Dear SPE Color and Appearance Division Members,

Winter is well entrenched in most of the country with record breaking snowfall in some areas. I have managed to miss most of it; however, it caught up with me this morning. Hopefully, we will be able to enjoy bright sunny days in Orlando, FL in March for ANTEC® 2015. Before discussing ANTEC®, I would like to thank Earl Balthazar and his team for the great job they did in managing last year’s CAD RETEC® 2014 in New Orleans. The technical program was excellent and I think we broke a record for the number of exhibitors. The support from our sponsors really helped to produce a successful conference. Thank you Earl! Earl provides a more detailed summary for CAD RETEC® 2014 is in this newsletter.

The success of our conferences allows us to support many educational activities. Last year, we awarded 13 scholarships for a total of $36,000. The application for 2015 scholarships is in the newsletter or available online at www.specad.org. If you know a student who is studying or plans to major in a STEM (science, technology, engineering, mathematics) field, encourage them to apply for the CAD scholarship. In the past, CAD has supported the plastic program at Terra Community College. We are looking for additional opportunities to work with colleges or universities interested in developing courses for color as part of a plastic or polymer program.

This year, CAD will sponsor The Plastics Race™ which was developed by SPE as an interactive program to educate college students and young professionals about the plastics industry. The first race was held at ANTEC® 2014 in Las Vegas with about 80 participants. This year, the SPE expects more than 200 participants to participate in the activity. The race will take place on Tuesday, March 24 on the NPE show floor. Participants will use a mobile-app designed specifically for the race to find the answers to questions they can only access by visiting race sponsors’

continued on page 2
booths. This provides educational opportunities and introductions to many industries involved in the plastics industry.

The Plastics Race™ is a good lead into ANTEC® 2015. The CAD Section will be held on Monday, March 23. Bruce Mulholland has gathered a great collection of papers and speakers so both the morning and afternoon section should be entertaining and educational. Jack Ladsen and Tom Rachel will moderate the morning and afternoon sessions respectively. Did you know SPE has a mobile-app for events? The SPE Events app for apple, google and other smart devices can be downloaded from the SPE website or from the respective device stores. It is a neat tool to manage your ANTEC® program. You can build a calendar with reminders for specific papers you would like to attend. Information about exhibitors can also be searched through the app. Earl worked with SPE to include CAD RETEC® 2014 event last year and the CAD RETEC® 2015 program will be accessible through the mobile-app later this year.

As a final note, CAD RETEC® 2015 will be October 4-6 in Indianapolis, Indiana. Scott Heitzman and I are working with a team of board members to bring an outstanding program and conference. We hope to restart the color seminar course with Bruce Mulholland stepping in for Bob Charvat. Bruce has received numerous awards for best papers and is an excellent teacher. A small example of his talent will be provided during his keynote address on Introduction to Color Theory, which opens the morning session for the CAD Section at ANTEC® 2015. The Indianapolis conference will be partially supported by ISCC, the Inter-Society Color Council. Jack Ladsen and Tom Chirayil are working on the technical program which is looking very promising. The panel discussion will also resume. As we get closer to the conference, more information will be available online at the CAD website, Linked and SPE eBlasts.

Best Regards,
Betty Puckerin
CAD Chairperson

Invitation to Attend Our Board Meetings

The Color and Appearance Division regularly holds Board of Director (BOD) meetings at the ANTEC® and the CAD RETEC®️. In addition, a Summer BOD meeting is typically held about 6 weeks prior to the next CAD RETEC®️.

The Summer meeting is scheduled in various locations. A Winter BOD meeting is held in January.
The Winter meeting is typically held at a site of a future CAD RETEC®️.

Any SPE CAD members who wish to attend are welcome at these meetings. If interested in attending the next Board meeting, please contact the Division Chairperson for more information.

Disclaimer:
The information submitted in this publication is based on current knowledge and experience. In view of the many factors that may affect processibility and application, this data/information does not relieve processors from the responsibility of carrying out their own tests and experiments; neither do they imply any legally binding assurance of certain properties or of suitability for a specific purpose. It is the responsibility of those to whom this information is supplied to ensure that any proprietary rights and existing laws and legislation are observed.
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Newsletter Sponsorship Opportunity
The Color and Appearance Division (CAD) commits to the publishing of at least three newsletters a year (four if there is sufficient material to justify the extra issue). Each newsletter is electronically distributed to our membership of nearly 1,000. Each sponsor’s art directly links to the company’s website.

In addition, we print one of these newsletters on 80#gloss coated stock, All electronic versions are also posted on the SPE website where it available for anyone to download.

For the small donation of $300 per year, we offer a business card sized (2 x 3.5 inches) mention in our newsletter.

We currently have the following slots available for sponsorship:
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2015 CAD BOD/ Councilor Election results

Incumbents:
Earl Balthazar  Alan Bodi
Hal Button      Sandra Davis
Jack Ladson     George Rangos

Newly elected members of the BOD:
Bruce Clatworthy  Alex Prosapio
Michael Willis

New CAD Councilor:
Bruce Mulholland

Respectfully submitted,
Jeffrey S. Drusda

Board Minutes

Dear Members:

Just a reminder that you can view past and current BOARD MINUTES on the SPECAD website.

We do not typically publish the minutes in the electronic versions of our newsletter, but they are always available for our members to view from our website. The site is not completely current at this time, as we are in the process of giving it a makeover and new launch in January.

Click here for the link to view:

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The Fall 2014 Council meeting was held on September 13 and 14, 2014 in New Orleans, LA with supporting meetings, including the Council Committee of the Whole (CCOW) being held immediately before the afternoon start of the Council meeting. It was announced that Russell Broome has been hired, effective October 1, as the managing director for SPE replacing Gail Bristol who as retired and Tom Conklin, who is now part time and will retire during the 2015 fiscal year.

Financial: The financial update for the Council indicated that while the operating income deficit for 2013 was expected to be more than $100,000, the final deficit was $87,173. At this point, 2014 is on track to be slightly better than expected; however, a deficit is still expected. The budget for 2015 is still in draft form awaiting finance committee approval. It is expected that once the budget is approved by the finance committee it will be available to Councilors for review; however, the Council has no role in approving the budget.

Membership: The official position on membership is that the organization membership remains stable between 13500 and 14000. Some concern remains regarding the robustness of the information being reported.

The Chain: The proposed social networking site is in beta testing and is expected to have a soft launch October 1, 2014. The full launch is scheduled for 1Q15.

As part of the Council meeting, a workshop was conducted to process three categories of questions related to the overall organization: SPE value (current and proposed), membership fees, and governance. The feedback was taken by SPE leadership for further consideration. Some of the feedback from the groups included:

Next Generation Advisory Board:
The NGAB remains active targeting members with less than 5-10 years’ experience in the plastics industry. This is a separate effort from the student activities, although on goal is to increase the number of memberships which are converted from student to full memberships. The metrics to measure the success of the NGAB include the number of young members, the retention rate of student members as they convert to full memberships, revenue and event participation.

Bylaws and Policies:
Several items were presented to the Council for voting. However, there was significant discussion because a number of the items were not presented with sufficient notice prior to the meeting for discussion with member group leadership. The most of the bylaw changes proposed and passed dealt with cleaning up structural items as related to the evolution of the organization – elimination of senior member status, eligibility for Society level offices, Councilor term of office and the method to change a bylaw. The item of most significance was the approval of the Council to grant the responsibility for the policy governing the use of the SPE brand including the logo to the Executive Committee. Initially, the proposal had included the elimination of the red logo as an acceptable option. The red logo was added back into the policy and the policy passed.

Respectfully submitted,
Sandra Davis
January 14, 2015

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CONNECT WITH SPE CAD VIA SOCIAL MEDIA

Join SPECAD’s Group On LinkedIn
to network with industry peers, participate in group discussions of industry and technical topics, find job opportunities, and get the latest division and conference announcements.

**Group Name:** SPE Color & Appearance Division  
**Group ID** 152108  
[www.linkedin.com/groups?gid=152108](http://www.linkedin.com/groups?gid=152108)
### MODERATOR: JACK LADSEN, COLOR SCIENCE CONSULTANCY

#### COLORED RESIN TOPICS

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<th>Time</th>
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<th>Company/Institution</th>
<th>Session Type</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:30 - 9:00</td>
<td>Bruce Mulholland</td>
<td>Celanese</td>
<td>Keynote</td>
<td>Introduction to Color Theory</td>
</tr>
<tr>
<td>9:00 - 9:30</td>
<td>Jonathan Till</td>
<td>Uniform Color Company</td>
<td>2090218</td>
<td>Optimizing Coloring Methods for Plastics: &quot;What's the best coloring method for your application?&quot;</td>
</tr>
<tr>
<td>9:30 - 10:00</td>
<td>Steve Blazey</td>
<td>A. Schulman, Inc.</td>
<td>2139678</td>
<td>Formulation Strategy to Achieve Highly Colorable and Weatherable ASA</td>
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<tr>
<td>10:00 - 10:30</td>
<td>Sharon Ehr</td>
<td>Uniform Color Company</td>
<td>2098608</td>
<td>Colorant Solutions to Meet Global Packaging Regulations</td>
</tr>
<tr>
<td>10:30 - 11:00</td>
<td>Shahid Ahmed</td>
<td>University of Ontario</td>
<td>2095651</td>
<td>Effect of Process Variables on Pigment Dispersion in a Polycarbonate Based Compounded Plastic</td>
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</tbody>
</table>

### MODERATOR: TOM RACHAL, TRONOX

#### COLORANT TOPICS

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Company/Institution</th>
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<tbody>
<tr>
<td>1:30 - 2:00</td>
<td>Steve Goldstein</td>
<td>Clariant Corporation</td>
<td>2097393/ Keynote</td>
<td>Specifications and Test Methods (A CAD Continuing Education Presentation)</td>
</tr>
<tr>
<td>2:00 - 2:30</td>
<td>Austin Reid</td>
<td>DuPont</td>
<td>2092676</td>
<td>X-Ray Methods: Examples of Contributions to the History of Pigments</td>
</tr>
<tr>
<td>2:30 - 3:00</td>
<td>Andrew Smith</td>
<td>The Shepherd Color Company</td>
<td>2138599</td>
<td>Pigment Design in the Modern Age</td>
</tr>
<tr>
<td>3:00 - 3:30</td>
<td>Dietmer Mäder</td>
<td>Eckart GmbH</td>
<td>2095794</td>
<td>Novel Effect Pigments For Cool Plastics</td>
</tr>
<tr>
<td>3:30 - 4:00</td>
<td>Phil Niedenzu</td>
<td>DuPont</td>
<td>2093885</td>
<td>A Walk Around the Color Sphere: Effect of Titanium Dioxide Particle Size Distribution on Color of Plastics</td>
</tr>
<tr>
<td>4:00 - 4:30</td>
<td>Nathan Karzses</td>
<td>Nubiola USA</td>
<td>2097848</td>
<td>Blue Undertone Enhancement of Black and Grey PP Injection Molded Parts for Automotive with Ultramarine Blues</td>
</tr>
<tr>
<td>4:30 - 5:00</td>
<td>Jim Rediske</td>
<td>BASF Corporation</td>
<td>2133420</td>
<td>Color Transfer from Point A to Point B: A Review and Examination of Crocking, Rub-off, Bleeding, Blooming, Blushing, Transfer, Migration, Extraction, Sublimation, Exudation, Plate Out, Diffusion and Any Other Means by Which Color Ends Up Where It Doesn't Belong.</td>
</tr>
<tr>
<td>5:00 - 5:30</td>
<td></td>
<td>Business Meeting</td>
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Technical Article

The following Technical Article was published in 2005- It was winner of the Best Paper of the same year.

A DAY IN THE COLOR APPLICATIONS LABORATORY/AND NOW THE REST OF THE STORY
Roger Reinicker, Brian Coleman, and Tad Finnegan
Ciba Specialty Chemicals, Inc., Ciba Specialty Chemicals Corporation

ABSTRACT
A color applications laboratory faces a variety of challenges on Monday morning: migration of a component out of a molding, crack propagation in a plastic part after weathering, an intractable color match in a packaging application, and dispersion failure in a concentrate for polypropylene. The laboratory seeks to find solutions based on classic pigment application data and knowledge. Solutions will incorporate the science behind each problem resolution, with discussions that focus on pigment characteristics of crystal stability in various substrates, change on exposure, nucleation, and the effects of particle size and particle size distribution significantly reduced.

INTRODUCTION
Problem solving is a critical skill of anyone working in a technical field, and those working in a plastics color application laboratory are no different. Presented below are several challenging situations based on real problems encountered in the laboratory that tested the problem solving skills of the technicians. A general discussion of the issues surrounding the problem, test methods used to isolate the critical variable in each problem, and the proposed solution are presented.

FAILURE OF A SINGLE PIGMENT DISPERSION AT A CUSTOMER’S CUSTOMER
DESCRIPTION OF THE PROBLEM
A customer has opened a new facility to produce single pigment dispersions (SPD) for a dispersion critical application. The customer has long used a particular organic powder pigment and been successful, but the first attempts at the new facility have been problematic and the end-user (the customer’s customer) has rejected a sample for being off-color. The direct customer is concerned about the quality of the lot received, but the Certificate of Analysis (COA) of the lot shows all parameters are within specification.

Further investigation reveals that the single pigment dispersion made by the customer actually passed all outgoing tests (among these are color, strength, pellet size, and pellet appearance) but failed in an incoming quality test at the end-user’s production site. It is also known that the dispersion composition, while held proprietary, is unchanged between the customer’s old site and the new satellite facility. Given that no composition or process information is forthcoming, should the lot be judged sub-standard and replaced?

POTENTIAL ISSUES CONTRIBUTING TO THE PROBLEM
Single pigment dispersions are used in some industries where the end-user has the ability and desire to control their own formulations by color matching and using stabilizers and other additives. Use of SPDs allows them to focus their efforts on these aspects and avoid the handling of powder pigments that some find difficult due to dusting issues. The SPD producer has learned to handle powders efficiently and has an economy of scale not available to his customer. However, the producer of the SPDs has limited scope for batch corrections with respect to color control, as there is no option to blend other pigments into the SPD to compensate for hue differences. Even strength differences are difficult to correct since the end-user might be using the SPD in any number of formulations and a significant strength compensation may work for one formula but is unlikely to work for all formulas. Given that the composition of the customer’s SPD is unchanged and the SPD actually passed the customer’s outgoing quality assurance tests, it is possible that some intrinsic, normally untested quality, such as heat stability or migration has failed. Such a property difference is not going to show up on the COA.

Just as pigment producers must demonstrate that a commercial lot of pigment fulfills certain quality specifications such as color, strength, fineness of grind, and purity, the producers of pigment dispersions must show that a commercial lot of SPD meets certain criteria including color, strength, and completeness of dispersion. In this case, the SPD manufacturer is using an effective quality control test in which the pigment dispersion is co-melted and mixed with titanium dioxide dispersion, pressed or molded into a plaque, and measured for color and strength. The resultant information gives a measure of confidence that quality is consistent from lot to lot. However, this test for consistency is not completely adequate for comparison of SPDs from different processes and should not be used alone in judging the viability of dispersions following a process change or when comparing
different manufacturing sources. The tint test is only a snapshot of the bulk of the particle size distribution curve of a pigment. As produced and delivered to the dispersion process the pigment will have a particular distribution of crystal aggregates and agglomerates. Dispersive work (shear, impact, and compression) applied to the pigment may narrow, broaden, or shift the particle size distribution curve. While it is not impossible to create identical dispersion processes in two locations, it is necessary to do more extensive testing when changing equipment.

For the fine or small end of the particle size distribution curve it is important to measure transparency. The reason is that, at least for organic pigments, there is a point of particle size below which there is no increase in strength of the pigment but only an increase in transparency (Figure 1). Hence two dispersions with similar tint strengths may remarkably different transparencies when viewed in medium that does not also contain a scattering pigment (whether white or other colorant with a high index of refraction).

At the high end of the particle size distribution curve reside the particles that contribute little to strength. These particles do not scatter light well (being supertransparent) nor do they absorb well because, while they have a larger mass per particle, they are few in number. Besides their lack of coloring power, the particles above a specific size are critically damaging to the efficiency of some processes (for example, fiber extrusion) and must be eliminated in order to avoid poor quality end-product.

A wide variety of methods are being used in practice to judge the quantity of oversized particles in dispersions, but the preferred test is the filter pressure test because it delivers a quantifiable number that relates to the quantity of oversize particles. Unfortunately, there is no standard test used in the US industry, as suppliers and customers have evolved any number of tests in which a fine screen filters the colored melt under pressure and the resulting increase in pressure is measured over time. Recently, though, a new standard test called the “EN 13900-5” has been proposed and adopted by a number of pigment producers. This test is doing what standardized testing is supposed to do: create a common language for judging quality and improve the quality of communication among all users. In fact, the pigment in question is a product that has a specified filter value, insuring that the powder particles are virtually free of aggregates over about 20 microns in size.

IDENTIFICATION OF THE KEY VARIABLES
The key variables here relate to the dynamic balance and timing of forces in the two dispersion operations and the effect that they have collectively on the particle size distribution. In the dispersing steps of pigment in plastic, it is important that wetting of the pigment surface precedes the application of shear or pressure. Application of pressure or shear prior to wetting is likely to cause the creation of aggregates through compaction. Since organic pigments are frequently very small in particle size and smaller particles have higher surface energies, compaction and wetting are critical variables in this situation.

A comparison can be made of the filter value of the SPD with the filter value of the pigment as already known from the COA. If the SPD has a higher filter value per weight of pigment than before processing, the most likely cause is poor wetting prior to shear.

SUGGESTED SOLUTION
While it is possible that the lot of pigment in question was changed in quality, the more fruitful are of inquiry is going to be the process at the customer’s new facility. Replacing the lot and having the customer repeat a production run is likely to simply delay the resolution of the problem.

Since no composition or process information was given, a direct solution cannot be provided to the customer. However, a set of tools and methodology can be provided to the customer to help them evaluate their material and processes. The customer needs to look at all parts of the particle size curve of the SPD by making a judgment of transparency, tint strength (at more than one level) and filter value (for characterizing the quantity of oversize particles). Process parameters can then be manipulated to bring each part of the size distribution into line with the previous standards. Once a new process is determined, quality testing can return to only those tests needed to insure product consistency.

The absolute number of the filter value is also very useful in determining if the dispersion is adequate for the application. The creators of the EN13900-5 test have stated that
The fourth potential issue is common, but more difficult to address. Frequently, color targets are provided that do not match the polymer system for the color match itself. Pantone® colors, painted metal, and colors in different polymer systems are all frequently provided as color targets to color matchers. In some cases, the color space of the target may not be achievable for technical reasons. For example, many pigments used in paint systems are not sufficiently heat stable to work in polymeric systems. Thus, a color target may indicate that a region of color space is accessible theoretically, but practical and technical constraints may limit our ability to actually reach that space.

The last two considerations, relating to the transparency of the pigment, are less widely known but can have an impact on the chroma of the material. To understand the influence of pigment and system transparency on chroma, a review of light dynamics is needed.

Color is our observation of the wavelengths of light "left over" after absorption by the pigment in an object. For a translucent or semi-opaque object, part of this "left over" light striking the object is transmitted through the object and part of this light is scattered, as shown in Figure 2.

Transmitted light passes through the object essentially unchanged, traveling in the same direction as the incident light striking the object. Scattered light is caused by the interaction of light with heterogeneities within the material. Scattered light no longer moves in the same direction as the incident light; it is diffused by the interactions and moves in many different directions. The scattering of light is primarily a function of three properties of the system:

1) the relative difference in the index of refraction between the medium (i.e., the polymer) and particles within the medium (i.e., the pigment);
2) the size of the particles distributed in the medium;
3) the absorption characteristics of the particles and the medium.

a value of 2 bar/gram of pigment is sufficient for many dispersion critical applications. Further efforts in the USA to align the new protocol with older screen test methods have refined this figure to a value of less than 1 bar/gram for general fiber applications.ii

With all parts of the particle size distribution curve evaluated and successfully matched to a previous acceptable offering, there is every confidence that the new process will deliver the quality expected by the downstream customer.

LACK OF CHROMA USING PIGMENT WITH A HIGH COLOR STRENGTH

DESCRIPTION OF THE PROBLEM
A customer called with a problem relating to the color saturation (chroma) of a tint for medium-to-deep shade translucent polypropylene product. Despite his best efforts, he was unable to achieve the necessary chroma to within the desired tolerance. "I'm using the strongest pigment available in this chemistry, and I still can't achieve the chroma I need for this application. Do you have anything stronger? What else can you suggest?"

POTENTIAL ISSUES CONTRIBUTING TO THE PROBLEM
Many factors can lead to a low chroma when color matching a material. The key considerations to addressing this problem include:

1) Is this a masstone or tint color to be matched?
2) Is the pigment well dispersed in the material?
3) Is the material contaminated?
4) Was the target a "real" target in the same polymer system?
5) What transparency or opacity is required for the polymer?
6) What was the transparency of the pigment used?

The first four considerations are very common issues relating to chroma issues. The nature of the color match, masstone or tint, is fundamental to any questions regarding the color itself. Since masstone colors and tints interact with light in different ways, knowing the nature of the color match is key. Our considerations should always start with the boundaries we are working within.

If a pigment is not well dispersed, the full strength and chroma of the pigment will not be achieved. If the pigment is contaminated (such as with carbon black or by an opponent color), the chroma of the material may be suppressed by the contaminant. These two problems are quite common and can frequently be addressed through quality control systems in place at the manufacturing site.
If the difference in the index of refraction between the polymer and the pigment is large, more scattering will occur than if the difference is small. Typically, the index of refraction for an organic pigment is similar to that of the polymer, while for inorganic pigments the difference is usually larger.

If the particles within the medium are very large, little scattering will occur. As the particles get smaller, more scattering occurs until it reaches a maximum. Scattering is strongest at particle sizes close to the wavelength of light (i.e., 0.3 to 0.7 µm). As the particles get even smaller, the amount of scattering decreases again so that very small particles scatter little light. Figure 3 shows the influence of particle size on light scattering.

![Figure 3](image)

**Figure 3** Effect of particle size on scattering.

The ability and efficiency of a particle to absorb and re-emit light also plays a role in scattering.

Pigment opacity is governed by light scattering. The maximum opacity of a pigment particle occurs at the size where maximum light scattering occurs. Particles that are smaller or larger than this critical size will appear to be more transparent.

The color strength of a pigment within a given chemistry is related to the particle size of the pigment and its absorption and scattering properties at a particular wavelength. A frequent measure of color strength is the K/S ratio, the ratio of absorbed light (K) to scattered light (S). This color strength can be measured at the wavelength of maximum absorption, or averaged over all wavelengths along with a weighting factor. Typically, within a given pigment chemistry, the pigment with a smaller particle size will be stronger and more transparent. By reducing the particle size, we have effectively maintained the light absorption (K) while reducing the scattering (S) to create the increase in color strength.

Conceptually, let's take a look at the color strength of two systems that have the same amount of scattering but use pigments with different absorption characteristics. In the material with low absorption, a large amount of white light is scattered by the pigment, making the object look pale and washed out. Its color strength would be described as weak. On the other hand, if the material has a high absorption, the only wavelengths scattered are those not absorbed, so the object would have a vivid color. Its color strength would be described as strong.

For translucent materials, both light scattering AND light transmission are required. In order to achieve a specific contrast ratio (a measure of the degree of translucency) for a color match in a translucent system, a "fixed" amount of scattered light relative to the incoming light is required. If a stronger, more transparent (i.e., less opaque) pigment is used, less light scattering will occur from the pigment than if a weaker, more opaque pigment is used. Since the degree of scattering is fixed for the application, the use of a stronger, more transparent pigment will necessitate the use of additional opacifying pigment (such as titanium dioxide). At a given lightness level, the additional opacifying pigment will not contribute to the chroma and can ultimately drive the saturation down. If a more opaque pigment is used, we take advantage of the scattering properties of the organic pigment and less opacifying pigment is required and higher chromas can be achieved.

In this manner, the transparency of a pigment can have an impact on the chroma achievable in a translucent system.

**IDENTIFICATION OF THE KEY VARIABLES**

Further discussions with the customer revealed that the pigment in question was Pigment Red 254, a diketopyrrolopyrrole (DPP), in combination with titanium dioxide. The quality of dispersion was excellent when measured through filter pressure value testing. Spectral curves revealed no evidence of contamination. The color target used by the customer was a physical sample in polypropylene, so it was clear that the color space was achievable in practice. The sample was 2mm thick and had a contrast ratio of 7.

The maximum chroma achieved in the color match for this sample was obtained at 0.10% pigment concentration and 0.058% TiO₂ while maintaining a contrast ratio of 7. The chroma, C* was 58 and the lightness, L*, was 48.

1 Contrast ratio is defined here as the total color difference (LE*) of a sample measured over a white background and over a black background for a given thickness and pigment concentration.
The fact that the customer stated he was using the "strongest pigment available" for the chemistry in a translucent application led us to believe that the pigment opacity may be the issue.

VERIFICATION OF THE KEY VARIABLES
The pigment used by the customer, PR 254-A, had a 1/3 International Depth of Shade (ISD) of 0.10%. The customer's pigment was then compared to a more opaque pigment, PR 254-B, with a 1/3 ISD of 0.15% (33% weaker in color strength).

To meet the same contrast ratio and \( L^* \) value, 0.10% of PR 254-B was used with 0.018% TiO\(_2\). The chroma for this formula was approximately 63, or 5 units higher than when using PR 254-A. Table 1 summarizes the property and formula differences for the two pigments.

Table 1. Properties of Transparent & Opaque Pigment Red 254

<table>
<thead>
<tr>
<th>Property</th>
<th>PR 254-A</th>
<th>PR 254-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3 ISD (with 1.0% TiO(_2))</td>
<td>0.10%</td>
<td>0.15%</td>
</tr>
<tr>
<td>Amount of pigment used in formula</td>
<td>0.10%</td>
<td>0.10%</td>
</tr>
<tr>
<td>Amount of TiO(_2) need to provide contrast ratio of 7.0</td>
<td>0.058%</td>
<td>0.018%</td>
</tr>
<tr>
<td>Chroma, C*</td>
<td>58</td>
<td>63</td>
</tr>
<tr>
<td>Lightness, L*</td>
<td>48</td>
<td>48</td>
</tr>
</tbody>
</table>

SUGGESTED SOLUTION
Based on the results presented above, the customer was informed that the color space and chroma he was seeking was achievable using a more opaque Pigment Red 254. While it may seem counterintuitive to use a weaker pigment grade to achieve a higher chroma, it is important for the color matcher to remember that color strength is only one factor contributing to the value of a pigment; in this case, the particle size and opacity of the pigment was more critical than the color strength. Keeping transparent and opaque pigments of the same chemistry on hand can help ensure that the best color match for any system, transparent, translucent, or opaque, is available.

MIGRATION OF A COLOR COMPONENT
DESCRIPTION OF THE PROBLEM
A customer has called early Monday morning concerned over discoloration that has not been seen before. At the end of the previous Friday, one of her color formulators had stacked the day’s series of PVC mill sheets on top of each other to tidy his workspace. While separating to measure the color on each sheet after the weekend, he notices that one side of a white sheet is spotted with yellow splotches. Curious about the cause, the formulator notes that the discoloration occurred on only one side of the sheet and he notes that a yellow sheet was in contact with his white sheet.

POTENTIAL ISSUES CONTRIBUTING TO THE PROBLEM
Because the color change was yellow and occurred only on the side adjacent to the yellow sheet, a transfer to the white sheet is the most likely explanation. After questioning the color formulator, it was confirmed that no color change had been observed in areas where the sheets had not been in contact due to imperfect stacking. Further confirmation came from the yellow stain that resulted from light rubbing of a white cloth on the surface of the yellow mill sheet. When the formulator repeated the preparation of the color, staining was not evident on the rolls nor were significant quantities rubbed off of the sheet. At this point, the color appears to be migrating from the interior of the mill sheet to its surface. To determine the cause of this movement, a number of questions need to be addressed:

1) Were the sheets stored for an unusually long period or under unusually high temperature or pressure?
2) Has the polymer and/or plasticizer been changed recently? Has the plasticizer concentration been increased?
3) Was the mill sheet prepared using higher roll temperatures?
4) Are there colorants that are inherently unsuitable for plasticized PVC?
5) Are the colorant concentrations appropriate?
6) Is there an uncolored migratory species in the system that is acting as a vehicle for the colorant?
7) Has a migratory foreign colorant been introduced unbeknownst to the formulator?

Migration of colored or uncolored species from inside a plastic article to its surface is driven by forces attempting to achieve an equilibrium state. A system can be at a high-energy non-equilibrium condition as a result of incompatibility or from a supersaturated solution of the soluble fraction of the pigment. In situations where a component and the system are incompatible, perhaps because of a polarity mismatch, the component will seek a more agreeable environment outside of the system until equilibrium is reached. Migration of this type is not always unplanned and detrimental; indeed sometimes it is integral to a solution.
Traditional antistatic additives like glycerol monostearate (GMS) and ethoxylated amines are successful in dissipating a charge only after a fraction has migrated to the surface; this migration is due to a polarity mismatch. And while it is unlikely that a large, immobile pigment crystal will diffuse through a polymer network, species like antistatics, some lubricants and stabilizers that migrate to the surface, whether intentionally or not, can act as a vehicle to carry pigments out with them by swelling and "loosening" the polymer network. The deposition of pigment particles on equipment or the surface of the plastic itself following this mechanism is known as plate-out. Processing plastics at unusually high temperatures or with high pigment concentration can exacerbate the problem.

The movement of colored species themselves can occur when there is a supersaturated solution of the soluble portion of a colorant in its vehicle system. Supersaturation refers to a condition in which there is more of a material in solution than could normally be dissolved by the solvent at the current temperature and pressure conditions. Modified thermoplastics facilitate the creation of supersaturated solutions by virtue of their preparation: they are processed at higher temperatures than their end use. So if a pigment is partially soluble in the PVC, its plasticizer or both, the vehicle will hold more of the dissolved pigment at the higher temperature seen during processing. Once cooled, the supersaturated system is a thermodynamically unstable condition; the solubility limit of the dissolved pigment has been exceeded. One of the routes to mitigating this high-energy state is for the pigment molecules to migrate to the surface and recrystallize. This process, referred to as blooming, will continue until the supersaturated condition is alleviated.

The speed at which blooming occurs and the degree to which it is the preferred mechanism depends on several factors. Many systems have a window of pigment concentration where blooming is likely to occur. At low concentrations, the limit has not been exceeded and therefore the system is relatively stable. At high concentrations, the excess solid pigment creates a situation where crystallization on the interior of the plastic is energetically preferred to crystallization on the surface. Other systems may not allow for pigment solubility at any level under the end-use conditions in which case there may be blooming even at very low concentrations. The likelihood of a species to bloom is dependent upon its ease of travel, i.e. the amount of mobility in the system at the conditions of use. Pigments dispersed in polymers like plasticized PVC and polyethylene will enjoy mobility because the conditions of use (typically ambient conditions) are above their glass transition temperature \(T_g\). The rigid matrix formed below the \(T_g\) significantly impedes the movement of dissolved particles. Plasticizers in PVC like dioctyl phthalate (DOP) and diethylhexyl phthalate (DEHP) serve to open the molecular structure of the plastic, allow the chains to slide along one another and thereby impart flexibility. The openness created by various plasticizers may differ but within the same type, the openness increases with increasing concentration. Some stabilizers and even the PVC itself affect the tendency of a given pigment to bloom. Migration from both blooming and plate-out will increase as the temperature of the system increases simply due to the increased motion.

Last, the chemical constitution of the pigment and its particle size distribution also govern the likelihood of migration. Some pigments are inherently more prone to migration than others. There exist no hard and fast rules that allow for prediction of migration resistance from a pigment’s structure alone but some general trends are recognized. These trends include increasing molecular weights, the presence of insoluble substituents and the formation of insoluble polar salts. Particle size distribution becomes important when the distribution is broad and contains very small particles. For a given chemistry solubility increases with decreasing particle size so the small particles at the low end of a broad distribution would contribute to a supersaturated state more readily than would a narrow distribution of larger particles.

Because prediction of migration resistance from chemical structure is so difficult, pigment manufacturers will typically supply data from standardized tests that serve as a relative ranking and afford the user some level of confidence. Migration resistance in plasticized PVC is sometimes assessed by placing a colored sheet in contact with a white sheet and subjecting it to a controlled pressure and temperature for a specified period. After the specified period, the white sheet is assessed for color change due to staining. The amount of color transferred is directly related to the pigment’s tendency to migrate. To ensure a reliable correlation, the many variables must be carefully controlled. In addition to time, temperature and pressure, these variables would include: the type and concentration of the plasticizer; the identity of the base PVC; the entire preparation method; the concentration of all ingredients and the interval between test completion and assessment.

\(^2\) By contrast, room temperature is well below the glass transition temperature of polystyrene and as a result, polymer soluble dyes can be used under normal circumstances without significant migration.

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IDENTIFICATION OF THE KEY VARIABLES
Eliminating potential issues contributing to this problem was achieved quickly through communication with the formulator. It was determined that the sheets were placed on a desk, in a small stack (no excessive pressure) and isolated from a heat source. Leaving samples like this over a weekend had been a common practice for years. A check of the ingredients and their lot numbers from the colorist’s notebook confirmed that the PVC and plasticizer had not been changed and that the plasticizer had been incorporated at the standard 30% level. Additionally, the mill’s process log indicated that roll temperatures remained within an acceptable range for the entire day of trials. The rest of the formula was remarkably simple. To create a bright mid shade yellow, he had used 0.277% Pigment Yellow 62 (PY 62) and just 0.053% Pigment White 6 (TiO2) to impart a bit of scattering. Based on a long history of successful use, the excellent migration resistance of PY 62 described in the literature, and the reasonable loading level, the PY 62 appeared to be an appropriate choice. With the ingredients, preparation and handling consistent with current procedure, the focus shifted to the quality of the current PY 62 lot. The stain could be the result of an unusually high percentage of small particles in this particular lot’s distribution: this condition would be more conducive to migration. Perhaps the yellow stain could be the result of unwanted foreign colorant introduced somewhere between the synthesis and this match trial. We knew we were onto something when the manager checked her records and found that the pigment supplier had changed, although the pigment was still identified as a PY 62.

VERIFICATION OF THE KEY VARIABLES
A sample of the alternate PY 62 was supplied to the laboratory. To confirm that the PVC system was not contributing to the migration, a known, high purity PY 62 sample was tested under standard conditions versus the other material. As expected, the alternate source showed noticeable staining even under the low temperature conditions. The two powders were then analyzed using a proprietary analytical technique capable of identifying pigments via molecular weight. The unknown PY 62 sample contained a species consistent with PY 62 and a species consistent with yellow pigment historically associated with migratory issues and decomposition above 200°C.

SUGGESTED SOLUTIONS
Because of the widespread use of PY 62 at this facility, including in polymer systems that operate at or above 200°C, it was agreed that the priority be placed on identifying the source of the contamination. The manager investigated the possibility of contamination of intermediate containers within her facility. She also began to question her alternate supplier about their means to minimize contamination and whether their capacity allowed them to dedicate vessels to specific pigment chemistries.

MECHANICAL FAILURE IN A PART FOR OUTDOOR USE

DESCRIPTION OF THE PROBLEM
After a routine conversation with a customer, the customer mentioned in passing an odd problem he was having with an injection-molded, high-density polyethylene (HDPE) seat for children's swingsets. After approximately six months outdoors, some of the seats were cracking in the same location (the junction of the armrest where the suspension chain is attached and the seat) when the child sat down. "But the odd thing is," he said, "that the cracking is only happening for one of our six colors – blue. Do you think the pigment could be contributing to the problem?"

POTENTIAL ISSUES CONTRIBUTING TO THE PROBLEM
In fact, it is known that pigments can have an impact on the mechanical properties of plastic materials. The fact that only a single color is failing in this particular case may lead one to believe that the pigment is directly or indirectly responsible for the problem. However, before this problem can be attributed to the pigment exclusively, several other possible factors must be ruled out:

1) Is the seat design flawed?
2) Are the molding conditions appropriate for the material and application?
3) Is the system properly stabilized for weatherfastness and outdoor durability?
4) Is the pigment weatherfast and durable?
5) Does the pigment affect the mechanical properties of the finished part?

Whenever a finished part prematurely fails in the same way repeatedly, it is indicative of a flaw in the design of the part and/or in the manufacturing process for the part. This fact must not be overlooked simply because the problem is occurring only for a single color. The geometry of the part, the type and grade of polymer used, the mold design, and the molding conditions are all critical components of the product that contribute to the mechanical performance of the finished part. Inconsistencies between different manufacturing sites’ molds or variability in molding cycles can...
often lead to this sort of problem. Thus, the first two considerations for consistent mechanical failure of a part should be whether or not the part design and manufacturing process are robust. The burden of assessing the robustness of the system is ultimately the responsibility of the product designer and not the color supplier.

Additionally, whenever plastics are used outdoors, the weatherfastness and durability of the system must be considered. Exposure to ultraviolet (UV) light will damage plastic over time, possibly leading to cracking, chalking, and even mechanical failure. If the pigment used in the system is not weatherfast, it can degrade as well. The pigment degradation by-products can then attack the polymer, leading to polymer degradation. Light stabilizers, such as ultraviolet light absorbers (UVA) and hindered-amine light stabilizers (HALS) are used to prevent the UV light from damaging the polymer or to mitigate the damage caused by UV light and thus maintain the durability of the plastic. Furthermore, some pigments are known to interact negatively with certain light stabilizers. Because these interactions can occur, one light stabilizer package may need to be optimized for a given color. The proper selection of a light stabilizer package for a specific color and application is critical to ensure the maximum protection from weathering is offered. In addition to light stabilizers, the pigments used in plastics for outdoor use must be carefully selected to ensure their weatherfastness and durability in the application.

Last, it is known that some organic pigments will affect the crystallization properties of polyolefins, and in particular HDPE. Certain pigments, such as copper phthalocyanines, serve as nucleators for polymer crystallization and can cause warping and shrinkage of injection molded part. Since the mechanical properties of HDPE are related to its microstructure, a pigment that alters the crystallization of HDPE can have an impact on the mechanical properties of the HDPE. Besides the pigment itself, the molding conditions (e.g., the cooling rate) can exacerbate the nucleation and crystallization problem, leading to parts with anisotropic properties and built-in stresses. The crystallization kinetics of HDPE makes relaxation of internal stresses after molding unlikely, leaving a molded part susceptible to mechanical failure. Careful selection of pigments with little or no influence on the crystallization properties of injection molded HDPE is often required to preserve the shape and mechanical integrity of the finished part.

IDENTIFICATION OF THE KEY VARIABLES
Further conversations with the customer revealed that the blue pigment used in the system was Pigment Blue 15:1, a copper phthalocyanine, at a concentration of 0.08% in masstone. The blue seats were molded at multiple facilities, with each facility showing the same failures at approximately the same frequency. Seats of other colors were molded at the same facilities on the same equipment without similar failures. No significant differences existed between molds and molding conditions between the different facilities.

Finite element analysis of the seat performed by the customer revealed that when under load (i.e., when a child was sitting in the seat), there was a concentration of stress at the location where the cracks were occurring. The concentration of stress was high but well below the yield point for the HDPE.

A light stabilization package containing both a UVA and a HALS was used to improve the weatherfastness of the seat. Accelerated weathering studies were performed on molded HDPE chips of each color, and each color showed acceptable durability for the duration of the test.

The correlation of the stress concentration determined by finite element analysis and the actual location of the cracking does indicate that the design of the seat is contributing to the failures. However, the fact that multiple facilities show the problem, and that multiple colors are run at each facility on the same equipment, does seem to indicate that the blue pigment is contributing to the cracking as well. If the problem were solely attributable to the stress concentration, it would be expected that the frequency of failure would be approximately the same for all seat colors.

The use of the light stabilization package and accelerated weathering study can help us rule out weathering as the primary source of the problem.

The pigment used, Pigment Blue 15:1, is generally weatherfast when used in masstone, as is the case here. However, the pigment is known to have a strong influence on the crystallization behavior of HDPE. A review of the other five colors used showed that each had little or no influence on the crystallization behavior of HDPE.

Based on this information, it appeared that two factors were working together to cause the mechanical failures. First, the design of the seat itself led to the creation of a line of stress concentration within the part. Second, the pigment was also contributing to the internal stress of the seat, allowing for cracking to occur.
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VERIFICATION OF THE KEY VARIABLES

Internally standardized warpage and shrinkage tests were conducted to determine the degree of influence on the crystallization behavior of the customer's HDPE. These tests use injection molded HDPE with controlled cooling cycles to obtain a measure of warping and shrinkage induced by a pigment. Results of the tests are shown in Figures 4. The results indicate that the pigment exerted a strong influence on the crystallization kinetics of the HDPE. Even though the customer has not observed warping during the manufacturing of the seats, the strong influence exerted on HDPE crystallization by the pigment cannot be ignored. It is likely that the warping is manifesting as an increase in the internal stresses of the part, exacerbating the stress concentration problem that already exists.

SUGGESTED SOLUTIONS

While the root cause of the cracking has not been established, the customer's question of whether the pigment could be contributing to the problem has been answered - "yes." The additional information will hopefully allow the customer to find the underlying mechanism of the warping and prevent it. The customer should also consider redesigning the seat to alleviate the stress concentration line designed into the seat.

Additionally, a recommendation to use pigments with a low influence on the warping behavior of HDPE may prevent failures. There is no low-warping Pigment Blue 15:1 currently available in the market; however, there are low-warping grades of Pigment Blue 15:3 available. Though Pigment Blue 15:3 is a green-shade blue, it's color can be shaded to match PB 15:1 using Pigment Blue 60, a very red-shade blue based on indanthrone chemistry. The warping results for that pigment combination are shown in Figure 5. This solution would not compromise the weatherfastness of the system and would minimize the problems associated with warping.

CONCLUSIONS

The challenging problems discussed in this paper were chosen to illustrate several points. First, the role of problem solving in the daily life of a technical service representative cannot be under-emphasized. To some extent, a tech service rep is a detective, looking for the clues to put him/her on the right track to solve a problem. A wide breadth of knowledge not only on the pigment's properties but how the pigment interacts with the system overall is essential. An understanding of the underlying science, whether its thermodynamics or light physics, is also a key skill.

In addition to the skills needed by the technical representative, each of these problems illustrates that the value of a pigment isn't one-dimensional (e.g., color strength). Manufacturers attempt to give their pigments properties for the broadest applicability. Frequently, the pigment best-suited for a wide range of applications isn't the best choice for a specific application. Particle size and particle size distribution, influence on mechanical properties, and pigment crystal stability can all provide critical value to the end user. Color matchers must not lose sight of this fact when developing a solution for their customers.

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  r.todesco@xxinternational.com
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