



# Recent Aspects of Polypropylene and Polyethylene Stabilization

February 27, 2017

---

Jungdu(Jack) Kim, Thomas Schmutz,  
Heejung Kwon & Klaus Keck

It's all about **the chemistry**



# Table of content

## Background & introduction

### Polyethylene

- General purpose processing stabilization of LLDPE film grades
- New requirements
- Improved processing stabilization of LLDPE film grades

### Polypropylene

- General purpose thermal stabilization of PP injection molding grades
- New requirements
- Improved thermal stabilization of PP injection molding grades

### Conclusions

## Background & introduction

It's all about **the chemistry**



# Background

## Background

- Polyolefins are intrinsically unstable to survive melt conversion w/o damage to the molecular architecture.
- For the same reasons, polyolefins are intrinsically not suitable for durable applications.
- Hence, polyolefins need to be protected against thermo-oxidative degradation.
- Chemicals added for this purpose are termed ... stabilizers or antioxidants.
- Since the mid 70s, the basic stabilization strategies for anti-oxidative protection of polyolefins were derived from polypropylene and extended into polyethylene.

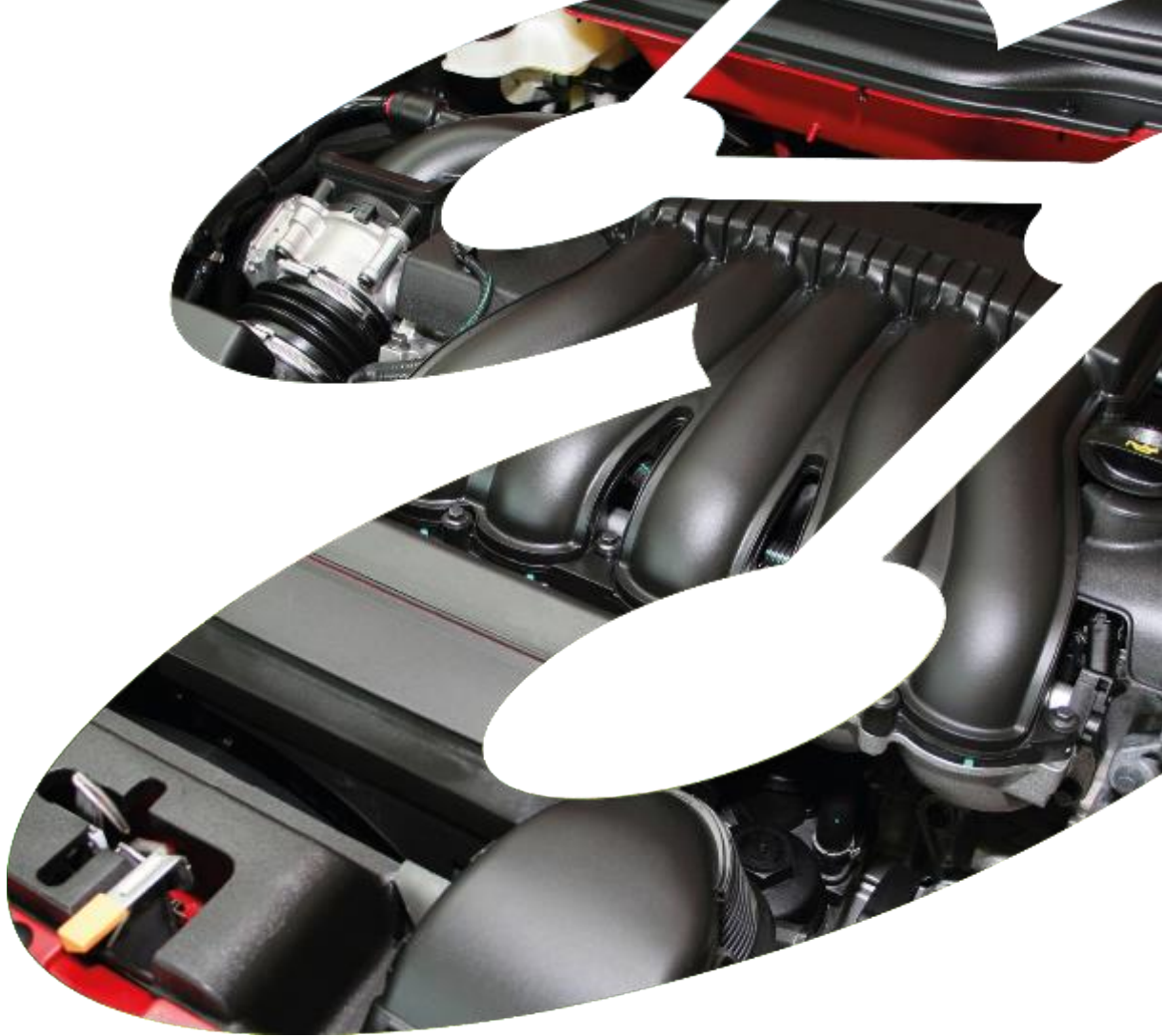
# Introduction

## Introduction

- This contribution reviews those basic stabilization strategies ... including their limitations.
- In select examples, high-end stabilization strategies for polyethylene and polypropylene are introduced to overcome above limitations.

## Polyethylene

- General purpose processing stabilization of LLDPE film grades
- New requirements
- Improved processing stabilization of LLDPE film grades



It's all about **the chemistry**



# Processing stabilization of polyolefins

## ... For Polyethylene

- Stabilization strategy for polypropylene extended into polyethylene Combination of [hindered phenol + phosphite] ... “B-Blend”
- Lower LTTS contribution of hindered phenol required due to lower LTTS (test) temperature and lower melting behavior
- Lower LTTS requirements (in non-durable applications ... e.g. packaging film)

### [hindered phenol + phosphite]

SONGNOX® 1010

or

SONGNOX® 1076

Moderate “thermal” stabilizer  
Reasonable balance between  
contribution to LTTS and  
processing

SONGNOX® 1680

or

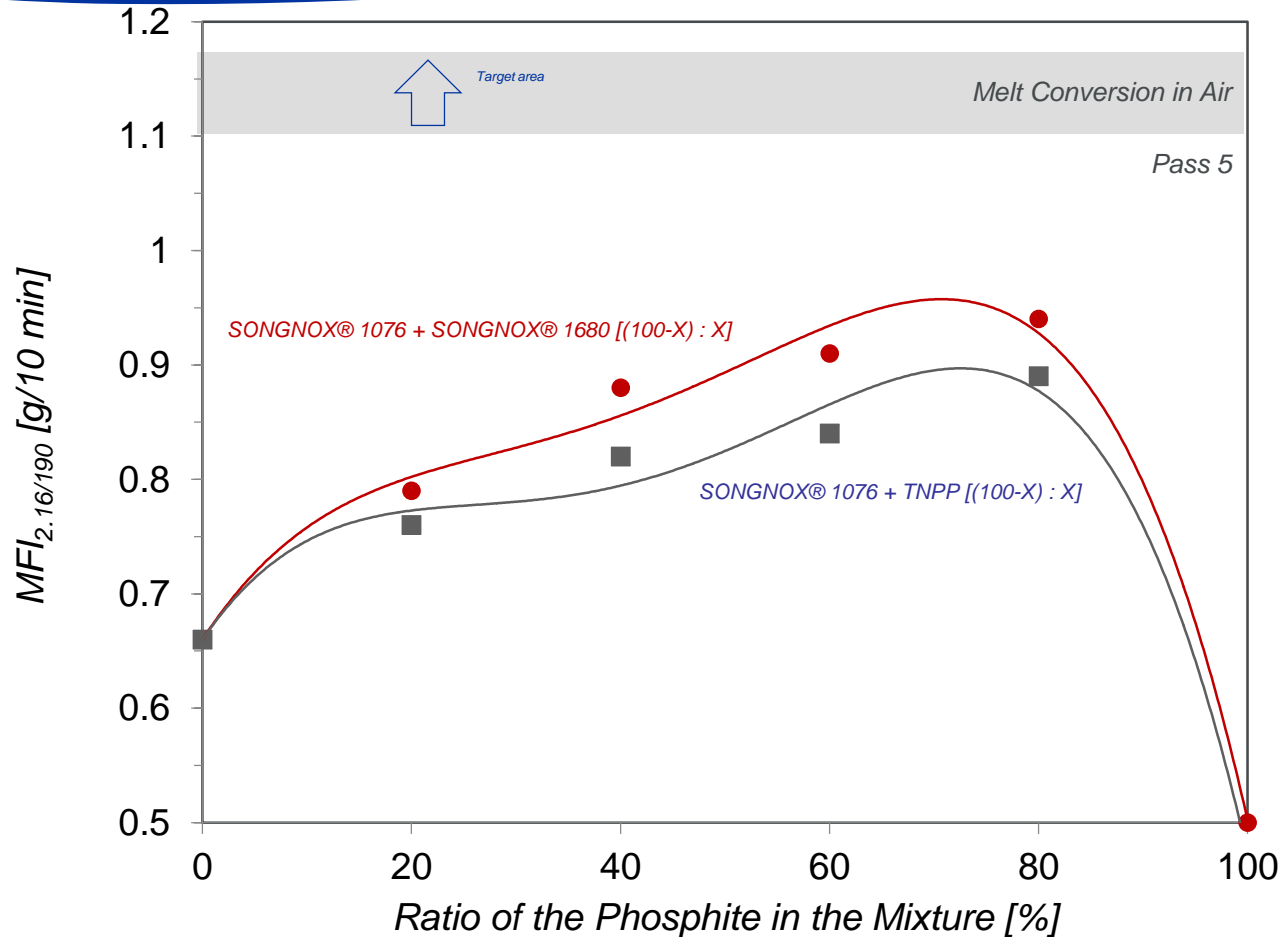
“TNPP” (liquid)

or

P-17 (liquid; recent introduction)

Mono-phosphite (one P center)  
Synergistic co-stabilizer for  
processing & moderate color  
regulator

# General Purpose Processing stabilization

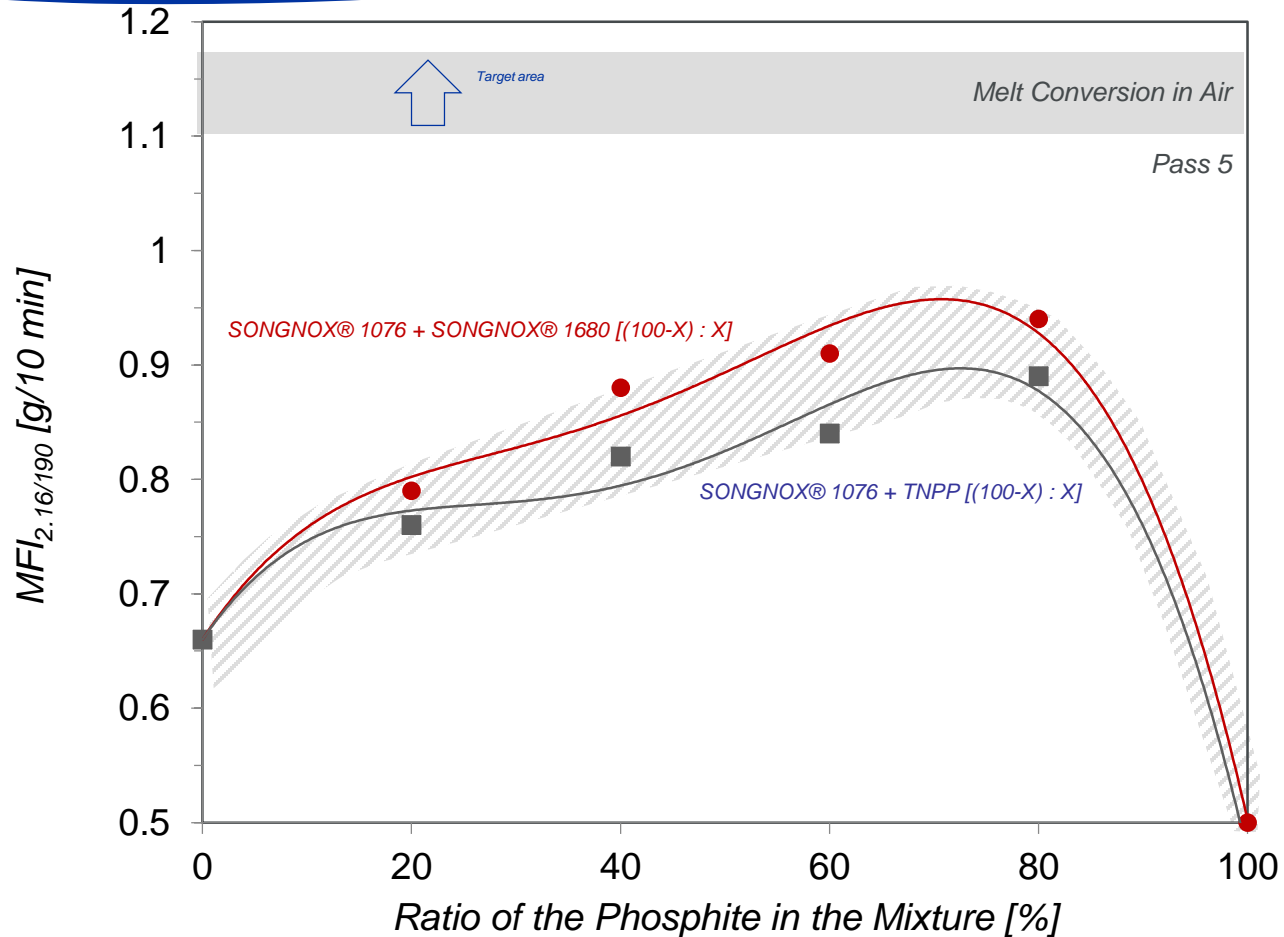


Substrate: Z/N C<sub>4</sub>-LLDPE ( $MFI_{2.16/190} \sim 1.0$  [g/10 min])

Reference: ADP # 14-030 (2014)



# General Purpose Processing stabilization



Substrate: Z/N C<sub>4</sub>-LLDPE ( $MFI_{2.16/190} \sim 1.0$  [g/10 min])

Reference: ADP # 14-030 (2014)

# General Purpose Processing stabilization

- Optimum synergism [hindered phenol + mono-phosphite] [40 : 60] to [20 : 80]
- Shape of the curve (grey hatched area) identical for all mono-phosphites with P content of approx. 5%
- Optimum point and best achievable performance limited by mono-phosphite (one P center) and limited P content
- Suitability and limitation of the basic processing stabilization strategy for polyethylene?

# New requirements

## [hindered phenol + phosphite]

SONGNOX® 1010  
or  
SONGNOX® 1076

Moderate “thermal” stabilizer  
Reasonable balance between  
contribution to LTTS and  
processing

SONGNOX® 1680  
or  
“TNPP” (liquid)  
or  
P-17 (liquid; recent introduction)

Mono-phosphite (one P center)  
Synergistic co-stabilizer for  
processing & moderate color  
regulator

Molecular weight protection during melt conversion

Discoloration during melt conversion

LTTS (service life)

Robustness (easy to handle)

Cost/performance (within area of suitability)

General regulatory clearance

New regulatory requirements for the substrate



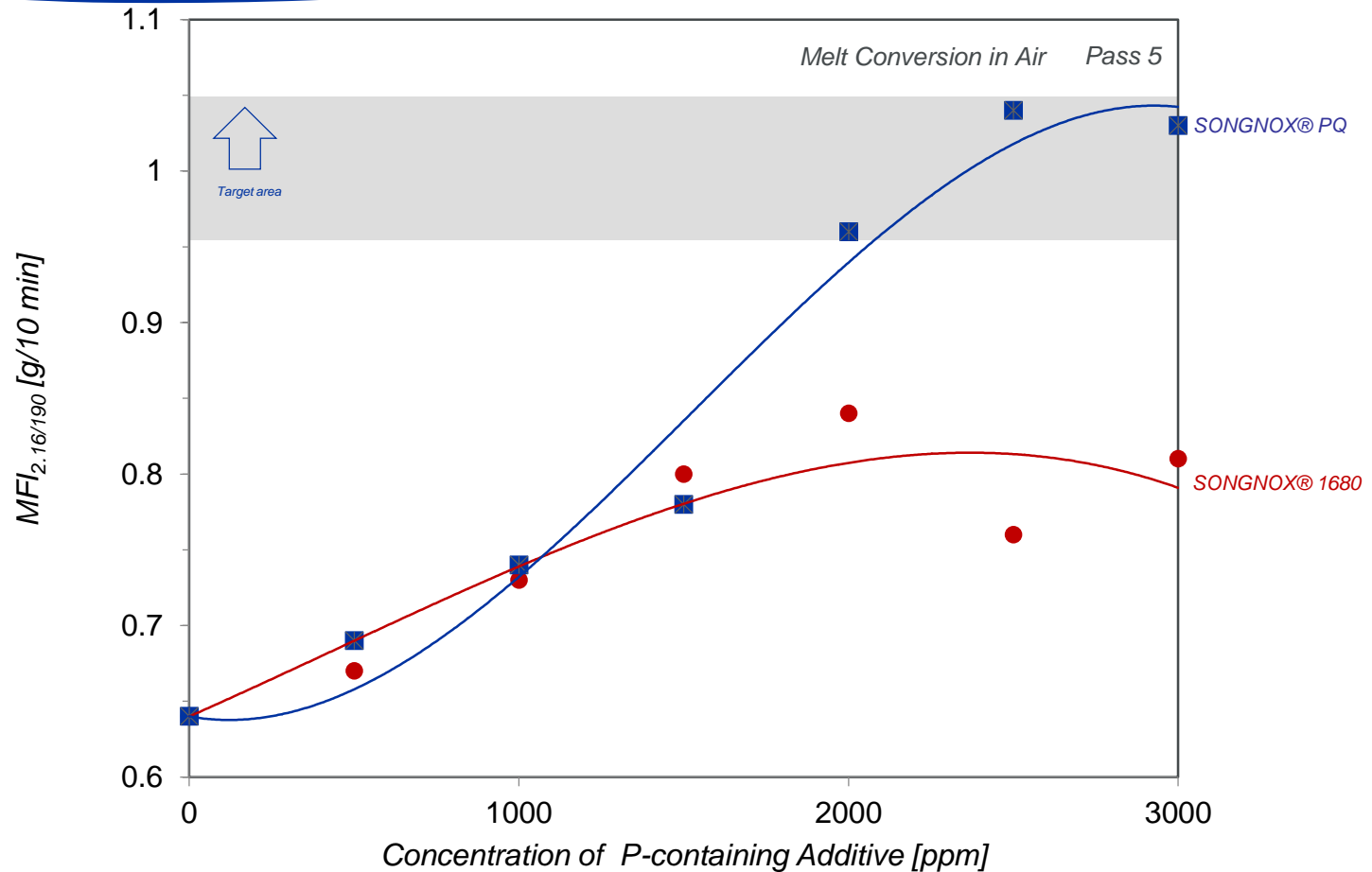
Improved technical  
requirement

Technical requirement for select PE

Potential downgrading depending  
upon global Inventories

New technical requirement

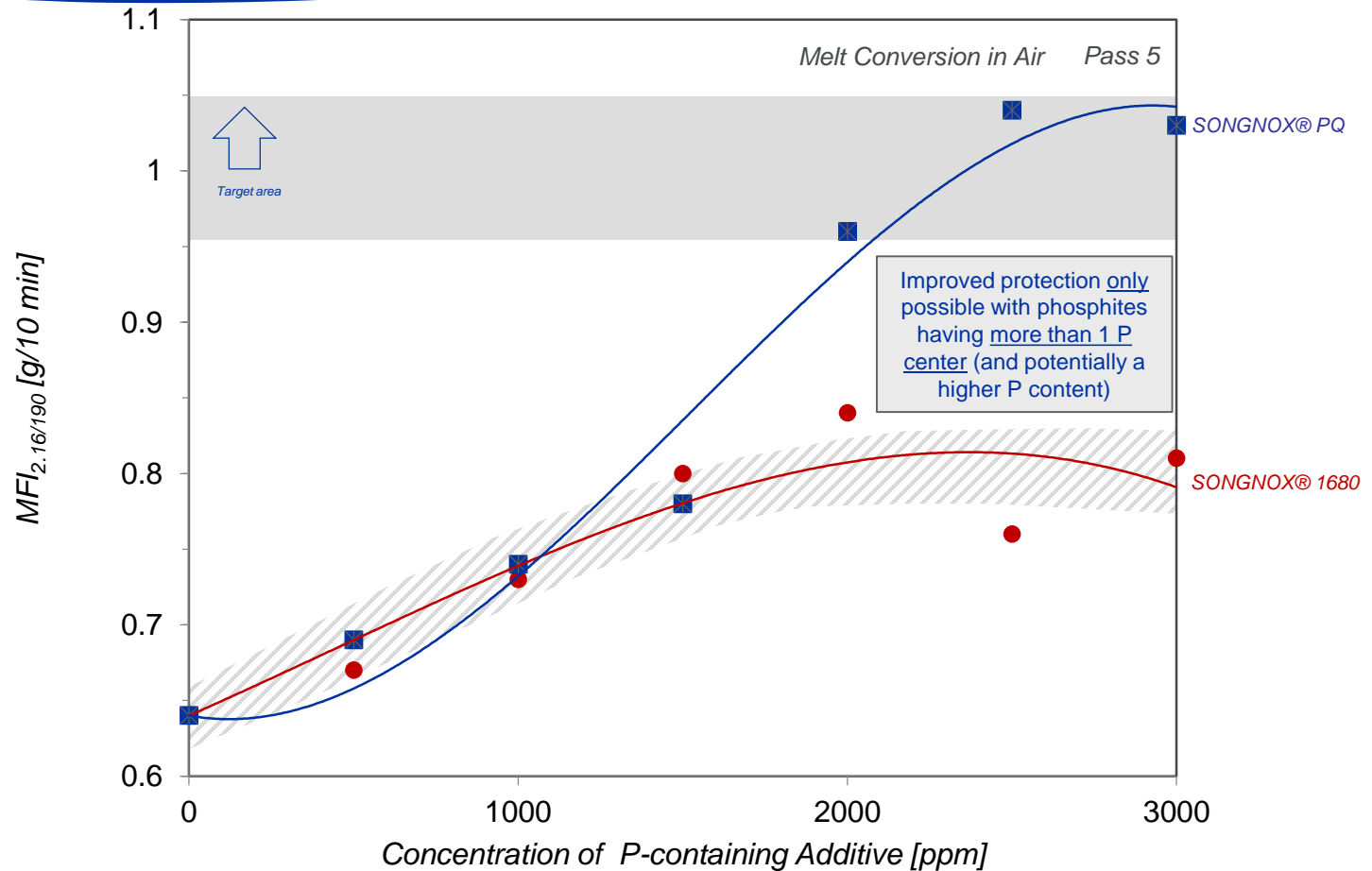
# Use alternative processing stabilizer (approach A)



Substrate: Z/N C<sub>6</sub>-LLDPE ( $MFI_{2.16/190}$  = 0.9 [g/10 min])

Reference: ADP # 14-030 (2014)

# Use alternative processing stabilizer (approach A)



Substrate: Z/N C<sub>6</sub>-LLDPE (MFI<sub>2.16/190</sub> = 0.9 [g/10 min])

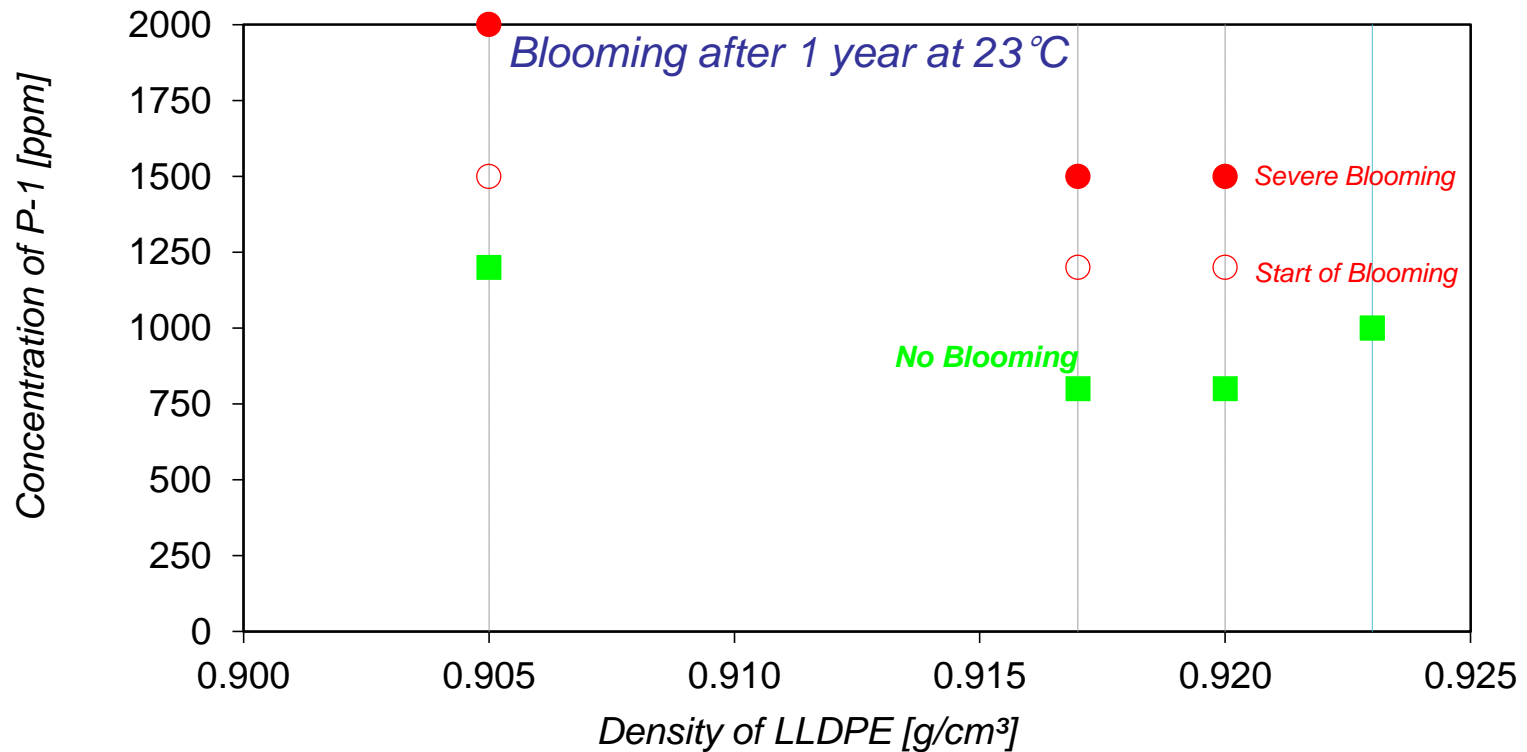
Reference: ADP # 14-030 (2014)

# Summary (approach A)

- Saturation behavior. Shape of the curve (grey hatched area) identical for all mono-phosphites with P content of approx. 5%
- Complete protection of the molecular structure cannot be achieved
- Acceptable for e.g. general purpose blown film grades ... but not sufficient for
  - mPE (narrow molecular weight distribution)
  - Pipe (oxygen deficiency during compounding)
  - Rotational molding (long cycle time)
  - Cast film
  - High T and shear processing (in general)
  - ...
- Improved protection only possible with phosphites having more than 1 P center (and potentially a higher P content)

# Improved processing stabilization (approach B)

## Solubility of Solid Phosphite P-1 in LLDPE

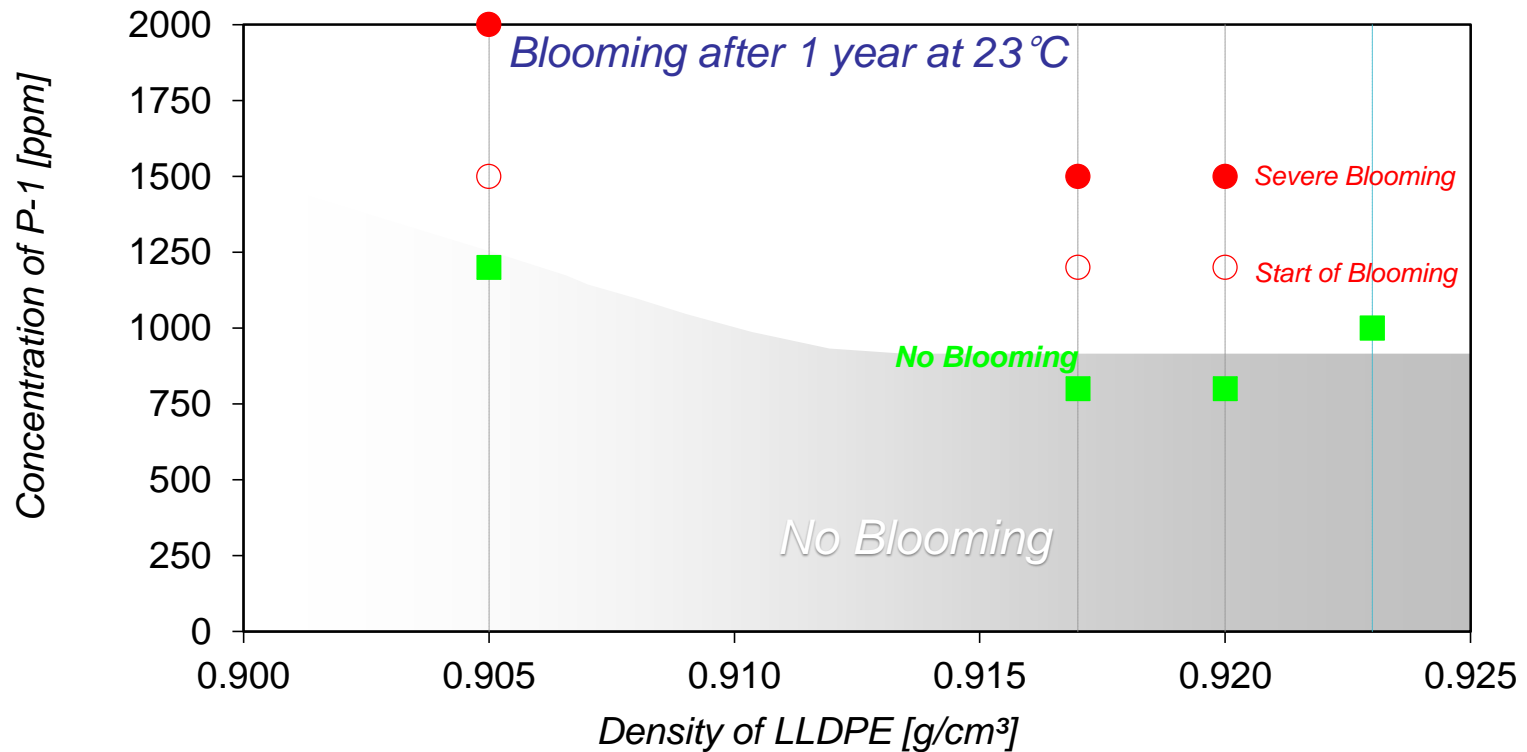


Reference:

KKA Literature # 393a; Private communication  
KKA Literature # 411; Svein Jamtvedt, Norner Innovation AS

# Improved processing stabilization (approach B)

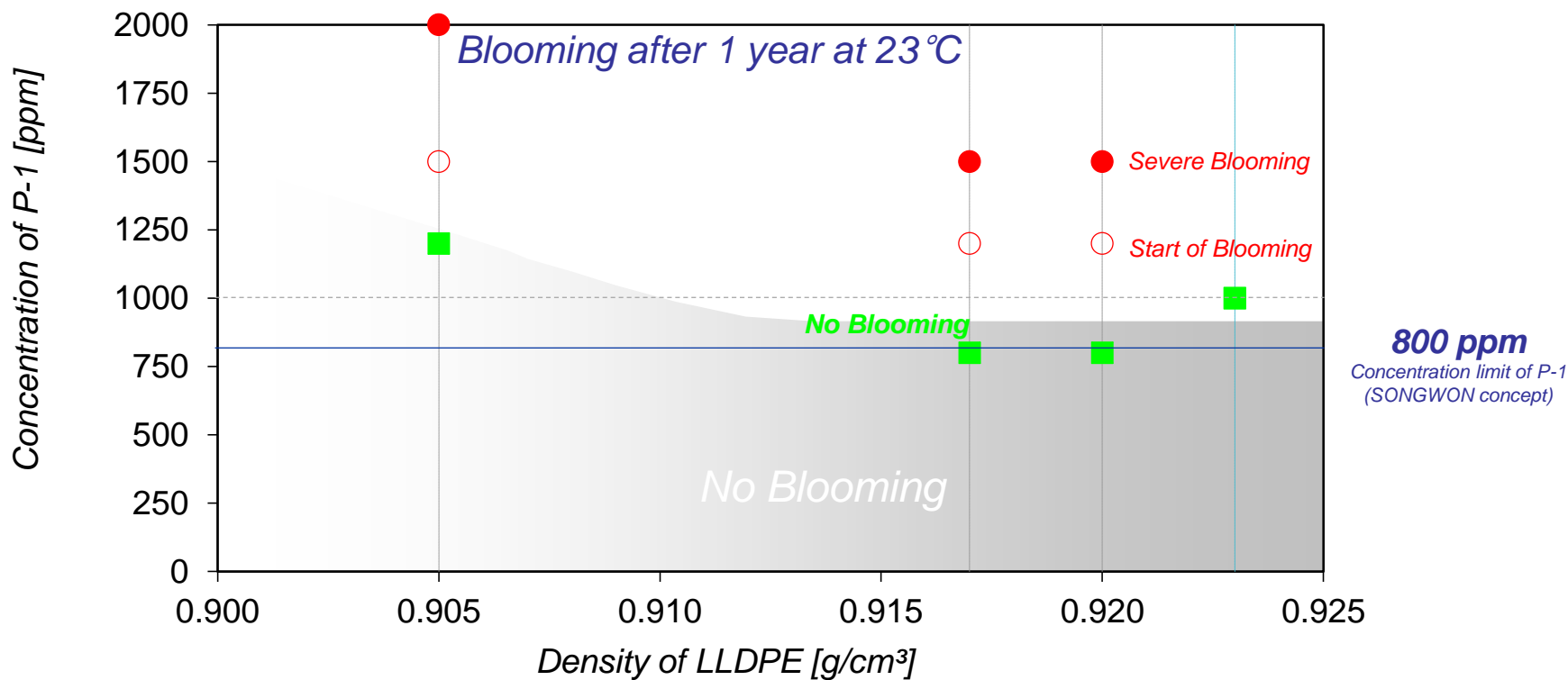
## Solubility of Solid Phosphite P-1 in LLDPE





# Improved processing stabilization (approach B)

## Solubility of Solid Phosphite P-1 in LLDPE



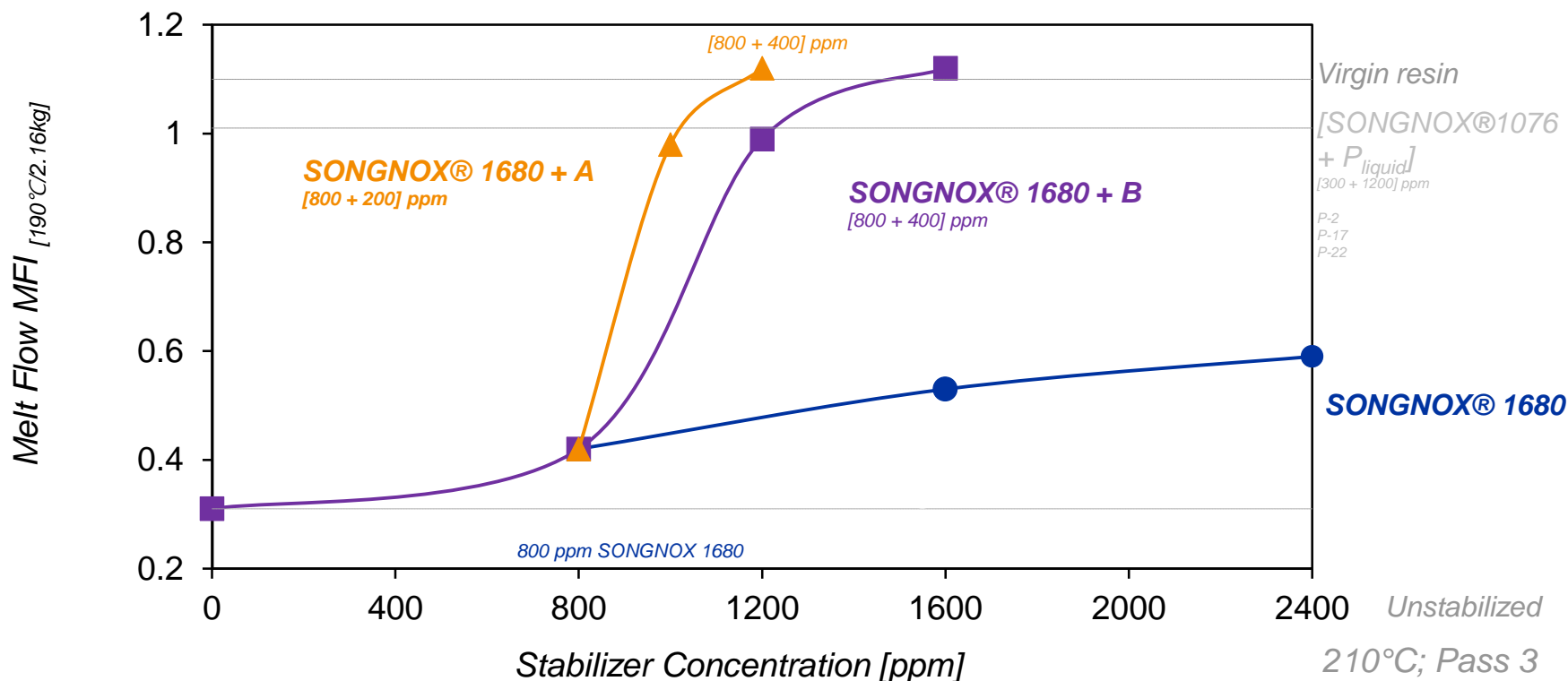
# Improved processing stabilization (approach B)

## Solubility of Additives in C4-LLDPE Solid Phosphite P-1

- Difference between solubility vs. diffusion rate
- Solubility increase with increasing temperature
- No solubility issue of P-1 during processing/conversion (blown film)
- Solubility limit of P-1 during service life 800 – 1000 ppm (blown film)
- No blooming of P-1 at 800 ppm
- Keep P-1 at 800 ppm or below

# Improved processing stabilization (approach B)

## Top-Up with high-end radical scavenger



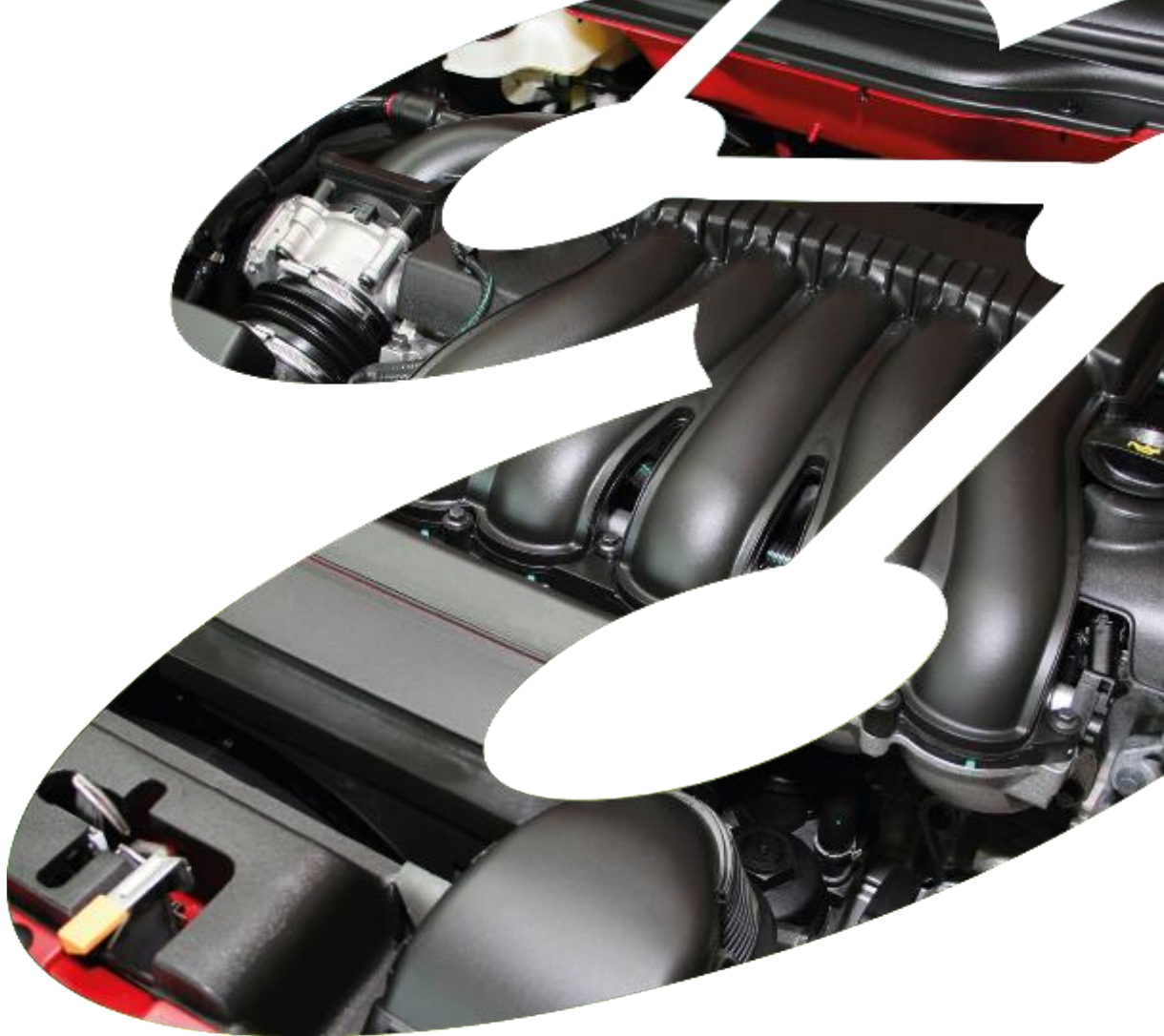
## Summary (approach B)

- Limit concentration of P-1 at 800 ppm
- Top-up with high-end radical scavenger
- Performance boost beyond the performance limits of mono-phosphites (P-1, P-2, ...)

## Polypropylene

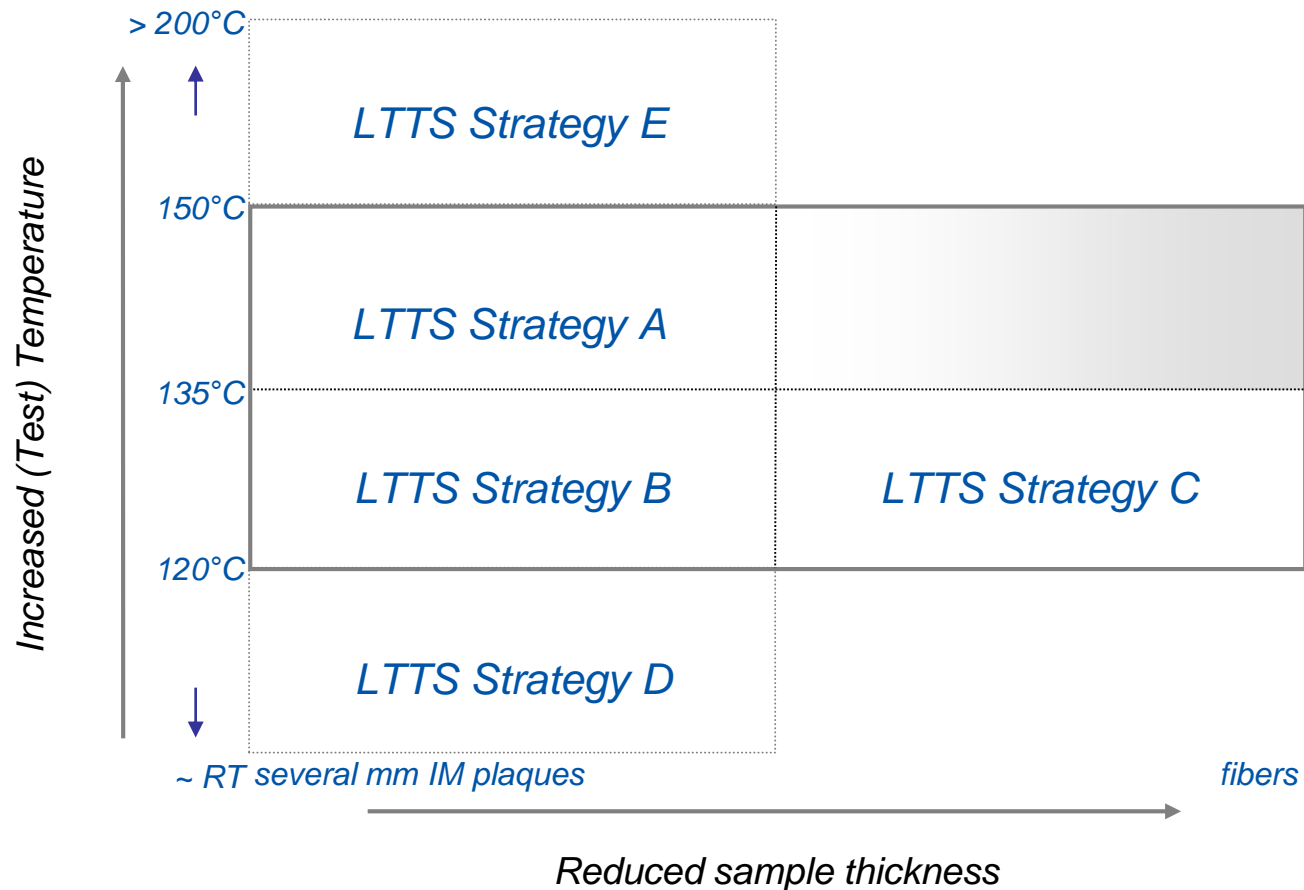
- General purpose thermal stabilization of PP injection molding grades
- New requirements
- Improved thermal stabilization of PP injection molding grades

It's all about **the chemistry**



# LTTS Stabilization Strategies

## SONGWON Classification of LTTS (Long Term Thermal Stability)

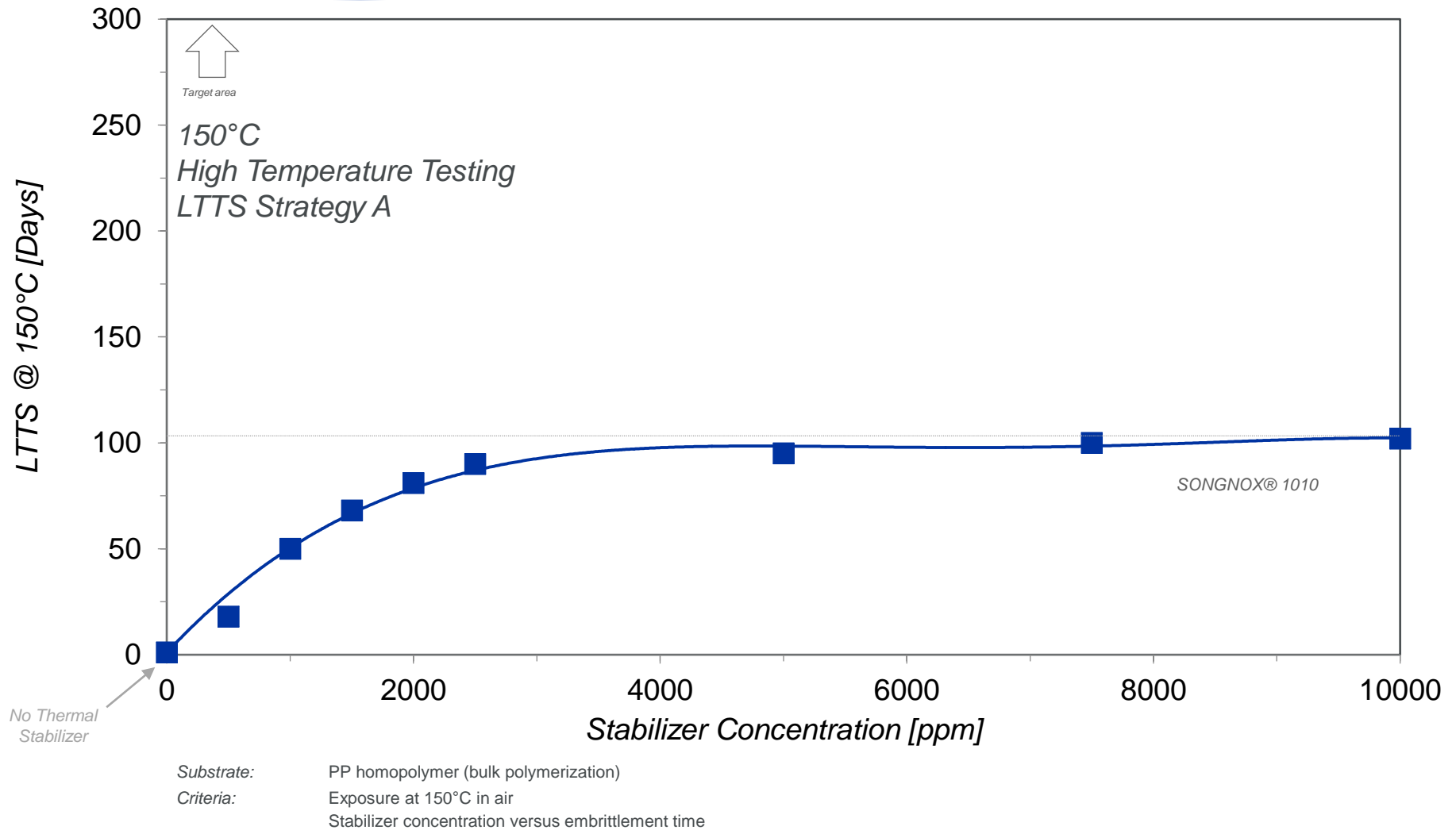


# LTTS Stabilisation Strategies

## Stabilization Strategy A

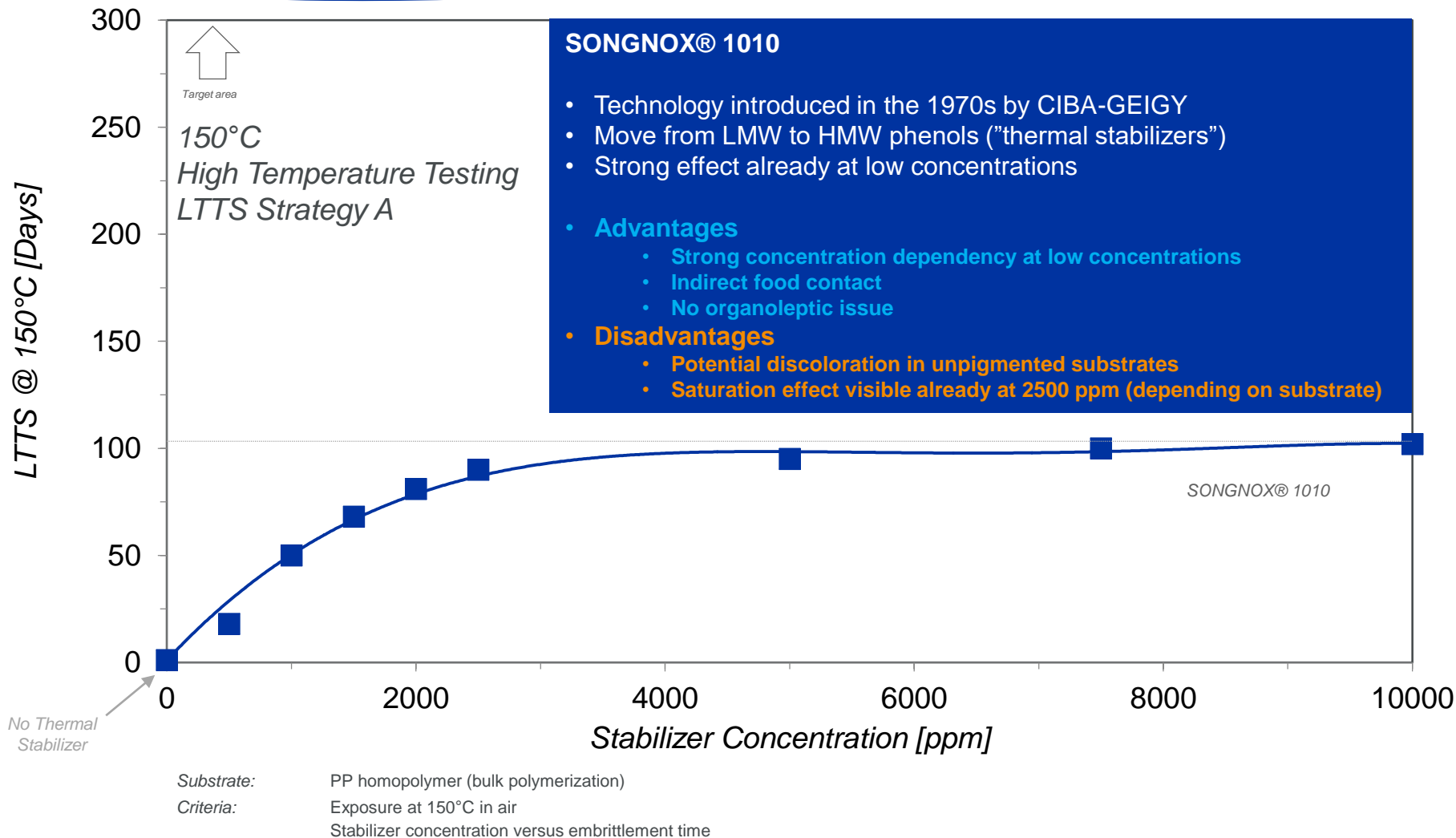
- Thick section ( $> 0.5$  mm)
- (Testing) temperature  $> 135^{\circ}\text{C}$ ; preferably  $150^{\circ}\text{C}$
- Mainly polypropylene homopolymer
- No specific other effects (e.g. extraction, filler interaction)
- Principle requirements ...
  - Low volatility (molecular weight  $> 500$  dalton)
  - Sufficient compatibility
  - “Kinetics adapted to oxidation rate”
- Suitable chemical classes ...
  - High molecular weight hindered phenols
  - High molecular weight hindered amines (HALS; very selected molecules & conditions only)
  - New chemistry ?

# General purpose LTTS strategy

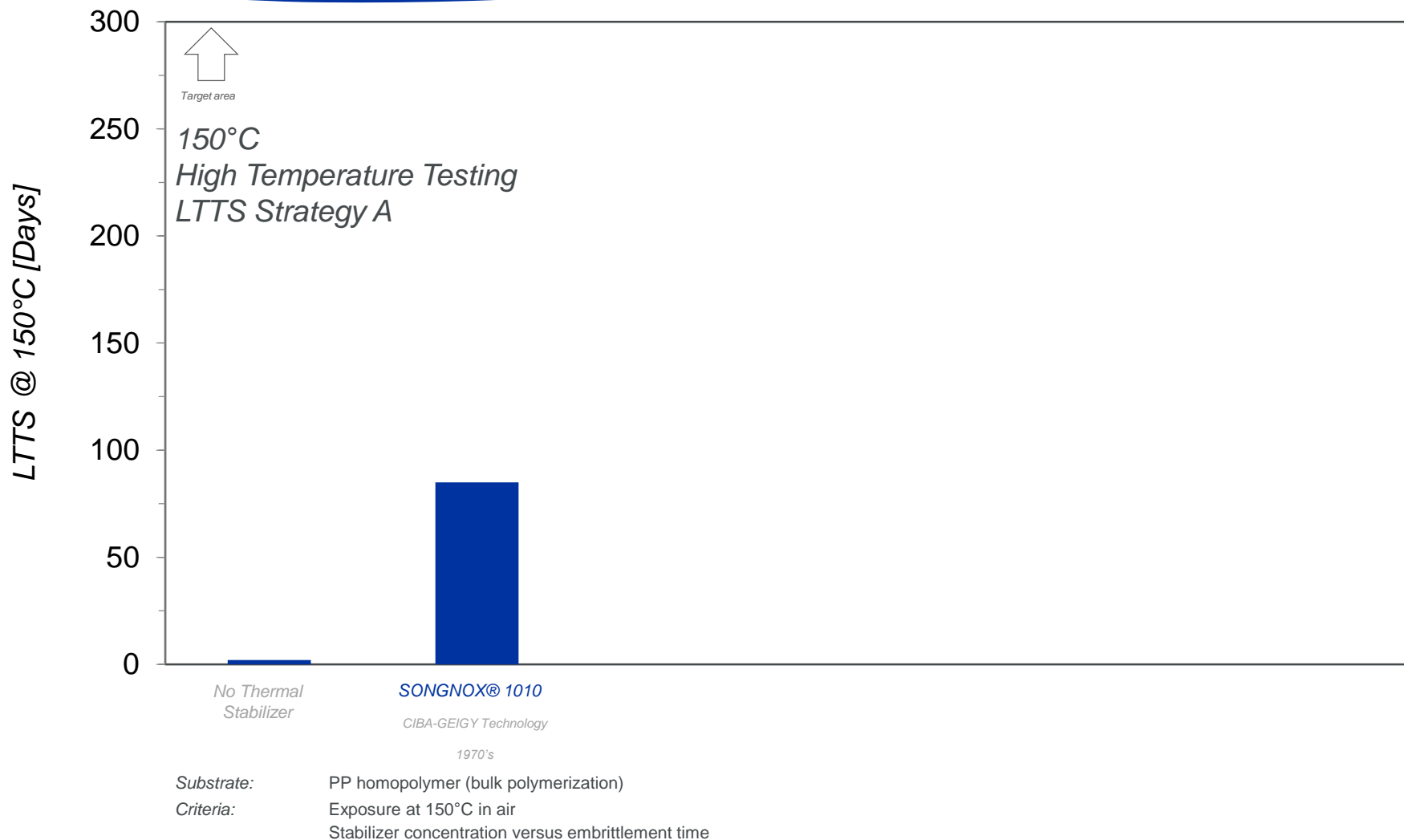




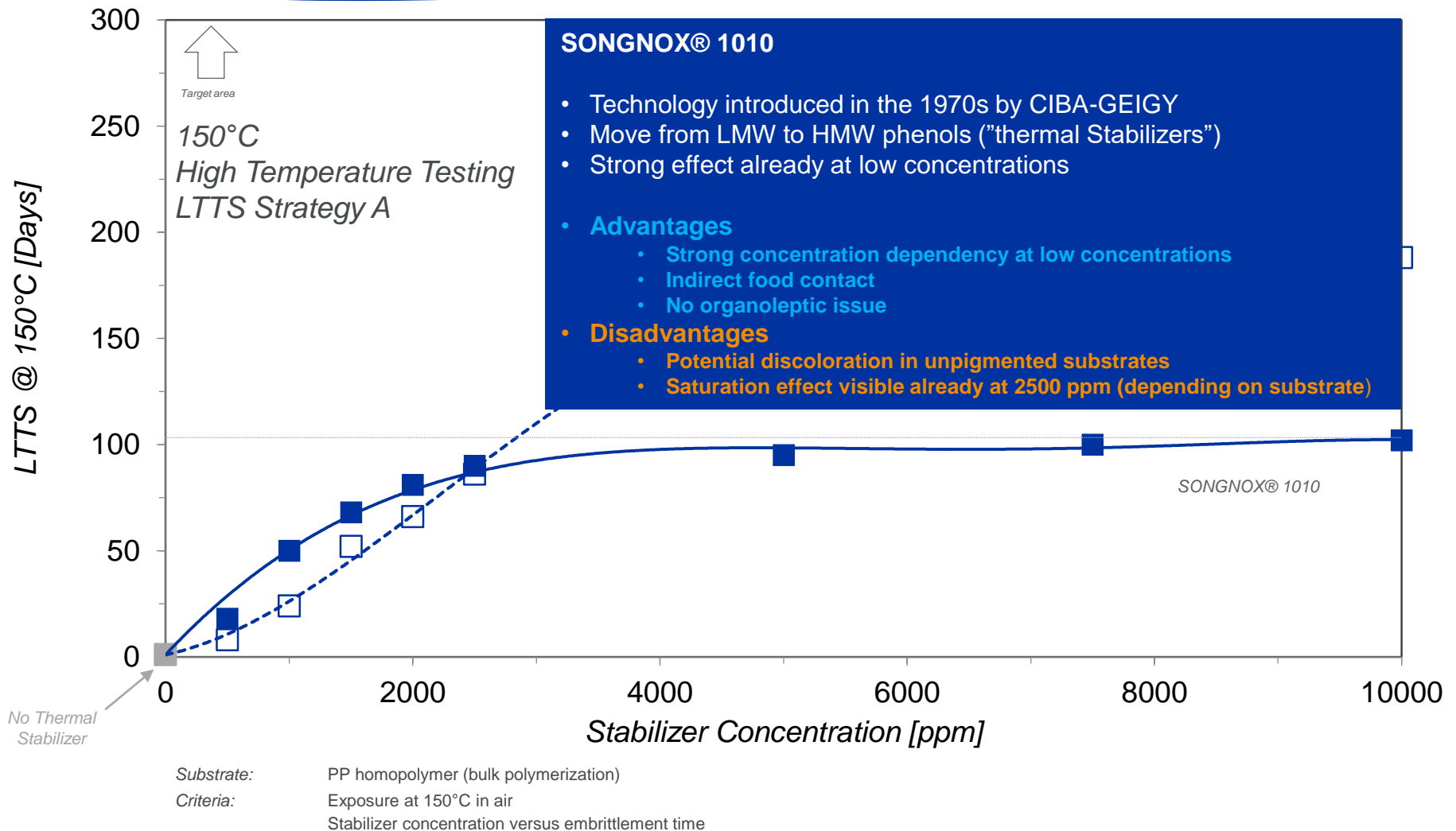
# General purpose LTTS strategy



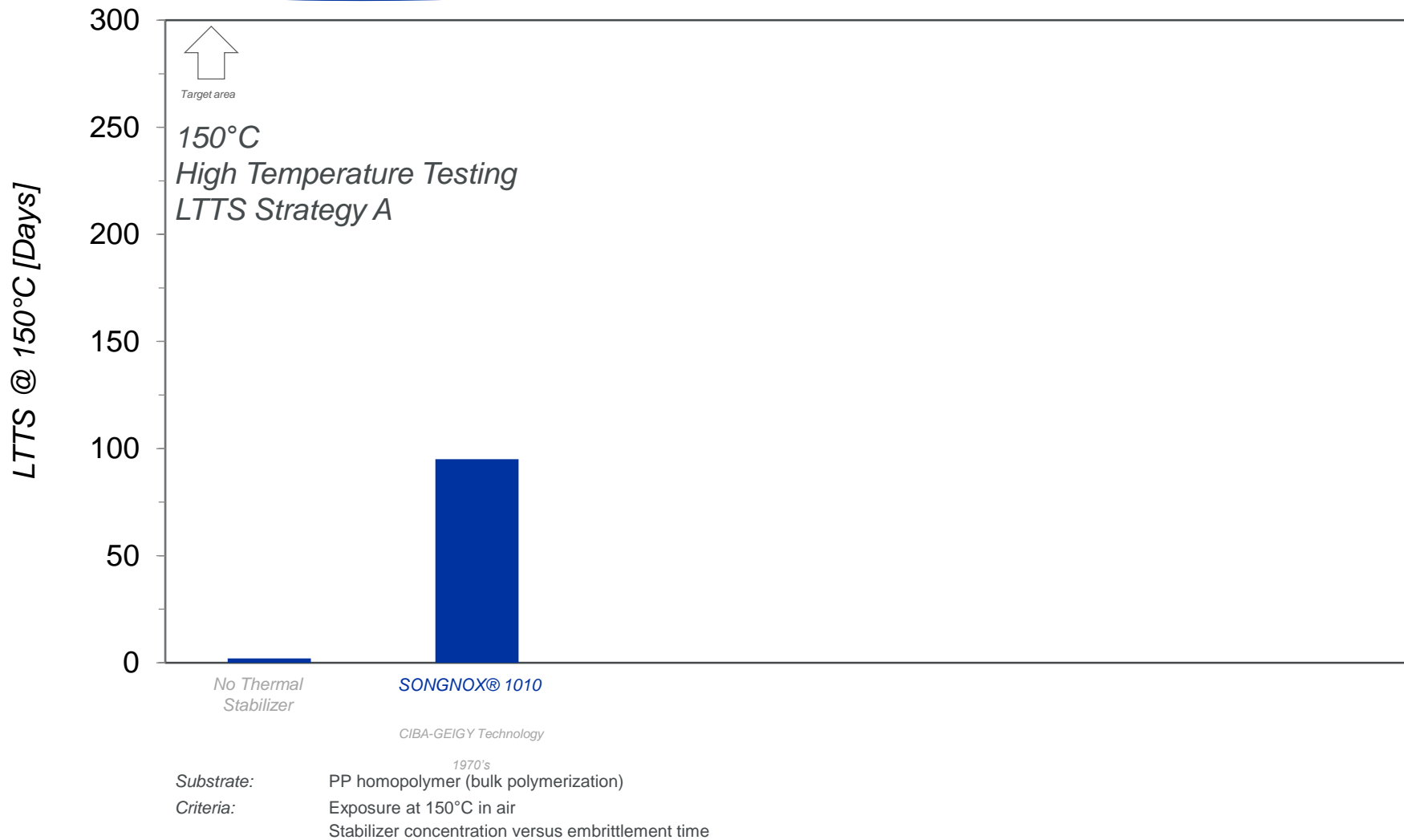
# General purpose LTTS strategy



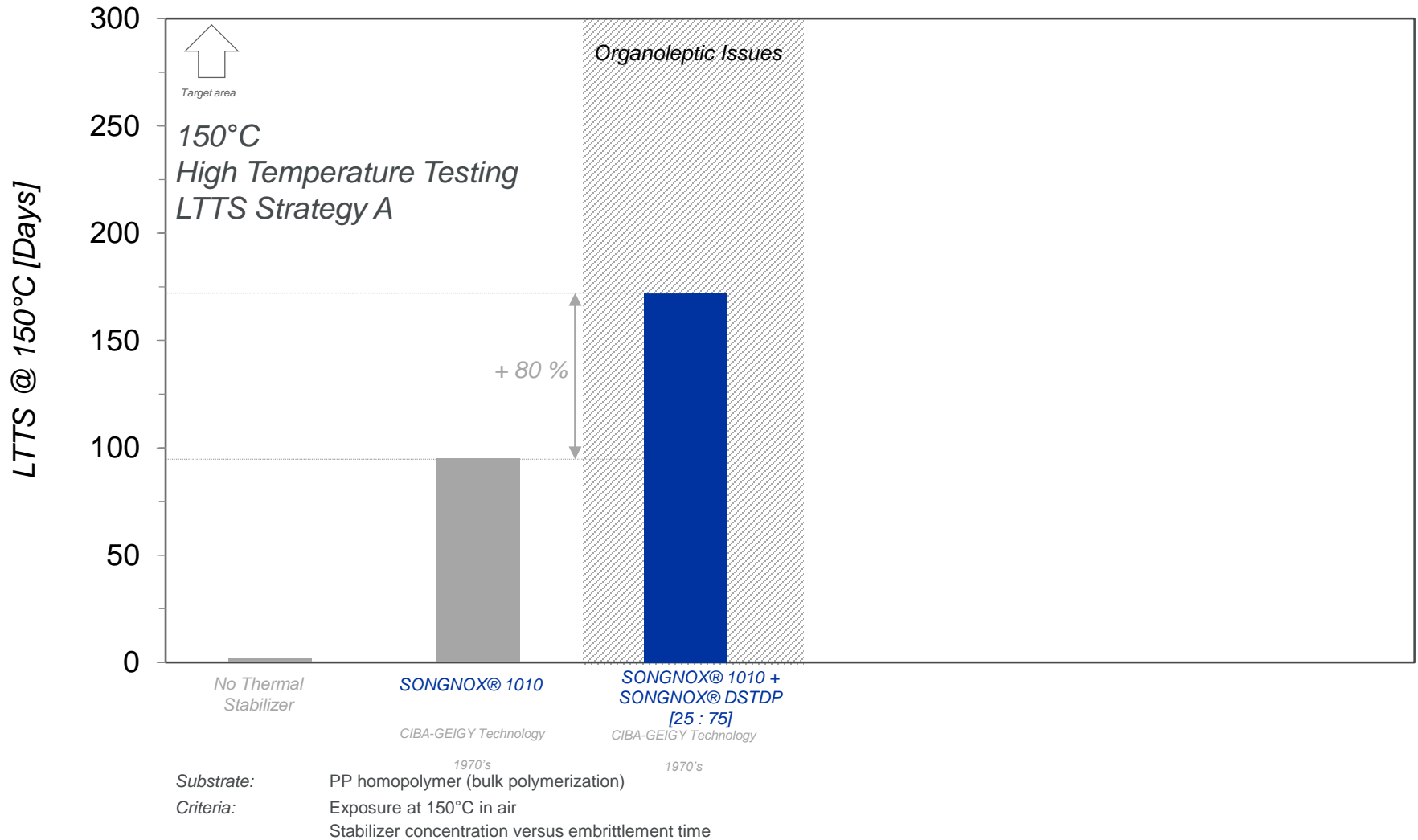
# General purpose LTTS strategy



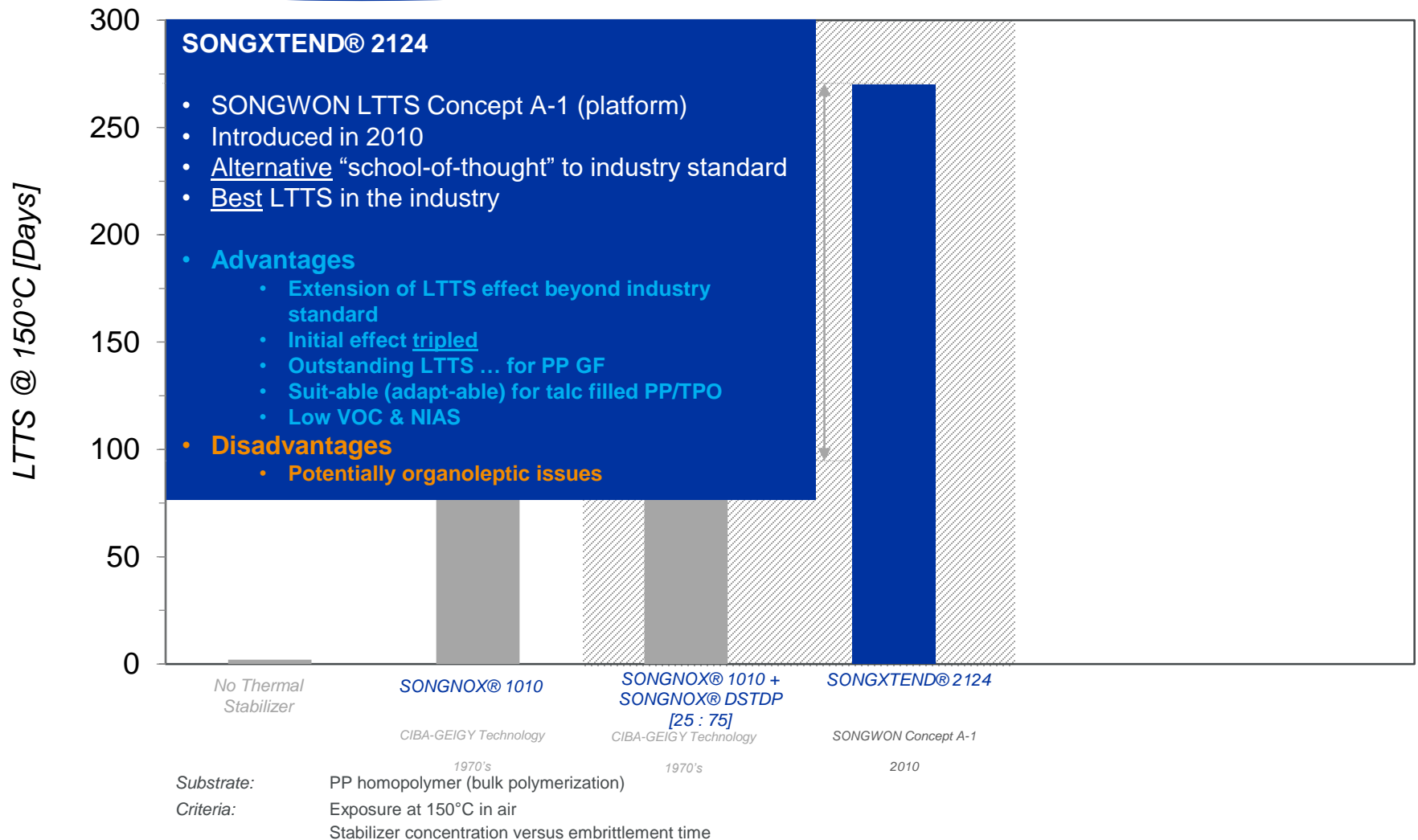
# General purpose LTTS strategy



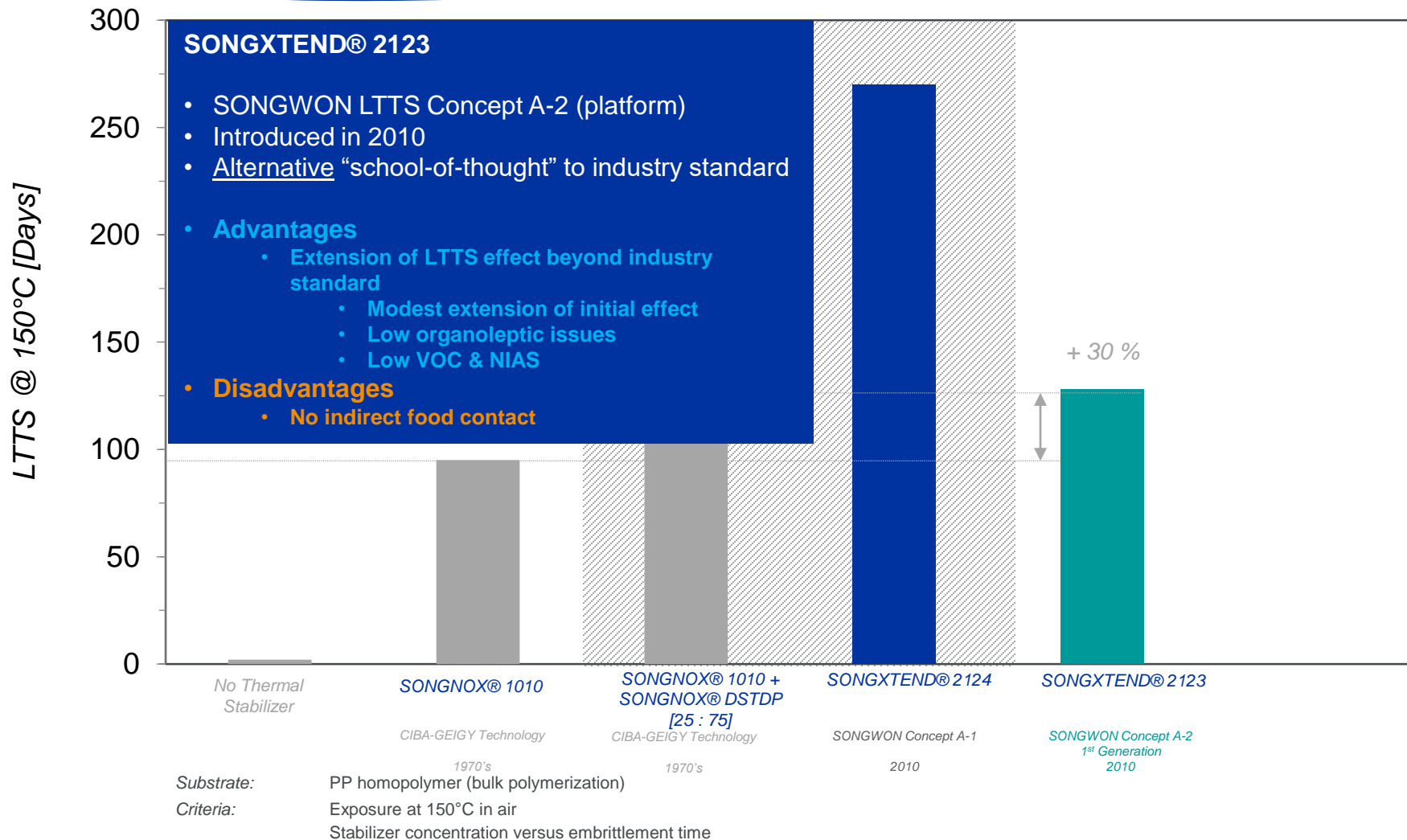
# General purpose LTTS strategy



# General purpose LTTS strategy



# General purpose LTTS strategy



## Conclusion



It's all about **the chemistry**





# Conclusion

## Basic stabilization strategy for polyethylene ...

[hindered phenol + phosphite]	
SONGNOX® 1010 or SONGNOX® 1076	SONGNOX® 1680 or “TNPP” (liquid) or P-17 (liquid; recent introduction)
Moderate “thermal” stabilizer Reasonable balance between contribution to LTTS and processing	Mono-phosphite (one P center) Synergistic co-stabilizer for processing & moderate color regulator

- ... yields acceptable protection of the molecular architecture during melt conversion of “general purpose” PE grades (i.e., blown film)
- Excellent cost / performance (within area of suitability)
- Increased demands of existing technical requirements or appearance of new ones results in limitations which cannot be overlooked
- Limitations are fundamentally related to the nature of the mono-phosphites

# Conclusion

## Higher end processing stabilization of PE ...

- Select examples were presented where the basic stabilization strategy (B-Blends) no longer fulfill the technical requirements.
- For these examples alternative “high-end” processing strategies exist.
- Select “high-end” processing strategies for PE were briefly highlighted.

# Conclusion

## Extension of the durability of PP / TPO ...

- PP / TPO can be used in durable applications ... only due to the addition of “long-term” Thermal Stabilizers
- Since years main(stream) “school-of-thought” stabilizer packages are established for LTTS (and UV) ... with suitable performance
- Stabilization strategies based on alternative “school-of-thought” yield significant better effects ...

Significantly better (longer) durability .. at same concentration

Same durability .. at notice-able lower concentration

Less secondary effects

- SONGWON has developed alternative approaches

Thank you for your  
attention

**Jungdu (Jack) Kim,**

Global Technical Service  
Americas

[jungdu.kim@songwon.com](mailto:jungdu.kim@songwon.com)

SONGWON Industrial Group

It's all about **the chemistry**



# Disclaimer

SONGWON provides customers with warranties and representations as to the chemical or technical specifications, compositions and/or the suitability for use for any particular purpose exclusively in individual written agreements.

The facts and figures contained herein have been carefully compiled to the best of SONGWON's knowledge but are essentially intended for informational purposes only.

SONGWON Industrial Group does not accept any liability whatsoever for any information, reference or advice provided in this document or any similar SONGWON publication.