PHOSPHITE ANTIOXIDANT KINETICS: MODEL STUDIES PART 1

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Addivant Global Technology

CONTENT

- Polymer degradation and stabilization
- Phosphite model study
- Polyethylene stabilization requirements (CTQ's)
- Technology innovation WESTON® 705 for polyethylene film
- Summary & Conclusions

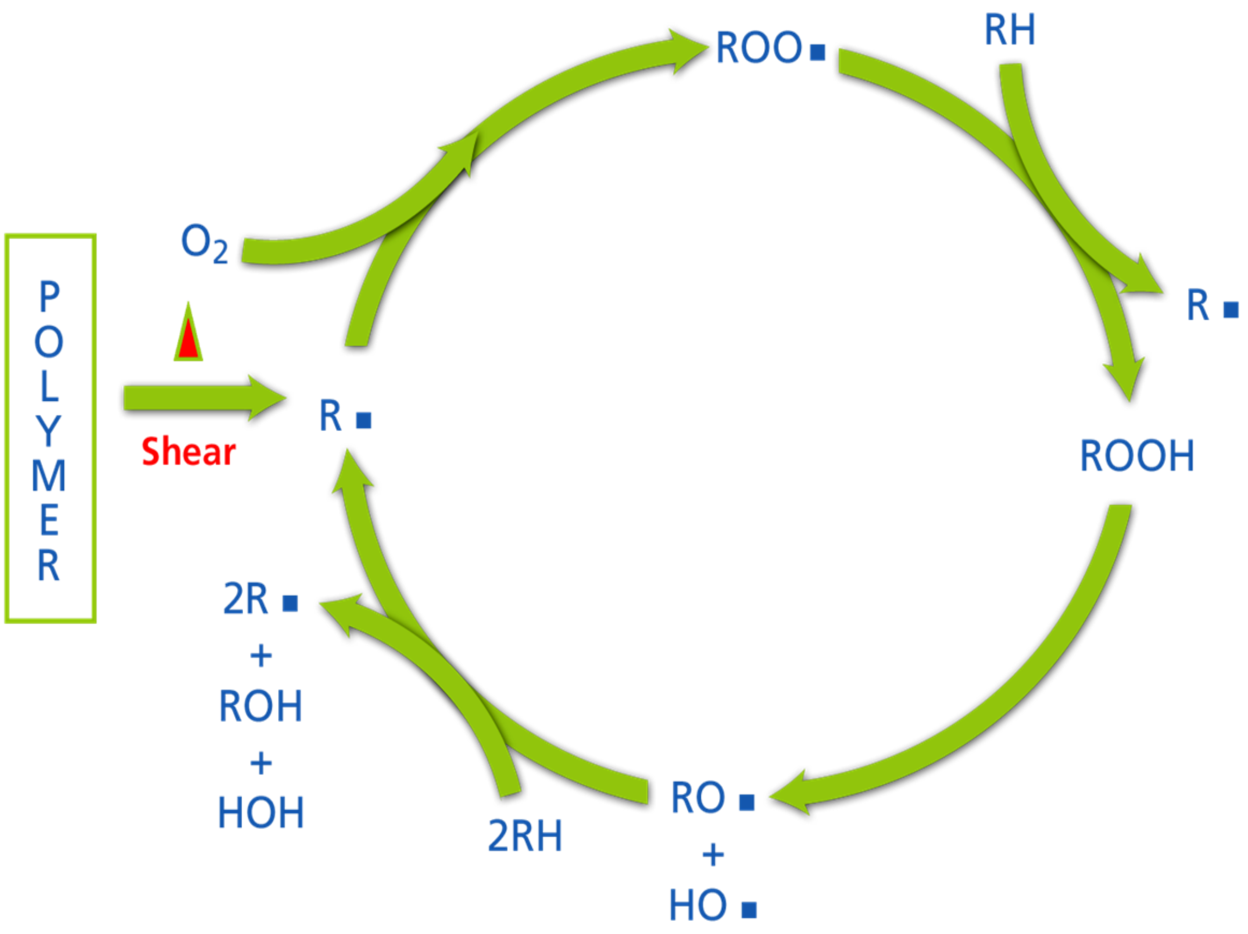
KEY FACTS

- **World's largest provider of**
  - Powder-free solutions
  - Liquid phosphites
  - Specialty antioxidants
- **Regional technical centres**
  - Morgantown (USA)
  - Trafford Park (UK)
  - Al-Jubail, GSI (KSA)
  - Waldkraiburg (Germany)
- **Commitment for innovation, global manufacture and supply**
- **Significant investment in regulatory compliance and new production capacities**

COMMITMENT FOR INNOVATION, GLOBAL MANUFACTURE and SUPPLY

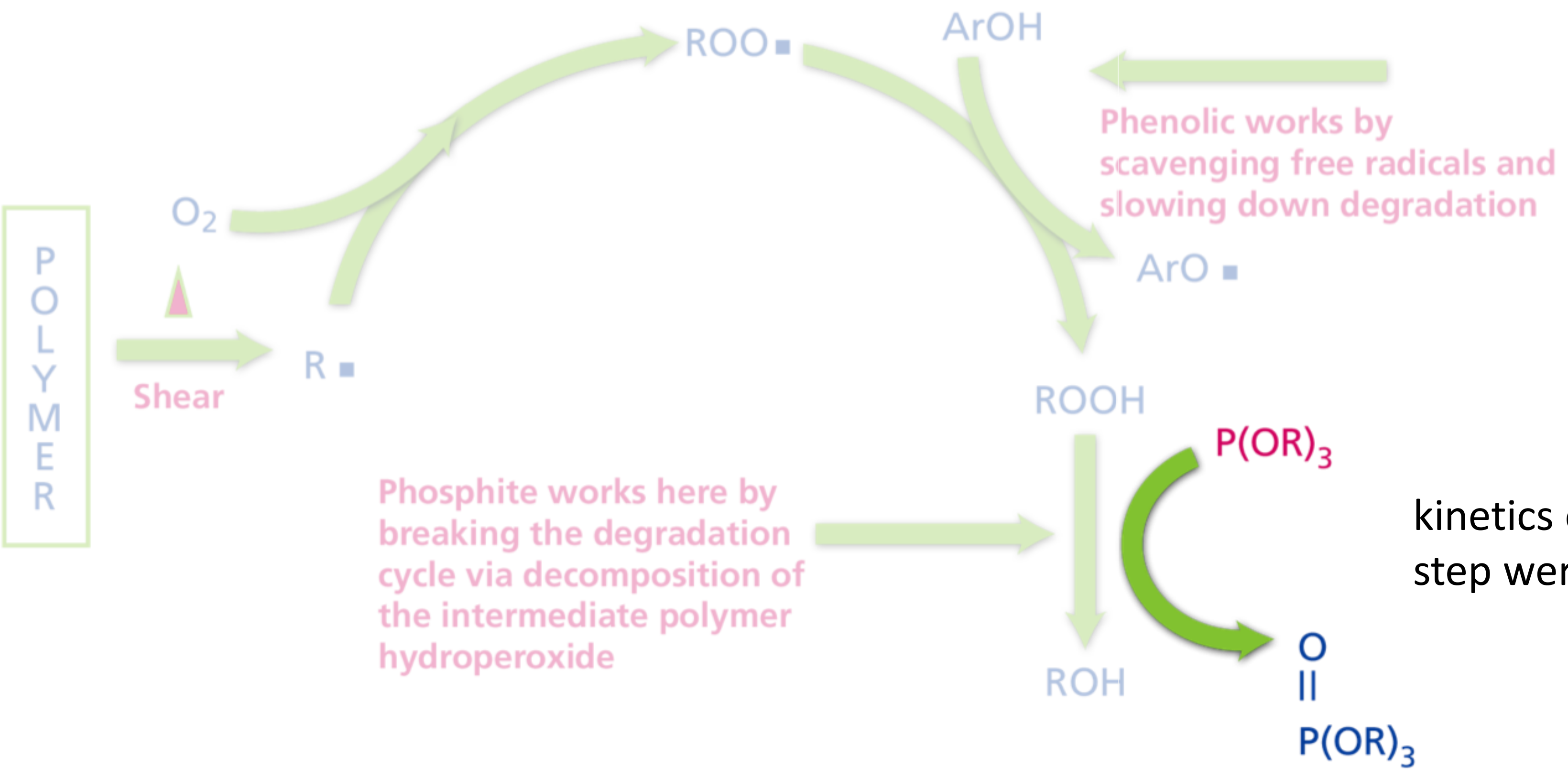
POLYMER DEGRADATION & STABILIZATION

POLYMER AUTO-OXIDATION CYCLE



ANTIOXIDANTS REQUIRED FOR POLYMER STABILIZATION

PRIMARY AND SECONDARY ANTIOXIDANT



kinetics of this step were studied

PHOSPHITES MOST EFFECTIVE SECONDARY ANTIOXIDANTS

FACTORS AFFECTING PHOSPHITE PERFORMANCE

- **% Phosphorus**
- **Chemical structure**
  - Tris Hindered Aryl
  - Tris Alkyl
  - Mixed Alkyl Hindered Aryl
- **Stabilizer hydrolytic stability**
- **Inherent thermal stability**
- **Melting point**
- **Formulation/loading level**
  - Stabilizer solubility
- **Resin type**

ALL FACTORS NEED TO BE CONSIDERED

NEXT GENERATION LIQUID PHOSPHITE FOR POLYETHYLENE STABILIZATION

MODEL STUDIES

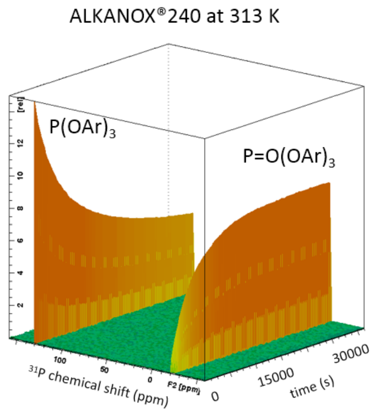
KINETICS STUDY OVERVIEW

- **Phosphites investigated:**
  - ALKANOX®240
  - WESTON®705
- **Reacted with tBuOOH in $CDCl_3$ at a range of temperatures between 25 and 40 ˚C**
  - tBuOOH is a model peroxide that was selected as it reacts with phosphites at optimal rates for measurement. Not too fast and not too slow.
- **Reaction monitored by ^{31}P NMR, with care taken to provide quantitative results ("qNMR")**

PHOSPHITE OXIDATION REACTIONS MONITORED IN SOLUTION BY NMR

REACTION MONITORING BY ^{31}P NMR

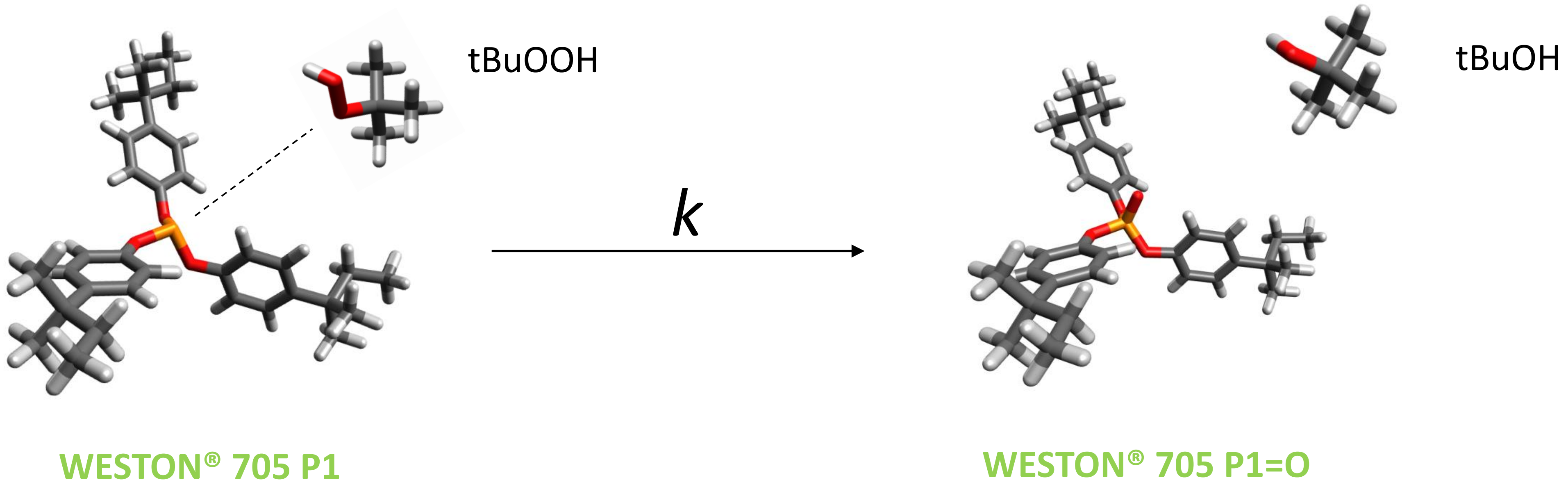
- Bruker AVANCE III 400 MHz spectrometer.
- 1D ^{31}P spectrum acquired every 300 s (5 mins). Total experiment time between 2 – 8 hours.
- Concentrations of phosphite(s) and tBuOOH were chosen to provide suitable reaction rates.
- Care was taken to achieve quantitative measurements: *Cr(III) relaxation agent used to ensure full relaxation of all P nuclei.*
- Peak areas were converted to concentrations using measured masses and volumes added to reaction mixture.



NMR USED TO MONITOR CONCENTRATIONS OVER TIME

PHOSPHITE OXIDATION REACTION MECHANISM

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



PHOSPHITES REACT WITH PEROXIDES: BIMOLECULAR REACTION MECHANISM

ALKANOX® 240: RATE CONSTANT MEASUREMENT

Calculate *k* using:

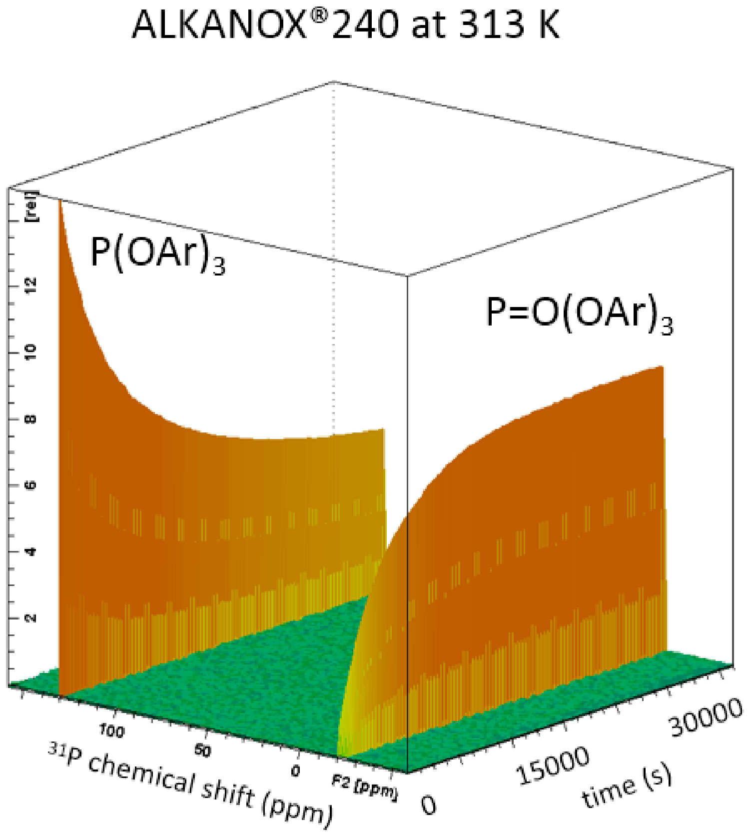
$$\ln\left(\frac{[\mathrm{tBuOOH}]\,[\mathrm{P}]_o}{[\mathrm{P}][\mathrm{tBuOOH}]_o}\right) = ([\mathrm{tBuOOH}]_o - [\mathrm{P}]_o)kt$$

rearranged to give:

$$k = \ln\left(\frac{[\mathrm{tBuOOH}]\,[\mathrm{P}]_o}{[\mathrm{P}][\mathrm{tBuOOH}]_o}\right) * \frac{1}{([\mathrm{tBuOOH}]_o - [\mathrm{P}]_o)t}$$

MEASURE K BY FITTING EXPERIMENTAL DATA TO SECOND ORDER INTEGRATED RATE LAW

EXAMPLE RESULTS : ALKANOX® 240 AT 313 K



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

$[P]_o$ = 61.53 mM
$[tBuOOH]_o$ = 40.17 mM

TYPICAL DATA

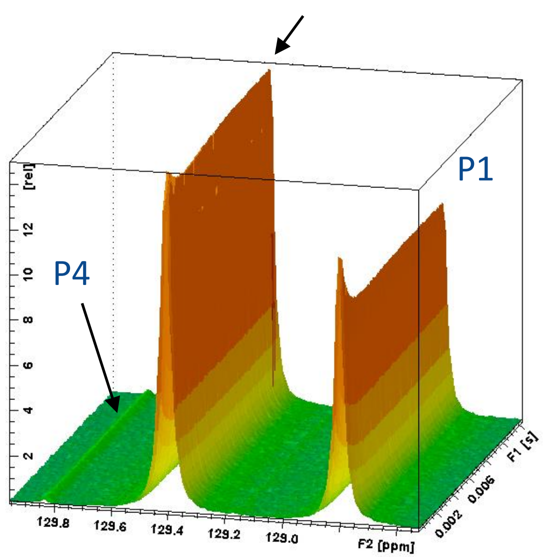
WESTON® 705: RATE CONSTANTS

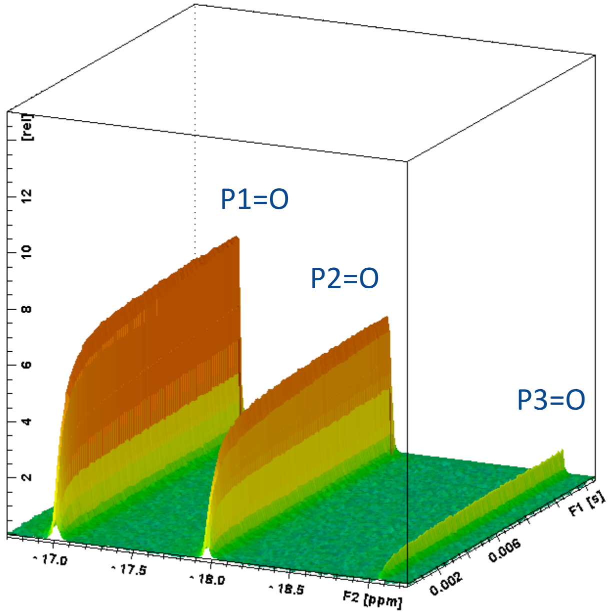
- Measure k_1 *and* k_4 values for pure P1 and P4 using the method described for ALKANOX®240.
- React WESTON®705 with tBuOOH, measuring P1 –P3 phosphite concentrations over time.
- Obtain k_2 and k_3 from k_1 via:
-

$$\ln \frac{[P2]}{[P2]_0} = \frac{k_2}{k_1} * \ln \frac{[P1]}{[P1]_0} \quad ; \quad \ln \frac{[P3]}{[P3]_0} = \frac{k_3}{k_1} * \ln \frac{[P1]}{[P1]_0}$$

CALCULATE RATE CONSTANTS OF WESTON® 705 P2/P3 INDIRECTLY

EXAMPLE RESULTS : WESTON® 705 AT 298 K





phosphite concentrations decrease

phosphate concentrations increase

$k_1 = 5.047 \times 10^{-3}$, $k_2 = 3.673 \times 10^{-3}$, $k3 = 1.799 \times 10^{-3}$, $k_4 = 1.365 \times 10^{-3}$ L mol^{-1} s^{-1}

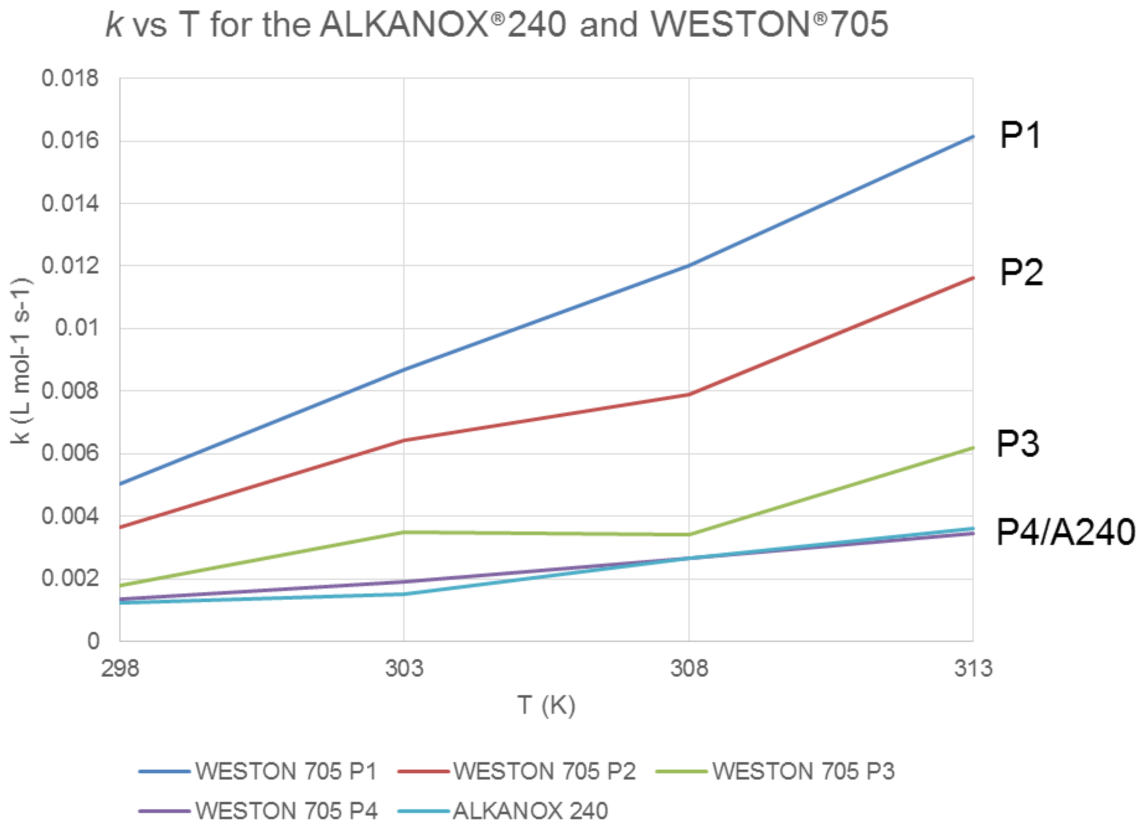
WESTON® 705 PHOSPHITES: SECOND ORDER REACTIONS

RESULTS: MEASURED RATE CONSTANTS

- Reactivity order is:
  P1 > P2 > P3 > P4 ≈ A240
- ALKANOX® 240 has similar reactivity to P4, the least reactive component of WESTON®705
- Rate constants at 313 K:

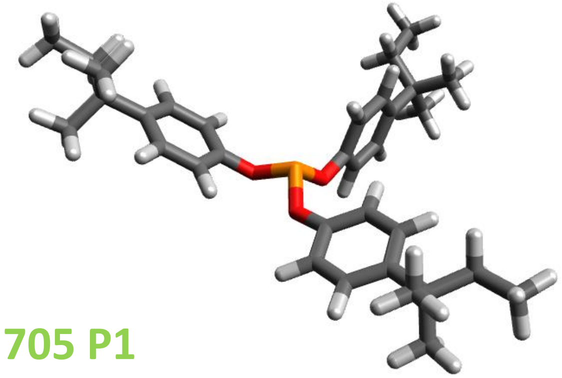
	P1	P2	P3	P4	A240
k	16.2	11.6	6.2	3.5	3.6

units of *k* are 10^{-3} L mol^{-1} s^{-1}

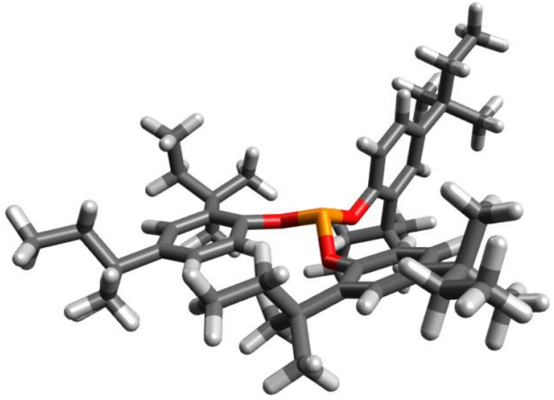


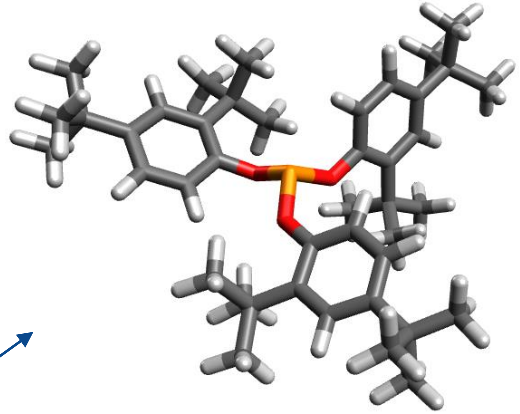
WESTON® 705 P1 REACTS >4X FASTER THAN ALKANOX® 240 AT 313 K

DISCUSSION: STERIC HINDRANCE AND REACTIVITY



WESTON® 705 P1
has least steric
hindrance around P





similar steric hindrance

	P1 of WESTON® 705	P4 of WESTON® 705	ALKANOX® 240
k at 303 K	16.2	3.5	3.6

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

PHOSPHITE REACTIVITY IS DETERMINED BY AVAILABILITY OF CENTRAL P ATOM

addivant™
SOLUTIONS TO BREAKTHROUGH

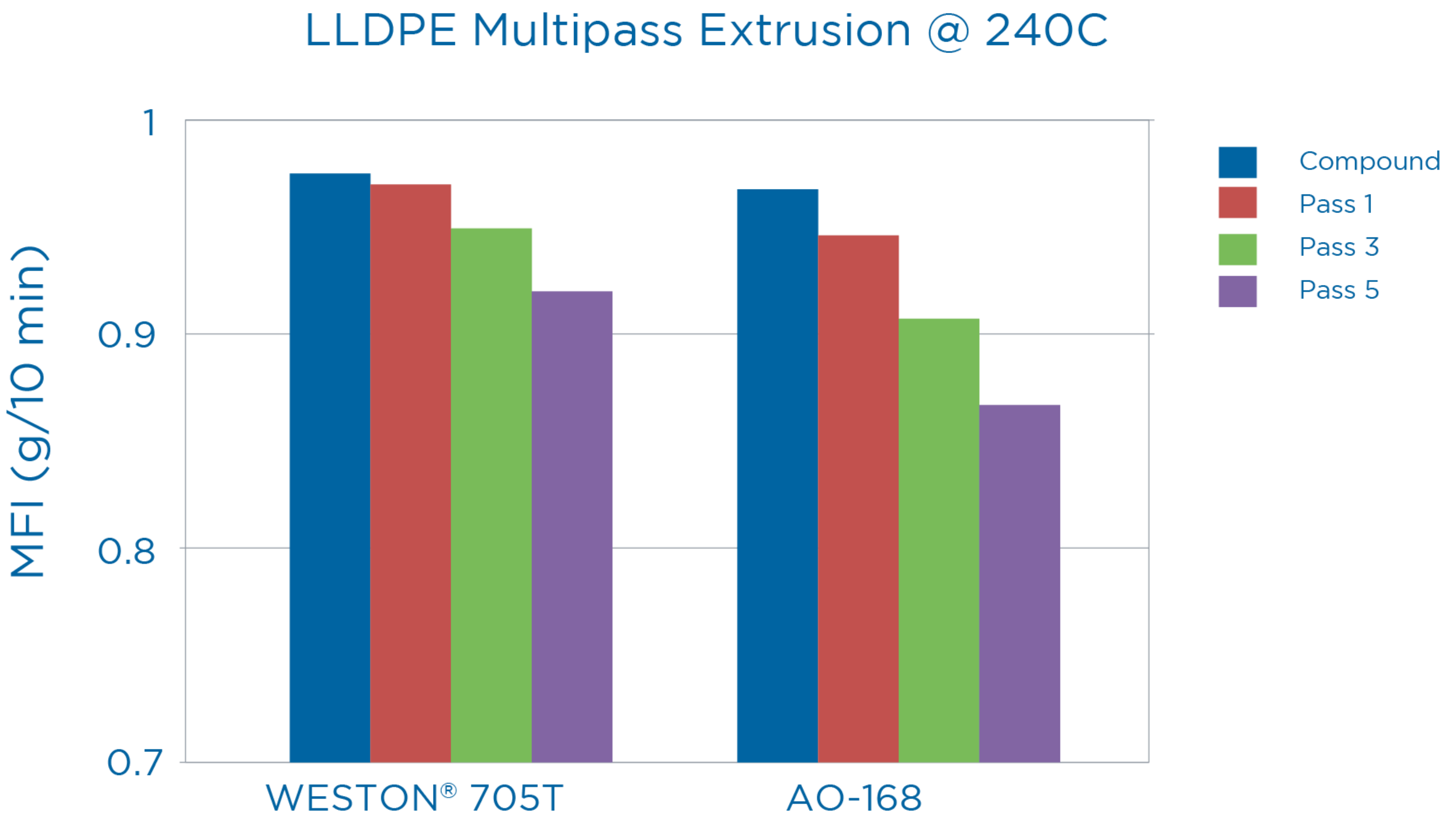
TECHNOLOGY INNOVATION:
WESTON® 705 NEXT GENERATION LIQUID PHOSPHITE FOR POLYETHYLENE FILM

POLYETHYLENE STABILIZATION CTQ'S

- Processing stability
- Low gel formation
- No black specks
- Resistance to gas fading (NOx pollutants)
- Excellent optical properties
- No discoloration
- No plate-out or blooming of additives
- Good surface properties, sealability, printability
- Good organoleptics
- Global food contact approvals

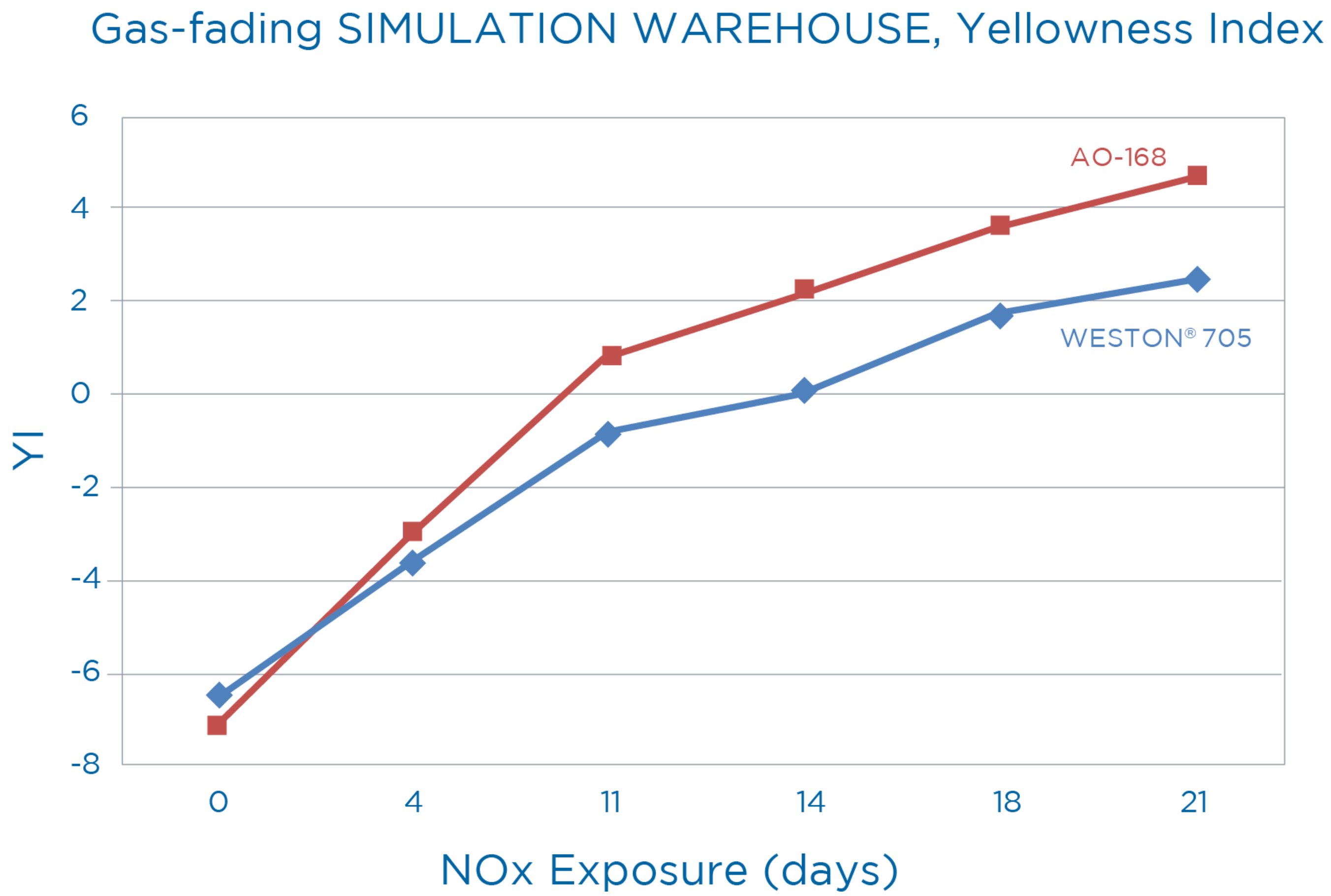
WESTON® 705: HIGH PERFORMANCE LIQUID PHOSPHITE

MFI COMPARISON AT EQUAL PHOSPHORUS



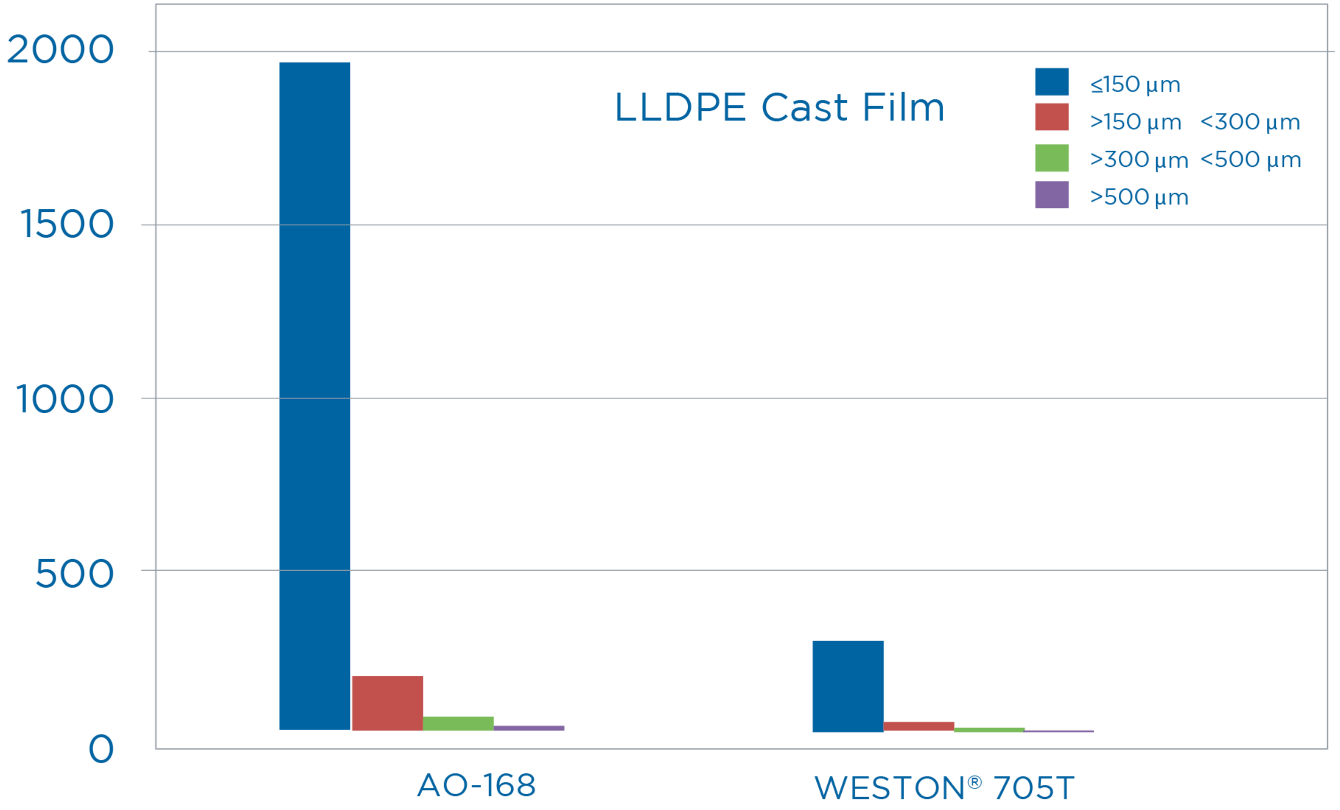
WESTON® 705 EXHIBITS EXCELLENT MFI RETENTION

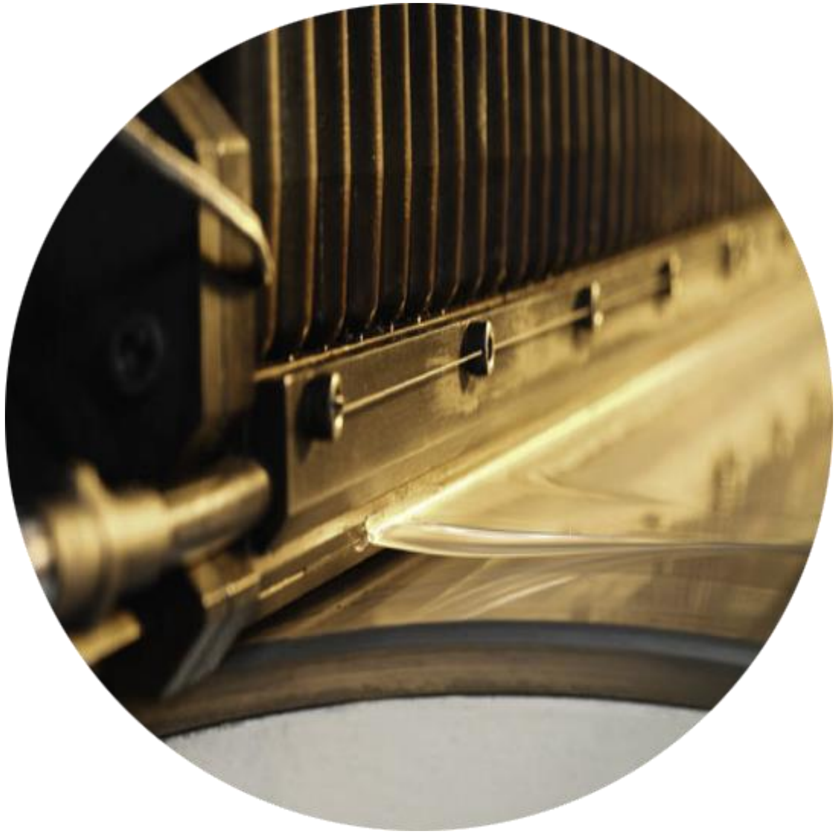
IMPROVED COLOR RETENTION DURING STORAGE



WESTON® 705 EXHIBITS SUPERIOR COLOR RETENTION

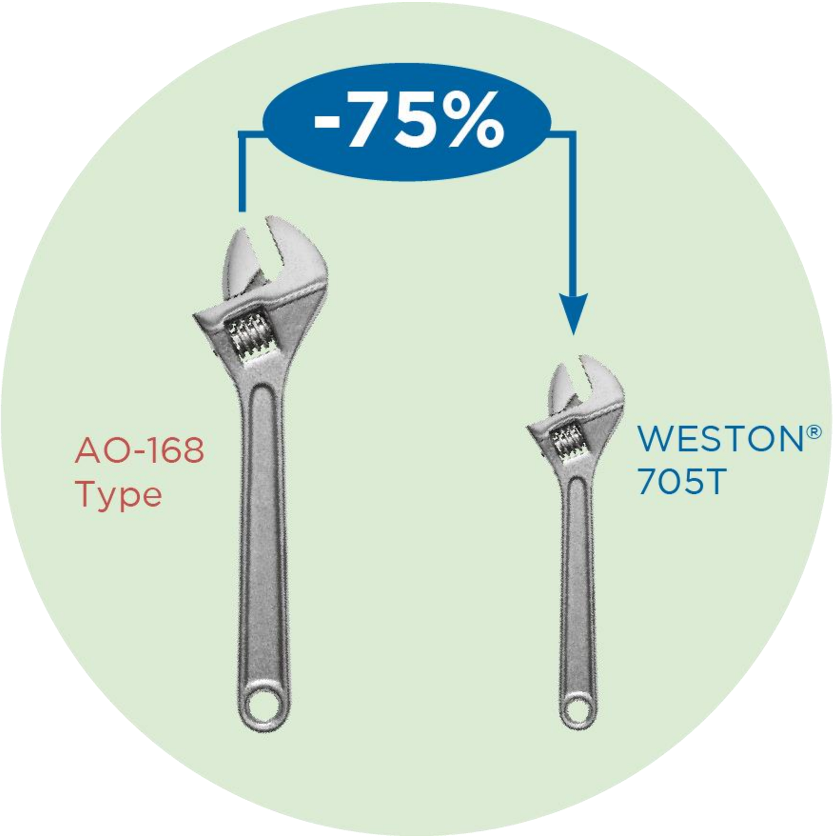
REDUCED GEL FORMATION IN LLDPE





WESTON® 705: LESS GEL FORMATION

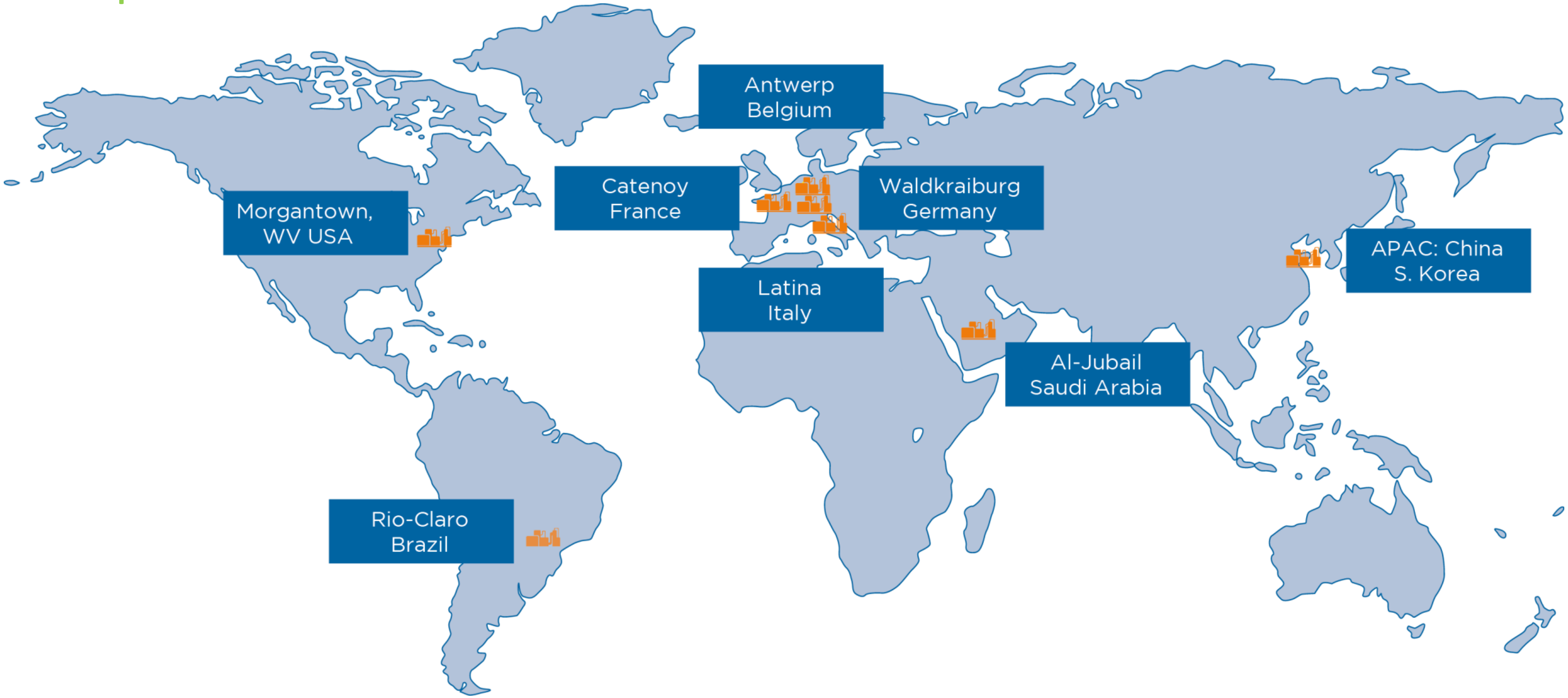
WESTON® 705: REDUCED PLATE OUT



WESTON® 705 PROVIDES HIGHER PRODUCTIVITY: LESS DOWN-TIME

SUPPLY SECURITY

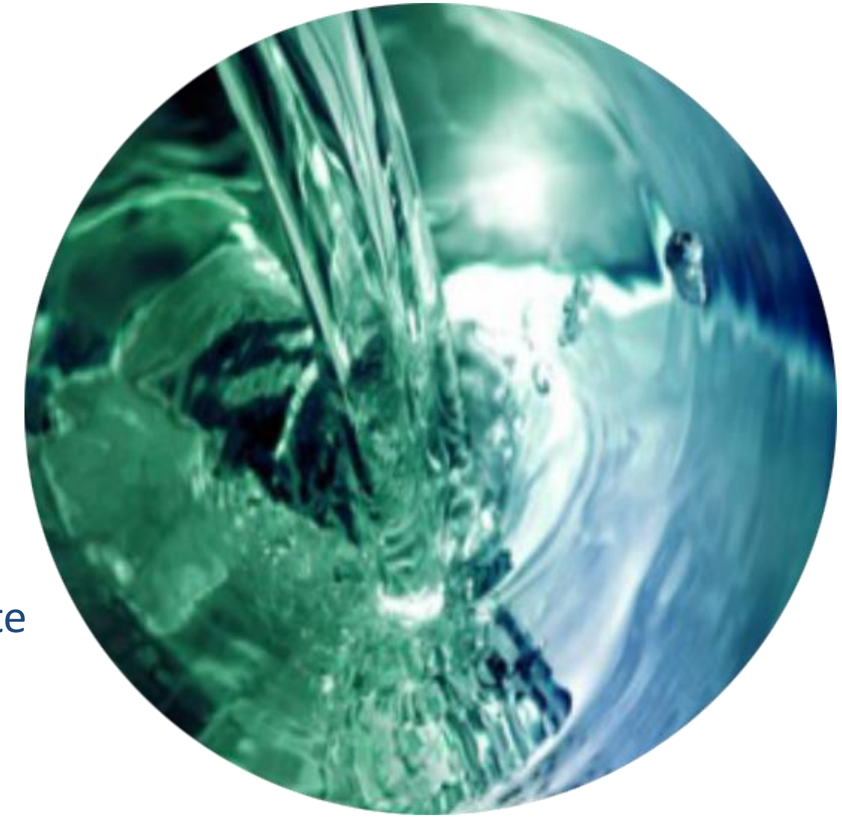
Liquid and powder-free blend solutions



GLOBAL MANUFACTURING TO MEET THE NEEDS OF THE GLOBAL POLYOLEFIN INDUSTRY

SUMMARY & CONCLUSIONS

1. Weston® 705: high active phosphorus content
2. Containing well balanced fast & slow active components
3. Completely nonylphenol free
4. Wide global registrations and food contact approvals
5. Able to blend with other additives to create single dose liquid system
6. Synergistic performance when blended with other antioxidants
7. Higher in-polymer solubility compared to solid AO168 type
8. Superior in-polymer performance compared with AO 168 type phosphite
9. QC methods to quantify WESTON® 705 in polymer
10. Global supply network



WESTON® 705: HIGH PERFORMANCE LIQUID PHOSPHITE

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For your
success