Phosphite Antioxidant Kinetics and in-Polymer Performance: PART 2

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Global Technology- Polymer Additives

SI Group
The Substance Inside

Agenda

- SI Group Overview
- Solid Phosphite Kinetics
- In-Polymer Performance
- Summary & Conclusions

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Our Global Reach

30
Manufacturing Facilities & 5 Joint Ventures

3,000
Global Workforce

$2+
Billion in Annual Sales

STRATEGIC
market focus

ACCELERATES
access to
technology

LEVERAGING
backward integration
capabilities

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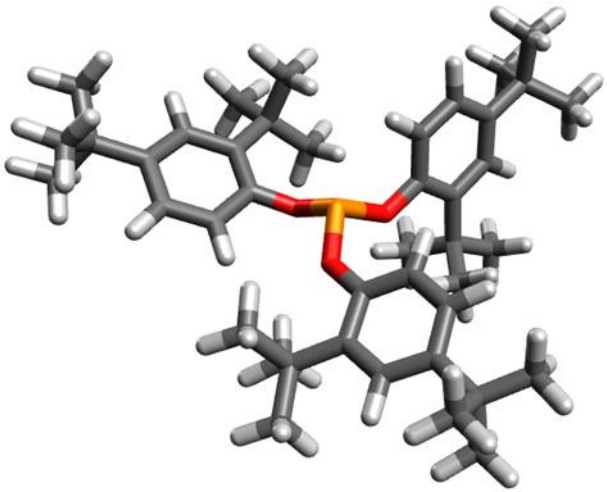
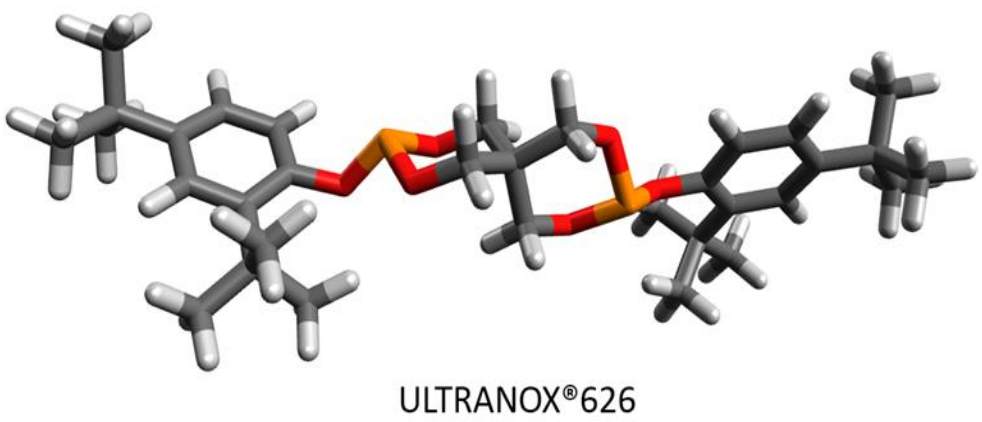
Model Studies: Solid Phosphites



ALKANOX®240



ULTRANOX® 626

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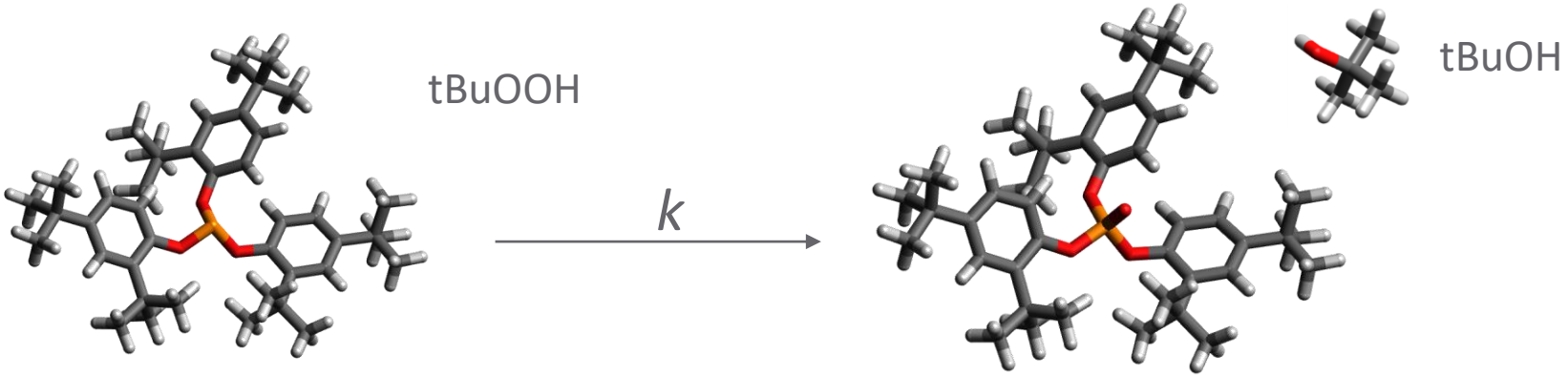
ALKANOX® 240 Oxidation: Model Study

- Second order elementary bimolecular reaction
- *rate* = *k*[P][tBuOOH]



ALKANOX®240 **ALKANOX®240 phosphate**

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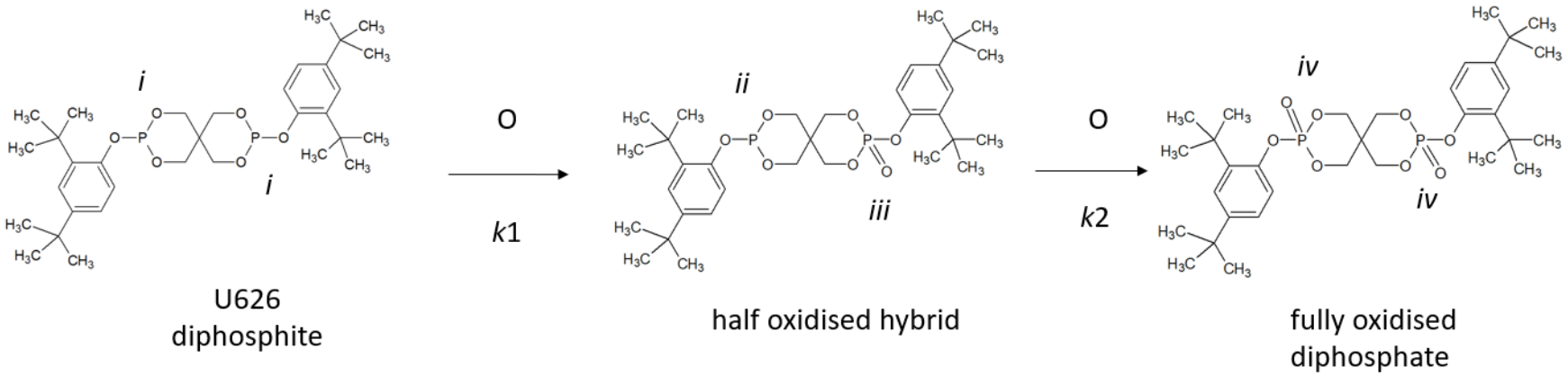
ULTRANOX® 626 Kinetics

- React ULTRANOX®626 with tBuOOH, measuring concentrations of all species over time.
- Calculate rate constants k_1 *and* k_2 by fitting measured NMR data to a sequential oxidation model.



U626 diphosphite

half oxidised hybrid

fully oxidised diphosphate

$$-\frac{d[\mathrm{U626}]}{dt} = k1\ [\mathrm{U626}]\ [\mathrm{TBHP}]$$

$$-\frac{d[hybrid]}{dt} = k2\ [\mathrm{hybrid}]\ [\mathrm{TBHP}]$$

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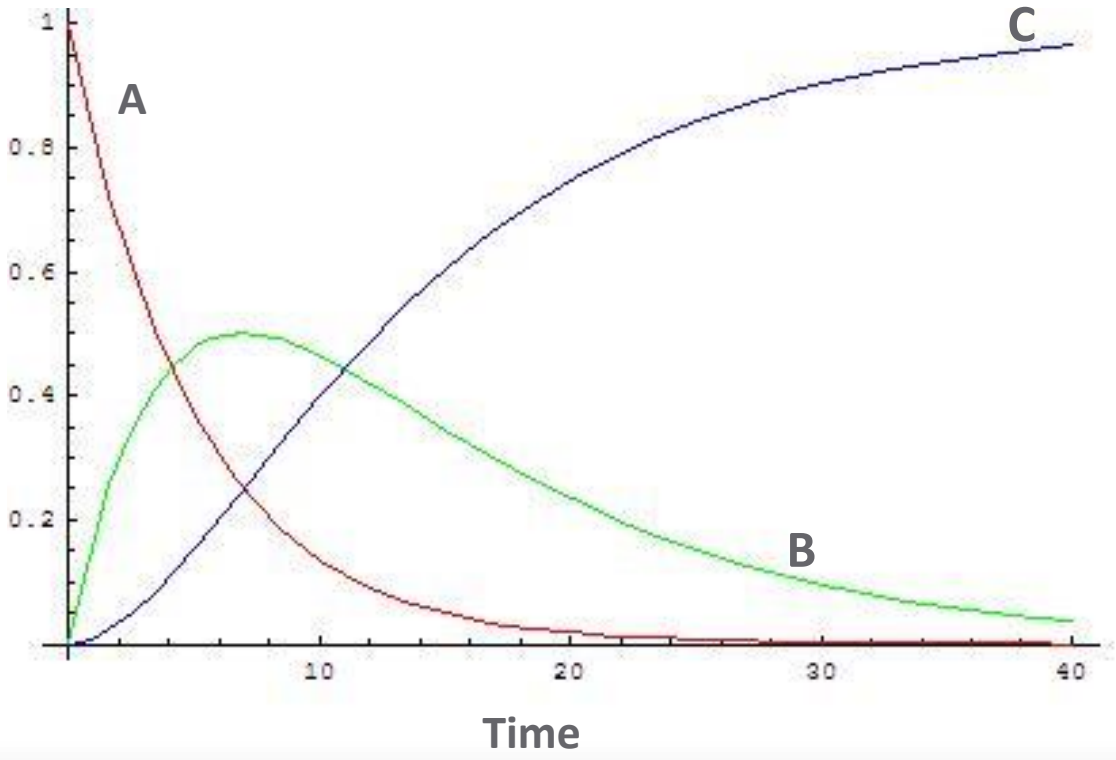
Consecutive Reaction

- Consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_1} C$$



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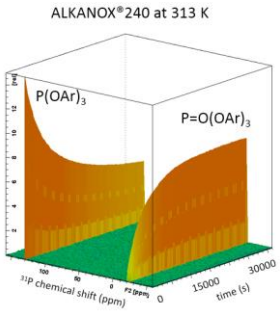
Reaction Monitoring by ^{31}P NMR

- Bruker AVANCE III 400 MHz spectrometer.
- 1D ^{31}P spectrum acquired every 300 s (5 mins). Total experiment time between 2 – 8 hours.
- Concentrations of phosphite(s) and tBuOOH were chosen to provide suitable reaction rates.



Phosphites investigated:

ALKANOX®240

ULTRANOX®626

- Reacted with tBuOOH in $CDCl_3$ at a range of temperatures between 25 and 40 ˚C
- Reaction monitored by ^{31}P NMR, with care taken to provide quantitative results (“qNMR”)
- Peak areas were converted to concentrations using measured masses and volumes added to reaction mixture.

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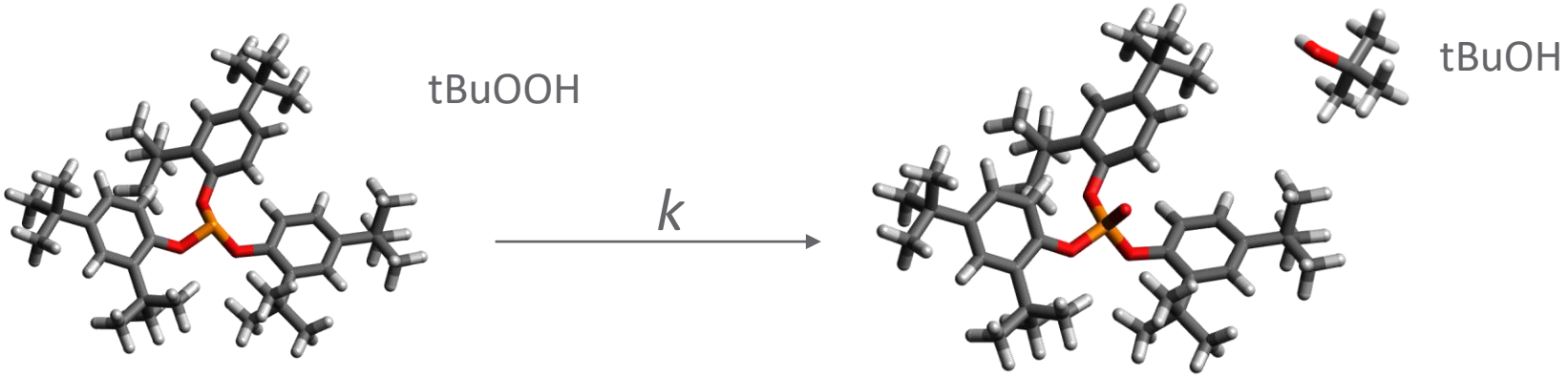
ALKANOX® 240 Oxidation: Model Study

- Second order elementary bimolecular reaction
- *rate* = *k*[P][tBuOOH]



ALKANOX®240 → **ALKANOX®240 phosphate**

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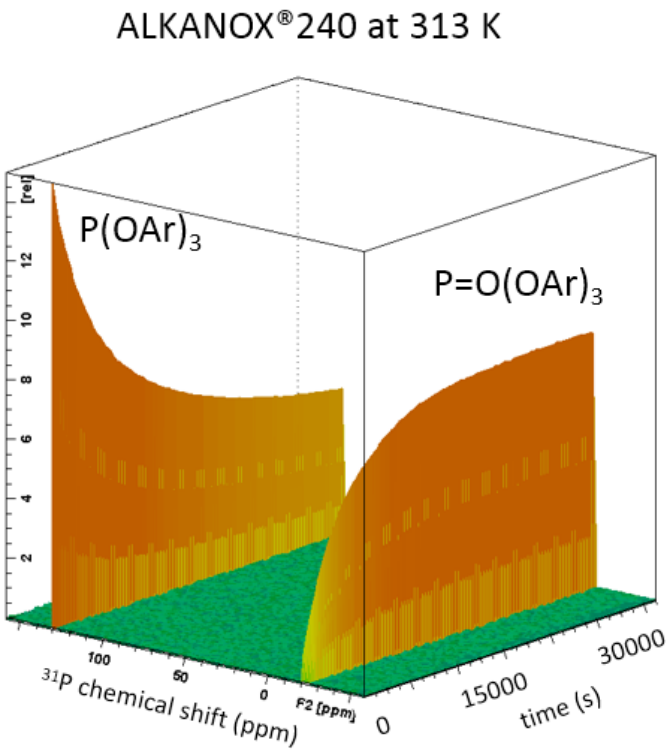
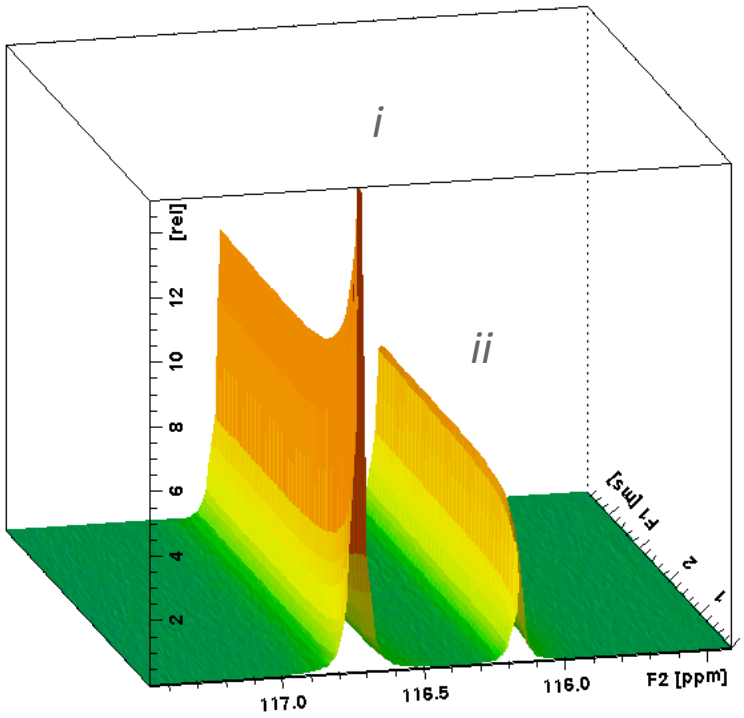
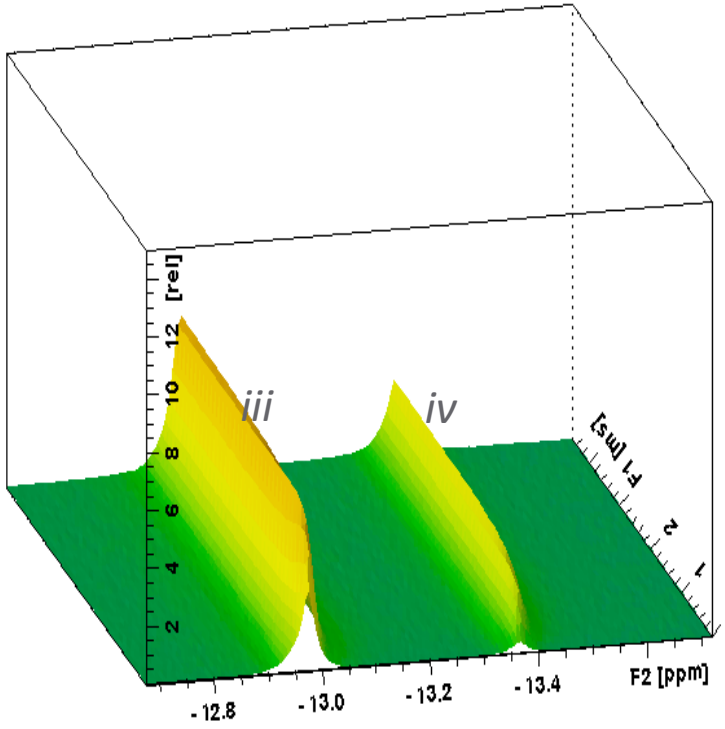
ALKANOX® 240 AT 313 K

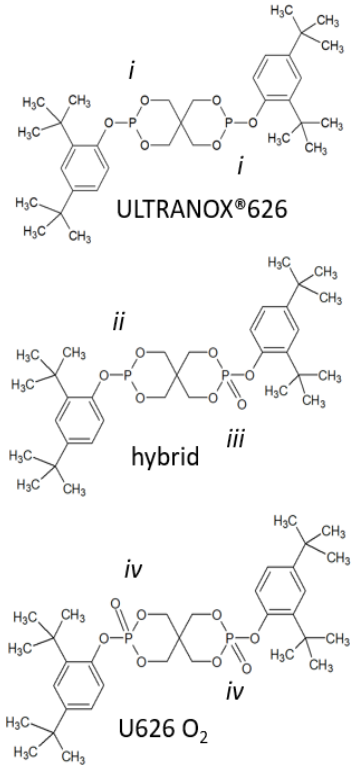


k = 3.64 x10^{-3} L mol^{-1} s^{-1}

ULTRANOX®626 AT 313 K







k_1 = 29.4 x 10^{-3} L mol^{-1} s^{-1}

k_2 = 11.8 x 10^{-3} L mol^{-1} s^{-1}

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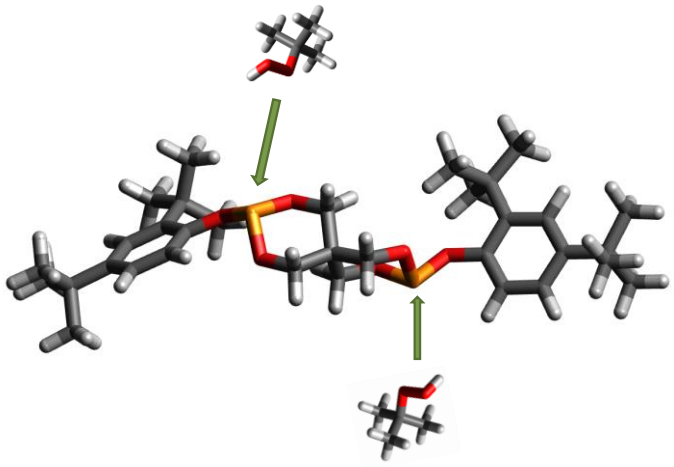
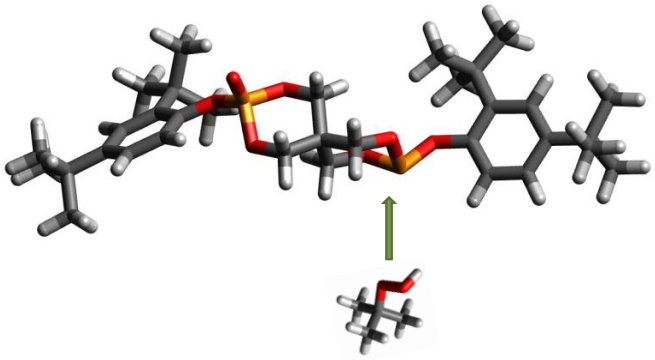
DISCUSSION: U626 k_1 vs k_2 reactivity



ULTRANOX® 626 k_1



ULTRANOX® 626 k_2

k at 313 K	29.4	11.8

units 10^{-3} L mol^{-1} s^{-1}

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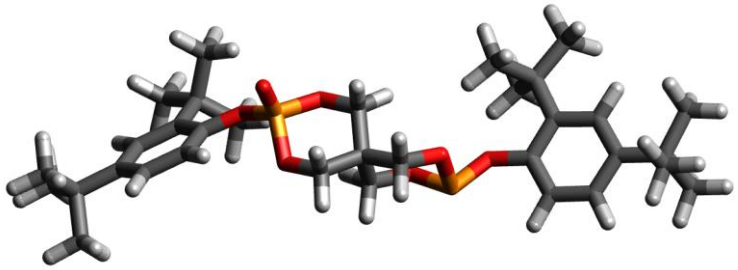
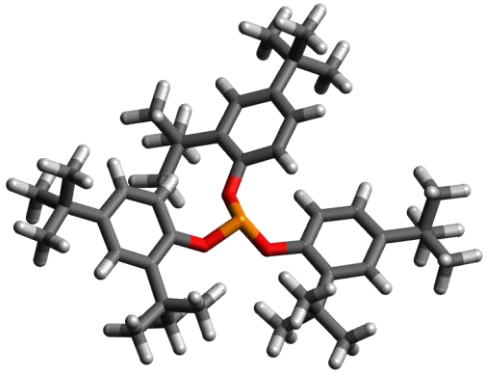
DISCUSSION: Triaryl vs Aryl-Alkyl





	ULTRANOX® 626 k_1	ULTRANOX® 626 k_2	ALKANOX®240
k at 313 K	29.4	11.8	3.6

units 10^{-3} L mol^{-1} s^{-1}

- Reactivity order is:
  U626 k_1 > U626 k_2 > A240

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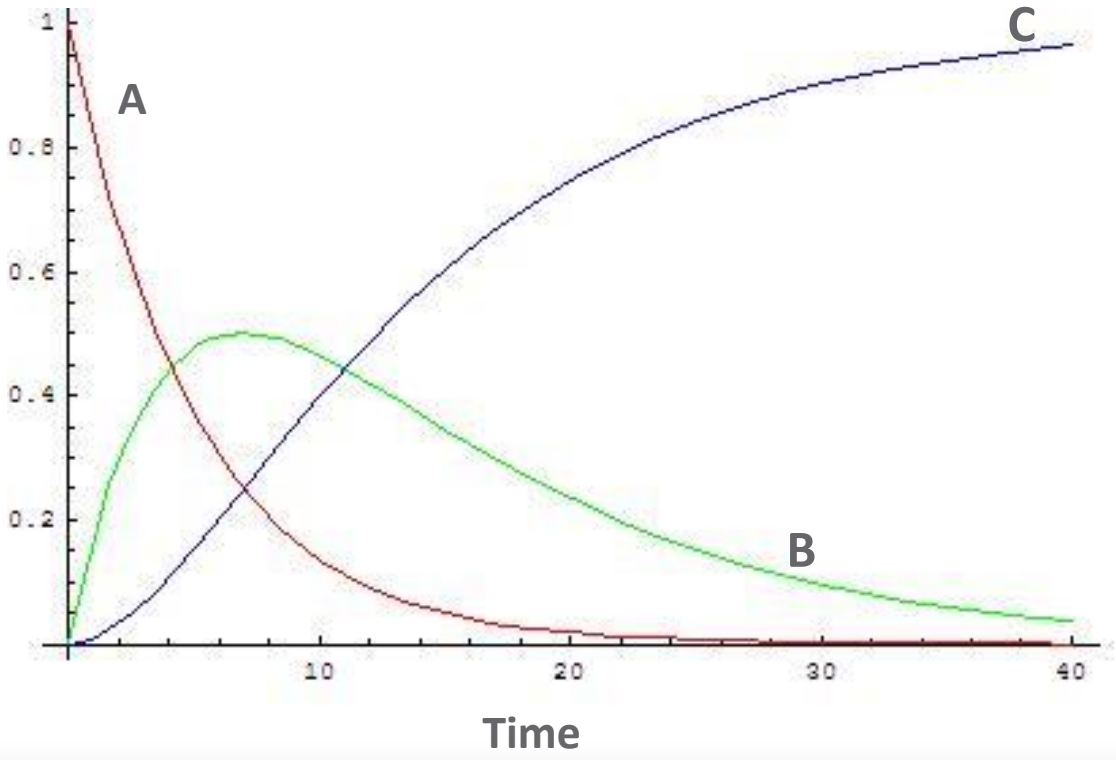
ULTRANOX® 626: High Performance Phosphite

PP Homopolymer Multipass Extrusion @ 260C

Consecutive Reaction

- Consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_1} C$$



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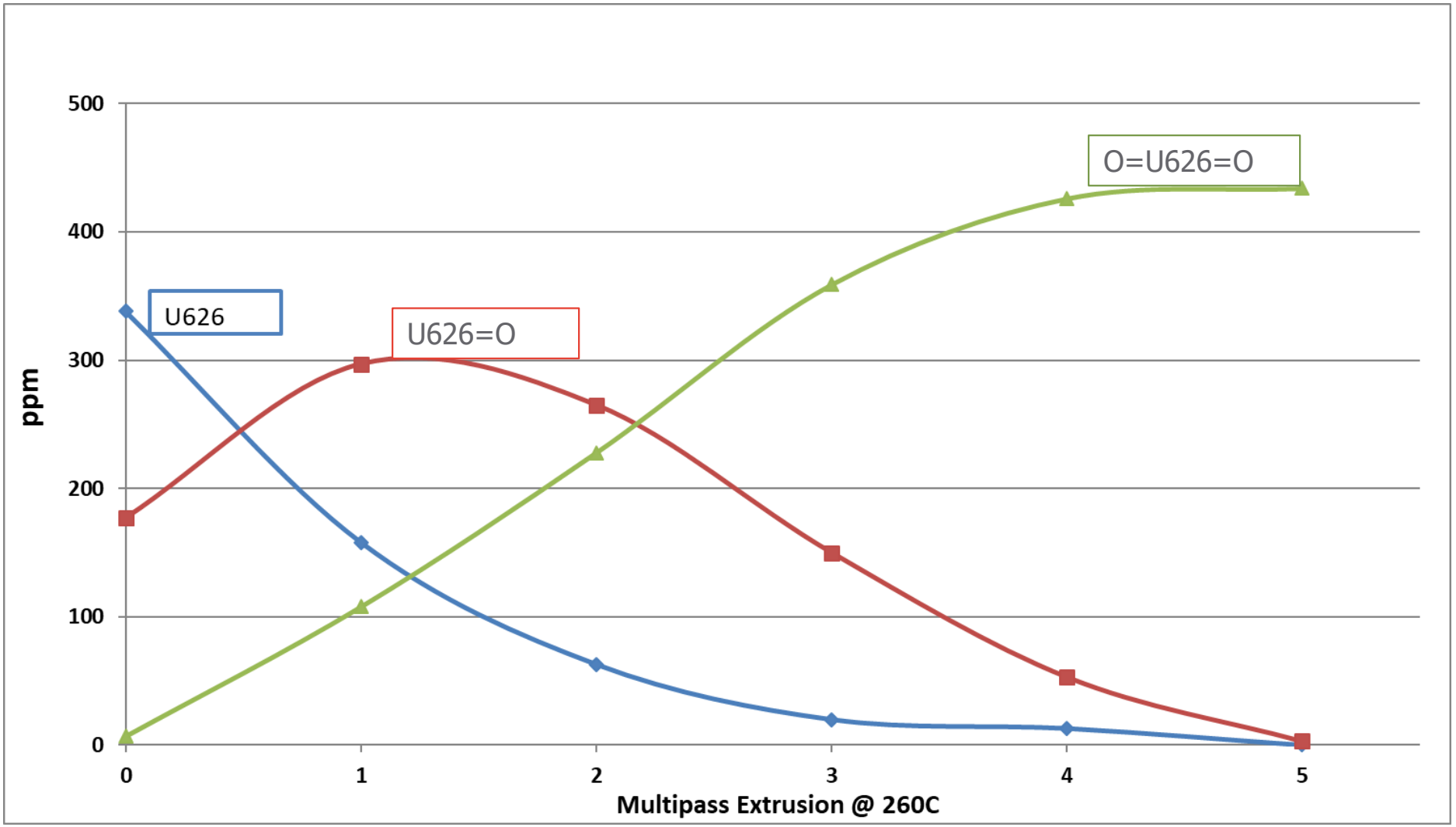
ULTRANOX® 626: PP Multipass Extrusion



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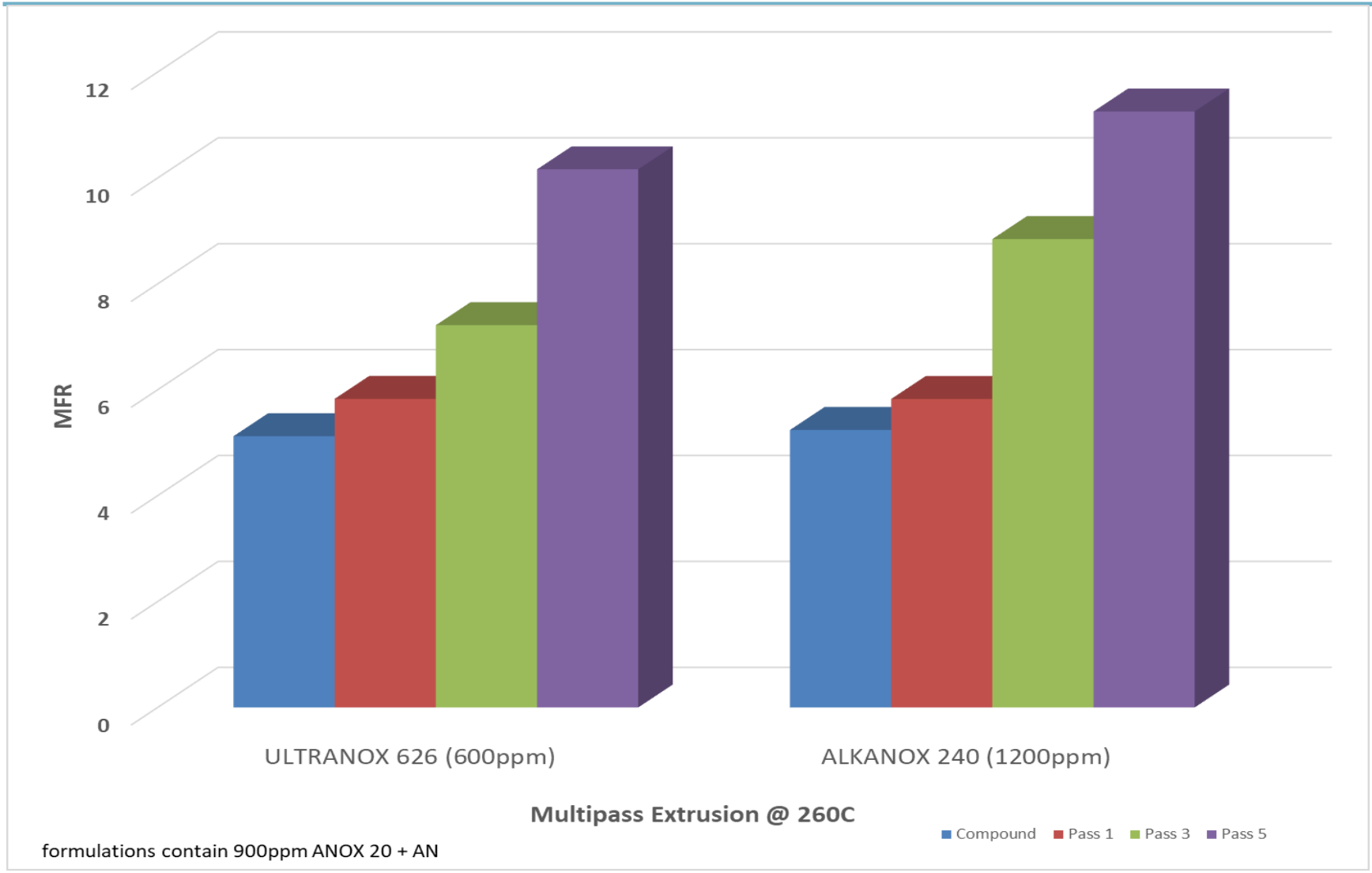
MFR Comparison: PP Multipass Extrusion



formulations contain 900ppm ANOX 20 + AN

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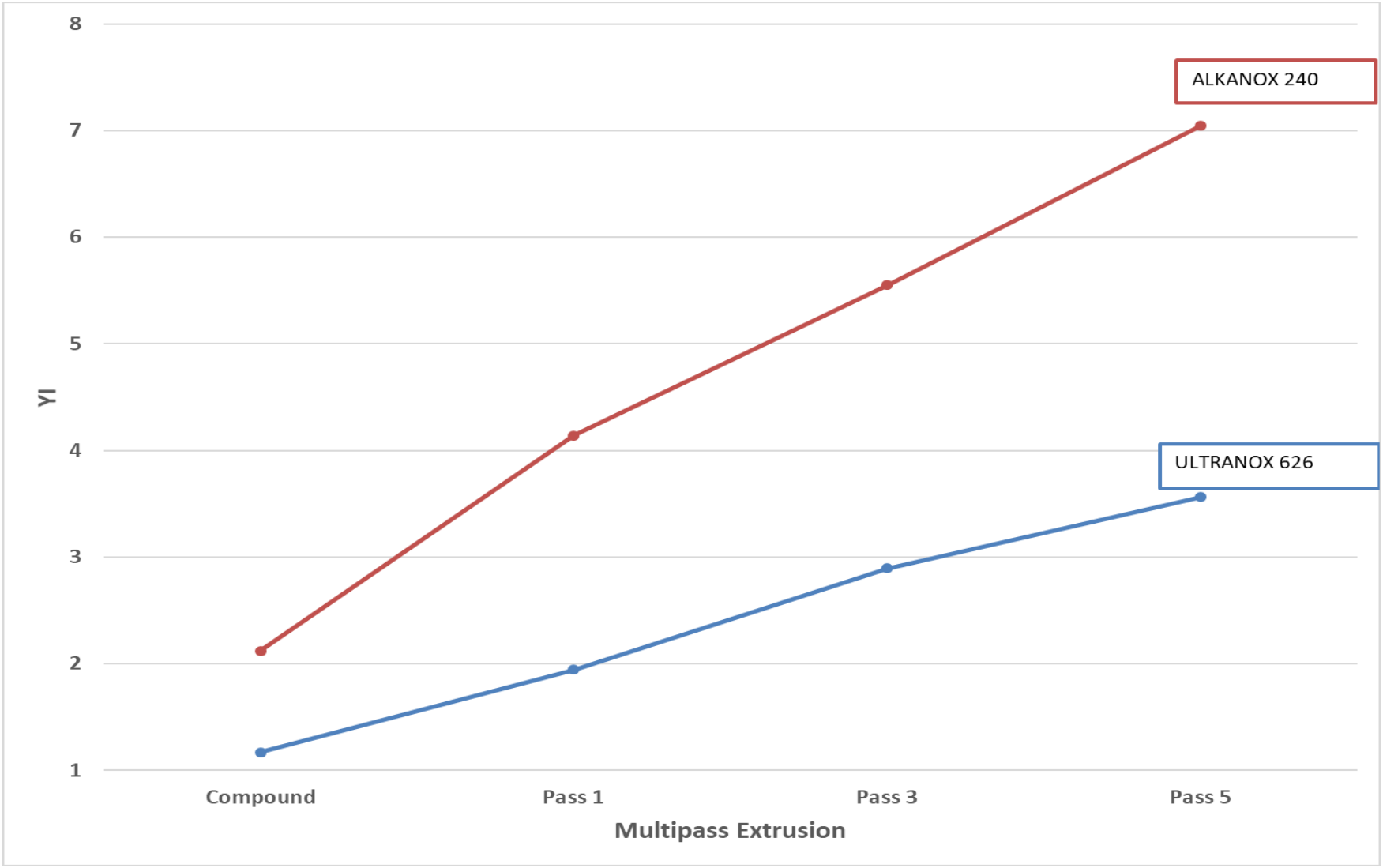
YI Comparison: PP Multipass Extrusion



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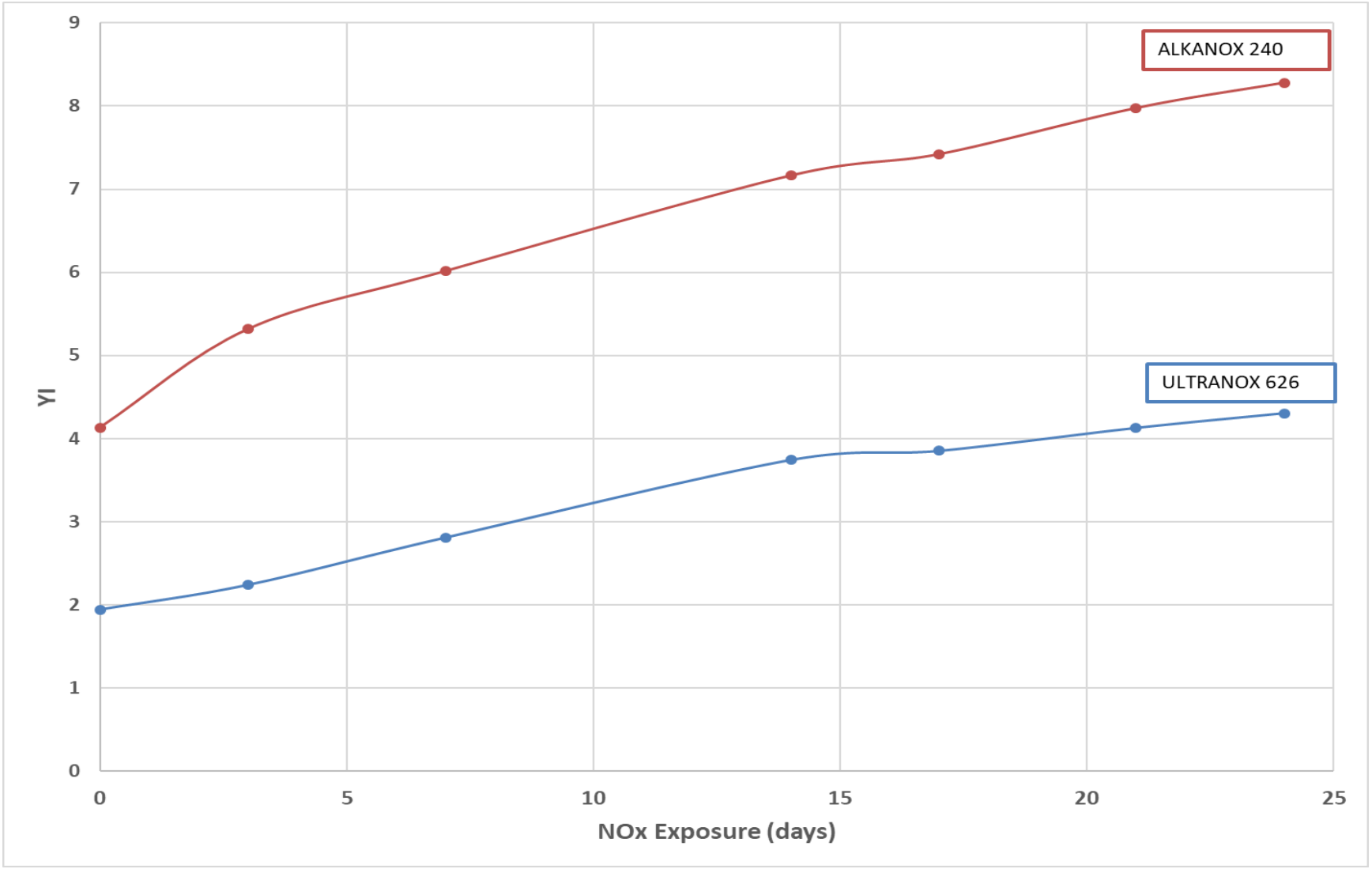
YI Comparison: Gas-Fading



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Summary & Conclusions

ULTRANOX® 626:

- High active phosphorous content
- Reacts 8X faster than ALKANOX® 240 at 313K
- Superior in-polymer performance compared with ALKANOX® 240 (AO-168 type phosphite) at half loading.
- Blends with other additives to create NDB with enhanced HR
- QC methods to quantify Phosphite/Phosphate in polymer
- Global supply network

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THANK YOU!!

SI Group®

The Substance Inside