Recent Aspects of Polypropylene and Polyethylene Stabilization

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Background & introduction

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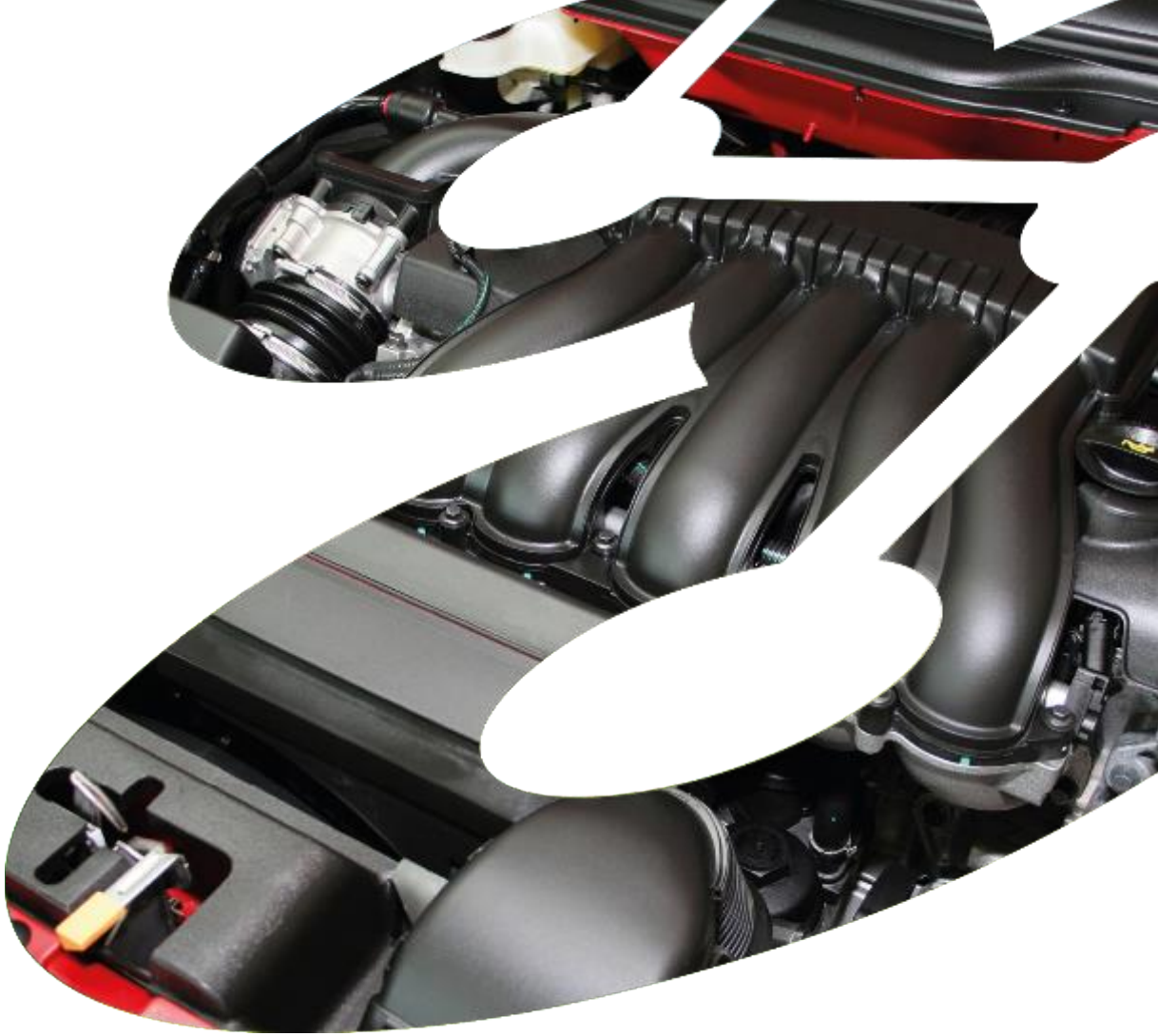
Background

- 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

- 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

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Processing stabilization of polyolefins

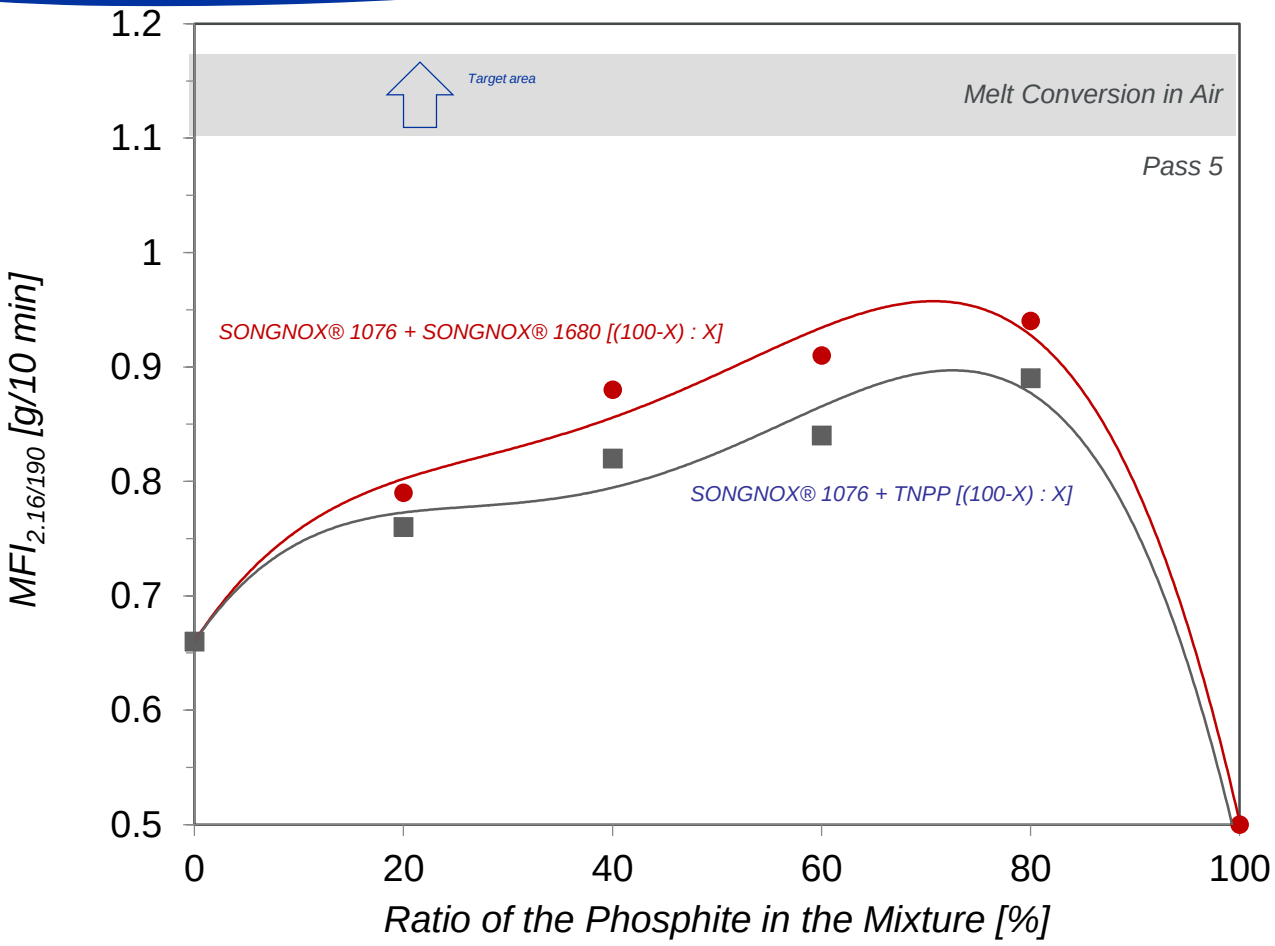
… For Polyethylene

- 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	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

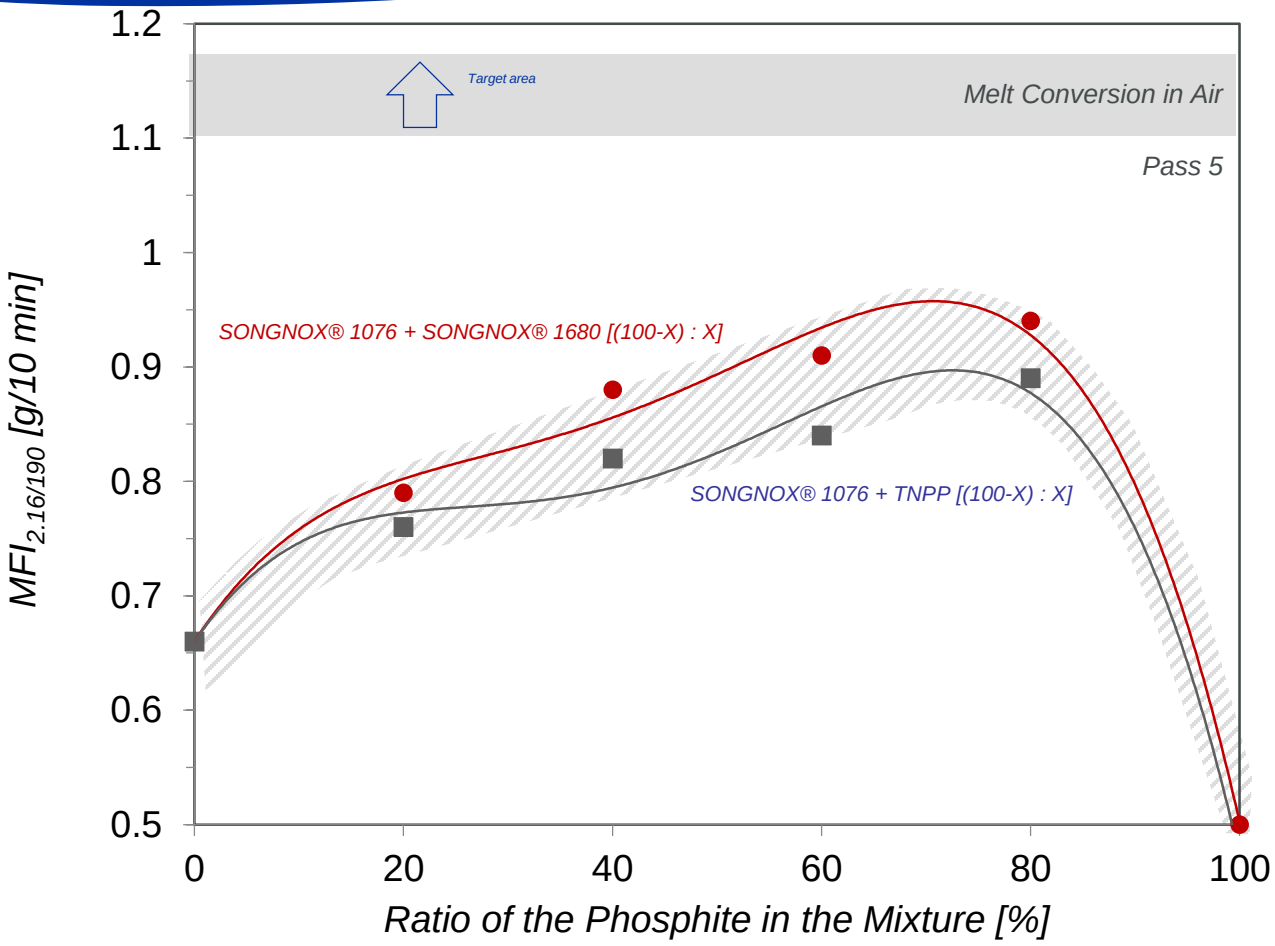
General Purpose Processing stabilization



Substrate: Z/N C_4-LLDPE ($MFI_{2.16/190}$ ~ 1.0 [g/10 min])

Reference: ADP # 14-030 (2014)

General Purpose Processing stabilization



Substrate: Z/N C_4-LLDPE ($MFI_{2.16/190}$ ~ 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	SONGNOX® 1680 or "TNPP" (liquid) or P-17 (liquid; recent introduction)
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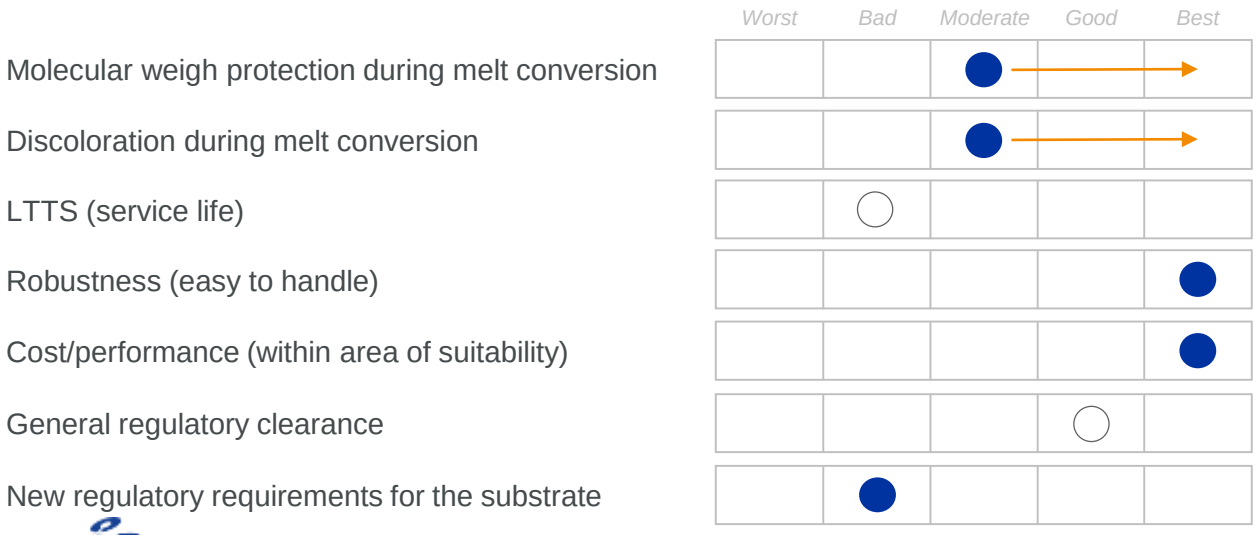


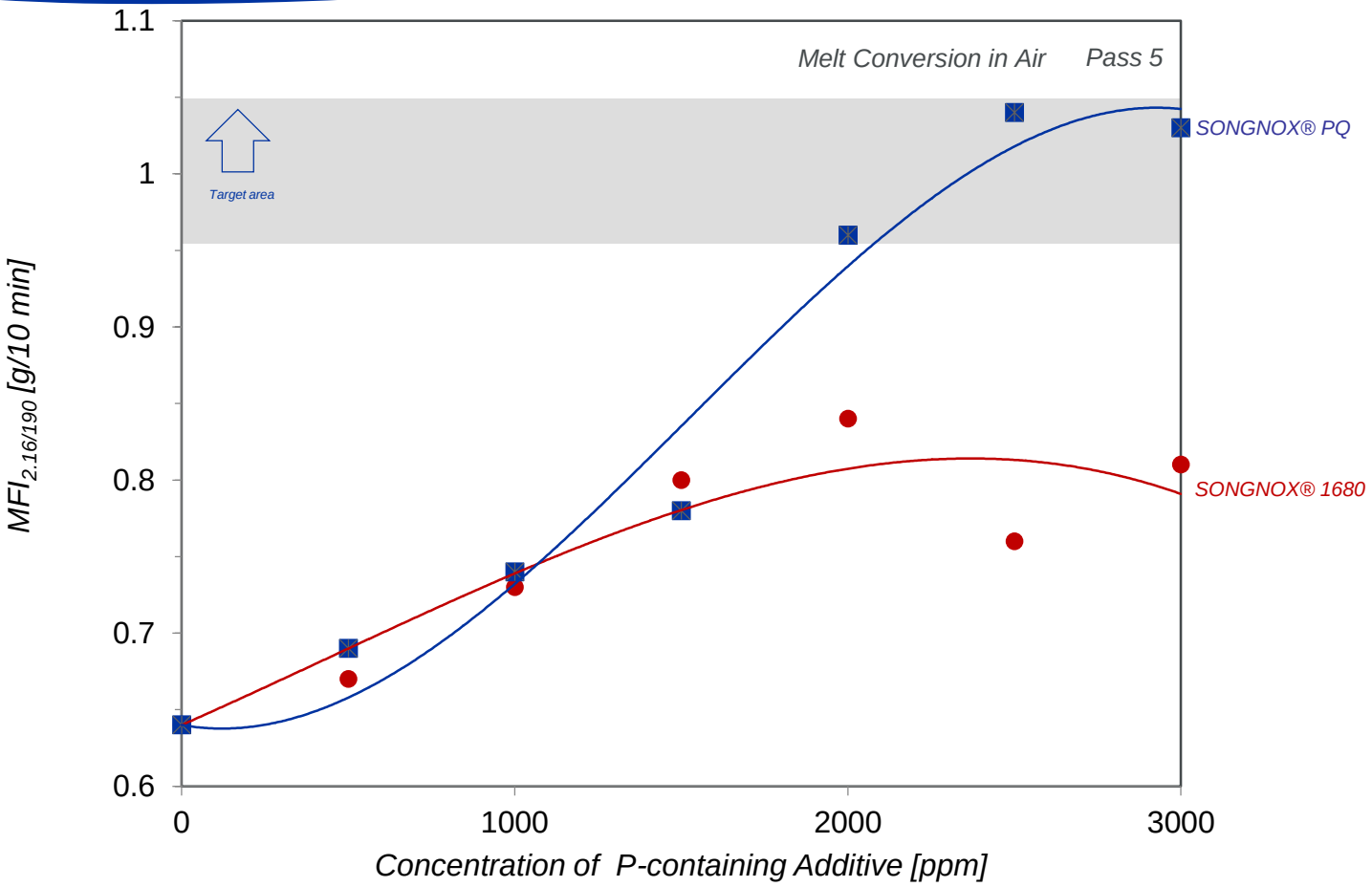
Improved technical requirement

Technical requirement for select PE

Potential downgrading depending upon global Inventories

New technical requirement

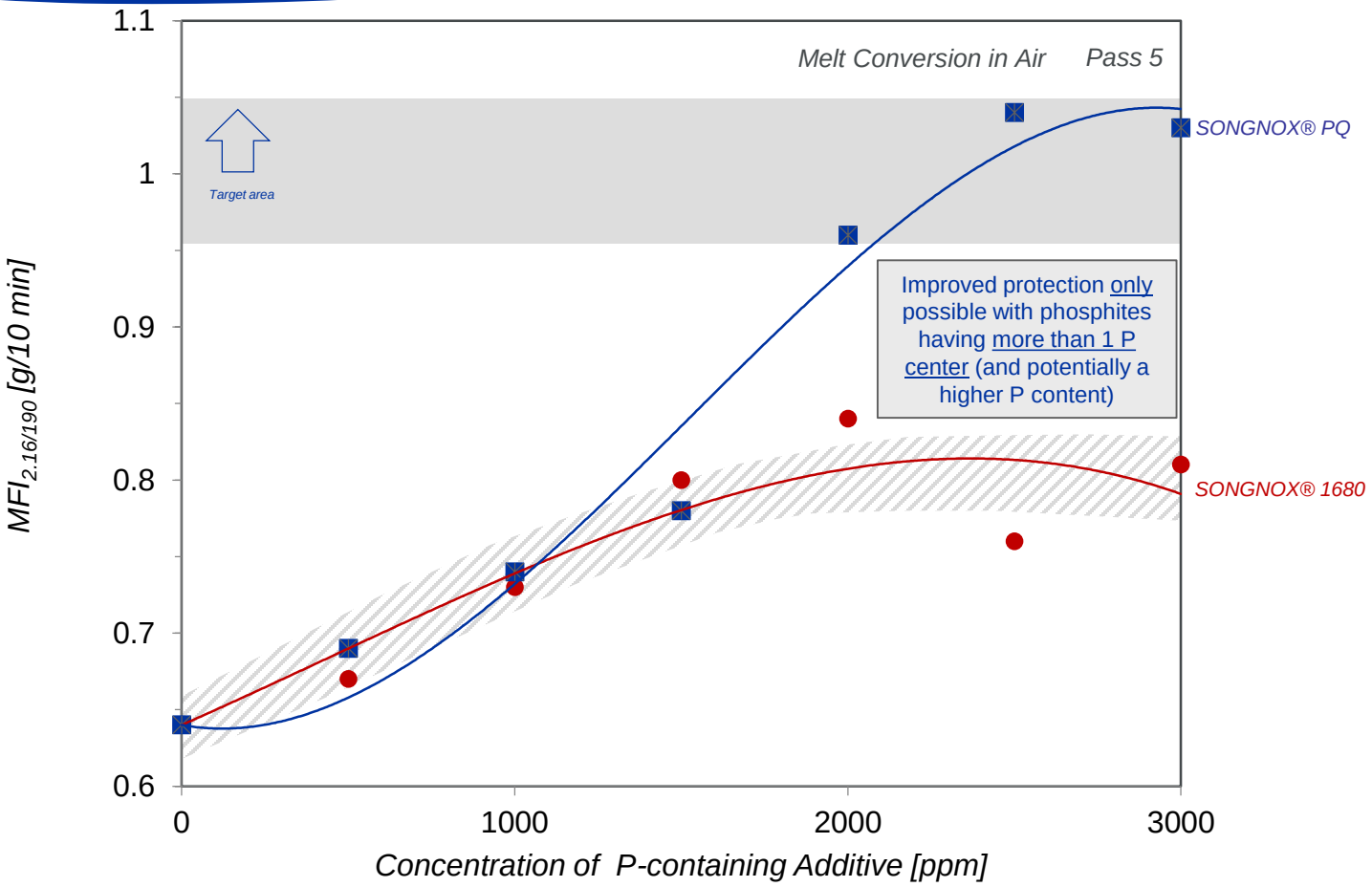
Use alternative processing stabilizer (approach A)



Substrate: Z/N C_6-LLDPE ($MFI_{2.16/190}$ = 0.9 [g/10 min])

Reference: ADP # 14-030 (2014)

Use alternative processing stabilizer (approach A)



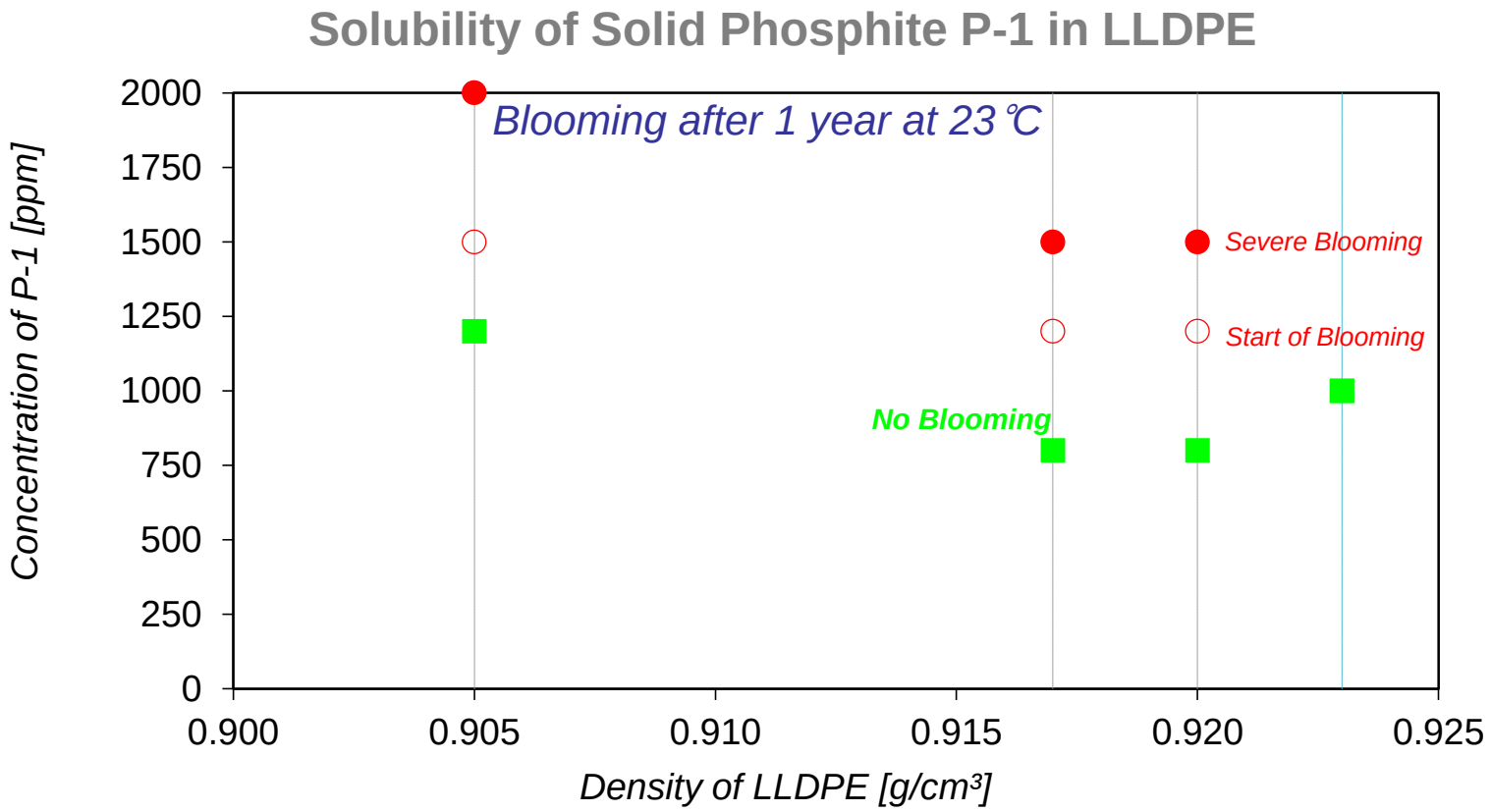
Substrate: Z/N C_6-LLDPE ($MFI_{2.16/190}$ = 0.9 [g/10 min])

Reference: ADP # 14-030 (2014)

Summary (approach A)

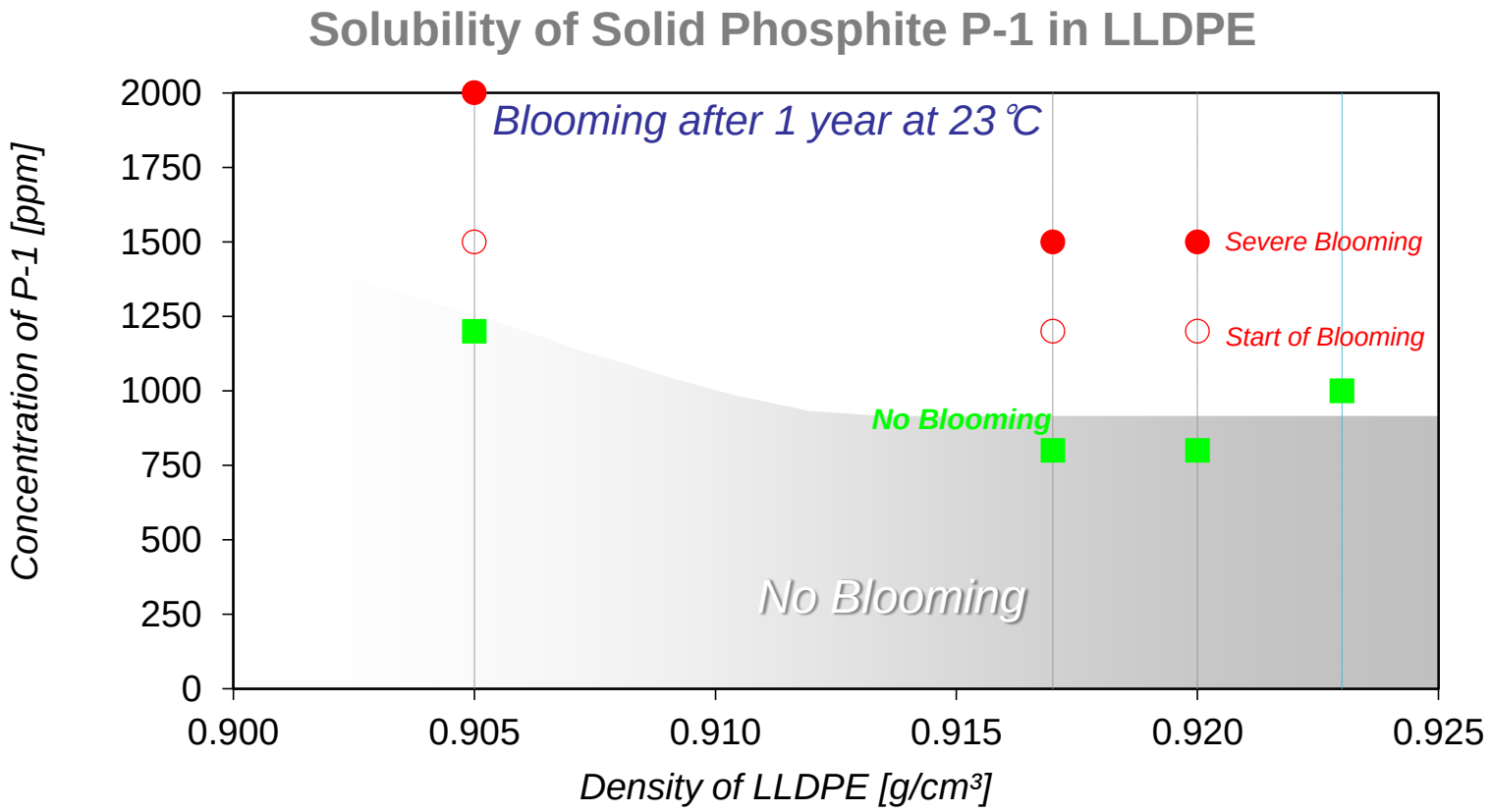
- Saturation behavior. Shape of the curve (grey hatched area) identical for all mono-phosphites with P content of approx. 5%
- Complete protection of the molecular structure cannot be achieved
- Acceptable for e.g. general purpose blown film grades … but not sufficient for
  - mPE (narrow molecular weight 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)

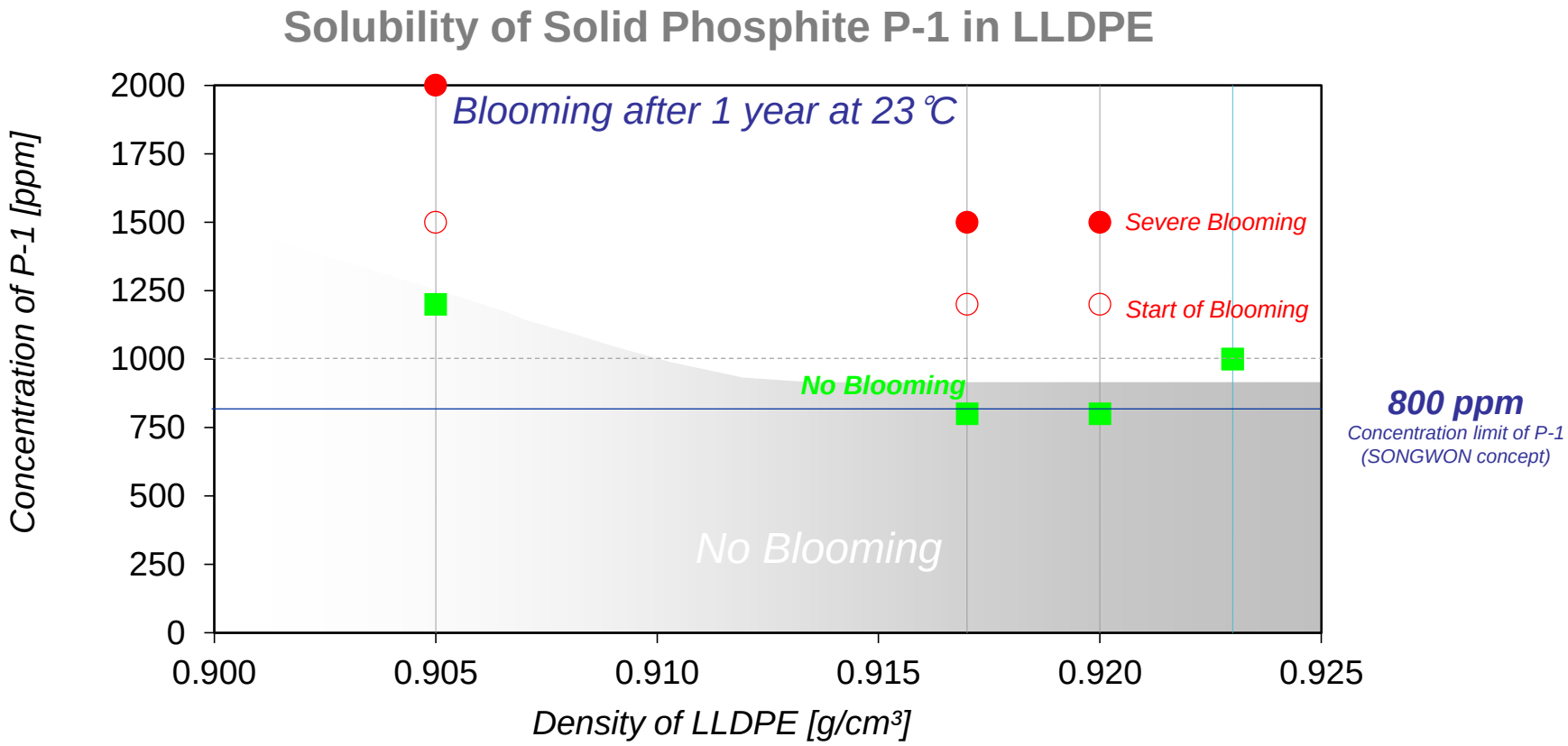


Reference: KKA Literature # 393a; Private communication
KKA Literature # 411; Svein Jamtvedt, Norner Innovation AS

Improved processing stabilization (approach B)



Improved processing stabilization (approach B)



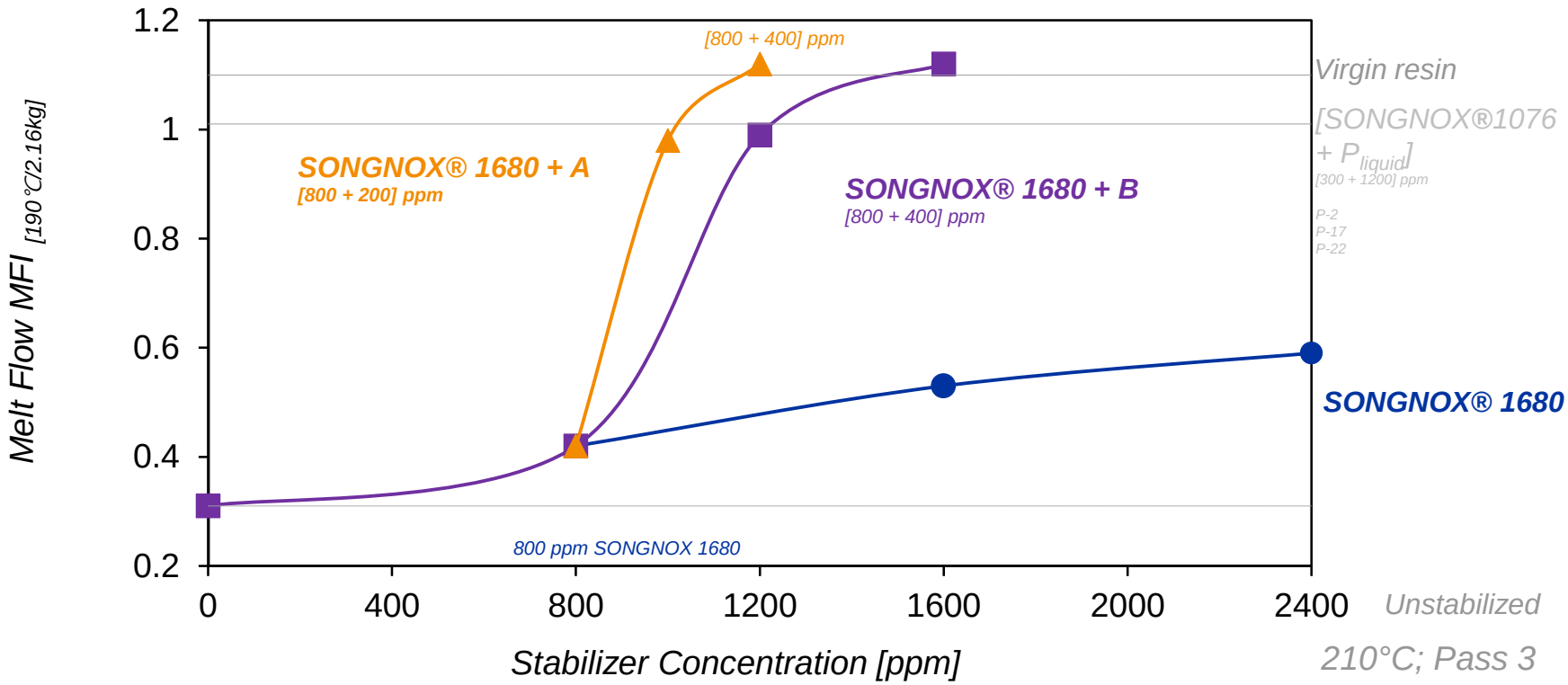
Improved processing stabilization (approach B)

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

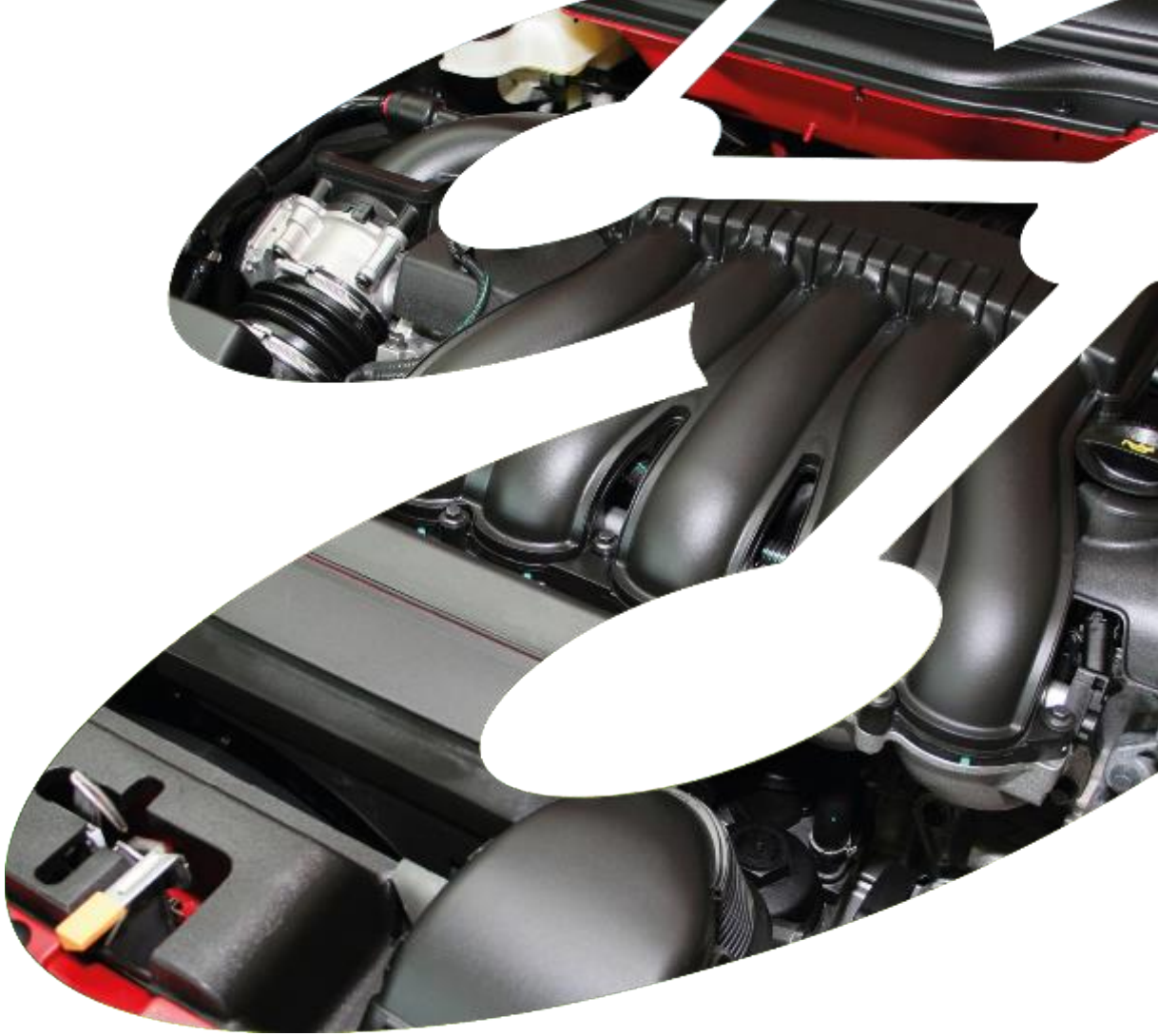


Substrate: C_4-LLDPE (gas phase process A)
$MFI_{190/2.16}$ 1.2; density 0.919 [dg/min]

Reference: ADP # 11-006

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

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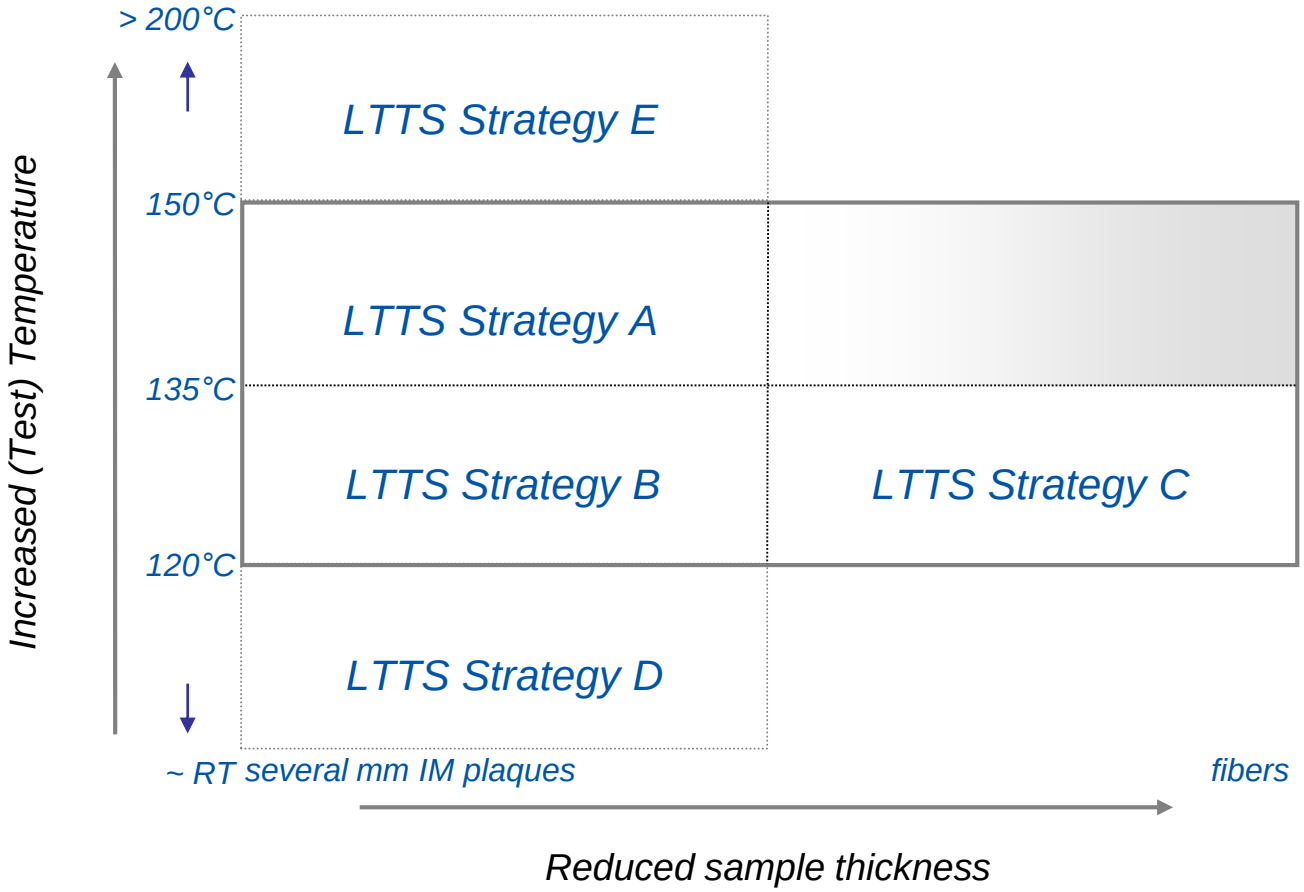
LTTS Stabilization Strategies

SONGWON Classification of LTTS (Long Term Thermal Stability)

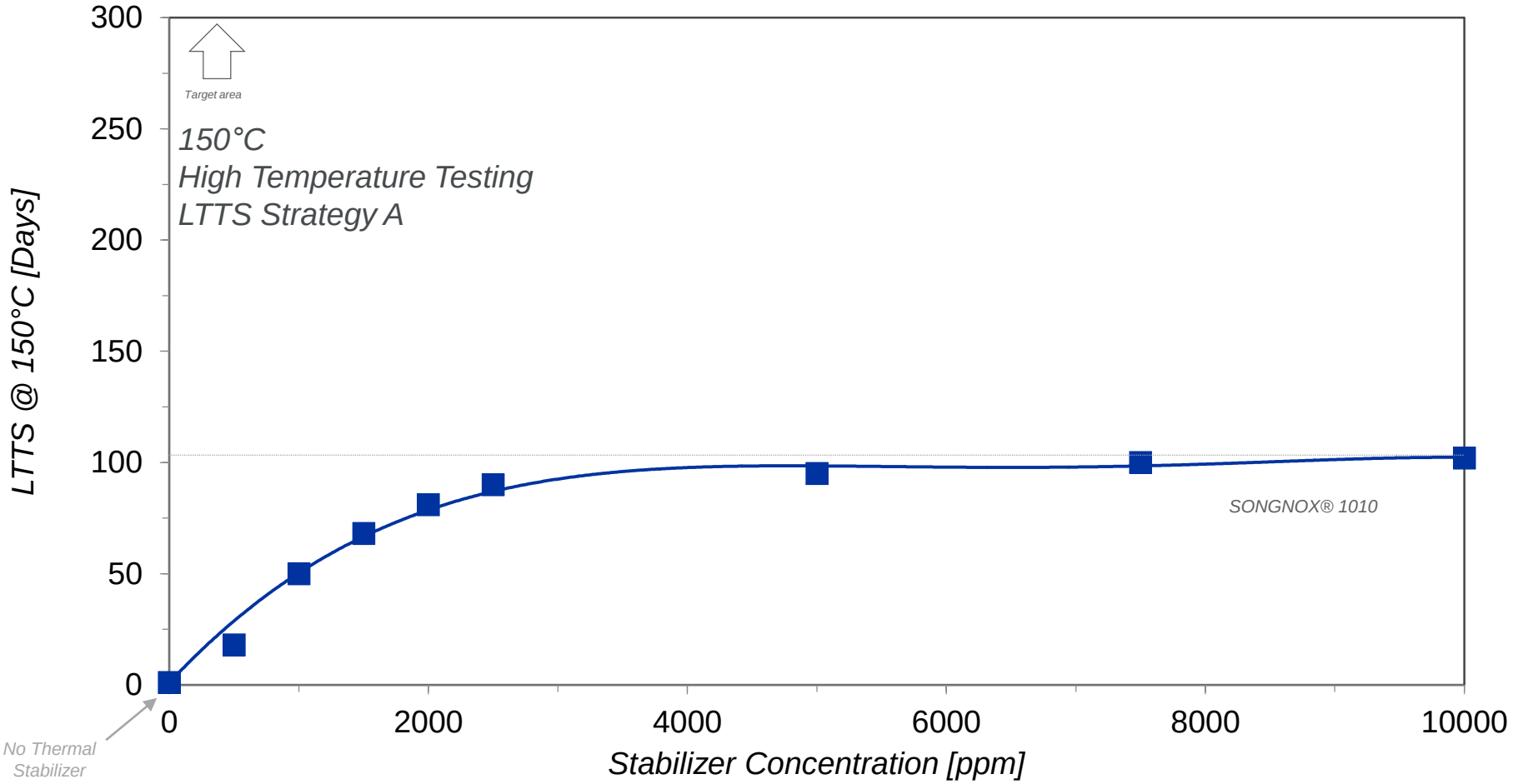


LTTS Stabilisation Strategies

Stabilization Strategy A

- Thick section (> 0.5 mm)
- (Testing) temperature > 135°C; preferably 150°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 ?

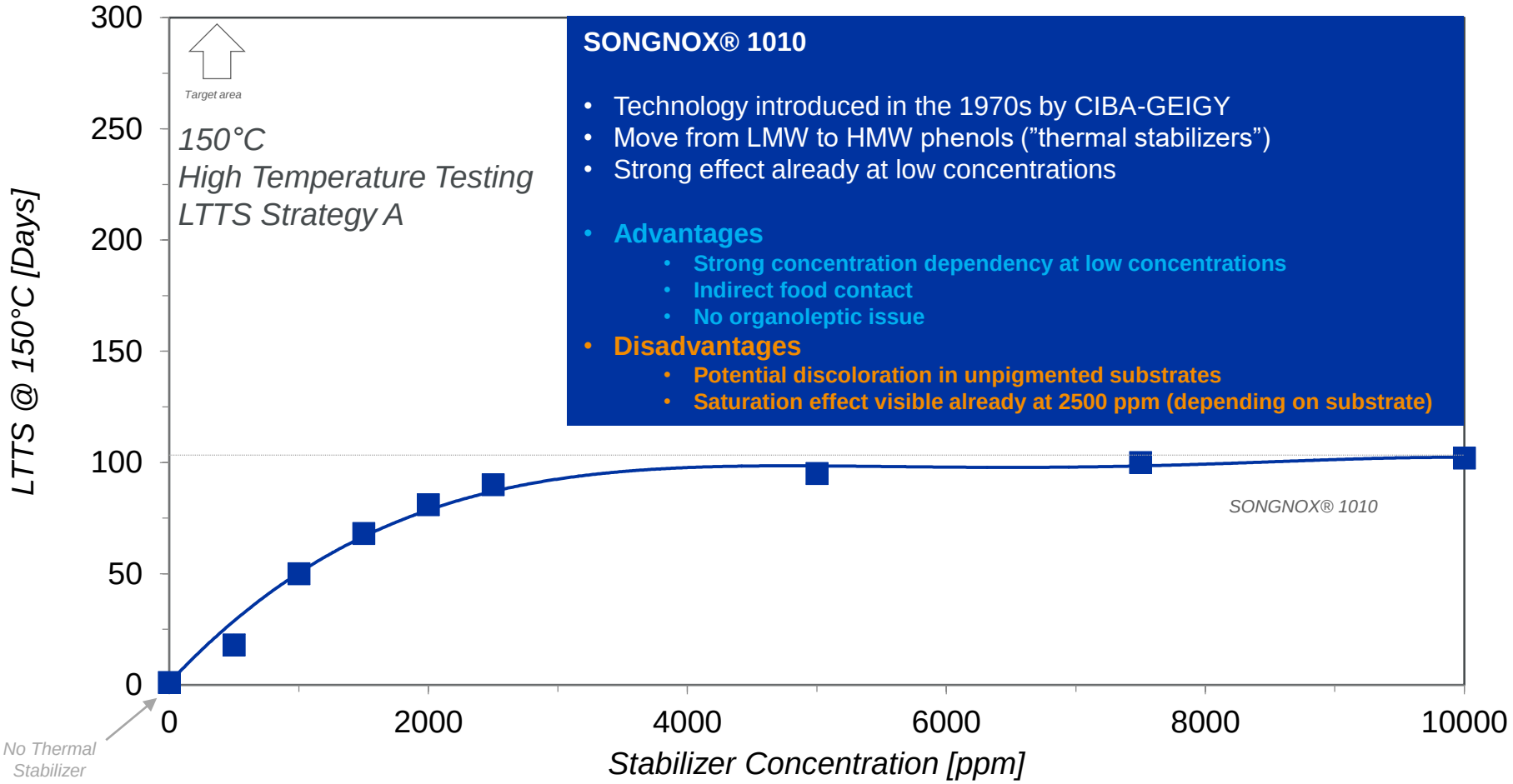
General purpose LTTS strategy



Substrate: PP homopolymer (bulk polymerization)

Criteria: Exposure at 150°C in air
Stabilizer concentration versus embrittlement time

General purpose LTTS strategy



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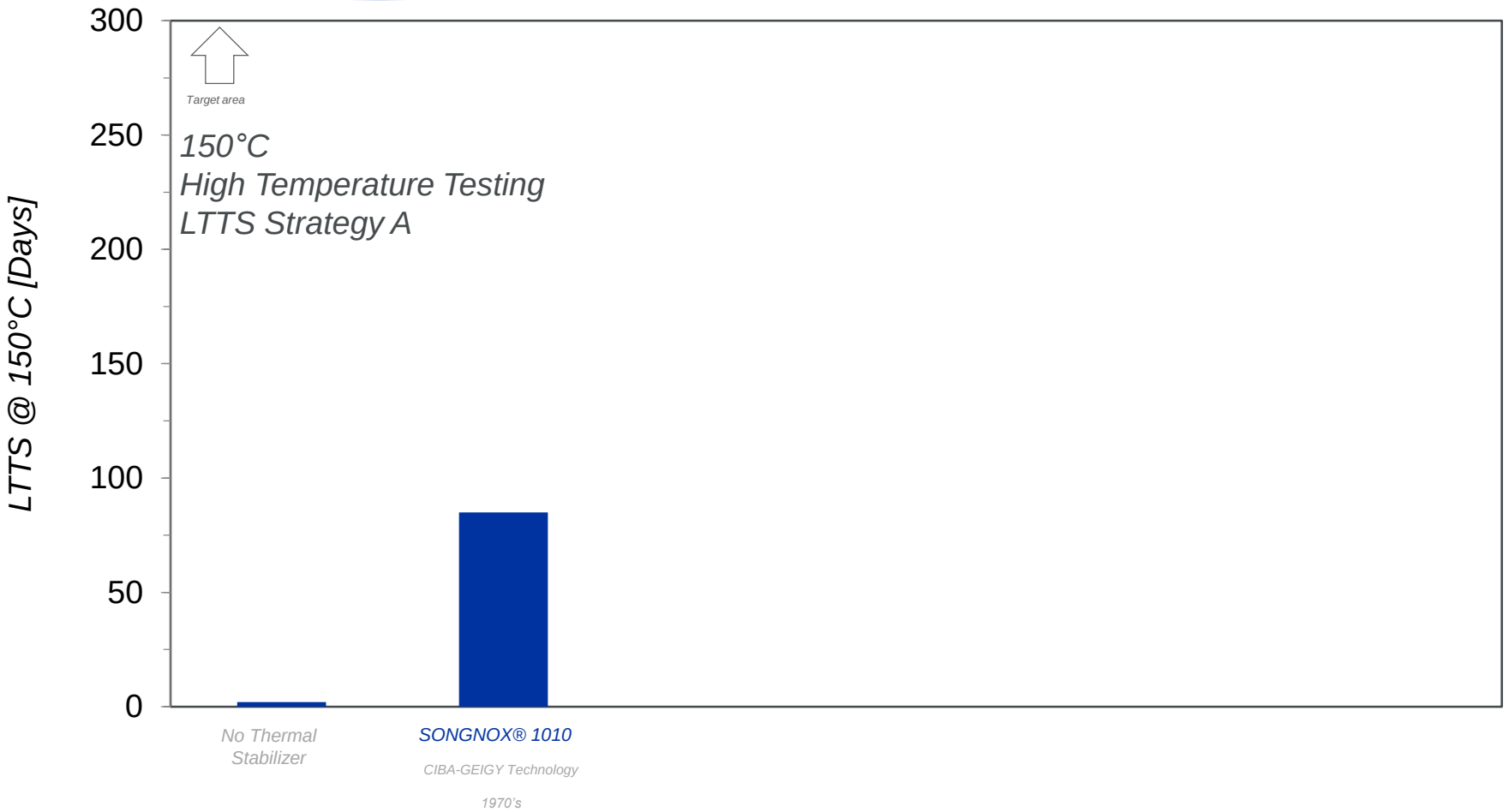

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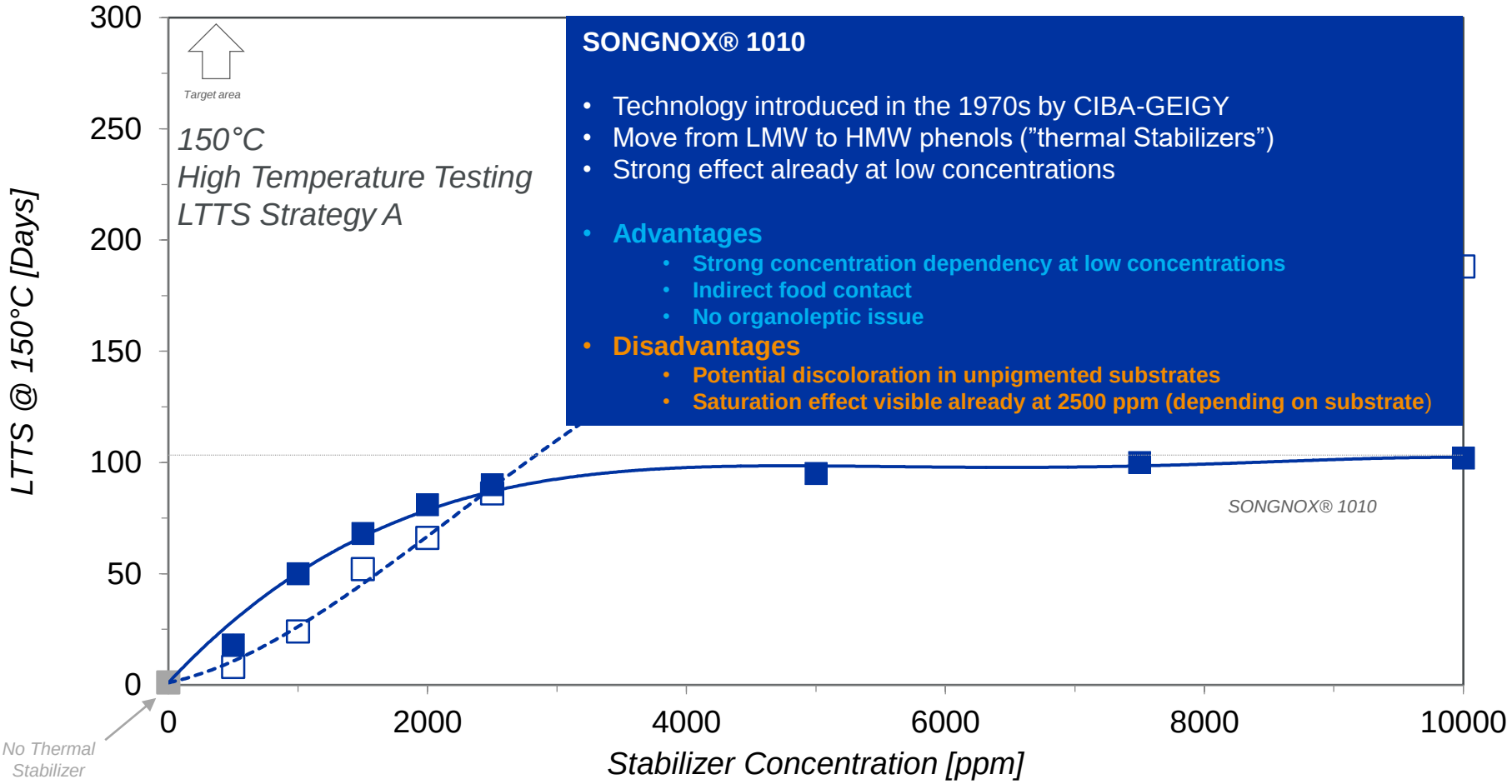

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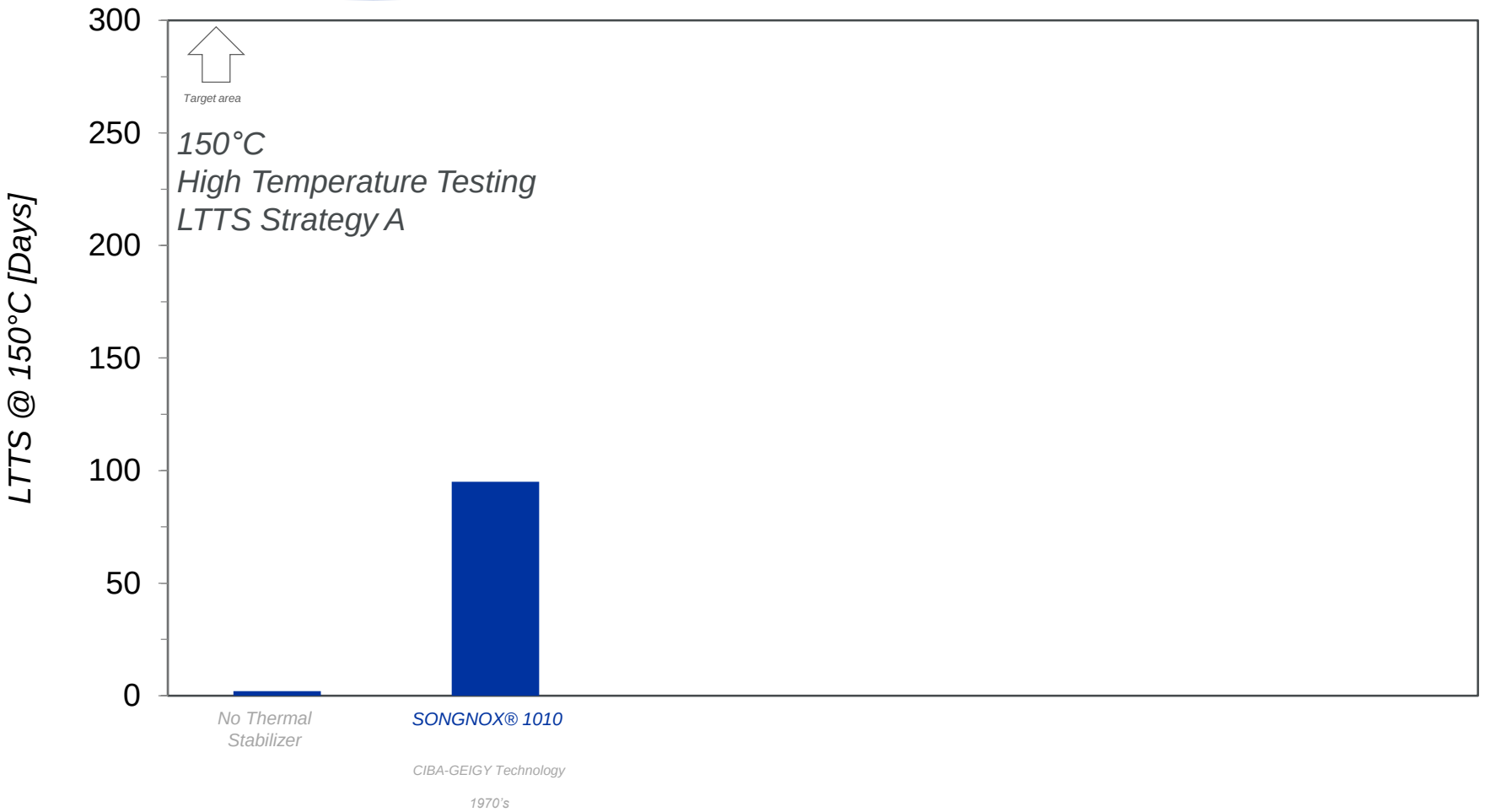

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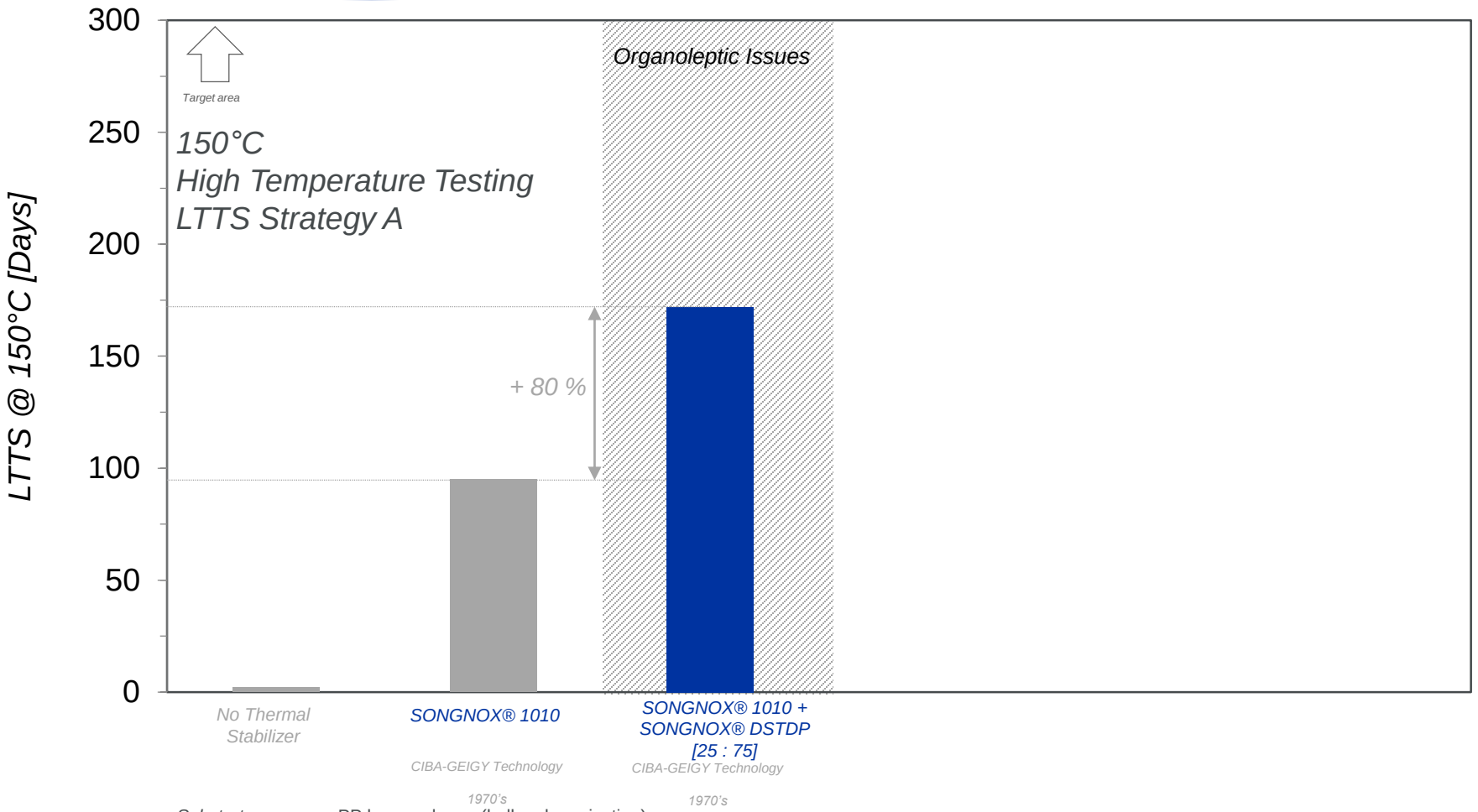

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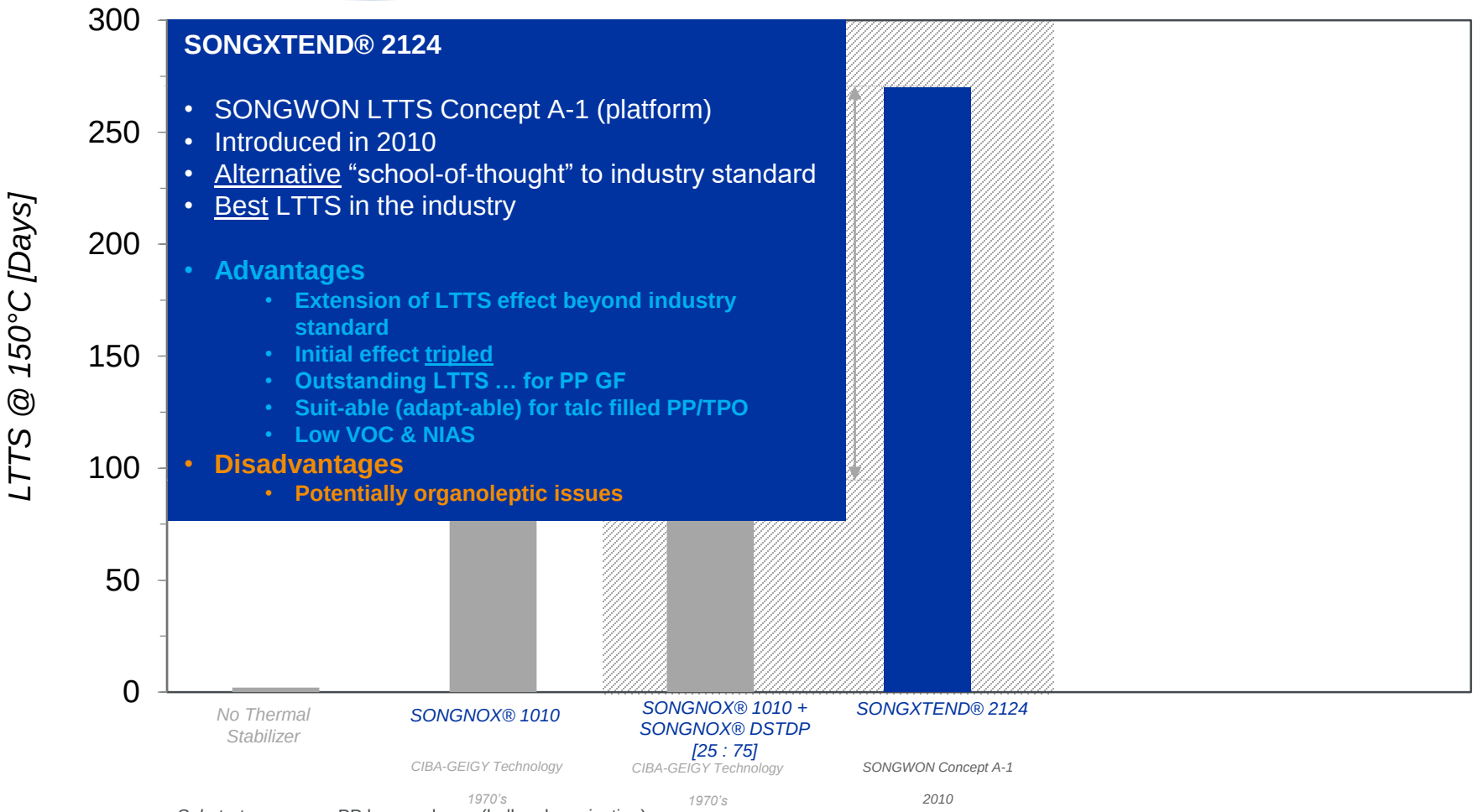

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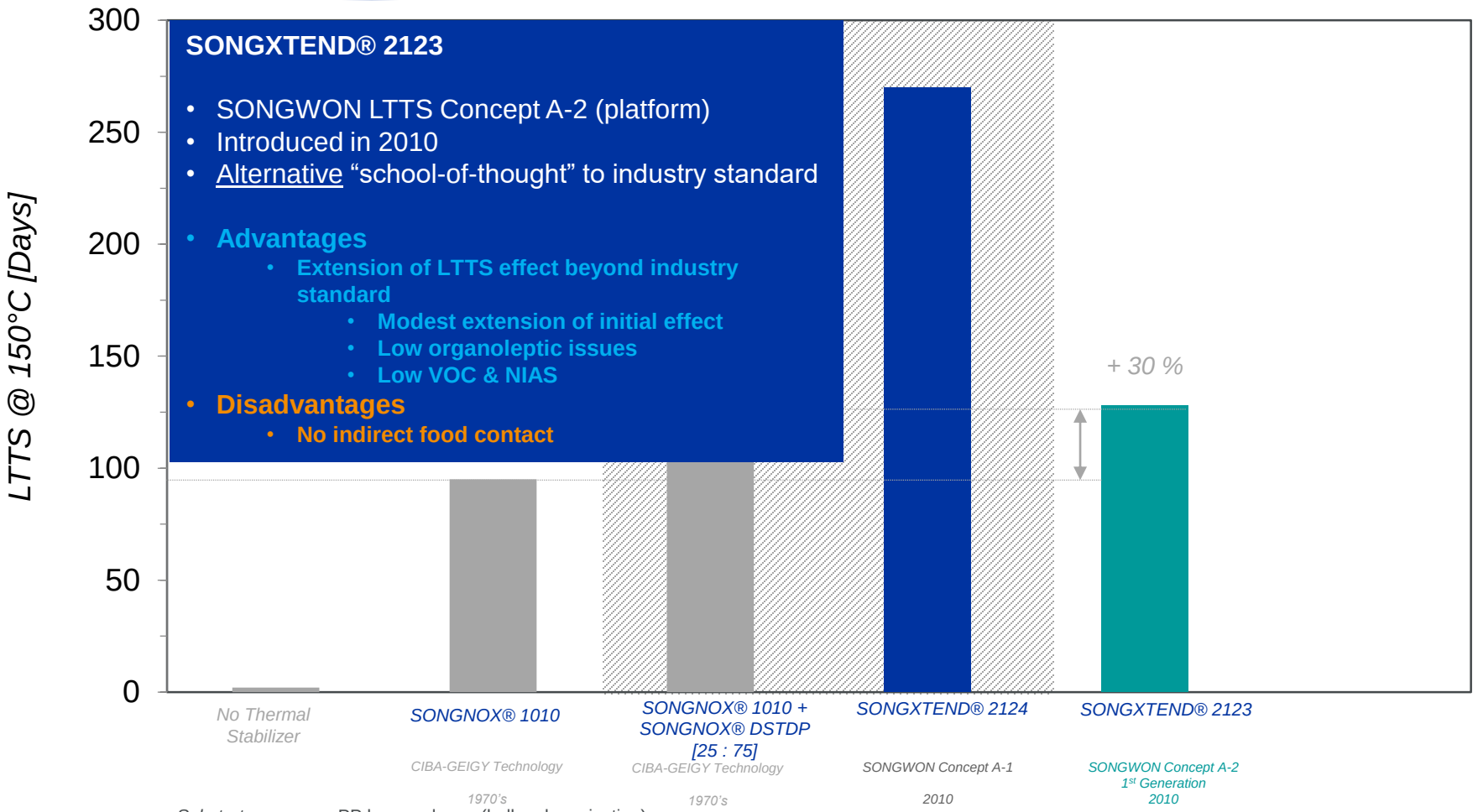

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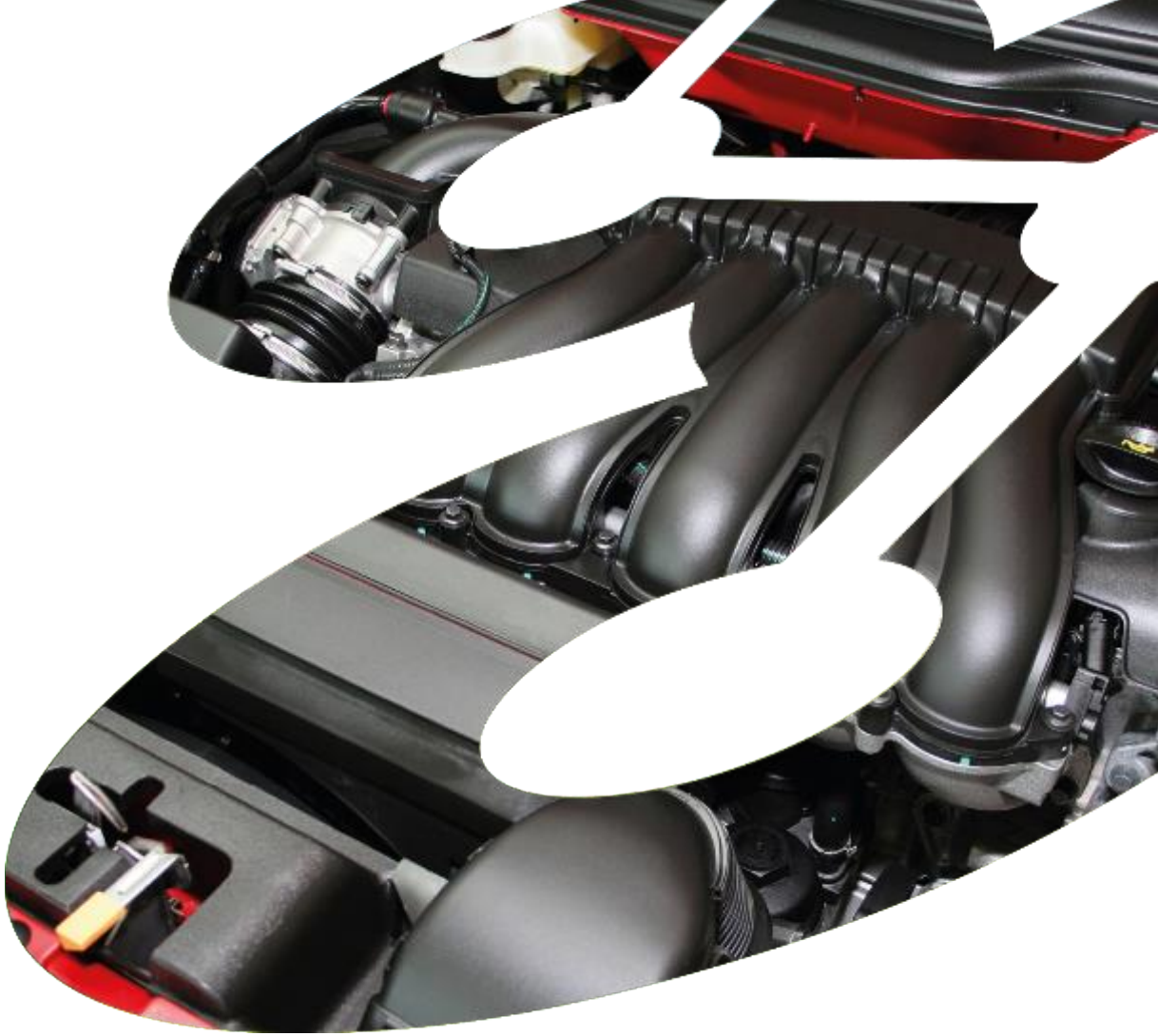
Conclusion



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Conclusion

Basic stabilization strategy for polyethylene …

[hindered phenol + phosphite]

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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

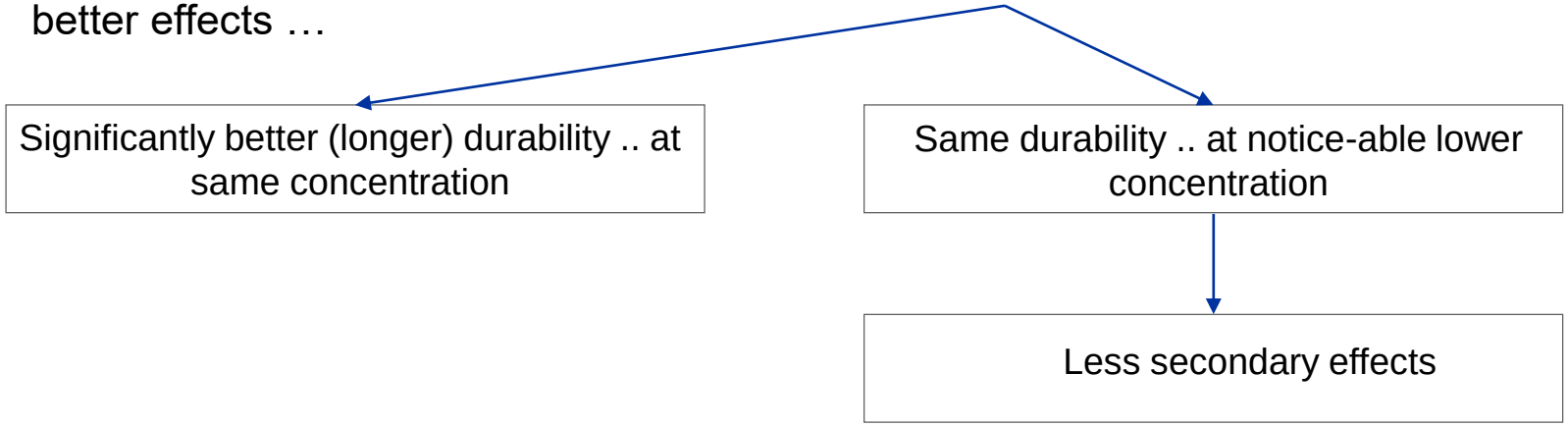
Higher end processing stabilization of PE …

- 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 …



- SONGWON has developed alternative approaches

Thank you for your attention

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