



COLOR &
APPEARANCE

CAD NEWS[®]
SUMMER 2023 NEWSLETTER

RETEC 2023

TECHNICAL ARTICLE

*UNDERSTANDING WARPAGE IN
INJECTION-MOLDED THERMOPLASTICS*

Brian D. Coleman | BASF Colors & Effects USA LLC, Southfield MI

ELECTION RESULTS



SUMMER 2023 CHAIRMAN'S MESSAGE

Hello CAD members and visitors. Welcome to the SUMMER 2023 CADNEWS® edition. D65 sets yet again on another Chair term. It is not without deep appreciation to all CAD members and their company sponsors that my term concludes. In my first CADNEWS® letter I mentioned following in the footsteps of giants. I do wish incoming chair Alex Prosapio the same feeling and much success and look forward to the continuation of programs the board provides for education and the coloring of plastics industry.

We have two newly elected board members, Bennett Chin and Cory Singleton, welcome aboard! I do want to thank Breeze Briggs for her work on the board as RETEC Technical Conference Chair, Technical Program Chair, Education Chair, and other involvements in the various committees. Thank you!

Speaking of RETEC, the RETEC Diamond year was well-attended in Orlando. Our conference committee is already busy working on RETEC 2023 in Columbus Ohio. I encourage every company to attend RETEC especially the technical talks. New members in your organization can surely benefit from the technical talks and panel experts as well as tabletop exhibitions. Registration information can be found at specad.org (advanced registration should be opening soon). Information on SPE and SPE CAD scholarships can also be found on the website.

One item to point out if you've never noticed them is the RETEC logo created each year for that specific location. These colorful and clever designs are made into conference pins you receive when checking in. Start your collection this year and see how many you or your colleague can collect.

May D65 shine upon you and weatherometer mist fall upon the fields.

Thank You Everyone!

MICHAEL WILLIS

Color and Appearance Division Chair
michael.willis@sunchemical.com

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Milliken presents

Milliken: The Color Experts

Milliken & Company understands the power and value of color as it relates to branding. Humans are visual creatures, and color plays a key role in purchasing decisions, as it helps to inform, personalize and speak the brand language.

The company continues to tap into its vast experience in this space to develop solutions for a wide variety of end markets and end-use applications.

Milliken's color journey began in 1964, when it launched its proprietary Versatint® washable colorants for textile identification. In 1981, it introduced its Reactint® range of colorants for polyurethane (PU). Five years later, Milliken unveiled its ClearTint™ polymeric colorants for use in NX® UltraClear™ polypropylene (PP), which can be made only with its Millad® NX® 8000 clarifier.

The year 2019 marked a major step forward, with the introduction of both its KeyPlast® products, as well as its KeyPlast RESIST™ high-performance colorants for plastics.

Milliken technology helps to color a vast range of sectors, including agriculture and turf; automotive and transportation; building and construction; coatings, paints and inks; home and laundry care; and plastics.

Milliken's KeyPlast RESIST colorants address another key challenge — coloring high-performance engineering polymers with bright and vibrant hues. These colorants are used in the high demanding applications such as high voltage connectors, control systems, structural parts and metal replacement.

Using KeyPlast RESIST colorants compounders and resin producers, offer a vast spectrum of stable and reproducible colors suitable for use with a wide range of resins such as Polyamides, PPA's, Poly Sulphones and other high heat polymer blends and alloys.

Additionally, Milliken continues to keep its finger on the pulse of end-user and market trends, which it documents each year in its ColorDirection report that forecasts the key shades and hues for the coming year. In doing so, it offers a palette of carefully curated colors, while providing the stories behind the inspiration and motivation driving their popularity. Brand owners can leverage this expert information to help capture the mood of consumers through effective branding and personalization.



Milliken's diverse portfolio of colorants can enable product makers to realize their aims to deliver on those colors that will help drive and shape consumer preferences in the coming year.

From the R&D lab to the production floor, Milliken's Chemical Division stands ready to help customers leverage color to design new products, reinvigorate existing products, and create opportunities to grow in new markets and applications.



SPE CAD RETEC® Coloring of Plastics Tutorial

The Color and Appearance Division of SPE has been presenting the "Coloring of Plastics" tutorial at the start of the CAD RETEC® conference for many years. Many SPE members and non-members have benefited from this program. The tutorial is a great starting point for those just beginning a career, or an excellent continuing improvement opportunity to those who wish to add to their base knowledge of coloring of plastics. The course is full of practical information which is embellished and enlightened by the active participation of all the attendees.

The tutorial runs a full day on Monday prior to CAD RETEC® and does require a separate registration and fee. The attendance is limited to 20 persons, so register soon. Attendees receive a full-color manual to use as a reference when they return home.

Who might benefit from attending the tutorial?

- Executives needing to better understand their company's coloring issues
- Managers newly appointed and/or desiring to communicate more effectively with peers and subordinates
- Color formulators/matchers to better understand the theory behind their work
- Color specifiers/approvers to understand limitations in coloring of plastics
- Sales personnel hoping to gain more technical knowledge to better serve their customers
- Product designers wishing to better understand the technology behind the coloring of plastics, to make better and more informed decisions
- Color manufacturing personnel to understand the impact of compounding on color
- Color processors (injection molding, extrusion, etc) to better understand the technology ways they can impact the final color

Attendees will leave the course with a better understanding of color technology and should be more effective in their careers around color.

For more information about Color of Plastics Tutorial, please contact the Conference Chair and Tutorial Instructor Bruce Mulholland @ captcolour@aol.com or call 859-982-5256

To register for this opportunity please visit the [SPECAD Website](#)

CONFERENCE REGISTRATION

(SELECT ONLY ONE TYPE OF REGISTRATION)

SPE Member	2023
<input type="checkbox"/> Advance	\$480
<input type="checkbox"/> Late / Onsite (After 8/18/23)	\$580

SPE Non-Member:	
<input type="checkbox"/> Advance	\$740
<input type="checkbox"/> Late/Onsite (After 8/18/23)	\$840

OTHER Registration Types:	
<input type="checkbox"/> RETEC Committee	\$225
<input type="checkbox"/> CAD BOD member	\$335
<input type="checkbox"/> Speakers/Moderator	\$225
<input type="checkbox"/> Student (w/ Valid Student ID):	\$100
<input type="checkbox"/> Emeritus:	\$200
<input type="checkbox"/> Tabletop advanced registration	\$1,650
<input type="checkbox"/> Tabletop late reg (After 8/18/23)	\$1,850

EXTRA CONFERENCE LITERATURE:

<input type="checkbox"/> Extra RETEC 2023	\$115 x ____ = \$ ____
<input type="checkbox"/> Archive DVD (1961-2007)	\$175 x ____ = \$ ____

(available on site)

OTHER EVENTS REGISTRATION / RSVIP

<input type="checkbox"/> Golf Outing (Sunday):	\$105
<input type="checkbox"/> 5K Fun Walk (Tuesday):	\$25
<input type="checkbox"/> "Coloring of Plastics" Tutorial (Sunday):	\$550

- * Full refunds available thru August 25, 2023
- * Refunds less a \$100 fee August 26 to September 8, 2023
- * No refunds after September 8, 2023

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SOCIETY OF PLASTICS ENGINEERS

2023 CAD RETEC® GOLF OUTING

Monday September 18th, 2022

Northstar Golf Club

Schedule (EST)

Registration and Lunch: 9:30am to 11:00

11:00am Shotgun Start

Price: \$105.00 per golfer

Includes: Range

Green and Cart Fees

Buffet Lunch

Course Location

1150 Wilson Rd

Sunbury, OH 43074

PH: (740) 524-4653

Awards (hole prizes)

Scramble format – Teams will be

drawn based on handicaps

again this year

When registering, input your Handicap typical 18 hole score. Please be honest to make this fair



NorthStar Golf Club, a private golf club in north central Ohio, boasts a John Cook-designed 18-hole, 7,516 yard, par 72 golf course with six sets of tees to accommodate players of all skill levels.

Founded in 2007, NorthStar has played host to the 2013 U.S. Amateur Qualifier and the 2015 and 2016 Ohio Public Golf Championships. It has also been the home of either the Division 2 or 3 Ohio High School Boys Golf Championship competition since 2009. The course is situated in a large area of preserved natural beauty, featuring numerous ponds, creeks and extensive wetlands.

Questions Contact:

[Mark Tyler](#) (570) 952.5255 or

[Mark Freshwater](#) (201) 665.0091 or

[Alex Prosapio](#) 845-641-0596

 NorthStar Golf Club

Colorful COLUMBUS



CAD RETEC® 2023
COLUMBUS OHIO



CAD RETEC®

Columbus, Ohio • September 18-20, 2023
Presented by SPE Color and Appearance Division

COLORFUL COLUMBUS



Pre-registration online Go to [2023 CAD RETEC HOME](#)

Onsite Registration Hyatt Regency Columbus

- Monday, September 18 1:00 PM – 7:00 PM
- Tuesday, September 19 7:30 AM – 5:00 PM
- Wednesday, September 20 7:30 AM – 3:00 PM

Preconference Tutorial [Coloring of Plastics](#)

Presented by Bruce Mulholland, SPE Fellow

Monday, September 18, 2023 8:00 AM – 4:30 PM

Fee: \$550 (Must Pre-register for event. Extra fee not included with CAD RETEC® 2023 registration)

CAD RETEC® 2023 Golf Outing



Monday September 18th, 2023

NorthStar Golf Club

Registration and lunch 9:30am – 11:00am

Shotgun start at 11:00am

Price: \$ 105.00 per golfer

Includes: the range, green fees, cart fee, lunch, Awards (hole prizes), scramble format

For more details, visit [CAD RETEC 2023\(R\) Golf Outing](#)

Welcome Reception

Monday 18 September 2023



8:00pm – 11:00pm

Sponsored by Milliken



Tuesday, September 19th, 2023

For more information go visit [SPE PlastiVan](#)

CAD RETEC® 2023 Fun Run/Walk

Wednesday 20 September 2023

Sponsored by DCL

\$25 Registration fee

All proceeds go to Habitat for Humanity

SPE CAD will match every \$25 donation



Proceeds this year will be donated to [Habitat for Humanity of Ohio](#)

Preliminary Technical Program Tuesday September 19th, 2023

Time	Category	Speaker/Company	Title/Sponsor
7:30-8:30 AM	Breakfast		DCL
8:55 AM	Opening Remarks	Kimberly Williamson - Techmer PM	Welcome to CAD RETEC® 2023 in Columbus, OH
9:00 AM	Keynote	Mark Ryan - Shepherd Color	<i>Do Robots Dream of Plastic Sheep?: The Effect of AI on Plastics Industry</i>
9:30 AM	Paper	Romesh Kumar, Heubach	<i>Pigment Purity Remains a Key Element of Sustainable Colors</i>
10:00 AM	Break	Exhibits open Exhibit Hall	Sponsored By Heubach
10:30 AM	Paper	Eric Andrews - Colour Synthesis Solutions	<i>Comparing the Migration of Genotoxic Impurities in Colorants to Their Total Extracted Content - An Analysis of Plastic Additive Risk in Food-Contact Applications</i>
11:00 AM	Panel		Regulatory (TBD)
12:00-1:30 PM	Lunch	On your Own	
1:30 PM	Keynote	Doreen Becker - Ampacet	<i>CMF Developments for Plastics: Sustainability Perspectives</i>
2:00 PM	Paper	Breeze Briggs - Sun Chemical	<i>High Heat Pigments for E-Mobility</i>
2:30 AM	Paper	Bonnie Piro - Sudarshan	<i>The Performance Impact of Laking Monoazo Organic Pigment Red 48</i>
3:00 PM	Break	Exhibit Hall	Sponsored
3:30 PM	Keynote	Christine Gheres - Specialchem	<i>The Post-Pandemic Digital Changes in the Plastics Industry</i>
4:00 PM	Paper	Andy Francis - Q-Lab	<i>High-irradiance Laboratory Weathering Testing of Plastics</i>
4:45 PM	NTF	Scott Heitzman - Moderator	New Technology Forum

Network Reception



The Shepherd Color Company
We Brighten Lives

Tuesday, September 19, 2023

Exhibitor Area, 5:30 pm – 7 pm

Sponsored by *The Shepherd Color Company*

Preliminary Technical Program
Wednesday, September 20, 2023

Time	Category	Speaker/Company	Title/Sponsor
7:00 AM	Activity	Fun Run/Hyatt Regency Lobby	Sponsored By DCL
8:55 AM	Opening Remarks	Kimberly Williamson - Techmer PM	Welcome Day 2
9:00 AM	Keynote	Bruce Mulholland	<i>Effect of Additives on the Color & Appearance of Plastics</i>
9:30 AM	Paper	Jeff Drusda - Chemours	<i>Achieve Greater Sustainability with Performance for Plastics with New TiO2 Innovation</i>
10:00 AM	Break	Exhibit Area Exhibit Hall	Sponsored
10:30 AM	Paper	Kevin Lucero - EMD	<i>Additives for Durable, Flexible, and Accurate Laser Markings in Plastics</i>
11:00 AM	Paper	Curtis Ross - DCL	<i>Heat Stability = Color Change, True or False?"</i>
11:30 AM	Paper	Jeff Scherm - Lanxess	<i>NIR Detectable Pigment that Recycling Sorting Systems Can Detect</i>
12:00 PM – 1:30	Luncheon	Awards Luncheon	Sponsored by Tronox
1:30 PM	Keynote	Narss Lapinid	<i>The Power of the Collective Mind in CMF Design.</i>
2:30 PM	Paper	Phil Niedenzu - Chemours	<i>L* is a Valuable Component for Color</i>
3:00 PM	Break	Exhibit Area Exhibit Hall	Sponsored
3:30 PM	Keynote	Bruce Mulholland	<i>The Status of SPE: Inspiring Plastics Professionals</i>
4:00 PM	Paper	Frank Neuber - Clariant	<i>Improved Dispersion of Organic Pigments in Polyesters and Final Product Physicals, without Impacting Printing and Label Adhesion.</i>
4:30 PM	Closing Remarks	Kimberly Williamson - Techmer PM	Raffle (Prizes TBD) Must be present to win!!
5:00 PM			Conference Ends

See you next year!

CAD RETEC® 2024
 Tampa, Florida
 September 23-25, 2024
 Riverfront Marriott



SPE Color and Appearance Division Mission Statement

The Color and Appearance Division of SPE strives to educate, train, inform and provide professional interaction opportunities to the global community involved in visual performance and aesthetics of plastics.

INVITATION TO ATTEND CAD BOARD MEETING

The Color and Appearance Division (CAD) holds 4 Board of Directors (BOD) meetings each year, either in person or virtually. Any CAD members in good standing with in SPE and has Color and Appearance as their selected division are welcomed to attend these meetings. If interested in attending these meetings, please contact the current CAD Chairperson or any BOD for more information.

CADNEWS® Technical Content – Scott Heitzman

The Technical Content portion of our Summer 2023 edition of CADNEWS® Includes a go to reference when formulating or answering customer questions about shrinkage and warpage. Processing, Testing, Characterizing, and Mitigation are all discussed. Thanks to Brian D. Coleman for his 2018 ANTEC paper, Understanding Warpage in Injection-Molded Thermoplastics; Causes and the latest Pigmentary Solutions.

CADNEWS® Color Notes – Scott Heitzman

Welcome CADNEWS® Color Notes. The idea is to create discussion and provide comments regarding questions you may have related to color and appearance, color measurements, and colorants in general. Do not miss your opportunity to anonymously ask our team of experts a question. Use the link below to submit your questions. Our SPECAD Color Notes committee will provide a response to one or more of the submissions in the upcoming CADNEWS® letter.

<http://specad.org/color-questions-for-cad/>

Abstract

This paper seeks to enlighten the newcomer to formulating color and additives masterbatches for thermoplastics with an overview on the issues of shrinkage and warpage. First, the two concepts will be defined and differentiated followed by a description of how they are quantified or characterized in the literature. Some of the many variables that impact warpage will be touched on after which the special role organic pigments can play will be elucidated. Finally, there will be a brief review of the recent developments in non-warping pigments and other strategies formulators use to mitigate warping.

Introduction

The global consumption of thermoplastics continues to increase; chief among those are the polyolefins (polyethylene and polypropylene). Of the 322 million tons of plastics consumed globally in 2015, about 46% comprised polyolefins.¹ They can be shaped into useful articles or intermediate materials via myriad processes including blow molding, rotational molding, fiber spinning, profile extrusion and injection-molding.

Of the many processes employed today, injection-molding is one of the more dominant with one estimate that about 1/3 of all thermoplastics consumed globally undergo it.² The proliferation of injection-molding throughout the world of plastics is owed to its speed, efficiency, repeatability and flexibility. Articles from minute medical device parts to large, complex structural parts to multitudes of caps and closures are injection-molded. Often these parts require exacting dimensions, sometimes for mating with other parts, as with connectors and harnesses, and other times for proper nesting or stacking, as with buckets or crates. Hence the minimization of warping can be paramount to the overall success of the injection-molding process.

Though injection-molding may seem to be a simple process on the surface, its very nature introduces many variables that influence shrinkage and warpage. These variables can be so complex that modeling post mold shrinkage and warpage with precision is extremely challenging.

Injection-molding parameters can be impactful in shrinkage and warpage but are by no means the only causative elements. Indeed, it's been known for decades that the presence of particulates in the polymer melt can drastically change the shrinkage characteristics of the resin.³ Thus, mitigating warping of injection-molded parts should be considered a joint effort among the masterbatch formulator, the tool designer, the injection-molding engineer and others. This paper seeks to enlighten the masterbatch formulator on the causes of warpage, the strategies to combat it as reported in literature and the current state of non-warping organic pigments. Because many of the dimensionally sensitive applications occur in polyolefins, high density polyethylene (HDPE) will receive special attention.

Shrinkage and Warpage

It will help to use established terminology to describe the phenomenon about which this paper is concerned. After reviewing several sources, *shrinkage* is generally agreed to be the reduction in the size of a part relative to the size of the mold. Based on accepted international standards ASTM D 955-08 and ISO 294-4, this difference is commonly measured 1, 24 and 48 hours after molding. The specimens are allowed to condition under controlled temperature and relative humidity on a heat non-conductive surface. Measurements involve the use of micrometers or vernier calipers. Depending on the specimen chosen, shrinkage parallel and perpendicular to flow can be reported.

A change in size occurs in all materials that undergo changes in temperature. Indeed, size changes are seen when liquid metal is allowed to cool after being cast in a preform. Plastics behave similarly when injection-molded but their behavior is complicated significantly, relative to metals, by their long molecular chains and the inherent stresses experienced during molding. When considering the two main types of thermoplastics – semi-crystalline and amorphous – the former experience significantly more shrinkage due to their denser, crystalline regions.

The crystallization of semi-crystalline polymers is characterized by a contraction in the molecular chains to a

local regions of alignment between short lengths of adjacent chains. Once nucleated, these newly formed crystals draw from polymer chains in the local melt and grow radially from the nucleation point to form spherulites. The addition of a nucleating agent – a species that increases the temperature of crystallization – tends to form solids with smaller spherulites and higher crystallinity. The high crystallinity is responsible for the increased shrinkage and increased probability of warpage observed in nucleated polymers.

Warpage can simply be defined as a distortion in the shape of the final injection-molded article.⁴ It is widely held that this distortion is a result of differential or non-uniform shrinkage in the article. The stresses induced by non-uniform shrinkage are great enough to overcome the mechanic strength of the article and thus distortion occurs. Stresses are inherent to injection-molding. Non-uniform shrinkage can result from a number of causes including thermal stresses.

Thermal stresses result from heterogeneous cooling of the outer layer and the core layer of parts. The outer layer (contacting the mold cavity surface) cools first and faces minimal resistance from the still molten core as its volume contracts during cooling. The core of the part, however, experiences resistance from the solidified outer layer as it tries to contract. Internal stress of the part therefore builds from each edge to a maximum in the core in a parabolic shape (Figure 1).⁵

Characterizing warpage

In contrast to shrinkage, there appear to be no international standards describing the characterization of warpage. As a result, one finds a few variations of basically two techniques in the literature. One technique involves the use of a rectangular plate whose long dimension (when not a square) is parallel to the melt flow in the tool. These plates are generally about 2 mm in thickness. The plates are allowed to cool and their shrinkage is measured parallel and perpendicular to flow. Most sources compare the two shrinkage values (determined more or less consistent with ASTM 955-08 / ISO 294-4) to highlight where non-uniform shrinkage has been observed. A notable exception was Grimm who found it predictive to calculate an internal factor based solely on the shrinkage perpendicular to the flow.⁶

A second technique employs a center-gated disc. Again the parts are allowed to cool under controlled conditions and are assessed at specific periods following molding. The cooling protocol is not well documented so one suspects there is significant variation. West and Williamson describe an assessment technique where the discs are rated

“flat”, “warped” or “cupped” and assigned a numerical 0 to 5 ranking. The assessment method discussed in this paper involves a measurement of the amount of deflection. For clarity, the methods used to generate forthcoming data are described below.

The newly developed plate test involves the injection-molding of a fan-gated rectangle of the following dimensions: 174 mm x 49 mm x 2.5 mm. The direction of the molten polymer is along the longer dimension. Prior to introducing a sample, virgin 8 MFI injection-molding grade HDPE, henceforth HDPE-1, is molded for 60 minutes. When organic pigments are tested, they are pre-compounded at 0.2% in the HDPE-1. After molding, the specimens are immediately placed in a 90° C water bath for 30 minutes to accelerate relaxation. They are then allowed to acclimate to ambient conditions for at least 15 hours before measurement. Measurements along the length and width of the plates are captured and used to calculate shrinkage as follows:

$$\Delta \text{Length } (L) = [(L_{\text{plate}} - L_{\text{cavity}}) / L_{\text{cavity}}]1000$$

$$\Delta \text{Width } (W) = [(W_{\text{plate}} - W_{\text{cavity}}) / W_{\text{cavity}}]1000$$

The shrinkage values are then plotted in two dimensions along with values for the virgin HDPE-1. Based on correlation with real world performance, trapezoidal regions are overlaid denoting regions of no, low and high warping (Figure 2).

The newly developed disc test employs a center-gated disc with a radius of 60 mm and a thickness of 2.0 mm. Like in the plate test, virgin HDPE-1 is molded for 60 minutes prior to introducing samples. Discs are collected and afforded accelerated relaxation by placing in a 90° C water bath for 30 minutes. The discs are then allowed to condition at ambient conditions for at least 15 hours prior to measurement. The warpage of each disc is quantified by placing the disc on a flat surface, pressing down on one side of the disc (0°) and measuring the height at 180° to the nearest mm (Figure 3). The greater the height, the more pronounced the warping.

Variables impacting warpage

It is important to understand that warpage in plastics can be a consequence of many factors. These factors are related to part design, mold design, processing and materials. The following speaks to some of those variables but is not intended to be all-inclusive.

First, the shrinkage characteristics of the polymer itself may vary considerably. As seen in Table 1, among semi-crystalline polymers there is wide variation in their inherent shrinkage behavior ranging from around 0.4% shrinkage

for 30% glass-filled polyamide to as much as 4.0% shrinkage for HDPE. Even within the same HDPE grade, there can be variation. Figure 4 shows the position of multiple moldings of HDPE-1 over time.

Part design is critically important to minimizing warpage as it the most difficult to overcome once in use.⁷ Wall thickness is positively correlated with shrinkage: the thicker the wall, the more shrinkage will occur. Very briefly, the thicker sections take longer to cool and, in semi-crystalline polymers, allow for more crystallization and thus more shrinkage. In parts with different wall thicknesses, differential shrinkage is likely to occur with the thicker walls shrinking more than their thinner counterparts. When changes in wall thickness cannot be avoided, the change should be introduced gradually. Abrupt changes can impart significant stresses in the change area. Ribs and bosses can also encourage warping if their thickness and radius at the adjoining point are not properly designed.⁸

Almost all molding conditions influence shrinkage to some degree. Table 2 shows how increasing some of the process conditions influences shrinkage. In the specific plate test described herein, it is clearly demonstrated that melt temperature is impactful. With the HDPE-1, it is observed that a lower melt temperature consistently yields a higher degree of warpage (Figure 5). It is believed that the more viscous lower temperature melt induces more molded-in stresses. Holding pressure also plays a role as shown in Figure 6. Increasing the pressure from 250 bar to 500 bar results in less shrinkage along both the length and width of the plate. The higher the holding pressure, or the longer the holding time, the more uniform and gradual the crystallization process. Cooling time of the part in the closed mold (hold time) showed a consistent influence over two grades of HDPE (Figure 7 shows HDPE-1). With both grades there was an increase in the dimension perpendicular to flow as more time elapsed. This behavior is likely the result of the plastic having the time to stretch slightly while it is “trapped in the mold”.⁹ It seems well established that increases in the holding phase, be it time or pressure, yields less shrinkage.

Finally, fillers can have a remarkable effect on shrinkage and therefore likelihood of warping. It's long been established that fiber fillers (those with a high aspect ratio) significantly decrease shrinkage in the flow direction. The fibers tend to orient along the melt flow in the filling stage and, unlike the polymer chains, stay “locked” in that orientation during the cooling phase. Because the fiber shrinks less than the resin and because the fiber is in effect replacing the resin, shrinkage is less in the flow direction. This behavior is correlated with concentration: the higher the fiber filler content, the lower the in-flow shrinkage. The cross-flow shrinkage, however, is not dramatically

decreased, and can even increase, so shrinkage can become non-uniform and lead to warpage especially with increasing concentration of fiber.

Fillers with a low aspect ratio like beads or flakes tend have no influence on non-uniform shrinkage. Indeed, their use is generally associated with the lower shrinkage in each direction. This behavior is attributed to their low coefficient of thermal expansion and their geometric uniformity. Like most high aspect ratio fillers, these low aspect ratio fillers are usually inorganic and shrink significantly less than the polymer. Unlike the fibrous fillers, these beads, powders and particulates are about the same size in each direction, therefore they do not “orient” in the flow direction. They influence shrinkage in all directions about equally. They reduce shrinkage in all directions by simply replacing “shrink-prone” polymer chains with a “shrinkless” inorganic; it's a matter of displacement.

Pigments may be considered a special case of a filler. Inorganic pigments like C.I. Pigment White 6 and C.I. Pigment Brown 24 have almost no influence on the shrinkage of semi-crystalline polymers. However, their organic counterparts can have dramatic impacts on shrinkage and can induce warpage to a degree that cannot be corrected through process adjustments. Interestingly, organic pigments behave in a range from no influence (like inorganic pigments) to significant influence. It appears in pigments that do encourage warping that the degree of warpage correlates with concentration. In Figure 8 that relationship is seen with an untreated C.I. Pigment Red 254 (PR 254). In contrast, the behavior of the non-warping C.I. Pigment Yellow 93 is unchanged with concentration (Figure 9). Organic pigments can exist as low and high aspect particles (like needles) so is their behavior explained simply by their particle shape? It does not appear to be based on Grimm's findings. He and his colleagues tested two C.I. Pigment Blue 15 (known high-warping pigment family) pigments varying only in their crystal shape: one was needle-like, the other had short and thick crystals. They found the needle-like crystals actually induced less warpage than the more uniform crystals! Rather than their crystal morphology, it is believed the nucleating behavior of certain organic pigments may be the driving force.¹⁰

Organic pigments' role in nucleation

Organic pigments have long been known to influence the mechanical properties of the polymers which it colors. A number of studies have been published showing the nucleating effect of pigments in polymers. Suzuki and Mizuguchi investigated the effect of organic pigments on the nucleation of polypropylene (PP) and HDPE by assessing both the onset temperature of crystallization and the crystallization rate. They confirmed that in both PP and

HDPE systems, inorganic pigments had minimal to no impact on differential shrinkage; they performed like the uncolored virgin polymer. Furthermore, they confirmed a range exists for organic pigments: some approach the behavior of inorganics while others influence shrinkage significantly. With regard to the onset temperature of crystallization, strong positive correlation was found: the higher the temperature, the greater the influence on shrinkage. The rate of crystallization was also evaluated for the same selection of pigments. Consistent with theory, pigments with faster rates of crystallization impacted shrinkage more profoundly. The correlation found between the spherulite size and influence on shrinkage was such that the authors concluded “mold shrinkage becomes more significant as the nucleation frequency is increased.” They further concluded modifications to the pigments' surface seemed a logical strategy to combat the nucleation tendency and by extension shrinkage and warpage.¹¹

Rather than an inspiration for a new research direction, Suzuki's work served more as a confirmation of work that had been started years before. In the mid 1970's, Hiromitsu Katsura and colleagues described warp-free coloration of polyolefins by treating organic pigments with methylol groups esterified by carboxylic acids.¹² Around the same time Sawai and others patented a low-warp treatment for several organic pigments based on organotitanium compounds.¹³ Elsener and colleagues appear to be the first to suggest a polymeric treatment of the pigment surface could yield warp-free coloration of polyolefins.¹⁴ Several other patents follow all demonstrating lower warping of certain organic pigments following an organic and/or inorganic surface treatment. Surface treatment techniques largely fell into three categories: treatment with pigment derivatives, treatment with inorganic materials and treatment with polymers.¹⁵ It was the latter two techniques that Bugnon and colleagues utilized to generate first and second generation low-warp PR 254 products. PR 254 was to that point untreatable for warping via other techniques. Ultimately Bugnon developed his “warping antidote” for PR 254 by using a derivative that interfered with the activity of specific crystal faces most linked to warpage in the final article. His derivative was polymer soluble and was found to associate with untreated faces as new faces were exposed during processing; it was essentially, a self-healing antidote!¹⁶ Later, in the 1990's, Joerg Schroeder introduced the use of a low temperature plasma treatment as a means of creating an inert pigment surface.¹⁷

Low warp pigments state of the art

The work of Bugnon and others has been utilized to develop non-warping versions of some of the most important pigment chemistries for polymers, especially

polyolefins. The aforementioned derivative technology has been applied to the most challenging pigment chemistries with regard to warping and has yielded performance nearly identical to the uncolored HDPE! These pigments include: C.I. Pigment Red 254, C.I. Pigment Blue 15:3, C.I. Pigment Green 7 and C.I. Pigment Yellow 110. The more a pigment can be rendered shrinkage neutral the greater the probability that a dimensionally stable article can be injection-molded.

Other strategies to mitigate warpage

Even with the use of the most advanced pigment chemistry and computer-aided analysis, there still are occasions where warping is problematic. Adjustments to be made to injection-molding processing conditions are myriad and well beyond the scope of this paper. Indeed, entire books and theses have been dedicated to the topic!^{18 19 20}

Masterbatch and compound formulators have developed ways to reduce their products' contribution to warping at the press. These “fixes” constitute a technical advantage over competition so not surprisingly the literature is meager with specifics. As stated earlier, the use of low aspect ratio fillers generally reduce shrinkage. These fillers can include glass beads²¹, talc²² and some metal stearates. As described previously, these fillers have little thermal expansion relative to the polymer thus do not shrink upon cooling. Their efficacy generally increases with increasing concentration. Nucleators have proven successful in lowering warping in LDPE but are not being promoted as such for HDPE. West and Williamson have shown that some additives can improve upon even the “low-warp” pigments. They also demonstrated pigments do not respond equally to additives so significant know-how and customization are required on the part of the formulator.

Conclusions

Shrinkage and warpage are straightforward concepts. Shrinkage will always occur to some extent as thermoplastics undergo the injection molding process. Warpage is the result of non-uniform shrinkage throughout the article, particularly parallel and perpendicular to the melt flow. There are myriad contributors to shrinkage and warpage, not the least of which are material properties. A significant amount of research has addressed the role of organic pigments as nucleators that interfere with normal crystal growth and yield warpage. New developments in advanced surface chemistries have created warping neutral pigments for some of the most important organic pigments used in thermoplastics today. These products coupled with the formulators' own fillers, nucleators and other proprietary additives render a robust material solution for dimensionally sensitive articles. Ultimately, each part of

the injection-molding process – material, part design, mold design, processing conditions, etc. – must consider dimensional stability to yield success.

Acknowledgements

Figure 1. Example of thermal residual stress distribution²³

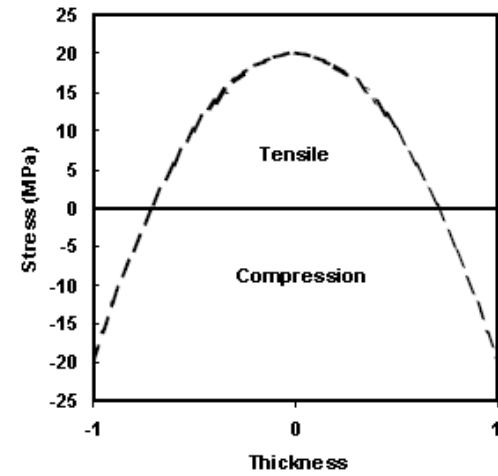


Figure 2. Generic layout used to plot results of the plate test

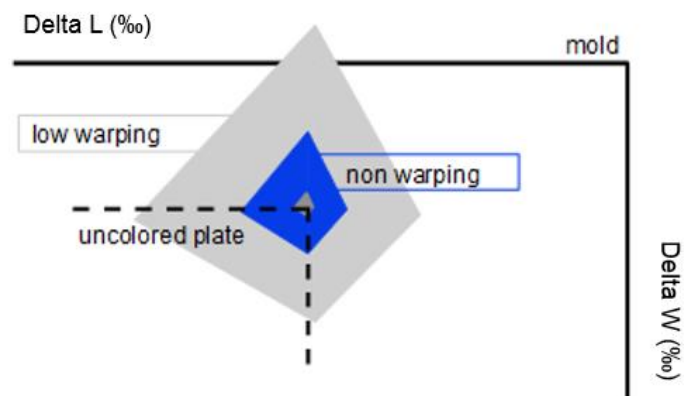
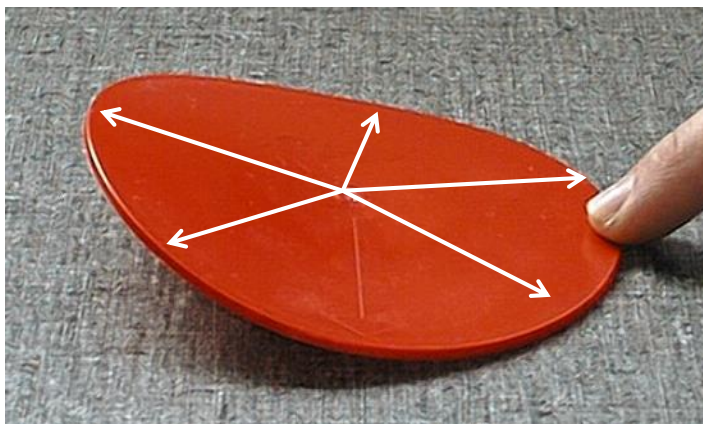


Figure 3. Position of a warped disc for measurement



The author wishes to thank Joachim Jandke, Juerg Zingg and James Rediske for their support.

Table 1. Shrinkage of various semi-crystalline polymers²⁴

Polymer	% Shrinkage
Unfilled PP	1.0 - 2.5
40% talc filled PP	0.8 - 1.5
40% calcium carbonate filled PP	0.7 - 1.4
HDPE	1.5 - 4.0
Polyamide 6	0.5 - 1.5
Polyamide 6.6	0.8 - 1.5
Polyamide with 30% glass fiber	0.3 - 0.5
Acetal	2.0 - 2.5

Figure 4. Distribution of uncolored HDPE-1 over several molding trials

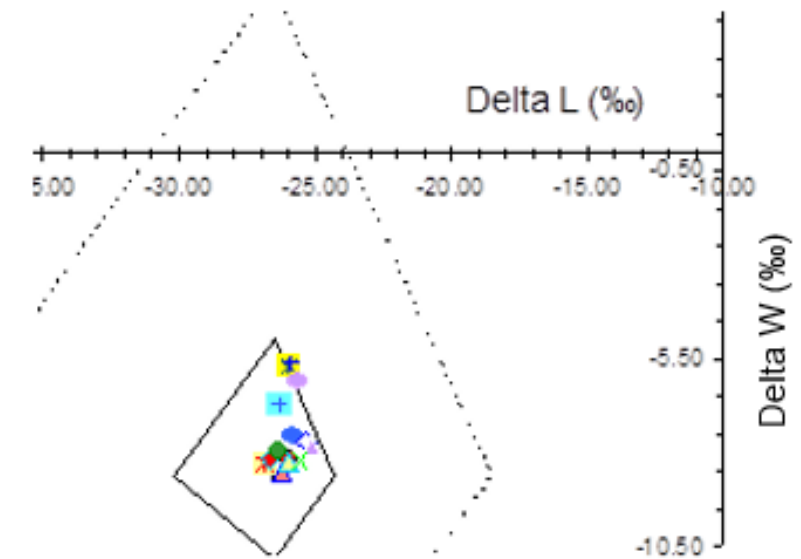


Table 2. Influence of process conditions on shrinkage²⁵

An increase in:	Has the following effect on shrinkage:
Injection pressure	Decreases (usually)
Injection rate	May increase or decrease
Holding pressure	Decreases
Holding pressure time	Decrease (until gate freeze)
Melt temperature	May increase or decrease
Mold temperature	Increases
Clamping pressure	Usually none; may decrease
Cooling time	Decreases

Figure 5. Effect of melt temperature on warpage

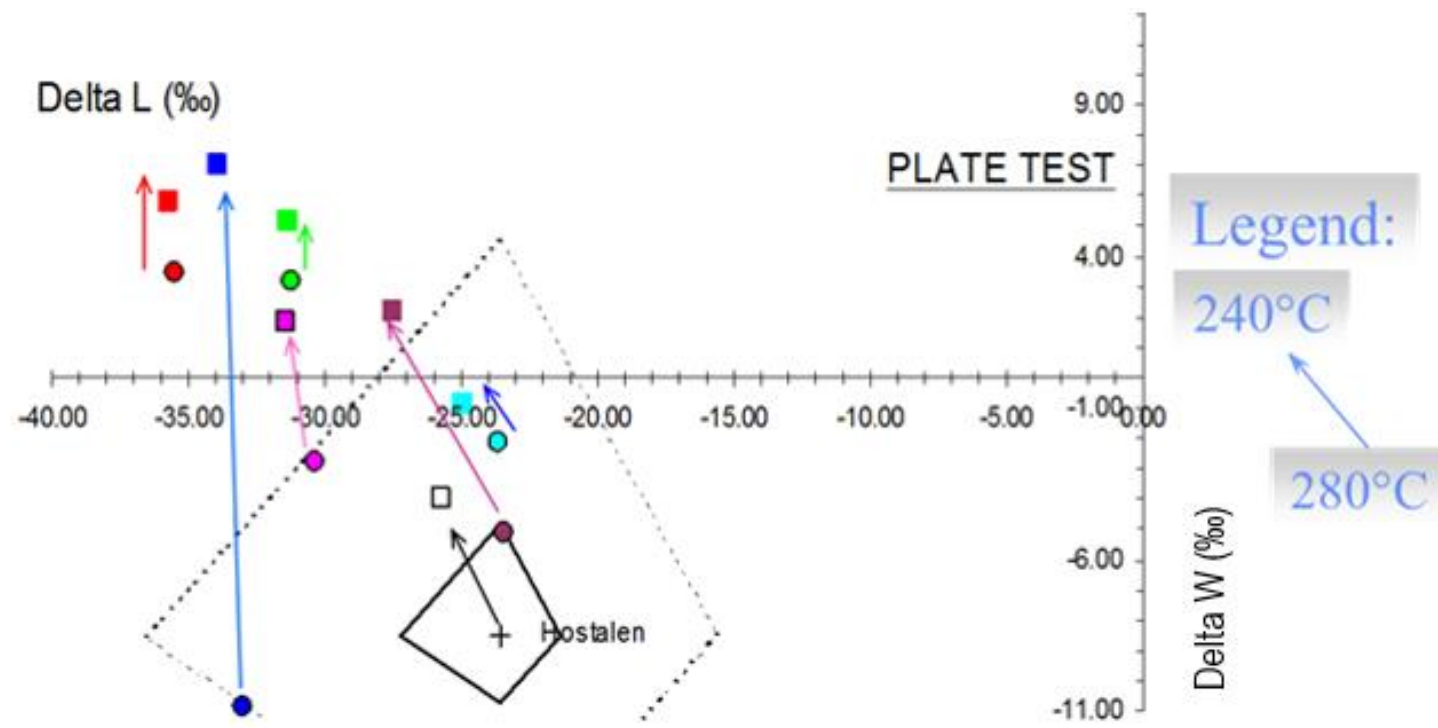


Figure 6. Effect of hold pressure and mold temperature on uncolored HDPE-1

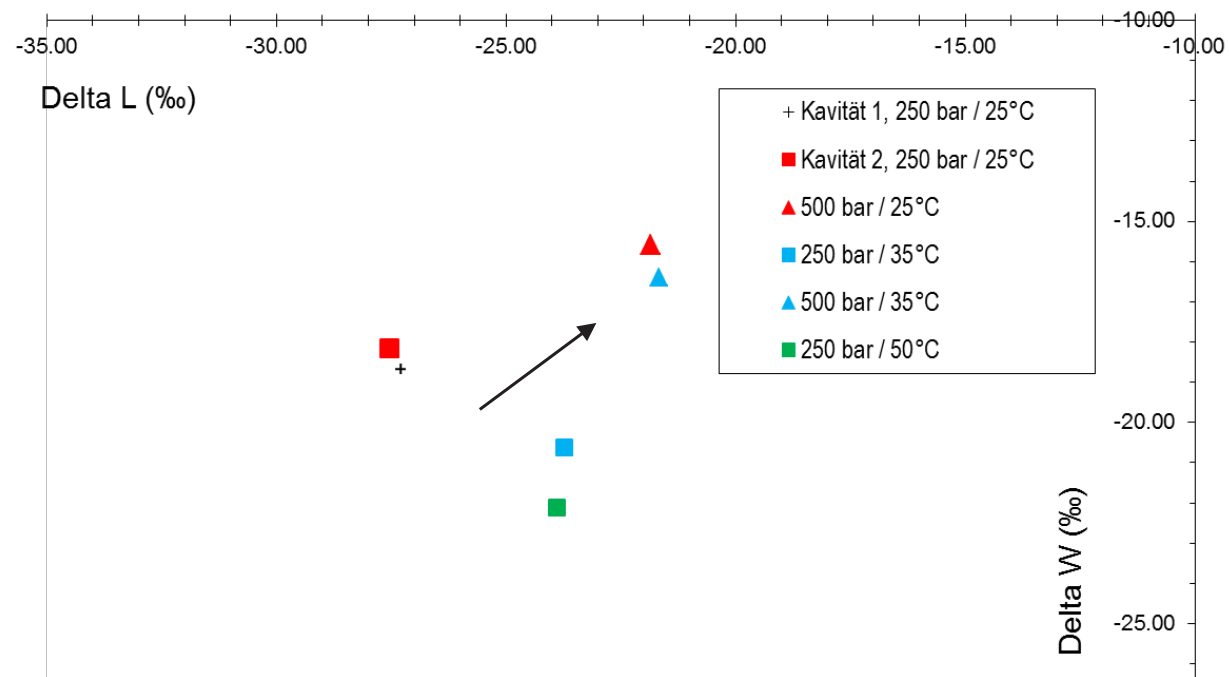


Figure 7. Effect of cooling time on three colored preparations of HDPE-1

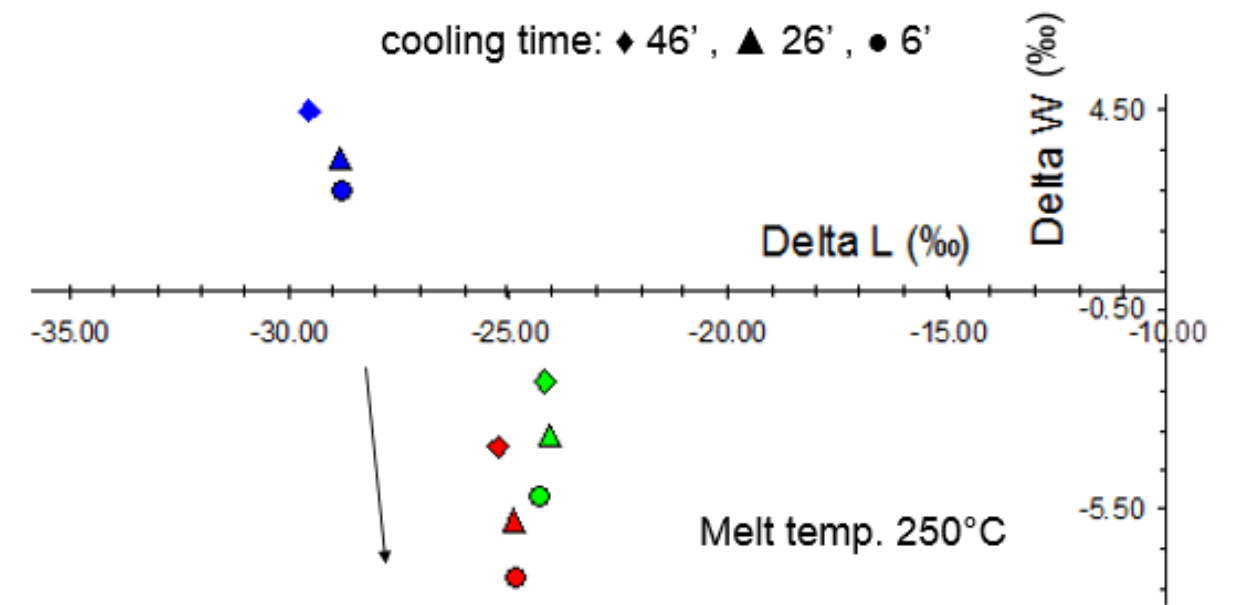


Figure 8. Effect of organic pigment concentration with untreated PR 254 at 0.01 – 0.2%

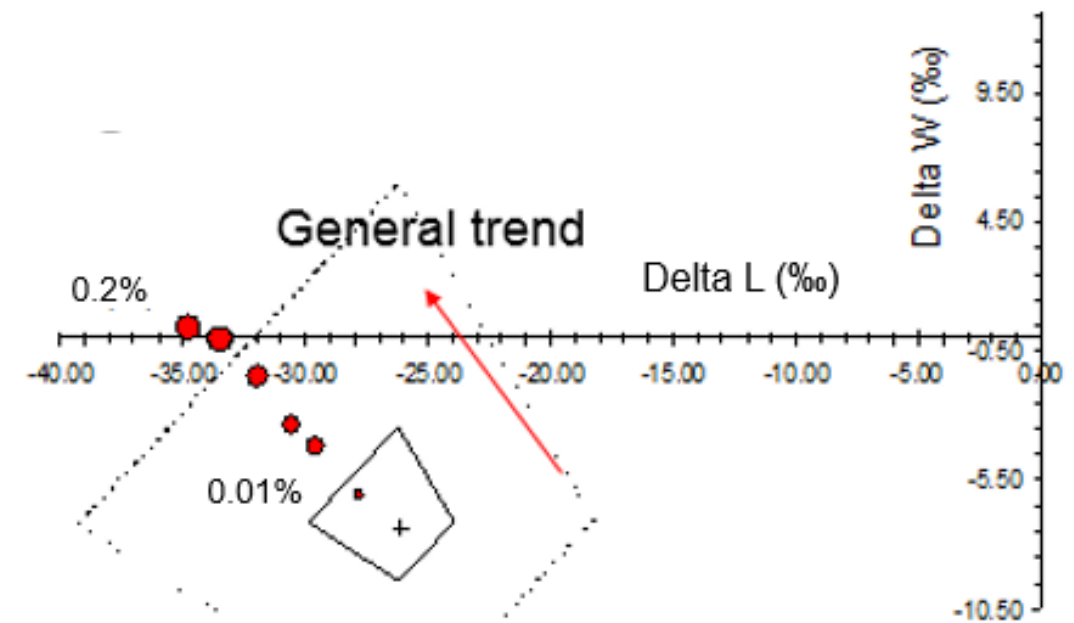
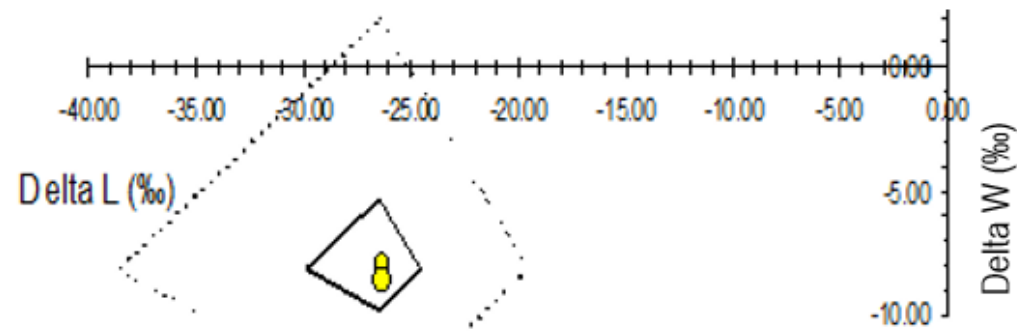


Figure 9. Effect of organic pigment concentration with untreated C.I. Pigment Yellow 93 (PY 93) at 0.01% - 0.2%



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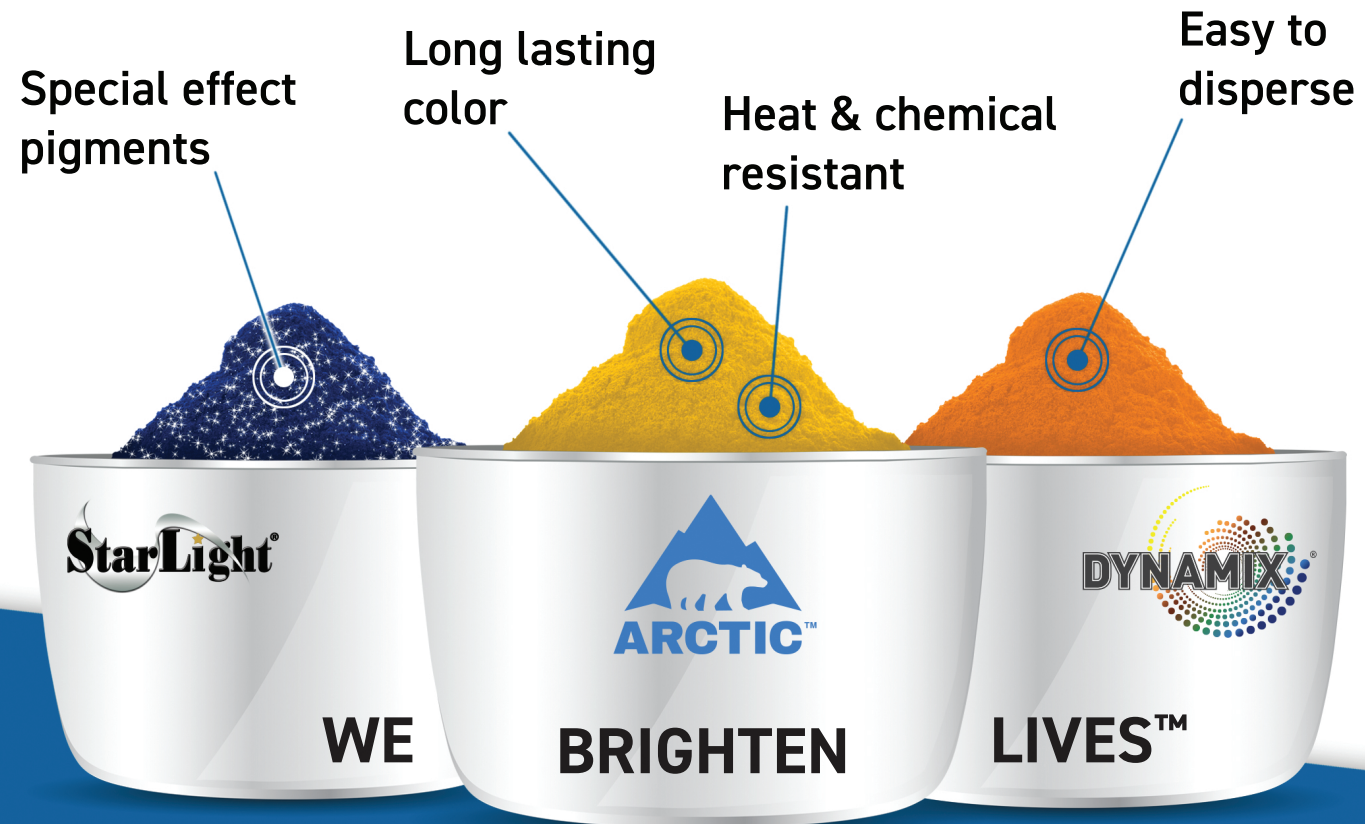
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CAD BOD SPRING MEETING

COUNCILOR'S REPORT - MAY 2, 2023

ATTENDEES

BOARD OF DIRECTORS

- Bruce Mulholland, President
- Jason Lyons, Past President
- Conor Carlin, President-Elect
- James Waddell, Director of Finance, Treasurer
- Lynzie Nebel, Director, Secretary
- Todd Bier, Director
- Praveen Boopalachandran, Director
- *Ray Pearson – resigned from BOD*

4 NEW DIRECTORS ON 1-YEAR APPOINTMENTS:

- Diane Marret – Sustainability Director, Consumer Pkg NA, Berry Global
- Meg Sobkowicz – Prof. Plastics Engineering, UMass Lowell
- Jeremy Dworshak – Research Scientist, Injection Molding, 3M
- Gustavo Nechar – VP & Chief Human Resources Officer, Ascend Performance Materials

2022 STRATEGIC GOALS SUMMARY

Knowledge Sharing

- Identified SMEs to participate in SME workshops at ANTEC 2023
- National Weeks of Learning – reached 620 viewers, 2022
- Ivan Lopez – Executive Director of Technical Programs, completed an analysis of technical education in the plastics field. This analysis will be used to identify our niche and develop new programs for SPE.

Increased Engagement & Networking

- ANTEC 2023, Denver
- Webinars for member directory & communities
- Non-technical courses

Enhanced Reputation

- Hosted first DEI virtual event – 12 speakers, 103 attendees, 16 pre-recorded talks available on-demand
- SPE Certificate in Leadership program – first program finished just before ANTEC, second group started in February
- Teach the Geek launched in March
- BadgeCert platform selected for micro-credentials for participation in SPE programs, workshops, etc.

2023 STRATEGIC PLAN

Identify two new revenue streams for SPE

- Re-work weeks of learning model to focus on attracting OEMs
- Conduct workshops in conjunction with ANTEC 2023
- Develop and conduct live virtual workshops
- Develop one new in-person HQ event: FlexPackCon – October 10-12, Montreal

Increased Engagement & Networking

- Define & implement leadership cohort group networking
- Student posters return to ANTEC 2023

Enhanced Reputation

- Promote DEI content to members
- Expand Girl Scout Patch program
- Expand Essentials of Management & Leadership in Plastics (two more cohort groups enrolled in 2023)
- Potentially develop Advanced Leadership course
- Promote Teach the Geek course
- Microcredential program
- Extrusion Division mid-career recognition platform
- “One SPE” – complete integration of SPE Foundation into SPE operations
- Define desired end state for chapter model & map out plan

3D Natives Acquisition

- 3Dnatives acquisition – French-based for-profit media & events company for the additive manufacturing market.
- >1.2 million people visit 3Dnatives platform monthly
- Content created for specific markets in each region's native languages (currently French, Italian, Spanish, German, English & planning to add more)
 - Principals Alexandre Martel & Filippou Voulpiotis attended ANTEC 2023


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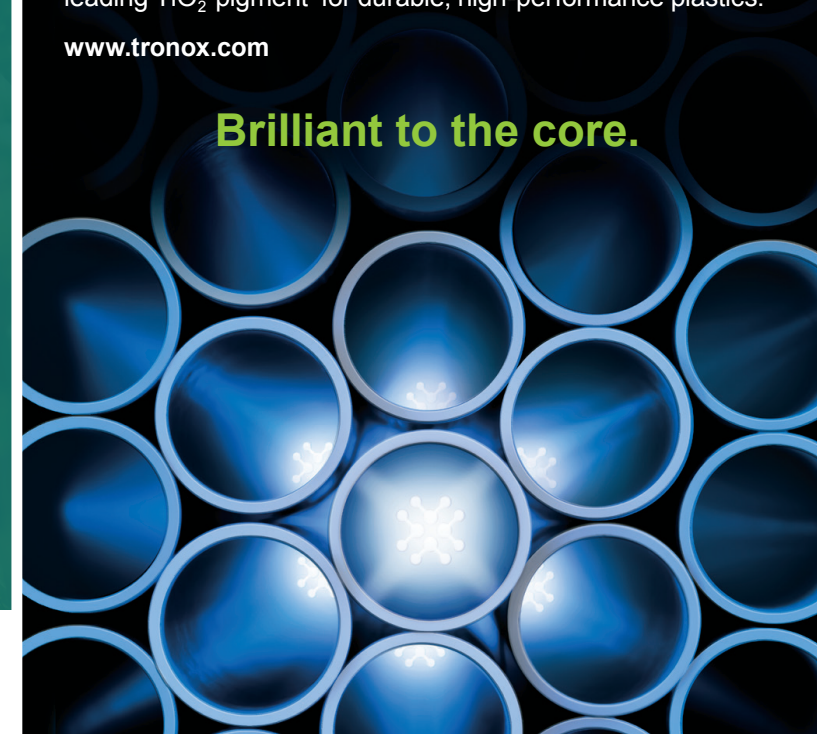



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Cory T. Singleton
Steve Esker
Matthew Billiter
Tony Tanner

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