

Superior Weathering Solution for PO-Based Automotive Parts Using Advanced Hindered Amine Light Stabilizers



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Amfine Chemical Corporation

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● Introduction

- PP degradation and stabilization
- Function of HALS as Light stabilizer

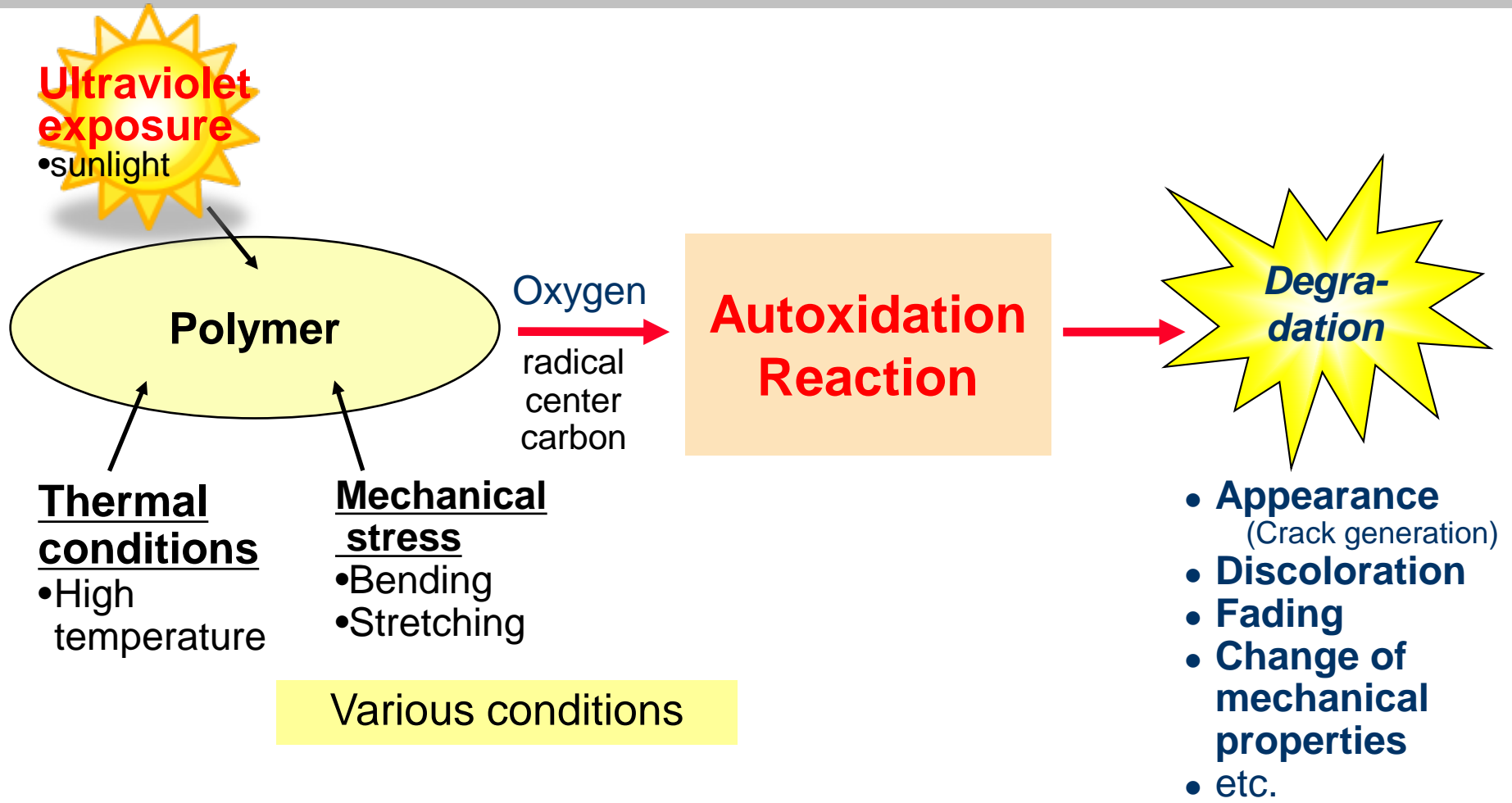
● Advanced HALS technologies in automotive parts

- Light stabilization of hard application
- Suited HALS system for soft application(TPE)

● Summary & Conclusions

Introduction

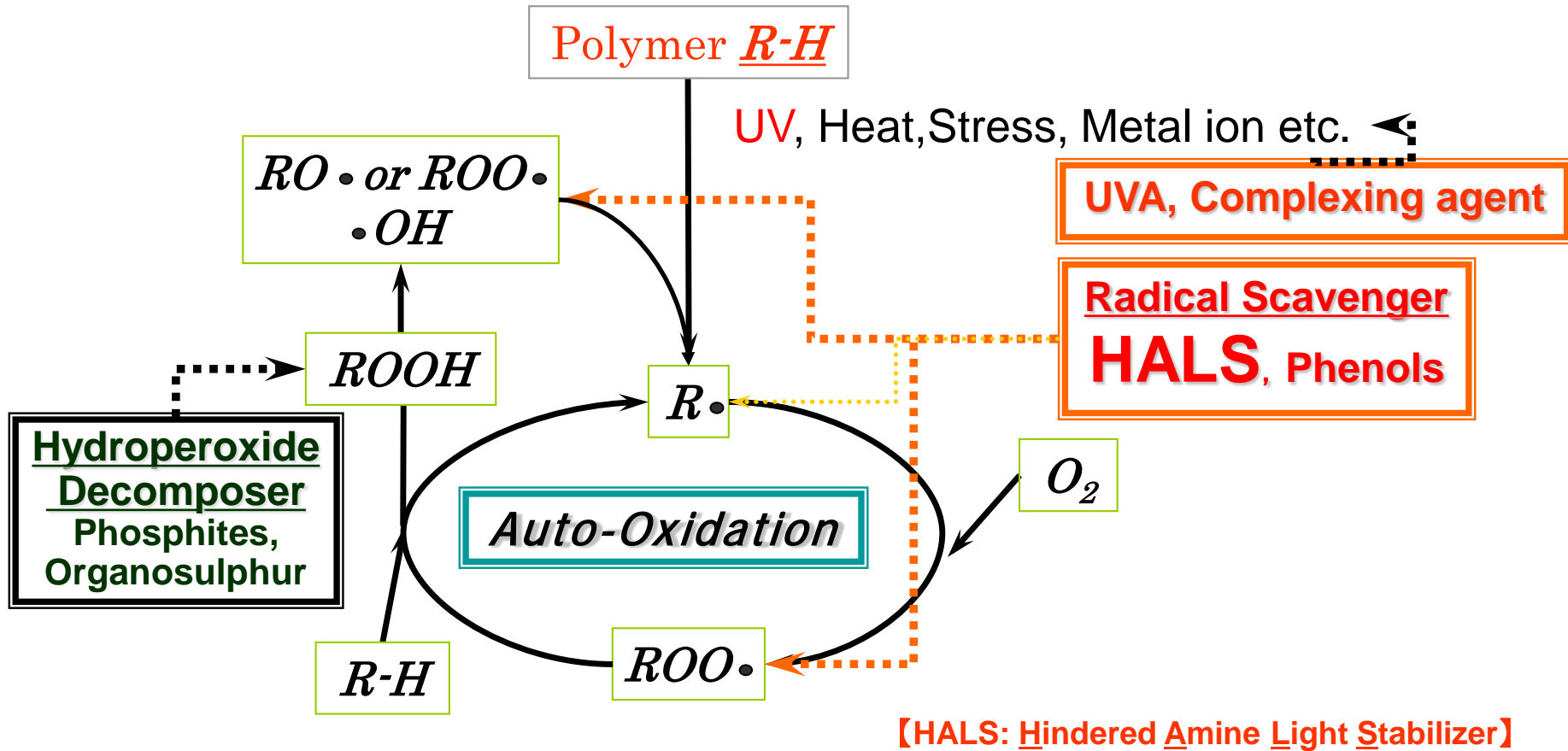
Degradation of Polymer



Various conditions

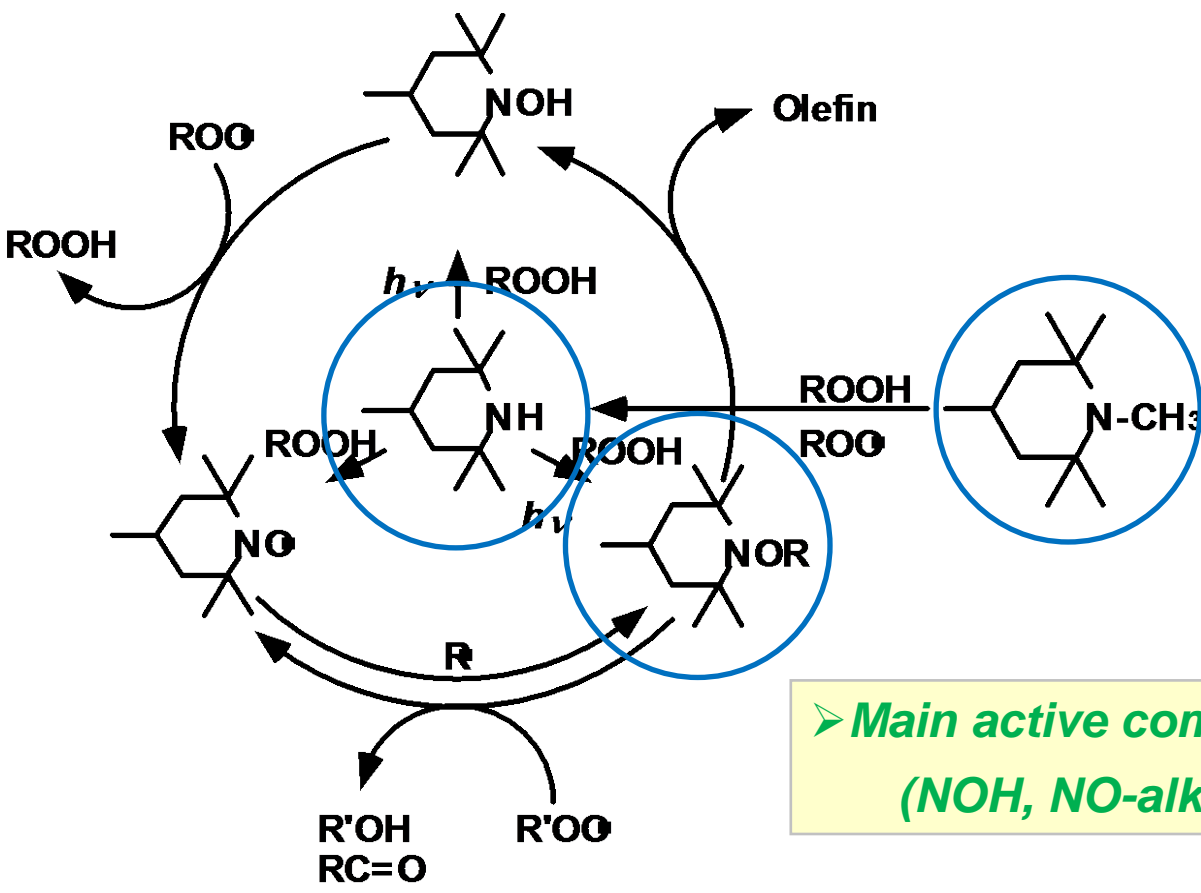
✓ Unstabilized polymer degrades easily under various conditions and the addition of antioxidants and light stabilizers is indispensable for long term utilization

Polymer Degradation and Stabilization



- Degradation inducing species: R^* , ROO^* , Hydroperoxide
- Additives: Trapping degradation inducing species
- HALS: Mainly Radical Scavenger

Stabilization Mechanism of HALS in Polymers



- Species accelerating degradation in polymer**
- ✓ $R\cdot$ Alkyl Radical
 - ✓ $RO\cdot$ Alkoxy Radical
 - ✓ $ROO\cdot$ Peroxy Radical
 - ✓ $HO\cdot$ Hydroxy Radical
 - ✓ $ROOH$ Hydroperoxide

Stabilization via cyclic mechanism for HALS

➤ *Main active compounds in the cycle (NOH, NO-alkyl and NO radical)*

✓ **HALS** traps unintentionally generated free radicals or unstable intermediates, which results in inhibition of auto-oxidation

Identifying Suitable HALS for Applications

Type of HALS

- **N-H**
- **N-Me**
- **NO-Alkyl**

-Reactivity against radicals
-Adsorption to filler
-Basicity → Formation of salt with acidic substance which leads to deactivation of HALS

Sustainability(persistency)

HALS must stay inside the resin but migrating toward the surface is also important

• **Molecular weight**

- Mobility in resin(High MW=low mobility)
- Stability to heat, (volatility, etc)

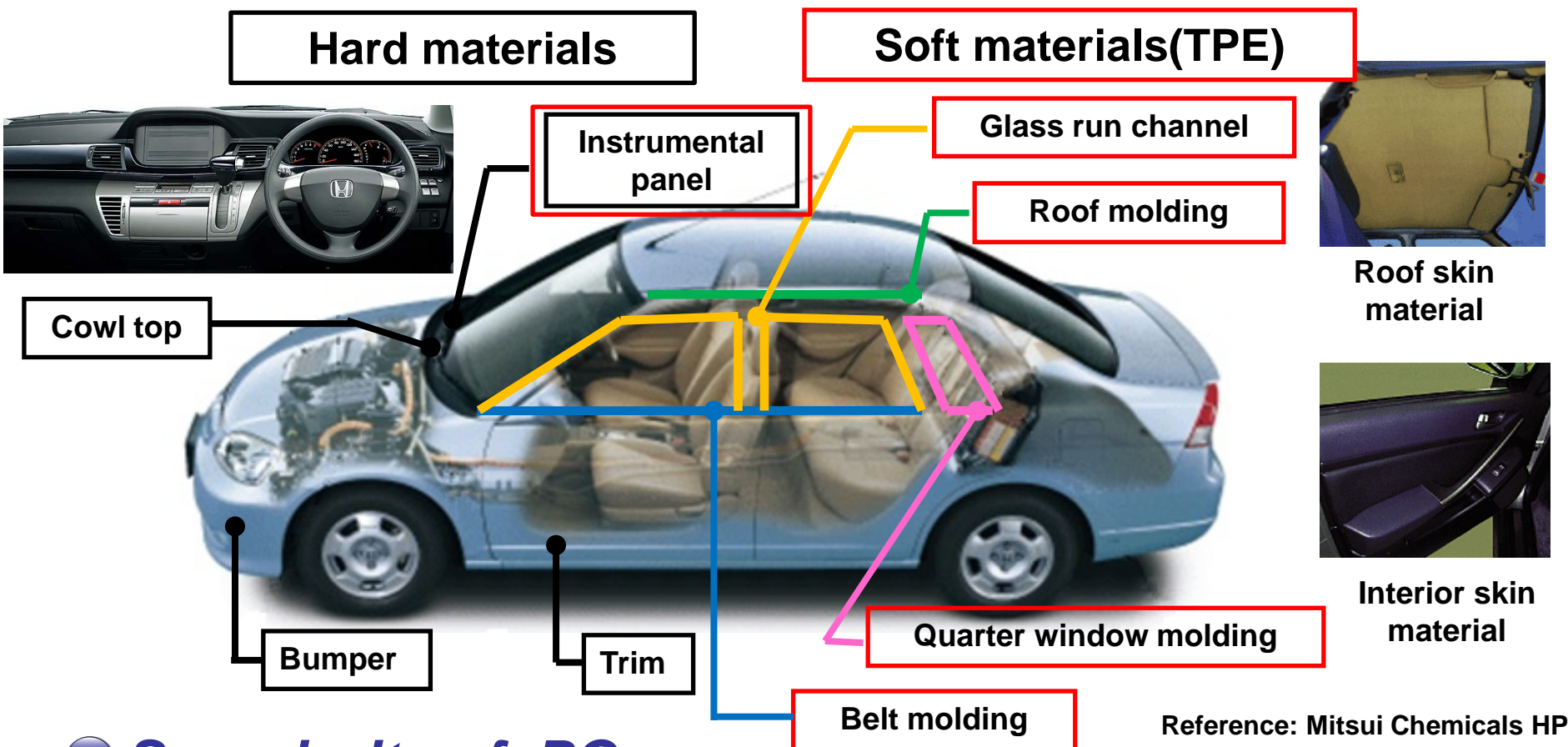
• **Compatibility**

- Similarity of the chemical structure, polarity, etc.

- ✓ **Suited HALS depends on the application**
- ✓ **Combination of different types of HALS can also be effective**

Advanced HALS technologies in automotive parts

Automotive polyolefin parts



● Superiority of PO

- Low density
- Superior mechanical properties
- Excellent chemical resistance
- Recyclability
- Ease of processing and molding
- Low cost, etc.

Requirement on HALS for automotive parts

Exterior



Exterior parts such as bumpers is exposed to **direct sun light** which leads to necessity of high weatherability and thermal stability. In addition, low compatibility of HALS can affect the **paintability**.

Interior



Although the effect of sun light is suppressed by the window, interior parts require weatherability and high thermal stability because **temperature** inside the car could become **higher than outside**. Also, high compatibility with the resin is required to avoid **fogging on front window**.

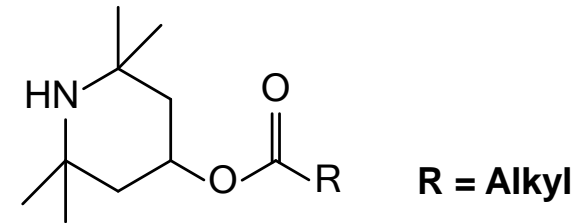
Requirement :
High performance & High compatibility

Advanced HALS system for automotive

LA-1 (ADK STABILIZER LA-402AF): **N-H HALS** + synergist

➤ Benefits

- **Excellent stabilizing ability**
Surface gloss and color sustainability
- **Superior compatibility with polymers**
Lower volatility
- **Easy handling master batch form**
50% PP Master Batch



➤ Applications

- **Exterior & Interior parts**

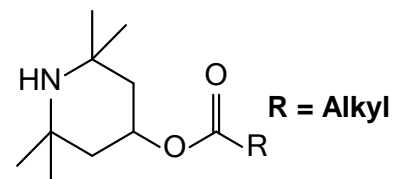


Additives used in Evaluation

HALS

LA-1

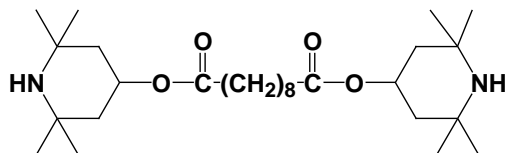
(ADK STABILIZER LA-402AF)



+ synergist

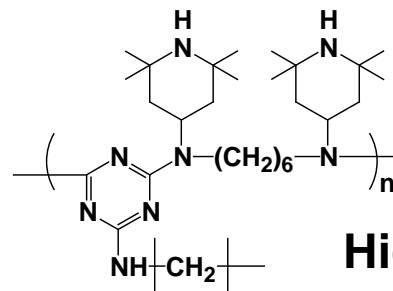
M.W. (420)

Ref 1 (ADK STABILIZER LA-77Y)



Low M.W. (481)

Ref 2 (ADK STABILIZER LA-94G)



High M.W. (>2000)

Additive Package for Evaluation

Phenolic AO

Phosphites AO

Catalyst Residue Scavengers

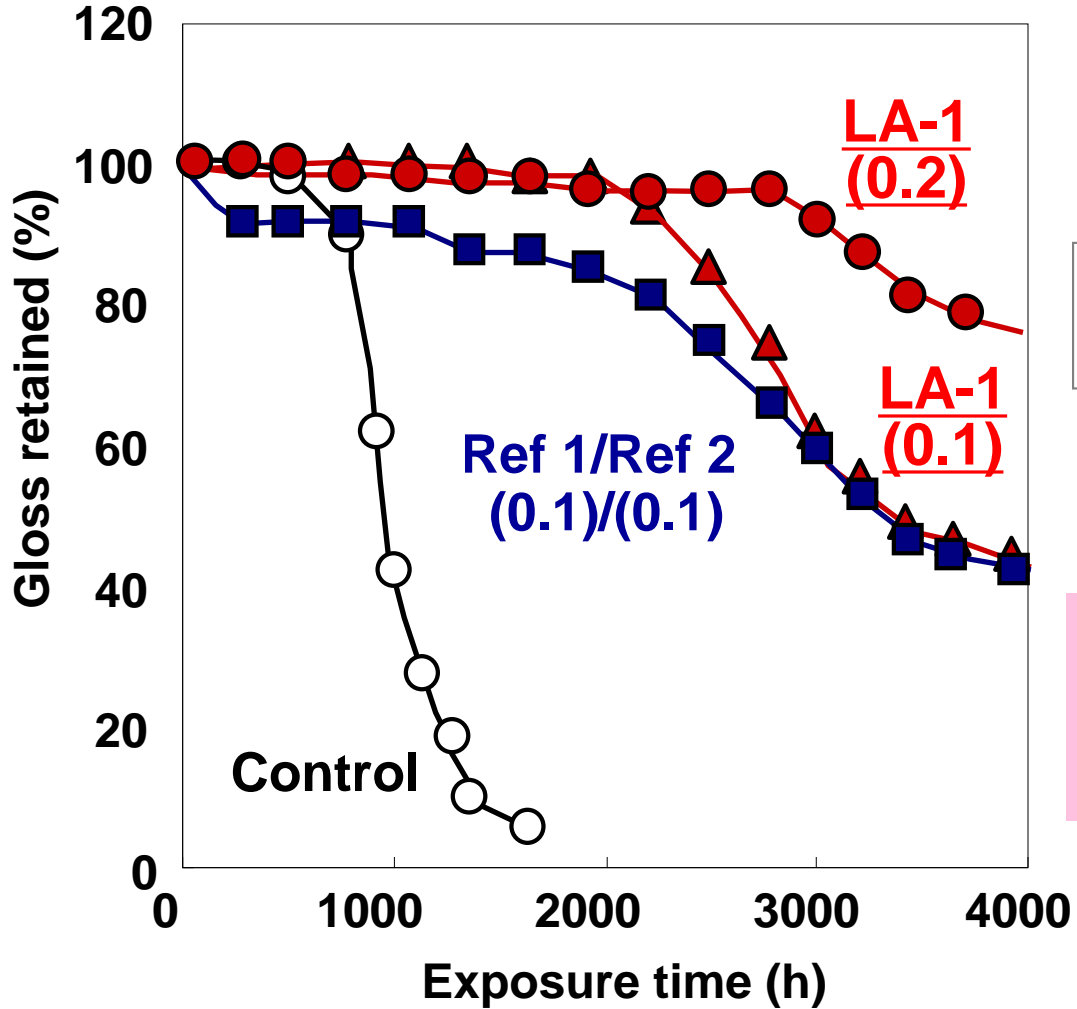
AO-1 (ADK STABILIZER AO-60)

PO-1 (ADK STABILIZER 2112)

Ca-Stearate

Weatherability of Exterior Parts : Surface Gloss

Comparison of light stabilizers in surface gloss stability



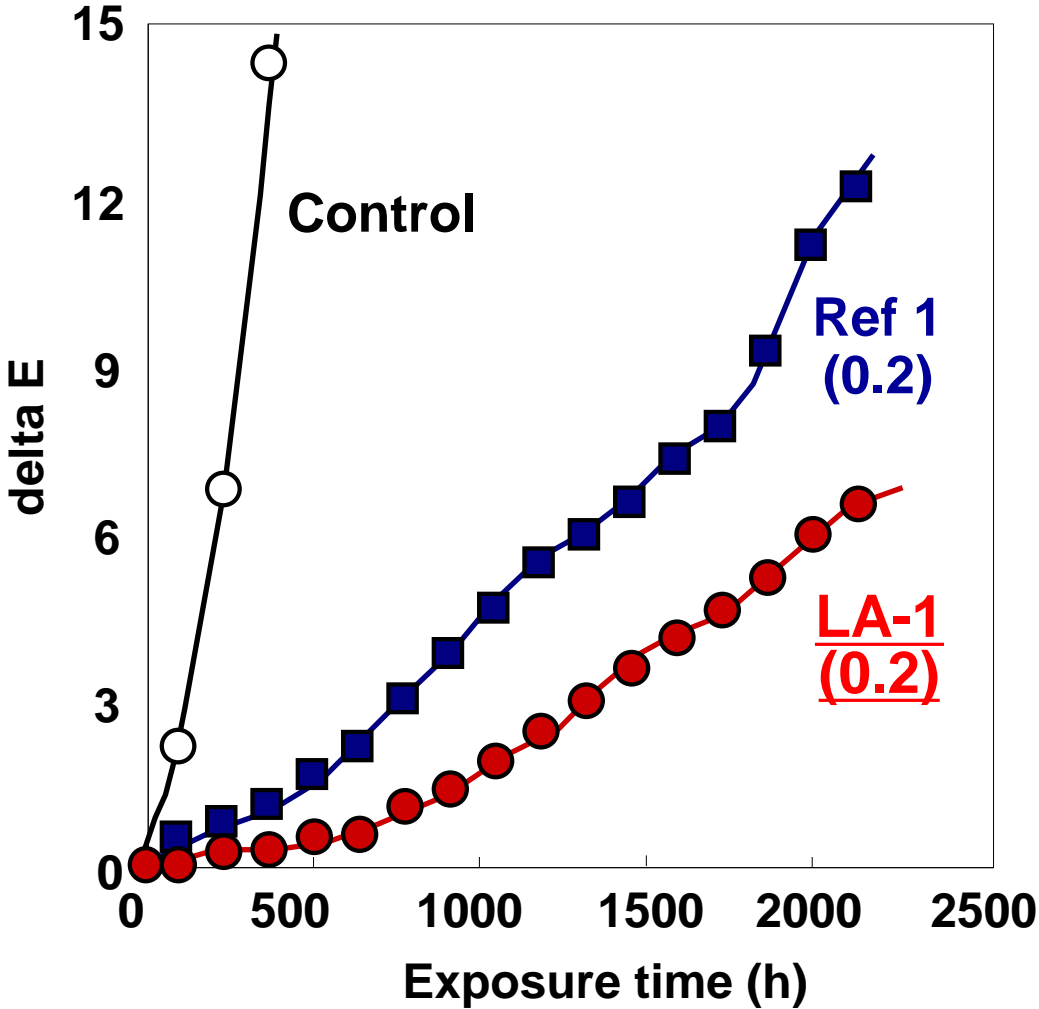
Acceleration test
Xenon Weather-O-Meter
(63°C, with Water spray)

Formulation
ICP [60] / Engage8100 [30] / Talc[10] Black [3]
AO-1 [0.1] / PO-1 [0.1] / Ca-St [0.1] / HALS

✓ **LA-1** improved surface gloss stability greatly as compared with conventional type at lower loading level

Weatherability of Interior Parts : Color stability

Comparison of light stabilizers in color stability



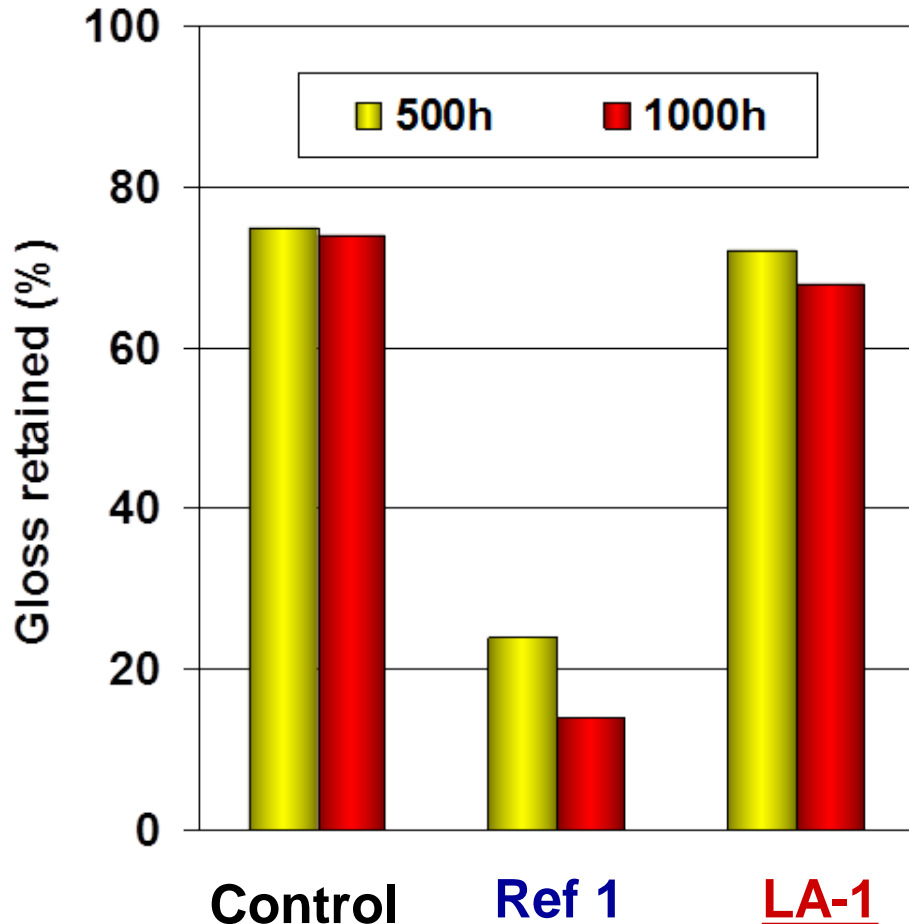
Acceleration test
Xenon Weather-O-Meter
(89°C, without spray)

Formulation
ICP [70] / Engage8100 [10] / Talc[20] Beige [3]
PO-1 [0.1] / PO-1 [0.1] / Ca-St [0.1] / HALS

✓ **LA-1** improved color stability greatly when compared with conventional type at lower loading level

Blooming of HALS from PP

Comparison of light stabilizers on surface gloss at oven



Acceleration test ***Oven aging at 80°C***

Formulation

ICP [70] / Engage8100 [10] / Talc[20] Beige [3]
AO-1 [0.1] / PO-1 [0.1] / Ca-St [0.1] / HALS [0.2]

✓ **LA-1** demonstrated lower blooming on the surface of PP compared with other low molecular weight HALS

N-Me HALS system especially for interior parts

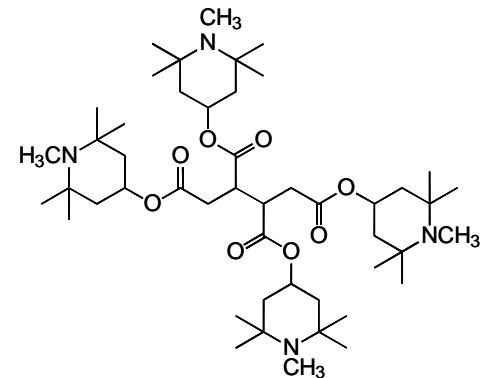
LA-2 (ADK STABILIZER **LA-502XP**): **N-Me HALS** + synergist

➤ Benefits

- **Superior thermal and light stabilizing activity**
Color sustainability and long term heat resistance
- **Superior compatibility with polymers**
Lower volatility
- **Easy handling master batch form**
50% PP master Batch

➤ Applications

- **Especially for Interior parts**

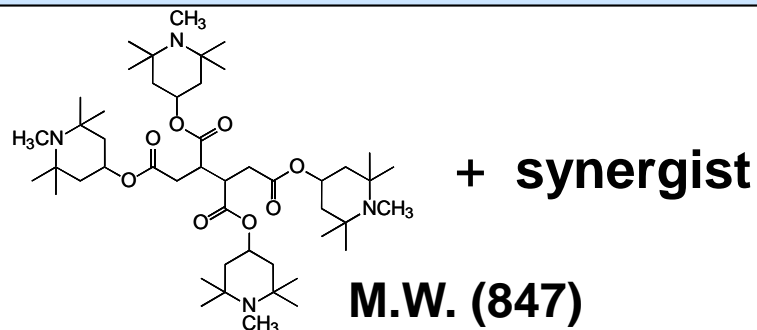


Additives used in Evaluation

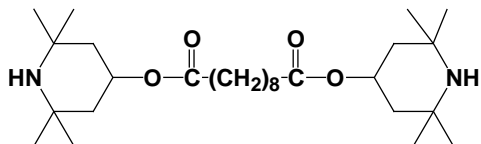
HALS

LA-2

(ADK STABILIZER LA-502XP)

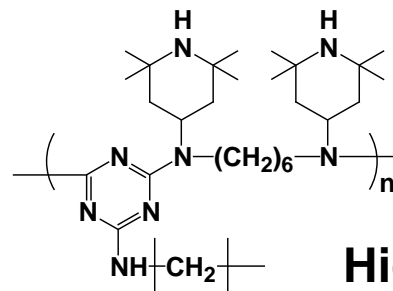


Ref 1 (ADK STABILIZER LA-77Y)



Low M.W. (481)

Ref 2 (ADK STABILIZER LA-94G)



High M.W. (>2000)

Additive Package for Evaluation

Phenolic AO

Phosphites AO

Catalyst Residue Scavengers

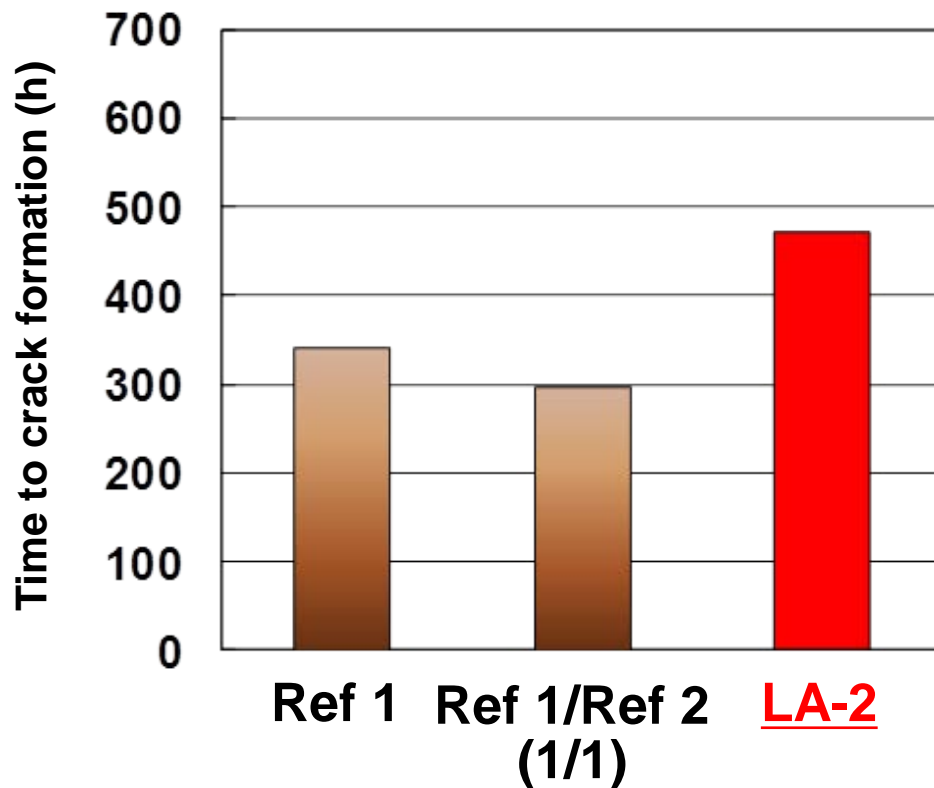
AO-1 (ADK STABILIZER AO-60)

PO-1 (ADK STABILIZER 2112)

Ca-Stearate

AO-2 (ADK STABILIZER AO-50)

Effect of HALS on thermal-stability of PP



Acceleration test
Oven aging at 150°C
2mm plaque

Formulation

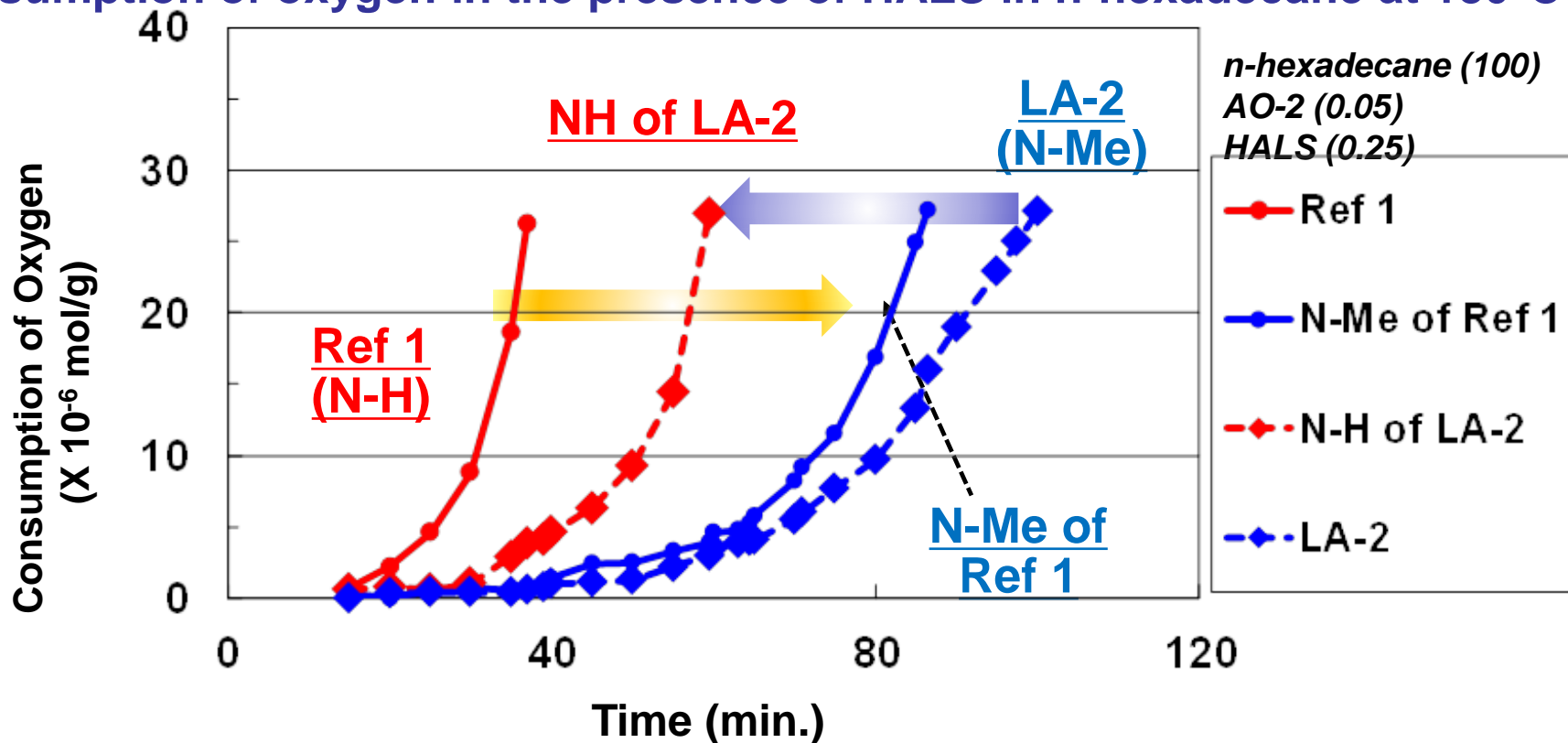
ICP [83] / Talc[17] Blue [3]
AO-1 [0.1] / PO-1 [0.1] / Ca-St [0.1] / HALS [0.2]

✓ LA-2 provided higher thermal stability compared with commodity HALS

Effect of N-Me HALS

- Model experiment -

Consumption of oxygen in the presence of HALS in n-hexadecane at 180°C



✓ N-Me HALS have higher activity to trap free radicals or unstable intermediates, resulting in inhibition of the chain propagation reaction in auto-oxidation

Summary : Hard application

- ✓ **Advanced N-H HALS system LA-1 provided remarkable weathering resistance compared with conventional type at low loading level in both exterior and interior formulation**
- ✓ **Advanced N-Me HALS system LA-2 provided high thermal stability which is especially required for interior parts**

HALS for soft application (TPE)

	Exterior	Interior
NOx gas resistance	Required	
Blooming / Bleeding		Required
Thermal stability		Required
Weatherability	Required	
Fogging resistance		Required

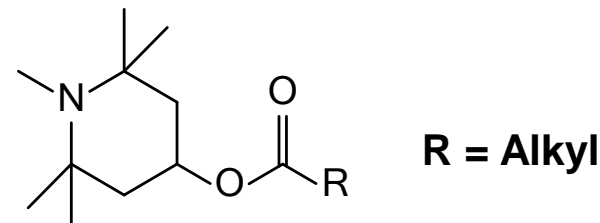
General Formulation of TPV

Materials	Rate[%]
PP, PE	20~40
EPDM	20~40
Oil	4~40
Filler	0-20

Due to difference in the compound formulation, performance of HALS may differ from hard PP application

Novel N-Methyl HALS system

LA-3 (ADK STABILIZER LA-704type): **N-Me HALS** + synergist



➤ Benefits

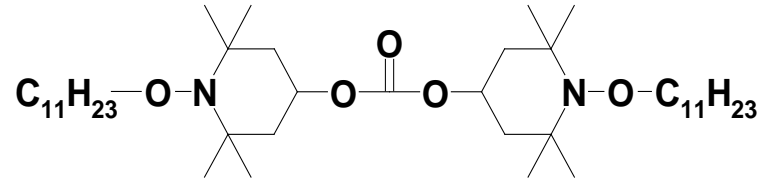
- Superior performance against NO_x discoloration
Low basicity compared to LA-1 with equal weatherability
- Good compatibility to poly olefins

➤ Applications

- Automotive parts particularly with light color

Novel NO-Alkyl HALS system

LA-4 (ADK STABILIZER LA-81 type): **NO-alkyl HALS**+ synergist



➤ Benefits

- **Excellent stabilizing ability under acidic conditions**
Low basicity compared to conventional HALS
- **Good compatibility to polyolefins**

➤ Applications

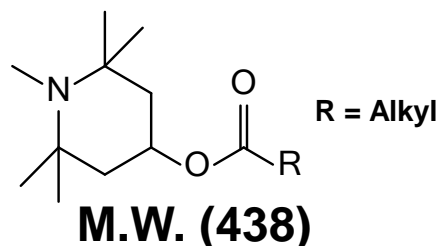
- **Automotive parts with acidic substance inside**
ex. Thioether AO

Additives used in Evaluation

HALS

LA-3

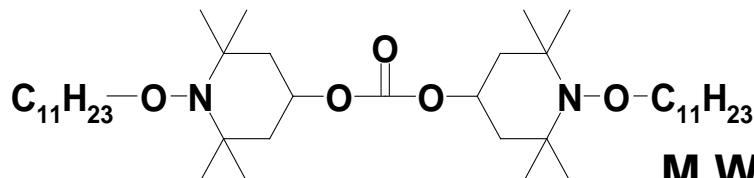
(ADK STABILIZER LA-704)



M.W. (438)

+ synergist

LA-4 (ADK STABILIZER LA-81 type)



M.W. (681)

+ synergist

Ref 3, Ref 4 (Competitor NO-alkyl)

Ref 5 (Competitor N-alkyl)

Additive Package for Evaluation

Phenolic AO

Phosphites AO

Catalyst Residue Scavengers

AO-1 (ADK STABILIZER AO-60)

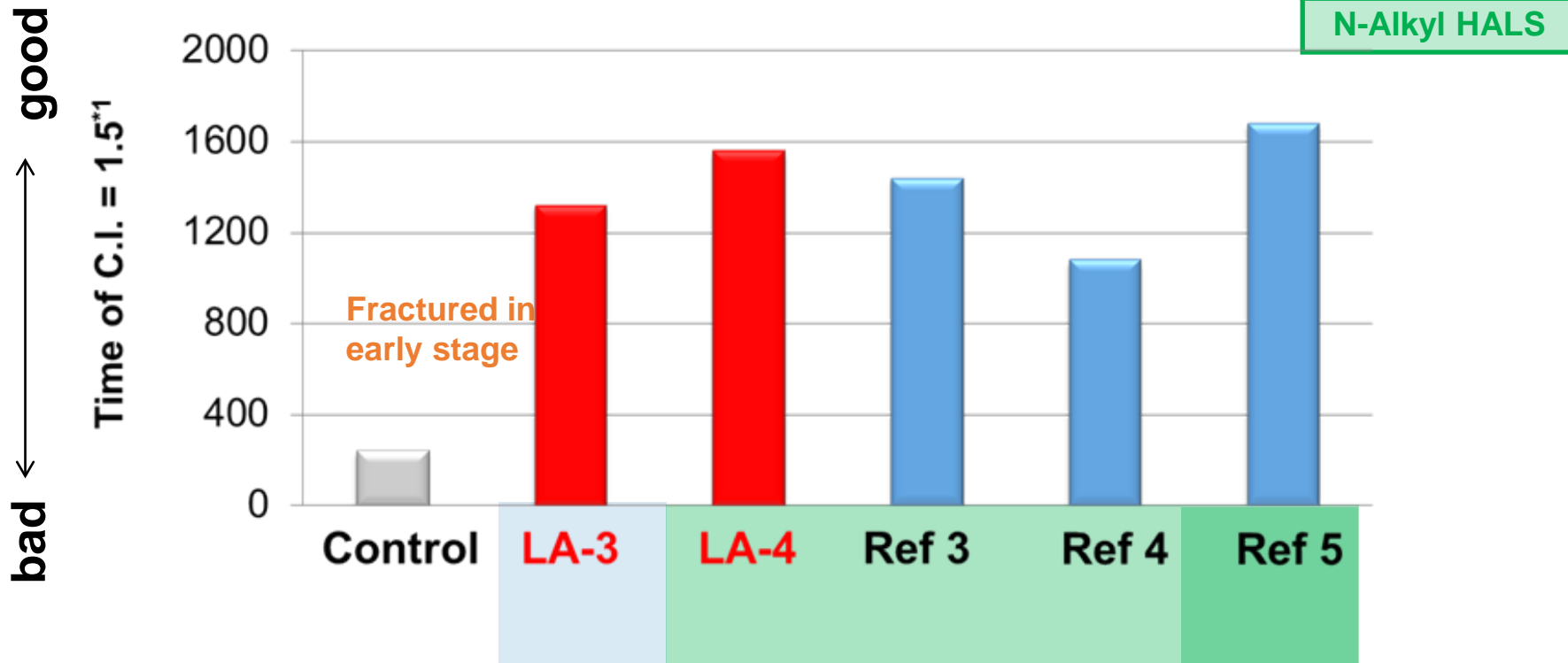
PO-1 (ADK STABILIZER 2112)

Ca-Stearate

AO-3 (ADK STABILIZER AO-20)

Weatherability -Surface deterioration(IR)-

Acceleration test
Xenon Weather-O-Meter
(89°C, without Spray)



*calculated from C=O peak at 1715 cm⁻¹ of IR chart

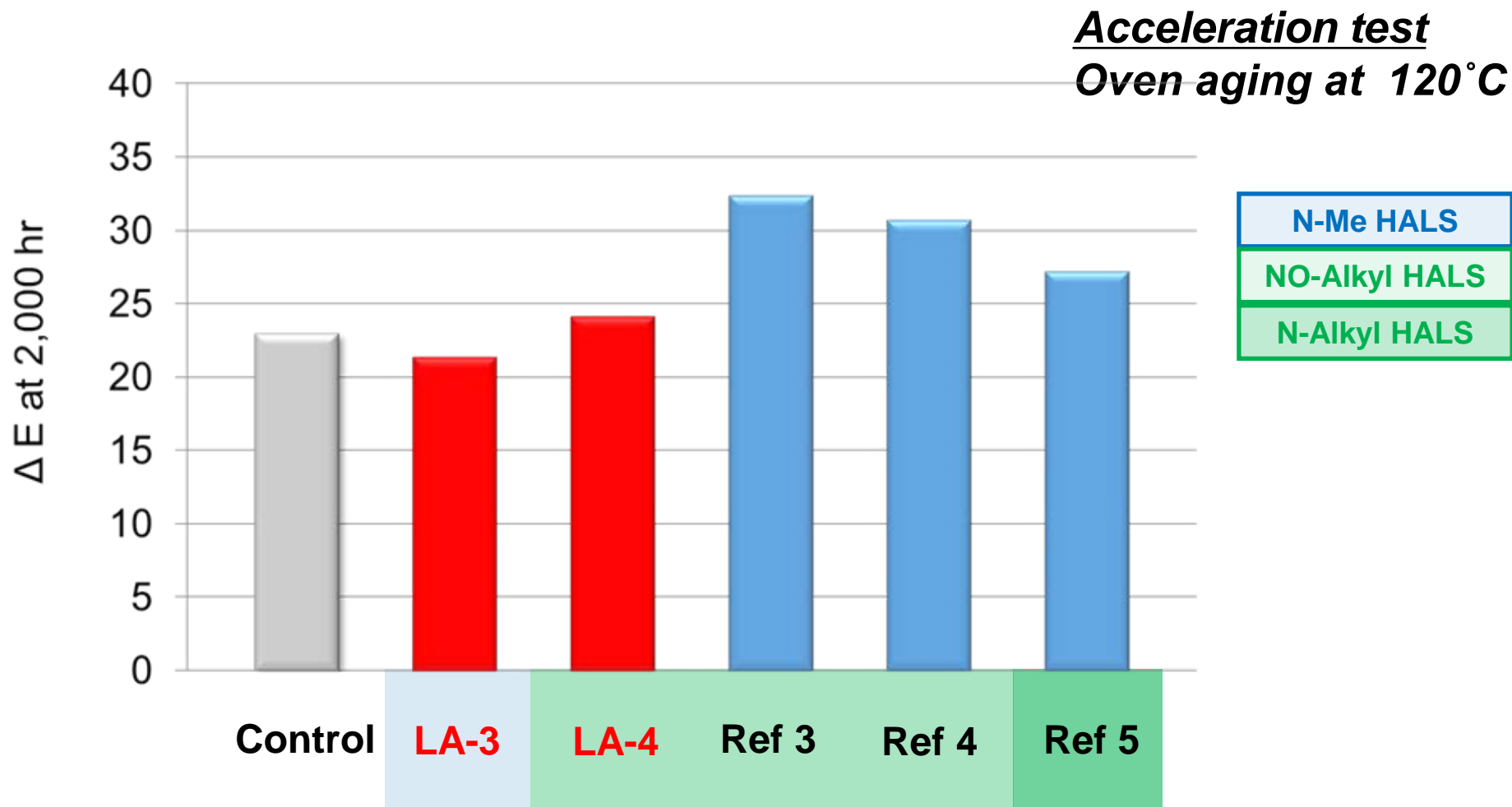
Formulation:

TPV (100) / AO-1 (0.05) / PO-1 (0.05) / UVA (0.15) / HALS* (0.2)

*Active component

Roll : 180 °C, Press: 180 °C Thickness: 0.4 mm

Thermal Stability - ΔE -



Formulation:

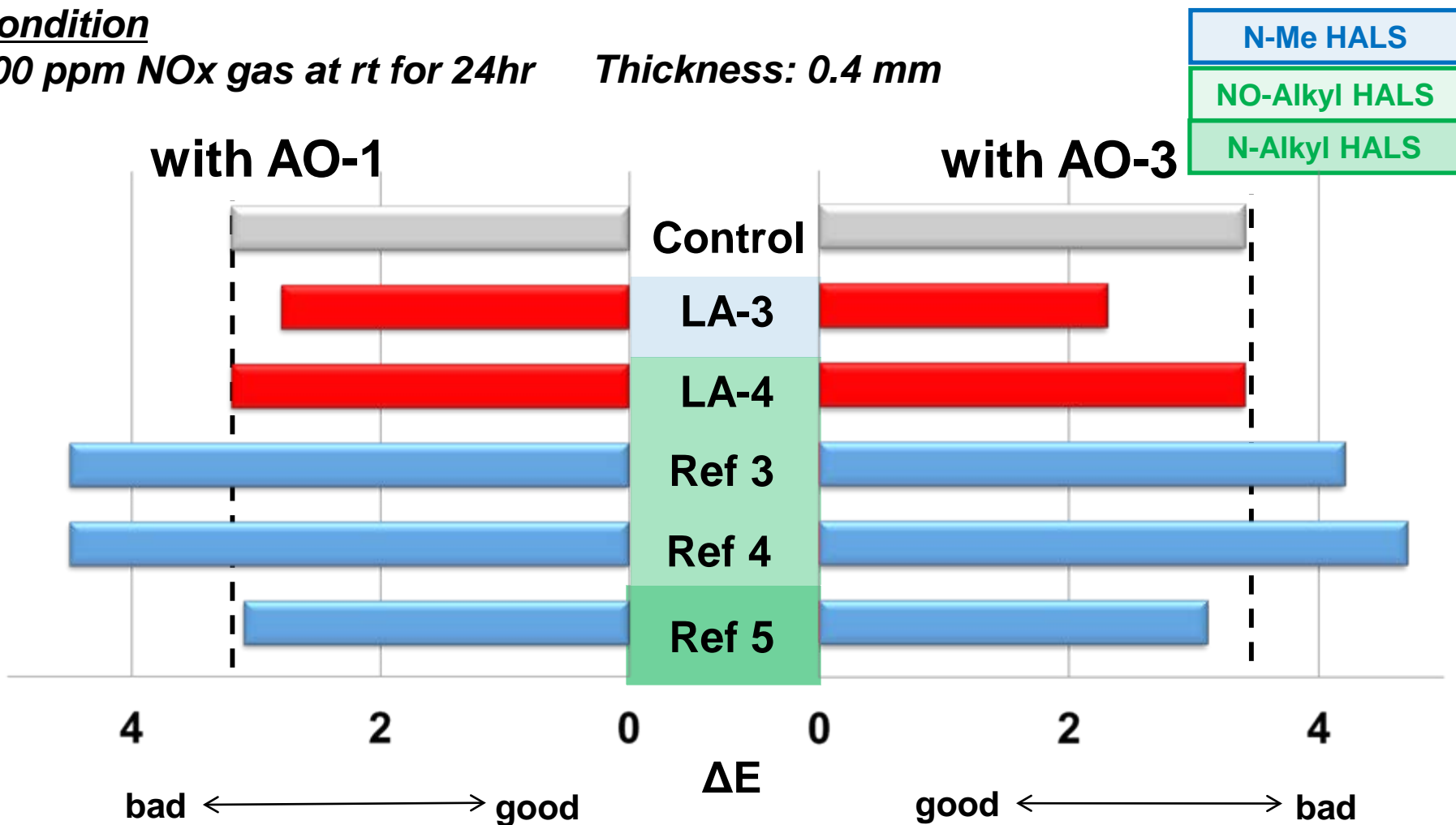
TPV(100) / AO-1 (0.05) / PO-1 (0.05) / UVA (0.15) / HALS (0.15)

Extrusion: 200 °C, Injection: 200 °C Mold: 50 °C Thickness: 2.0 mm

Anti NOx discoloration(Beige)

Condition

700 ppm NOx gas at rt for 24hr Thickness: 0.4 mm

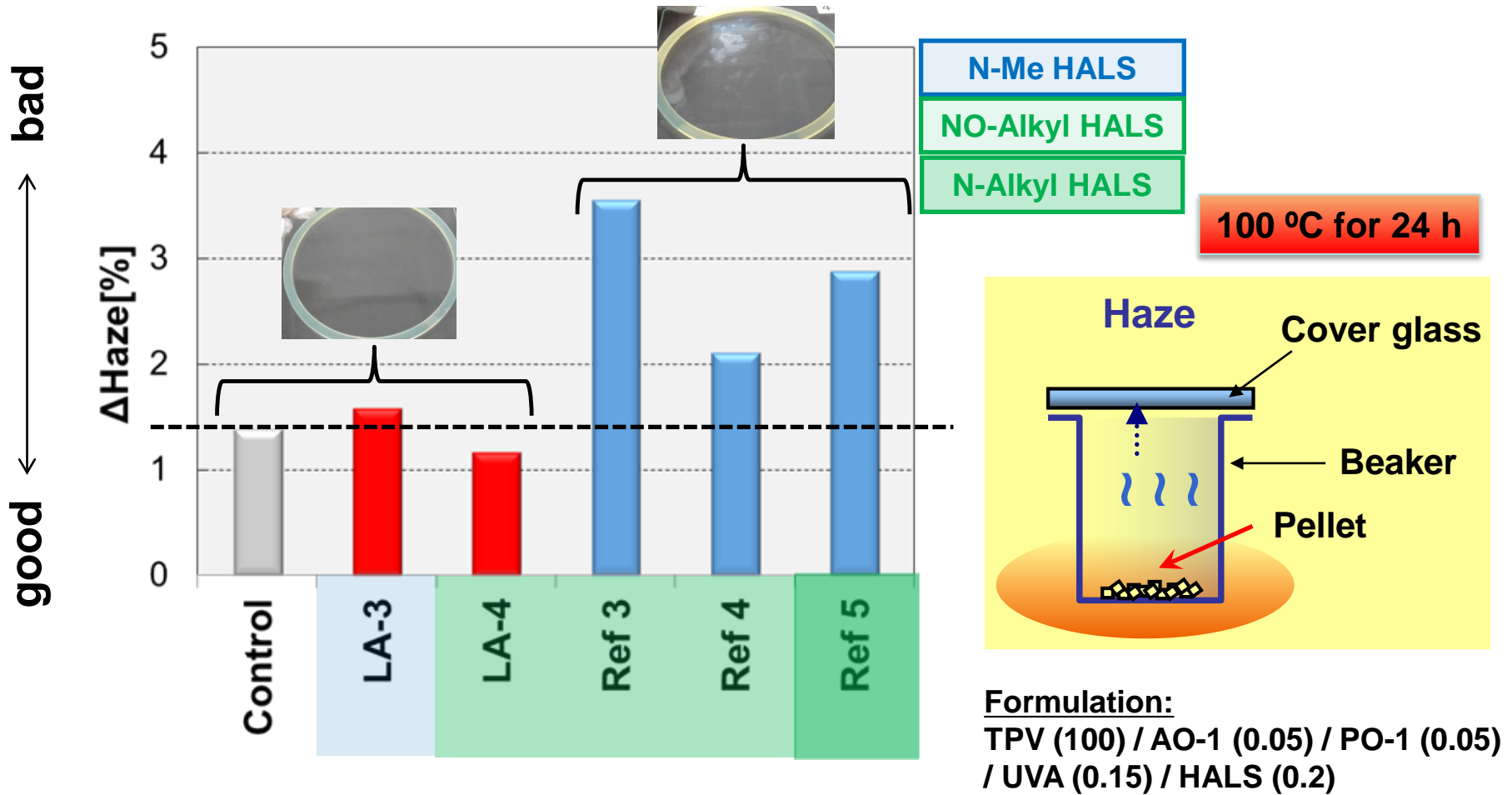


Formulation:

TPV (HS=80, 100) / AO-1 or 2 (0.05) / PO-1 (0.05) /
UVA (0.15) / HALS (0.2)

Condition: 700ppm NOx gas, R.T, 24 h Thickness: 0.40 mm

Fogging resistance (Photometric)



✓ Both **LA-3** and **LA-4** showed better compatibility and fogging resistance than competitor's HALS

Compatibility of HALS with Polymer

Solubility of HALS

HALS	<i>Heptane</i>
<u>LA-3* (N-Me)</u>	>50
<u>LA-4* (NO-alkyl)</u>	>50
Ref 3 (NO-alkyl)	0.5
Ref 4 (NO-alkyl)	>50
Ref 5 (N-alkyl)	0.5

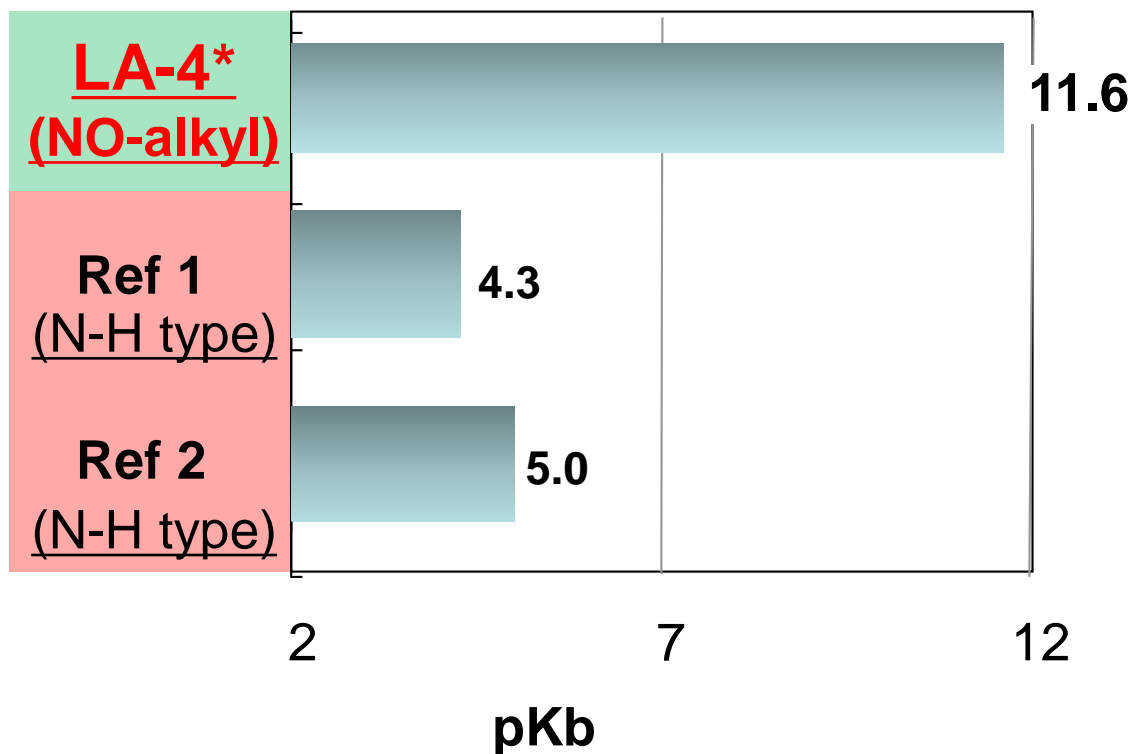
* without the synergist

(g/100g-Solvent)

- Heptane : model substance for polar polymer such as polyolefin

✓ LA-3 & LA-4 is expected to have an excellent compatibility with polyolefins

Basicity of HALS



*measured by using pH meter in MeOH

Salt formation with carboxylic acid



Ref 1

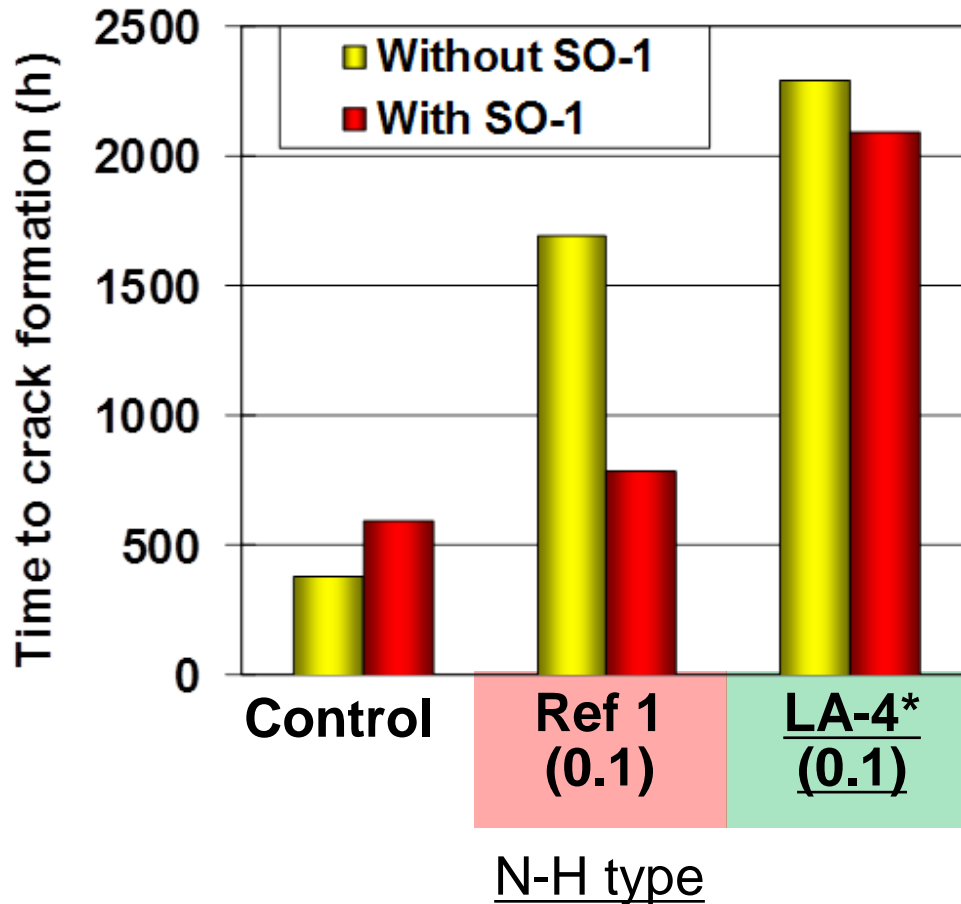
LA-4*

*without synergist

➤ LA-4 has no salt formation with carboxylic acid.

✓ LA-4 is possible to function with the existence of acidic substances

Effect of HALS with Organosulfur



***Acceleration test
Xenon Weather-O-Meter
(89°C, without Spray)***

Formulation

ICP [100]
AO-1 [0.1] / PO-1 [0.1] / Ca-St [0.1] / HALS

***without synergist**

✓ **LA-4** can coexist with thioether AO which makes it possible to give thermal stability and weaherability at the same time

Summary : soft application

- ✓ Novel HALS system LA-3 & LA-4 had good compatibility in polyolefins and showed high performance in formulation of soft application
- ✓ LA-4 showed excellent light stabilizing activity in compounds containing acidic substances

Summary and Conclusions

- ✓ **There are multiple factors that determines the performance of HALS**
- ✓ **By selecting the suited HALS for the application, it will give the compound the performance necessary for automotive parts**



By combining these HALS with other additives, it should enlarge the possibility of resin for automotive parts

Thank you for your attention !