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

Dear SPE CAD Members,

Nature is displaying fall colors and RETEC<sup>®</sup> is behind us, so we must be going into winter. Thanks again to our team of volunteers led by Breeze Briggs for putting on another great CAD RETEC<sup>®</sup>, and wasn't it fantastic! Look elsewhere in this issue for more details, but every year the team makes it look easy; but trust me, it isn't. Much work goes on behind the scenes beginning around three years out with the initial site selection, negotiating a contract, selecting a theme and building a program.



Our next public event is ANTEC<sup>®</sup> 2019 being held in Detroit where it all began. The Society will be celebrating 75 years of the SPE. Look for a mixture of talks contrasting then and now with sessions aligned by applications. Just think about the amount of plastic in an automobile 75 years ago versus today and the importance of plastics in every aspect of modern living!

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ANTEC<sup>®</sup> is March 18-20, 2019 at the Renaissance Center Detroit. Because ANTEC<sup>®</sup> is so early in the year our CAD BOD elections must be held early also. Each year a third of the board seats come up for election and we vote on a new class of board members. The officers, in turn, are elected from the BOD. The elections committee is working on the slate of candidates right now so look for an announcement soon on who is running.

In the last issue I said I would reveal how I got into the succession to the chairmanship the first time around. I know what you're all wondering. Was it outstanding color vision, exhaustive color chemistry knowledge, or an uncanny foreknowledge of future colors of the year? Well you are all wrong! Here is what really happened. When I attended my 1st meeting I sat next to the person who turned out to be the TPC chairman. Quite possibly it was the only open chair and was left open for the secretary, or maybe everyone else knew better than to sit there (an indication of better mentoring for all the other newbies perhaps). The new secretary was absent and so I would take the minutes. I had to do it again at 2nd meeting as the secretary couldn't make it again, so guess who took the minutes. Now with six months experience I was nominated for the next election and it was made official. This is what put me into the progression of chairs leading up to Division Chair seven years later and the rest is history.

Well, enjoy the rest of the issue and see you in Detroit.



Best Regards,

*Brian West* Chairman

#### Terry Golding Outstanding Achievement Award

The Terry Golding Outstanding Achievement Award was formerly known as the Outstanding Achievement Award, but Terry did so much good work organizing the awards format that we named the award after him. This year we have two very deserving persons of this prestigious award, Austin Reid and Robert (Bob) Trinklein.



Austin was on the CAD Board of Directors for 30 years, starting on the Technical Program Committee. Austin served in the leadership positions and was chairman of CAD in 2001. He also helped chair and organize the 1999 and 2010 CAD RETEC<sup>®</sup> 's. Austin served as overall ANTEC<sup>®</sup> technical program Chair for the Division for over 15 years. At the Society level, he served as a Vice-President of SPE. Austin has played in the "Color Eye Blind" Band for 20 years, and this year was the 20th Anniversary for the band. Austin is also an Honored Fellow of the Society, having achieve both Fellow and Honored Service Member status.



Robert was also a long-time member of the CAD Board of Directors where he served as a past chair and was the Conference Chair in Toronto in 2002. Robert was also awarded Honored Service Member of SPE and served as editor of this CAD Newsletter for many years.

Both these gentlemen have dedicated their time and their knowledge and their skills to serve the Color and Appearance industry and we are so thankful for these efforts. We are a better industry because of them and cannot thank them enough.

#### **Editor's Note**



Welcome to the Fall edition of the Color and Appearance Division Newsletter. Hope the Fall has been good to all so far. RETEC<sup>®</sup> 2018 in Charleston was another great success with very good attendance and a spectacular technical program that demonstrated many topics and a great session on the weathering of plastics. Kudos to

Breeze Briggs and Brenda Mullins and their committee for putting on another great RETEC<sup>®</sup>!

As 2018 is coming to a close, we would like to send out a huge thank you to all the sponsors to our division. Without their continued support, we could not do all the things we do to make the Color and Appearance Division one of the best divisions of SPE. From supporting RETEC<sup>®</sup> to supporting this Newsletter, the sponsors really step up when it comes to our division.

As we look ahead to 2019, the process for voting the Board of Directors for 2019 to 2022 term begins in February. *See page 4 in this Newsletter for details*. ANTEC<sup>®</sup> 2019 will be in Detroit celebrating 75 years of SPE and will take place March 18th to the 21st. CAD RETEC<sup>®</sup>2019 will be in Cleveland, Ohio on September 23rd to 25th. It will be a Monday start instead of traditional Sunday start so save the date! Scholarship opportunities will be available for the 2019 /2020 school year (*See page 7 in this newsletter on how to obtain information on these scholarship opportunities*).

Last but not least, there is still time to let us know your interest in sponsoring this Newsletter with an ad for your company. These sponsorship ads allow us to do these Newsletters to help maintain a solvent division of the SPE and allows us to keep getting pertinent information out to the division members. See page 18 in this Newsletter that shows the different sizes available and contact information. Ads will run from winter issue through the fall issue, if content is available, with a minimum of three Newsletters being published. We would need to know you're interest by the end of the year and your sponsorship ad by the end of January.

Hopefully there is something for you in the Newsletter and as always if you have any suggestions or comments please me or someone on the BOD know.

Mark Tuler

Color and Appearance Newsletter Editor tylerm@silberline.com







We Need Your Help - Continue The Excellence!

- Interested candidates for the 2019 Board of Directors should contact Doreen Becker any Board Member, or indicate your interest on the questionnaire
- We will be soliciting candidates through the end of November, 2018
- **Biographies due December 14, 2018**
- Elections start in January, 2019 and run throughout the month
- If elected, term is 3-years (serve until 2022)
- There are 4 Board meetings per year to attend: ANTEC<sup>®</sup>, CAD RETEC<sup>®</sup>, Winter, and Summer meetings



Renaissance Cleveland Hotel Cleveland, Ohio September 23 – 25, 2019 (Monday – Wednesday format) Deadline for Abstracts is February 2019

Chairperson: Steve Esker, Paramount Colors steve@paramountchemicals.com

Technical Program: Ann Smeltzer, Clariant ann.smeltzer@clariant.com

Alex Prosapio, Sudarshan aprosapio@sudarshan.com

COLOR & APPEARANCE

#### CAD RETEC<sup>®</sup>2018 RECAP



SPE CAD-RETEC<sup>®</sup> has been supporting HfH since 2005 when Hurricane Katrina struck the Gulf Coast causing catastrophic damage from central Florida to eastern Texas. That year SPE CAD-RE-TEC<sup>®</sup> was held in Charlotte, North Carolina and in support of the vast rebuilding that would take place, SPE CAD-RETEC donated 25% of the profits from the event to HfH. Since that time the relationship between the two organizations has grown from strength to strength.

For over 10 years, DCC LANSCO (formerly known as *Dominion Colour Corporation*) has supported the Habitat for Humanity in their mission to bring people together to build homes, communities and raise hope through sponsorship of the 5K Fun Run. This past September DCC LANSCO once again hosted the annual 5K Fun Run. It raised almost \$1,000! We are grateful to the runners who helped make this possible, as well as the matched donation made by the Society of Plastics Engineers.

The photo to the right pictures Dr. Bruce Howie (*DCC LANSCO*, *Global Product Marketing Manager*) presenting the cheque to Lynn Bowley (*Habitat for Humanity*).



#### Scholarship Winners Attend CAD RETEC<sup>®</sup> 2018

Every year, the Color & Appearance Division awards thousands of dollars in scholarships to undergraduate students across the country. Our scholarship winners come from a broad range of fields of study, from plastics engineering to earth systems science to international business. This year, in addition to the scholarships, we gave winners the opportunity to attend CAD RETEC\*2018 in Charleston. Two of our 19 winners were able to attend; Annalie Fitzgibbon, a senior at Penn State Behrend, and Nathan Rader-Edkin, a junior at Pennsylvania College of Technology. The students got to attend talks, walk the expo floor and network with industry professionals at the conference and at many of the evening events.

"It was a great conference, great topics, great networking, all around great experience!" said Rader-Edkin.

"RETEC was an amazing experience," said Fitzgibbon, "because is was really in depth about one of the most creative plastic industries. The networking was so valuable that it even led to a job interview one month after."

For more information on our scholarships, visit www.specad.org/scholarships.



Annalie Fitzgibbon, a senior at Penn State Behrend



Nathan Rader-Edkin, a junior at Pennsylvania College of Technology

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#### Society of Plastics Engineers Color & Appearance Division Endowment Scholarship Program for the 2019 – 2020 School Year

The Endowment Scholarship Program offered by the Color & Appearance Division of the Society of Plastics Engineers awards multiple scholarships each year to students who have demonstrated or expressed an interest in the coloring of plastics industry. The students must be majoring in or taking courses that would be beneficial to a career in this industry. This would include, but is not limited to, plastics engineering, polymer science, coloring of plastics, chemistry, physics, chemical engineering, mechanical engineering, industrial design and industrial engineering. All applicants must be in good standing with their colleges. Financial need is considered for most scholarships.

Undergraduate and graduate scholarships range up to \$4,000 annually. Scholarships are awarded for one year only, but applicants may apply for a re-award for each year they are enrolled in school.

#### Scholarship Eligibility

- 1. Applicants for these scholarships must be full-time undergraduate students in either a four-year college or a twoyear technical program or enrolled in a graduate program.
- 2. All applicants must be graduates of public or private high schools.

#### Scholarship Criteria

- 1. Applicants must have a demonstrated or expressed interest in the coloring of plastics industry.
- 2. Applicants must be majoring in or taking courses that would be beneficial to a career in the coloring of plastics industry.
- 3. An applicant must be in good academic standing with his or her school.
- 4. Preference is given to student members of SPE and also to students who have a parent(s) as a member of the Color & Appearance Division of the SPE.
- 5. Financial need of an applicant will be considered for most scholarships.

#### **Application Procedure**

To be considered for a scholarship from the Color & Appearance Division Endowment Scholarship Program, applicants must complete an application available on our website and return it to the address specified on the application by June 1, 2019 All submitted applications must include:

- 1. A completed application form.
- 2. Three recommendation letters: two from a teacher or school official and one from an employer or non-relative.
- 3. A high school and/or college transcript for the last two years.
- 4. An essay by the student (500 words or less) telling why the applicant is applying for the scholarship, the applicant's qualifications, and the applicant's educational and career goals in the coloring of plastics industry.

Please feel free to contact Ann Smeltzer by email or by phone at 412-298-4373 with any questions.

#### All scholarships will be paid directly to the recipients' schools.

*The Color & Appearance Division Endowment Scholarship Program will not award scholarships to applicants who are not qualified and reserves the right to not award a scholarship in a given year if it so chooses.* 

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#### **Best Paper:**

#### Relationship of Different Grades of Titanium Dioxide with the Decay of Polypropylene Gloss under Accelerated Exposure Conditions

Joseph Bidwell, Kevin Brinker, Sandra P. Davis, Peter Jernakoff, Philipp M. Niedenzu, Austin Reid, Maria de los Angeles Torres Salazar

The Chemours Company

#### ABSTRACT

Titanium dioxide is a common pigment used in plastic applications to provide opacity and protection of the polymer matrix against photo-oxidation The color attributes and photo-durable functions of pigmentary titanium dioxide are most relevant for plastic applications which experience exposure to wavelengths less than 700 nm and greater than 300 nm from solar or artificial light exposure, i.e., visible and ultraviolet wavelengths. Shorter wavelengths can induce the greatest damage to polymers, being of higher energy. TiO<sub>2</sub> efficiency to deliver the functions of color and photo-durability is related to the TiO<sub>2</sub> surface coating, concentration of TiO<sub>2</sub> and formulation design. This paper describes the relationship of these factors by monitoring the decay of polypropylene gloss based under accelerated exposure conditions.



#### Introduction

Titanium dioxide pigments are widely used in plastics primarily to provide opacity which may also be described by terms as hiding power, tint strength or scattering. A secondary attribute of titanium dioxide, especially the rutile crystalline phase, is the ability absorb UV wavelengths of light 1. The wavelengths of particular importance are those which pass through the atmosphere. The wavelengths which are acutely damaging to hydrocarbon based materials such as plastics are UVA (320 to 400 nm) and UVB (290-320 nm). Table One is a useful scale to calibrate the bond strength of hydrocarbons with the band gaps of various forms of titanium dioxide in three energy scales, kJ/mol, nm and eV. The UVA region is particularly damaging to carbon-carbon bonds and when this wavelength interacts, photo-degradation of the plastic matrix can occur.

Fortunately, wavelengths of 380 nm or smaller can be absorbed by rutile pigmentary TiO<sub>2</sub> particles and the absorbed energy is converted to either heat or chemical species which can oxidize polymer matrices. Hence, to preserve the polymer matrix, the desired effect is for TiO<sub>2</sub> particles to absorb damaging UV wavelengths and convert the energy into heat 2. The conversion of absorbed energy into "oxidizing agents" is undesirable.

TiO<sub>2</sub> owes its photochemical behavior to the crystalline structure. The combination of the titanium and oxygen atoms in pigmentary rutile results in a lattice with two characteristic bands wherein electrons reside. Between the two bands is a defined band gap. This band gap (*approximately 3.05 eV for rutile*) is the source of the absorption and photo-catalyst behavior of TiO<sub>2</sub>.

When TiO<sub>2</sub> is irradiated at wavelengths of less than 380 nanometers, the incident energy results in electron excitation from one band (*the "valence" band*), across the gap, and into another band (*the "conductance" band*). The energy absorbed by the TiO<sub>2</sub> lattice forces electrons across the band gap. The consequences of the electron transition from valence to conductance band are two-fold:

- 1) an electron is present in an "uncomfortable" higher energy state
- 2) a hole is created in the valence band

The electron and hole are in a metastable energy state, i.e., the electron will react with nearby species having an unpaired electron and the hole will likewise "steal" an electron from any nearby donor species.

Typically, the excited electron will jump back down to the valence band and fill the hole; hence, the electron and hole recombine. As the electron jumps back down to the valence band, it releases energy in the form of heat. Alternatively, the electrons and holes can lower their energy state by reacting with other molecular species present at the surface of the titanium dioxide particle. For example, the holes will react with water and/or surface hydroxyl groups to form hydroxyl radicals. The excited electron will react with an organic matrix, resulting in extensive oxidation and degradation of the organic matrix. The following sequence of reactions describes the process:

TiO<sub>2</sub> + UV light → electron + hole O<sub>2</sub>- + H<sub>2</sub>O → HO<sub>2</sub> + OH- electron + hole  $\rightarrow$  TiO<sub>2</sub> + heat Hole + OH- surface  $\rightarrow$  OH electron + O<sub>2</sub> surface  $\rightarrow$  O<sub>2</sub>-

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#### **BEST PAPER CONTINUED**

OH. + -(CH2-CH(CH3))n-  $\rightarrow$  degradation HOO. + -(CH2-CH(CH3))n-  $\rightarrow$  degradation

In most exterior applications, particularly those that are not purely white formulations, the photocatalytic role of TiO2 must be minimized. TiO2, acting as a photo-catalyst *(that is, holes and electrons escape from the surface of the TiO2 particles),* can participate in the chemical breakdown of the organic matrix. Several options are available to diminish the role TiO2 plays in the degradation of polypropylene.

Two strategies can be employed:

- 1) prevent the formation and migration of the hole and electron WITHIN the TiO2
- 2) prevent the hole and electron from ESCAPING the TiO2 surface

In theory, there are many ways of achieving either strategy:

- 1) alter the band gap so that the titanium dioxide crystal higher or lower
- 2) reduce the ability of the electron and hole to separate in the  ${\rm TiO_2}\ crystal$
- 3) insulate the TiO<sub>2</sub> to prevent escape of the electron and provide a barrier between the organic matrix and the TiO<sub>2</sub> surface

Alteration of the band gap may be looked upon in two different ways. The first possibility is to change the band gap in the TiO<sub>2</sub> so that the TiO<sub>2</sub> has to absorb a greater amount of energy to allow the electron to reach the conductance band. This type of alteration would require a redistribution of the atomic arrangement within the TiO<sub>2</sub>.

Such a re-arrangement would result in a different crystal structure. This type of rearrangement will be noted by inspection of the two most prevalent TiO<sub>2</sub> crystal structures: anatase and rutile. Rutile has a smaller band gap and as a result absorbs more of the UV wavelengths. From a practical standpoint, this role of TiO<sub>2</sub> must be preserved since the TiO<sub>2</sub> will always provide durability to pigmented systems by absorbing damaging UV light. Anatase has a higher energy band gap and only absorbs the smaller wavelengths of the UV portion in the electromagnetic spectrum. Since anatase does not absorb the longer UV wavelengths, the organic matrix is not protected and degrades more rapidly than in a rutile pigmented system. Therefore, the creation of a TiO<sub>2</sub> band gap that is larger would not be desirable if the TiO<sub>2</sub> is to provide the characteristics of opacity and durability.

Lowering the energy gap relative to the rutile systems is also possible by introducing dopants. The dopant can provide a lowerenergy state in which the electron can reside. For a lower energy state, the likelihood of recombination between the hole and electron is higher as compared to pure TiO<sub>2</sub>. The primary hindrance to incorporation of dopants in a rutile crystal is that the resulting energy level for the vast majority of these hybrid systems is near the visible region of the electromagnetic spectrum. As a result, the TiO<sub>2</sub> develops a visible coloration and is no longer useful as a white pigment. Dopants are defects that result in the formation of chromophores within the rutile crystal and will decrease the overall brightness and adversely affect the inherent color of the TiO<sub>2</sub>.

A second method is to reduce the tendency for the electron and hole from separating in the crystal. There are two methods to accomplishing this task: surface insulation or sometimes referred to as "site capping" and surface olation. Both techniques lower the electronic energy gradient within the TiO<sub>2</sub> crystal.

Site capping is the reaction of surface hydroxyl groups with other non-TiO<sub>2</sub> materials *(inorganic or organic)*. This reaction can be viewed as lowering the electronic energy gradient within the TiO<sub>2</sub> crystal. As a result, the mobility of the hole in the valence band is not as high and increases the probability of recombination with the electron from the conductance band.

A second method of achieving the same result is by removing the surface hydroxyl groups by heat treatment – "olation". The heat treatment removes the surface hydroxyl groups to form water and a Ti-O-Ti bond on the surface of the TiO<sub>2</sub> crystal.

The typical technique to encourage UV absorption and repress redox chemistry on the pigment surface is insulating the surface. The common technique is site capping with the use of colorless inorganic coatings. For example, one form of site capping is the reaction of surface hydroxyl groups with silica, alumina, and phosphate containing oxides or hydrous oxides. The insulating surface layer permits UV waves passage and transmittance of heat to the polymer matrix but denies interaction of the surface with atmospheric reagents such as elemental oxygen and water. The insulation technique may appear conceptually quite simple, but actual demonstration of encapsulation presents difficulties. One difficulty is the level of oxide needed for complete encapsulation. In theory, only 0.3 to 0.7% by weight of an amorphous material needs to be precipitated onto the surface of the TiO<sub>2</sub> particle for complete monolayer encapsulation. In reality, much more hydrous oxide is needed to achieve complete encapsulation. The cause of this is related to the statistics of precipitation.

#### **BEST PAPER CONTINUED**

Precipitation of solids from a solution onto a particle surface is much like trying to completely wet an area of sidewalk with rain droplets. At first, the rain falls onto the sidewalk and the raindrops strike a dry area on the sidewalk. However, after a certain percentage of the square is wetted with rain droplets, raindrops will start to fall onto areas that are already wet. The precipitation process used to coat pigmentary particles is no different. At first, the precipitation coats only the TiO<sub>2</sub> surface; but as the surface gets coated, the exposed TiO<sub>2</sub> surface area decreases. At some point, the precipitate will deposit upon itself rather than the TiO<sub>2</sub> surface and add no "insulating" characteristics to the coating. Approximately three monolayers are needed on the surface to cover approximately 95% of the TiO<sub>2</sub> surface.

The preamble of the techniques which encourage UV energy absorption by rutile titanium dioxide and prevent release of chemical energy from the particle surface was necessary to guide the experimental design. Based on the discussion concerning suppressing the formation of radicals from a TiO<sub>2</sub> surface, a review of three pigmentary rutile materials was conducted based on the surface treatment. Several types of titanium dioxide materials were reviewed (**Table Two**). The photo-oxidative impact of the surface modifications is registered as a gloss loss for injected molded polypropylene.

#### Experimental

All samples were prepared using a 50% by weight masterbatch in NA206 LDPE. Each pigment masterbatch was hand mixed, i.e., "let-down", with Profax 6331 PP material in plastic bag to produce a final product containing a prescribed % by weight pigment (0.5, 1.0, 2.0, 4.0, 8.0, 15). The resulting heterogeneous mixture, approximately 4 lbs., was placed in the injection molder hopper to produce approximately chips with the dimensions of 3 inch X 1¾ inch X 1/8 inch. The following molding parameters were used to produce samples on the Cincinnati Vista Toggle Injection Molder NO. Vista 85-1: PP injection molder conditions are described below for all samples:

		<u>Timer set-up in seconds</u>		
Location_	Set point in degrees F	Injection high	2.5	
Nozzle	400	Injection pack	4.0	
Zone #1	400	Injection hold	4.0	
Zone #2	400	Cooling	15.0	
Zone #3	400	Clamp open	0.5	
Feed throat monitor	104	Eject forward dwell	0	
Hydraulic oil	100	Hydraulic delay	0	
Setting on temperature controller	120			
с <u>г</u>		<u>Eject control in inches</u>		
Clamp set-up in inches		Forward stroke	1.75	
Open limit	12.00	Retract stroke	0.50	
Close blowdown	6.50	Start eject set point	11.00	
Mold touch	3.00	Retract override set point	11.00	
Open fast	6.50	Actual clamp position	0.00 - closed 12.54 - open	
Open slowdown	11.00	Actual ejector position	0.28	
Close velocity	14.00 in./sec.			
Breakaway velocity	4.00 in./sec.	Extruder control		
Open velocity	14.00 in./sec.	Initial back pressure	50 PSI	
Actual clamp position	12.54 – open 0.0– closed	Final back pressure	50 PSI	
		Initial extruder speed	50%	
Injection Settings in Pounds per squa	<u>re inch (PSI)</u>	Final extruder speed 50%		
Injection high pressure limit	450	Shot size	1.25 inch	
Injection pack pressure #1	450	Transfer position	0.25 inch	
Injection pack pressure #2	450	Decompression distance	0.25 inch	
Injection hold pressure #1				
, -	500			
Injection hold pressure #2	500 500			

All samples were exposed using Atlas Ci-65A Weather-OMeter Atlas Eprom program number 1 (*102 minutes of light only followed by 18 minutes of light and specimen spray. This 2 hour cycle was repeated until the test was complete. Chamber temperature was held constant at approx. 65 deg. C and dropped to approximately 40 deg. C during each spray cycle.*) All gloss measurements were collected using BYK-Gardner AG 4601 using the ASTM D2457 or ASTM D523 test method.

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#### **BEST PAPER CONTINUED**

#### **Results and Discussion**

To monitor the level of photo-oxidation performance of the chosen pigments, each pigment was compounded into the same polypropylene resin at various weight percentages (see Table Three). The evaluation monitored the decrease of gloss performance of the polypropylene article during exposure. The hypothesis is that as the pigment oxidizes the polypropylene matrix surface, the roughness of the surface increases and gloss decreases. Gloss is primarily determined by the smoothness of the initial first five microns. An assumption is made that oxygen and water can permeate the polymer surface and saturate the first five microns. Therefore, level of gloss decay would be related to the photo-oxidative performance from the pigment.

The typical gloss loss profile during an exposure can be segmented into three portions (see Figure One): - "incubation" time frame is where the gloss performance does not change during exposure time - "gloss decrease" time frame is where there is a linear relationship of gloss decrease with time - "gloss failure" time frame is where the surface is too rough to note any dramatic gloss changes with exposure time.

The major metric to distinguish the pigment photooxidation in the polypropylene gloss is the "t50" point in **Figure One.** The t50 represents the time frame required for the gloss level to drop to 50% of the initial value. The t50 is typically noted in the "gloss decrease" portion and will incorporate the initial incubation time frame and rapid gloss decrease. This metric permits the evaluation to be shortened and provides the ability to compare the various pigments with a single metric. Using the t50 metric, comparison of the three pigments material at different weight percentages can be done. **Table Four** contains the various t50 values for all three pigments at different weight percentages. **Figure Two** highlights the impact of pigment choice and weight percentage on the t50 performance. The first observation is to note the level of the natural polymer system, 0 weight % pigment. The natural polymer system demonstrates the longest t50 time frame. Two of the three pigments, Pigment A and C, decrease the t50 values as the weight percentage increases. Pigment B seems to have a little impact on the t50 performance, and implies its photo-activity performance is very low. The decrease in t50 as function of pigment concentration is most pronounced with Pigment A. The implication is that Pigment A has the highest level of photo-activity at the polymer surface. Pigment C photo-activity seems to be a compromise between pigments A and B based on the t50 performance.

The titration also provides an insight about the pigment surface technology. The efficacy of the insulating technique to coat the rutile particle becomes more apparent in the titration. Pigment A demonstrates an immediate decay of the t50 performance once the pigment is introduced to the polypropylene matrix even at 0.5% by weight. Assuming a pigment surface area of 10 m^2/g for Pigment A, 5 m^2/100 gram of sample is photo-active. This value should increase as the photo-activity decreases for a pigment when using the insulating technique. In other words, to get the same level of t50 decay as Pigment A, more area from a coated pigment is required. This hypothesis can be seen with Pigment C. Pigment C demonstrates the same t50 performance as Pigment A, but requires 1 weight %, i.e. more surface area of the pigment. The titration experiment also shows that there is a saturation. By adding more and more pigment, the t50 values start to reach an asymptote. After about 5 weight% pigment, the change of t50 values starts to plateau, which indicates a saturation point for the gloss deterioration.

A second experiment to highlight the photo-activity of uncoated pigment is to blend it with a coated one, i.e., blend Pigment A with C at a constant total weight percentage. **Figure Three** shows the t50 ratio values at a constant pigment 10 weight percentage but where the amount of Pigment C is decreases with increasing amounts of Pigment A. The t50 ratio is done to normalize the impact of Pigment A. A conclusion from the Pigment C titration was that Pigment C basically had very little photo-activity as indicated by gloss loss. Therefore, the t50 values of the blends can be divided by the t50 of the 10% by weight Pigment C sample set. This manipulation allows to monitor the impact of the Pigment A impurity as its level increases and Pigment C decreases. For example, the addition of 0.5% by weight of Pigment A results in a 20% decrease in t50 values (ratio is approximately 0.8).

The striking feature of the **Figure Three** is the additional data from the Pigment A titration. The Pigment A titration data are at various total amounts of Pigment A whereas the blend data are at constant weight percentage of 10; hence, it is not a direct comparison. Nonetheless, the photoactivity of the Pigment A in the blend is similar to the titration experiment. This observation indicates that the photo-active potency of Pigment A; a small amount of the pigment in the overall polymer matrix can cause t50 values to decrease such that the blend photo-activity is dominated by Pigment A.

continued on page 15

# QUALITY RESISTS.



**Colortherm**<sup>®</sup> pigments have been particularly developed for the coloring of plastics. All pigments are easily dispersed and rapidly reach their final tinting strength. Their excellent properties in terms of heat stability, migration resistance, lightfastness and weather stability make them suited for almost any type of plastic. Thus, LANXESS quality ensures long lasting color stability combined with the highest technical standards.



### QUALITY WORKS.



CAD NEWS<sup>®</sup>

#### **BEST PAPER CONTINUED**

#### Conclusions

The blend experiment indicates that at constant weight percentage of pigment, the overall photo-activity of the blend is determined by the amount of the most photo-active pigment. The titration experiments of the three chosen pigments indicate the following order of photo-activity in terms of t50 performance:

Pigment A> Pigment C> Pigment B

The explanation for the observed photo-activity is the different inorganic surface modifications amongst the three rutile based pigments. The experiments highlight the efficacy of the insulating technology in reducing the photoactivity of rutile pigments.

#### References

1. T. A. Egerton; Molecules, 19, 18192-18214 (2014)

2. Y. Tezuka, S. Shin, T. Lshii, T. Ejima, S. Suzuki, and S. Sato, J. Phys. Soc. Jpn. 63, 347 (1994); J. Pascual, J. Camassel, and H. Mathieu, Phys. Rev. B 18, 5606 (1978)

#### Table 1: Typical bond energies in a hydrocarbon polymer compared with band gap of titanium dioxide

	C-C	С-Н	C-0	C=O	O-H	N-H		
	bond	bond	bond	bond	bond	bond	rutile	anatase
kJ/mol	348	440	358	745	467	391	289	328
nm	347	274	337	162	258	308	391	368
eV	3.61	4.56	3.71	7.72	4.84	4.05	3	3.4

#### Table 2: Empirical description of rutile titanium dioxide particles used in this evaluation

Pigment	added Al2O3	added SiO2	organic type
А	none	none	hydrophobic
В	yes	yes	hydrophobic
С	yes	no	hydrophilic

#### Table 3: Polypropylene gloss data as a function of pigment type, pigment %wt. and hours exposure

		0	100	200	100	500	(00	700	000	000	1000	
pigment A	1	0	100	200	400	500	600	700	800	900	1000	hours
% wt.	0	85.4	85.1	83.0	70.6	68.4	59.9	50.0	43.5	38.1	34.9	
pigment	0.5	86.6	86.3	84.7	67.5	57.4	44.7	36.0	31.1	28.2	25.1	
	1	87.2	86.4	84.9	60.3	46.3	35.2	29.0	27.0	22.1	22.6	
	2	87.7	87.5	80.2	57.3	39.5	34.9	27.6	25.8	22.0	17.9	
	4	85.0	88.0	81.8	42.6	32.6	27.1	21.1	18.5	17.0	13.3	
	6	85.5	84.5	80.9	41.3	31.9	24.0	19.3	15.6	14.3	10.5	
	8	84.1	81.4	77.3	39.6	29.7	23.6	18.3	15.4	12.1	9.2	
	15	76.1	75.3	74.4	28.7	21.0	14.7	9.1	5.0	3.0	2.2	
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pigment E	3	0.0	100	200	400	500	600	700	800	900	1000	
% wt.	0	85.4	85.1	83.0	70.6	68.4	59.9	50.0	43.5	38.1	34.9	
pigment	0.5	86.6	86.2	85.6	78.5	72.0	65.8	56.5	45.1	38.2	33.9	
	1	86.1	87.1	87.2	77.1	69.2	62.2	52.2	43.1	36.4	30.6	
	2	87.6	87.1	83.1	71.2	69.2	60.8	51.7	41.2	34.7	30.1	
	4	86.2	86.9	84.0	76.7	68.1	58.6	49.4	42.7	36.0	31.2	
	6	86.4	86.4	85.4	72.7	63.9	54.5	47.4	40.5	35.1	29.6	
	8	86.8	86.0	84.9	74.7	65.6	56.5	48.8	43.0	36.4	32.4	
	15	83.8	87.5	83.1	74.8	66.5	57.8	50.8	47.6	40.6	35.9	

#### **BEST PAPER CONTINUED**

pigment C		0	100	200	400	500	600	700	800	900	1000
% wt.	0	85.4	85.1	83.0	70.6	68.4	59.9	50.0	43.5	38.1	34.9
pigment	0.5	86.9	86.8	82.7	75.2	69.8	60.6	49.2	40.1	36.9	32.6
	1	87.8	86.4	87.4	73.3	67.6	57.0	45.3	39.1	32.3	28.8
	2	89.1	86.3	86.3	72.4	66.4	51.1	40.0	35.8	28.6	23.8
	4	86.6	86.2	86.6	65.9	53.3	42.8	34.7	28.7	24.7	21.0
	6	86.4	86.2	85.7	62.8	52.7	41.8	34.0	26.7	22.3	18.2
	8	85.3	85.6	85.0	62.4	53.8	41.9	33.9	27.9	21.3	16.5
	15	85.0	83.3	83.8	67.8	57.3	47.0	38.9	33.2	24.8	17.0

Table 4: t50 values for different pigments at various weight percentages



Figure 1: Typical gloss loss profile during exposure at various weight percentages 4, 6, and 8%





Figure 2: t50 in hours of three pigments at various weight percentages





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# CAD NEWS®

#### About 2018 CAD NEWS<sup>®</sup> Sponsorships Deadline for the 2018 newsletter period is

the end of December 2018.

Mark Tyler, the CAD Newsletter Editor, publishes at least (3) issues of the CAD Newsletter per calendar year. This publication is e-mailed to approximately 700 Plastic Color Industry professionals and is also posted on our website at http://www.specad. org/ and the Parent SPE website on the Divisional pages.

In addition, the newsletter is posted on the Society of Plastics Engineers website technical area. Three (3) issues appear in electronic form annually and each sponsor placement is automatically linked directly to your website when the viewer clicks on your ad, provided you supply us with your website address. Participating in a sponsorship in the CADNEWS<sup>\*</sup> is a great way to connect with plastic coloring industry professionals by promoting your company and the services you offer.

If interested in learning more, please contact: Mark Tyler 570-952-5255, tylerm@silberline.com

EXAMPLE TO A WARD WINNING NEW SLEETTER Deadline for placing your company's sponsorship for the 2019/2020 Year:

December 31, 2018

OPTIONS	HEIGHT X WIDTH
1–unit	2 x 3.5
2-unit	4 x 5
3-unit	6 x 3.5
4–unit	4 x 7.5
1/2-page	5 x 7.5
Full page	8.5 x 11

#### **Invitation to Attend Our Board Meetings**

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

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<sup>®</sup>.

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.





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