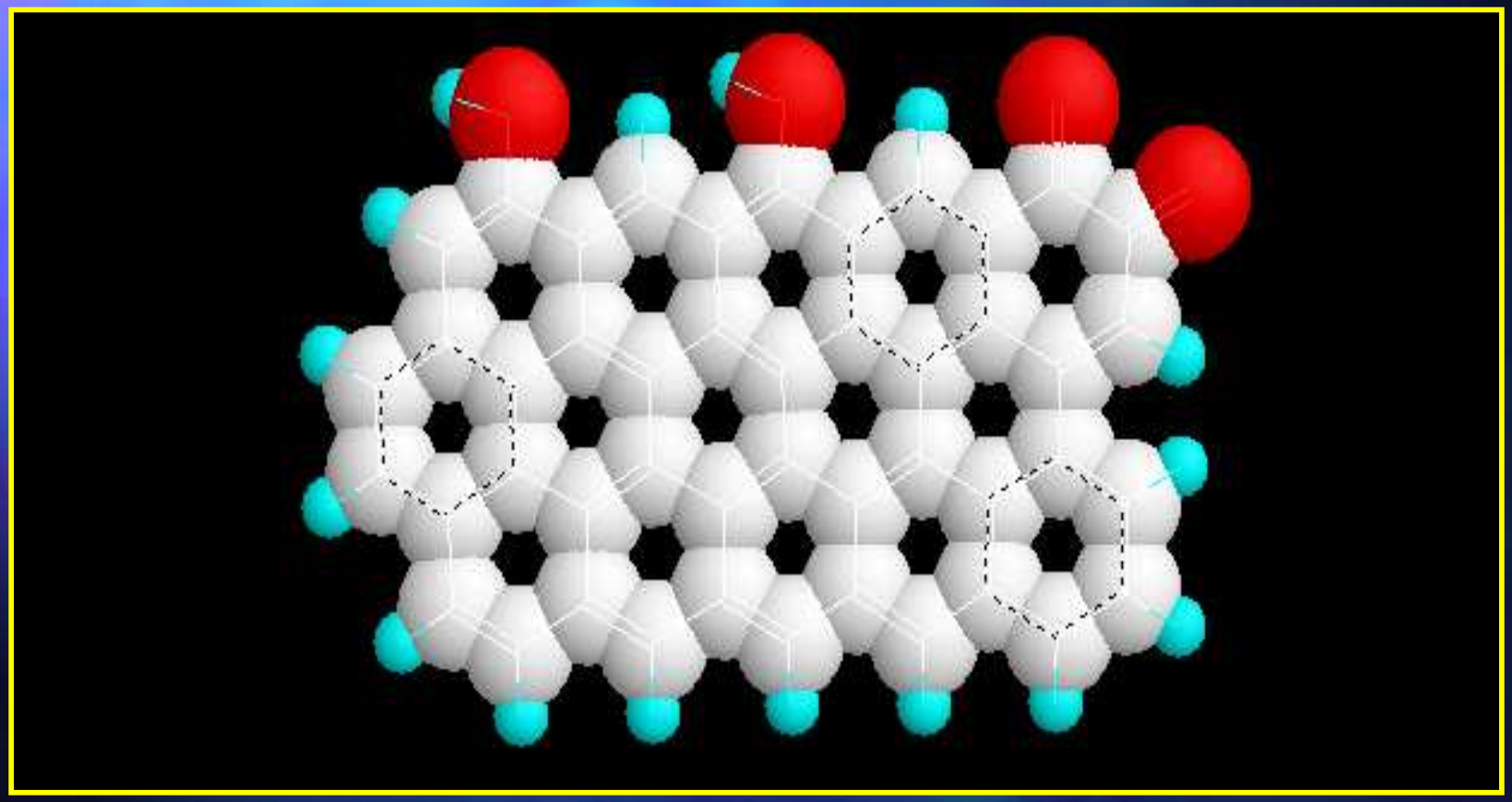
Oligomeric Catalysts in Study
Catalyst C-2



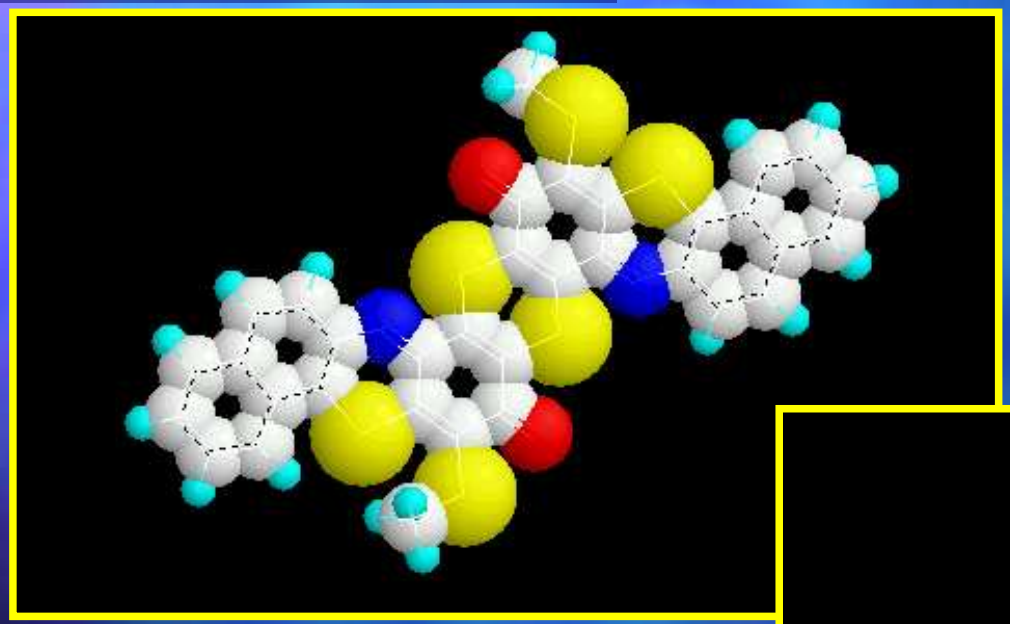
Polyester of Succinic Acid
Catalyst C-3

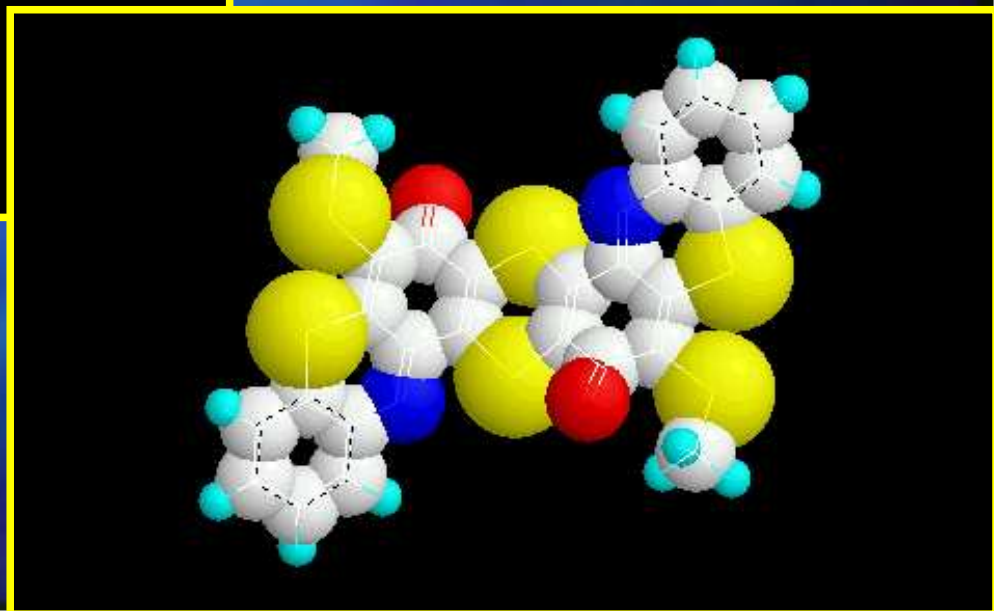


Black Pigments Used in Study



Black Antioxidant Used in Study

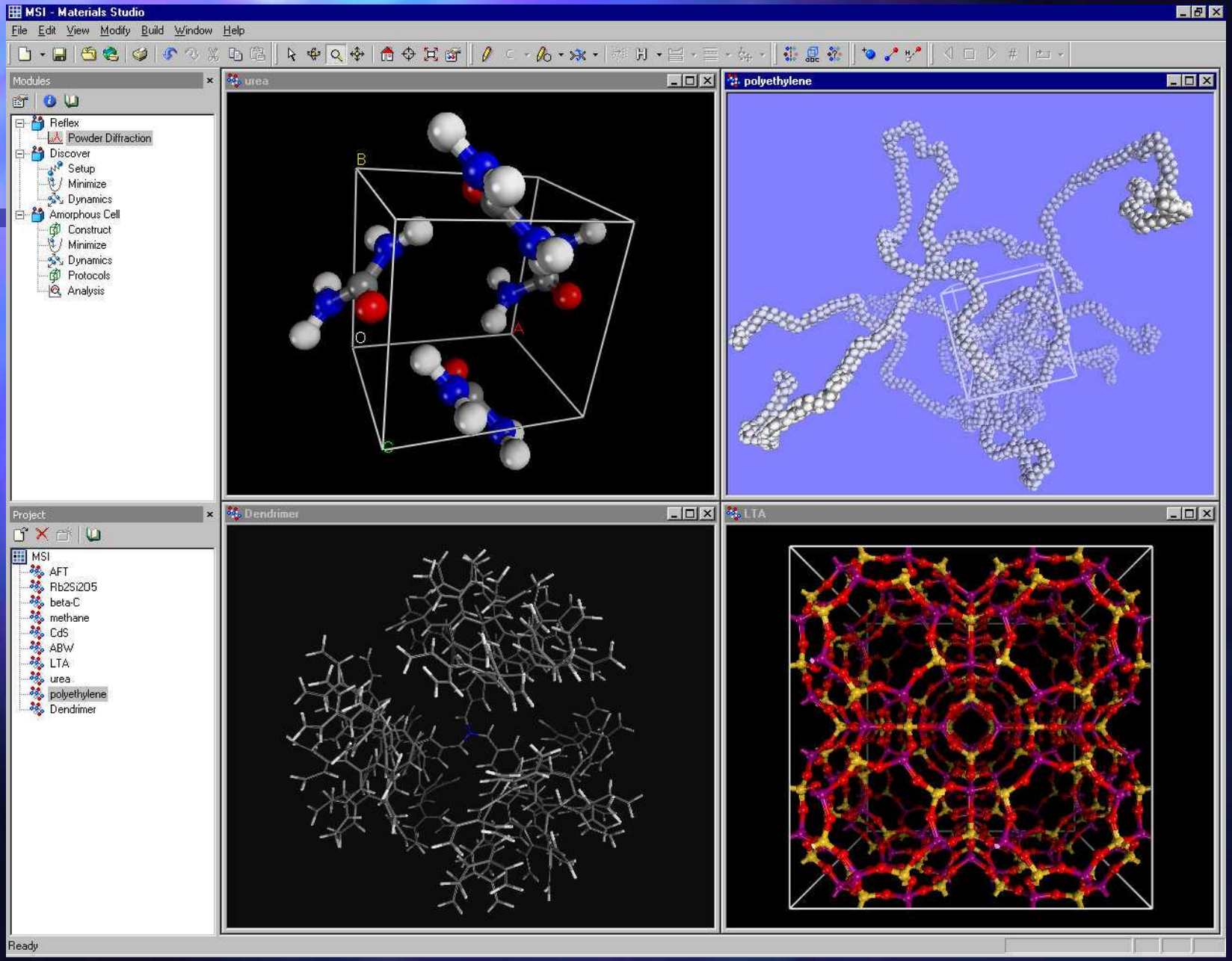


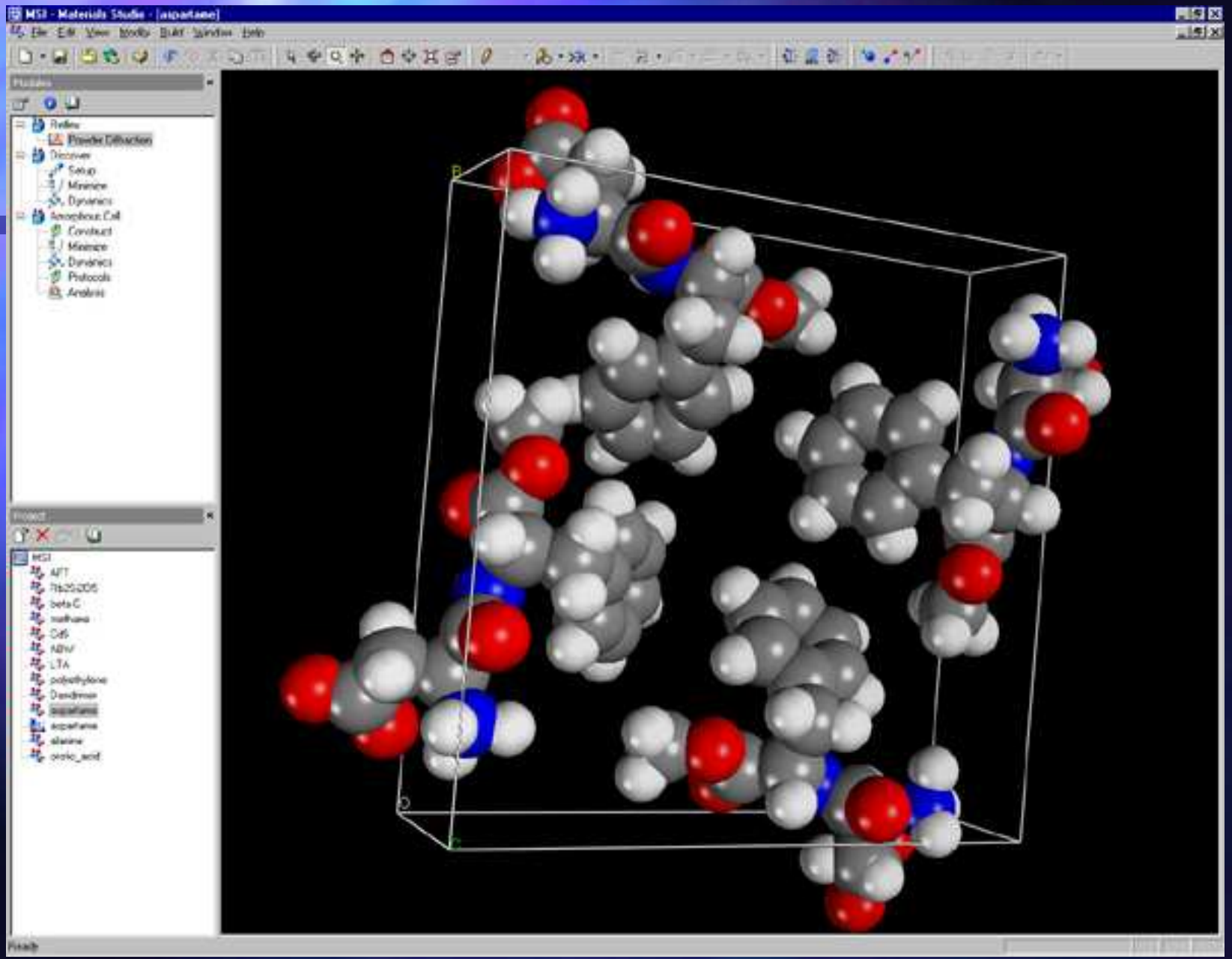


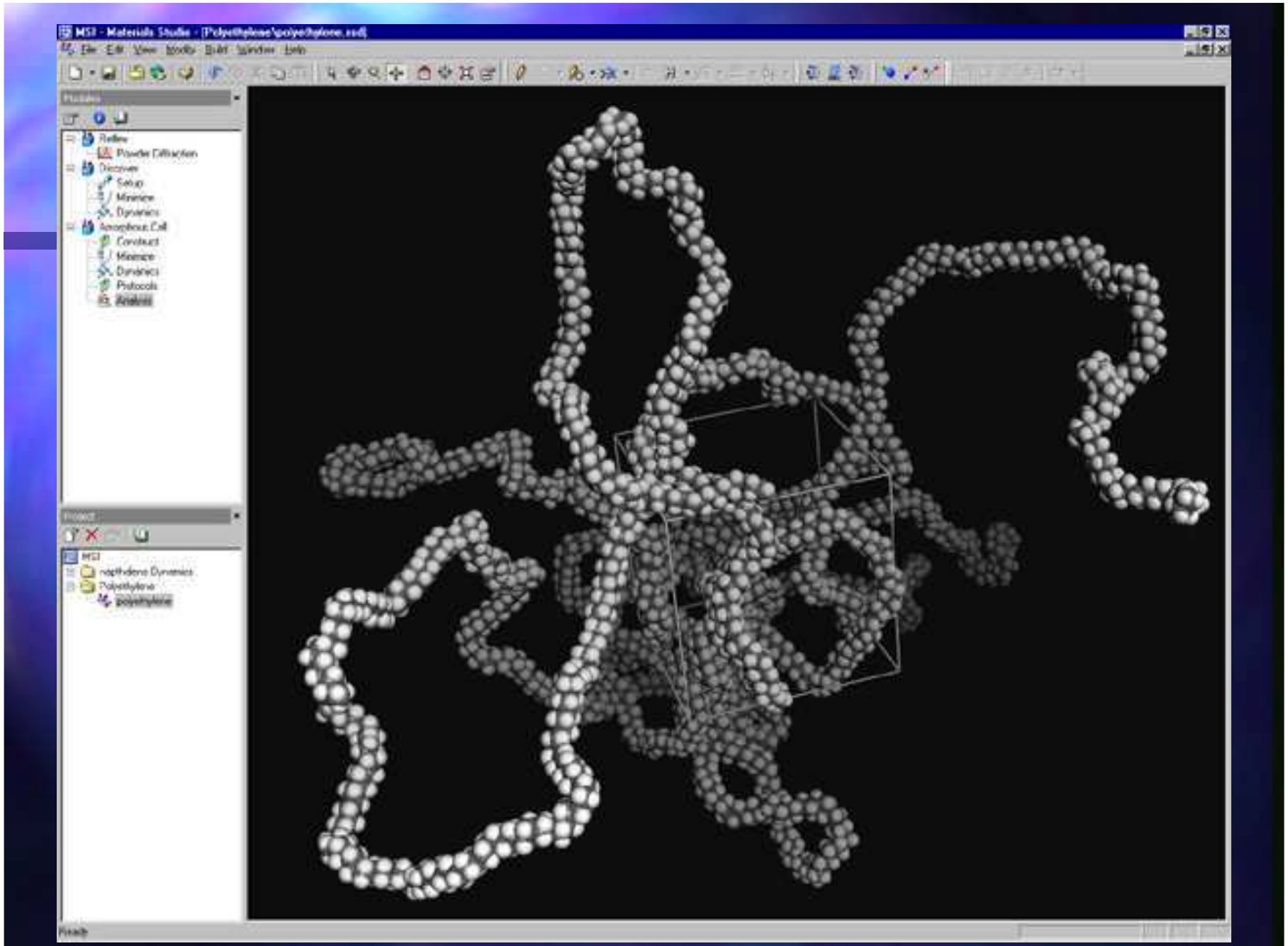
Molecular Modeling Computational Chemistry

Carbon Black versus Sulfur Black Chemistries

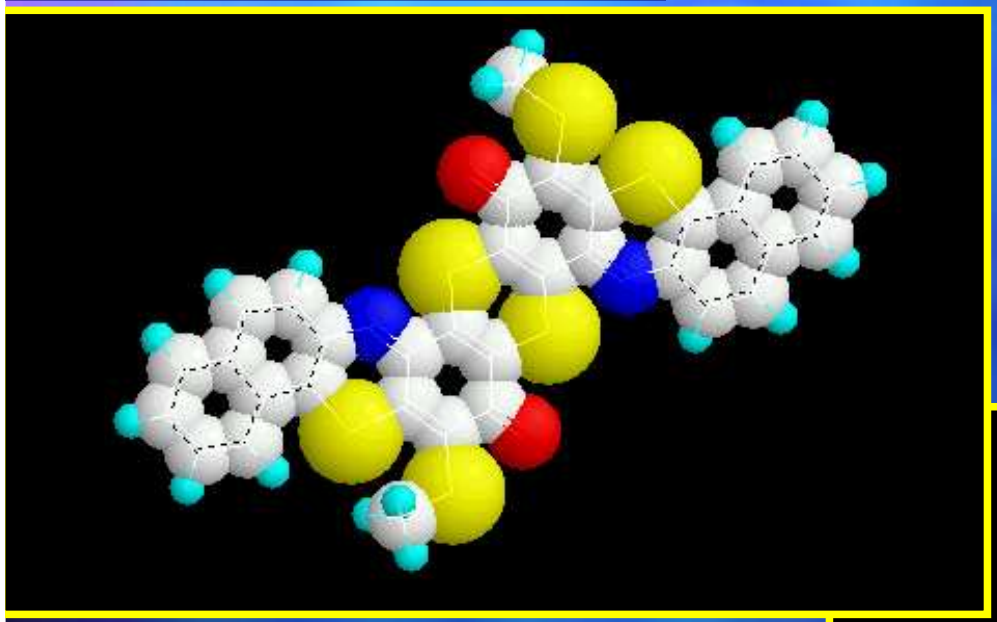
Chemical Interactions

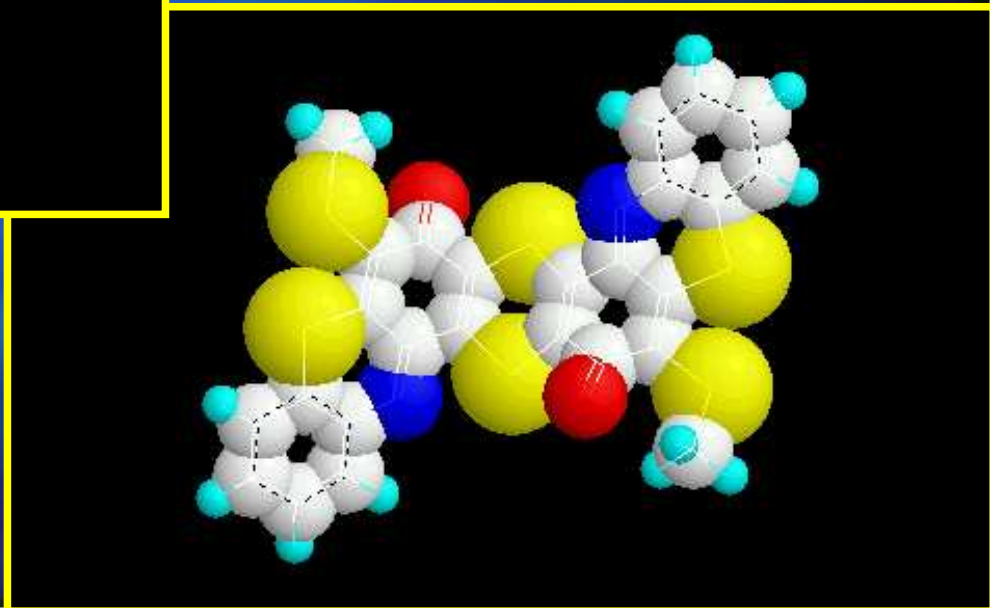

MSI - Materials Studio
File Edit View Modify Build Window Help
Modules
Reflex
Powder Diffraction
Discover
Setup
Minimize
Dynamics
Amorphous Cell
Construct
Minimize
Dynamics
Protocols
Analysis
urea
B
A
C
polyethylene
Project
MSI
AFT
Rb2Si2O5
beta-C
methane
CdS
ABW
LTA
urea
polyethylene
Dendrimer
Dendrimer
LTA
Ready


MSI - Materials Studio - [aspartame]
File Edit View Modify Build Window Help
Modules
Project
Ready


MSI - Materials Studio - [Polyethylene\polyethylene.xsd]
File Edit View Modify Build Window Help
Modules
Reflex
Powder Diffraction
Discover
Setup
Minimize
Dynamics
Amorphous Cell
Construct
Minimize
Dynamics
Protocols
Analysis
Project
MSI
naphthalene Dynamics
Polyethylene
polyethylene
Ready

Modeling of Sulfur Structures
" Black Stabilizer"

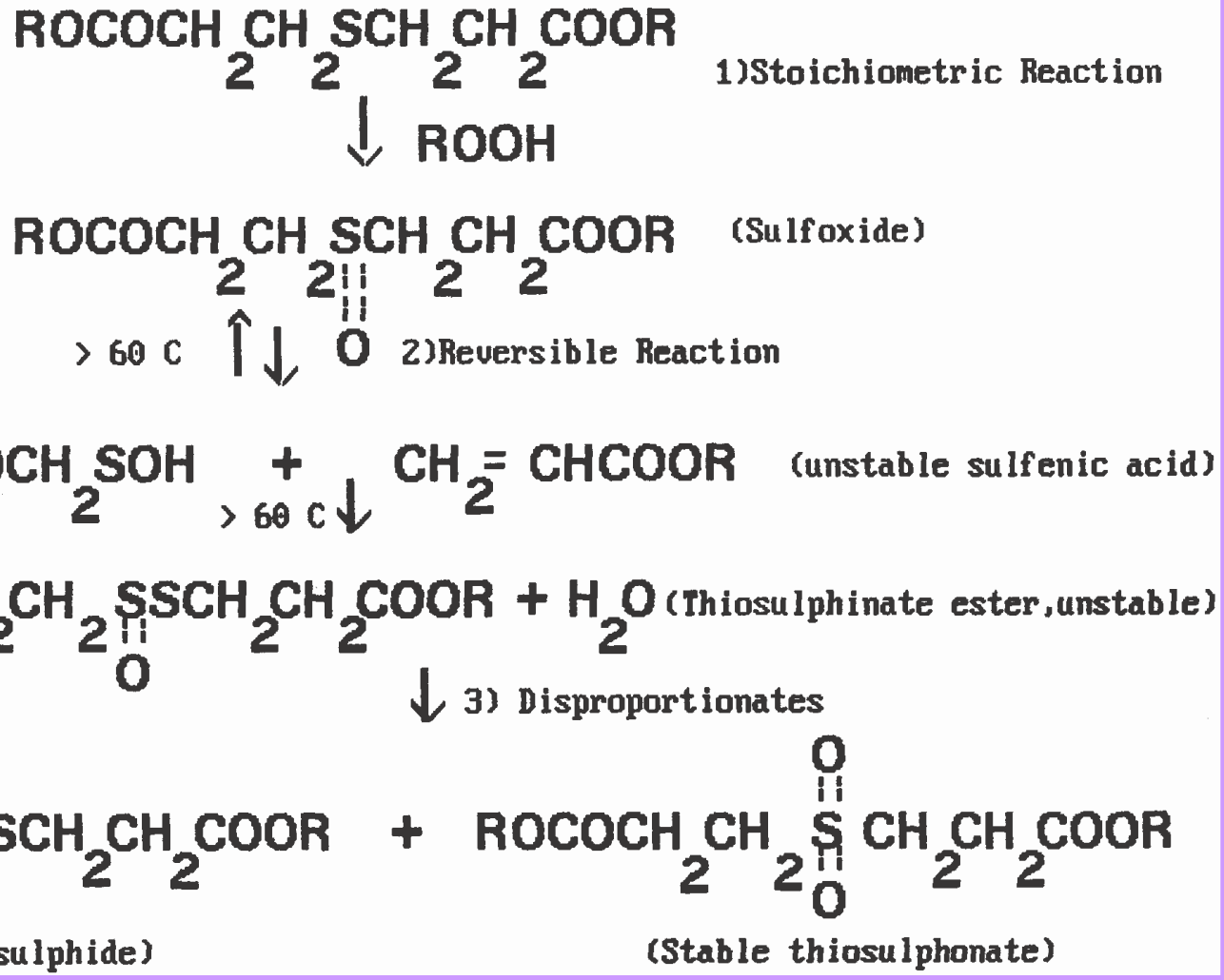




OXIDATION OF THIODIPROPIONATE ESTERS

R = $C_{12}H_{25}$ DLTDP

R = $C_{18}H_{37}$ DSTDP



Peroxidolytic Species

RSOH (Sulfenic Acids)

RSOH (Sulphinic Acids)

RSOH (Sulfonic Acids)

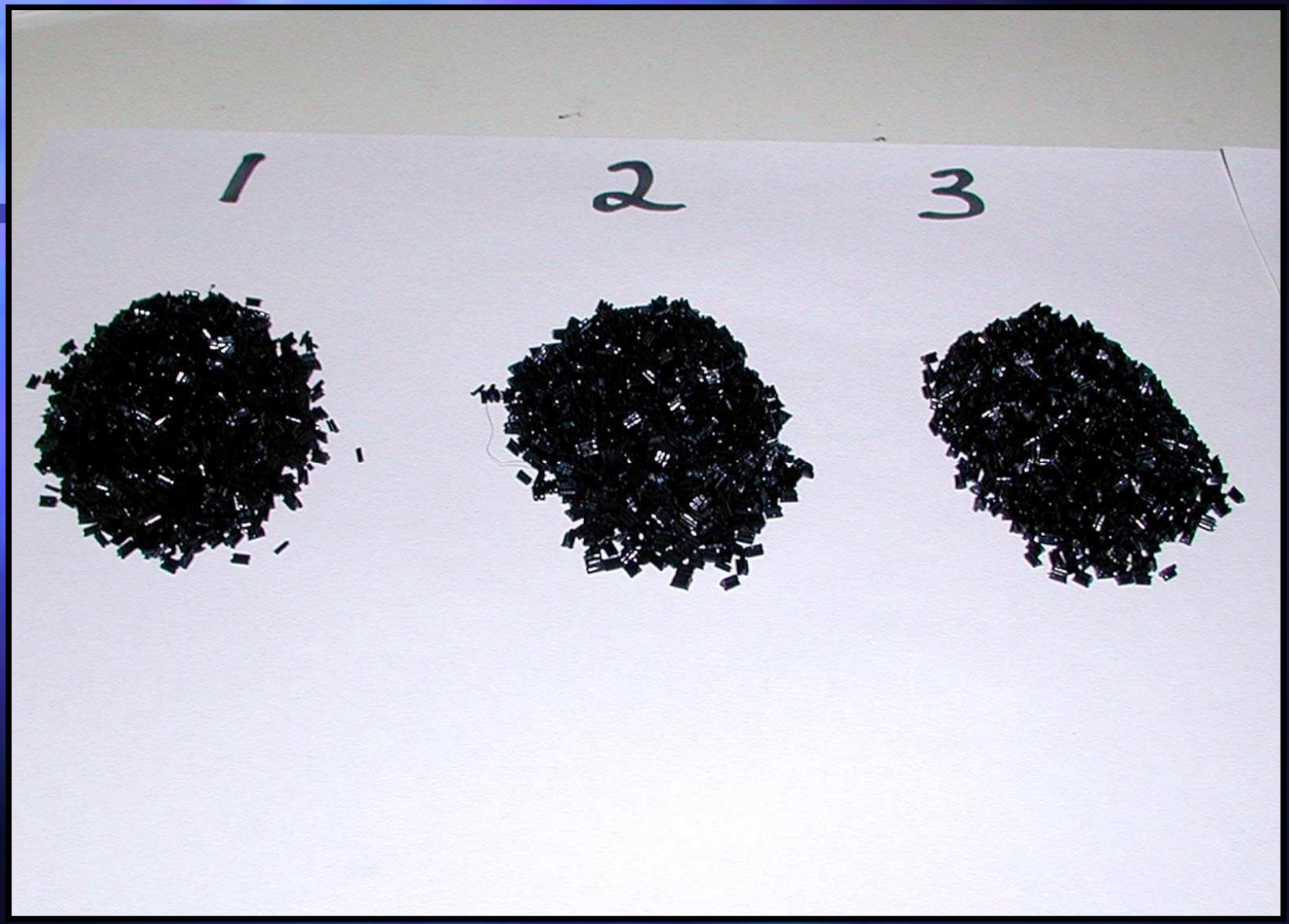
RSSR (Thiosulfinates)

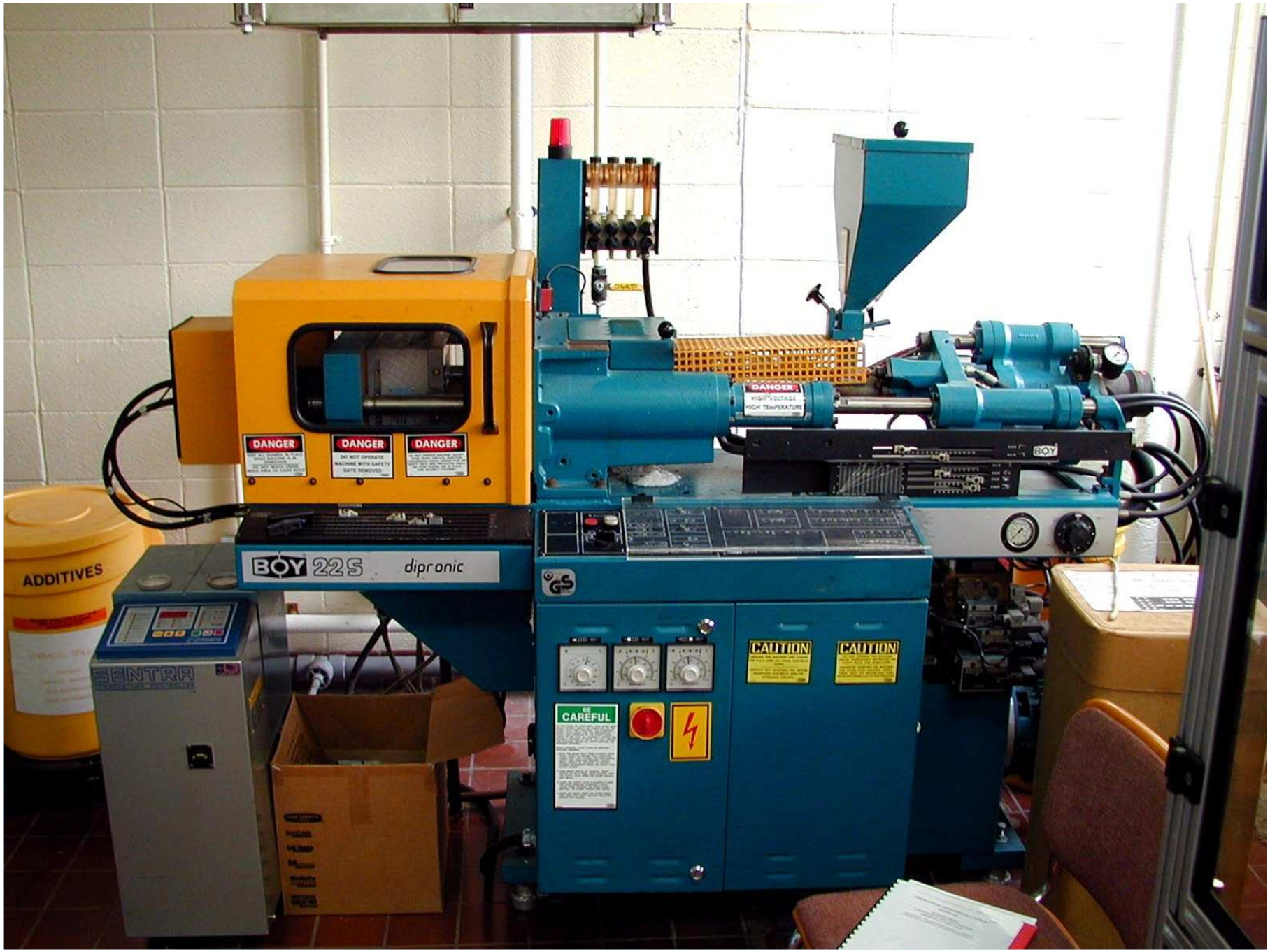
Peroxidolytic Antioxidants by In-situ Oxidation of Thiols

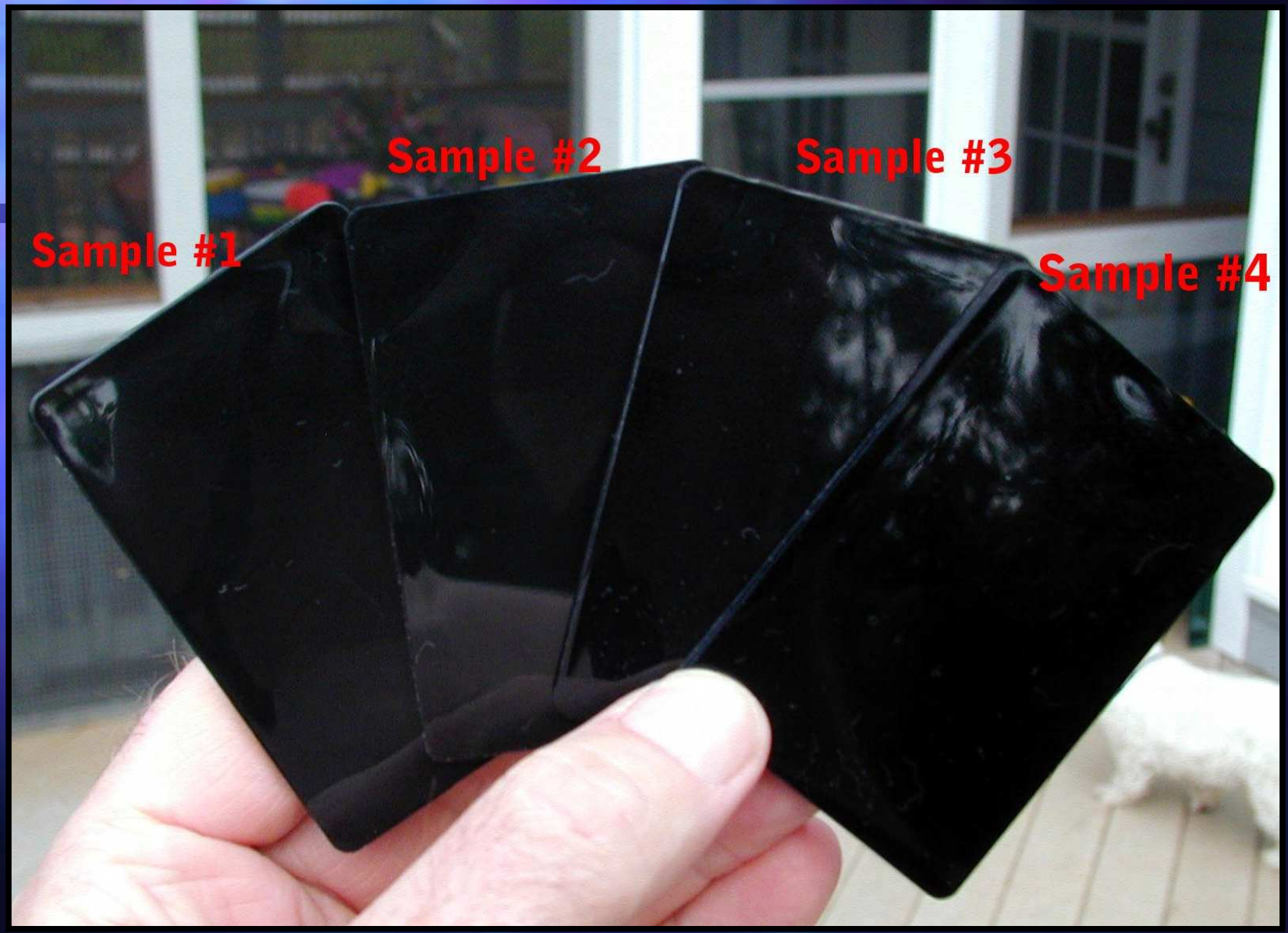
aliphatic thiol oxidation to disulfide and regeneration of the amine

Molding Melt Compounded Pellets

Preparation For Long Term
Testing at Elevated Temperatures

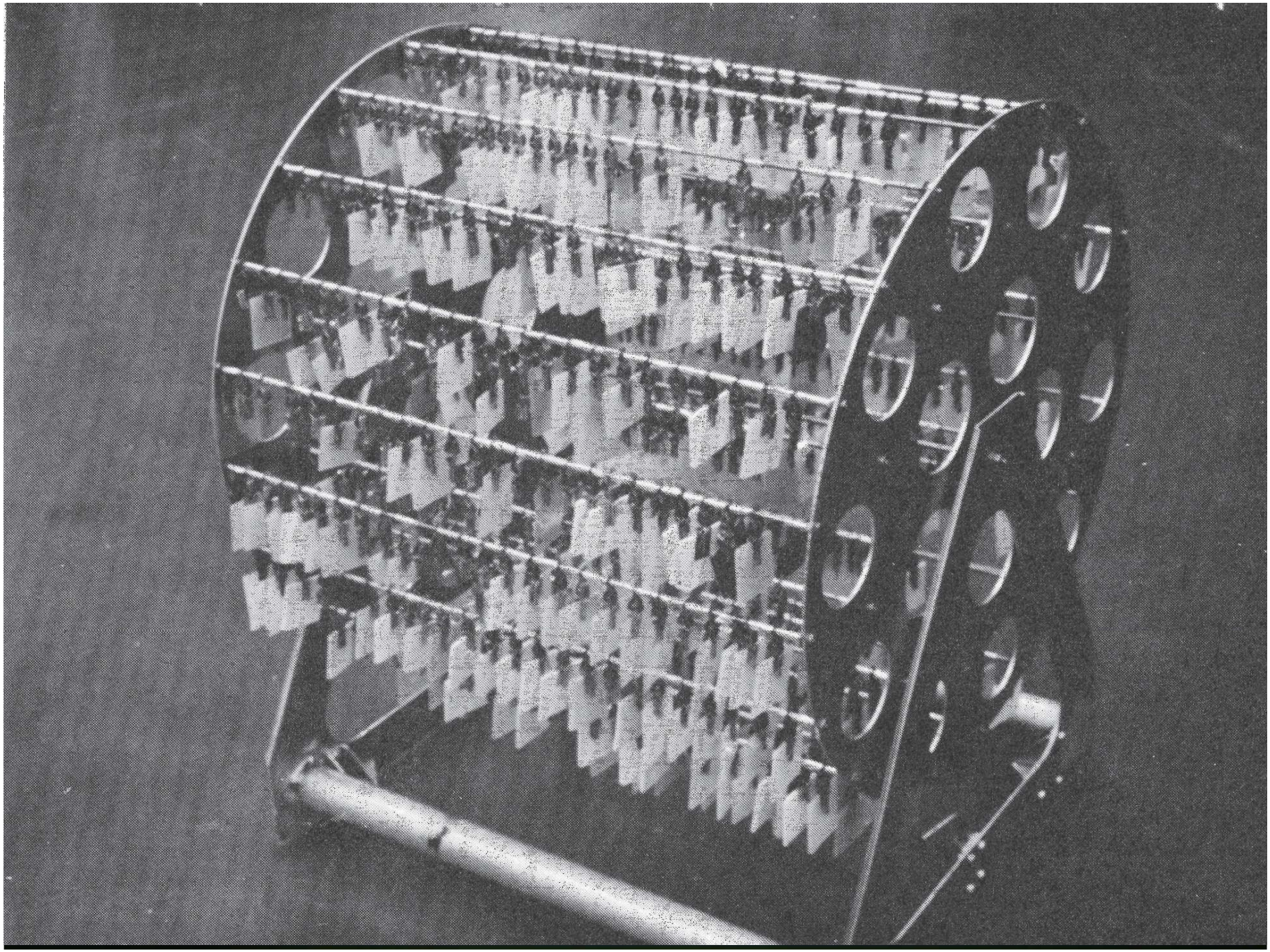

1
2
3

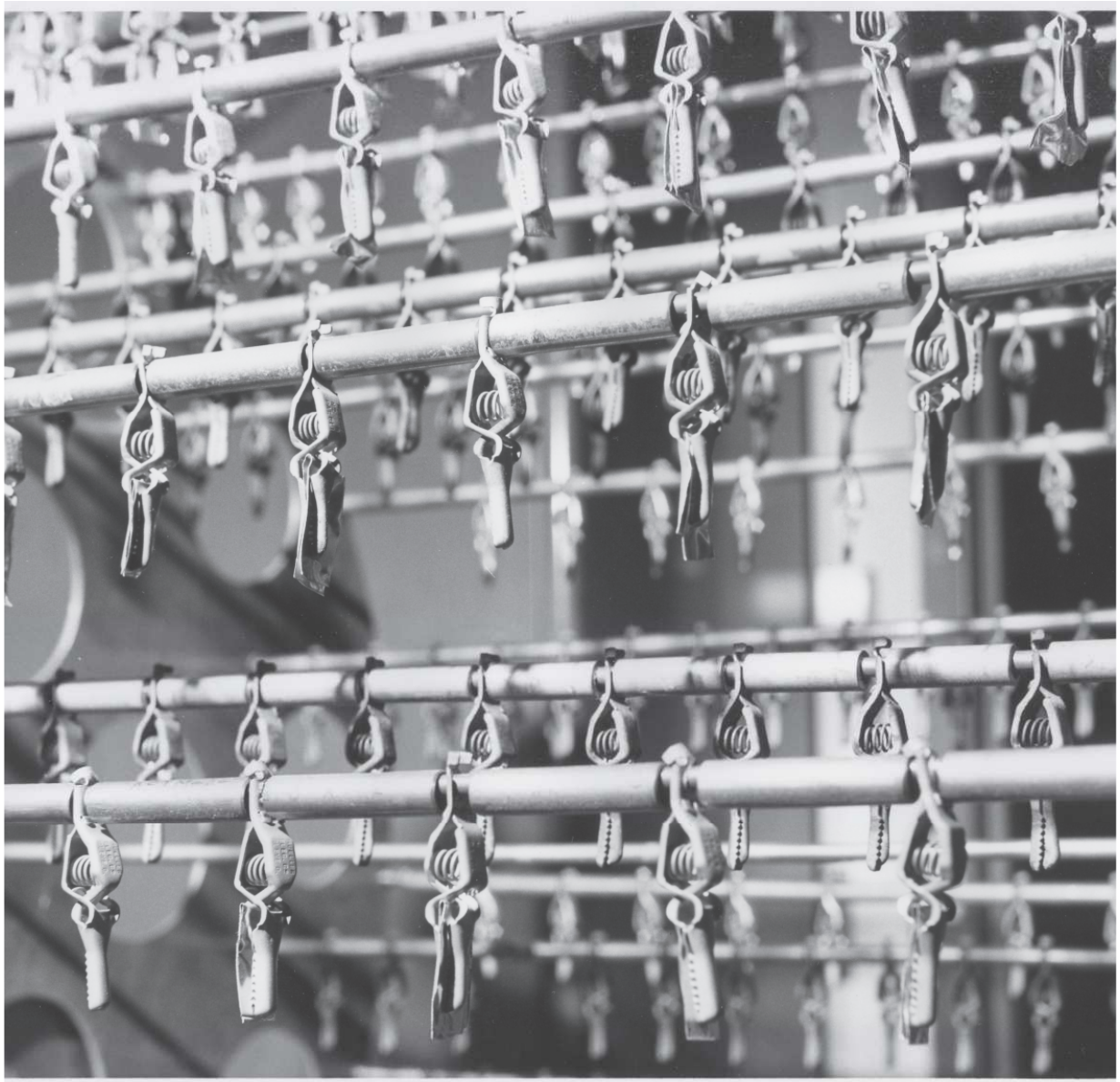

DANGER
DANGER
DANGER
DANGER
HIGH VOLTAGE
HIGH TEMPERATURE
BOY
ADDITIVES
BOY 22S dipronic
CAUTION
CAUTION
BE CAREFUL
SENTRA


Sample #1
Sample #2
Sample #3
Sample #4

1% Carbon Black

1% 4G Black

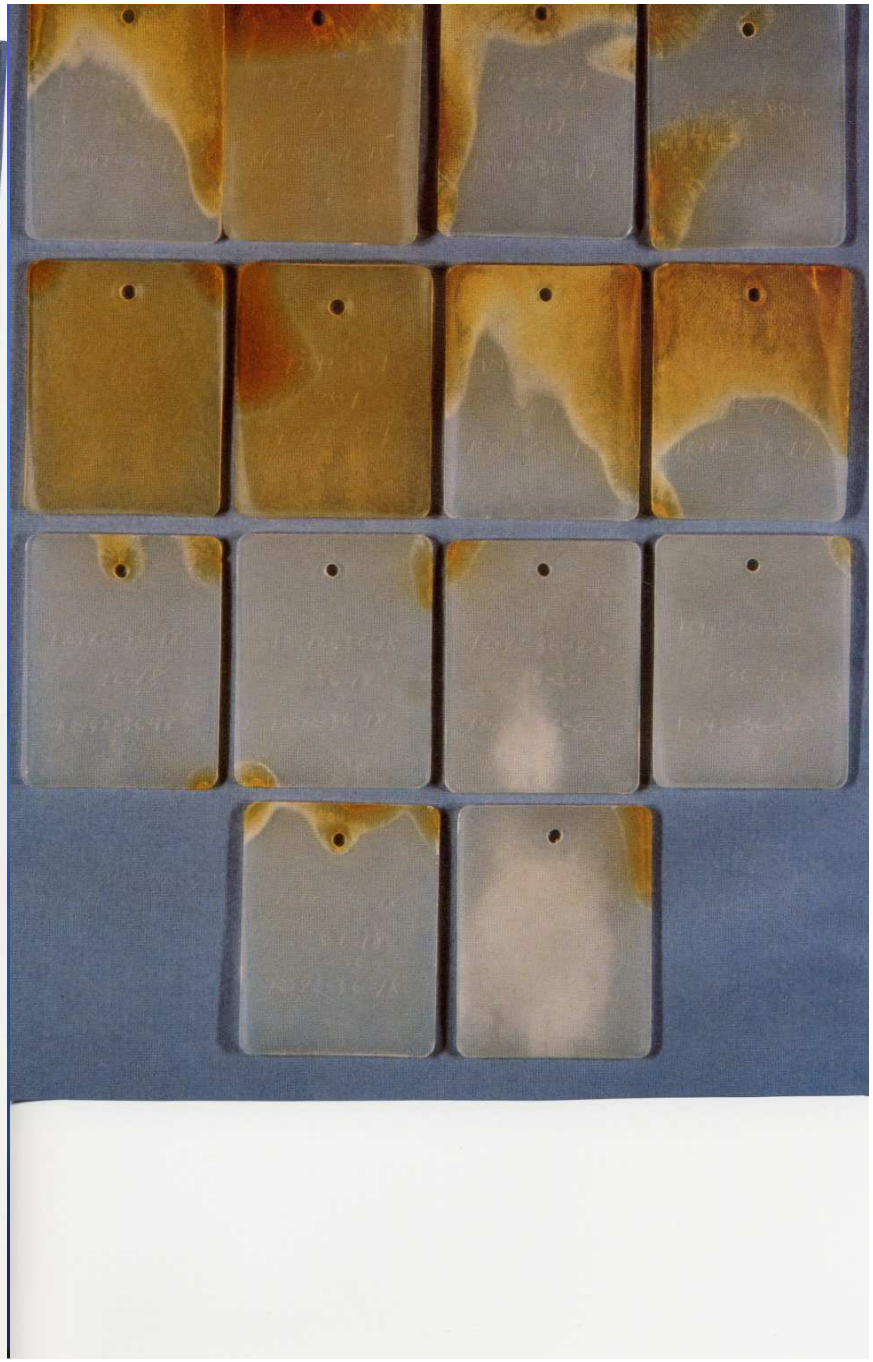




Suspension Clips on Rotary Oven Testing Rack

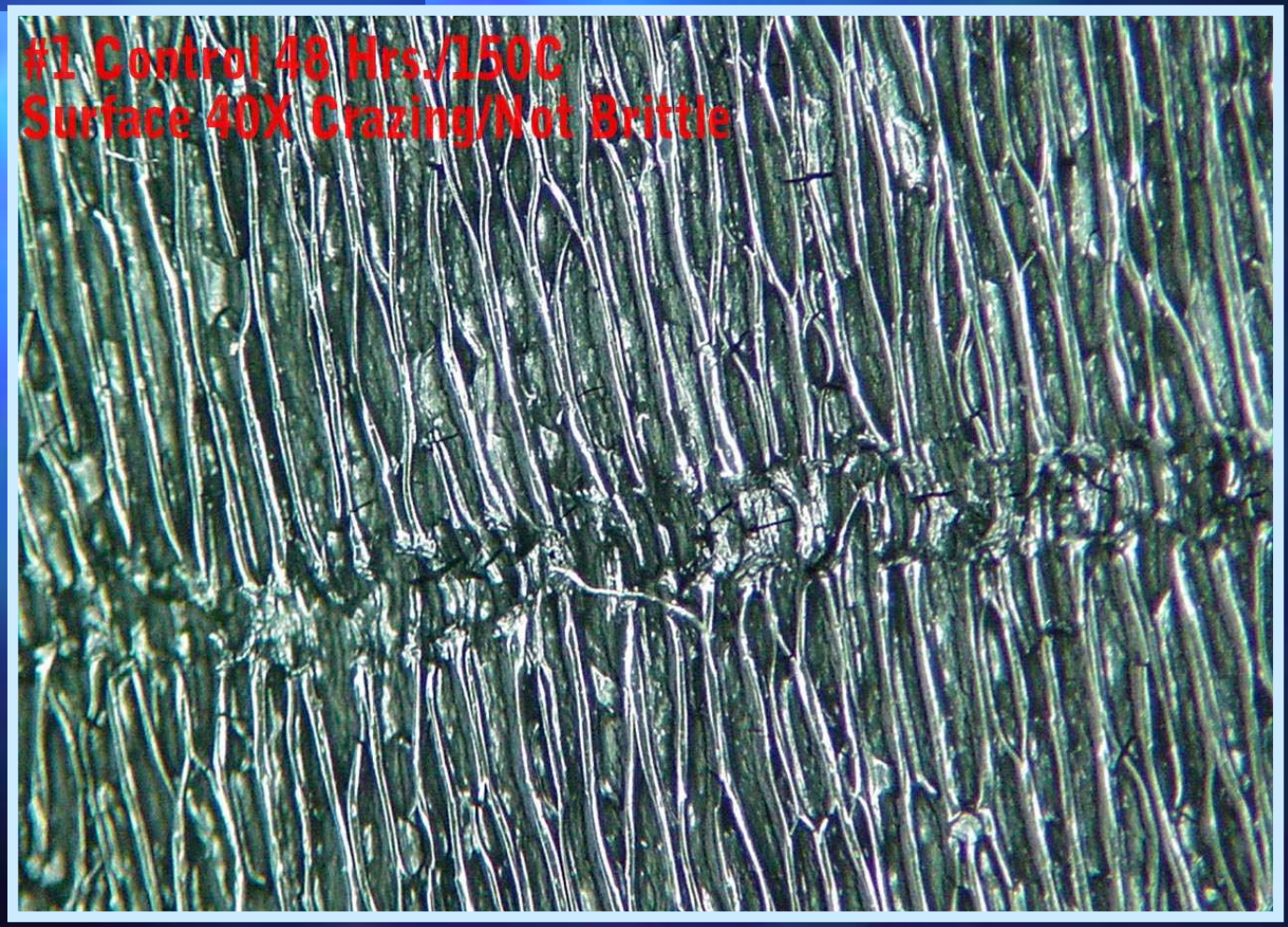
Unstabilized Natural Polypropylene at 150 C

Surface Crazing & Embrittlement After 24 hours at 150 C

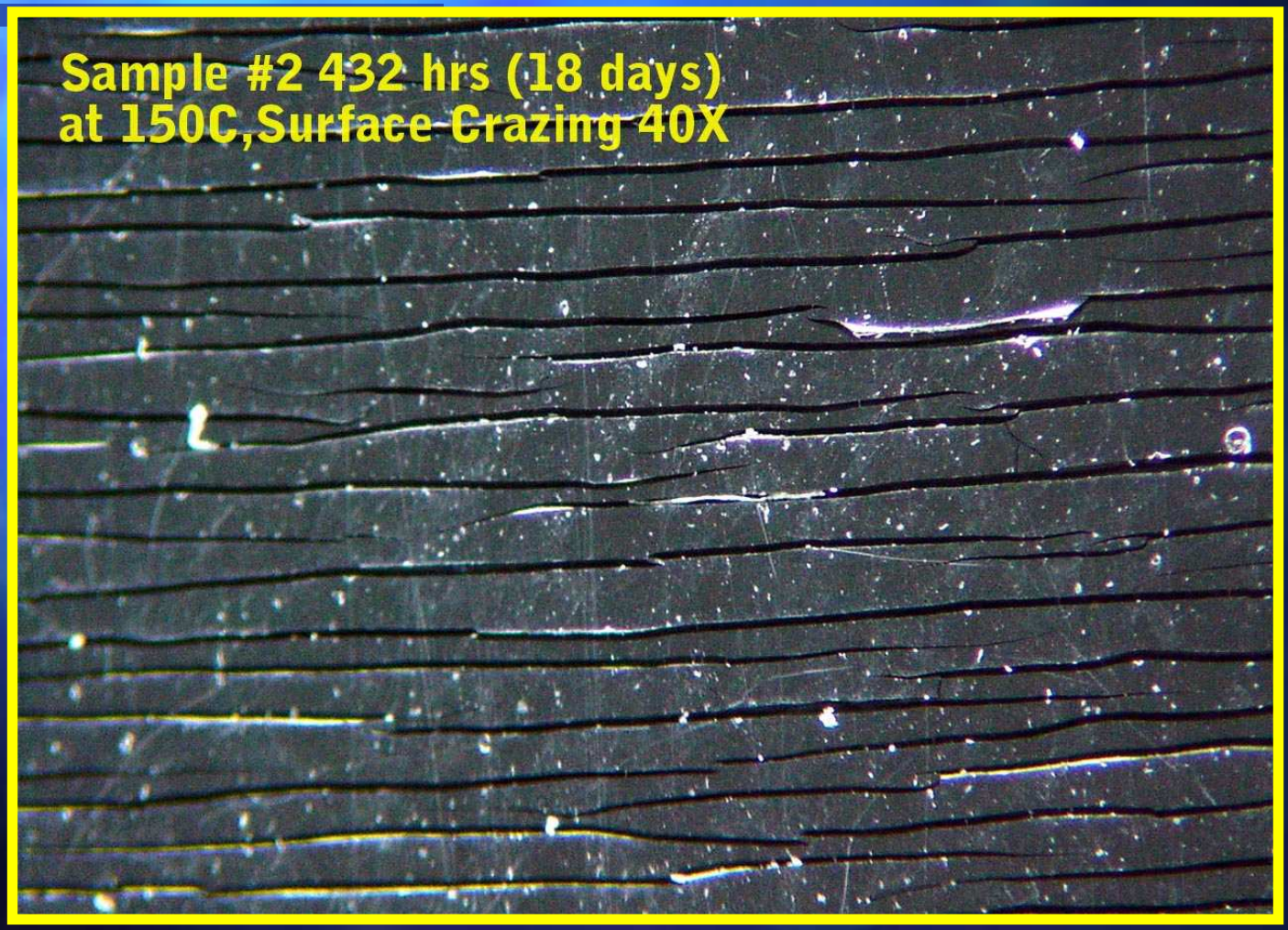


Stabilized Plastic Failures at 150 C Oven Stability

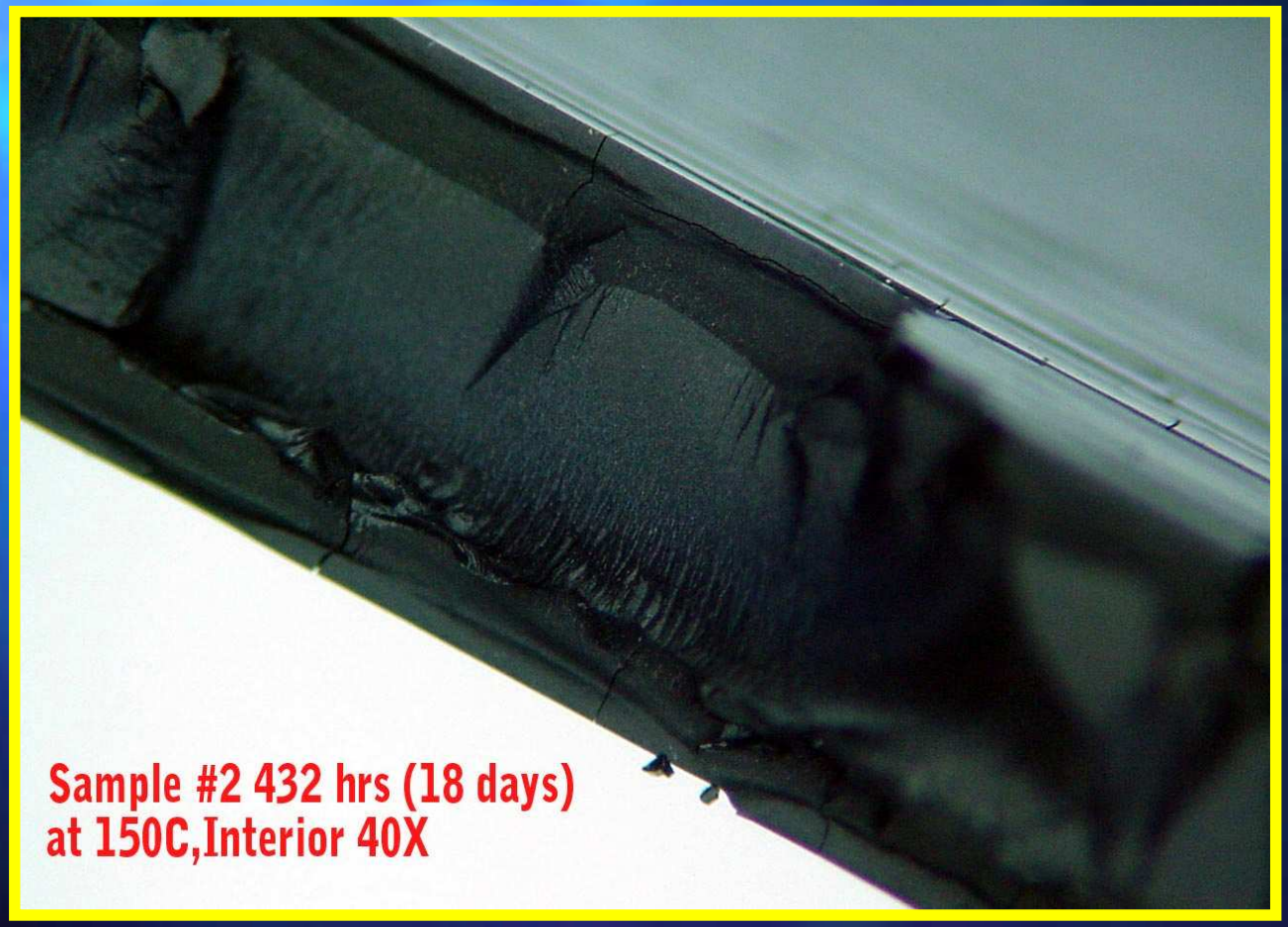
Unstabilized Control Carbon Black



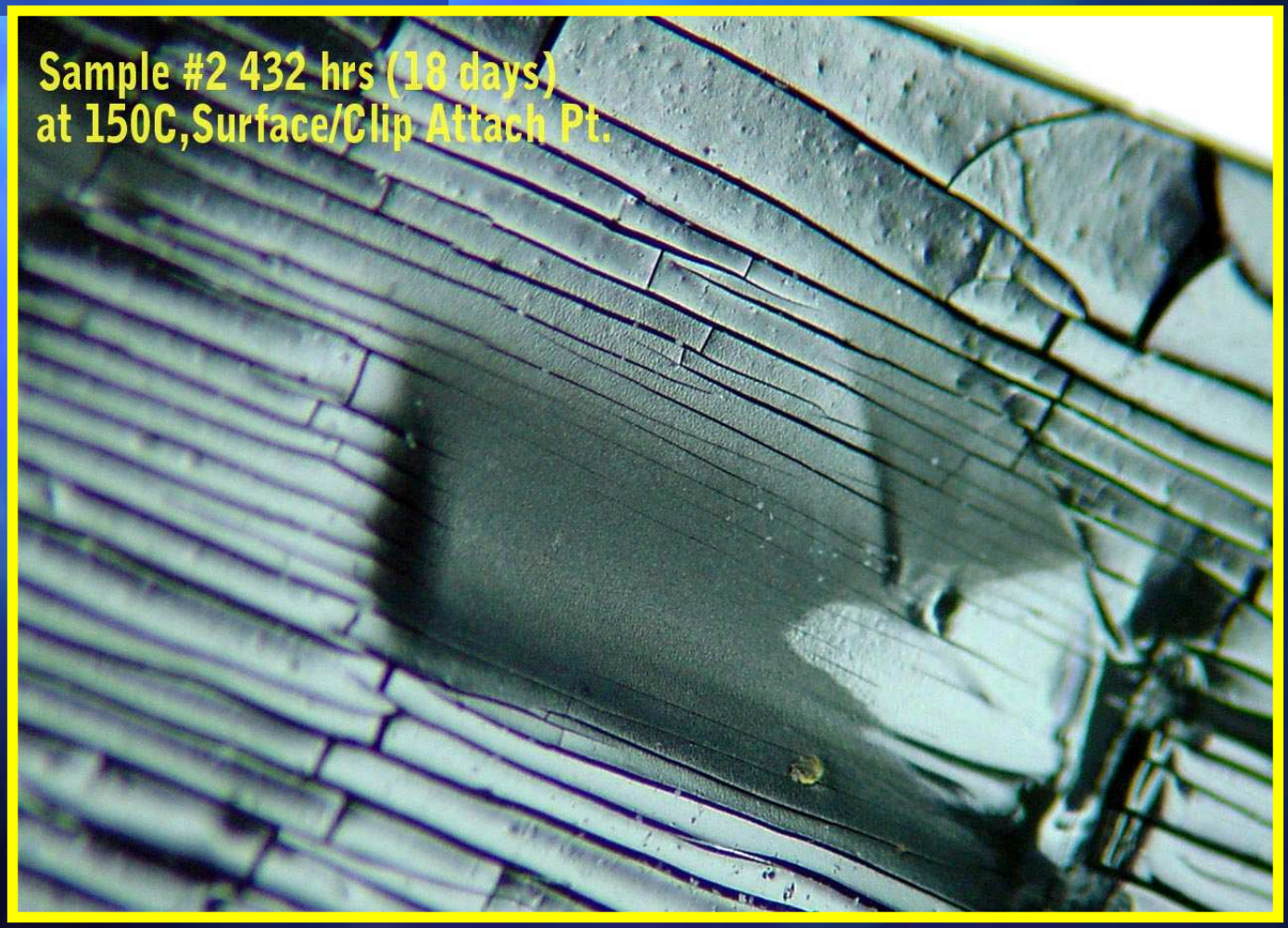
Fortified Carbon Black in Polypropylene 150 C



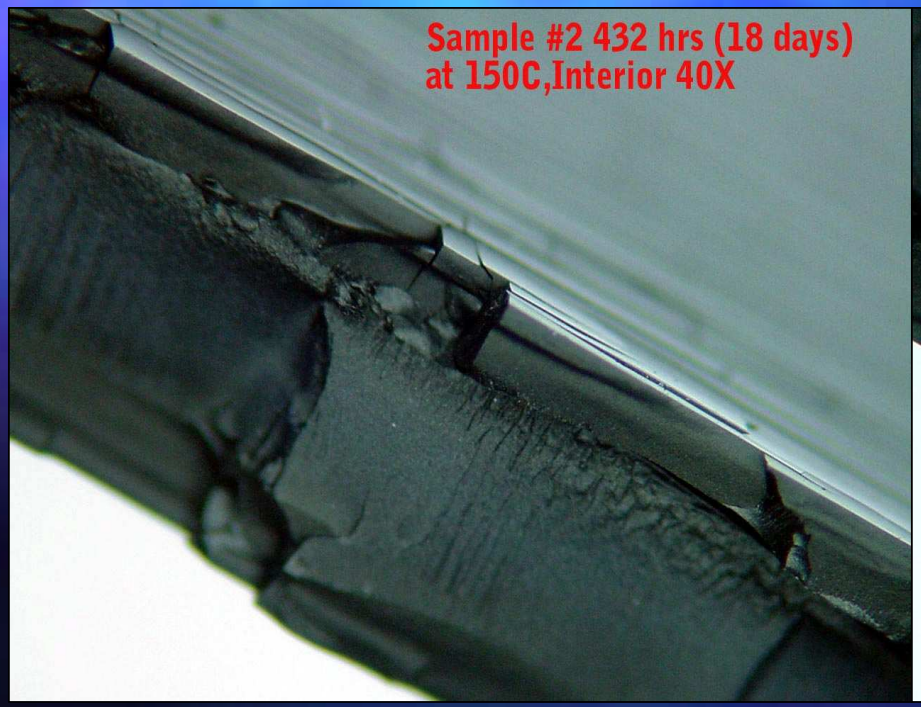
Fortified Carbon Black 150 C Interior of Degraded Plaque

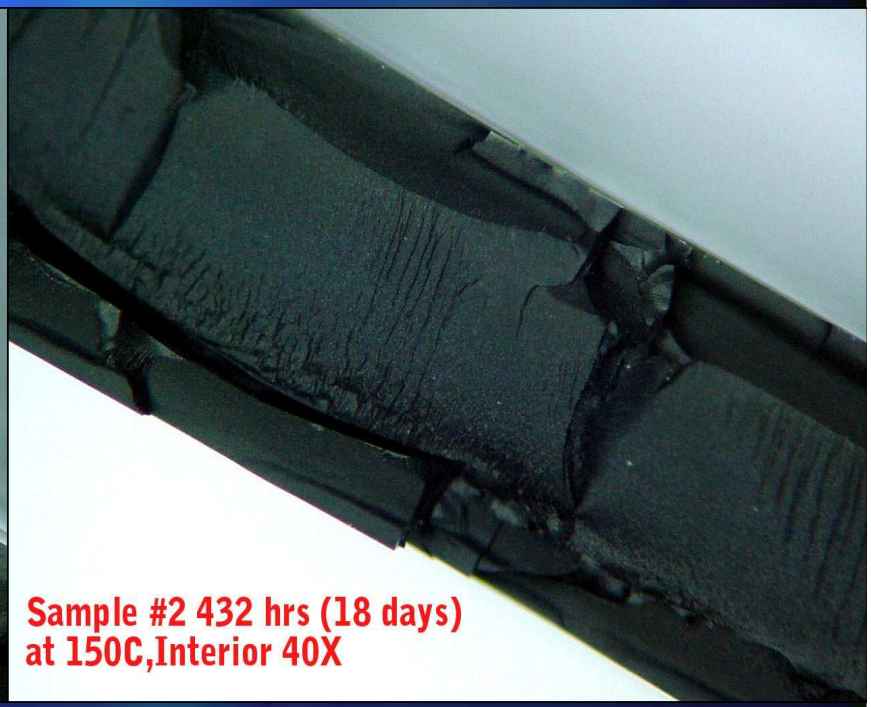


Surface of Degraded PP 150C Control with Carbon Black

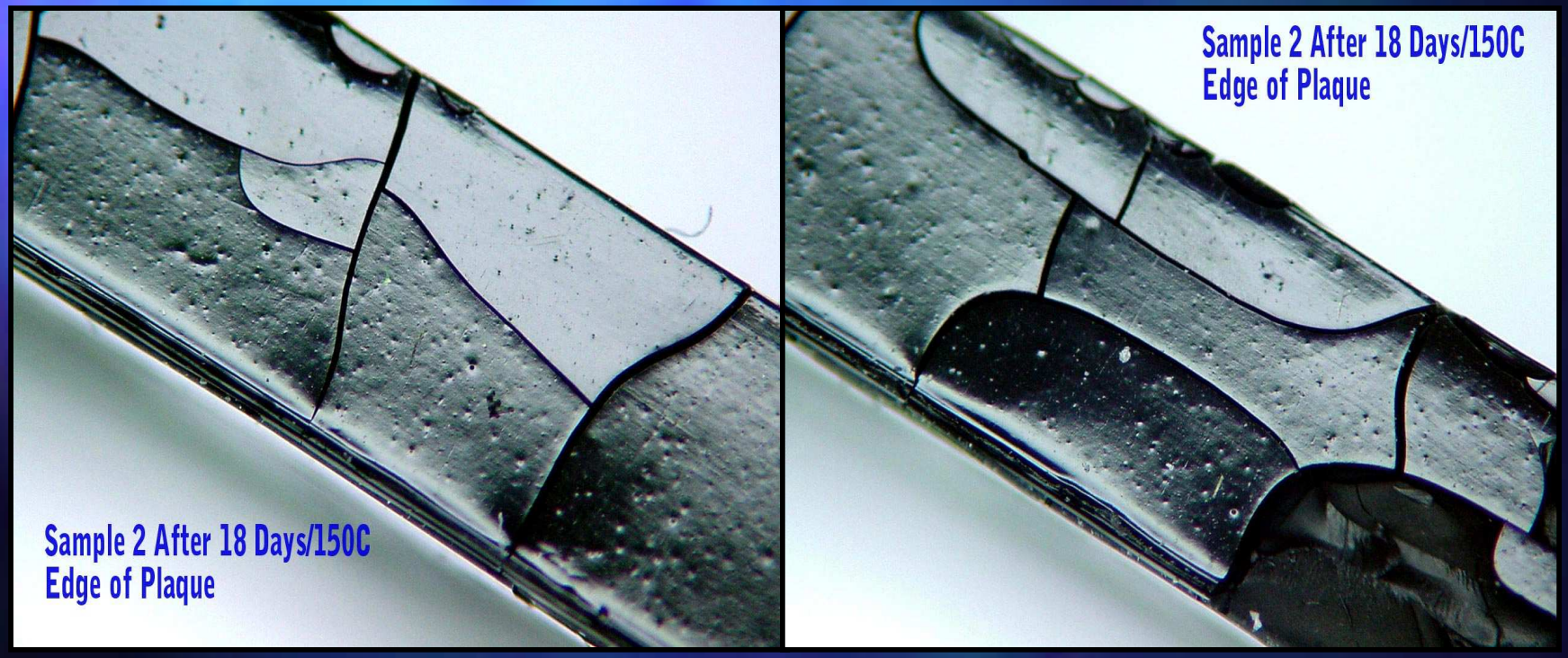


Fortified Control Carbon Black in Polypropylene Interior View





Fortified Carbon Black PP
150 C Degradation Side View



Phase 1 Testing of New Black 150 C Oven Testing Fortified

Thermo-Oxidative Stability 150C
600 Hrs (25 Days)
PP Plaques

#5 No Degradation #6

Degraded 150 C Fortified PP Phase One Results

43 Days/150C
Edge Failure Only

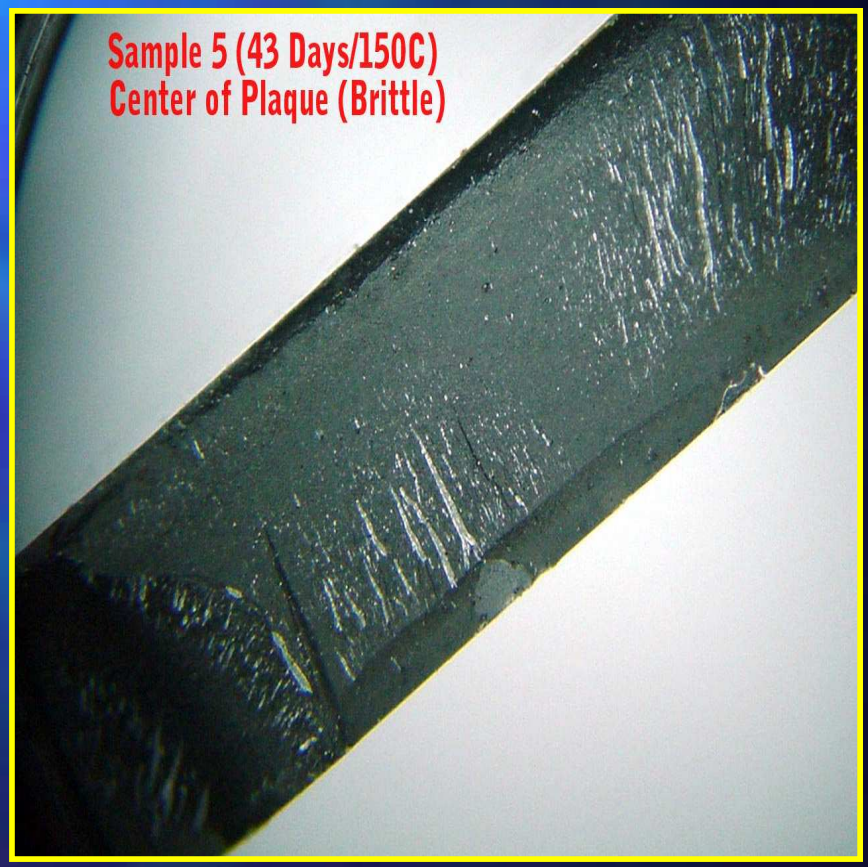
41 Days/150C
Surface and Edge Failure

Degraded Surface at Edge
Phase One Testing

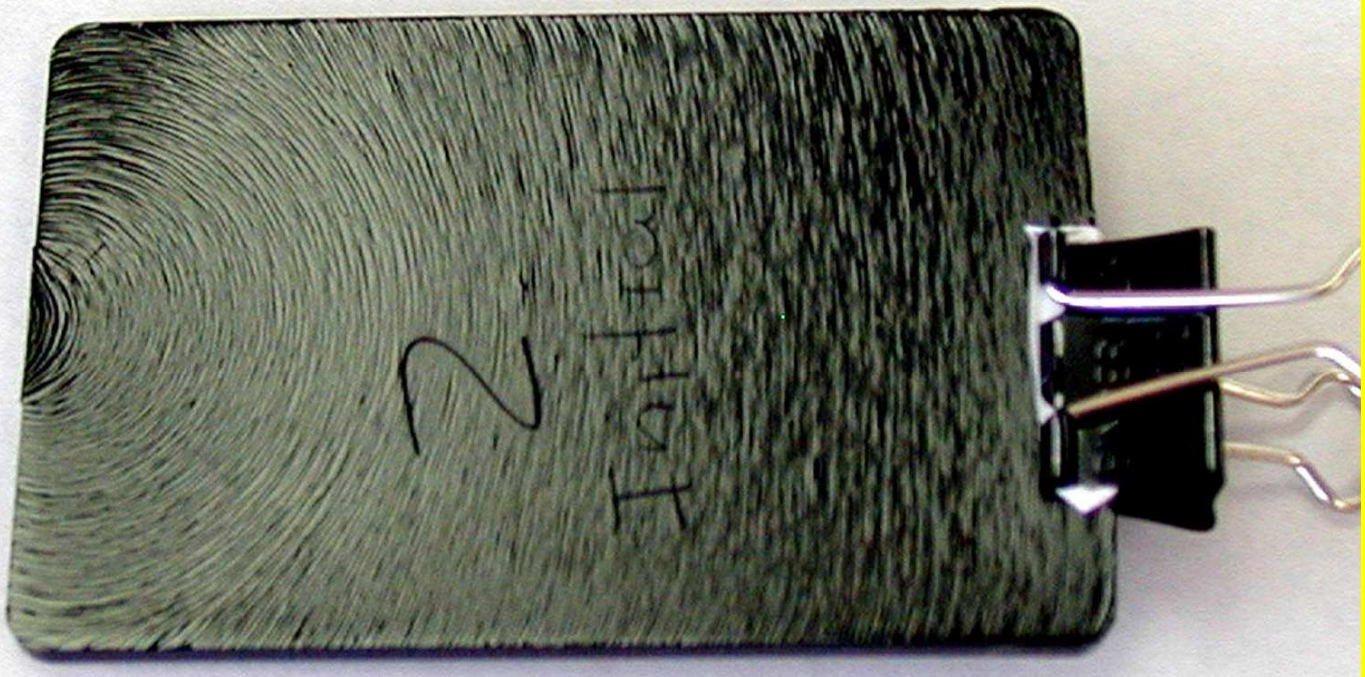
Surface After 43 Days/150C

Edge Degradation Only.

Interior of Fortified New Black After Embrittlement



Phase 2 Carbon Black Testing



5/24/01 INTERNAL CONTROL
2.5% CB,0.1/0.6% 1010/STDP/
0.1% CALCIUM STEARATE

17 DAYS/150C

5/25/01

18 DAYS/150C

COMPLETE FAILURE

* 2.5% CB,0.1% 1010,0.6% STDP;0.1% CAST2

INTERNAL CONTROL
2.5% CB 0.1/0.6/0.1% 1010/STDP/CAST2

17 DAYS/150C **100 MIL**

60 MIL **90 MIL** **120 MIL**

Results of All Phases of Study

Graphic Analysis of Carbon Black

versus

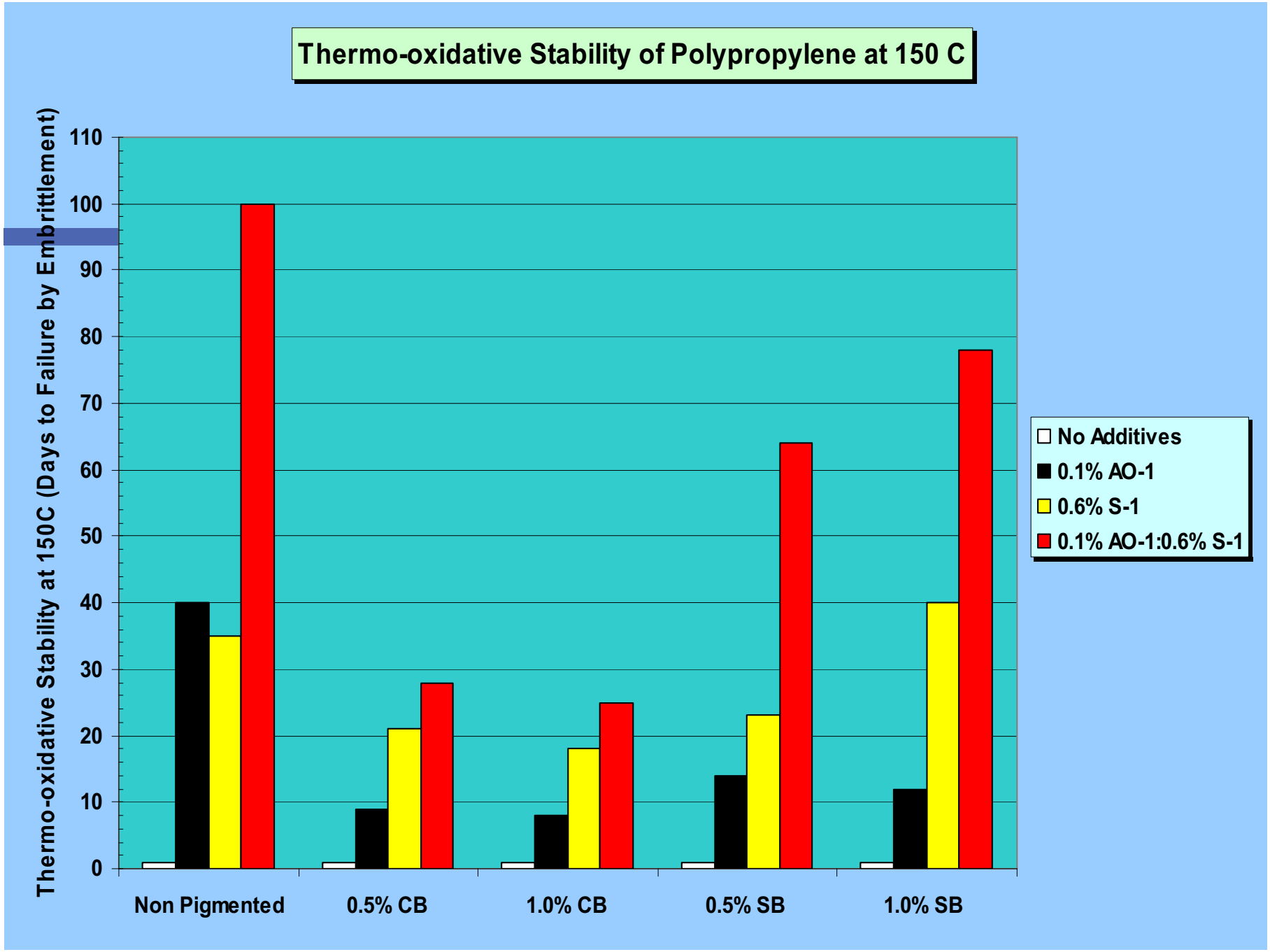
Oxidized Sulfur Black

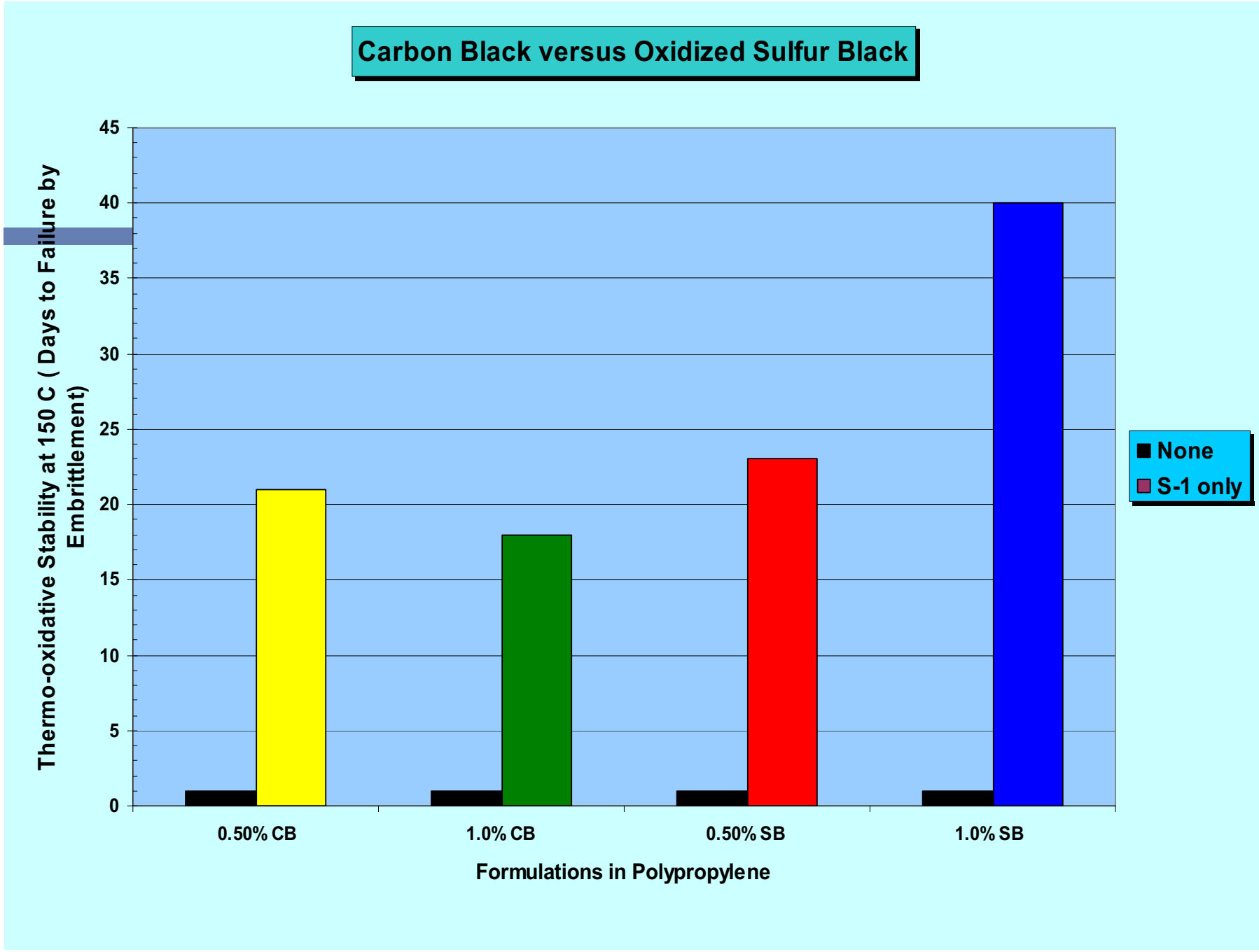
Codes For Slides

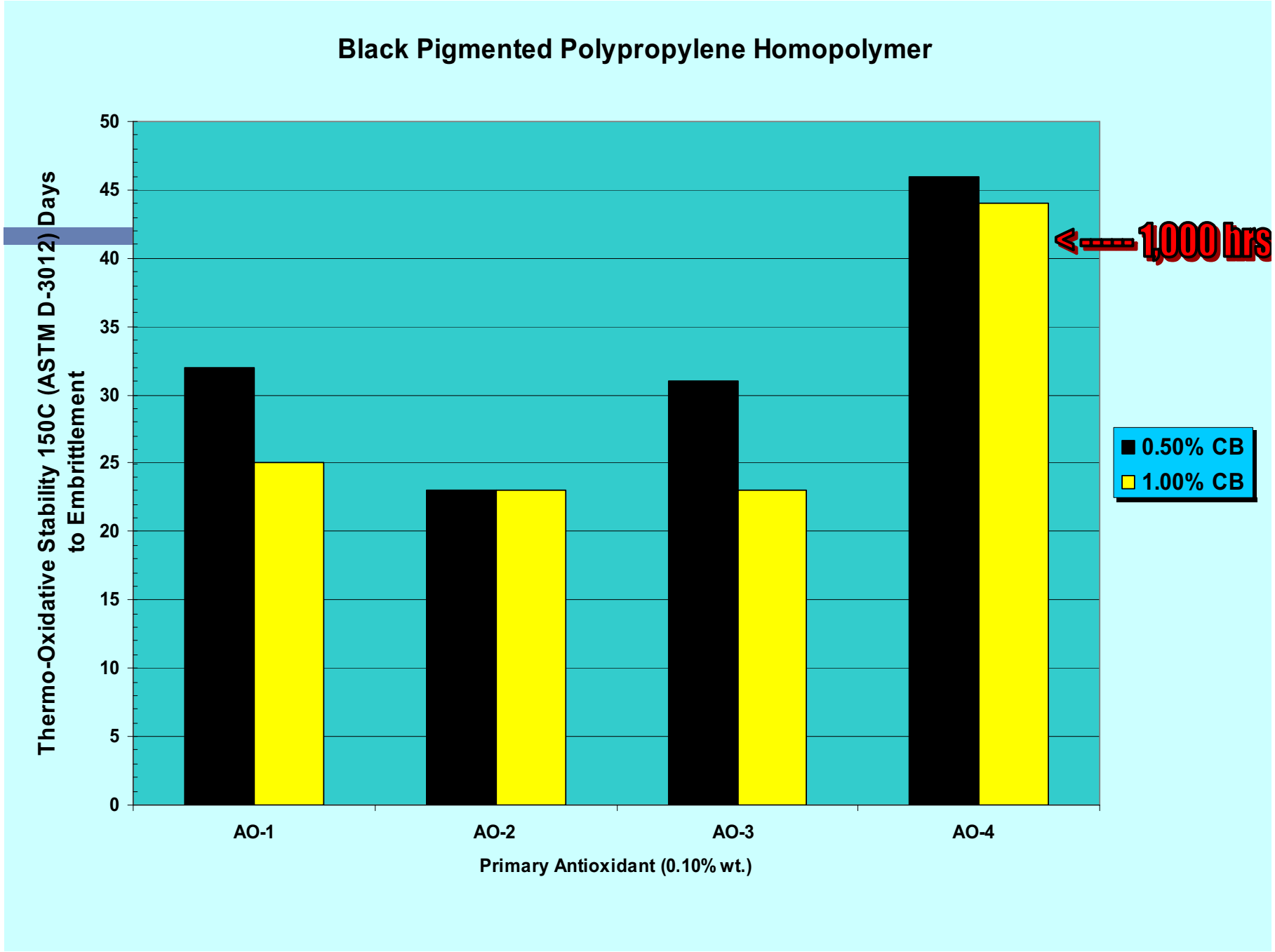
- AO-1 to AO-4 represent standard stabilization using one part AO to six parts of thioester and acid acceptor.
- AO-1 to AO-4 coded as AO-C1 to AO-C4 represent co-stabilizers or catalysts added to the standard stabilization systems at 0.1% unless noted.
- S-1 Ester of Propionic Acid

Carbon Black Pigmented Systems

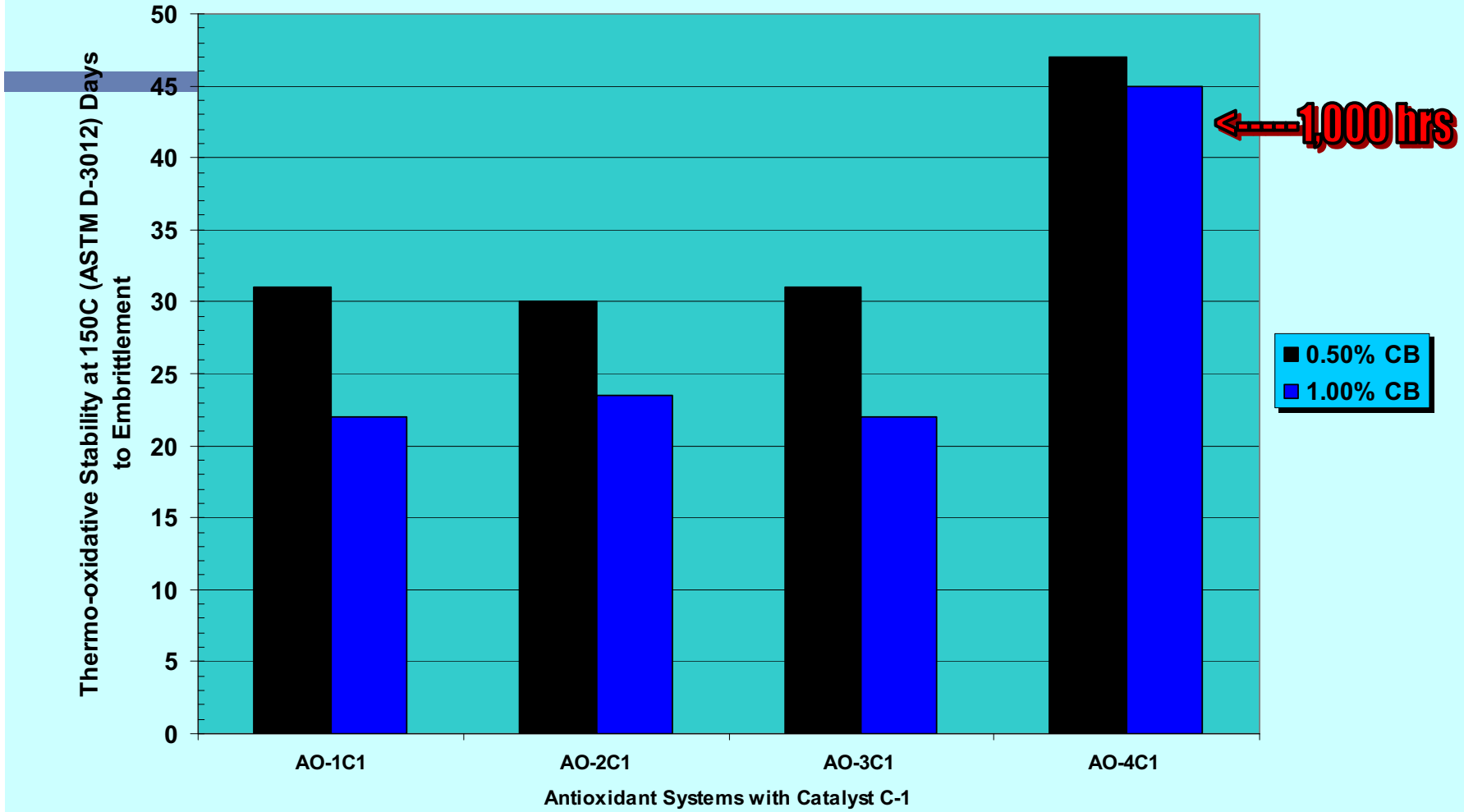
Relationships between Primary Antioxidants with Carbon Black and the Addition of Catalysts


Thermo-oxidative Stability of Polypropylene at 150 C
Thermo-oxidative Stability at 150C (Days to Failure by Embrittlement)
110
100
90
80
70
60
50
40
30
20
10
0
Non Pigmented
0.5% CB
1.0% CB
0.5% SB
1.0% SB
No Additives
0.1% AO-1
0.6% S-1
0.1% AO-1:0.6% S-1

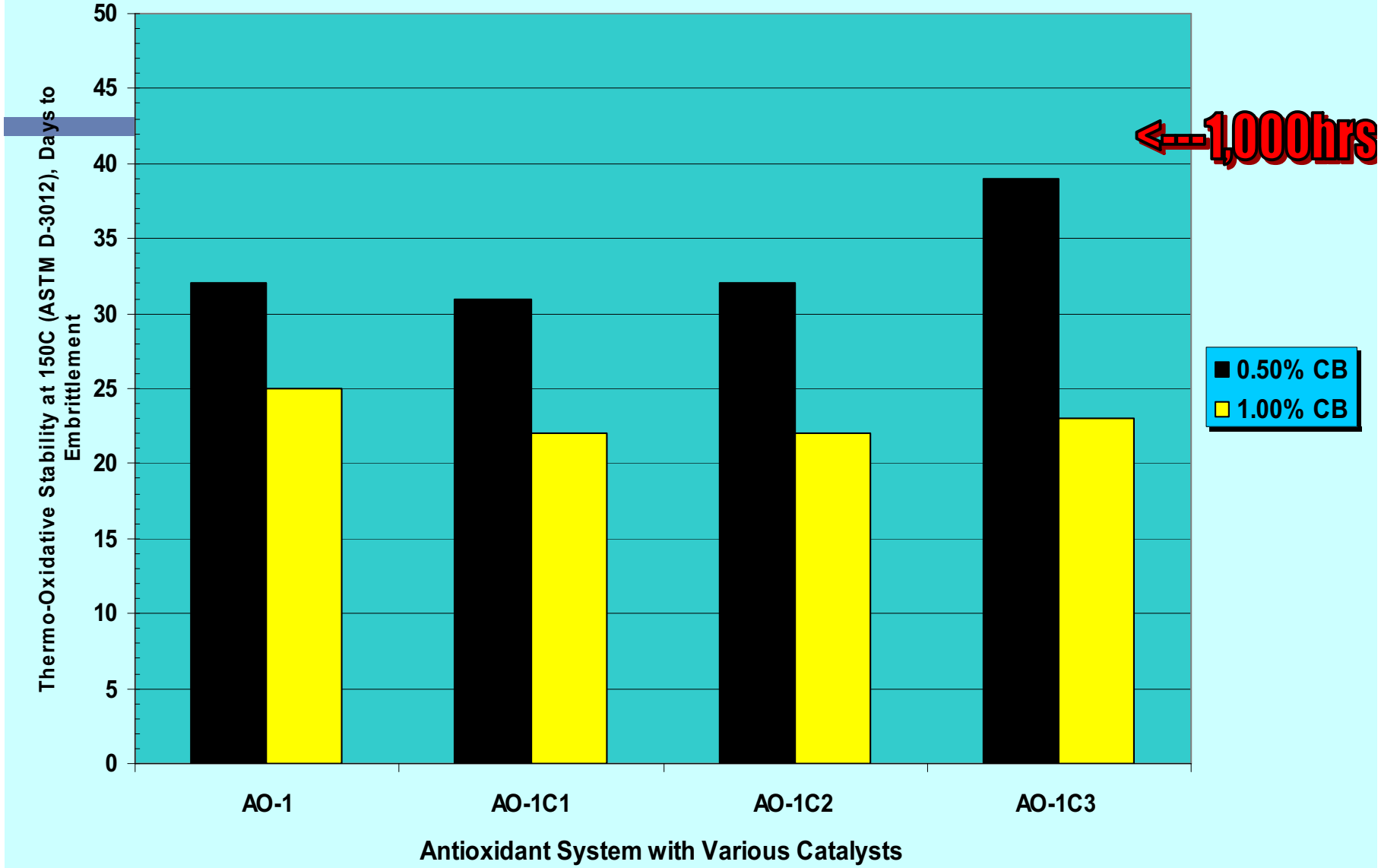

Carbon Black versus Oxidized Sulfur Black
Thermo-oxidative Stability at 150 C (Days to Failure by Embrittlement)
45
40
35
30
25
20
15
10
5
0
0.50% CB
1.0% CB
0.50% SB
1.0% SB
Formulations in Polypropylene
None
S-1 only

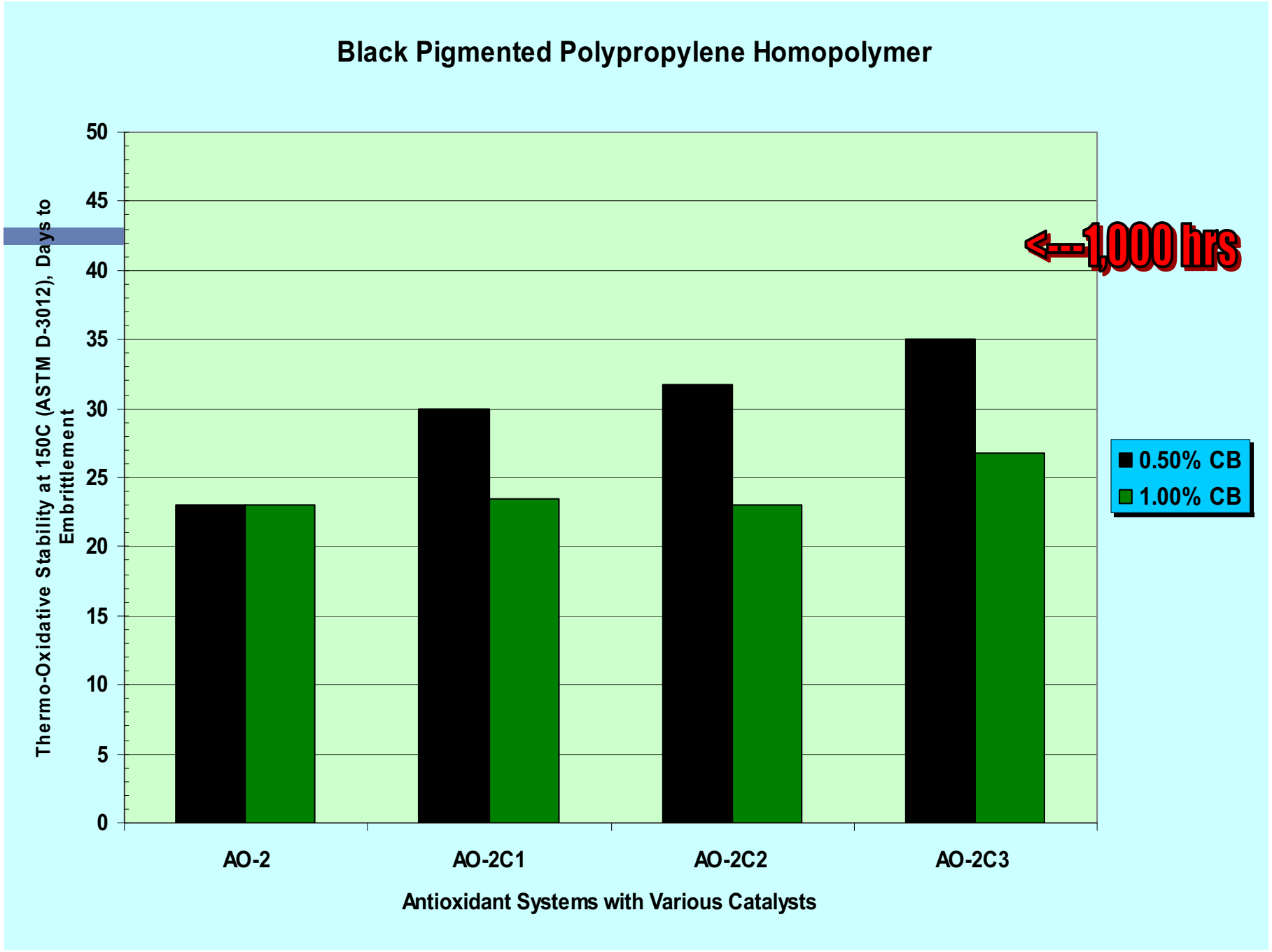

Black Pigmented Polypropylene Homopolymer
Thermo-Oxidative Stability 150C (ASTM D-3012) Days to Embrittlement
50
45
40
35
30
25
20
15
10
5
0
<----1,000 hrs
0.50% CB
1.00% CB
AO-1
AO-2
AO-3
AO-4
Primary Antioxidant (0.10% wt.)

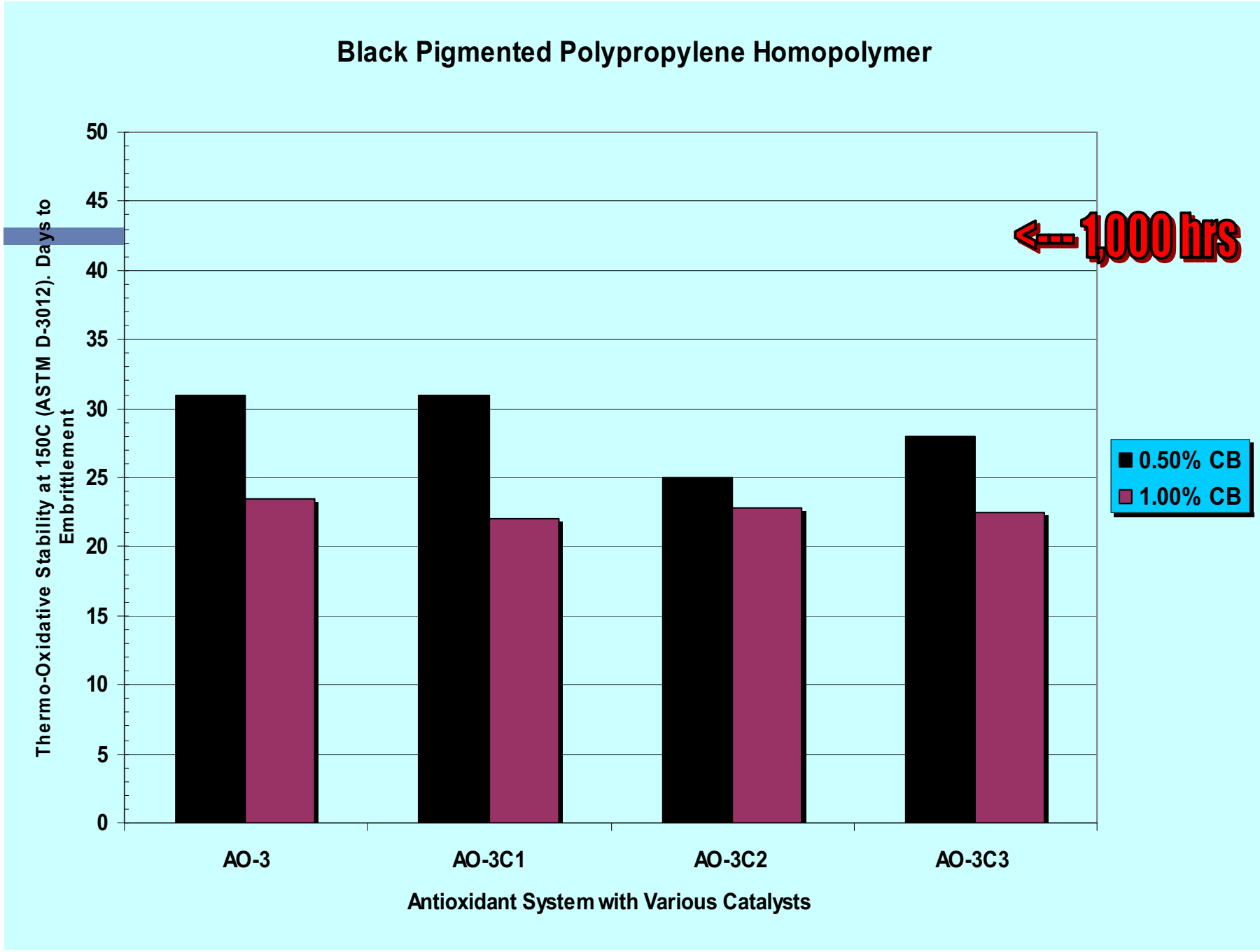
Black Pigmented Polypropylene Homopolymer

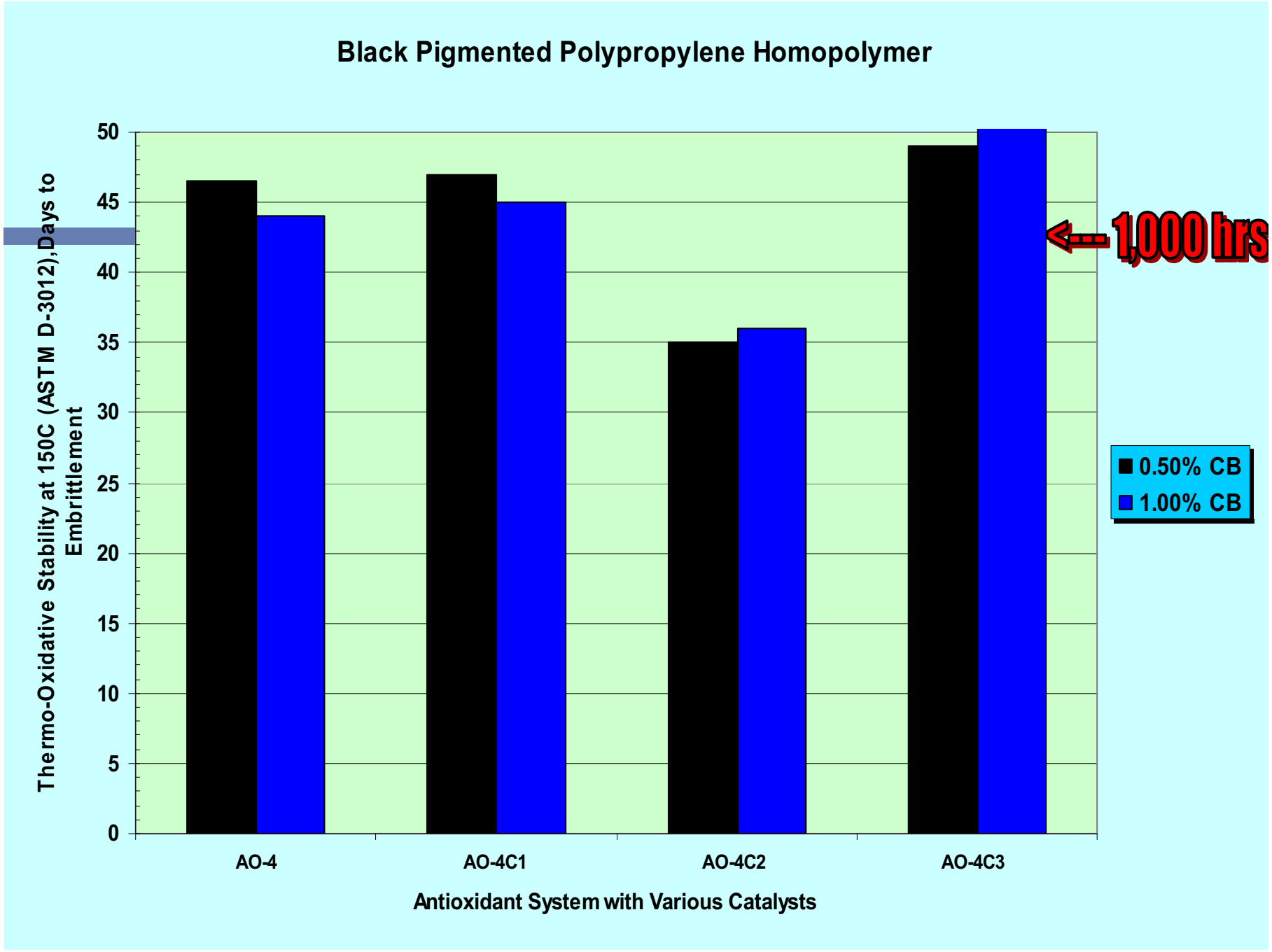


Black Pigmented Polypropylene Homopolymer




Black Pigmented Polypropylene Homopolymer
Thermo-Oxidative Stability at 150C (ASTM D-3012), Days to Embrittlement
50
45
40
35
30
25
20
15
10
5
0
<---1,000 hrs
0.50% CB
1.00% CB
AO-2
AO-2C1
AO-2C2
AO-2C3
Antioxidant Systems with Various Catalysts


Black Pigmented Polypropylene Homopolymer
Thermo-Oxidative Stability at 150C (ASTM D-3012). Days to Embrittlement
50
45
40
35
30
25
20
15
10
5
0
<-- 1,000 hrs
0.50% CB
1.00% CB
AO-3
AO-3C1
AO-3C2
AO-3C3
Antioxidant System with Various Catalysts


Black Pigmented Polypropylene Homopolymer
Thermo-Oxidative Stability at 150C (ASTM D-3012),Days to Embrittlement
50
45
40
35
30
25
20
15
10
5
0
<--- 1,000 hrs
0.50% CB
1.00% CB
AO-4
AO-4C1
AO-4C2
AO-4C3
Antioxidant System with Various Catalysts

Oxidized Sulfur Black Pigmented Polypropylene

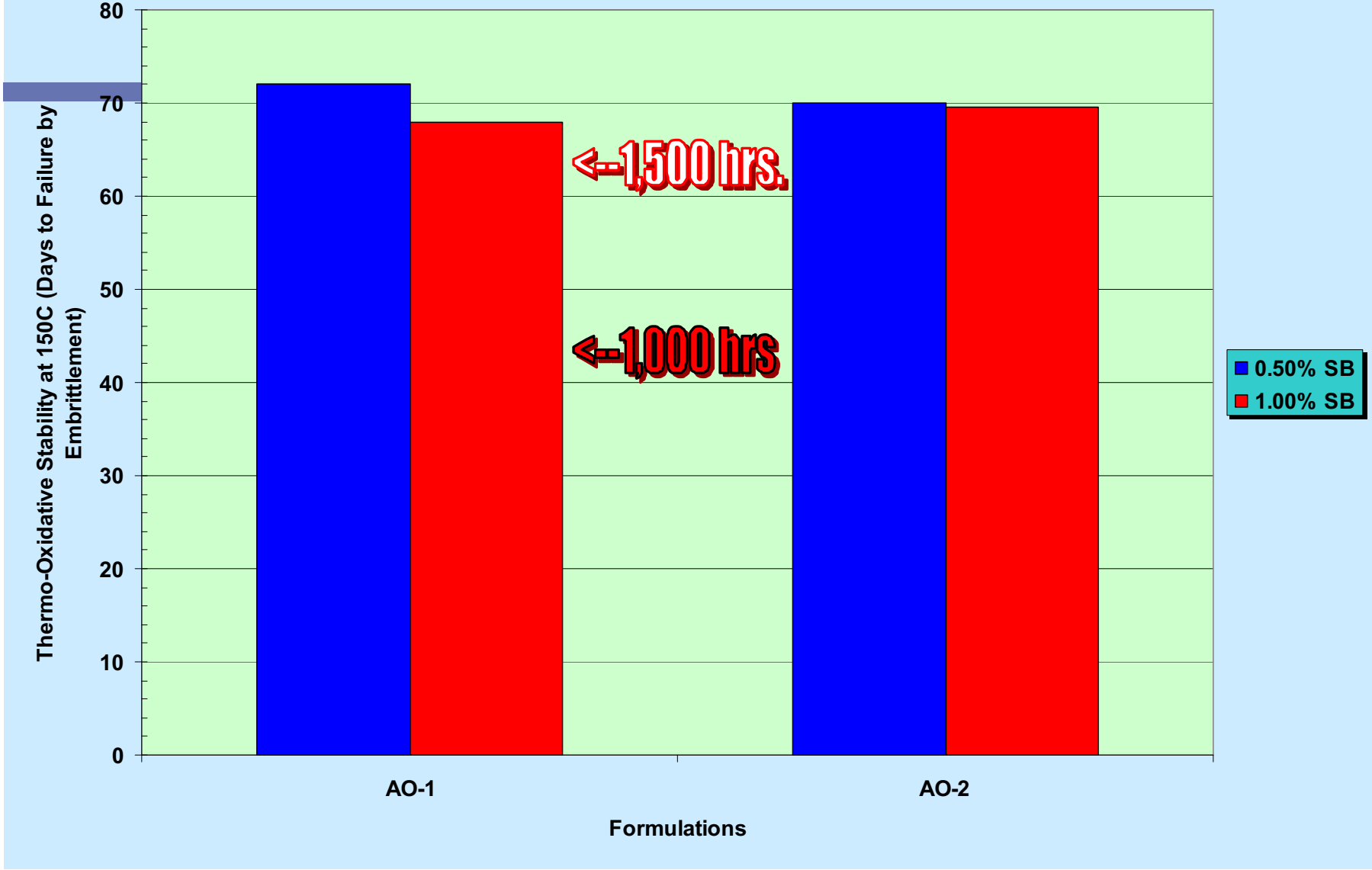
Relationship Between Primary Antioxidants and Catalysed Systems on Thermo-Oxidative Stability

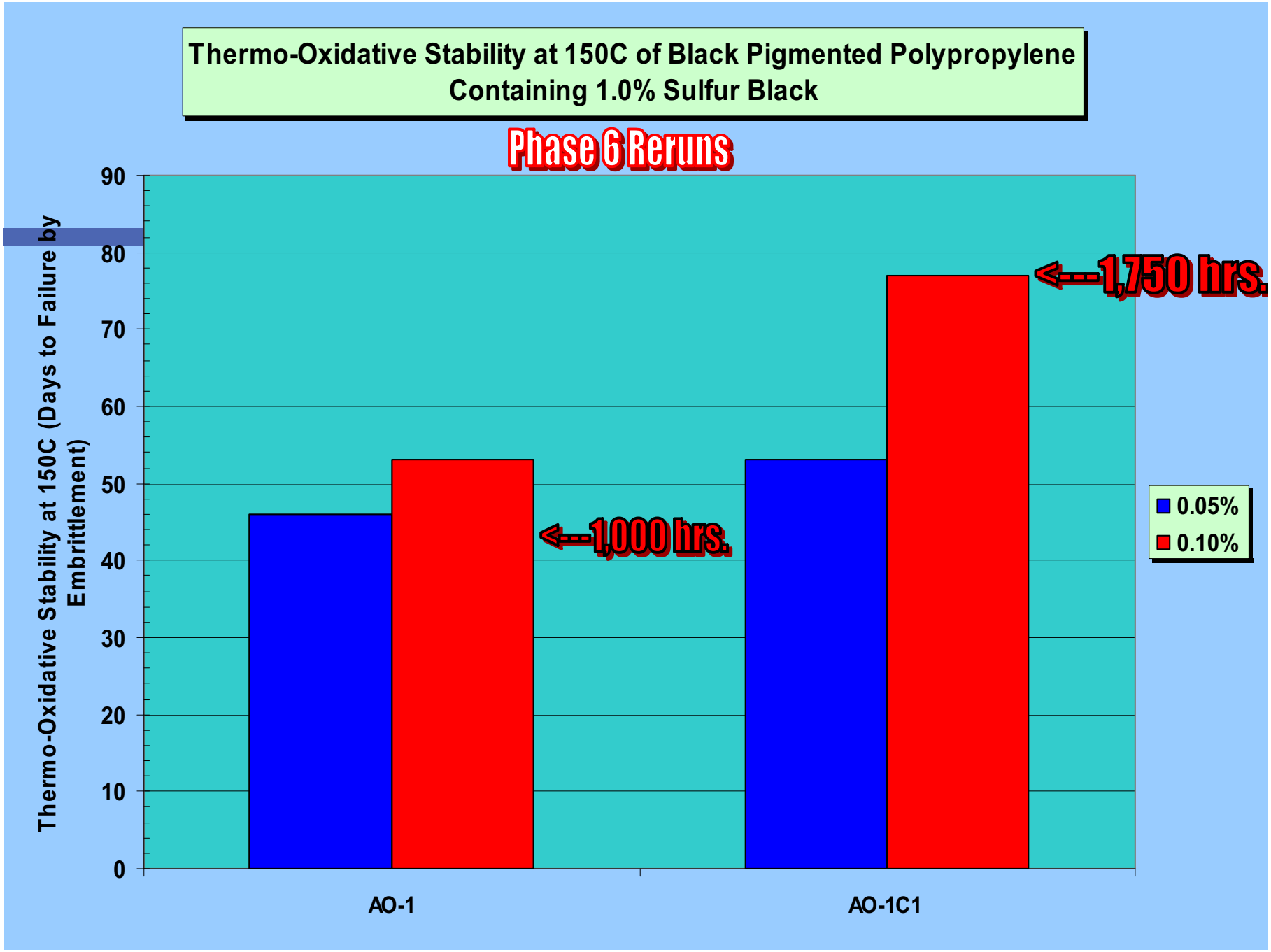
Thermo-Oxidative Stability at 150C Carbon Black vs Sulfur Black

	150 C Thermo-Oxidative Stability (Days to Embrittlement)
0.50% Sulfur Black	23 Days (552 hours)
1.00% Sulfur Black	40 Days (960 hours)
0.50% Carbon Black	21 Days (504 hours)
1.00% Carbon Black	18 Days (432 hours)

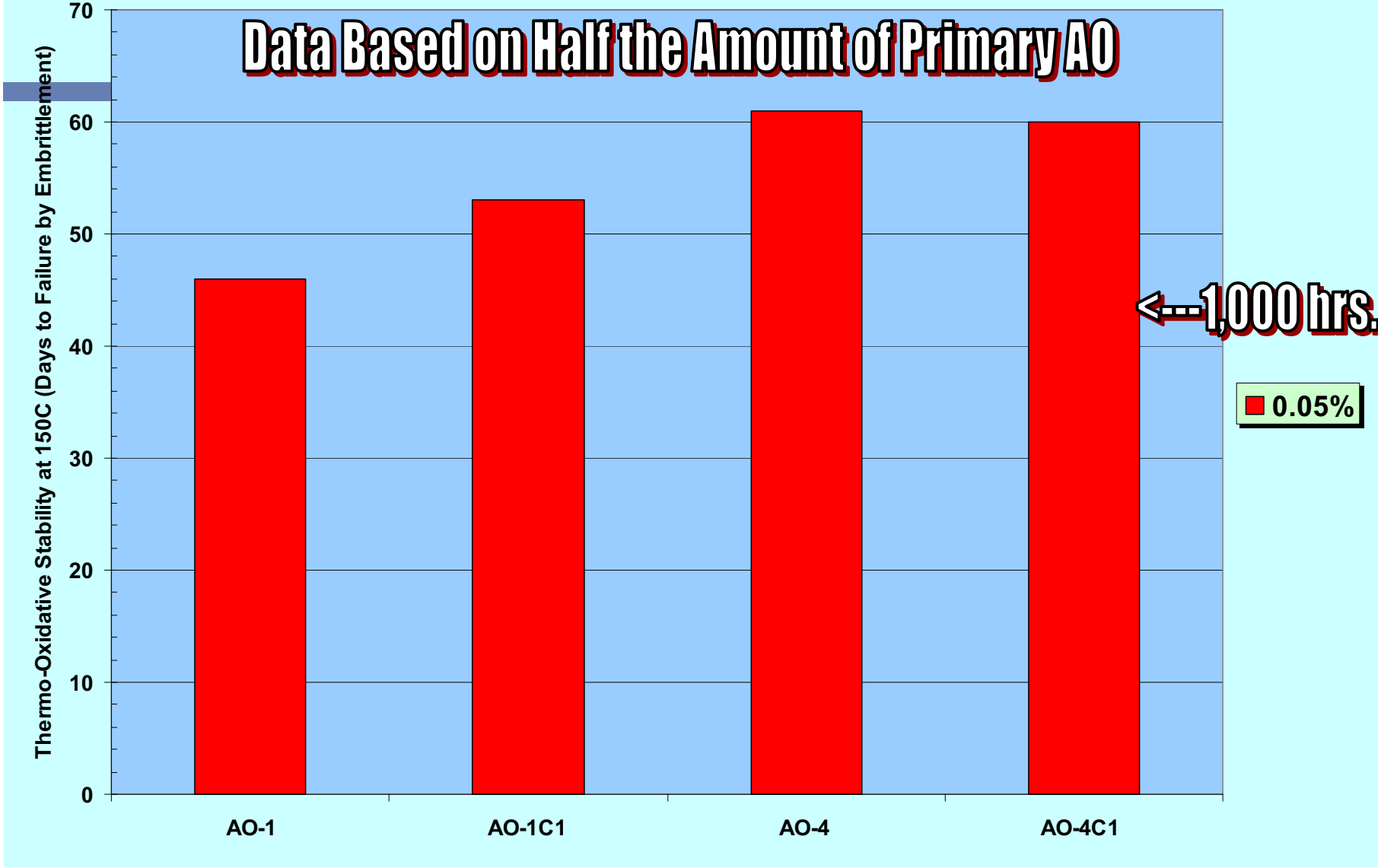
** No Primary AO, 0.6% S1 with calcium stearate*

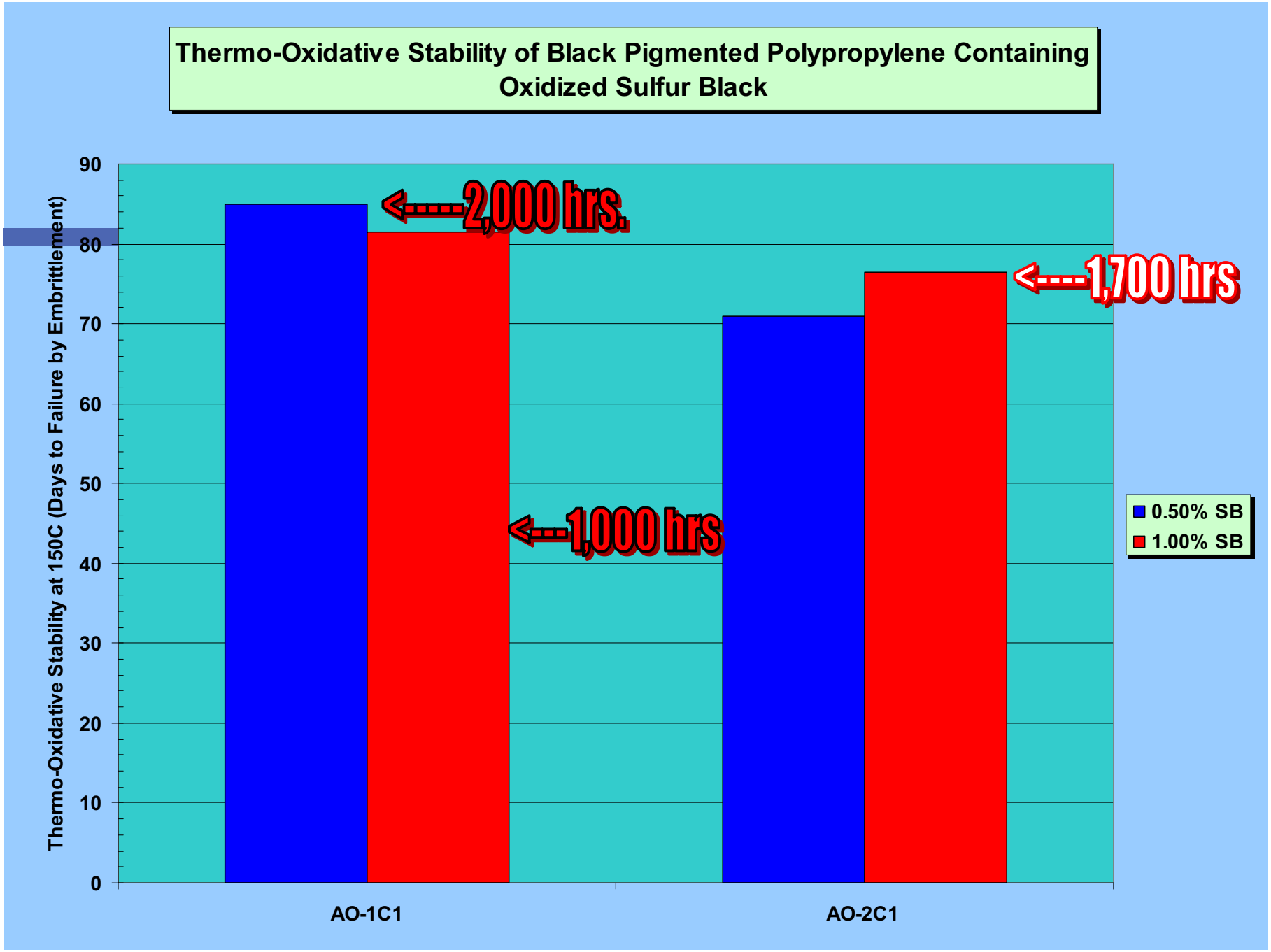
Thermo-Oxidative Stability of Black Pigmented Polypropylene with Sulfur Black



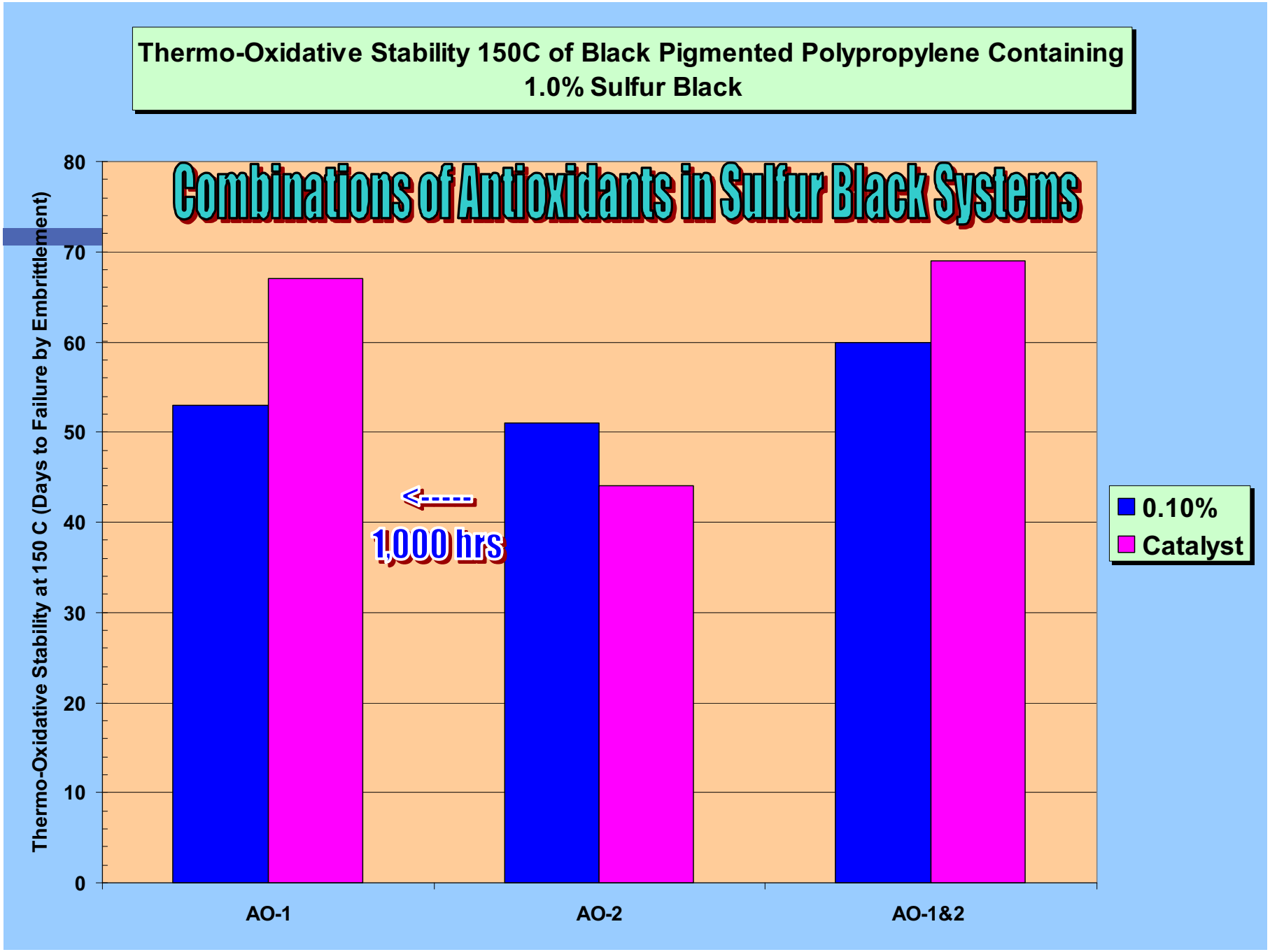

Thermo-Oxidative Stability at 150C of Black Pigmented Polypropylene Containing 1.0% Sulfur Black
Phase 6 Reruns
Thermo-Oxidative Stability at 150C (Days to Failure by Embrittlement)
90
80
70
60
50
40
30
20
10
0
<---1,000 hrs.
<---1,750 hrs.
0.05%
0.10%
AO-1
AO-1C1

Thermo-Oxidative Stability of Black Pigmented Polypropylene Containing 1.0% Sulfur Black




Thermo-Oxidative Stability of Black Pigmented Polypropylene Containing Oxidized Sulfur Black
Thermo-Oxidative Stability at 150C (Days to Failure by Embrittlement)
90
80
70
60
50
40
30
20
10
0
<----2,000 hrs.
<---1,000 hrs
<----1,700 hrs
AO-1C1
AO-2C1
0.50% SB
1.00% SB

Thermo-Oxidative Stability 150C of Black Pigmented Polypropylene Containing 1.0% Sulfur Black



Thermo-Oxidative Stability at 150 C (No Catalyst Present)

Antioxidant Type&%wt.	Carbon Black		Sulfur Black	
	0.50 %	1.00 %	0.50 %	1.00 %
AO-1	32 days	25 days	53 days	53 days
AO-2	23 days	23 days	57 days	51 days
AO-3	31 days	23 days	71 days	66 days
AO-4	46 days	44 days	104 days	93 days

1,000 hrs equals 42 days

Thermo-Oxidative Stability at 150 C (Catalyst Present)

Antioxidant Type&%wt.	Carbon Black		Sulfur Black	
	0.50%	1.00 %	0.50 %	1.00 %
AO-1	31 days	22 days	77 days	67 days
AO-2	30 days	23 days	51 days	44 days
AO-3	31 days	22 days	77 days	>145 days
AO-4	47 days	45 days	113 days	95 days

1,000 hrs equals 42 days

145 days = 3,480 hours

Thermo-Oxidative Stability 150C Affect of Catalyst on Sulfur Bk.

0.50% Sulfur Bk.	No Catalyst	C-1	C-2	C-3
AO-1	53 days	77 days	81 days	69 days
AO-2	57 days	51 days	59 days	63 days
AO-3	71 days	77 days	77 days	78 days
AO-4	104 days	113 days	>145 days	>145 days

145 days = 3,480 hours

Catalyst 0.10% w/0.10% AO,0.6% S-1

Thermo-Oxidative Stability 150C Affect of Catalyst on Sulfur Black

1.0% Sulfur Bk.	No Catalyst	C-1	C-2	C-3
AO-1	53 days	67 days	79 days	64 days
AO-2	51 days	44 days	45 days	43 days
AO-3	66 days	>145 days	72 days	78 days
AO-4	93 days	95 days	99 days	93 days

Catalyst at 0.10% w/0.1% AO & 0.6% S1

" Future "

Thermal Stability in Excess of - 3,000 Hours

Tomorrow !

Oxidized Sulfur Black Systems:

0.50% Black: From a min. of 1,272 hours to 2,456 hours.
With catalyst up to 2,712 hours.

1.00% Black: From a min. of 1,272 hours to >2,736

Today !

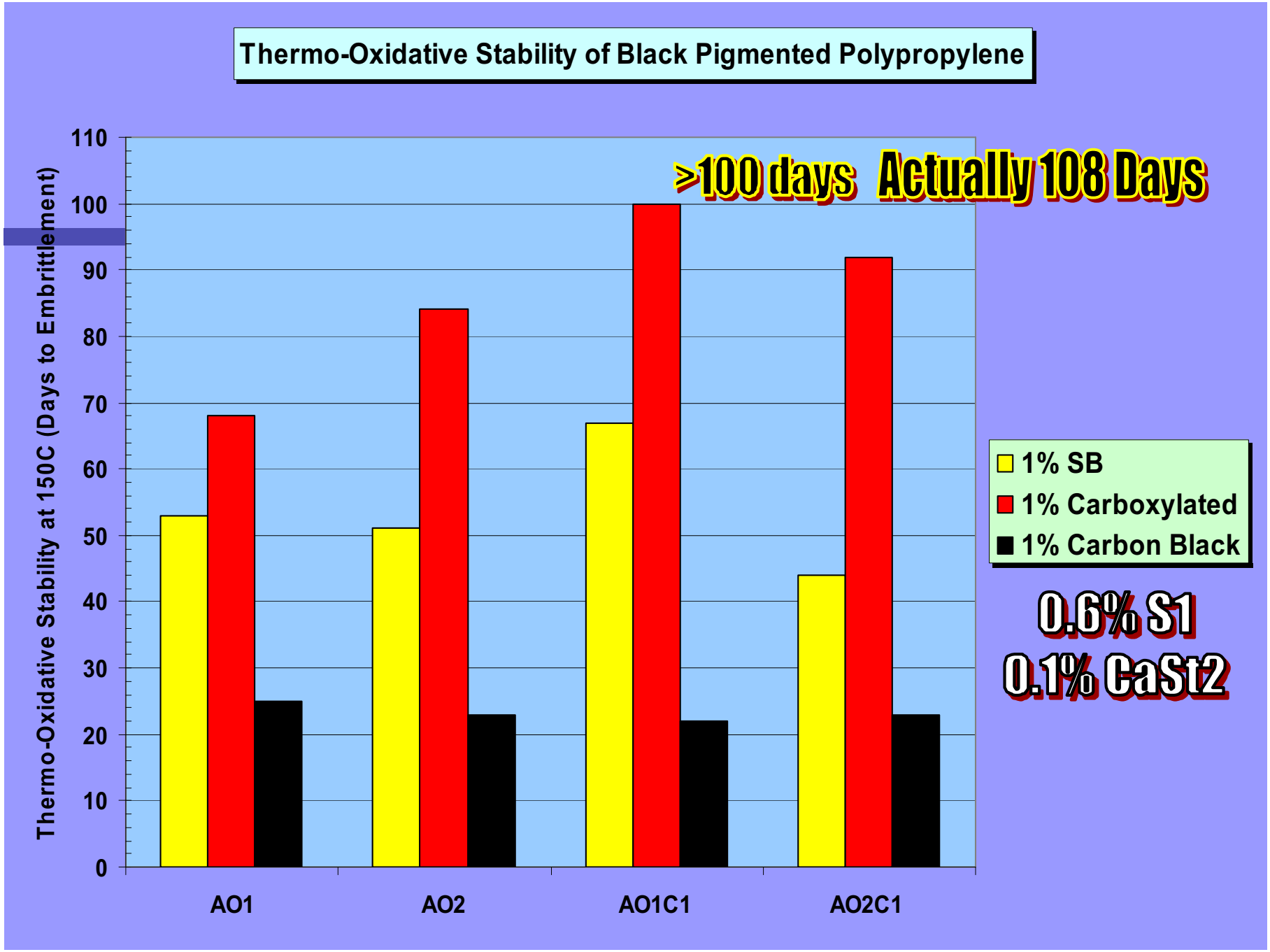
Carbon Black Systems:

0.50% Black: From 552 hours to 1,116 hours maximum today regardless of antioxidant used

1.00% Black: From 552 hours to 1,056 hours maximum today regardless of antioxidant us

Chemical Modification of Sulfur Black via Carboxylation

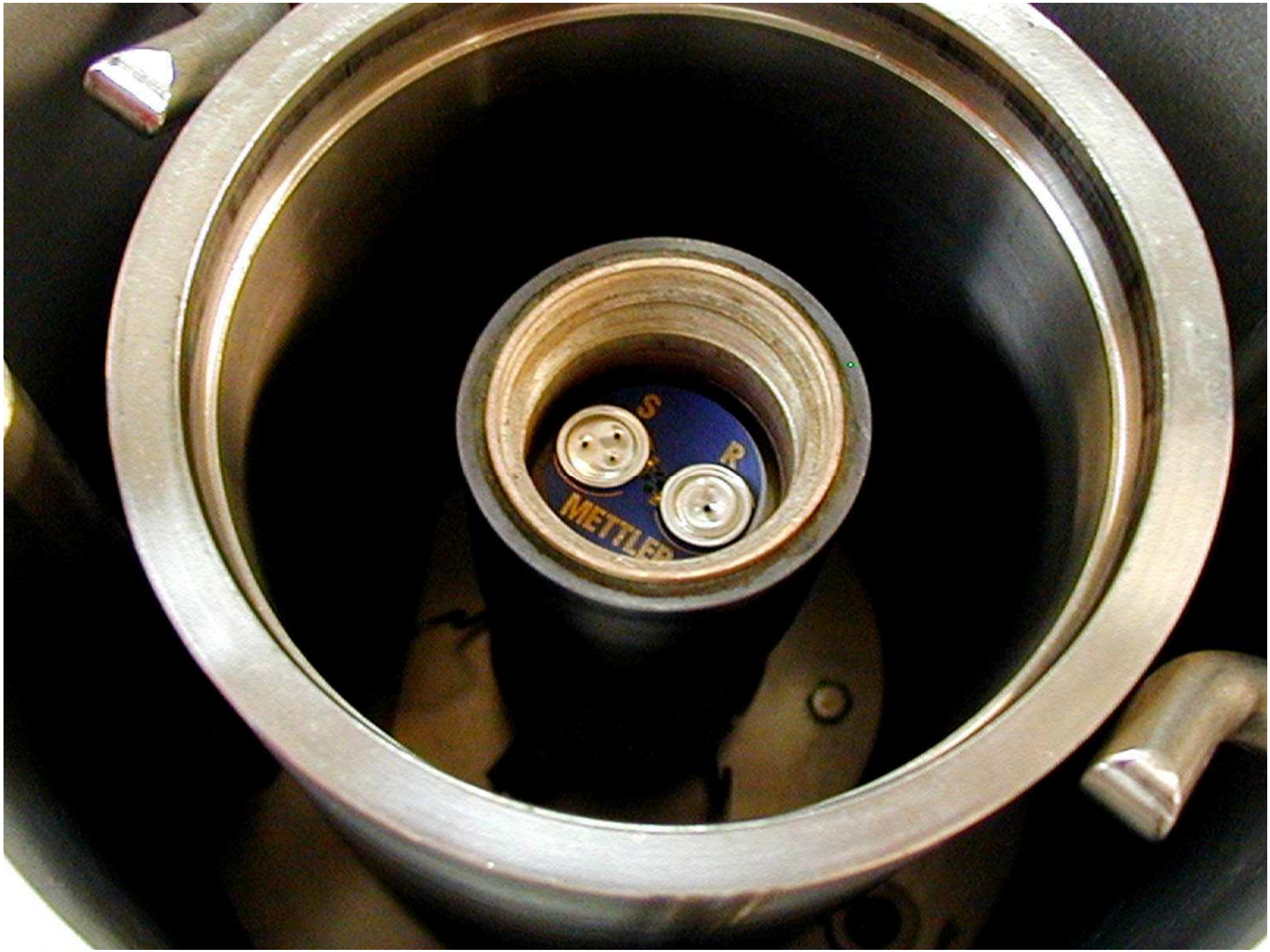
Conversion to a metal salt

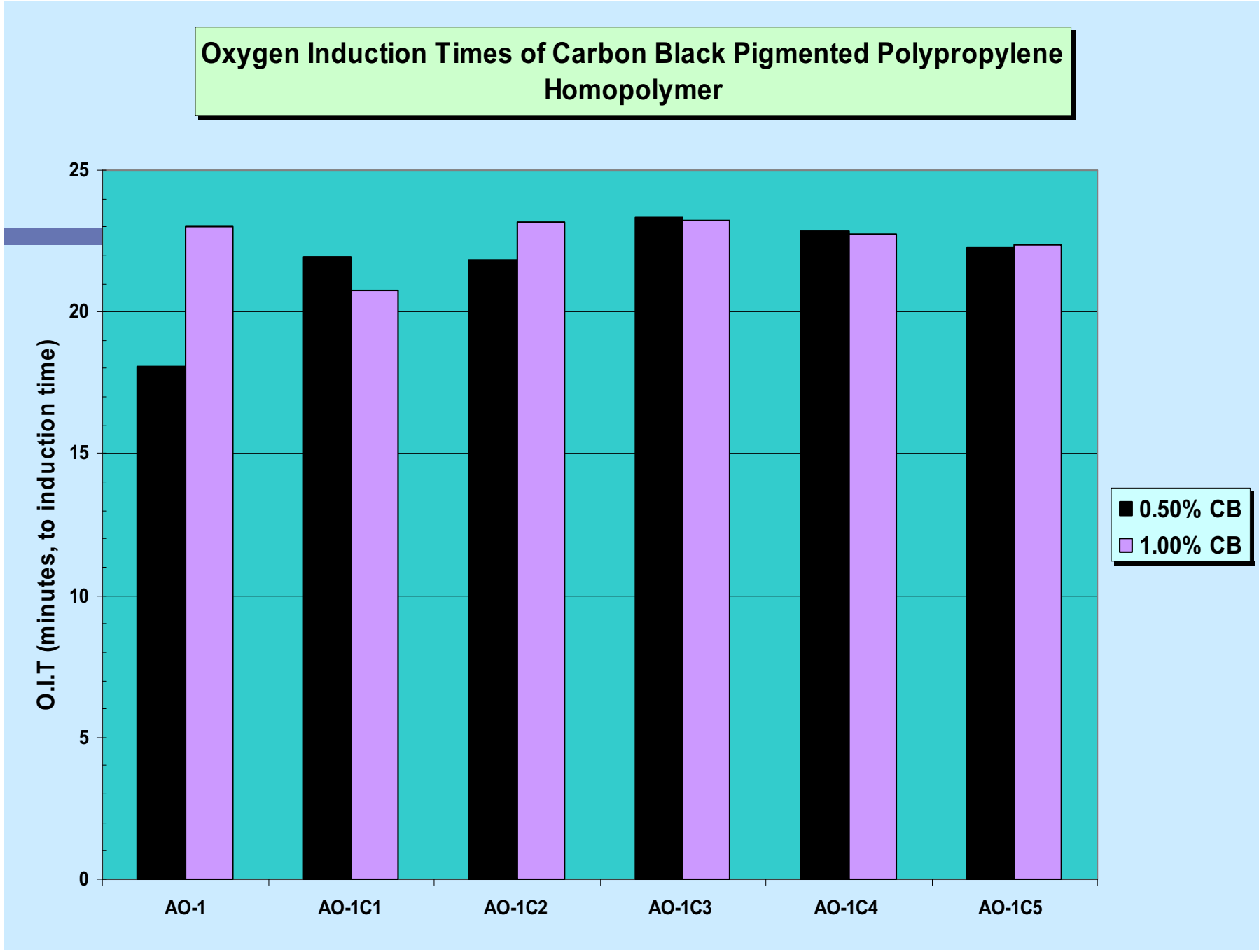

Thermo-Oxidative Stability of Black Pigmented Polypropylene
Thermo-Oxidative Stability at 150C (Days to Embrittlement)
110
100
90
80
70
60
50
40
30
20
10
0
AO1
AO2
AO1C1
AO2C1
>100 days
Actually 108 Days
1% SB
1% Carboxylated
1% Carbon Black
0.6% S1
0.1% CaSt2

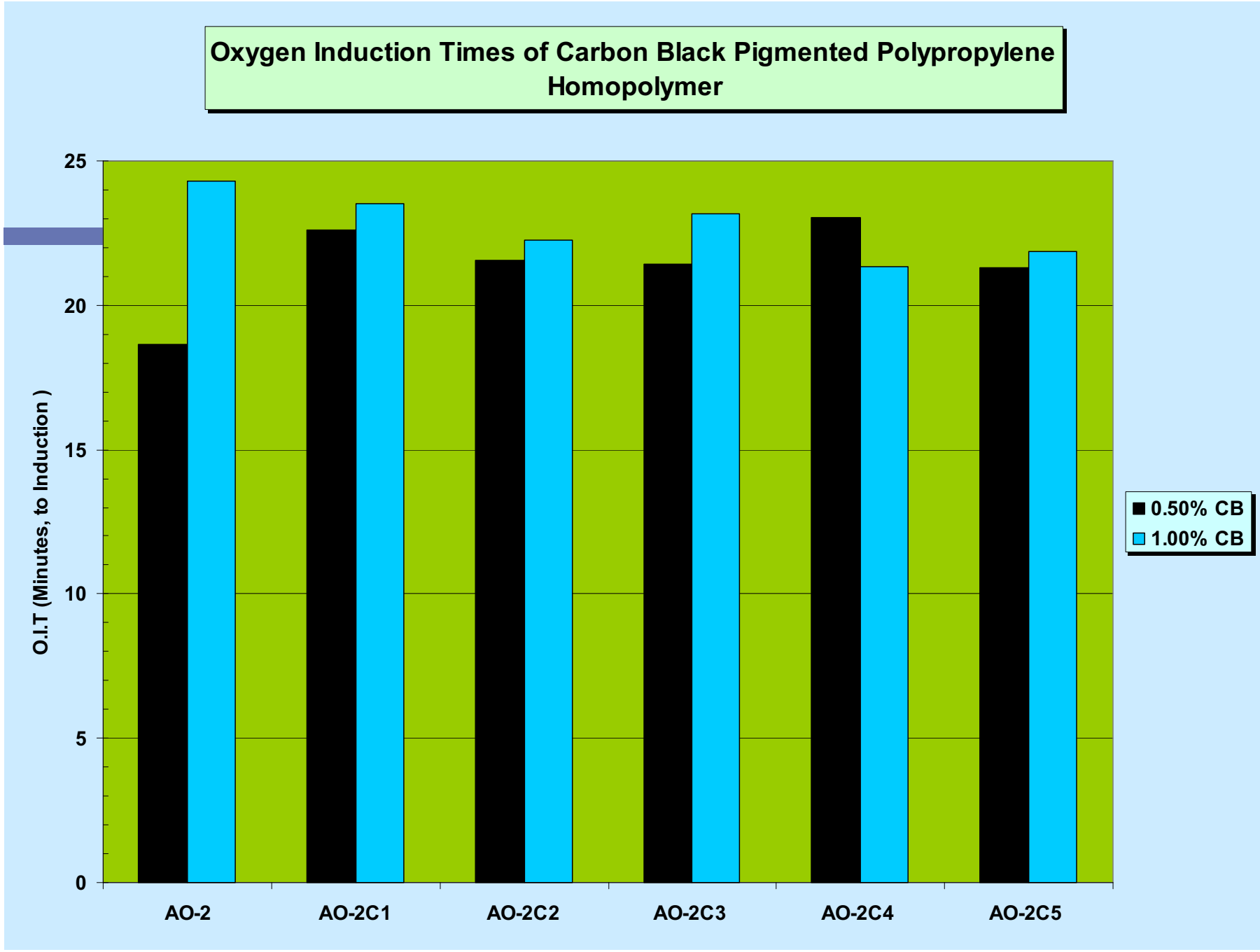
Oxygen Induction Time Data Carbon Blk. Vs Sulfur Blk.

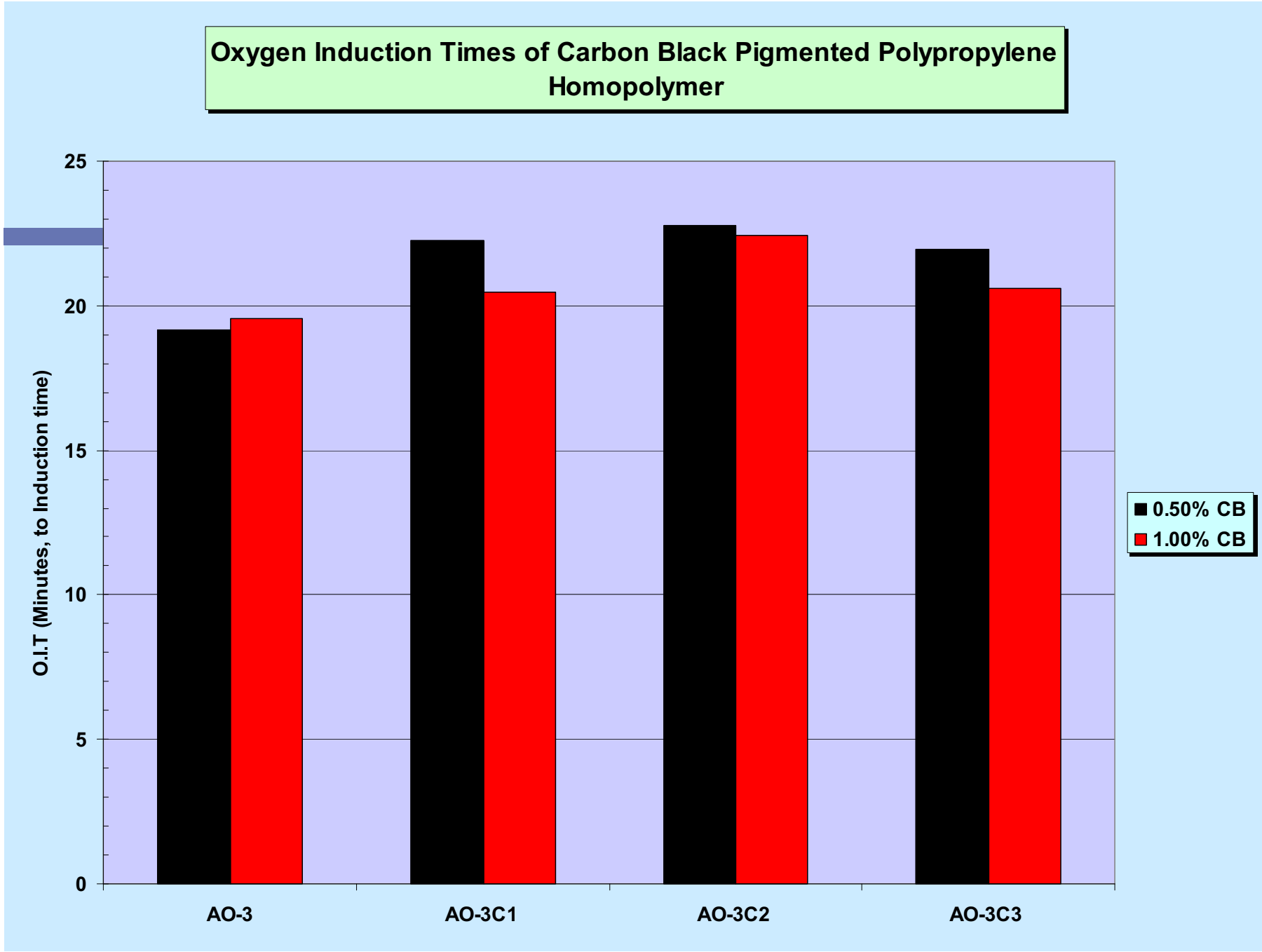
Expressed in Minutes to Induction of Rapid Oxidation at 190 C

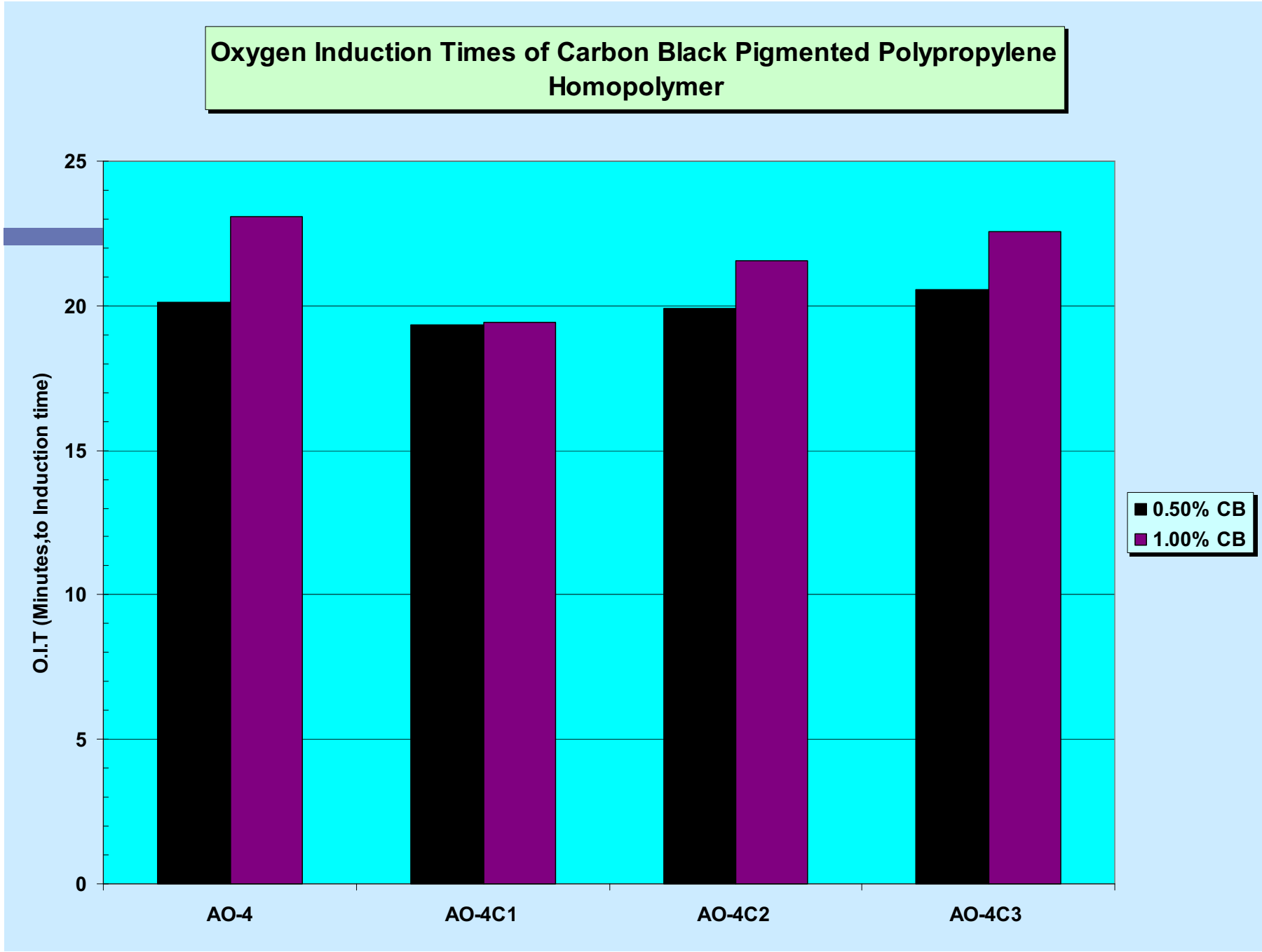

Not an
Exit
DELL

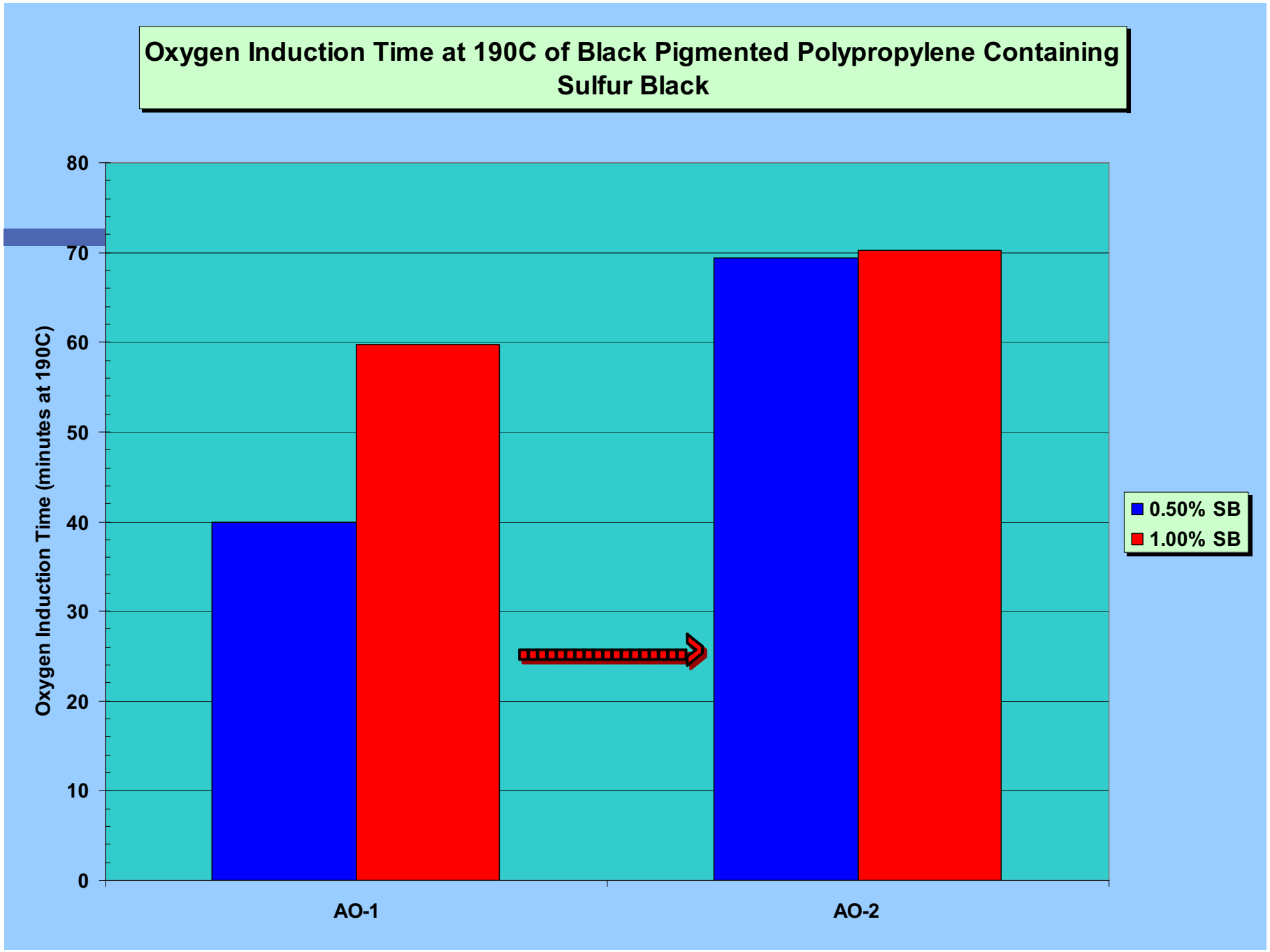

S
R
METTLER

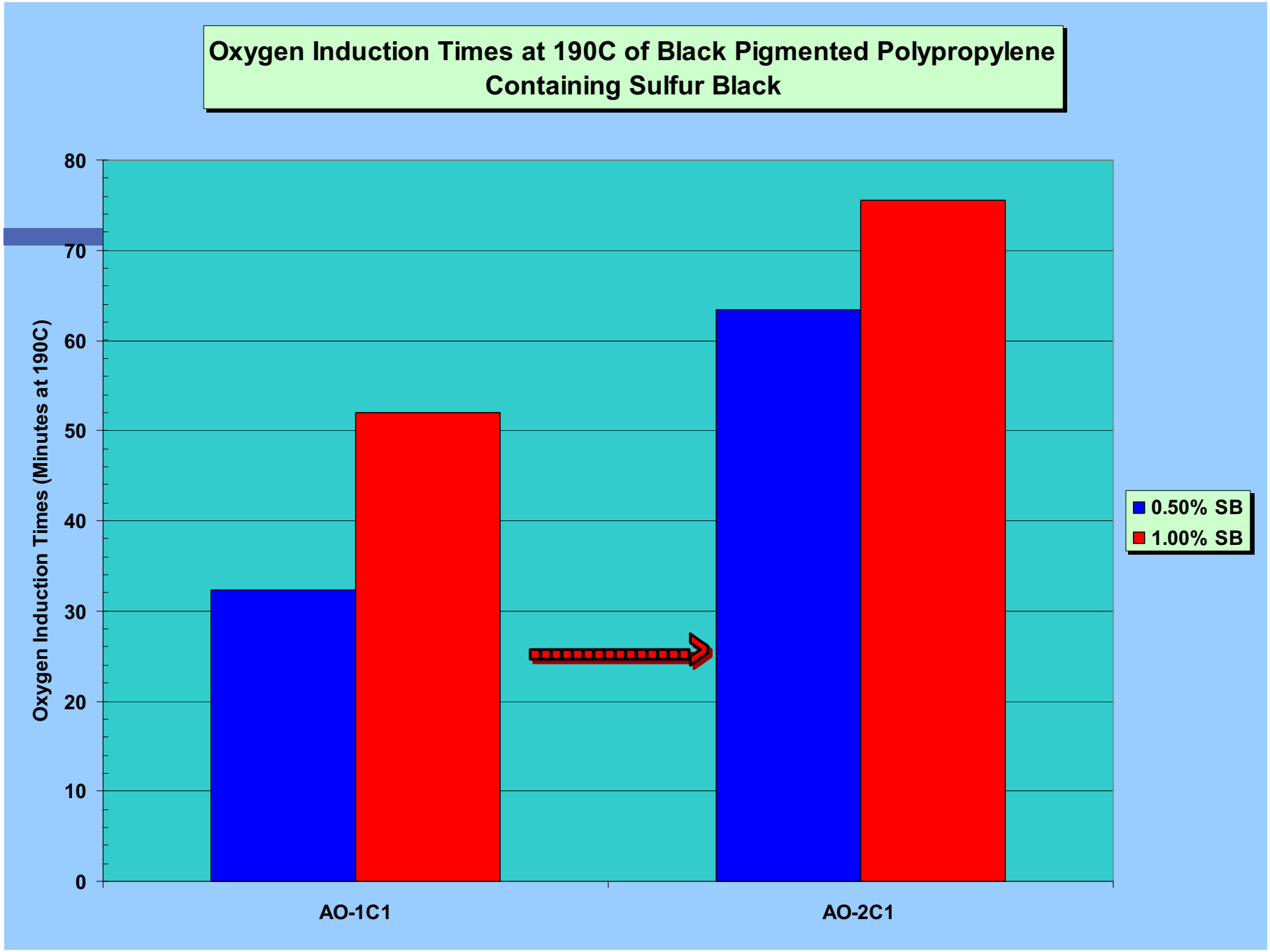

Oxygen Induction Times of Carbon Black Pigmented Polypropylene Homopolymer
O.I.T (minutes, to induction time)
25
20
15
10
5
0
AO-1
AO-1C1
AO-1C2
AO-1C3
AO-1C4
AO-1C5
0.50% CB
1.00% CB


Oxygen Induction Times of Carbon Black Pigmented Polypropylene Homopolymer
O.I.T (Minutes, to Induction)
25
20
15
10
5
0
AO-2
AO-2C1
AO-2C2
AO-2C3
AO-2C4
AO-2C5
0.50% CB
1.00% CB


Oxygen Induction Times of Carbon Black Pigmented Polypropylene Homopolymer
O.I.T (Minutes, to Induction time)
25
20
15
10
5
0
AO-3
AO-3C1
AO-3C2
AO-3C3
0.50% CB
1.00% CB


Oxygen Induction Times of Carbon Black Pigmented Polypropylene Homopolymer
O.I.T (Minutes,to Induction time)
25
20
15
10
5
0
AO-4
AO-4C1
AO-4C2
AO-4C3
0.50% CB
1.00% CB


Oxygen Induction Time at 190C of Black Pigmented Polypropylene Containing Sulfur Black
Oxygen Induction Time (minutes at 190C)
80
70
60
50
40
30
20
10
0
AO-1
AO-2
0.50% SB
1.00% SB


Oxygen Induction Times at 190C of Black Pigmented Polypropylene Containing Sulfur Black
Oxygen Induction Times (Minutes at 190C)
80
70
60
50
40
30
20
10
0
AO-1C1
AO-2C1
0.50% SB
1.00% SB

Conclusions

- Carbon Black Pigmented Polyolefins Continue to Show Significant Limitations to extend LTHA at 150C and O.I.T at 190C.
- Oxidized Sulfur Black is a cost performance alternative and has no limitations with antioxidants and can be catalyzed in-situ to further extend LTHA & OIT.

Next Year Non-Warping Colorants

A Photo of Non-Warping Blue in HDPE Beverage Crate

Thermally and UV Stable Colorants at 200 ppm