

Enhancing the Properties of Polyolefins to Accelerate Market Adoption

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Abstract:

As the use of polyolefins continues to increase in new markets and applications, resin producers, compounders, masterbatchers and molders must keep pace with complex, changing technical requirements. Leveraging its experience in polyolefin stabilization, Solvay is helping companies throughout the plastics value chain deliver exceptional performance and improve operational efficiencies. This presentation will highlight our technical innovations to meet demanding requirements in the building and construction as well as molding markets.

Background

Sunlight contains harmful energy that can decrease the useful life of many plastic articles. Polymers are inherently unstable when exposed to sunlight. Ultraviolet photons from the sun contain sufficient energy to cleave chemical bonds, forming radical species. These harmful radicals go on to attack polymer chains, pigment, etc. in the presence of oxygen. The use of UV stabilizing chemistries is essential for polymer articles intended to be placed outdoors. For especially rugged applications, for example roofing/building materials, extra care must be taken in the formulation of UV stabilizers, as these materials are exposed to both intense sunlight and heat, and consumers expect service lives in excess of 10 years, and in some cases multiple decades.

As time goes on, compounders, extruders, and molders, as well as consumers, are demanding extra improvements in the performance of stabilizers for polymer articles. For some applications, it is customary for the manufacturer to warranty the product for some length of time, including against photo-bleaching and physical degradation by sunlight. Large changes in performance can be realized from minimal increases in the cost of a formulation, and producers are further realizing the value of well-stabilized materials and products for their customers. Solvay, from the days of American Cyanamid and Cytec, has been committed to delivering new innovative UV stabilizer solutions that enable customers to obtain additional value from performance differentiated products.

In a customer and market driven business structure, it is important to understand how to use advanced technology to better meet the unmet needs of customer. In a competitive environment, customer seeks product differentiation to increase the product value to the final end customer. Product innovation can manifest itself as enhanced performance, ease of use, improved manufacturing efficiency, reduced complexity in operations or improved product quality.

As a major supplier of innovation stabilizer solutions to the polymer industry, the development of technology is guided by the unmet needs described by the customer and industry. Several key

unmet needs were discovered in the building/construction and also in the resin/masterbatching industrial segments. New technology and proprietary products were developed to meet the industrial unmet needs in building/construction and also in the resin/masterbatching segments.

Introduction – Stabilizer Innovation for Building and Construction

Polyolefins, especially TPO, TPV and TPE, are replacing other materials in construction for reasons including: their physical properties, ease of fabrication, barrier properties, relative cost effectiveness, lower weight, and recyclability. For some building applications, including roofing membranes, the performance requirements are even more demanding, with some manufacturers looking to meet and even exceed both the current long-term heat aging and weather resistance specifications set forward by the ASTM D6878 (Table 1). A product that far surpasses the current long-term heat aging standards could help a producer find new markets in desert regions or in equatorial locations; at the extremes, a roof could be hotter than 90°C due to location, design, materials and radiant heat from surrounding surfaces. In addition to the aforementioned environmental stresses on a roofing sheet, often these sheets will be in contact with tar and other building materials that could contain stabilizer-inactivating chemicals.

Table 1 - Thermoplastic Polyolefin-based Sheet Roofing Standards & Specifications

ASTM D6878 -17 Standard for Thermoplastic Based Sheet Roofing (2017)			
Test	ASTM Test Method	Test Condition	Passing Requirement
Heating Ageing	ASTM D573	<ul style="list-style-type: none"> • 5,376 hours (32 weeks) at 240°F (116°C) or • 1,344 hours (8 weeks) at 275°F (135°C) 	<ul style="list-style-type: none"> • 3" Mandrel Bend Test No cracks/crazing inspected at 7X magnification • Weight loss < 1.5%
Weathering Resistance	ASTM G155	<ul style="list-style-type: none"> • 10,080 kJ/m² at 340 nm and 80°C BPT, 50°C air temperature • Water spray cycle = 102 min. light & 18 min. light + water 	<ul style="list-style-type: none"> • 3" Mandrel Bend Test No cracks/crazing inspected at 7X magnification

Market trends in the UV weathering of TPO roofing material have been evolving in the recent years. In 2003, ASTM D6878 describes the performance requirement as 5,040 kJ/m² Xenon Arc exposure (mandrel bend test with no cracks at 7x magnification). In 2006, ASTM D6878 describes the performance requirement as 10,080 kJ/m² Xenon Arc exposure (mandrel bend test with no cracks at 7x magnification). Currently in 2019, the product differentiation trends are discussed at increasing UV performance to >30,240 kJ/m². Generally most other companies simply recommends increase the dosage of the UV system to meet the higher performance trends. The industry observed that increasing the UV dosage often leads to additive blooming issues resulting in an unsightly powdery deposit on the surface of the TPO roofing membrane. Also in other cases,

membrane to membrane weldability is negatively affected which can lead to product failure. New innovative technologies are required to meet the roofing industry unmet needs. Figure 1 illustrates the mandrel bend test showing a sample that passed and a sample that failed.

Figure 1 – Illustration of a Mandrel Bend Test – Sample Passed and Failed



New innovative technologies are required to address the roofing industry unmet needs. Meeting the roofing trend of $>30,240 \text{ kJ/m}^2$ of Xenon Arc exposure is not a trivial innovation target. Surface blooming, minimal processing volatilization, low to no odor, high performance duration for physical property retention combined with thermal stabilization needs to be considered in the product development. Table 2 describes the new product, CYASORB CYNERGY SOLUTIONS® B878T Stabilizer which meets the unmet performance requirements of the industrial trend.

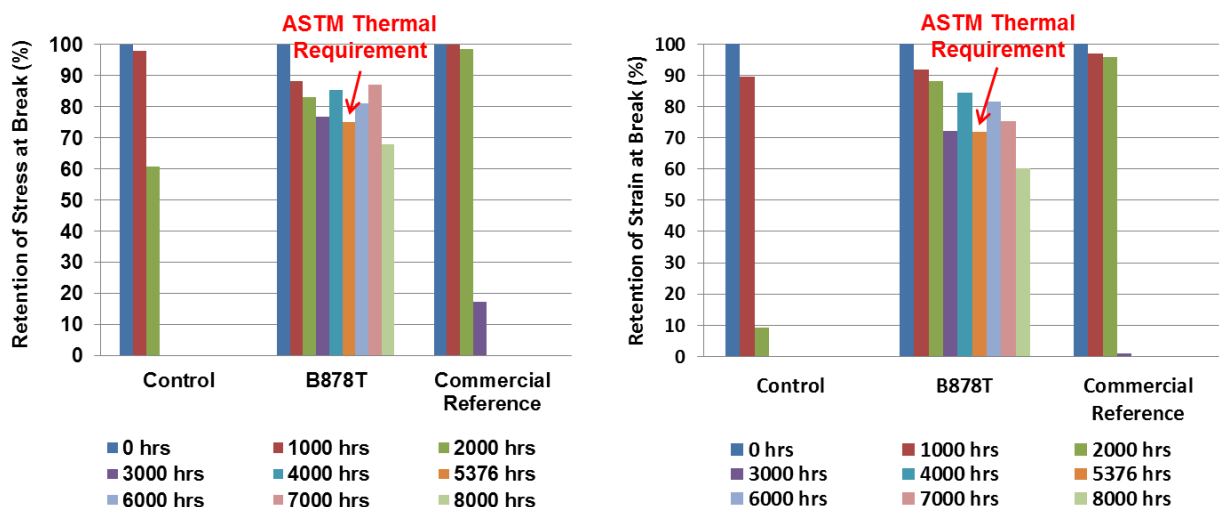
Table 2 – CYNERGY B878T UV Weathering Performance - Mandrel Bend Test

		ASTM D6878 UV Requirement			Industry Trend	Solvay Innovation B878T	
	kJ/m²	5,040	10,080	20,160	30,240	35,280	50,400
Control (No UV)		Failed					
B878T		Passed	Passed	Passed	Passed	Passed	Passed
Commercial Reference		Passed	Passed	Passed	Failed		

Heat Aging requirement for TPO roofing membranes have also experienced changing requirements and performance increasing trends. In 2003, the heat aging requirement was described at 4 weeks at 240°F (mandrel bend test with no cracks at 7x magnification) by ASTM. In 2011, the performance requirements were increased to 32 weeks at 240°F. In 2017, heat

ageing at 275°F for 8 weeks was offered as alternative. There is a clear need for a new product that can deliver a higher performance to meet/exceed the defined unmet industrial needs. Figure 2 describes the thermal stabilizing performance of CYASORB CYNERGY SOLUTIONS® B878T Stabilizer after 8000 hours of thermal aging at 240°F (116°C). B878T surpassed the 5376 hours of thermal exposure and showed 60% of retention of strain at break after 8000 hours at 240°F. The commercial reference sample failed after 3000 hours at 240°F.

Figure 2 – Heat Ageing Performance (240°F/116°C) of B878T – Physical Properties



Also important in the roofing membrane requirement is the ability to withstand extended time at high temperatures. Without the aid of stabilizers, roofing membrane shows signs of degradation after 1 year outdoor. Current ASTM requirement is 32 weeks (5376 hours) at 240°F (116°C). The new CYASORB CYNERGY SOLUTIONS® B878T Stabilizer is able to provide thermal stabilization effectiveness approaching an unprecedented 8000 hours at 240°F, far exceeding the ASTM D6878 requirements. See Table 3 below.

Table 3 – CYNERGY B878T Thermal Stabilizing Performance – 240°F (116°C)

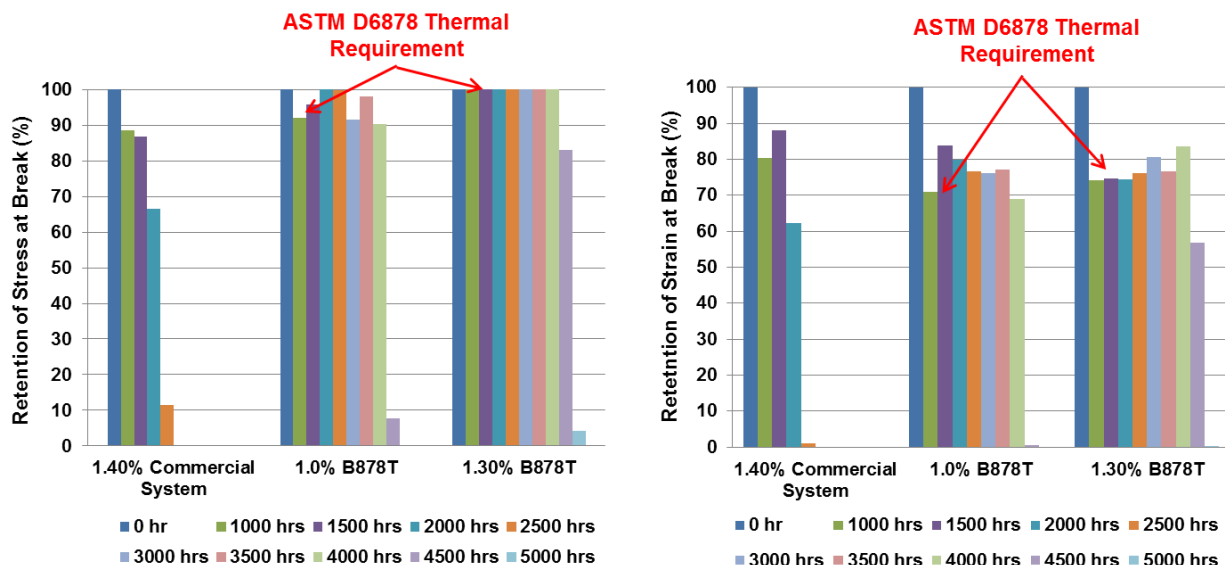
ASTM D6878
Thermal
Requirement



Hours	1,000	2,000	3,000	5,376	6,500	7,500	8,000
Control	Passed	Failed					
B878T	Passed	Passed	Passed	Passed	Passed	Passed	Failed
Commercial Reference	Passed	Passed	Failed				

As thermal specifications are moving toward higher performance requirements, new stabilizers are required to meet future targets as well. In Table 4, CYASORB CYNERGY SOLUTIONS® B878T Stabilizer demonstrated thermal stabilization effectiveness at the higher thermal conditions of 8 weeks (1344 hours) at 275-280°F (135-138°C). Roofing samples containing B878T retained greater than 50% of strain at break after an unprecedented 4500 hours of thermal exposure at 280°F (138°C), far exceeding the standard requirements. See Figure 3 below.

Figure 3 – Heat Ageing Performance (240°F/116°C) of B878T – Physical Properties



Outstanding weathering performance of CYASORB CYNERGY SOLUTIONS® B878T Stabilizer was also verified in natural outdoor weathering in Arizona. Single Ply TPO Roofing Membrane samples were sent to New River, Arizona for exposure under the Ultra-Accelerated EMMAQUA

weathering conditions (ASTM G90-17). In Table 4, after 4,650 MJ/m² radiant exposure in a Ultra-Accelerated EMMAQUA test (approximately equivalent to 15 years natural outdoor exposure in Miami, Florida), the sample containing B878T showed no sign of cracks/crazing at 7X magnification in the 3" Mandrel Bend Test.

Table 4 – CYNERGY B878T Weathering Stabilizing Performance – Ultra-Accelerated EMMAQUA New River, Arizona

Radiant Energy (295-385 nm); MJ/m ²	1,550	3,100	4,650	6,200	7,750	9,300
Miami 5° South (Years)	5 years	10 years	15 years	20 years	25 years	30 years
B878T	Passed	Passed	Passed	Weathering Continues		

In summary, CYASORB CYNERGY SOLUTIONS® B878T Stabilizer has demonstrated excellent UV performance, in TPO roofing membrane, far exceeding the ASTM D6878 specification and ability to meet future higher performance specifications. Furthermore, B878T has also demonstrated unprecedented thermal stabilization performance, in TPO roofing membrane, surpassing the newer ASTM D6878-17 heat ageing specification.

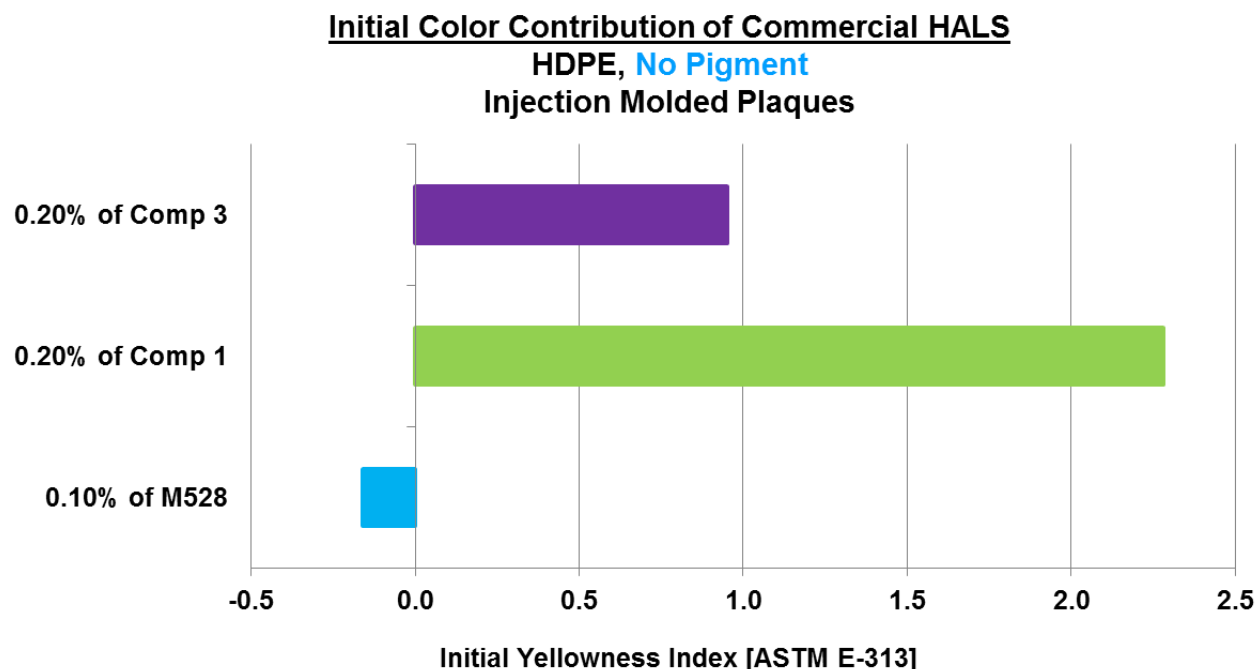
Introduction – Stabilizer Innovation for Resin Producers and Matchbatchers

Injection molding is a major polymer processing technique. Many thick sectioned parts are made from injection molding, such as trash cans, roll out carts, IBC tanks, plastic pallets, electrical boxes, containers, etc. The global injection molded plastic market is expected to reach +290 billion USD by 2020. Much of this growth is driven by the replacement of metals and other materials with polymers. The performance requirements for polyolefin injection molded articles vary drastically depending on application. Typical high-end products require a decade or more of outdoor exposure with requirements to protect appearance and physical properties. CYASORB CYNERGY SOLUTIONS® M528 Stabilizer is a new UV stabilizer solution recommended to resin producers and masterbatchers for short to long term weathering performance requirements.

For the resin producers, important features of a new product are low color contribution, FDA sanctioning, tunable concentration with ability to provide UV performance from 2 years to 10 years outdoor stability, non-dusting, non-blooming, good flowability, high storage stability and cost competitiveness.

CYASORB CYNERGY SOLUTIONS® M528 Stabilizer is able to provide low initial color contribution while at the same time provide equivalent UV stabilizing performance of traditional HALS at **HALF** the concentration/dosage.

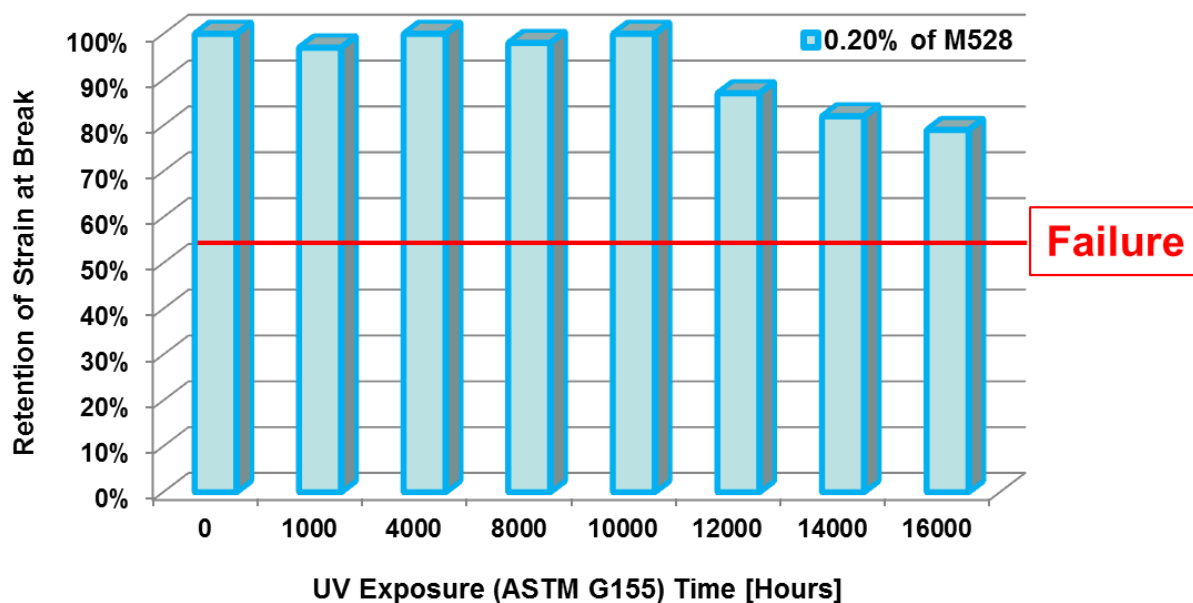
Figure 4 – **Minimal Color Contribution with CYNERGY M528**



The preservation of the water-whiteness of resin is an important property for resin producers. CYASORB CYNERGY SOLUTIONS® M528 Stabilizer imparted little color to resin, as the yellowness is negative which can be seen in Figure 4. (Still blueish). On the other hand, the traditional HALS imparted a shift to a noticeable yellow color in polyethylene resin. In addition, at the same time M528 can provide an unprecedented stability of +16,000 hours of Xenon Arc weathering (ASTM G155) for polyethylene. In Figure 5, M528 loaded at only 0.20% can provided excellent retention of HDPE initial properties after 16,000 hours of weathering. M528 is tunable to meet all short, mid, and long term weathering needs.

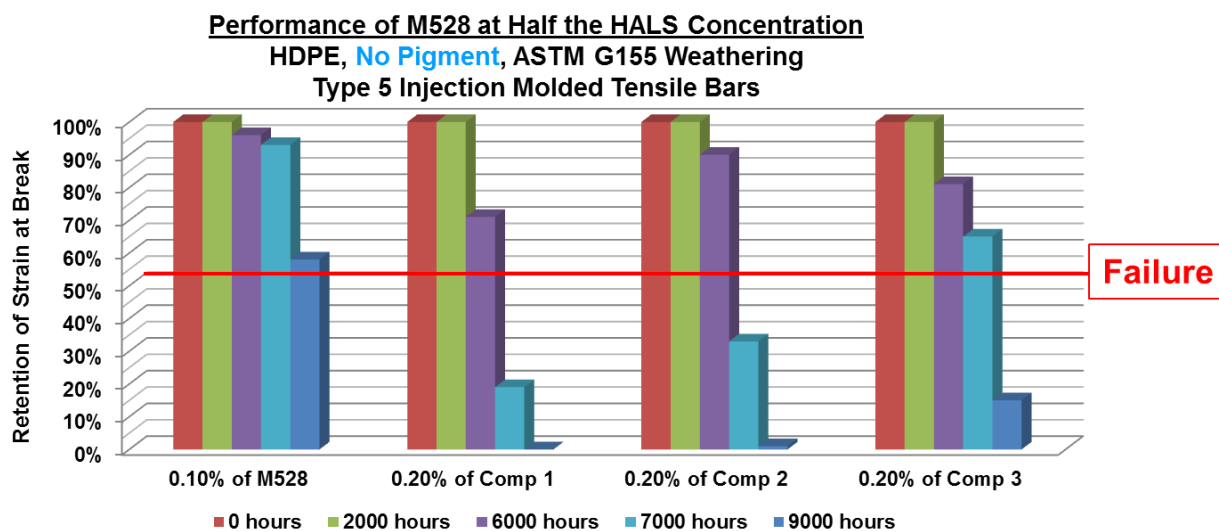
Figure 5 – M528 provides an unprecedented +16,000 hours of weathering (ASTM G155)

Extended UV Performance Provided by M528
HDPE, No Pigment, ASTM G155 Weathering
Type 5 Injection Molded Tensile Bars



For general performance requirements, the M528 concentration can be tuned downward to lower concentrations for meeting 4,000, 8,000 or 12,000 hours performance targets. Additionally, experimentation showed that new M528 can be used at half the concentration of the traditional HALS to provide equivalent UV stabilizing performance. In Figure 6, M528 was loaded in HDPE resin at 0.10% while the competitive HALS was loaded at 0.20% concentration. At half the concentration of the current traditional HALS technology, CYASORB CYNERGY SOLUTIONS® M528 Stabilizer showed outstanding retention of stabilizing performance (strain at break) which equaled or exceeded those of the current commercial HALS products.

Figure 6 – M528 at half the dosage provides equal or improved retention of physical properties over current HALS



Exceptional UV stabilizing performance of CYASORB CYNERGY SOLUTIONS® M528 Stabilizer is evident in blue and green pigmented polyethylene (Figures 7 and 8), 0.10% M528 outperformed competitive HALS product at half the concentration of traditional HALS at 0.20%.

Figure 7 – M528 surface and appearance protection at half the concentration of commercial HALS

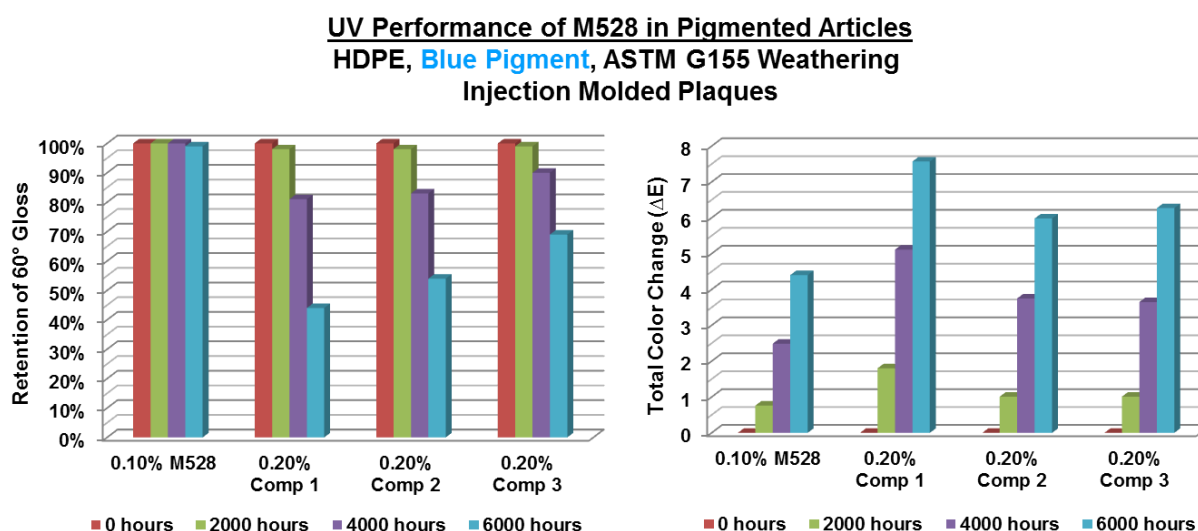
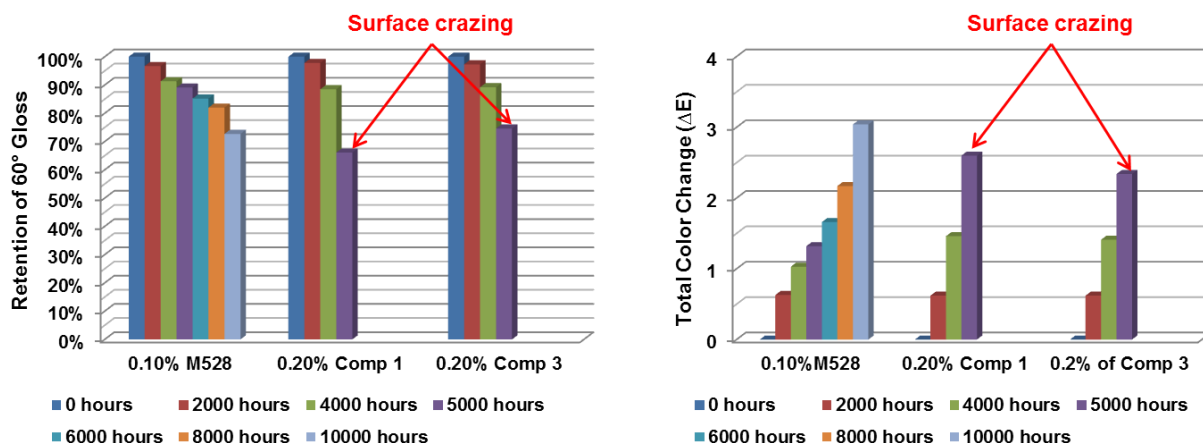


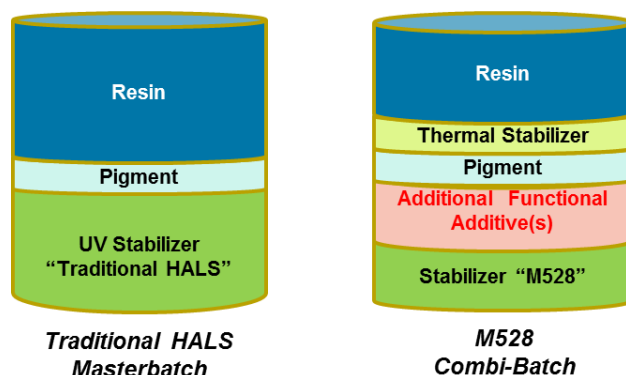
Figure 8 – M528 surface and appearance protection at half the concentration of commercial HALS

UV Performance of M528 in Pigmented Articles
HDPE, Green Pigment, ASTM G155 Weathering
Injection Molded Plaques



For the masterbatchers, the ability to use lower dosage (e.g. half the concentration of the current stabilizer) in the final article, allows for lower concentration in the masterbatch. With the lower loading in the masterbatch, the 'extra space' in the masterbatch can be used for adding more pigment or functional additives. This allows for the creation of a 'combi-batch' where a single masterbatch can deliver multi-functional properties to a polymeric article. For example a masterbatch in the past can deliver UV and AO. With the 'combi-batch', the masterbatch can deliver UV, AO, pigments and anti-slip properties. Figure 9 illustrates the expanded potential from masterbatch to combi-batch. The extra free volume created by the use of M528 can be used for adding other functional additives, creating value-added multi-functional masterbatch (combi-batch).

Figure 9 – CYNERGY M528 opens the possibilities for a multi-functional masterbatch (Combi-batch)



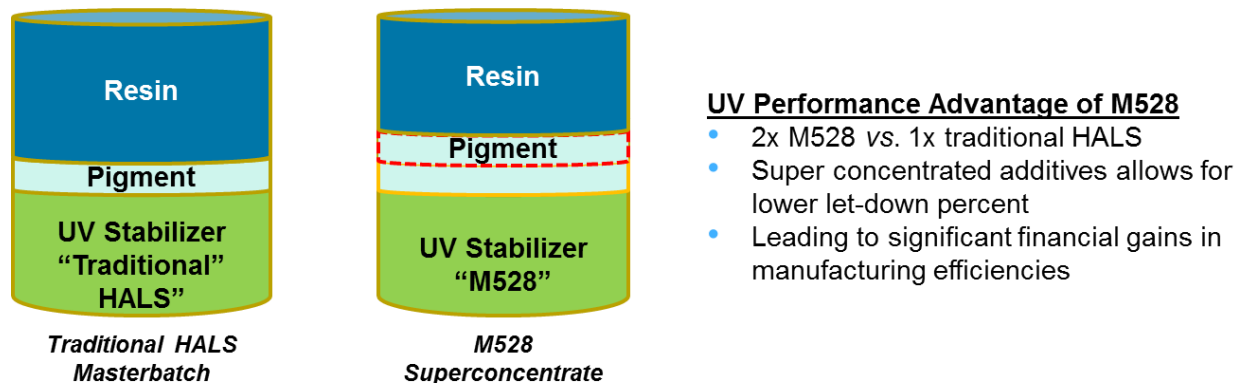
UV Performance Advantage of M528

- 2x M528 vs. 1x traditional HALS
- Equal performance at half the concentration of traditional HALS
- Extra free volume enables the addition of other functional additives

Alternatively, CYNERGY M528 can be the foundation for the creation of a UV superconcentrate masterbatch. Since M528 at half concentration provides the same performance of the traditional

HALS, loading the M528 at the same concentration as the traditional HALS lead to the masterbatches with lower let-down ratios. The super concentrated M528 masterbatch would require less manufactured volume of the masterbatch resulting in increased operational efficiency and profits. For example, masterbatcher can fill an order using only 5 mt of M528 containing super-concentrate vs. 10 mt of masterbatch with traditional HALS. Figure 10 illustrates the upgrading of traditional UV masterbatch to highly concentrated M528 superconcentrate.

Figure 10 – CYNERGY M528 enables the manufacturing of Superconcentrates



Summary

This paper highlights the UV and thermal performance of two new innovative stabilizer solutions from Solvay: CYASORB CYNERGY SOLUTIONS® B878T Stabilizer for highly demanding building and construction applications and CYASORB CYNERGY SOLUTIONS® M528 Stabilizer for injection and blow molding.

In TPO roofing materials, CYASORB CYNERGY SOLUTIONS® B878T Stabilizer demonstrated excellent retention of physical properties and strong resistance to cracking in both highly-intense ASTM D6878 Xenon Arc weathering conditions and two different high temperature heat ageing conditions.

In HDPE injection molded parts, modest levels of CYASORB CYNERGY SOLUTIONS® M528 Stabilizer have shown to deliver good surface protection, physical property retention, and colorfastness through various weathering experiments in an ASTM G155 Cycle 1 weatherometer. At higher dosing of the M528, unsurpassed UV performance can be achieved in reaching UV-20 grade.

Solvay continues to lead technology innovation to extend the performance of plastics and open additional high-value opportunities for polyolefins, highlighting Solvay's company-wide commitment in *Asking More from Chemistry*.