Improved UV stabilization with hydroxybenzoates for polyolefins

September 23, 2022

JungDu Kim, Heejung Kwon &
Thomas Schmutz

It's all about **the chemistry™**

SONGWON

Content

- About SONGWON Industrial Group
- Background and objectives
- Auto-oxidation cycle and light stabilizers
  - Filter – absorption mechanism
  - Radical scavenging mechanism
  - Hydroxybenzoates
- Hydroxybenzoates in polyolefins
- Conclusions

About SONGWON Industrial Group

- Founded in 1965, SONGWON is **headquartered in Ulsan, South Korea** and operates group companies all over the world.

- SONGWON is **100% dedicated** to additives and the 2nd largest producer of polymer stabilizers worldwide.

- Our clients benefit from a **global framework** combined with readily accessible local organizations, including customer service offices and technical support centers in numerous countries.

No.1 Maeam Plant

Production expertise and consistent quality

Our customers benefit from:

- **Large capacity** & flexible approach
- **Fully integrated** manufacturing processes for SONGNOX® 1076, SONGNOX® 1010 and SONGNOX® 1680 antioxidants
- **Long-term relationships** with strategic suppliers
- **100% commitment** to our additives business and to continuous process optimization

Value focused

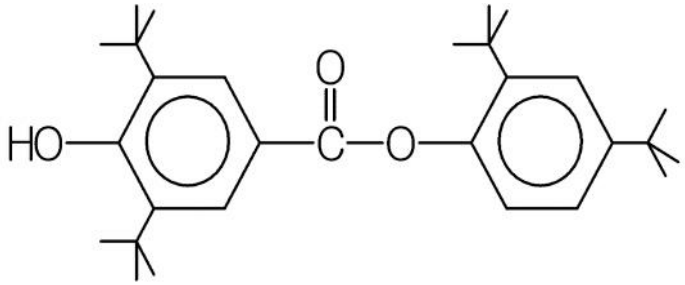
Global quality consistency, manufacturing excellence, backward integration and economy of scale

Hydroxybenzoates

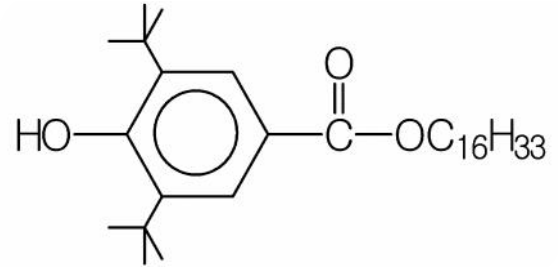
Production expertise and consistent quality

Our customers benefit from:

- **Dedicated production line** for SONGSORB® 2908 and SONGSORB® 7120 hydroxybenzoates
- **Fully integrated** manufacturing processes



SONGSORB® 7120



SONGSORB® 2908

Content

Background and Objectives

Background

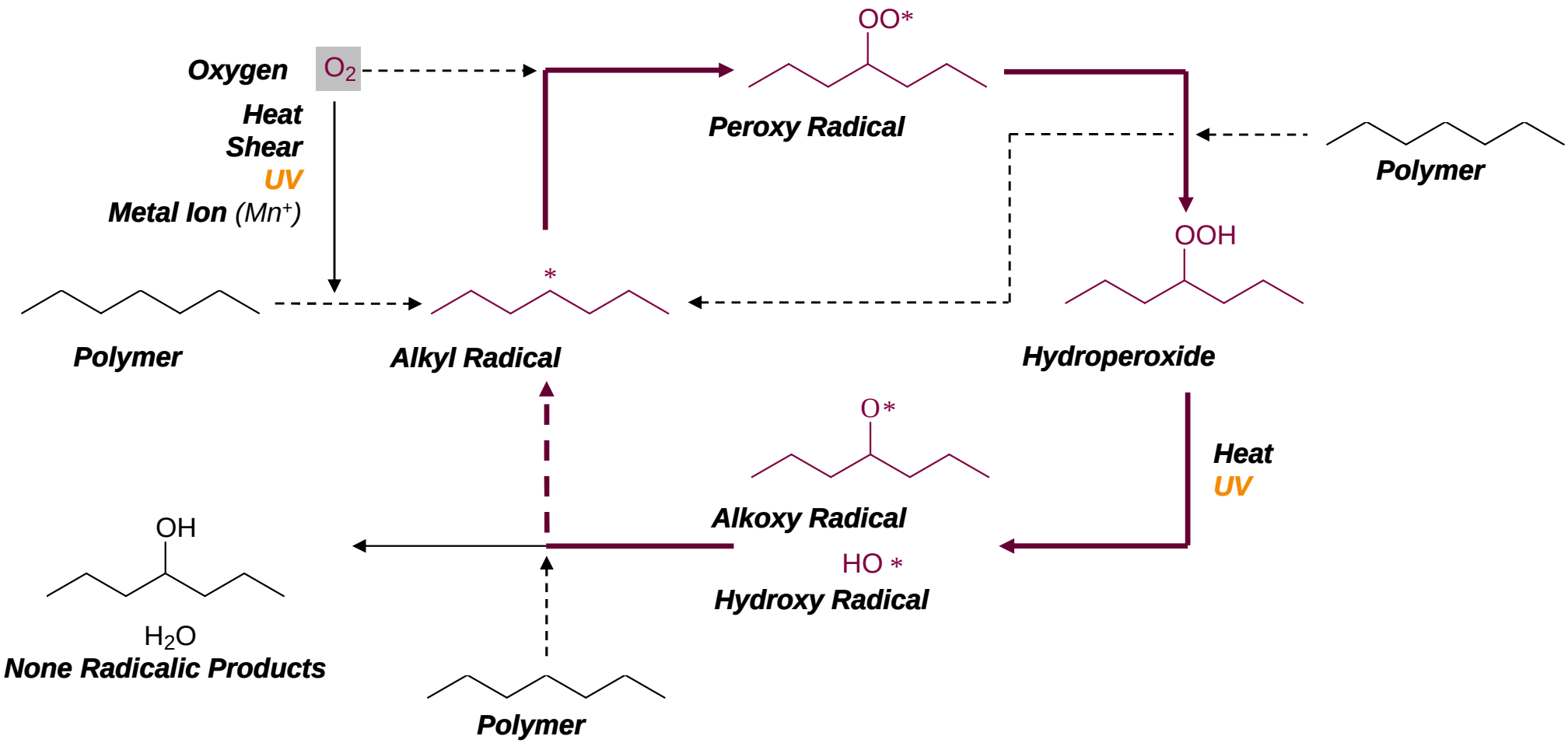
- SONGWON presented “Hydroxybenzoates as UV stabilization strategies for polyolefins” in the 2008 polyolefin conference. This is a continuation of the background and gives commercial examples in specific applications.
- Hydroxybenzoates (HB) type light stabilizers, such as SONGSORB® 2908 & SONGSORB® 7120 are special and can act as both radical scavenger and UV screener (UV absorber (UVA)) to protect polyolefins.

Objectives

- This presentation overviews light stabilization and use of HB in combination with hindered amine light stabilizers (HALS) for polyolefins.
- We intend to emphasize hydroxybenzoates as an alternative to overcome limitation of classical light stabilization systems in specific applications.

Content

Simplified Auto-oxidation Cycle of Polymers



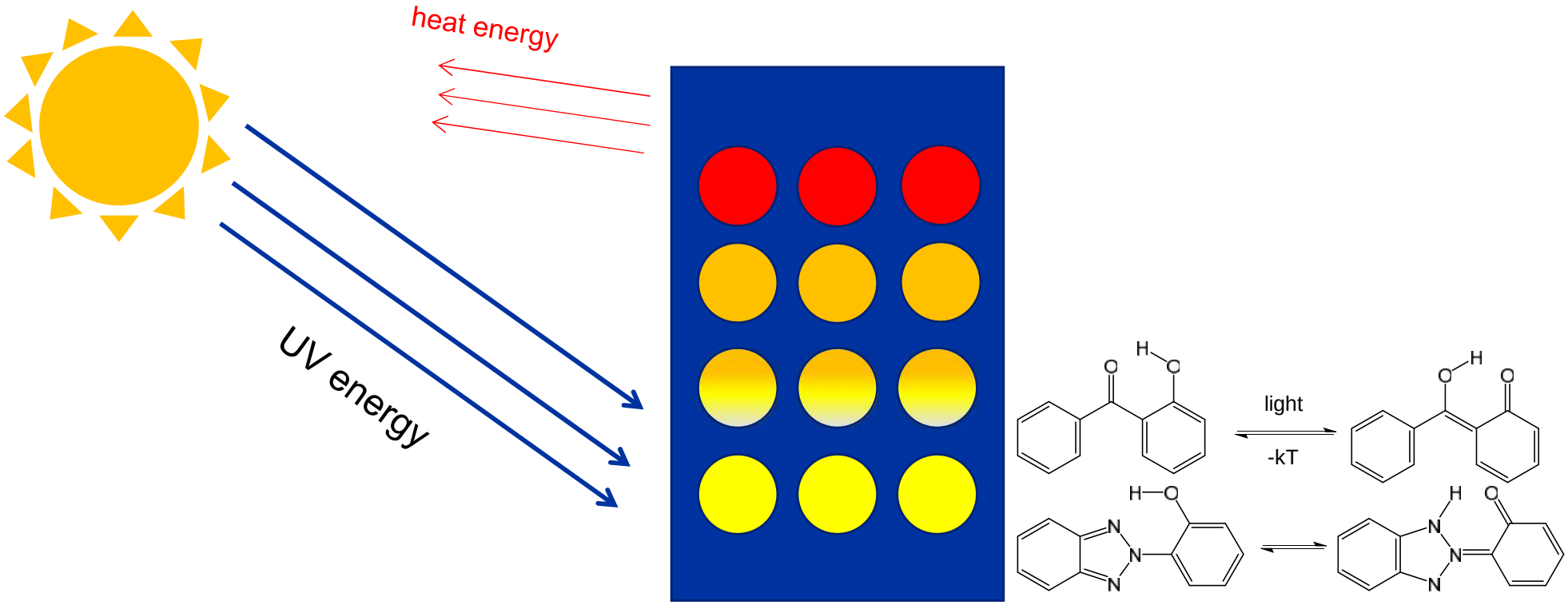
Inhibition of Photo-oxidation with Light Stabilizers

Light stabilizers by functionality

- **Filter – absorption mechanism**
  - Benzophenones, benzotriazoles, HB, hydroxyphenyl triazines & other UVAs
- **Free radical scavenging mechanism**
  - HALS
  - HB

Filter – Absorption Mechanism
UV Absorbers

Mechanism

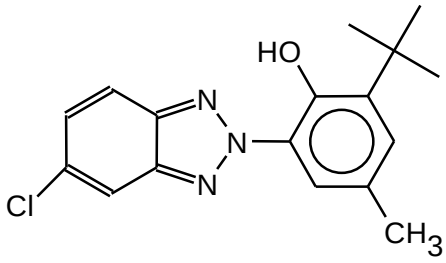


UVA absorbs harmful UV radiation instead of the chromophoric groups in the polymer.

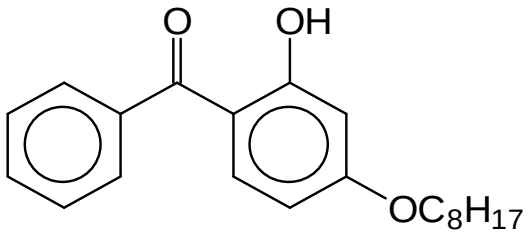
Absorbed radiation is dissipated as heat into the polymer matrix.

Filter – Absorption Mechanism
UV Absorbers

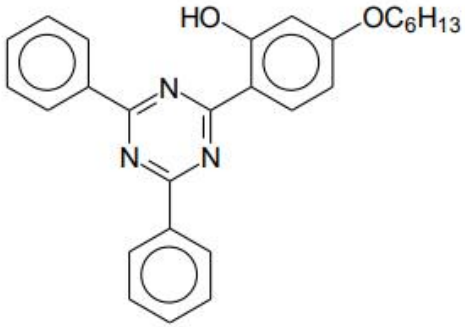
5 different types of UVAs



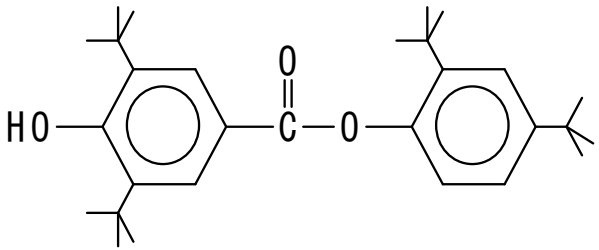
SONGSORB® 3260
HBZ-1 (Benzotriazole)



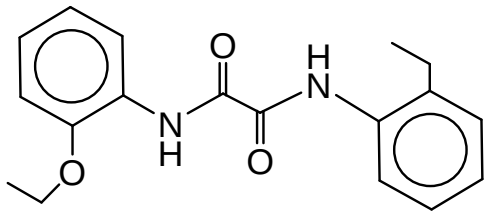
SONGSORB® 8100
HBP-1 (Benzophenone)



SONGSORB® 1577
(Triazine)



SONGSORB® 7120 HB-1
(Hydroxybenzoate)



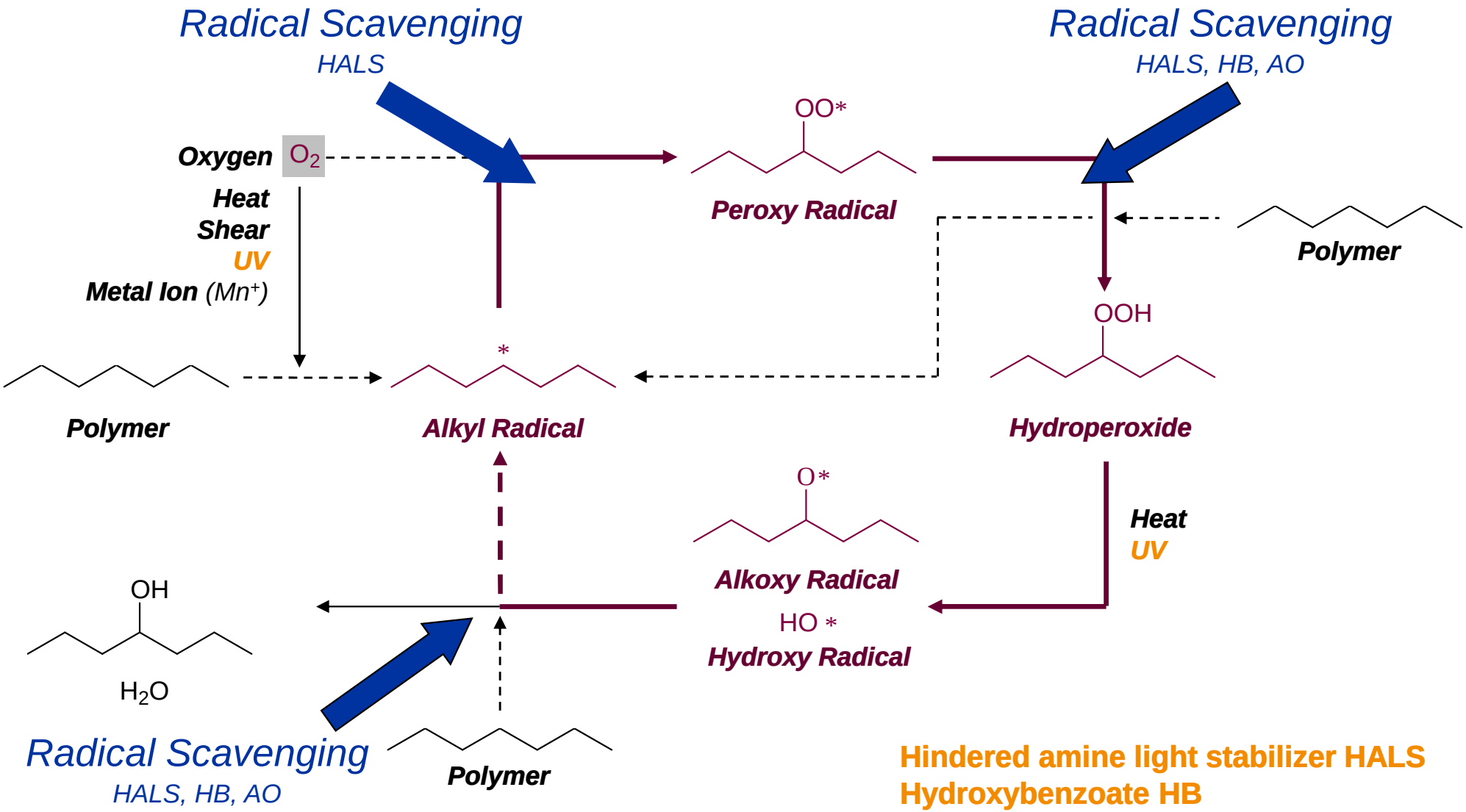
SABOSTAB® UV 312
(Oxanilide)

Filter – Absorption Mechanism
UV Absorbers

UV absorbers

- Protection of bulk (mechanical properties) of polymer in thick section applications
- Limited protection of surface & thin sections (high surface to volume ratio, film and fiber, e.g., < 100micron)
- Protection of content (packaging)
- Protection of other additives in thick sections (e.g., organic pigments)
- Less effective in polyolefins
- SONGSORB® 8100 benzophenone UVA has better compatibility with PE
- SONGSORB® 3260 benzotriazole UVA is more effective in polyolefins
- Triazine UVA (UVA 1164) can be an alternative to a benzotriazole UVA with a regulatory issue
- Very effective in UV absorbing substrates (e.g., styrenics, polycarbonate and polyesters)

Radical Scavenging Mechanism

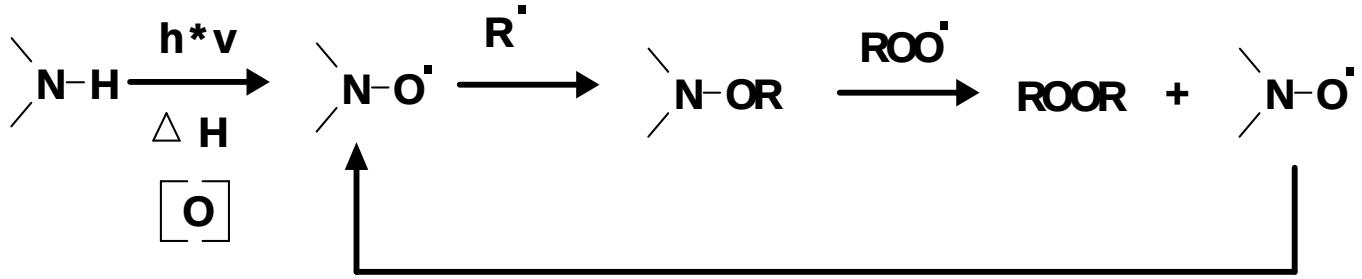


Hindered amine light stabilizer HALS
Hydroxybenzoate HB
Antioxidant AO

Radical Scavenging Mechanism
HALS

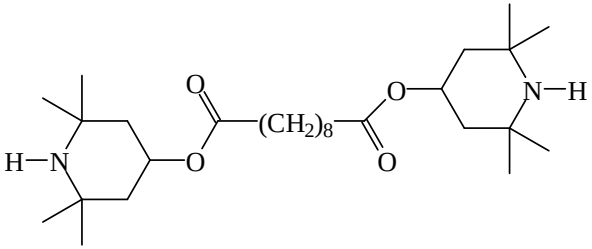
Hindered amine light stabilizers (HALS) - basic principles

- Function via free radical scavenging mechanism
- Through light exposure, nitroxyl radicals are generated trapping carbon centered radicals and peroxide radicals. Active unit is recycled; hence, highly effective

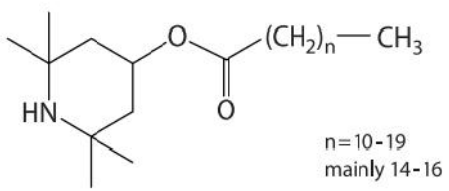


- Differentiated according to physico-chemical features:
  - Substitution of the amine group (secondary HALS, tertiary HALS, N-OR HALS)
  - Molar activity
  - Melting range
  - pKa value (alkalinity)
- Sensitive to acidic, sulphur, and bromine (FR) containing species

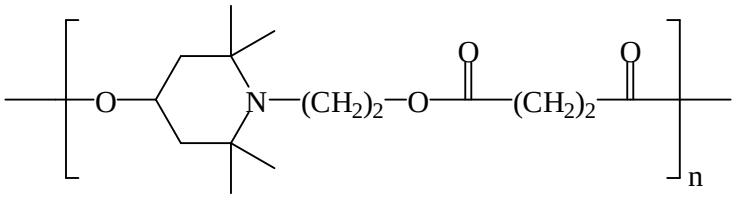
Radical Scavenging Mechanism
HALS



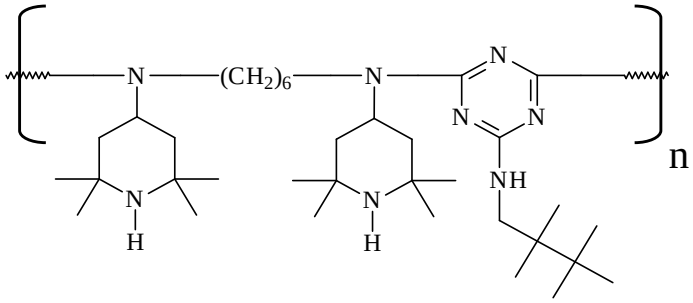
SABOSTAB® UV 70
Low molecular weight (LMW)
Secondary HALS-1



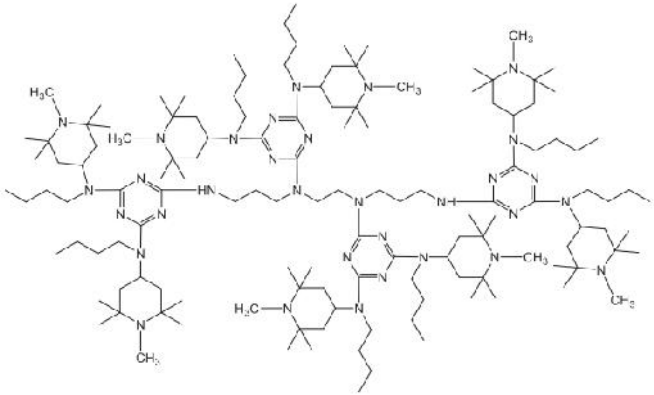
SABOSTAB® UV 91
LMW secondary HALS-5



SABOSTAB® UV 62
Polymeric, high molecular weight (HMW)
Tertiary HALS-3



SABOSTAB® UV 94
Polymeric, HMW
Secondary HALS-2



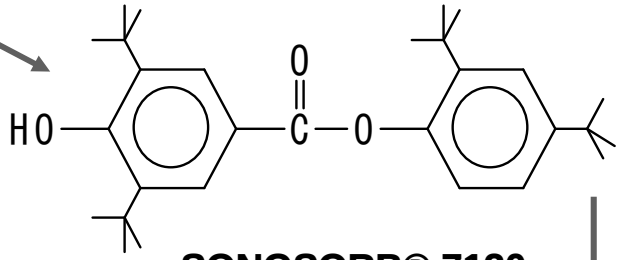
SABOSTAB® UV 119
HMW Tertiary HALS-4

SABOSTAB® UV 65, SABOSTAB® UV 40, SABOSTAB® UV 78

Radical Scavenging Mechanism
HB

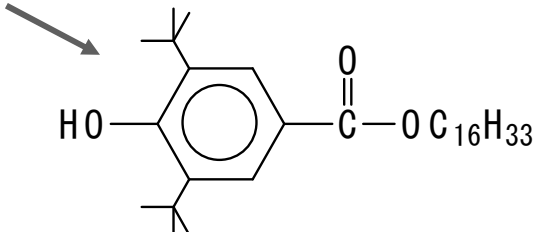
Hydroxybenzoates (HB)

Phenolic group



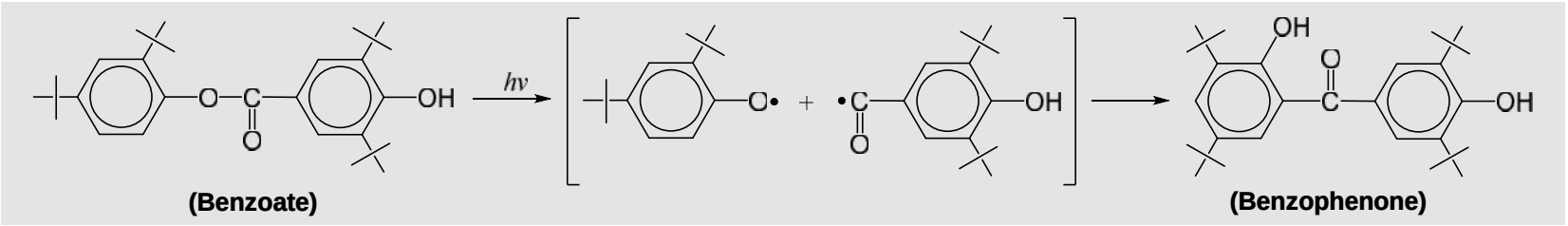
SONGSORB® 7120
(HB-1)

Phenolic group



SONGSORB® 2908
(HB-2)

Chemical rearrangement



(Benzoate) **(Benzophenone)**

- SONGSORB® 2908 has “high” solubility in polyolefins and offers better compatibility & low blooming.
- SONGSORB® 7120 has a broader UV absorption spectra as a benzophenone type after chemical rearrangement in UV exposure and can be discoloring.

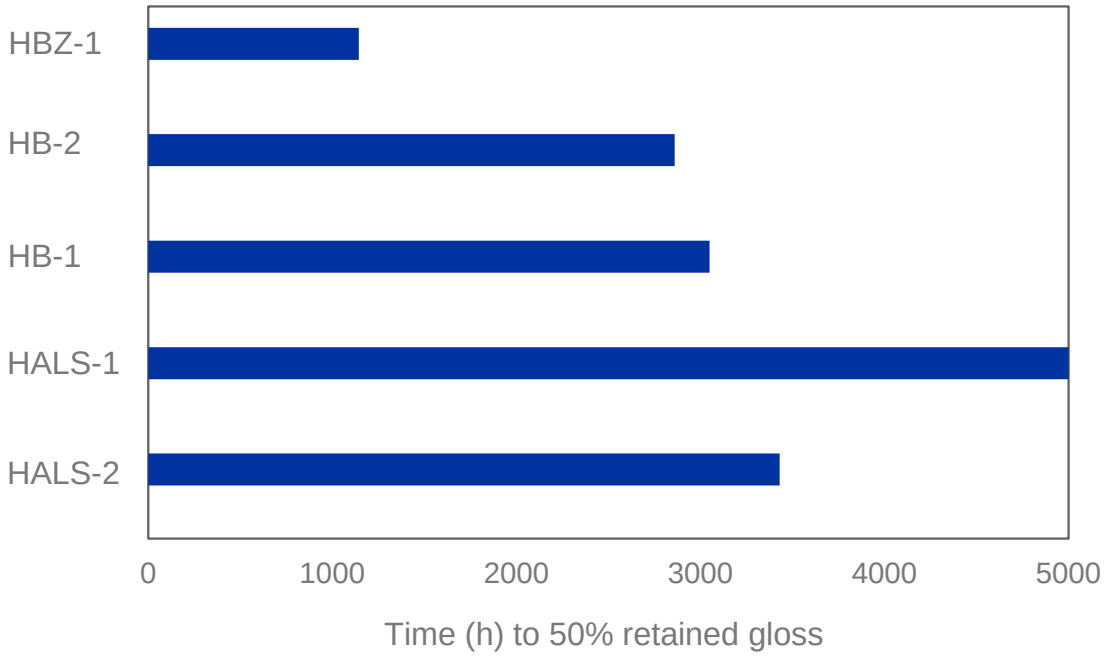
Radical Scavenging Mechanism
HB

- Non-basic, free radical scavengers (with phenolic group) under UV conditions
- Efficacy as radical scavengers second only to HALS (although inferior)
- Absorption spectra at short wavelength (< 300 nm)
- Non-yellowing (do not absorb in visible regions)
- Not adversely affected by thiosynergists
- Synergism with HALS
- Offer indirect food contact registrations in polyolefins

Content

Hydroxybenzoates in Polyolefins

Single stabilizer system / gloss

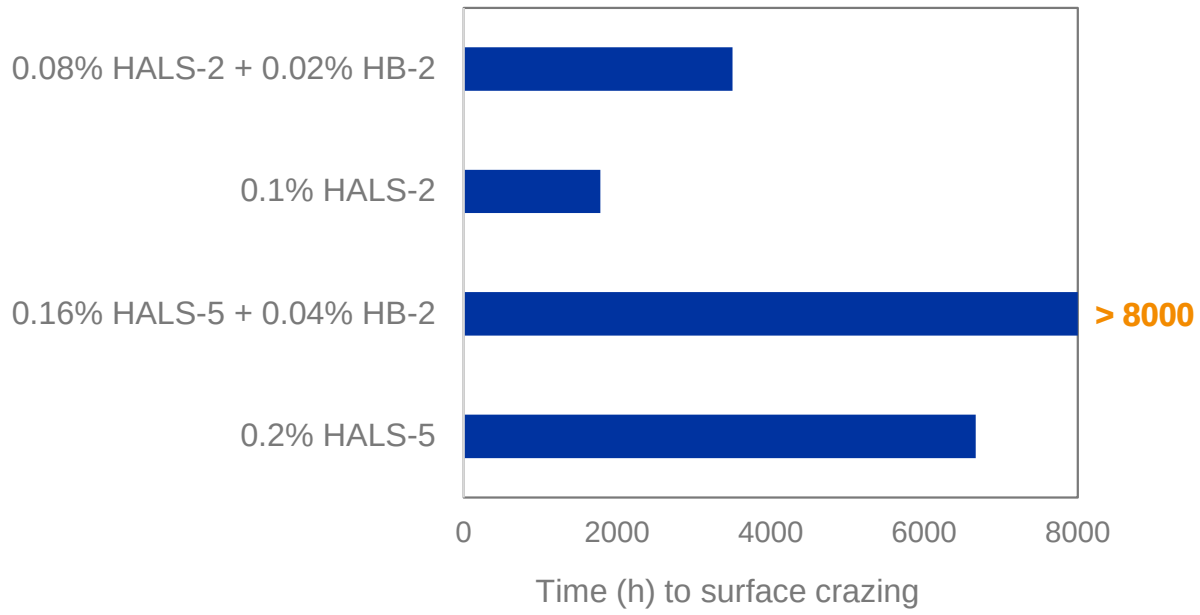


Substrate:	PP homopolymer (unpigmented)	*Stabilization:*	0.15% SONGNOX® 1680 + 0.05% Ca-stearate
Sample:	3.0 mm IM plaques		+ 0.20% UV stabilizers
Exposure:	WOM Ci65; ASTM G155 Cycle1(excluding rain cycle)		
Criterion:	Time (h) to 50% retained gloss (60°) , ADP#08-001		

HALS is the most powerful UV stabilizer in PP

Hydroxybenzoates in Polyolefins

[HALS + HB] / surface crazing



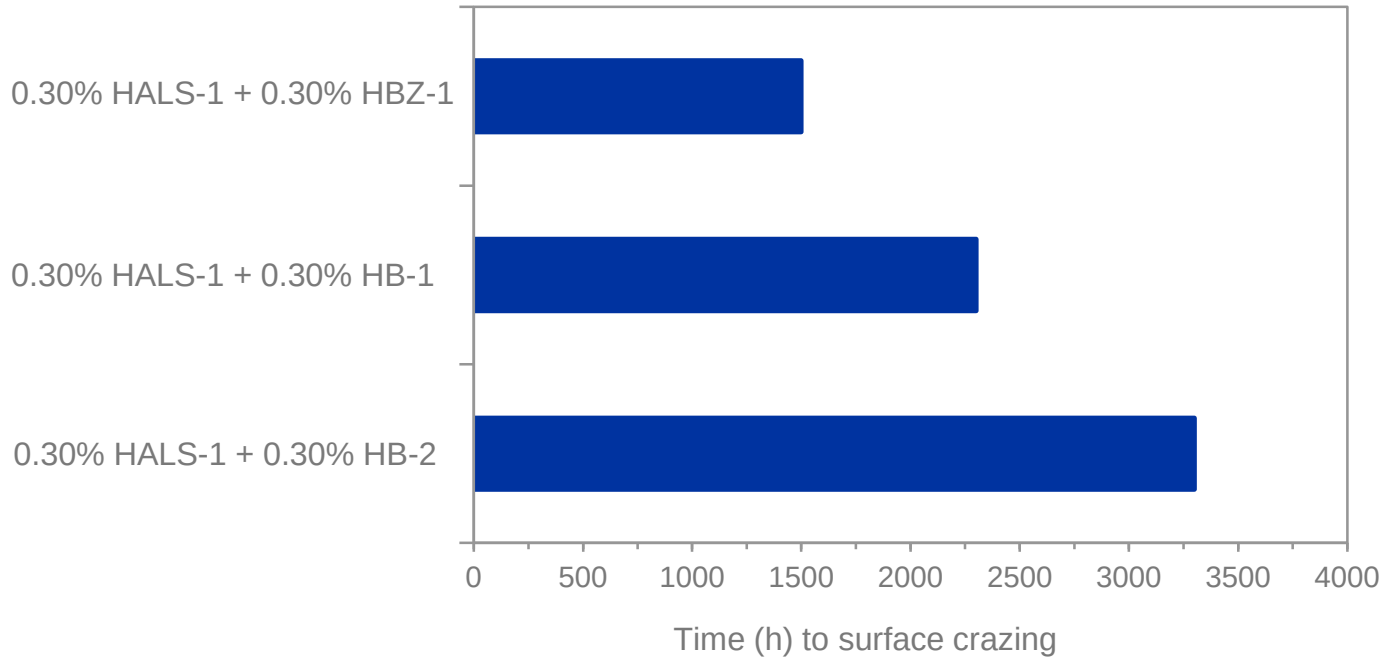
Substrate: PP homopolymer (unpigmented)
Sample: 3.0 mm IM plaques
Exposure: WOM Ci 4000; ASTM G155 Cycle1(excluding rain cycle)
Criterion: Time (h) to surface crazing, ADP#08-001

Stabilization: 0.15% SONGNOX® 1680 + 0.05% Ca-stearate + 0.20% UV stabilizers

[HALS + HB] shows strong synergistic behavior in terms of surface property

PP/TPO Automotive

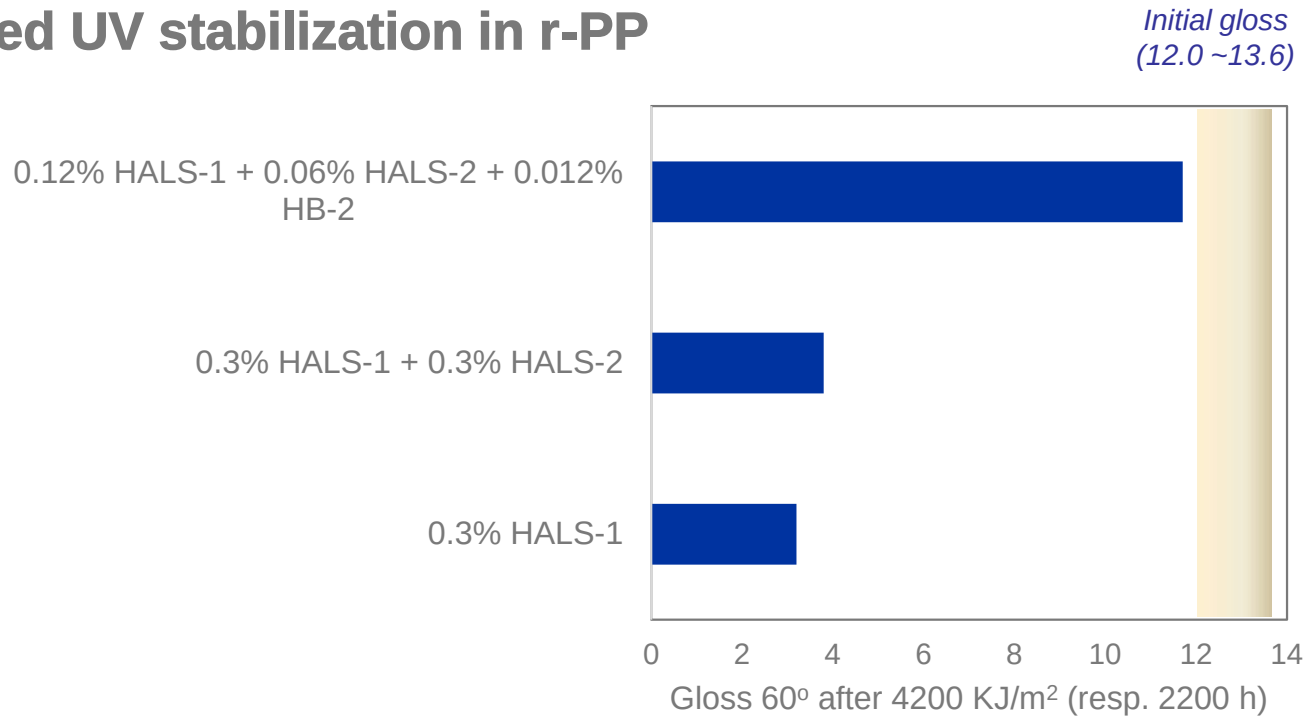
Good surface protection



Substrate:	Ethylene-propylene-copolymer	*Stabilization:*	0.20% Ca-stearate + 0.20% SONGNOX® 1010 + 0.20% P-9
Sample:	2 mm plaques		
Exposure:	WOM Ci65; ASTM G155 Cycle1(excluding rain cycle)	*Pigmentation:*	Blue
Criterion:	Time (h) to surface crazing [$t_{crazing}$]		

[HALS + HB] is more efficient than [HALS + benzotriazole UVA] in PP/TPO compounds

Improved UV stabilization in r-PP



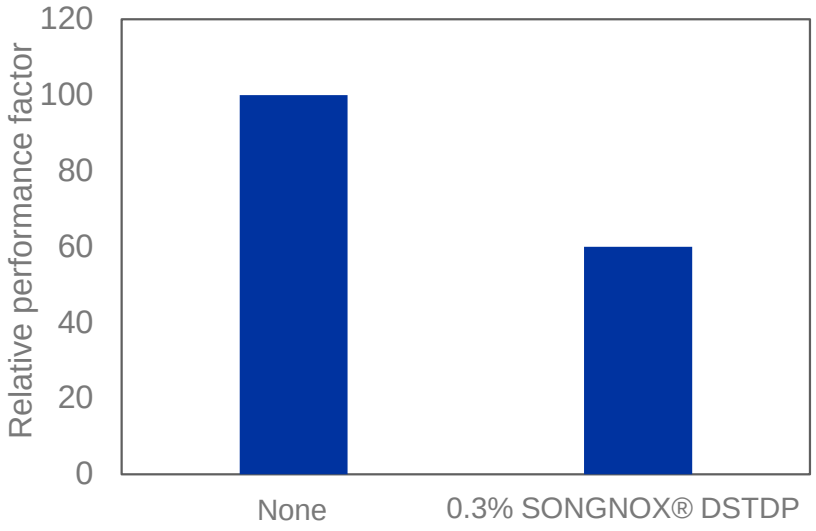
Substrate: r-PP
Sample: 2 mm plaques
Exposure: WOM according to ISO 4892-2,ADP0#9-008

Pigmentation: Black
Criterion: Gloss 60° after 4200 KJ/m²

[HALS + HB] synergistic combination provides excellent UV stability in r-PP compounds

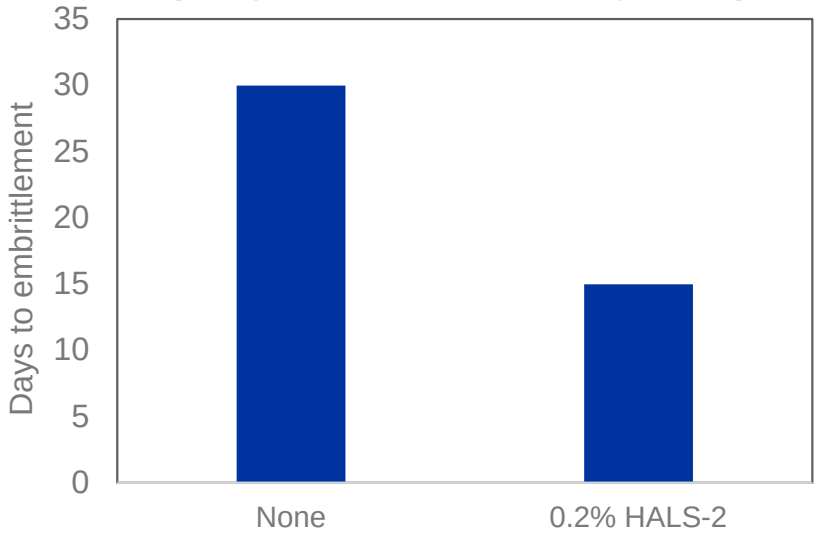
Less antagonism between HALS with other additives

Interaction between HALS and thioster (UV stability)



Substrate: PP, Injection plaques
Exposure: WOM
Stabilization: 0.15% HALS-1 + base antioxidants
Criterion: Relative factor

Interaction between HALS and phenolic AO (Long-term thermal stability, LTTS)



Substrate: PP, Injection plaques
Exposure: 150 °C Oven
Stabilization: 0.15% SONGNOX® 21B
Criterion: Embrittlement (days)

HALS can interact with other stabilizers, and it can be partially replaced by HB, yields better UV stability and LTTS

PP/TPO Automotive

[HALS + HB] vs. other stabilization concepts (HALS, HALS+UVA)

- Improved surface protection (gloss, delta E, crack and gray scale)
- Reduced (negative) secondary effects (gas fading, blooming & fogging)
- Substitution of UVA (as benzotriazole type UVA with regulatory issue)

[HALS + HB + long-term thermal stabilizers]

- Less antagonism with long-term stabilizers (phenolic antioxidant & thioester)
- High UV stability and high LTTS protection technically not feasible
- Good balance between UV stability and LTTS

PP/TPO Roofing Membrane

[HALS + HB] vs. other classical HALS systems

- Improved thermal and UV stability
- Reduced (negative) secondary effects (in particular gas fading in natural and light-colored applications)
- [HALS-4 + HB-2] having excellent balance between UV stability & LTTS, and good chemical resistance (e.g., acid rain)

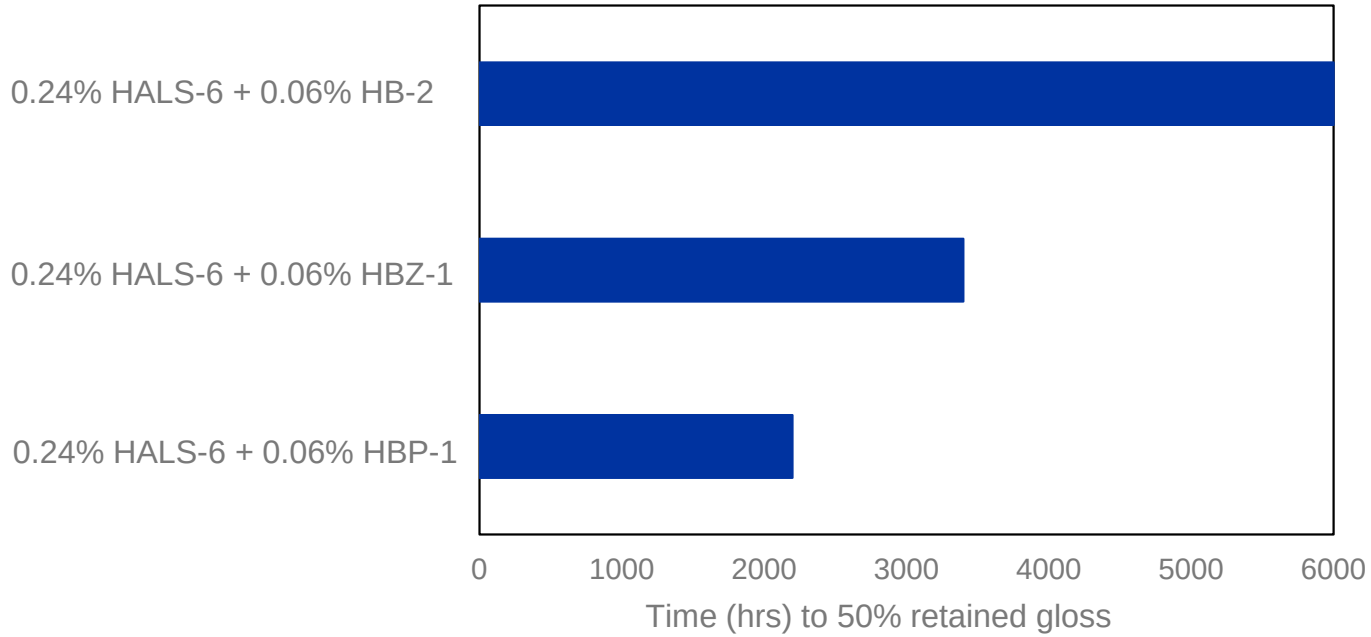
PP Film and Tape

[HMW HALS + HB] in PP thin applications

- Reduced adverse secondary effects (discoloration, gas-fading, water-carry-over (WCO) and die-build up) vs. HALS alone
- Good balance between UV stability and secondary effect
- Compliance with indirect food contact regulations

Pigmented PO Thick Section

Good surface protection in pigmented LLDPE thick section



Substrate:	LLDPE	*Stabilization:*	0.15% phenolic antioxidant + 0.10% Ca-stearate
Sample:	1mm compression moulded		HALS-6 (HMW HALS)
Exposure:	SONGWON Exposure condition B	*Pigmentation:*	green 50
Criterion:	Exposure time h until 50% retained gloss		

[HALS + HB] provides excellent UV stability in terms of surface property

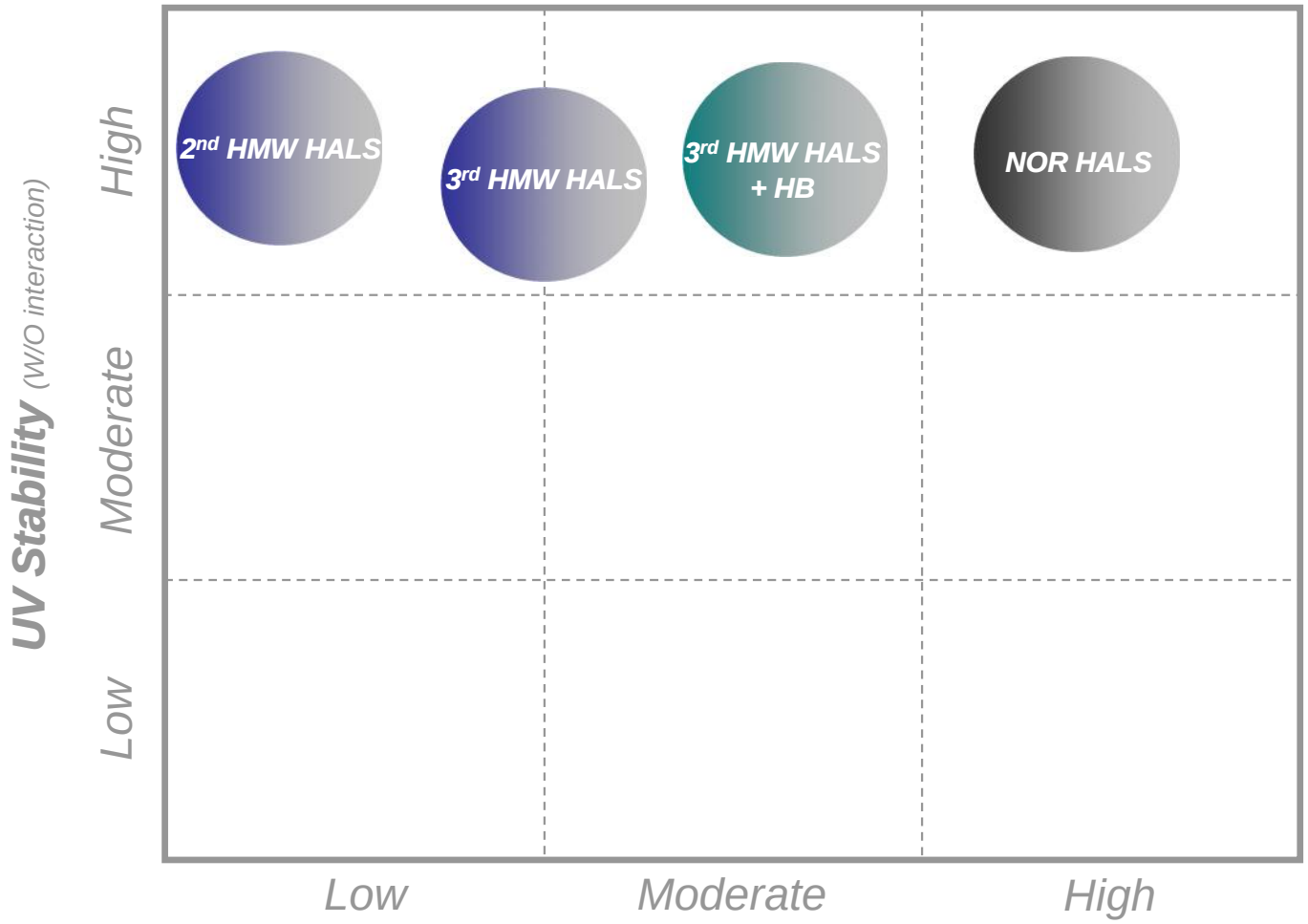
Pigmented PO Thick Section

[HMW HALS + HB] vs. other stabilization concepts in pigmented PO thick section

- Strong synergistic effect of HALS with HB vs. HALS alone and [HALS + other UVA classes]
- Improved surface protection and better color stability
- Compliance with indirect food contact regulations (vs. LMW HALS)
- Case by case assessment

PE Greenhouse

[3rd HMW HALS + HB] in PE greenhouse



+ UVAs (Benzotriazole, Benzophenone or Triazine)

PE Greenhouse

Less antagonism with agrochemicals in greenhouse

- Alkaline HALS (2nd HALS) shows antagonism with agrochemicals
- High UV stabilization with agrochemicals not possible (2nd HALS)
- [HMW HALS + HB] shows synergistic effect and has less antagonism with agrochemicals
- [3rd HMW HALS (HALS-4) + HB-2] can be used as a substitution for non-basic HALS system and other solution packages in greenhouse film under certain level of agrochemicals
- Better cost performance vs. NOR HALS (when technically feasible)

Content

Conclusions

- UV stabilization and the strategies were reviewed in polyolefins
- Overall, HALS is the most efficient single UV stabilizer class for polyolefins
- However, HALS alone is not an adequate choice in various applications
- Several alternative strategies where HALS were partially replaced by other UV stabilizer classes, including HB's, yielded significantly better UV protection

- Hydroxybenzoates, SONGSORB® 7120 and SONGSORB® 2908
  - Free radical scavenger
  - Not alkaline (unlike most HALS)
  - Superior efficacy and alternative concepts vs. "UV absorber" in specific applications
  - Strong synergism with HALS (primary effect)
  - Excellent surface protection
  - Partial substitution of HALS (reduced adverse secondary effects)

Thank you for your time and interest

Thomas Schmutz

Leader Global Technical Service,
Testing & Application Development

Thomas.Schmutz@songwon.com

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.