

Color and
Appearance
Division



CAD NEWS

PUBLISHED BY THE COLOR AND APPEARANCE DIVISION OF THE SOCIETY OF PLASTICS ENGINEERS

CHAIRMAN'S MESSAGE

Growing up on a farm in Eastern Canada, near the capital city of Ottawa, we grew corn...lots and lots of corn... in huge 200 acre fields. I remember being out in the middle of one of those fields on a hot, windless August day. The only noise that I could hear apart from a few crows flying overhead was the dull rustle of the corn growing. That's right, you could actually hear the corn growing. You certainly could not see the corn grow and normally you could not hear it grow over the day to day noise of tractors cars, animals and other typical farm and country sounds. However, by the fall, there was no question that the small yellow corn seed had grown into a huge 6' tall corn plant with two or three gigantic ears of corn.

In a way, our economy is the same as the corn fields of my youth. Right now it is pretty quiet but if you listen carefully...very carefully, you can hear it...the '*green shoots*' as Federal Reserve Chairman Ben Bernanke calls them, of the global economy starting to grow. There is no question the noise of cost cutting, inventory cutbacks, plant closing, job losses and mortgage foreclosures is pretty loud and it is doing a doing a good job, of blocking out much of the sound of growth but it is certainly there.

Just like the growing season, recessions come and go in cycles. Given that this recession is/was the worst since 30's with and it was exacerbated by a significant amount of financial chicanery, the analogy to corn farming is a bit stretched. It's as if the farmer set off a couple truckloads of dynamite in the middle of the cornfield and then takes three years to grow corn again. The signs of growth though, are solid.

After shrinking at an annualized rate of approx. 4% from October 2008 to March 2009, the International Monetary Fund predicts the economy will grow at a rate of 2.5% in 2010. Macroeconomic Advisers says that the US economy is already growing at a rate of 2.5%. The stock

market has rallied over 50% since March. Seven of the ten indicators in the Conference Board Leading Economic Index pointed upward in June. General Motors and Chrysler have made it through bankruptcy (*and the world did not end*). In the micro sense, there are companies in the plastics industry that have become stronger by buying weaker competitors, that are increasing production and that are hiring.

At the 'end of the day', the recession will come to an end and the countries, economies, industries, companies and people that have taken the opportunity to adapt and improve themselves will survive and grow stronger for the next cycle of the economy.

The Color and Appearance Divisions mission is to '*educate, train, inform and provide networking opportunities*' to those involved in '*Coloring the World of Plastics*'. Our Color RETEC® this year in Savannah will work towards that mission and will help you to grow with those '*green shoots*'. You just have to listen for them.

Howard Kennedy
CAD Chairperson

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EDITOR'S NOTE

Since this is the CAD Newsletter preceding RETEC®, it was produced in both electronic and printed form. The rest of the Newsletters for the year will be in an electronic form only. Spring is a time of changeover for the CAD. Howard Kennedy has replaced Tracy Philips as Chairman. Tracy did a fantastic job of moving the CAD forward, I am confident that Howard will continue the excellent leadership the division has enjoyed. See the back page for the new officers and Board members.



I have included a short article from the latest PMAD Newsletter about Elliot Weinberg who passed away after many years in the industry. Many of you will remember Elliot from his participation in CAD RETEC®s.

In addition to a technical article from Bruce Mulholland, which was awarded Best Paper at the 2007 ANTEC™, I have included an interesting historical article by Robert Baptista. It investigates the effect that prohibition had on the colorant industry in the 1929's. Robert has an interesting website that contains many such articles about the history of the colorant industry. He has had contributions from several members of our group. The link to his site is: <http://www.colorantshistory.org>

Hope to see you at this year's RETEC® in beautiful Savannah, GA in October, it promises to be fun and informative. See the further information in the newsletter.



Jamie Przybylski

Editor

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In general, you must be a registered user on these websites to join the SPECAD Group hosted there. These websites are not affiliated with SPE. To find the SPECAD group, go to the Groups directory and search for "SPE Color and Appearance Division". Or, go to www.specad.org home page for a link to the groups on each website.

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ANTEC™ 2009 WRAPUP. By Roger Reinicker and Tracy Phillips

ANTEC™ 2009 was held in June in Chicago in conjunction with the 2009 edition of the NPE at the McCormick Center. Thank yous to all the authors/presenters for CAD and to moderators Jim O'Dwyer and Betty Puckerin for making the program a success. CAD was able to offer a full program of two keynotes and ten technical papers to fulfill our obligations as a division to the SPE.

Not everything always goes according to plans: I want to offer my special appreciation to Doreen Becker of BASF who filled in for a missing keynote speaker at the very last minute to open up our morning session and give her "Trendance Trends" talk about current and upcoming color stylings. Also to Steve Goldstein who authored and presented not just one but two papers: one on measuring heat buildup in plastics due to IR absorption and one on NIR absorbers.

"Green" themes were prevalent during the overall ANTEC™ sessions. Included in these were biopolymers, which generated extensive interest as *Plastics Engineering* magazine has recently noted (*July/August issue*). In our own sessions, Phil Niedenzu was right on theme with the paper "Evaluation of Titanium Dioxide in a Renewably Resourced Polymer." Tad Finnegan's paper discussing strategies for replacing lead and chrome - based pigments also echoed environmental concern over the use of heavy metal based coloration.

In the area of innovative mixing, both Tatanya Samoylova's paper on extensional mixing and Dave Zumbrunnen's talk on smart blenders to make realistic wood grains challenged our usual conceptions of shear and mixing in extruders.

Rounding out the presentations were Lisa Swain's introduction of a new modified form of titanium dioxide, John Hollendonner on titanium dioxide extension (*a topic surely to*

be re-visited next year), and Dieter Gruber's paper on a new technique for measuring distinctness of image of high gloss surfaces.



Pictured are moderator Betty Puckerin and Linda Carroll of Ampacet who gave the second keynote of the day on color trends.

ANTEC™ 2010 will take place on May 16-20, at Orlando World Center Marriott Resort & Convention Center in Orlando, Florida. Jim O'Dwyer (*Croda Inc.*) and Sharyl Reid (*A. Schulman Inc.*) are Technical Program Chairs for CAD. The abstract submission website has opened for submissions, and the link to the site is: ANTEC™ 2010 Submission Site.

Roger Reinicker and Tracy Phillips
Technical Program Chairs
ANTEC™ 2009



INVITATION TO ATTEND OUR CAD BOARD MEETINGS

The Color and Appearance Division regularly holds Technical Program Committee (TPC) and Board of Director (BOD) meetings at the ANTEC™ and the RETEC®. In addition, a Summer BOD and TPC meeting are typically held about 6-weeks prior to the RETEC®, and a Winter BOD and TPC meeting are held in early January. The Summer meeting is scheduled in various locations; the Winter meeting is typically held at the site of the RETEC® that is a year and a half away.

Any SPE/CAD members who wish to attend are welcome at these meetings. Contact the Division Chairman (*see the back cover*) for information on the location and times of any of these meetings.

May 16-20

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Engineers, scientists, professors and business professionals attend ANTEC™ to share ideas, to learn about the latest advances in technology and to network amongst their peers. ANTEC™ 2010 will take place May 16-20 in Orlando, Florida and we expect excellent attendance and hope you will join us in this experience.

The Color and Appearance Division (CAD) of the Society of Plastics Engineers (SPE) will be hosting our annual technical session during this conference and would like to encourage you and your company to participate by presenting a paper. We would consider any paper related to the color and/or appearance of plastic and the following categories would be typical topics:

Color Trends
Decorative or Special Effects
Color Measurement
Color Matching Techniques
Materials (*Colorants, Additives, Plastics*)

Instrumentation/Test Methods/Quality Control
Property Retention/Durability
Regulatory Issues
Processing and Equipment
Other Color/Appearance Related Topics

For more detailed information or guidelines for writing the paper please visit our website www.specad.org and it will be listed under conferences or you can contact Sharyl Reid at (864) 915-7253.

The entire submission and review process is conducted online. To submit an abstract or paper by the deadlines, please do so via the following website: www.anteccad.org. Please remember to specify "Color and Appearance Division" (D21) when submitting your abstract.

Sharyl Reid
ANTEC™ 2010 CAD Technical Program Chair
A. Schulman, Inc. (864) 915-7253
sharyl_reid@us.aschulman.com

CALL FOR PAPERS

Abstract Deadline:

September 4, 2009-5:00pm E.S.T.

Paper Deadline:

November 13, 2009-5:00pm E.S.T.

Final Paper Revision Deadline:

January 8, 2010-5:00pm E.S.T.

The Annual Technical Conference (ANTEC™) of the Society of Plastics Engineers is the largest gathering of individuals representing industry, academia and government in the fields of plastics and synthetic polymers. Engineers, scientists, professors and business professionals attend ANTEC™ to share ideas, to learn about the latest advances in technology and to network amongst their peers. ANTEC™ 2010 will take place May 16-20 in Orlando, Florida and we expect excellent attendance and hope you will join us in this experience.



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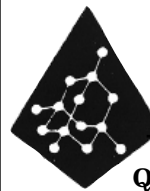
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PLASTICS HALL OF FAME TAPS NEW MEMBER



The Plastics Academy has announced nine new members will be inducted into the Plastics Hall of Fame at NPE 2009 in Chicago. The "Class of 2009" covers a global spectrum of leaders in the fields of equipment, packaging, polymer science, processing and compounding. Included is Robert D. Swain who founded color master batch manufacturer, Chroma Corporation, in 1967.

Swain, a chemical engineer, worked at Union Carbide's Bakelite Division in 1951 and was later assigned to Mellon Institute when the phenolic and vinyl business were merged. Later, he joined Exxon as they entered into the polypropylene business. His innovations included the first commercial use of polypropylene in steering wheels by Ford Motor Company.

He developed the first talc filled polypropylene coil bobbins used by Essex Wire and the first high performance polypropylene agitator used commercially by Maytag for over 25 years. Swain was recognized for his innovation in the formulation of more highly concentrated master batches in the late sixties and early seventies.

In the mid-seventies Chroma was the first color compounder to offer custom formulated GMP colorants. Widespread acceptance of these concentrates helped Chroma to develop a niche market for pharmaceutical master batches.

In the mid-eighties a disastrous fire totally destroyed Chroma's production facility yet they shipped product four days later from a competitor's plant. They operated out of this plant for four months thanks to the kindness of the Bill Bradbury family. *(Bill Bradbury Sr., founder of the PMS color business and a true pioneer in the world of plastics colors, was inducted into the Plastics Hall of Fame posthumously in the late eighties.)*

Bob's role as an educator spawned in the late eighties with Chroma's introduction of seminars on the In-Plant Color Control. He partnered in this endeavor with Ralph Stanziola. They were so well received that in the nineties he constructed a classroom/library dedicating it as the RALPH STANZIOLA LEARNING CENTER where over 500 people learned about the fundamentals of color technology.

During the nineties the emergence of the "HEAVY METAL JUNK SCIENCE" was noted with the introduction of the CONEG bill. Continuing his role as an educator, Swain became a spokesman against this junk science. He wrote several articles for the Society of Plastics Engineers (SPE) Color and Appearance Division RETEC®S and delivered technical presentations throughout North America, Europe, Australia, and New Zealand.

Swain has been a member of SPE since 1962. He had an active role in the Color and Appearance Division serving on the Technical Program Committee, RETEC Chairman, Board of Directors, and as a volunteer for SPE's Speaker Bureau. Chroma has been a member of the Society of the Plastics Industry (SPI) serving on their Food, Drug, and Cosmetic Packaging Materials Committee for 40 years. Chroma was a charter member in the founding of SPI's Rigid Packaging Container Division under the leadership of Dick Landis of Landis Plastics.

With the help of Pat Toner, Bob formed a new SPI Division, the Color & Additive Compounders Division, and served as its initial chairman. He served six years on the SPI Board of Directors. When he stepped down as chairman the division had grown to 120 company members.

Today, Bob resides in East China, Michigan with his wife Judy. They have six children and eleven grandchildren. He is actively involved as Chairman of the Board of Chroma Corporation, Technical Director for its Rotational Molding Division, a member of the Detroit Colour Council, and a member of both the Rotomolding and the Color and Appearance Division of SPE.

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PROHIBITION BREWED DYES AND DRUGS

By ROBERT J. BAPTISTA, JULY 29, 2009

The late 1800s was the golden age for American breweries with close to 4,000 breweries in operation across the country. Temperance groups, however, alarmed by the social unrest from the influx of alcohol-imbibing immigrants from eastern and southern Europe, pressed for a ban on alcohol, hoping to return social order to their communities. The onset of World War I further fueled anti-German, and thus anti-brewing, sentiment. Groups such as the National Prohibition Party, the Woman's Christian Temperance Union, and the Anti-Saloon League succeeded in pressing for legislation banning the manufacture, transportation, and sale of alcohol.

The United States Senate proposed the 18th Amendment on December 18, 1917. After approval by 36 states, the Amendment was ratified in 1919 and became law on January 16, 1920. Many breweries had closed earlier-by 1918 there were only 1,000 breweries left and by the time Prohibition took effect, there were half that number. Hard liquor distilleries also shutdown.

The remaining breweries survived by making non-alcoholic near beer, soft drinks, ice cream, candy or yeast. Some surviving breweries had diversified their holdings and investments prior to Prohibition and had a cushion of cash. Anheuser Busch used the refrigerated trucks they had invented for transporting beer to ship the ice cream they now manufactured. Pabst made malt syrup, which was widely purchased in grocery stores to make home brew.

But other opportunities arose for some innovative beverage makers. The British blockade of German shipping in World War I prevented the importation of dyes and created a dye famine. Dye prices soared and U.S. manufacturers, including small entrepreneurial firms and large corporations like DuPont, rushed to setup dye-making facilities to capitalize on the emerging opportunity. Alcoholic beverage makers could enter the dyes manufacturing field themselves or sell their closed facility to investors seeking to enter the dye or even pharmaceutical business with a plant requiring relatively few modifications.

Breweries and distilleries had a significant technology advantage since they were basically chemical plants with process equipment and infrastructure readily adaptable to synthetic organic chemicals. They typically had a good supply of clean water, storage tanks, fermentation tanks, stills, filter presses,



Fig. 1 Typical Multi-Story Brewery Designed for Gravity Flow

pumps, steam boilers, cooling capacity, warehouses, laboratories and chemists. The multi-story arrangement of the brewery process, enabling gravity feed of one step to the next, was similar to the layout developed by the German dye makers (Fig. 1, 2).

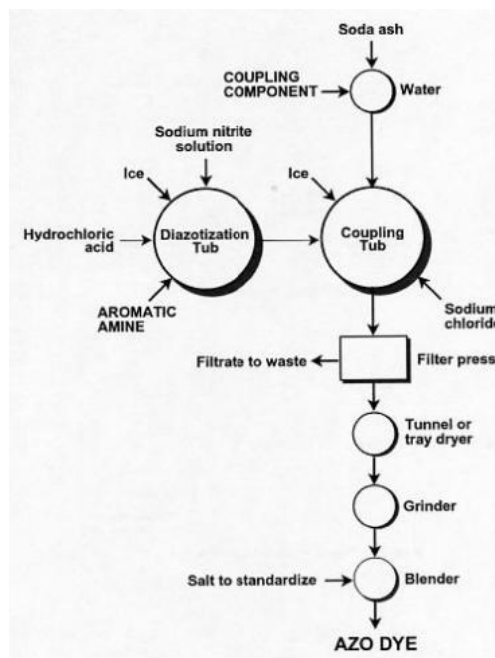


Fig. 2 Typical Process Schematic for Azo Dyes. Image: Travis, *Dyes Made in America 1915-1980*, 2004

The classical azo dye process began with raw materials at the top of the building, where the diazo step was made in a small

continued on page 10

PROHIBITION BREWED DYES AND DRUGS (CONTINUED)

continued from page 9

tank, and moved downwards by gravity to the coupling step in a larger tank where the dye was formed, and finally to a filter press, for isolating the wet dye cake, both located on the ground floor.

One of the modifications necessary to switch from beer making to dye manufacture would be the addition of a cover and an agitator, driven by an overhead belt at the time, to convert the cypress wood lager tanks to dye coupling tanks (Fig. 3).

Other necessary changes would be the installation of shelf dryers, grinders and blenders to produce the finished dyes. This equipment could be placed in the idle warehouse of the former brewery.



Fig. 3 Wood Lager Tanks Were Modified for Dye Manufacture.

Image: Library of Congress

One of the first breweries to convert to dye manufacturing in World War I was the Lion Brewery located at 140-156 West 108th Street in New York City. The new company was called the Noil Color & Chemical Works. The Noil name was derived by spelling Lion backwards. The brewing operation continued but was now restricted to near beer.

The company was led by Franklin P. Summers, a chemist who directed production and the research staff of four chemists. An impressive line of direct, developed, acid, and chrome colors was produced for cotton, wool and silk fabrics. The dyes were said to equal in quality and fastness properties the pre-war dyes imported from Germany. A Noil dye swatch ad is shown in Fig. 4.

Another New York brewery that converted to dye manufacture was the F. & M. Schaefer Brewing Company, which had built a brewery in Brooklyn at South 9th Street and Kent Avenue in 1915-1916 (Fig. 5). With Prohibition looming, Rudolph J. and F. M. E. Schaefer prepared for the change by organizing the Kent Color Corporation in 1918 with \$25,000 capital. When Prohibition



Fig. 4 Noil Dye Swatches.

Image: American Dyestuff Reporter, 1925

was enacted in 1920, the brewery switched to making dyes and near beer in order to survive. Methyl violet base and toner were among the dyes produced. Ice was made for use in the diazotization step of dye making and for sale.

Nuyens & Co., a Bordeaux based maker of vermouths, brandies, cordials, and other liqueurs, had a beverage business in the U.S. which had to

be abandoned due to Prohibition. One of these investments was a distillery established in 1914 on West 52nd Street in Bayonne, New Jersey. In 1919 Albert J. Farmer, a New York financier of Nuyens, met with Dr. Eugene A. Markush, who had formed the Pharma Chemical Company in Bayonne in 1917, to discuss the sale of the distillery. Markush at the time was operating a small pharmaceuticals plant near 45th Street and was eager to expand. With financial help from Farmer and other Nuyens investors, Pharma Chemical took over the distillery and its equipment (Fig. 6).



Fig. 5 Schaefer Brewery in Brooklyn Made Dyes During Prohibition Era.

Photo: Library of Congress, 1948

The first products made were creosote and guaiacol carbonates, expectorants with some antiseptic properties. The pharmaceutical line included salophen and phenacitin, which had

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PROHIBITION BREWED DYES AND DRUGS (CONTINUED)



Fig. 6 Pharma Chemical Dye Plant in Bayonne, NJ, a Former Distillery; ca. 1920s

analgesic and fever-reducing properties, in addition to the sleeping aids sulfonal and trional. But postwar imports of pharmaceuticals from Germany and Switzerland, along with the startup of larger drug makers in the U.S., convinced Pharma Chemical to switch to dye manufacturing in the early 1920s (Fig. 7).

While some breweries converted to dye manufacture, traditionally established dye manufacturing plants attracted illegal distillery operations. At the defunct Central Dyestuff & Chemical Company in Newark, Federal agents raided an alcohol still operating in 1930. There were six wooden vats of 20,000 gallons capacity each. Five vats contained a corn syrup mash and the sixth vat contained yeast. Four 5,000 gallon stills, with thermostatic temperature regulation, were capable of producing 20,000 gallons of high proof alcohol daily. The still operator was arrested.

An even larger illegal distillery was raided by Federal agents at the Heller & Merz dye plant in Newark in 1931. The unit was valued at \$500,000 of which \$240,000 represented equipment and supplies. It had been operating for seven months, producing 12,000 gallons of alcohol, valued at \$35,000, daily. The distillery had been receiving carloads of molasses from Puerto Rico, delivered to the rail siding adjoining the plant. A pipeline was used to pump the high grade alcohol into railroad tank cars. No arrests were made since an accomplice sounded the plant siren as soon as the Federal agents walked through the main gate, giving the moonshiners time to escape.

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- 4) "American-Made Colors", American Dyestuff Reporter, Vol. 11, No. 11, November 20, 1922, pp. 373-374
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Despite the Prohibition ban on alcohol, people who wanted to drink could get bootleg liquor or visit "speakeasy" taverns run by the Mob. The growth of organized crime and the loss of tax revenue convinced the government to repeal Prohibition in 1933. The Noil Chemical and Color Works business was acquired by the Calco Chemical division of American Cyanamid on December 1, 1932. The specialized



Fig. 7 Dye Coupling Tanks of Pharma Chemical ca. 1930. The Autoclave in Upper Left Was Part of the Original Distillery in 1914.

Noil line of dyes was a good fit with the Calco line. Dye production was transferred to the large Calco plant in Bound Brook, New Jersey. Arthur L. Benkert and several other former Noil managers formed the Young Aniline Company to make dyes in Baltimore. The Lion Brewery resumed beer making and operated until 1942. The brewery was demolished in 1944. American Cyanamid quit the dye business in 1980. In 1933 the Kent Color business was also sold to the Calco Chemical and Schaefer returned to brewing beer in its Brooklyn facility. This brewery, one of the last in New York City, closed in 1976. Pharma Chemical became a successful dye producer and merged with intermediates manufacturer Verona Chemical of Newark in 1957. In the same year the merged company was acquired by Bayer. Later the name Verona Dyestuffs Corporation was adopted. This company eventually became part of DyStar, a joint venture of Bayer and Hoechst that is now privately owned. DyStar makes textile dyes today in the former Bayer facility in Goose Creek, South Carolina. Specialty dyes once made by Verona are now produced by Lanxess and Kemira Chemical, both companies operating at the Goose Creek site.

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TRIBUTE TO ELLIOT WEINBERG

Reprinted from the PMAD newsletter dedicated to the memory of Elliott Weinberg, who has made his present felt at many CAD RETEC®S:



Elliott Weinberg, scientist, raconteur, inventor, editor, Fellow of the SPE, a Founding Member of PMAD, and one of the good men given by God to every generation passed away on May 6, 2009

For the technical paper featured in this issue, I have included the first page of US 2,648,650, filed by Elliott and Ernest Johnson of M&T in 1951. (*Ed. Note: not included*). It discloses the preparation of organotin mercaptide heat stabilizers and

their use in vinyl, a development on which the huge North American rigid PVC industry is based. I urge you to read the entire patent, nine pages, downloaded from uspto.gov. It is well worth the \$3.00 charge as an example of how to carry out and document research in the field of plastics additives. Elliott was originally an inorganic chemist whose early work related to isotope separation for the Manhattan Project. This background led to generalization of the action of heat stabilizers underlying his development of tin, and later, antimony mercaptides.

Elliott added to this the ability to formulate the right questions. "Doubt", said Richard Feynman, "is the essence of knowledge." Elliott had the depth and breadth of knowledge to formulate the questions raised by doubt into paths leading to solutions. Underlying this was the curiosity into every possible field that characterizes the great scientist as well as the great artist. No subject was not of interest to Elliott. This is the identifying mark of Homo sapiens, the man who thinks.

In recent years Elliott was active in refuting the pseudoscience that attacks all chlorine-containing compounds with pretended ignorance that life on Earth would not exist without this vital element. To Elliott this was a moral matter; truth is good, falsehoods, evil. I cannot help but feel that this is also a distinguishing mark of Homo sapiens.

In brief remarks at the Palisades/ PMAD Golf Outing, I said that Elliott is, not was, my friend because he will remain with me always. I know I am one of a great many who feel that way. A final characteristic of thinking man is that the great and good men and women never pass away but will be here in their moral convictions and in their perpetual curiosity for all of the generations.

Dick Grossman

EFFECT OF ADDITIVES ON THE COLOR & APPEARANCE OF PLASTICS

Bruce M. Mulholland, Ticona

INTRODUCTION

To many people, color is at best a necessary evil. The coloring process amounts to adding a contaminant (*the colorant*) to a perfectly good polymer system to achieve a color while reducing all other properties! This perception can be transformed into reality when color is an afterthought in the whole product development cycle. That cycle typically progresses as follows:

- 1) the customer has a problem
- 2) a new resin formulation is developed to solve it
- 3) the new resin (*in natural, uncolored form*) is molded and tested
- 4) the new resin indeed solves the problem
- 5) the customer now reports they need the resin in dark green
- 6) the color group formulates the dark green using three times the normal pigment loading
- 7) the new resin in dark green is molded and tested by the customer
- 8) the new resin in dark green no longer solves the problem due to strength and warpage issues
- 9) back to step 1!

Of course, all of this can be avoided if the color and appearance of the resin are engineered along with other desired thermal and mechanical properties. That way, when the desired engineering properties are met, so is the color (*at least the closest achievable color anyway*). Because one must also be aware that including the colorability of the resin early in the development process is no guarantee that all desired colors can be achieved. What this work will accomplish is to help define problems and limitations in achieving colors up front. And if there are limitations, this information can then be used with the customer to help select colors that are achievable without detrimental side effects.

None of this of course is new information. But it can be forgotten. The purpose of this paper is to present information that unequivocally shows that color should not be an afterthought in the development cycle. Discussion will be focused on describing adverse effects on colorability attributed to the base polymer itself, other blended polymers, modifiers, additives and stabilizers.

[Note: since this paper is written by a colorist, information will be presented in the spirit of the pure colorant being adulterated by the polymer system and all of its additives!]

VISUAL COLOR PERCEPTION PROCESS

Before we can discuss color concerns in polymers and blends, it is important that the reader has an understanding of the visual color perception process. In order to see color, three things must exist: a light source, an object and an observer. For purposes of this paper, describing the light

source and observer are not included other than to say we assume the light source contains all wavelengths (*i.e., white light*). The object in our case is an article molded from our colored resin. A beam of light reaches the surface of our object. A portion of the light is reflected due to the surface interface and is called the specular reflection or gloss component. The remainder of the light penetrates the surface of the object where it is modified through selective absorption, reflection, and scattering by the colorants, polymers and additives. Selective absorption and reflection by wavelength create color. For example, if an object absorbs all wavelengths of light other than blue, blue light will be reflected or transmitted and the object will appear blue.

Scattering occurs when the light beam contacts particles or regions within the polymer system that have an index of refractive which is different from that of the base polymer. The change in refractive index that the light beam encounters causes the light to be redirected and, if the index of refraction is increasing, to slow down. The index of refraction is a physical property of the substance. It is determined by the equation:

$$\frac{\sin \theta_1}{\sin \theta_2} = \eta$$

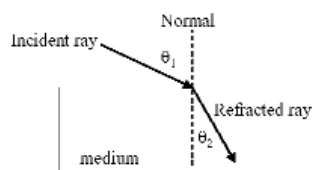
where 1 and 2 are the angles formed by the incident ray and the refracted ray versus the normal as shown in **Figure 1**.

The index of refraction for a substance depends on the wavelength of incident light. This relationship is most often observed by refracting light with a prism. In a prism, the blue wavelengths of light are refracted more than the red region of the spectrum because of this function. The result is the obvious separation of wavelengths and our ability to see the individual colors of the spectrum. For anisotropic crystals, the index of refraction also depends on the crystal axis on which the light is incident. For these materials, the index of refraction as a number is typically reported as an average value of the various axes.

If scattering occurs nearly equally at all wavelengths with no absorption, the object will look white. That is how titanium dioxide appears to impart its white

Continued on page 15

Figure 1
Refractive Index Diagram

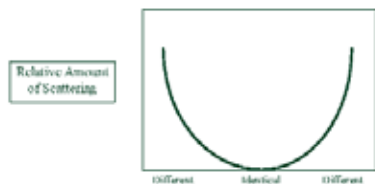


color to objects – by scattering virtually all of the incident light. In mixtures of titanium dioxide and dark pigments such as carbon black, the index of refraction as a function of wavelength becomes apparent. Because the index of refraction for the titanium dioxide is higher for shorter wavelengths of light (*blue light*), the net result is that more blue light will be reflected than red light in these dark colors. Blue wavelengths of light see greater light scatter from the titanium dioxide and do not penetrate as deeply into the medium as longer wavelengths do (*red light*). The resulting shorter path length for the blue portion of the incident light cause less absorption by the carbon black so that more blue light emerges and is reflected towards the observer compared to the red light. This scattering causes the blue flop which is observed when titanium dioxide is present in black color formulations.

This discussion was included here because this phenomenon can also hold true for any additive which has an index of refraction significantly different from the base polymer. In the case of the titanium dioxide example, if the blue flop was problematic in color matching, one can most likely reduce or remove the pigment from the formulation minimizing this problem. In the case where this blue flop is caused by the additive system, the effect can only be minimized by increased pigment loading. This phenomenon is also a characteristic of the base polymer as well. Most crystalline polymers will exhibit more bluish flop compared to amorphous or semi-crystalline resins due to this dependence of index of refraction on the wavelength of incident light. The amount of scattering as you might expect depends on the magnitude of difference in refractive index between the polymer and the scattering substance. The direction of difference does not matter, only the magnitude as depicted in **Figure 2**. Finally, there is an optimum particle size for scattering to occur that is dependent on the index of refraction of the substance and

the medium, and the wavelength of light. This optimum particle size is generally in the range of $\frac{1}{2}$ the wavelength of the incident light. Smaller or larger particle sizes will scatter less light as shown in **Figure 3**.

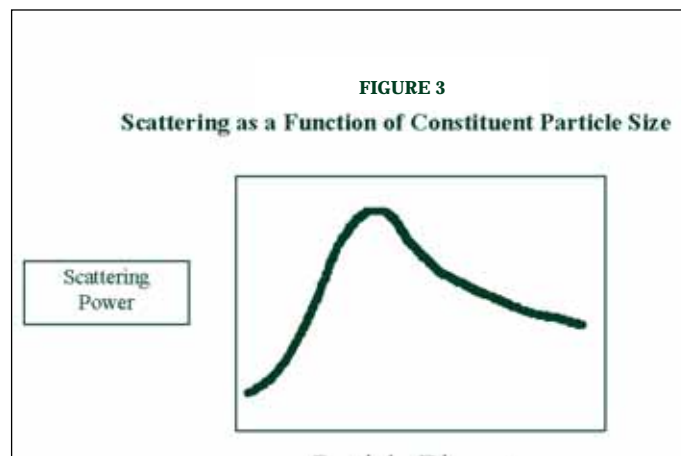
Figure 2
Scattering as a Function of Refractive Index Difference



particle sizes will scatter less light as shown in **Figure 3**.

It is important to understand the mechanism of scattering because the majority of the problems in coloring polymers and blends can be related to the intrinsic whiteness or scattering of the polymer system itself. Increasing the amount of scattering in our resin system will increase the amount of diffuse reflection (*white light*) which is mixed with the reflected colored light generated by our pigment interactions. This

mixing will dilute the color strength and the color of our object will appear lighter and less bright to the observer. An analogy can be percolated from everyday life: coffee. Coffee without cream is said to be black (*actually more like dark brown*) due to light absorption by the coffee extract dispersed in water. Adding cream to the coffee increases the light scattering and the color is transformed from dark brown to light tan. And it is obvious that once the cream is added, it is impossible to color the mix with more coffee extract to achieve the original black color. So is the case in polymers



containing additive systems. As will be shown, some additive systems can impart so much light scattering to the base resin that certain colors can no longer be achieved. Or if they can be achieved, other properties may be adversely affected such as impact strength and cost. In either case, the practical color gamut or palette that is obtainable with this particular resin system is reduced. The discussion below presents the effects that the polymer and its additives can have on colorability.

POLYMER TYPES

Transparent Resins

From the discussion above, it should be intuitive that transparent resins such as polystyrene or polycarbonate do not scatter light and therefore can achieve the most brilliant colors. Colors are generated through transmitted or reflected light without having to mix with white light from diffuse reflection since none exists from the polymer. The difficulty here is making the system opaque (*no light transmission*). If opacity is required, a scattering opacifier such as titanium dioxide is needed and apparent color strength will be reduced.

Translucent & Opaque Resins

Most polymers fall in the class of translucent resins. These include acetal, polyamide, polybutyleneterephthalate (PBT), polyethylene and polypropylene as examples. There are very few neat polymers that are truly opaque (*this depends on thickness as well*). Liquid crystal polymer (LCP) is an example of a typically opaque polymer. It is theorized that these semi-crystalline and crystalline resins will

Continued on page 16

scatter some portion of incident light due to spherulitic crystal structure and the amorphous-crystalline region interfaces themselves. The degree of translucency can be measured by calculating a contrast ratio. This number is the ratio of the L-value in color measurement obtained when backing the natural sample with a black tile divided by the L-value of the sample backed with a white tile. A completely opaque sample will have a contrast ratio of 1.00. Contrast ratio measurements are specific to the thickness of the sample and the intensity of the light source.

Table 1
Contrast Ratios of Selected Resins

Resin	L-value†	L-value	Contrast Ratio @ 3.2mm
	White	Black	
Nylon 6,6	85.65	66.75	0.78
Acetal	93.01	82.05	0.88
PBT	92.70	87.14	0.94
PBT (annealed)	92.80	90.94	0.98
LCP	84.10	84.10	1.00

† Specular excluded, expressed in HunterLab units

resins, the contrast ratio generally increases with increased degree of crystallinity. Nylon 6,6 has the lowest contrast ratio (*less opaque*) compared to liquid crystal polymer that has an extremely high crystallinity and is completely opaque. Furthermore, the two PBT samples show that the annealed sample (*higher crystallinity*) is also more opaque. The higher opacity indicates that more light scattering is occurring by the polymer and typically a more restricted color gamut will be achieved. Polymers with a high degree of intrinsic whiteness will exclude deep, dark colors and bright, high chroma colors from the achievable color gamut.

To illustrate this effect on colors, three single pigment colors (*blue, red and yellow*) were developed in three different resin systems. Blue and yellow were produced in acetal (POM), polyphenylene sulfide (PPS) and LCP. The red color was prepared in nylon 6,6, PPS and LCP. The acetal and nylon resins are translucent while the PPS and LCP are opaque at the 3.2mm sample thickness. In all three colors, the more translucent resins produced visually more brilliant, higher chroma colors than the more opaque resins with increased diffuse scattering. **Table 2** presents color data generated from these same samples. Numerically, PPS and LCP produced lighter colors (*higher L* values*) and/or lower chroma (*C* values*) compared to the acetal and nylon controls which is consistent with what is seen visually. The base resin light scattering will increase the L* value and decrease chroma in these colors. What's more, the PPS and LCP were evaluated from 2 times to 15 times the pigment loading (*relative concentration*) of the acetal and nylon, and this still holds true. Another indication of the increased scattering from the PPS and LCP is the rel-

ative strength data of Table 2. As shown, even at the higher relative pigment concentrations, these resins produce colors that appear only 16 to 50% as strong.

This discussion illustrates the effect light scattering of the polymer has on the resulting color. In real life, if LCP is required for a particular application, the examples in Table 2 show that deep, dark colors or bright, high chroma ones can not be achieved. If the customer is currently using these higher chroma colors in other resins such as polycarbonate, he needs to be educated that these same colors can not be achieved in LCP.

Contrast ratios for several resins are presented in **Table 1**.

The data in Table 1 shows that for these crystalline

Table 2
Relative Color Strength in Various Resins

Color	Resin	Relative Concentration	Relative		Relative Strength
			L*	C*	
Blue	POM	X	37.05	55.01	
	PPS	3X	47.78	34.34	42 %
	LCP	3X	61.60	27.93	16 %
	LCP	6X	56.14	35.09	26 %
Red	Nylon 6,6	X	35.91	41.61	
	PPS	3X	44.43	33.67	48 %
	LCP	3X	56.87	34.13	23 %
Yellow	POM	X	77.52	77.94	
	PPS	2X	69.35	52.45	50 %
	LCP	15X	78.13	51.03	31 %

The other limiting factor in coloring a specific polymer is the stability and suitability of the colorant for a particular polymer and application. A general rule of thumb is that as the recommended processing temperature for a resin increases, the number of colorants that can withstand those temperatures decreases. Most of the colorants that drop out are organic pigments that are typically used to achieve the bright, high chroma colors or the deep, dark colors. Furthermore, polymers with harsh chemical environments like PVC, acetal or nylon limit colorants based on chemical stability. Conversely, the chemistry of the colorant can also render the polymer unstable, making it unsuitable for use as well. Finally, end use requirements such as agency compliance (FDA) or UV stability will further restrict the number of colorants that can be used in a specific polymer. Thus the achievable color gamut for a resin system not only depends on the light scattering of the polymer but also on the types of colorants that can be utilized.

POLYMER BLENDS

One can assume that blends of polymers will be more difficult to color than any component by themselves. Diffuse reflection can increase due to internal light reflection or scattering at phase interfaces if the polymers are at least partially immiscible or their refractive indexes are significantly differ-

Continued on page 17

Continued from page 16

ent. Blends of translucent polymers are typically more opaque than either resin alone. Furthermore, colorant stability (thermal or chemical) can be adversely affected by the presence of the other polymer(s). As in the case of neat polymers, both circumstances will result in a restricted achievable color gamut for the polymer blend. An example of a prominent polymer blend is GE's Noryl® (PS/PPO) which certainly colors much differently than the polystyrene component by itself. Blends of polymers can pose their own unique problems as well. An example is cases where colorants exhibit preferential dispersion to one of the polymer phases. The other polymer phase remains virtually uncolored. Macroscopically, this may not be a problem as the molded part appears uniformly colored. But even at this level, if wall thickness is very thin, color striations may become apparent. Other performance measures may be adversely affected as well. At the microscopic level, since all of the colorant is dispersed in one phase, impact strength and other properties may be reduced at pigment concentrations that are much lower than expected. This would primarily occur in blends where the colorant prefers the resin phase that provides the toughness to the blend.

POLYMER ADDITIVES

A wide variety of additives and modifiers are incorporated into polymers and polymer blends to tailor specific properties. Unfortunately, these additives can also impact the colorability to the total resin system. Listed below are some common additives and modifiers used in polymers and a short discussion of their typical effect on colorability.

Antioxidants

In general, antioxidants will have little effect on colorability since they are typically used at low levels. At higher levels, they may increase light scattering and impact colorability depending on the polymer type. There are remote instances where antioxidants have been linked to problems with gray-ing bright colors or "pink-ing" whites. But these are very polymer specific and usually result from a chemical instability within the system.

Anti-stats

These additives are designed to be present on the surface of the molded part to achieve the full anti-static benefit. Furthermore, they are typically used at higher levels than other additives such as antioxidants. Therefore, anti-stats are likely to increase light scattering making it more difficult to achieve the higher chroma colors.

Coupling Agents

Coupling agents such as silanes and titanates will increase light scattering. Both types can impact colorability if they are incorporated at high levels.

Flame Retardants

Typical flame retardant formulations will include an antimony compound, a bromine compound, and possibly a drip suppressant. All three additives will significantly increase light scattering and reduce the color gamut of the resin.

Table 3

presents color data to show this effect. E i g h t f l a m e retardant polyester

Table 3
Effect of Flame Retardants on Colorability
(FR Resin Versus Neat Polymer)

Color	DL*	DC*	Relative Strength
Bright Yellow	2.3	-3.5	56 %
Bright Red	4.9	-7.1	53 %
Medium Tan	7.0	-2.4	57 %
Bright Orange	4.0	-1.5	74 %
Royal Blue	6.3	-3.2	78 %
Dark Green	9.3	n/a	52 %
Medium Gray	5.0	-0.5	n/a
Black	3.4	-0.9	72 %

colors are listed with lightness, chroma and strength differences calculated versus the same colors in neat polyester resin. All colors are lighter (positive DL*) and duller with lower chroma (negative DC*) with the presence of the flame retardant system. Relative color strength data also shows that the colors are weaker and less intense. It would be difficult if not impossible to exactly match the neat polymer color in the flame retardant system due to the light scattering of the additives.

Foaming Agents

The author has little experience with foamed resins. However, one would speculate based on all of the above information that foaming would increase light scattering since the molded parts would contain a complex cell structure with all of its polymer/gas interfaces.

Heat Stabilizers

Antioxidants can be referred to as heat stabilizers and were previously discussed. Other heat stabilizers are metal complexes used in PVC and nylon. The largest impact on colorability is with the metal complexes used to increase the continuous use temperature rating in nylon. In that resin, these metal complexes can significantly reduce colorability due to discoloration via reaction with the colorant, or by thermal degradation. Light colors in heat stabilized nylon are virtually impossible to control since a slight change in residence time or temperature will significantly drive the color to tan or brown. The presence of oxygen will accelerate this. Darker colors are less affected and are preferred in heat stabilized nylon.

Table 4
Effect of Lubricant on Colorability

Color	DL*	Relative Strength
Bright Red	1.6	85 %
Dark Blue	2.7	80 %

Continued on page 18

Impact Modifiers

This class of additives covers a broad range from butadiene to acrylic polymers. Since these additives are polymeric in nature, diffuse reflection will occur at the polymer/modifier interfaces similar to polymer blends. Again, this will result in colors that appear lighter and duller. **Table 5** contains three examples of impact modified colors compared to the neat resin without modifier. As expected, the impact modified colors are lighter and have lower chroma. In practice, ABS or HIPS would have a more restricted color gamut compared to their transparent SAN and PS base polymers.

Table 5
Effect of Impact Modifier on Colorability

Color	DL*	DC*
Gray	4.5	-1.8
Bright Red	2.8	-2.4
Bright Yellow	3.6	-4.0

Lubricants/Mold Releases

Like anti-stats, lubricants and mold releases are designed to reside on the molded part surface. Therefore, light scattering can be increased depending on the chemistry and concentration of additive. Generally this effect is not a problem unless these additives are used at high levels, or they have significantly different refractive indexes from the base polymer. **Table 4** shows color difference data for two colors containing a high level of lubricant versus a polymer with no lubricant. Increased light scattering is evident by the lighter color (positive DL*) and lower relative color strength.

Reinforcing Agents

Reinforcing agents are typically either a mineral such as talc and calcium carbonate, or fiberglass. As expected, mineral types used at their high levels can scatter a large portion of the incident light depending on the refractive index and particle size. In mineral filled resins, it is usually impossible to achieve deep, dark colors such as chocolate brown or forest green. Bright colors are also made duller. Because a high amount of mineral is generally used, bright white colors such as appliance white can also be difficult to achieve. Fiberglass poses a different problem in that colors are typically darker and more dingy looking in glass reinforced resins versus their unfilled counterparts.

Table 6 lists color difference data for several 30% glass reinforced PBT colors versus the same color in unfilled PBT. The darker, dingier look is evident by the negative lightness and chroma difference values. Brighter, high chroma colors in glass reinforced resins either require significantly more colorant to achieve (at higher cost) or can not be exactly matched due to the resin. Overcoming

Table 6
Effect of Fiberglass on Colorability

Color	DL*	DC*
Gray	-1.8	-0.2
Dark Blue	-1.5	-0.7
Bright Yellow	-5.9	-8.2
Dark Green	-3.5	-2.9
Bright Red	-1.7	-0.6

the darkness makes bright white colors difficult to achieve as well. Contributing factors to the dark, dingy appearance are most likely the glass sizing agent and the elevated processing temperatures for glass reinforced resin versus the unfilled product.

Fiberglass adds another problem to coloring: mechanical property retention. A number of widely used colorants will abrade glass fiber length or can affect fiber wetting significantly reducing properties. For example, in 30% glass reinforced PBT, certain colorants can reduce tensile strength up to 20% and notched izod impact by as much as 30%. And this reduction occurs using colorant concentrations that would be termed typical and not excessive. Mechanical property retention may further limit the types and numbers of colorants that can be used in the glass reinforced resin, further limiting its achievable color gamut.

UV Stabilizers

A large number of colored polymers and polymer blends are used in applications where UV stability is important. First and foremost, many common colorants do not possess satisfactory lightfastness to be used in UV applications. Therefore, the color gamut can be reduced due to limited availability of colorants with acceptable lightfastness in certain polymer systems. UV stabilizers themselves can also impact colorability. Many impart a yellowish tint to the polymer that must be overcome. Also, some do increase light scattering making the more popular automotive maroon and dark blue colors difficult to achieve.

CONCLUSION

Hopefully, the discussion and examples presented above have clearly shown that color should be engineered along with other desired thermal and mechanical properties. That way, either the desired color can be formulated to minimize property loss, or the closest achievable color can be developed. And understanding the color limitations early on can help steer customers to those colors that can be achieved, which may be different from those actually desired. Most of the discussion has been centered around just the neat polymer or the polymer plus a modifier or additive. Coloring issues further escalate when polymer blends are used or when multiple additives are incorporated. Would it be difficult, and would the color gamut be somewhat restricted, if one was to color an impact modified, flame retardant, glass reinforced PBT/polycarbonate alloy? The answer now better be a resounding YES!

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REGISTRATION FEES	EVENTS SCHEDULE
SUNDAY, OCTOBER 18	
Advance Registration (before 8/31) SPE or DCC Member \$325 SPE Member w/ membership renewal \$444 Non-Member w/ SPE Membership \$444 Non-Member declining SPE Membership \$470 Late or On-Site Registration (after 8/31) SPE or DCC Member \$425 SPE Member w/ membership renewal \$544 Non-Member w/ SPE Membership \$544 Non-Member declining SPE Membership \$570 Speaker/Moderator \$160 SPE Emeritus Member \$100 Student (<i>Valid ID required</i>) \$ 50 Conference Literature and Extras Extra Conference CD \$115 <i>(available on-site)</i> SPE CAD Archive DVD \$175 <i>(conference papers from 1962-2007)</i> Special Events Welcome Reception (<i>Sunday</i>) Included Golf Outing (<i>Sunday</i>) \$125 Skeet Shooting (<i>Sunday</i>) \$ 30 5K Fun Run/Walk (<i>Tuesday</i>) \$ 20 Networking Lunch (<i>Monday</i>) Included Networking Reception (<i>Monday</i>) Included Awards Lunch (<i>Tuesday</i>) Included Pre-Conference Tutorial -Sun, Oct 18 <i>(register separately) "Coloring of Plastics"</i> with Bob Charvat \$450	9:00a – 4:00p "Coloring of Plastics" Tutorial with Bob Charvat <i>(Register Separately)</i> 11:30a – 5:00p Golf Outing – The Club at Savannah Harbor <i>(Pre-register for this event)</i> 11:30a – 3:00p Skeet Shoot – <i>(Pre-register for this event)</i> 6:00p – 8:00p Welcome Reception
MONDAY, OCTOBER 19	
	8:00a – 4:00p Technical Program 10:00a – 6:00p Exhibits Open 12:00p – 1:30p Networking Lunch 4:00p New Technology Forum 5:00p Networking Reception in Exhibit Area
TUESDAY, OCTOBER 20	
	7:00a 5K Fun Run/Walk for Habitat for Humanity 8:30a – 3:00p Exhibits Open <i>Note: Exhibits will close during the Awards Luncheon</i> 8:30a – 4:00p Technical Program 12:00p – 1:30p Awards Luncheon 4:00p Survey Raffle/Closing Remarks
For more information or to register online, visit www.specad.org Advance registration deadline is September 18, 2009	

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