

New Products to Enhance the Light and Thermal Stability of Polyolefins for Automotive Applications

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ABSTRACT

Polyolefin-based materials such as polypropylene and TPO are widely used in the automotive industry due to their good balance of physical properties, ease of processing, recyclability, and low cost. Developing the proper stabilization formulations to meet the weatherability, long term thermal stability, and other requirements of automotive interior and exterior applications can be a challenging task. This paper will summarize the performance criteria that need to be considered in developing a stabilization system and will present an overview of several new products developed by Ciba to meet the needs of the automotive market. Data will be presented comparing the performance of new and existing stabilization systems for color and gloss retention of TPO and polypropylene during accelerated weathering (SAE J1960 and SAE J1885) and retention of tensile properties on long term heat aging at temperatures up to 150°C. The effect of stabilization systems on important secondary properties such as coating adhesion and resistance to warehouse discoloration will also be discussed. Ciba's new products enable TPO and polypropylene to meet current automotive requirements and will also facilitate their use in more demanding automotive applications by extending their weatherability and long term thermal stability.

INTRODUCTION

Polypropylene and thermoplastic polyolefin elastomers (TPO) are widely used in automotive interior, exterior, and under-the-hood components. The use of these materials in automotive applications would not be possible without the incorporation of stabilization systems to improve their stability to the effects of sunlight and heat as well as the high temperatures and mechanical shear encountered during melt processing operations. A wide variety of light, processing, and thermal stabilizers are commercially available, both as individual chemical products and fully formulated systems. This paper provides a brief overview of polyolefin degradation and stabilization as well as

guidelines for the selection of stabilization systems for interior and exterior applications.

DEGRADATION AND STABILIZATION OF POLYOLEFINS

DEGRADATION OF POLYOLEFINS

Like other organic materials, polyolefins are subject to oxidative degradation when exposed to heat or sunlight in the presence of air.[1] Oxidation produces undesirable changes in the appearance (i.e. color, gloss) and the mechanical properties (i.e. tensile properties, impact strength) of the material. The components of stabilization systems function primarily by decomposing the radical and/or hydroperoxide intermediates in this process.

LIGHT STABILIZERS

Light stabilization systems significantly extend the life of polyolefins on exposure to sunlight. Typical system components include **Hindered Amine Light Stabilizers (HALS)** and ultraviolet absorbers (UVAs, see Appendix). HALS act by scavenging the radical intermediates formed in the photo-oxidation process, while UVAs simply shield the polymer from ultraviolet radiation. In general, HALS provide the best performance in polyolefins. The high efficiency and longevity of HALS are thought to be due to a cyclic mechanism wherein the active species are continually regenerated rather than consumed [2]. HALS are often used in combination with UVAs to boost their performance. These combinations are particularly useful for stabilizing compositions containing organic pigments. Combinations of low and high molecular weight HALS (e.g. LS System 1) are also widely used for the light stabilization of polyolefins. A wide variety of HALS and UVAs are commercially available. Selection of specific system components is dependent on the substrate and the end use requirements of the application.

THERMAL/PROCESSING STABILIZERS

Processing and thermal stabilization systems extend the lifetime of polyolefins during melt processing and end use at elevated temperatures. Typical system components include hindered phenols (e.g. AO 1), phosphites (e.g. AO 2), thioethers (e.g. AO 4), and hydroxylamines (e.g. AO 3, see Appendix). Some types of hindered amine light stabilizers (e.g. HALS 3, 4) are also effective as long term thermal stabilizers in polyolefins, especially at moderate temperatures (up to ca. 130°C). Stabilization system components act by decomposing the radical and hydroperoxide intermediates formed in the oxidation process.[1] Hindered phenols are most widely used, often in combination with phosphites (as in AO System 1). Selection of system components is dependent on the processing conditions and the end use requirements of the application.

STABILIZATION FOR INTERIOR APPLICATIONS

Plastics in the interior automotive environment are exposed to light and high temperatures during the lifetime of the vehicle, and specifications typically require testing to ensure light and thermal oxidative stability. Important secondary properties that may be affected by stabilization system components include warehouse discoloration and fogging (especially for instrument panel components). All polyolefins used for interior applications also contain a processing stabilizer to guard against degradation during melt processing.

LIGHT STABILITY

Current specifications in NAFTA require minimal color change ($\Delta E < 3$) after exposure (typically 1240 kJ/m²) in a xenon arc weatherometer per SAE J1885 [3]. For polyolefins these requirements can usually be met using conventional light stabilization systems (e.g. hindered amine light stabilizers alone or in combination with UVAs).

THERMAL OXIDATIVE STABILITY

Specifications for interior plastics are severe, requiring stability during heat aging at temperatures up to 150°C. Hindered phenols (often in combination with thioethers) are widely used for the high temperature stabilization of polyolefins, but their use can be problematic for interior applications due to their tendency to give warehouse discoloration. Negative interactions between thioethers and hindered amine light stabilizers present another issue.

WAREHOUSE DISCOLORATION (GAS FADING)

Gas fading refers to the pink or yellowish discoloration sometimes observed when parts stabilized with hindered phenols are exposed to combustion gases, most often during warehouse storage. Hindered phenols used as stabilization system components (e.g. AO 1, AO System 1) are readily oxidized to highly colored quinonoid compounds by reaction with nitrogen oxides produced during combustion of natural gas [4]. The problem occurs most often in light-colored parts, although parts in darker colors may also be affected. It appears most frequently in the winter months due to the use of gas-fired heaters and the generally less effective ventilation of combustion gases. While the discoloration may not be permanent, the color changes are highly undesirable and present a real concern to production supervisors and plant managers.

SYSTEM RECOMMENDATIONS

Light stabilization requirements can usually be met using hindered amine light stabilizers (Table 1). The use of an ultraviolet absorber may be necessary for formulations containing organic pigments.

Table 1. Light Stabilization of Reactor TPO.

Color	Stabilization System	1250 kJ/m ² exposure	
		ΔE	60° Gloss (% Retn.)
Gray	0.2% LS System 1	0.1	96
Gray	0.2% LS System 2	0.1	97
Tan	0.2% LS System 1 + 0.2% UVA 1	0.5	98
Tan	0.2% LS System 2 + 0.2% UVA 1	0.5	97

All formulations contain 0.1% AO System 2 + 0.05% calcium stearate

Substrate: injection molded plaques

Exposure per SAE J1885 (interior automotive)

Process stabilizer systems based on hydroxylamine chemistry (Systems 2, 3, 4) have been developed which do not produce discoloration on exposure to combustion gases (Table 2). These systems provide processing stability in polyolefins comparable to conventional systems based on hindered phenols such as AO System 1 (Tables 3-4). While hydroxylamines by themselves do not impart long term thermal stability to polyolefins, the addition of a high molecular weight HALS (used as a component of the light stabilization system) provides excellent long term thermal stability at moderate temperatures (Table 5). More recently, AO System 4 has been developed which provides superior long-term thermal stability at high temperatures (up to 150°C, Table 6), excellent process stabilization (Tables 3-4), and resistance to gas fade discoloration (Table 2).

Table 2. Gas Fade Discoloration in Natural Polypropylene Homopolymer.

Stabilization System	ΔE 7 Gas Fade Cycles
0.20% AO System 1	3.8
0.20% AO System 3	0.8
0.25% AO System 4	0.8

AATCC test method 23-1988, compression molded plaques (0.040" thick). All formulations contain 0.2% HALS 1 + 0.1% calcium stearate.

Table 3. Process Stabilization of Polypropylene Homopolymer. Change in Melt Flow Rate after Multiple Pass Extrusion (525°F, 274°C).

Stabilization System	Melt Flow Rate (dg/min) ASTM D 1238, 230°C		
	1 st Pass	3 rd Pass	5 th Pass
0.20% AO System 1	3.7	5.4	5.6
0.20% AO System 3	3.9	5.2	5.4
0.25% AO System 4	3.7	4.6	4.9

All formulations contain 0.2% HALS 1 + 0.1% calcium stearate

Table 4. Process Stabilization of Polypropylene Homopolymer. Change in Color after Multiple Pass Extrusion (525°F, 274°C).

Stabilization System	Color (YI 1925)		
	1 st Pass	3 rd Pass	5 th Pass
0.20% AO System 1	10.8	13.7	15.7
0.20% AO System 3	10.6	11.2	11.5
0.25% AO System 4	10.7	11.4	12.0

All formulations contain 0.2% HALS 1 + 0.1% calcium stearate
Substrate: Compression molded plaques (0.040" thick)

Table 5. Thermal Oxidative Stability of Polypropylene Homopolymer: 120°C.

Stabilization System	% Retn. Tensile Strength		
	1000 h	2000 h	3000 h
0.4% LS System 1 + 0.20% AO System 1	94	91	91
0.4% LS System 1 + 0.1% AO System 2	103	110	100
0.2% LS System 1 + 0.1% AO System 2	103	100	88
0.2% LS System 2 + 0.1% AO System 2	103	112	91

All formulations contain 0.1% calcium stearate
Substrate: Injection molded microtensile bars, 0.125" thick

Table 6. Thermal Oxidative Stability of Polypropylene Homopolymer: 140-150°C.

Stabilization System	Days to Failure, 150°C	% Retn., 1000 h @ 140°C	
		Elongation	Tensile Strength
0.2% AO System 1	27	0	0
0.2% AO System 3	5	0	0
0.25% AO System 4	25	83	112

All formulations contain 0.2% HALS 1 + 0.1% calcium stearate

Substrate: Injection molded microtensile bars, 0.060" thick

STABILIZATION FOR EXTERIOR APPLICATIONS

Exterior automotive plastics must withstand prolonged exposure to UV radiation in sunlight and also elevated temperatures, particularly in darker colors. Specifications usually require testing to ensure light and thermal oxidative stability. In addition, for parts that are to be painted special care must be taken in selecting a stabilization system in order to avoid interactions with the cure which can sacrifice coating durability. As in the case of interior applications, processing stabilizers must be used to prevent degradation during melt processing operations.

LIGHT STABILITY

Current OEM specifications in the NAFTA region for automotive exterior applications require minimal changes in color ($\Delta E < 3$) and in some cases gloss after 2500 kJ/m² exposure in a xenon arc weatherometer per SAE J1960 [5]. It is likely that future OEM specifications will require longer exposures in order to bring requirements for molded-in-color plastics more in line with those for automotive coatings (typically requiring >4000 kJ/m² exposure). Achieving weatherability performance to meet even existing requirements can be problematic in colors other than black and in talc-filled TPO substrates.

THERMAL OXIDATIVE STABILITY

Requirements for exterior plastics are typically less severe than for interior applications, involving heat aging at temperatures of 120°C or less. These requirements can easily be met using high molecular weight hindered amines and/or hindered phenolic antioxidants.

COATING ADHESION

Exterior parts may be molded-in-color, fully painted, or partially painted. For partially painted applications the light stabilization system must be carefully selected in order to avoid interaction with paint cure. Acid-cured 1K automotive coatings are widely used for exterior applications such as bumper fascia in the NAFTA region. Strongly basic HALS are capable of interfering with the acid-catalyzed cure, resulting in poor paint adhesion to

the substrate.[6] The problem is particularly acute with low molecular weight HALS that have a tendency to migrate to the surface of the part (e.g. HALS 1). Light stabilization systems derived from nonbasic HALS (e.g. HALS 2 + HALS 3) have been recommended and used successfully in partially painted TPO applications.

SYSTEM RECOMMENDATIONS

The new “LS System 2” has been developed to provide improved weatherability and meet thermal oxidative stability requirements without sacrificing paintability. As shown in Table 7, a black, talc-filled reactor TPO can be stabilized to meet current exterior automotive requirements using a conventional light stabilization system (LS System 1). However, after extended exposure the use of the more robust LS System 2 is required to achieve a $\Delta E < 3$. In a red molded-in-color polypropylene homopolymer, formulations containing LS System 2 show excellent weatherability even after 4000 kJ/m² exposure (Table 8). LS System 2 is also noninteracting with acid-cured 1K automotive coatings to minimize adhesion problems (Table 9) and provides sufficient thermal oxidative stability to meet exterior automotive requirements (Table 5).

Table 7. Light Stabilization of Black Reactor TPO (15% Talc).

Stabilization System	ΔE	
	2500 kJ/m ²	3500 kJ/m ²
0.5% LS System 1	2.0	4.5
0.5% LS System 2	0.8	2.3

All formulations contain 0.15% AO System 1 + 0.1% calcium stearate + 0.25% carbon black
Substrate: Injection-molded plaques
Exposure per SAE J1960 (exterior automotive)

Table 8. Light Stabilization of Red Polypropylene Homopolymer.

Stabilization System	4000 kJ/m ²	
	ΔE	% Gloss Retn.
0.4% LS System 2 + 0.2% UVA 1	0.7	88
0.2% LS System 2 + 0.1% UVA 1	1.6	66

All formulations contain 0.05% AO 3 + 0.1% calcium stearate + 0.25% Pigment Red 3B
Substrate: Injection-molded plaques
Exposure per SAE J1960 (exterior automotive)

Table 9. Coating Adhesion to Natural TPO.

Stabilization System	% Loss Taber Scuff	Aggressive Adhesion Test
0.4% LS System 1	100	Fail
0.2% HALS 2 0.2% HALS 3	0	Pass
0.4% LS System 2	0	Pass

Injection molded samples (4" x 6") coated with chlorinated polyolefin primer, 1K basecoat, and 1K clearcoat. Testing conducted by TFI Labs using their proprietary methods.

CONCLUSION

Selection of a stabilization system for polyolefins in automotive applications can be a challenging task due to the large number of products available and the demanding weatherability and thermal exposure specifications that must be met. Also, the effect of stabilization system components on other important attributes must be considered, including coating adhesion and gas fading.

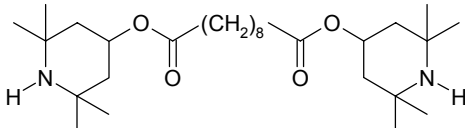
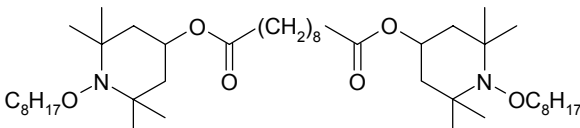
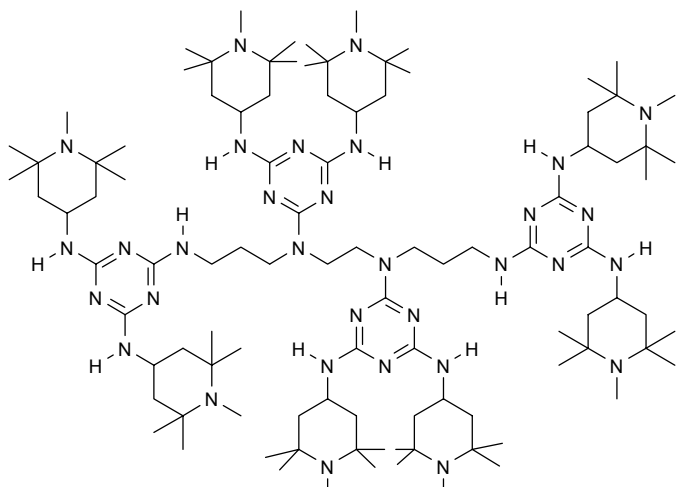
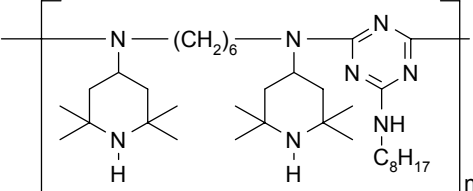
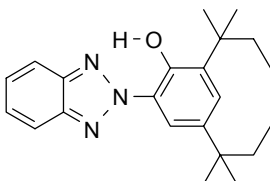
Several new stabilization systems have been developed with the versatility to meet OEM requirements while avoiding the problems sometimes encountered with existing systems. LS System 2 is a light stabilization system that provides outstanding weatherability to polyolefins while avoiding the negative effects on coating adhesion associated with some of the traditional systems. AO System 4 is a new processing and long-term thermal stabilization system for polyolefins which imparts excellent processing and thermal oxidative stability (even at high temperatures) as well as providing resistance to gas fade discoloration.

REFERENCES

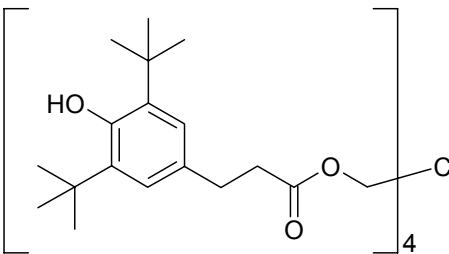
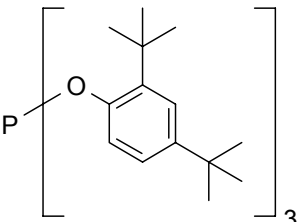
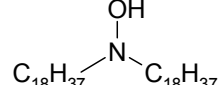
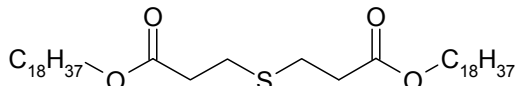
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4. P. Klemchuk & P. Horng *Polymer Degradation and Stability* **1991**, *34*, 333-346.
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APPENDIX

LIGHT STABILIZERS

<p style="text-align: center;">HALS 1</p> 
<p style="text-align: center;">TINUVIN® 770</p> <p style="text-align: center;">HALS 2</p> 
<p style="text-align: center;">TINUVIN® 123</p> <p style="text-align: center;">HALS 3</p> 
<p style="text-align: center;">CHIMASSORB® 119</p> <p style="text-align: center;">HALS 4</p> 
<p style="text-align: center;">CHIMASSORB® 944</p> <p style="text-align: center;">LS System 1 50% HALS 1 + 50% HALS 4</p> <p style="text-align: center;">TINUVIN® 791</p> <p style="text-align: center;">LS System 2 Proprietary composition</p> <p style="text-align: center;">TINUVIN® XT 850</p>
<p style="text-align: center;">UVA 1</p>  <p style="text-align: center;">TINUVIN® 328</p>

PROCESSING/THERMAL STABILIZERS

<p style="text-align: center;">AO 1</p>  <p style="text-align: center;">IRGANOX® 1010</p>
<p style="text-align: center;">AO 2</p>  <p style="text-align: center;">IRGAFOS® 168</p>
<p style="text-align: center;">AO 3</p>  <p style="text-align: center;">IRGASTAB™ FS 042</p>
<p style="text-align: center;">AO 4</p>  <p style="text-align: center;">IRGANOX® PS 802</p>
<p style="text-align: center;">AO System 1 50% AO 1 + 50% AO 2</p> <p style="text-align: center;">IRGANOX® B 225</p>
<p style="text-align: center;">AO System 2 50% AO 3 + 50% AO 2</p> <p style="text-align: center;">IRGASTAB™ FS 301</p>
<p style="text-align: center;">AO System 3 50% AO 3 + 50% HALS 3</p> <p style="text-align: center;">IRGASTAB™ FS 210</p>
<p style="text-align: center;">AO System 4 Proprietary Composition</p> <p style="text-align: center;">Developmental Product EB 41-63</p>

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