Fall 2020

CAD NEWS®

A publication of the Color and Appearance Division of the Society of Plastics Engineers

Chairman's Message

Dear SPE Colorant and Appearance Members,
As your new Chairperson, I would like to begin by expressing my appreciation for this opportunity. It is both an honor and a privilege to serve in this capacity. I would also like to thank Doreen Becker as outgoing chair for her leadership over the past year.

It is difficult to find words to appropriately describe what we are dealing with, collectively, regarding the Covid-19 pandemic. It has impacted our way of life unlike anything most of us have ever experienced before. It does not necessarily mean we cannot do the things that we are accustomed to doing; however, it does mean we must be responsible and do some things differently. Welcome to Virtual RETEC®!

Yes, our 58th annual conference for the coloration and appearance of plastics "Make a SPLASH with Color" will go on. Education is the core of our mission and a full technical program of papers will be offered virtually September 21st-23rd. Jeff Drusda and Cheryl Treat, RETEC® Chair and Vice Chair, have admirably demonstrated the resilience of our team by coordinating a virtual program that will be educational, provide meeting venues, and include some fun with the awards reception, the annual charity fun run/walk, and closing prize raffle.

I encourage all who have attended RETEC® in the past to join us again this year and anyone who may not have, to give it a shot. You will not be disappointed!

On behalf of the CAD BOD, I would like to offer our sincere gratitude to our Corporate Sponsors. Your commitment and generosity through sponsorship, membership, and employee attendance is essential and appreciated. Your support further enhances educational forums like RETEC® and more.

One of the first orders of business during our August 18th virtual summer meeting was the greeting of our newest CAD BOD members. Karen Carlson - EMD Performance Materials, Tony Tanner - Milliken, and Andrew Smith - AErnest.Consultech were recently elected to three-year terms and we are excited to have them as part of the team.

In closing, my appreciation for personal interaction has grown even stronger through these times and I look forward to seeing you all in person at a future conference or meeting. In the meantime, please remember "In uncertain times, kindness connects us all" and "we will get through this together."

Stay Healthy and Safe!

Mark A. Freshwater
2020-2021 CAD BOD Chair

SPE COLOR & APPEARANCE

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Editor's Note

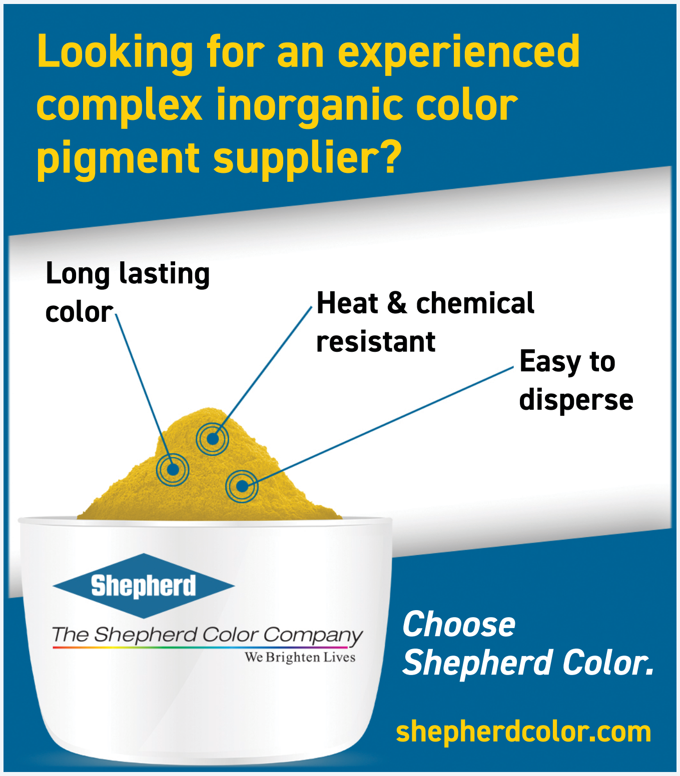
Hello Color and Appearance Division and welcome to the 2020 Fall issue of the Newsletter where you will find helpful information on upcoming events, especially the 2020 CADRETEC® which is Virtual for the first time due to COVID-19 concerns.

What a year 2020 has turned out to be and how it has greatly affected our lives in so many ways. The task of putting together a Virtual CADRETEC®, virtually, was something we never thought we would have to do. There were many people involved, as there is in a typical live event, that sacrificed many hours and days to put this event together. None of whom has had to do this before, so it was a great learning curve for all involved. Please consider coming to this year's Virtual CADRETEC® and check out all that was put together for the Division and see how it benefits our Division. A special thanks needs to be given out to this year's Chair, Jeff Drusda and Co-Chair Cheryl Treat for the organization and diligence in making sure everything gets converted from the live event to the virtual platform. It was not an easy task, but we feel we have captured what we could to make this year's CADRETEC®, although different, the best conference about Color and Appearance in the world.

We also need to thank each and every one of this year's sponsors for their continued support of the CADRETEC®. The support received by the conference sponsors is what is used to help spread the word of the importance of the coloring of plastics. This is demonstrated through the number of scholarships given out each year by CAD. Also, by supporting of the Plastivan *(details of Plastivan in this issue)* which educates students around the country about the importance of plastics in our world today. Just a couple examples of what is done with this support.

Please enjoy this edition of the CADNEWS® and check out what is inside. As always, if you have comments about the Newsletter or like to see certain content that is currently not being added or discussed, please let me know. Always looking ways to make the Newsletter better for all.

Mark Tyler
Newsletter Editor
tylerm@xxxsilberline.com



Scholarship Opportunities

This is an SPE CAD Scholarship Information Reminder for the 2021/2022 School Year. The Society of Plastics Engineers Color and Appearance Division have scholarships available for qualified individuals.

Each year, scholarships are awarded in honor of some of those who have influenced our industry through education of up to $4,000 each. Additional full or partial scholarships may be awarded based on available funding and on the number of qualified applicants.

Jack Graff Memorial Scholarship	up to $4000.00
Gary Beebe Memorial Scholarship	up to $4000.00
Bob Charvat Memorial Scholarship	up to $4000.00
Steve Goldstein Memorial Scholarship	up to $4000.00
George Rangos Memorial Scholarship	up to $4000.00

For questions on applications or process
please email Ann Smeltzer, or call her at 412-298-4373

Problems and Solutions for Coloring High Heat Polymers

Growth of the plastics industry depends on finding performance polymers that can replace traditional substrates and provide better performance, lower cost, extended durability or reduced weight. These performance polymers are generally processed for several minutes at temperatures in excess of 550°F (288°C), and therefore, require colorants that are equally heat stable. However, many organic pigments and solvent dyes degrade, sublimate, or migrate at these elevated temperatures. To further complicate matters, the amides in nylon react with many organic colorants. This reaction causes the chromphore to degrade, thus leaving very few options to color high performance high temperature polymers.

Seeing this problem, ColorChem has developed and commercialized a solution—a full line of heat resistant dyes specifically engineered for glass-filled nylon, polysulfones and other high heat polymer applications. Testing and commercial usage has shown that ColorChem's Amaplast® high heat dyes can withstand the elevated processing temperatures and extended dwell times that cause other colorants to degrade. These Amaplast® dyes provide the brightest hues on the market, and will not react with nylon, thereby maintaining their color and clarity throughout multiple processing cycles.

ColorChem's dyes are ideal for coloring all nylons and glass-filled nylons, polysulfones, PC, and PEEK. ColorChem's technology is proven, proprietary and domestically manufactured. Amaplast® dyes outperform the commercial alternatives offered by offshore manufacturers, such as Solvent Orange 116, Solvent Red 52, Solvent Red 149, Solvent Yellow 104 and Solvent Blue 7.

As a domestic manufacturer, ColorChem has complete control over the manufacturing process, purity, inputs, supply chain, and logistics, for these products.

ColorChem's high heat colorants include the following products:

Amaplast® Yellow NX: a bright neutral yellow
Amaplast® Orange YXL: a bright orange
Amaplast® Orange GXP: a bright red-shade orange
Amaplast® Blue HB: a strong blue
Amaplast® Violet PK: a strong violet
Amaplast® Red BSR: a blue-shade red (not suitable for polyamide)

In addition, ColorChem offers cerium sulfide based pigments for use in opacifying and coloring nylon and other high heat polymers. These pigments, now known as Greentop™ and Neolor™ pigments, can be used in conjunction with ColorChem's Amaplast® dyes to color the most demanding polymer applications and the combination is especially suitable for use in coloring glass-filled nylons.

The GreenTop™ and Neolor™ products, for which ColorChem is the exclusive U.S. distributor:

Neolor™ Light Orange H
GreenTop™ Orange S
GreenTop™ Red S

With the addition of the Greentop™ and Neolor™ pigments, ColorChem is a one-stop shop for high heat coloring solutions.

Please visit www.colorchem.com, or contact ColorChem directly at +1-770-993-5500 or sales@colorchem.com for additional regulatory or product information.

Fun Run

CAD RETEC® 2020 Fun Run

14th Annual 5K Virtual Fun Run

This year the annual 5K Fun Run is going virtual! Register and run (or walk) your distance around your neighborhood, on your treadmill, or anywhere you can physically distance. Register through the CAD RETEC® Website!

Use a fitness tracker or your cell phone to track your time and distance. Prizes (Two $50 Amazon Gift Cards) will be awarded for the fastest and most colorful runner, so make sure to share your time and/or a photo on Facebook (tag @ DCLCorporation2020) or email to amiller@pigments.com. Please submit your time and/or photo of yourself completing the run by Monday, September 21st at 7:00 PM. If you have any questions, please contact DCL Corporation!

MAKE A VIRTUAL SPLASH WITH COLOR
CAD RETEC® 2020

Join us virtually at CAD RETEC® 2020
September 21-23, 2020

For information go to www.4spe.org/CADRETEC
Check out the CAD RETEC Sizzle video

Still deciding on Registration?

With virtual venue, this is a great opportunity to educate yourself and make contact with the most informed professionals in your field, and all without leaving your home office. Join Us, It is easy. Click here.

Cost:

SPE MEMBER 2020	**$195**
SPE NON-MEMBER:	**$395**

CAD RETEC® Committee:

Chairperson:
Jeff Drusda, The Chemours Company
jeffrey.drusda@chemours.com

Vice Chairperson:
Cheryl Treat, BASF
cheryl.treat@basf.com

Technical Program:
Alex Prosapio, Sudarshan
aprosapio@sudarshan.com

Mark Tyler, Silberline Manufacturing
tylerm@silberline.com

A special thank you to all who responded to our survey a few months back, and to all our sponsors and team of organizers for your flexibility and support dedicated to this conference.

Please take time to view the sponsors recognized on the pages following our schedule.

MAKE A VIRTUAL SPLASH WITH COLOR
CAD RETEC® 2020

Monday

Eastern Time		Speaker	Company	Title
8:15	8:30	**Jeff Drusda**	**2020 RETEC Chair**	**Opening Remarks**
8:30	9:00	Jeralyn Camp	Byk Gardner	How Gloss and Texture Affect Visual Color
9:00	9:30	Salvatore Monte	Kenrich Petrochemicals	Functioning the Pigment Interface with 1.5-Nanometer Titanates and Zirconates
9:35	9:55	Monday Sponsor Time		
10:00	10:30	Breeze Briggs	BASF	Coloring Plastics for a Sustainable World
10:30	11:00	Nathan Noyes	Croda	Advances in Liquid Color Concentrate Formulation
11:05	11:25	Monday Sponsor Time		
12:00	1:00			PlastChicks Session
1:00	1:30	Curtis Ross	DCL	Increasing Pigment Black Jetness with Color Pigment Blending
1:30	2:00	Patrick Ryan	Silberline	The Effect of Particle Size, Morphology, and Loading Levels, of Aluminum Pigments in Polypropylene Molded Products
2:05	2:25	Monday Sponsor Time		
2:30	3:30			Platinum Sponsor Showcase (5 min talks from Platinum Sponsors)
3:30	5:00			Supplier Showcase (Exhibits Open)

Tuesday

Eastern Time		Speaker	Company	Title
8:30	9:00	Mark Ryan	Shepherd Color	Innovation in Unlikely Places: Hard Work, Attentiveness, and Luck Lead to New Pigment Chemistries
9:00	9:30	Mike Willis	Sun Chemical	Colorant Stability in Common Sanitizing Solutions
9:35	9:55	Tuesday Sponsor Time		
10:00	10:30	Eric Andrews	Colour Synthesis Solutions	Reconciling Risk Assesment of Colourants with Contemporary NIAS Strategy
10:30	11:00	George Iannuzzi		Consumer Packaging Directions for 2020+
11:05	11:25	Tuesday Sponsor Time		
11:30	12:30			Awards Presentation
1:00	1:30	Bruce Mulholland	Celanese	Design for Sustainability - A Case Study with Appearance Nylon
1:30	2:00	Jackie Anim	Ethicon	Role of Branding and Color Science in Medical Devices
2:05	2:25	Tuesday Sponsor Time		
2:30	3:30	**Panel Discussion** – Sustainability Challenges for Colors & Plastics		
3:30	5:00			Supplier Showcase (Exhibits Open)

Wednesday

Eastern Time		Speaker	Company	Title
9:00	9:30	Mike Willis	On behalf of SPE	Colorants - Part IV of the CAD Color Education Series
9:30	10:00	Joseph Fay	BASF	The Effect of Accelerated Weathering Conditions on the Appearance of Polymer Compounds Intended for Outdoor Applications
10:05	10:25			
10:30	11:00	Rob Lorenzini	Maroon Group	New Functional Inorganic Pigments for Laser Marking and Compostable Plastic Products
11:00	11:30	Philip Richards	Sasol	Improved Dispersibility with Fischer Tropsch Synthetic Waxes in Manufacturing Masterbatch and Colorants
11:35	11:55	Wednesday Sponsor Time		
12:00	12:30			Closing Remarks / Prize Give-Aways

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Milliken introduces KeyPlast RESIST™: A spectrum of bright, high-performance colorants for engineering plastics

New portfolio designed specifically for coloring polyamides and high-heat engineering plastics

Milliken & Company, recognized as a worldwide leader of plastic additives and colorants, announced the launch of KeyPlast RESIST™, a spectrum of bright, high-performance colorants for engineering plastics.

Polyamide resins and high-heat engineering polymers present unique challenges in the world of plastics. The materials of choice in demanding electrical, automotive and industrial applications, polyamide resins and high-heat engineering polymers are subject to high-temperature processing and require steady, reliable performance properties, making vibrancy of color difficult to achieve.

Milliken has addressed this challenge with its KeyPlast RESIST range of colorants. These products are specially designed for coloring engineering polymers such as polyamides, polyimides, PBT polysulfones, PEEK, PPO and other high-heat resins and alloys. KeyPlast RESIST colorants can be used effectively with unfilled, glass-filled, and flame-retardant grades of various polyamide types such as polyamide 6, 66, 46, and other high temperature engineering polymers.

"Keyplast RESIST meets the strong requirements in another fast-growing application area—that of electrical vehicles and their charging system requirements," said Sami T.K. Palanisami, Milliken Global Product Line Manager, Plastic Colorants.

The new range delivers the brilliant, consistent colors — including bright orange, yellow, red, blue and green—and the high-end properties that users demand. These colorants offer improved weather resistance and light fastness, are high purity and perform well in the high-temperature and chemically-reductive conditions typically associated with high-performance polymers.

Milliken introduces KeyPlast RESIST™: A spectrum of bright, high-performance colorants for engineering plastics. (Photos © 2020 Milliken & Company, all rights reserved, MKPR209)

For more details and information please contact us or visit us online at ***chemical.milliken.com***

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The SPE Color and Appearance Division generously donated $35,000 to PlastiVan® in 2019. Combined with their 2018 gift of $17,500, their support over two years of $52,500 provided a PlastiVan® visit to 30 classrooms, bringing the exciting world of plastics to thousands of students. Thank you, Color and Appearance Division, for this meaningful impact toward changing the perception of plastics one classroom at a time. And a big THANK YOU for committing to another $35,000 for 2020!

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PlastiVan®

PLASTIVAN®: CHANGING THE PERCEPTION OF PLASTICS ONE CLASSROOM AT A TIME

Through lively demonstrations and hands-on activities, the PlastiVan® Program is designed to excite students about opportunities in science and engineering within the plastics industry. Students are educated about the chemistry, history, processing, manufacturing, and sustainability of plastics and how the science and real-world applications relate to their everyday lives. PlastiVan® provides sound science and educational programs which spark scientific curiosity in students while increasing their knowledge of the contribution plastics make to modern life; encouraging them to seek careers in engineering.

PlastiVan® educators are skilled in tailoring the presentation to meet the needs and grade-level expectations of each classroom and teacher. The program is easily integrated into school curricula. A PlastiVan® visit typically consists of 5 classes/day for up to 40 students/class or is individually designed for STEM and science fairs.

Click here for more information on the PlastiVan®

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CALL FOR PAPERS

YOU ARE INVITED TO SUBMIT A PAPER FOR PUBLICATION & PRESENTATION
Podium and poster presentations showcasing the latest in industrial, national laboratory and academic work.
Share your findings in polymer research or new and improved products and technologies
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- Polymer Analysis
- Rotational Molding
- Thermosets
- Automotive
- Building and Infrastructure
- Decorating and Assembly / Joining
- Extrusion
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- Medical Plastics
- Plastic Pipe and Fittings
- Polymer Modifiers & Additives
- Thermoforming
- Sustainability
- Bioplastics
- Color & Appearance
- Electrical & Electronic
- Failure Analysis
- Injection Molding
- Mold Technology
- Plastics Recycling
- Product Design & Development
- Thermoplastics Materials
- Vinyl Plastics

A full manuscript submission is required and will be due towards end of October 2020. Your paper will be published as part of the ANTEC® 2021 proceedings.

FOR MORE INFORMATION PLEASE CONTACT
Mark Spalding
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THE INFLUENCE OF ADDITIVES ON POLYMER DISCOLORATION

Tad Finnegan and R. E. King III
BASF Corporation, Tarrytown, NY

ABSTRACT

Managing the color of a plastic article requires not only the appropriate selection of the colorants, but also careful selection of the processing, thermal, and light stabilization additives. Improper selection and use of these additives can lead to the formation of chromophores and discoloration of the polymer after processing, during storage, or upon exposure to heat or light. These chromophores may be either transient or durable, leading to unexpected and difficult-to-manage changes in the article's color during storage and use. The use of recycled polymer or regrind can exacerbate the potential for discoloration by introducing chromophore precursor compounds formed by thermo-oxidative stress on the polymer system. In this paper, common causes of discoloration and strategies to manage them through additive selection are presented.

INTRODUCTION

Polymers undergo oxidation during processing and storage that can negatively impact their properties. This oxidation can impact the polymer's molecular weight, melt flow behavior, and color in addition to other properties. Discoloration, because it is immediately evident to an observer, can be of special concern[1,2].

Color is how we perceive the absorbance, reflectance, and transmission of wavelengths of electromagnetic radiation between ~400 nm to 700 nm from an object. The portion of the molecule responsible for absorbing light is the *chromophore*. In organic molecules, the chromophore is a usually a region of highly conjugated chemical bonds where the electrons are delocalized. When an electron in the chromophore absorbs a photon of the right energy, the electron is excited from the ground state into the excited state, as illustrated in Figure 1. The electronic band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) shows us the energy required to excite the electron, and the wavelength of light required to provide that energy is given by Equation 1.

$$E = \frac{hc}{\lambda} \qquad \text{(Equation 1)}$$

where $\boldsymbol{E}$ is the energy of the photon, $\boldsymbol{h}$ is Planck's constant, $\boldsymbol{c}$ is the speed of light, and $\boldsymbol{\lambda}$ is the wavelength of the light.

Molecules with a low level of conjugation require higher energies (i.e., shorter wavelengths) to excite. As the level of conjugation increases, the energy required to excite the electron decreases until eventually the absorbed wavelengths of light will extend into the visible range. From Fieser-Kuhn rules for conjugated systems[3], we can determine the absorbance will enter the visible spectrum for a linear, conjugated system with 8 or 9 conjugated double bonds. As an example, β-carotene (a naturally-occurring pigment) has 11 conjugated double bonds, as shown in Figure 2. It has an absorption of

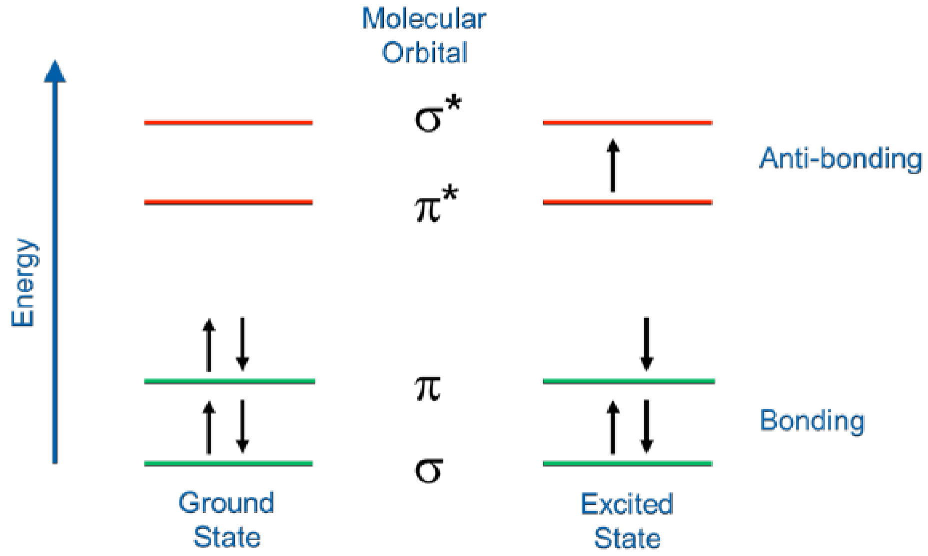


Figure 1. Ground state and excited state of electron in a conjugated chromophore

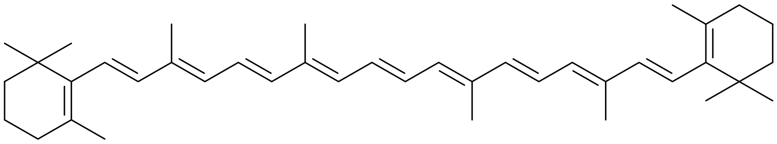


Figure 2. Molecular structure of β-carotene

452 nm. This value is well into the visible spectrum (400-700 nm) and corresponds to the absorption of blue light, giving the molecule its characteristic yellow/orange color.

In polymers, often the discoloration is not due to conjugation in the polymer itself; rather, it is other components in the polymer (e.g., antioxidants, light stabilizers, and impact modifiers) that lead to the discoloration. Furthermore, many of these ingredients are not inherently colored, but rather form chromophores as they are oxidized during processing, thermal aging, and weathering of the polymer in the autoxidation cycle.

Figure 3 shows the autoxidation cycle[4]. The process is started when the polymer is exposed to light (in particular, ultraviolet light), heat, or shear in the presence of oxygen. Improperly deactivated catalyst residues or the presence of transition metals can also initiate the process. In the initiation process, a highly reactive free radical (R•) is formed by carbon-carbon or carbon-hydrogen bond scission. Cycle I illustrates the formation of hydroperoxides from the free radical. The free radical interacts with molecular oxygen present in the polymer to form a peroxy radical (ROO•). This peroxy radical can abstract a hydrogen from the polymer or another molecular to form a new free radical (R•) and a

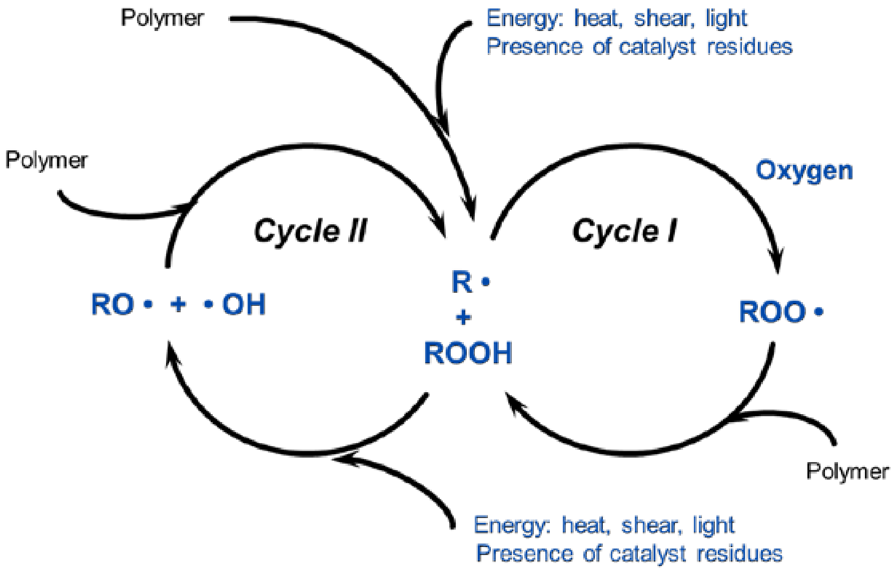


Figure 3. The autoxidation cycle

hydroperoxide molecule (ROOH). The newly generated free radical can then interact with molecular oxygen and repeat Cycle I.

Cycle II illustrates the breakdown of the unstable hydroperoxide to form additional free radicals. The hydroperoxide splits to form an alkoxy radical (RO•) and a hydroxy radical (HO•). These radicals can then interact with the polymer or other molecules to form new molecules (such as alcohols, ROH) and generate additional free radicals that can then enter Cycle I. The breakdown of the hydroperoxides in Cycle II increases the overall radical flux and accelerates the oxidation process.

Polymer additives, such as antioxidants and light stabilizers, are used to slow down and prevent autoxidation. Primary antioxidants, such as hindered phenol compounds, act as hydrogen donors and oxygen-centered radical scavengers, preventing the formation of hydroperoxides. Primary antioxidants are most effective in Cycle I, but also can act in Cycle II. Secondary antioxidants, such as hindered phosphite compounds, act to decompose the hydroperoxide without the formation of free radicals, slowing the creation of free radicals in Cycle II. Ultraviolet light absorbers can absorb ultraviolet light (UV) and dissipate the energy before it interacts with the polymer to form a free radical, preventing entrance into the autoxidation cycle.

While these additives can, and are intended to, reduce the discoloration of the polymer relative to unstabilized polymer, the additives can also *contribute* to color under certain conditions. As examples, three methods by which additives can contribute to color are

1. Over-oxidation of hindered phenols can lead to conjugated structures with strong color
2. Interactions between hindered phenols and oxides of nitrogen (N_xO_y) can lead to the formation of strongly-absorbing chromophores
3. High concentrations of ultraviolet light absorbers can begin to absorb short-wavelength visible light, directly discoloring the polymer

DISCUSSION

Over-Oxidation of Hindered Phenols

Hindered phenols, such as 2,6-di-*tert*-butyl-4-methylphenol (**AO-1**) or octadecyl-3-(3,5-di-*tert*-butyl-4-hydoxyphenyl)propionate (**AO-2**), have been long-established to act as antioxidants in polymer systems. Even at low concentrations, these molecules are very effective at preserving the architecture of the polymer. However, as the antioxidants donate hydrogen atoms to neutralize free radicals in the autoxidation cycle, they can undergo a variety of rearrangements and reactions that can lead to the formation of conjugated chromophores. AO-1, due to its simplicity as a molecule, offers a good model for examining how conjugated chromophores can arise from oxidation of the hindered phenol. Figures 4 and 5 illustrate the transformation of AO-1 into stilbenquinone and diphenoquinone respectively. The more complex conjugated chromophores for the oxidation of AO-2 are shown in Figure 6. Table 1 shows the wavelength of maximum absorption and the molar absorptivity of the transformation products relative to β-carotene.

As illustrated, chromophores do not arise from the loss of a single (or even second) hydrogen in the hindered phenol. To form a chromophore, the antioxidant must donate multiple hydrogens, undergo coupling reactions, and donate further hydrogens to conjugate the coupled molecule. This over-oxidation of the molecule is ultimately what results in the formation of the chromophore.

As polymer converters increase the use of regrind in their processes, and with a strong consumer focus on increasing the amount of recycled polymer used, there is a unique challenge relating to discoloration. In these cases, the starting material (i.e., the antioxidant) has already been partially oxidized or consumed. Each heat history applied to the polymer increases the level oxidation and consumes more

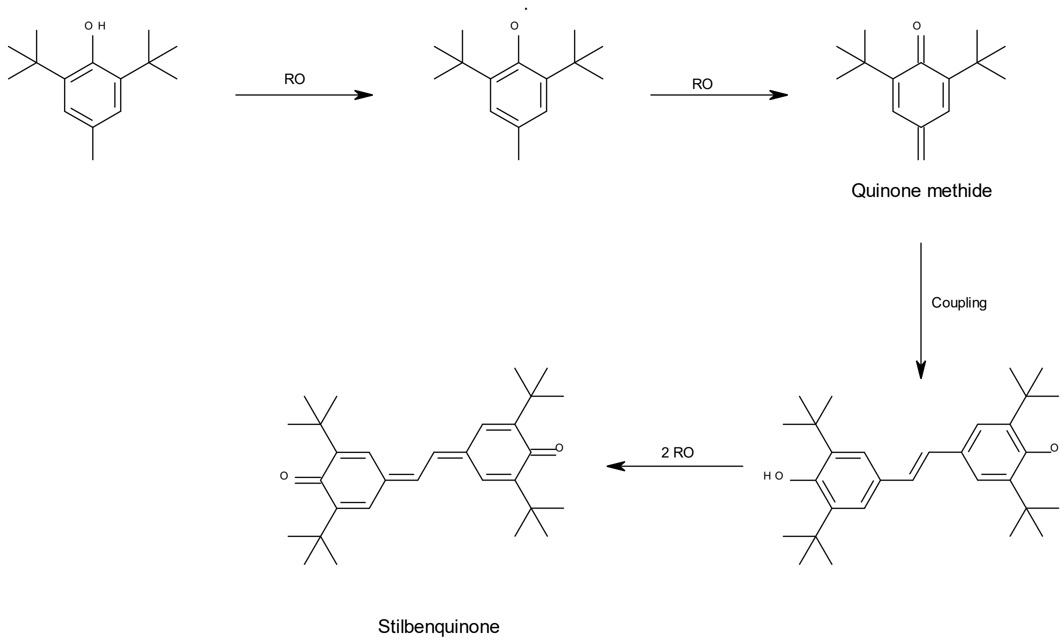


Figure 4. Oxidation of AO-1 to stilbenquinone

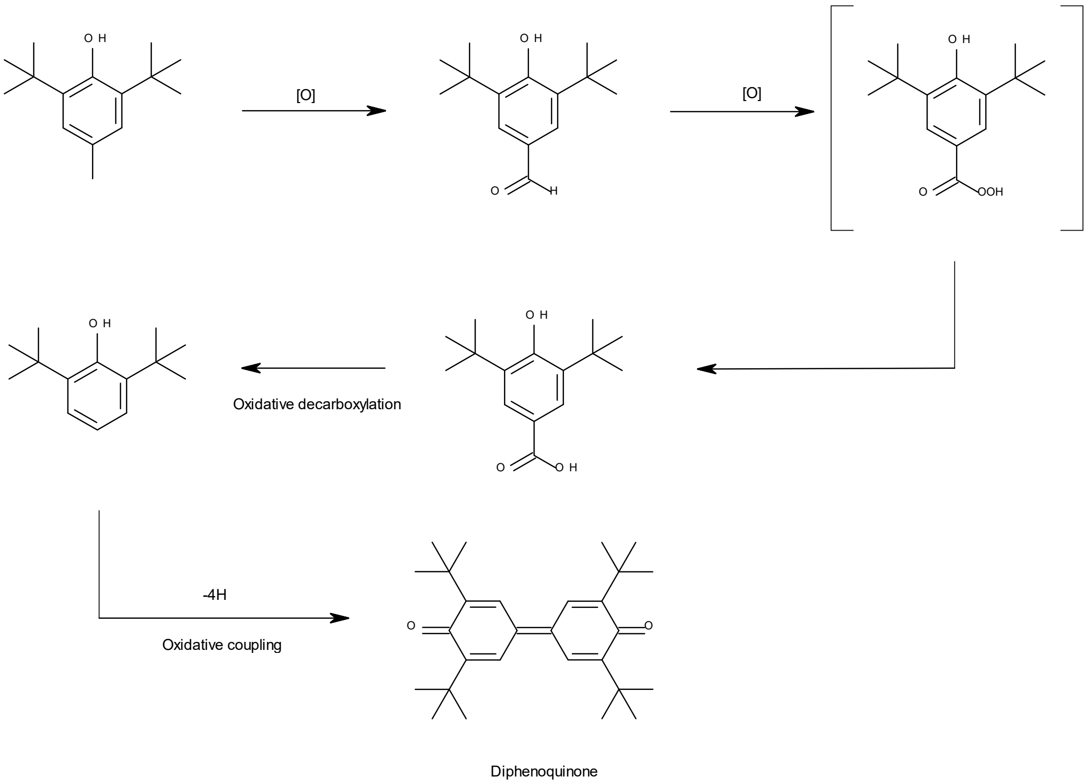


Figure 5. Oxidation of AO-1 to diphenoquinone

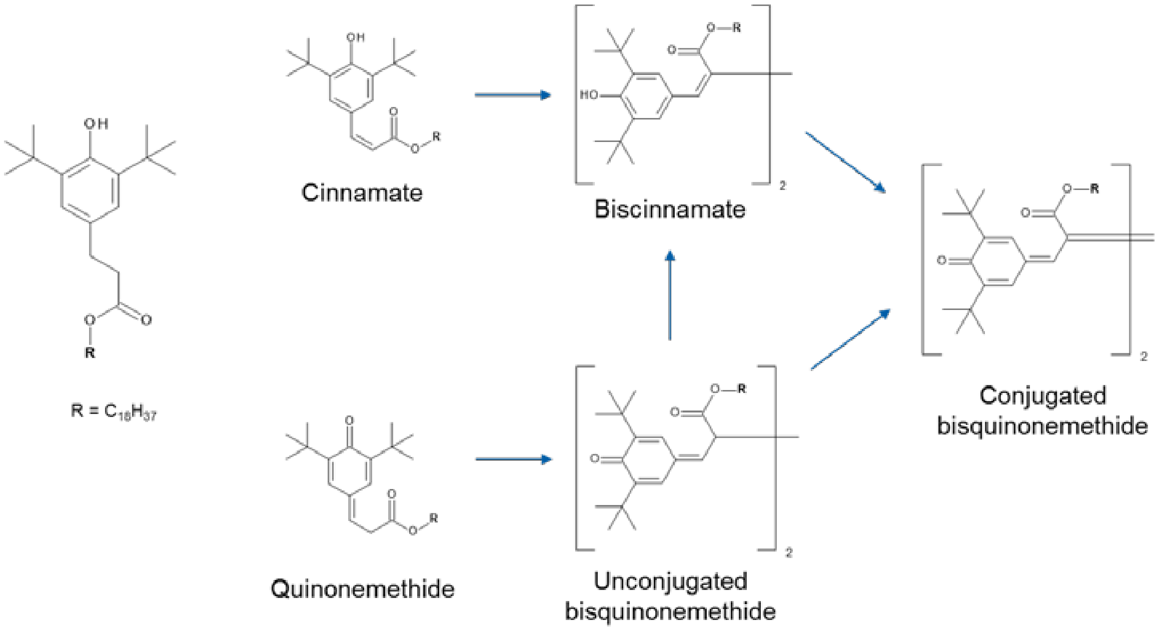
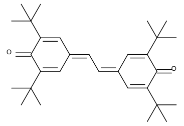
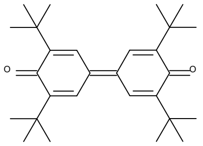
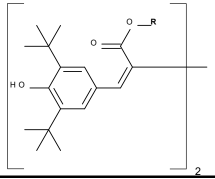
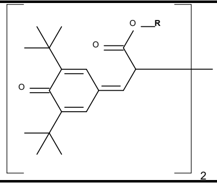
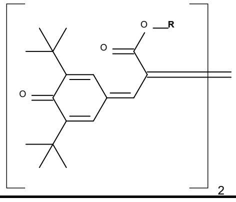
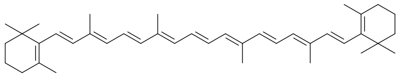


Figure 6. Oxidation products of AO-2

Table 1. Wavelength of maximum absorption and molar absorptivity of chromophores.

Chromophore	Structure	λ_{max}, nm	ε, l/mol·cm
Diphenoquinone		423	72,700
Stilbenquinone		452	106,000
Biscinnamate		450	106
Unconjugated bisquinonemethide		420	116
Conjugated bisquinonemethide		440	34,800
β-carotene		452	152,000

antioxidant. If supplemental antioxidant isn't used at each processing step, the probability of forming a chromophore increases. And since many of the chromophore precursors are nearly colorless, there may be little warning to the converter or consumer that there is a problem until the next stress to the polymer creates discoloration.

To minimize the formation of chromophores due to oxidation of hindered phenols, there are several strategies that can be employed[5].

1. *Select the correct hindered phenol (and concentration)*
   As an example, the formation of chromophores can be reduced by increasing the difficulty of the coupling reaction. The steric hindrance to coupling provided by the C_{18} fatty ester tail of AO-2 compared to the methyl group of AO-1 illustrates this principle. There are many phenolic antioxidants available commercially, with each product having strengths and weaknesses related to discoloration and melt flow control.
2. *Select and use secondary antioxidants (phosphite)*
   The use of secondary antioxidants such as a hindered phosphite to decompose hydroperoxides can reduce the formation of free radicals in the autoxidation cycle, and reduce the burden on the hindered phenol.

3. *Optimize the ratio of hindered phenol to phosphite*
   Because the performance of primary and secondary antioxidants is synergistic, finding the right ratio to will ensure neither component is over oxidized or consumed disproportionately. It is recommended that the ratio of phenol to phosphite be in the range of 1:1 to 1:4, with 1:2 being a good starting ratio.
4. *Select and use an appropriate acid scavenger*
   Since catalyst residues and certain types of acidic or alkaline species can accelerate reactions leading to discoloration, using an appropriate acid scavenger can help minimize the formation of chromophores.
5. *Consider employing phenol-free stabilization*
   The use of alternative chemistries, such as hydroxylamines, in place of hindered phenols can reduce the likelihood of forming chromophores and provide better polymer color.

Gas Fading / Pinking of Hindered Phenols

Hindered phenols are known to interact with oxides of nitrogen (N_xO_y) to create chromophores[7,8,9], as illustrated in Figure 7. In this instance, the degree of discoloration is also related to the exposure surface and the surface area to volume ratio of the plastic part. Materials will high surface area to volume ratios, like polymeric fibers or films, have a higher exposure to N_xO_y during storage, leading to a higher rate of discoloration.

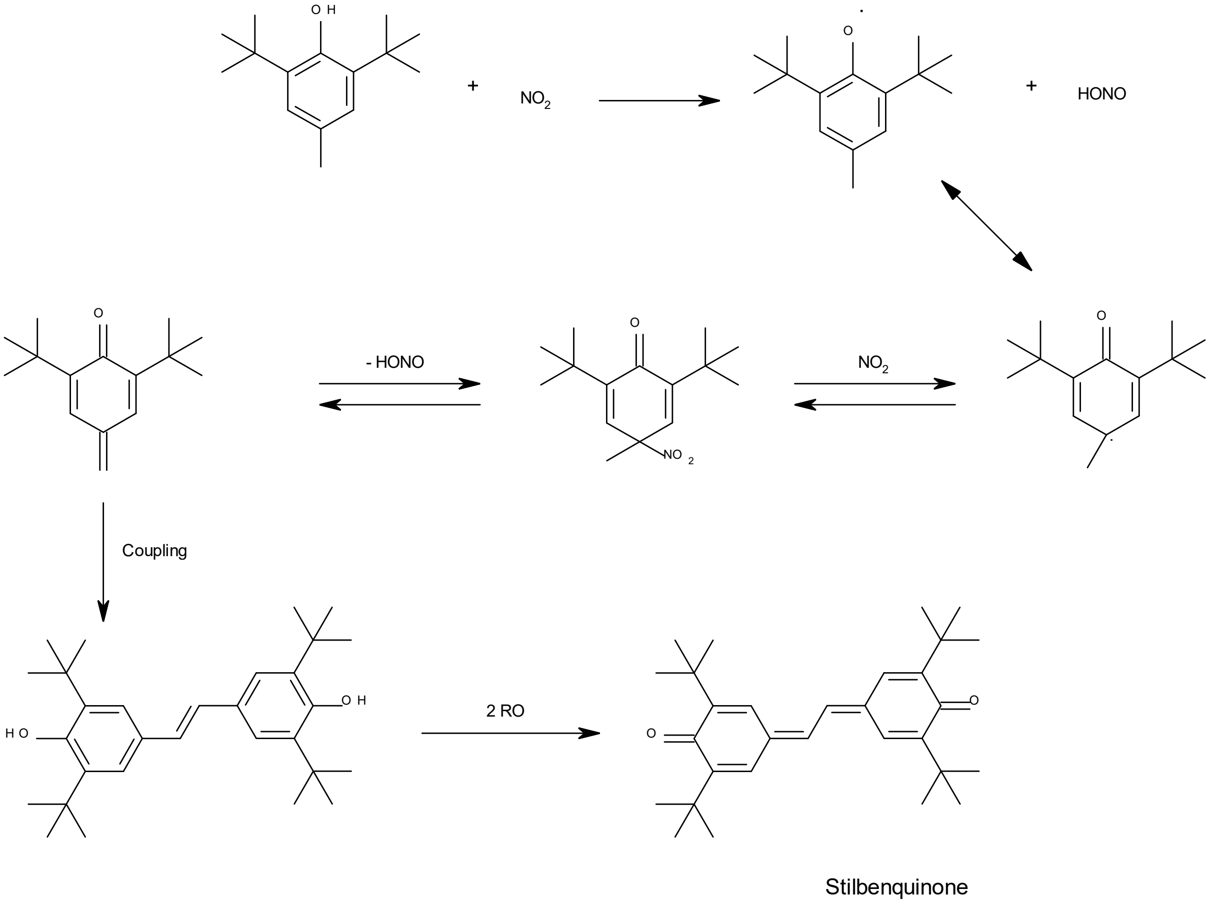


Figure 7. Gas fading reaction

To minimize the formation of chromophores due to gas fading, beyond limiting the exposure of the plastic part to N_xO_y, the strategies employed are similar to the strategies used to prevent over-oxidation of hindered phenols (see above). Selection of the correct phenol, phosphite, and acid scavenger, and using the appropriate concentration and ratio of ingredients can reduce the oxidation of the hindered phenol. The best option, however, may be moving to phenol-free stabilization systems, such as those based on hydroxylamine stabilizers.

Additionally, it should be noted that many polymer manufacturers include at least some hindered phenol in their polymers to provide melt processing stability. Phenol already present in the polymer cannot be removed and will always be prone to gas fading reactions. Selection of low gas fading grades of polymer may be required for sensitive applications.

Direct Absorbance by Ultraviolet Light Absorbers

Ultraviolet light absorbers are chromophores that prevent the photodegradation of polymers by absorbing ultraviolet light and dissipating the absorbed energy without breaking down or initiating oxidation. The mechanisms of absorption have been studied extensively[5].

UV absorbers are governed by Beer-Lambert law, which equates absorbance of light to the concentration of the absorber, the pathlength the light travels, and the molar absorptivity of the molecule itself as given in Equation 2:

$$A = -log_{10}\left(\frac{I}{I_0}\right) = \varepsilon l c \qquad \text{(Equation 2)}$$

where A is the absorbance, I is the intensity of transmitted light, I_0 is the intensity of incident light, ε is the molar absorptivity (a measure of the attenuation of a particular wavelength of light), l is the pathlength, and c is the concentration of the absorber.

For absorbers that block longer-wavelength UV radiation, at high concentrations their absorbance can impinge on the visible spectrum and absorb blue light, introducing yellow discoloration into the polymer. This discoloration will be present in the polymer from the start, rather than forming over time as we saw in the previous two cases. According to Beer's law, this impingement will be concentration-dependent, with higher concentrations of absorber acting to absorb more of the visible light.

As an example, Figure 8 show the reflectance curves of three UV absorbers (BTZ-5, BTZ-6, and CYA-1) at different concentrations in polycarbonate relative to a control[10]. At the start of the visible spectrum (400 nm) all the UV absorbers show some absorbance, but BTZ-6 shows strong absorbance than BTZ-5 at equal concentration. CYA-1 shows a longer absorbance tail into the visible spectrum, giving it intermediate performance between BTZ-5 and BTZ-6 in this case.

To minimize the discoloration due to the absorbance of visible light by UV absorbers, there are several considerations to take.

1. *Ensure the light stabilization package is well-designed*
   UV absorbers are only one class of light stabilizers. Other classes, such as hindered amine light stabilizers (HALS), may offer better protection in some polymers (such as polyolefins) without contributing significantly to discoloration. Optimizing the light stabilizer package will help

determine if a UV absorber is necessary in the formula, or if the same result can be achieved by a different mechanism.

2. *Minimize the concentration required for the UV absorber*
   Since absorbance is directly related to the concentration of the absorber and pathlength the light travels, understanding how much UV absorber is required can help. For thick parts, like those found in rotational molded water tanks, only a few hundred parts per million of UV absorber may be required to provide a benefit in light stability. In contrast, in polycarbonate glazing, up to several percent of absorber may be required to meet the durability requirements. Understanding the relationship between durability, concentration, and part thickness will ensure the system is optimized for the end-use application.

3. *Consider alternate chemical families of UV absorbers*
   Every UV absorber has its own absorption spectrum and characteristics. Every polymer has chemical bonds that are susceptible to absorption of UV light. By carefully selecting a UV absorber that covers the spectrum of concern for the polymer, one may be able to select a UV absorber that has less impingement into the visible spectrum while preventing photodegradation of the polymer.

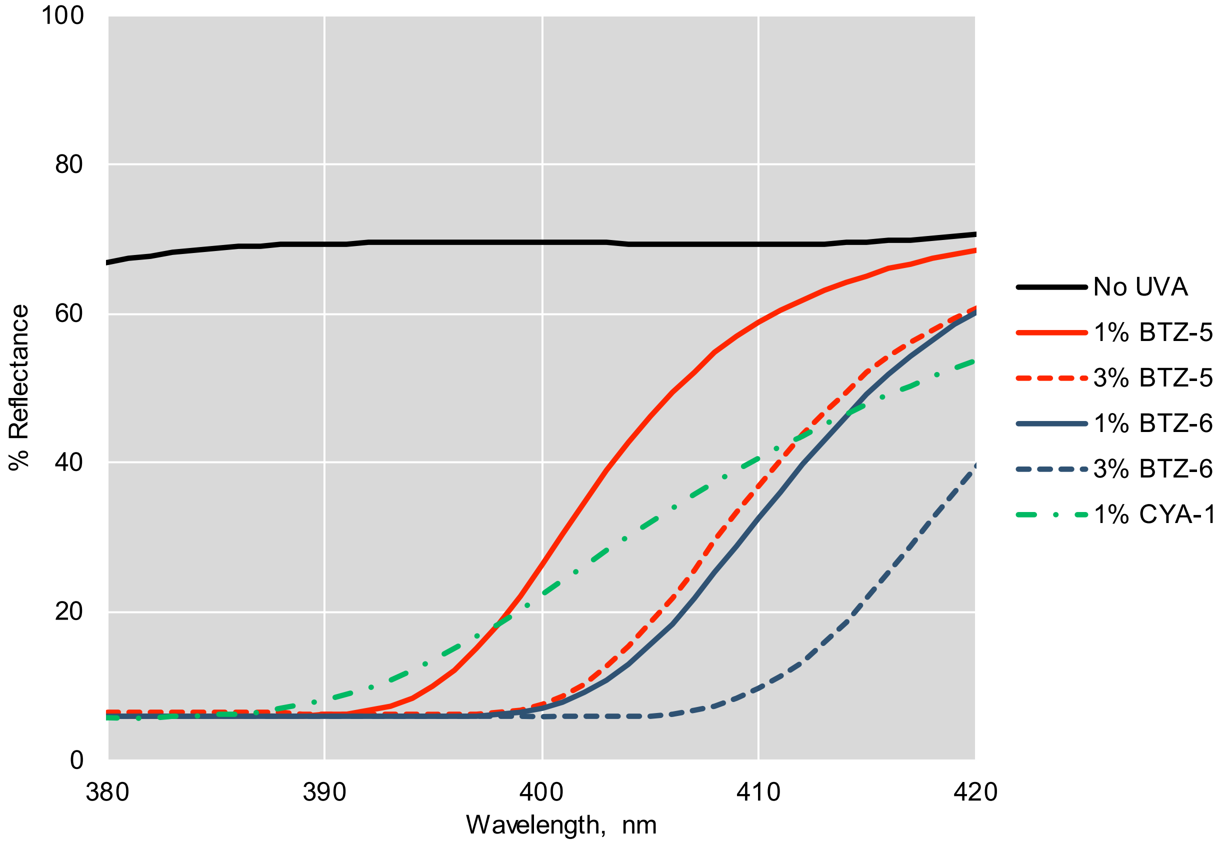


Figure 8. Reflectance curves for ultraviolet light absorbers in polycarbonate

CONCLUSION

While many polymer additives are intended to reduce the discoloration of polymers and ensure the polymer's performance, they can under certain conditions contribute to discoloration. By ensuring that additive packages are well-formulated, one can help mitigate some of the most common discoloration problems. Starting with the antioxidant package, selection of the hindered phenol, phosphite, and acid scavenger is the first step to minimize discoloration. Optimizing the ratio of the phenol to phosphite can also reduce excessive oxidation that can lead to discoloration. Understanding the role UV absorbers can play in initial color is also important. Formulating a robust light stabilizer package, selecting the right UV absorber, and optimizing its concentration are crucial steps to ensure the discoloration is minimized.

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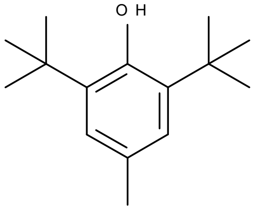
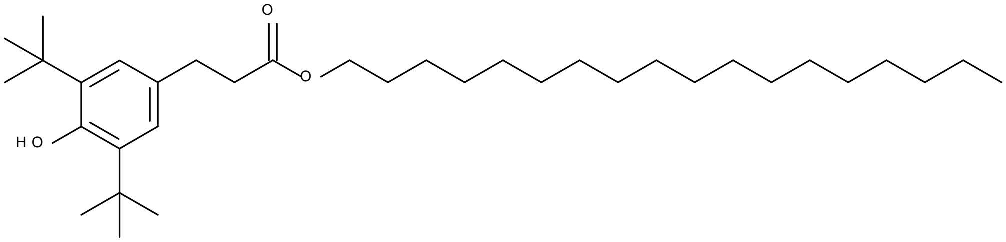
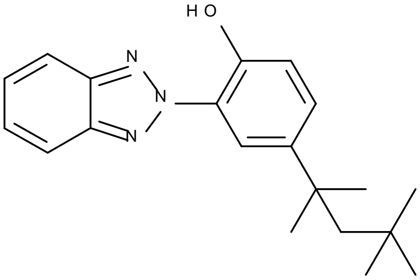
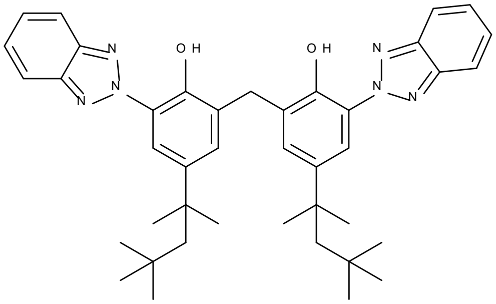
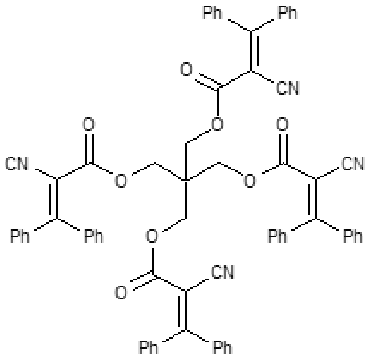
TABLE OF CHEMICAL STRUCTURES

Compound Identification	Structure
AO-1	
AO-2	
BTZ-5	
BTZ-6	
CYA-1	

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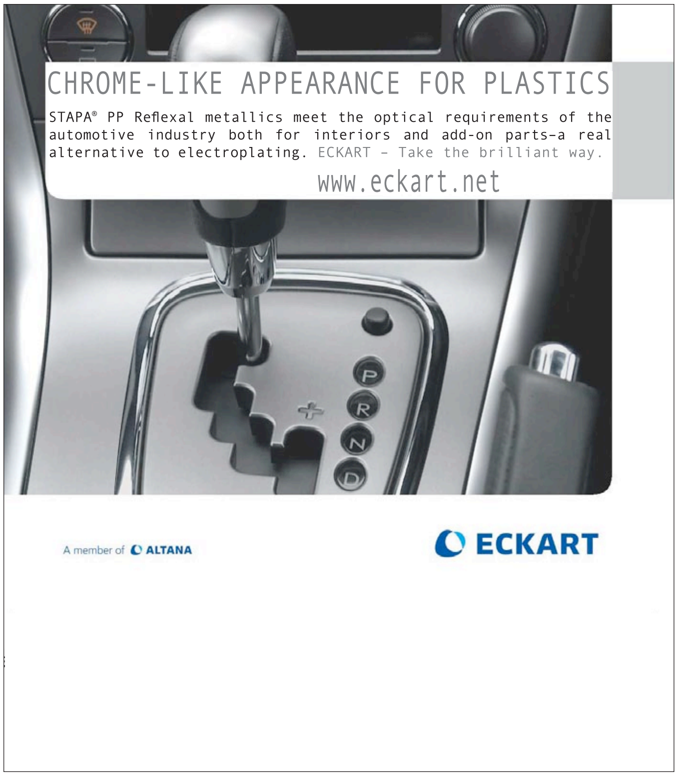

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