COLORANTS

Introduction

Colorants for plastics can be grouped into two broad categories: pigments and dyes. Pigments are organic or inorganic colored, white, or black materials. They are nearly insoluble in plastic. Dyes are intended to dissolve or go into solution in a given polymer. Physical forms for dyes and pigments can range from dry prills or powder to liquids. These forms can be used as is or can be preincorporated into compatible dispersions. The colorant supplier or concentrate supplier can manufacture predispersions. A concentrate supplier usually adds additional value-added steps such as additive packages and color matching.

The main considerations when selecting colorants usually include dispersion, migration resistance, heat stability, light stability, and cost. All are dynamic and change with concentration of the colorant, processing conditions, part thickness, and additives. Similarly, changes in properties can be expected for a single pigment type depending on supplier.

Dispersion

Dispersion relates mainly to pigment. The pigment manufacturing process usually leaves a variety of particle sizes and distributions. Primary particles are true single crystals of pigment. Nonetheless, aggregates and agglomerates are also present. These are single pigment particles that are joined together. To provide good color strength and physical properties these particles must be separated. Use of wetting agents combined with shear is the key to agglomerate and aggregate reduction.
Migration. Migration refers to dissolved portions of a dye or pigment bleeding or blooming (1). Simply, the color is transported to the surface and can be wiped off or imparts unwanted color to an adjoining part. Dyes should be thoroughly evaluated, as they are naturally soluble. A pigments' tendency to migrate increases with the processing temperatures. When pigments are being used at the thresholds of their heat stability and/or at very low levels, caution should be observed. Plasticizers are known to facilitate migration; therefore plasticized poly(vinyl chloride) (PVC) is a good medium for evaluation.

Thermal Stability. Thermal stability of a colorant is important as thermoplastics have different melt processing temperatures and thermosets have different cure temperatures. Color changes in a pigmented or dyed polymer system usually originate from one of the following mechanisms: Thermal decomposition – degradation occurs if a pigment is processed above its decomposition temperature. This can be rapid as in the case of pyrazolone, Pigment Red 38; it totally decomposes at 218°C and turns brown. Decomposition can also be a slow gradual process as in the case of some quinacridones. They decompose slowly at 300–350°C. Chemical substitution – it is less common but can occur. In PVC some of the azomethine pigments can shift color rapidly at temperature above 160°C. The copper complex can be substituted by atoms from barium/cadmium and lead stabilizers. Crystal shift – polymorphous materials may undergo crystal phase transitions. Phthalo blue is a classic example. The alpha crystal can convert back to the more stable beta crystal. Particle size or crystal growth – pigment particles can grow in a hot solvent. As they grow a decrease in chroma and tinting strength can be observed. Solubility – a pigment if processed at higher than recommended temperature range can fully or partially dissolve. The fugitive material will generally change color and reduce the other properties of the colorant.

Light Stability and Weatherfastness. Light stability and weatherfastness are defined by the ability of a pigment or dye, in plastic, to retain its color upon exposure to sunlight and/or atmospheric impacts. If the polymer is not correctly stabilized for uv it will degrade at a rate that may negate the colorants performance. Conversely, uv stabilizers cannot greatly improve the stability of a colorant that has poor fastness properties. Lightfastness and weatherfastness are largely dependent on the particle size of a colorant. This is understandable as the job of a colorant is to absorb and reflect light. Failure of the pigment in most cases is not abrupt. A darkening of color occurs when used in masstone, and a loss of chroma and strength can be observed in the tint. The color changes layer by layer.

Cost. The broad spectrum cost for colorants is from $6.00 to $200.00/kg. Accordingly cost is as important as the above properties. Color matching and color formulation is critical. An effective colorant package should meet the needs of the application, provide a slight safety factor but not significantly exceed the properties required. As with most things, “you get what you pay for.” This is also true for colorants. In most cases, the better the properties the higher the price. When comparing colorants for value, do not focus on the price alone, as this method can be misleading. Focus on the strength or amount needed for a specific application, ie “value in use.”

As in many raw materials there can be large differences in properties among a pigment type. A single supplier can have a variety of Pigment Blue 15:3s. The product line can cover a range of transparency, dispersions, heat stabilities, cost,
FDA approval, shade, and physical forms. By factoring in those Pigment Blue 15:3s offered by a multitude of other suppliers the number can grow exponentially. There are many varieties of each pigment type that is discussed.

**FDA Colorants.** Because of the large amount of pigment used in packaging, house wares, and food-processing equipment, a colorants impact on health and safety should be considered. The U.S. Federal Government by way of the Food and Drug Administration (FDA) regulates food additives. Pigments that are used to color materials that come in contact with food are deemed to be indirect additives (2). This is based on the assumption that the pigment will extract from the plastic article and become part of the food. The FDA has published a list of sanctioned colorants. The list was introduced in Title 21 of CFR 178.3297 “Colorants for Polymers” and 175.300 for resinous and polymeric coatings. CFR 178.2600 may also be of interest when dealing with rubber articles. In very general terms, the pigments listed in these articles are suitable as components for plastic products used in producing, manufacturing, packaging, transporting, or holding food. In recent years the FDA has added new colorants or expanded usage of previously listed colorants. Some have limitations in regard to a colorants percentage and the resin to be incorporated. Current FDA regulations should be referenced for details.

**Inorganic Pigments**

**Whites.**

*Titanium Dioxide.* Titanium dioxide is the most common white of choice and by weight; it is actually the most widely used pigment. Product selection can be difficult as the variety can be staggering. Focus on particle size and surface coating during the selection process. Particle sizes usually range from 0.20 to 0.35 µm. Most plastic grades are manufactured to minimize reactivity. Reactive sites are masked with surface coatings of alumina, silica, and silicone fluid. This process increases dispersion and improves weatherability.

Titanium dioxide has a high Mohs’ hardness and is very abrasive. Its outstanding importance is due to its light scattering properties, its FDA approval, and excellent properties. Its large particle size provides ease of dispersion, excellent heat stability, migration resistance, and lightfastness at a typical cost of less than $2.00/kg. Titanium dioxide is used in nearly all plastics to provide pastels and to adjust colors. The opacity is valued for ascetics and its ability to absorb uv radiation. In fiber, titanium dioxide pigments provide a matte finish that eliminates the undesirable oily appearance caused by translucence. *Rutile* titanium dioxide is the first choice for most plastic applications. The shade is slightly yellow. If desired, very small amounts of blue or violet can be used to provide a cooler white. *Anatase* titanium dioxide is less yellow, not highly recommended for outdoor use, blocks less uv radiation and is generally more reactive.

*Zinc Sulfide.* Zinc sulfide pigments were developed in 1850. They still have some use in plastic because they are less abrasive and can have a smaller particle size. However, after the introduction of titanium dioxide in the 1950s they have continually lost market share.
**Zinc Oxide.** Zinc oxide has lost importance as a pigment but is noteworthy for its use as an activator for accelerating vulcanization in rubber (3).

**Carbon Black.** Carbon blacks are not only valued as colorants but for the functional benefits they provide. They improve weatherability of plastics by blocking ultraviolet, visible, and infrared radiation. They can act as free-radical traps and provide a wide range of electrical properties. Fineness, structure, porosity, and surface chemistry are properties used in selection of a carbon black. Typical particle size is from 18 to 80 nm. Keep this in mind when considering loading levels. It can require a large quantity of resin to wet out the pigment.

For practical purposes there are two basic types of carbon black, channel and furnace. Burning enriched natural gas makes channel black. Channel black has become nearly obsolete with increased natural gas prices. They still find some use in plastics for FDA and special applications. Furnace black is produced by thermal decomposition of feedstock oil for petroleum refineries. Channel black has been all but replaced by furnace black.

**Iron Oxide.** Iron oxide pigments find value in plastics as they are nontoxic, chemically stable, and low in cost, and are offered in a variety of shades. They can be naturally occurring, natural iron oxides, or they can be synthesized, synthetic iron oxides. There are four basic types and thus four colors of iron oxide pigments, yellow, red, brown, and black. Synthetic iron oxides are much purer, have better tinting strength, and vary less in composition. As a consequence, they have nearly replaced natural iron oxides. Natural iron oxides still find use in cellulose and phenolics. In cases where black is required at low levels, iron oxide is often the pigment of choice. It has much lower strength than carbon black whereby larger amounts can be used. This allows for a more homogenous mixture and contributes less in weighing errors. Red, yellow, and brown can be used in most plastics. They have good durability but are dull. Use caution with the yellow (ferric hydrate) as water can be driven at temperatures above 175°C and shift the color red.

**Chromium Oxide Green.** Chromium oxide green is a dull olive green. It has excellent heat and weatherfastness. Its large particle size offers easy dispersion. Its reflectance is similar to that of chlorophyll, making it suitable for camouflage (3). However, its lack of tint strength and other suitable colorants in this color space exclude it from significant use.

**Iron Blue.** Iron Blue or Pigment Blue 27 has replaced the older names of Paris blue, Prussian blue, Berlin blue, and Toning blue, etc. It is ferric ammonium ferrocyanide \([\text{FeNH}_4\text{Fe(CN)}_6]\). It finds little use in plastics at present. It is mixed with chrome yellow to form chrome green. Chrome green offers a low cost opaque green that finds some use in polyethylene film. Caution should be used as it has little alkali resistance.

**Ultramarine Pigments.** Ultramarine pigments are a complex of aluminum sulfo-silicate. Pigment Blue 29 is most common though; Pigment Violet 15 and pink Pigment Red 259 are also available. The blue can be used in almost any polymer; the pink and violet have maximum processing temperatures of 200°C. All have poor acid resistance. Surface-treated grades do provide better acid resistance and dispersion. They do not promote shrinking or warpage and are approved worldwide for coloring of food-contact plastics. The most popular is blue. Blue has its uses in plastics but is now often replaced by phthalocyanines that have 10 times the tint strength.
**Mixed Metal Oxides.** The term MMO (mixed metal oxides) denotes a pigment that crystallizes in a stable oxide lattice. They are manufactured by heating combinations of metal salts to temperatures of 800–1400°C. They are regarded as solid solutions and so some prefer to call them “complex inorganic color pigments.” The following are some of the colors produced: Cobalt blue – Pigment Blue 28 (CoAl₂O₄) and Pigment Blue 36 (Co(Al,Cr)₂O₄), cobalt green – Pigment Green 50 ((Co,Ni,Zn)₂TiO₄), zinc iron brown – Pigment Yellow 119 (ZnFeO₄), spinel black – Pigment Black 28 (Cu(Cr,Mn)₂O₄) and Pigment Black 22 (Cu(Fe,Cr)₂O₄). Nickel rutile yellow – Pigment Yellow 53 and chromium rutile yellow – Pigment Brown 24 are commonly referred to as titanates.

Compared with organic pigments they lack clean hues and tinting strength. Compared with most inorganics they are considered expensive and hard to disperse. Nonetheless, they are indispensable in high heat applications and their weatherfastness and chemical resistance are outstanding. Use in engineering resins for automotive interior and under-the-hood application is common. MMOs are also important tools for coloring rigid PVC siding.

**Lead Chromates and Lead Molybdates.** Lead chromates and lead molybdates are characterized by their bright hues and good opacity. The pigments of importance are chrome yellow – Pigment Yellow 34 and molybdate red and orange – Pigment Red 104. Because of the toxicity of lead and hexavalent chromium these pigments are forbidden from many uses. As a result, formulation into plastic has declined at a considerable rate. They are susceptible to acids, alkalis, and hydrogen sulfide. Surface treating of the pigments improves the weathering, chemical resistance, and heat stability. They are readily blended with each other and are often shaded with quinacridones to provide a variety of colors. Environmental regulations have caused a significant downturn in use. They have been replaced by high performance inorganic pigments where applicable.

**Cadmium Pigments.** Among the inorganic pigments, cadmium pigments are known for their bright shades. Their physical properties allow their use in most plastics. They are very heat stable, weatherfast, chemical resistant, and easy to incorporate. They also show good dimensional stability in large injection molded parts. These pigments are sensitive to overgrinding. The colors range from yellow through maroon (yellow, orange, red, bordeaux).

The pigments are cadmium sulfides and selenides. These raw materials are precipitated, dried, and calcined at 600°C (3). They usually undergo a dilute acid wash to remove impurities. Cadmium orange (Pigment Orange 20) is pure cadmium sulfide. Cadmium yellow (Pigment Yellow 35) is cadmium sulfide mixed with crystals of zinc cadmium sulfide. Cadmium red (Pigment Red 108) is produced in similar fashion to the yellow. Selenium powder is added to obtain the desired shade. The maroon is manufactured in the same manner as the red, selenium replacing the sulfur, at 50 mol% the shade shifts to a maroon.

Lithapones are coprecipitates with up to 60% barium sulfate. The lithapones are offered in the full color range and provide slightly better dispersion and value in use. Also available are a variety of mercury cadmiums in shades of orange, red, and maroon. They contain mercuric sulfide to replace a quantity of selenium. The advantage is slightly better economics and heat stability. Shortages of raw materials have caused increases in the price of cadmiums. Environmental
regulations have also caused a significant downturn in use. They are/have been replaced by high performance organics (eg, perylene, quinacridone, and azo condensation pigments).

**Special Effect Pigments**

**Pearlescents.** Pearlescent, nacreous, or interference pigments are designed to simulate the natural luster of pearls. Simply put, pearlescents are constructed of various layers of platy particles with differing indices of refraction. The **index of refraction** is the degree to which light slows and is bent as it passes through a substance (eg, prism). Numerous effects can be achieved by altering the incident light via reflection, refraction, and transmission.

*Natural pearlescence* (Guanine) is produced from the scales of herring and Atlantic salmon caught in cold waters. It does not find much use in plastics as it is more fragile, expensive, and is only available in a paste. *Bismuth oxychloride* is produced by precipitating platelet crystals from an aqueous solution of BiCl₃ via hydrolysis. Bismuth oxychloride pigment is the closest to natural pearl but is fragile and has relatively poor light stability.

Oxide-coated micas are produced by precipitating a metal oxide onto the surface of refined mica. Titanated micas are produced by precipitating a layer of TiO₂ from an aqueous solution of titanium tetrachloride onto a refined mica substrate. The titanium precipitates as the hydrate that is in turn converted to the oxide by calcinations at 800°C. They offer a wide range of colors, good light stability, and are generally low cost. The factors that affect luster and color are particle size, mica quality and color, and TiO₂ layer thickness. The larger particles offer more luster and transparency. The smaller particles offer more of a satin finish. The iridescent titanated micas that are produced by increasing the thickness of the TiO₂ layers are called **interference colors**. Two-tone and intensified versions of these interference colors can be produced by the addition of absorption colors. Using an absorption color that is the same as the interference color will produce a deeper colored TCM (titanium dioxide-coated mica). Using an absorption color that is different from the interference color will produce a TCM with two-tone flop effect. In a “two-tone flop effect” the color will change to two distinctly different colors when observed at different angles.

When using any of the pearls, care must be taken during incorporation. The pigment has to be wet-out but care must be taken to keep from breaking down the particles. Try to avoid twin-screw extruders unless you use a downstream feed port. If using a banbury try avoiding long cycles. This is one of a few products where mold design should be considered in the product-engineering phase as controlling flow and weld lines may be required. A variety of colors and effects can be achieved with these pearl pigments. Varying the combination and loading of pearls and traditional pigments are common practice.

Over 95% of pearls used in plastics are oxide-coated micas. The major application for plastics is polyolefin packaging. Recent interest in mass coloration for automotive parts could spur the already strong growth rate of pearls.

**Metallic Pigments.** Plastics can be given a metallic appearance by incorporation of very thin platelets of aluminum, aluminum–bronze, zinc, copper, and
copper–zinc alloys. The metal effect is caused by the reflection of light at the pigment surface. Larger pigment particles increase reflectance and hence brilliance. A large particle also increases flop (color change when viewing at an angle).

Grinding aluminum powder produces aluminum pigments. Wet milling does this best as aluminum powder forms explosive mixtures with air. The pigment suspension is usually sieved, filtered, and vacuum-dried in the case of products for plastics. Copper, gold, and bronze pigments (powdered copper–zinc alloys) are produced by dry milling. Copper is produced using 100% copper. A variety of gold shades can be achieved by adding up to 25% zinc.

Unlike most pigments used in plastics, metallics may agglomerate after a shelf life of 1 year. Proper dispersion is important. In organic colorants the objective is to deagglomerate by use of shear. However, use of high shear will tear, ball up, or fold the metallics. This will change their color and hiding power. Avoid high intensity mixers or add pigment at the end of the cycle at low speeds. Try to avoid twin-screw extruders unless you use a downstream feed port. Plate-out on calendering rollers and extruder screws have been reported. Flakes with a polymer surface treatment may reduce or eliminate the problem. Controlling flow and weld lines should be considered in mold design.

Fluorescent Pigments. There are three basic types of fluorescent pigments: A thermoplastic pigment based on a polyamide resin, a thermoplastic pigment based on a polyester resin matrix, and a pigment based on a blend of polyether and polyamide resin.

Fluorescent pigments are based on dyes that not only absorb some visible light, but also photons of higher energy form from the invisible uv region of the electromagnetic spectrum. The dyes used for the red pigments are members of the rhodamine family. The yellows are typically members of the coumarin family. There are no blue or green fluorescent dyes. These colors are achieved by blending phthalocyanines green with fluorescent yellow and phthalocyanines blue with optical brightener respectively.

The compatibility and heat stability of the pigments is important. Polyamides exhibit the highest degree of heat stability, but lack good compatibility in polyolefin. Polyester resins have excellent compatibility in olefin but lack good heat resistance. The polyester/polyamide hybrid has good heat stability and good compatibility. All lack good light stability.

Plate-out is an area of concern when processing concentrate or molding parts. At higher temperatures the components of a fluorescent pigment can undergo sublimation. The colored material will be deposited on the barrels and molds. Plate-out can be reduced by a number of methods. The combined use of absorbent agents such as barium sulfate and reactive agents such as titanate coupling agents can greatly reduce or eliminate plate-out.

Organic Pigments

Azo Pigments. Many of the red, yellow, and orange pigments used in plastics are classified as azo pigments. This classification is attributed to the fact that they contain the azo chromophore (–N=N–). Further subdivisions of azo pigment are possible. They can be labeled as metallized or nonmetallized; the
latter are most common in plastics. Manufacture of a metallized azo pigment involves four basic steps:

1. **Diazotization**: reacting a primary aromatic amine with nitrous acid that was formed *in situ* by reacting sodium nitrite with hydrochloric acid; this forms a diazonium salt. Some common primary amines are Tobias acid, C acid, 4B acid, 2B acid, and anthranilic acid.

2. **Coupling**: the diazonium salt is coupled to form the pigment. Common couplers are β-naphthol and BON. This forms an azo dye or very unstable pigment.

3. **Metallization**: the azo dye is precipitated as a metallized salt such as calcium, manganese, strontium, or barium. This is accomplished in the presence of anionic groups. Consequently, the sulfonic or carboxylic acid on the dye can react with metals to form an insoluble pigment.

4. **Washing**: the suspension is then filtered and washed. This removes any unwanted impurities.

Figure 1 is an example of the process of manufacture for a metallized azo pigment, barium lithol red (1). Reaction with a metal salt causes the azo dye to precipitate, forming an insoluble metallized azo pigment. Most nonmetallized reds contain no anionic groups.

Azo pigments are the perfect workhorse pigments for non-high performance applications. Overall, azo pigments are low cost and have excellent tinting

1. **DIAZOTIZATION**

   ![Diazotization Diagram]

   2-Naphthylamine-1-sulfonic acid + HONO \( \rightarrow \) 2-Diazonium naphthalene-1-sulfonic acid + 2 H₂O

2. **COUPLING**

   ![Coupling Diagram]

   2-Diazoniumnaphthalene-1-sulfonic acid + β-Naphthol sodium salt \( \rightarrow \) Sodium lithol red

3. **METALLIZATION**

   ![Metallization Diagram]

   Sodium lithol red + BaCl₂ \( \rightarrow \) Barium chloride

**Fig. 1.** Lithol red manufacture.
strength. They have fair to good dispersion, migration, and light and heat stability properties. The following review will be focused on the most commonly used azos, as there are more azos than time for discussion allows.

**Metallized Azo Reds, Oranges, and Yellows.** *Pigment Red 48:1 (2)* – Barium 2B is a strong, very yellow shade pigment with heat stability up to 260°C. Lightfastness rates a 3 on the 1–8 blue-wool scale. It has good dispersion and is used in almost all thermoplastics, excluding the engineering polymers. It has good migration in PVC systems.

*Pigment Red 48:2 (3)* – Calcium 2B is the counterpart to Barium 2B. It fills color space for a formulator by offering a clean, strong, and economical blue shade red. Physical properties are similar to Barium 2B although the Calcium 2B has slightly better light stability.

*Pigment Red 53:1 (4)* – Red Lake C is almost identical in shade to Barium 2B. Its slightly better heat stability of 288°C allows its use in ABS (acrylonitrile–butadiene–styrene) where lightfastness is not important. Caution should be used in plasticized PVC since migration can occur.

*Pigment Red 57:1 (6)* – Calcium Lithol Rubine is bluer than Ca 2B, with slightly inferior fastness properties. In Europe it replaces Ca 2B as the blue shade red of choice.

*Pigment Red 60:1* – Pigment Scarlet is unique as it is laked using barium chloride and alumina hydrate. The shade is not the typical yellow shade usually offered by a Barium Lake. It is bluer, tends to be weaker but has much better physical properties than the 2Bs. Heat stability of 300°C and midrange light stability offers a pigment with properties between those of high performance pigments and the above-mentioned azos.

*Pigment Orange 46 (5)* – Clarion Red offers a brighter and yellower shade of Red Lake C. Properties are similar and caution should be used in plasticized PVC since migration can occur.

Monoazo yellow pigment lakes (Fig. 3) are synthesized by first adding the diazotizedamine to the coupler. This dye is then precipitated as an insoluble metal salt. Ordinarily they have large particle size for an organic. This offers good opacity, heat stability, and dispersion. However, the tinting strength in application is one-half that of a diarylide yellow. Major applications are low to medium
monoazo yellow pigment takes.

**Pigment Yellow 62** (7) is the most common red shade yellow and **Pigment Yellow 168** (8) is its counterpart on the green side.

**Naphthol Red.** **Pigment Red 170** (Naphthol red) is offered in a transparent and opaque version. Pigment’s particle size of crystal form controls the opacity. The opaque version has a larger particle size. It is yellower in masstone and has better heat and light stability. Napthol red finds use in some low cost exterior applications (eg, coolers) as they have better light stability as compared with metallized azo reds.

**Disazo Yellow and Red.** Diarylide yellows use dichlorobenzidine (DCB) as a difunctional amine. The coupler changes, as can be seen by the generic name AAOT, AAMX, AAA, etc; hence it is the coupler that imparts the differences seen in the pigment (see Fig. 4).

Pound-per-pound, diarylide yellows cannot be out-performed for value in use. They are used in low temperature olefin and PVC application. Caution is required in plasticized PVC as migration is possible. The amine DCB is suspected to release at temperatures above 200°C in polyolefins. This is an area where discussion with your pigment supplier is recommended.

**Pigment Yellow 12** (9) – AAA Yellow is a medium-to-red shade yellow with low heat stability. Pigment Yellow 12 finds use in rubber. Heat stability is generally too low for olefins. **Pigment Yellow 13** (10) – AAMX Yellow is a medium-to-red shade yellow with good opacity. **Pigment Yellow 14** (11) – AAOT Yellow is a very opaque medium shade yellow. **Pigment Yellow 17** (12) – AAOA Yellow is a slightly transparent green shade yellow. **Pigment Yellow 83** (13) – AADMCA Yellow is a very red shade yellow with slightly better properties than the other diarylides.
**Pigment Red 38** – Pyrazolone red is ideal for rubber and other low heat applications. The bright clean red masstone quickly shifts to brown or black at temperatures above 218°C. Alkali resistance is excellent. Pyrazolone red is FDA approved for use in rubber. *Pigment Orange 13* and *Pigment Orange 34* are also disazopyrazolones that find use in rubber or low temperature olefin applications. *Pigment Orange 34* is slightly redder than *Pigment Orange 13*.

**Benzimidazolone Yellow and Orange Pigments.** Benzimidazolone pigments contain 5-aminobenzimidazolone group (Fig. 5). This group is common to all the pigments and hence the name. They are a very important group of pigments for plastics despite their high cost. They are not as clean and strong as diarylides. Nevertheless, they find use in a variety of applications as they have excellent lightfastness, heat stability, and migration resistance. Dispersion is fair. Some specific grades are FDA approved and others are considered low warp.

*Pigment Yellow 154* (14) is medium-to-green shade with select codes having some FDA approval. Nevertheless, most usage is in PVC. This is due to its bleed resistance being excellent and its heat stability of 200°C being too low to find much use in olefins. *Pigment Yellow 151* (15) is somewhat greener than *Pigment Yellow 154* (16) and has better heat stability (260°C). It is often used with phthalocyanine green to provide a very yellow but stable green. *Pigment Yellow 180* (17) is a medium shade with select codes having some FDA approval and low warp qualities. It is stable up to 290°C in olefins and is useful in coloring engineering resins. It does not show migration in PVC. *Pigment Yellow 181* (18) is very red. Its heat stability is good in polyolefins and most engineering resins; however, *Pigment Yellow 181* is not recommended for use in nylon. Select codes have

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*Fig. 4.* Disazo yellows and reds.
restricted FDA approval. Pigment Orange 36 (19) is a reddish shade orange with very good lightfastness properties. It finds most of its use in plastisols and PVC since its heat stability is 220°C, much lower than that of the other benzimidazolones. It is often used with carbon black to create lightfast shades of organic browns.

**Disazo Condensation Pigments.** Disazo condensation pigments (Fig. 6) represent a multistep approach to disazo chemistry. For disazo pigments of the diarylide types both the amino groups of the DCB are diazotized simultaneously, followed by reaction with two equivalents of coupler, to form the pigment. In the category of condensation pigments the disazo components are coupled to afford monoazo carboxylic acids. In a separate stage these are converted to their respective acid chlorides. The condensation pigment then forms, in the final stage, when two equivalents of an acid chloride react with one equivalent of an appropriate diamine (22). By selecting the amines in the coupling or diamines in the condensation a variety of pigments can be made. The high molecular weight of these products brightens the shade and increases stability.
Because of the complex manufacturing process, azo condensations are expensive when compared with most organic pigments. The result is they are only used in high performance applications, the majority of that being polypropylene and polyacrylonitrile fiber. They have replaced lead and cadmium pigments where toxicity was an issue. All physical properties are excellent but shrinkage in large molded parts can be an issue. There are three important pigments for use in plastics. They are Pigment Yellow 93 (20), a medium-to-green shade yellow, Pigment Yellow 95 (21), a red shade yellow, and Pigment Red 144 (22), a medium shade red (its CI number is 20735). Select codes of Pigment Yellow 95 have restricted FDA approval.

**Fig. 6.** Disazo condensation pigments.
Miscellaneous Yellows.

Pigment Yellow 138 (23) is a quinophthalone. It is considered slightly more opaque and weaker in tint than some of the other high performance yellows. It has good light and heat stability. The pigment is known to nucleate, which can lead to shrinkage in large parts. Select codes have restricted FDA approval.

Pigment Yellow 139 (24) is a methine-type isoindoline that has a red shade.

Pigment Yellow 110 (25) is an azo methine-type tetrachloroisoindolinone that has a very red shade. Pigment Yellow 110 is hard to disperse and transparent. Its good performance in PVC, heat stability in olefins of 270°C, generally good lightfastness, and the fact that select codes are FDA approved, make it worth mentioning (1).
Pigment Yellow 109 (26) is an azo methine-type tetrachloroisindolinone. It has overall good properties and is considered a green shade yellow.

Pigment Yellow 150 (27) (Pyrimidine Yellow) is an azo/nickel complex. Its color is dull and it lacks tinting strength. It finds its importance in a good stable yellow for fiber applications. It can react with zinc sulfide.

**Phthalocyanine Pigments.** Presently, phthalocyanine blue and green are the most important organic pigments being used in plastics. They have bright clean shades and their physical properties are excellent. Lightfastness and weatherfastness are of automotive quality. Most can be used in all but the highest processing temperature resins. They are very high in tint strength and have excellent value in use. They are sold in high volumes and most domestic sources are FDA approved. Shrinkage in large molded parts can be an issue.

Phthalocyanines are planar molecules that comprise four isoindole moieties connected by four nitrogen atoms. This forms a 16-membered ring with the central atom being copper. Manufacture of the crude pigment is relatively straightforward (Fig. 7). Phthalic anhydride reacts with urea to form a compound that reacts at 190°C with copper salts. Molybdates and vanadates are often used as catalysts for this condensation reaction (4). This process produces crude pigment. Chemically replacing the hydrogen in the phthalo blue (28) with chlorine results in Pigment Green 7. Replacement of the hydrogen with bromine results in production of the yellower, Pigment Green 36.

The crude of all of these phthals has a very large particle size and needs to be conditioned in order to make it pigmentary. Conditioning can be completed using several processes: Salt attrition – The crude is ground in a ball mill or a double-arm
mixer in the presence of salt and optionally a solvent such as diethylene glycol. This provides the green shade beta crystal in the case of blue crude. **Solvent free attrition** – The crude is ground in a ball mill in the presence of a large excess of salt, excluding the solvent; this is used exclusively for production of red shade or alpha crystal blue. **Acid pasting** – The crude is dissolved in a large excess of concentrated sulfuric acid, then reprecipitated by drown-out in iced water. **Acid swelling** – The crude is treated with a smaller amount of concentrated sulfuric acid than used in acid pasting technique. This acid-swelled paste is added to iced water to precipitate the pigment.

**Phthalocyanine Blue Pigment.** Phthalocyanine blue pigment (28) exhibits polymorphism. Although chemically the same, changes in crystal shape change the color and properties. The beta phase or green shade is more inherently stable. The alpha shade or red shade will readily convert back to the more stable green shade if not stabilized. Current methods of stabilization are essentially proprietary. They offer added heat stability and resistance to flocculation in coatings applications. Light stability remains consistent for the different crystals phases.

**Pigment Blue 15** is a nonstabilized alpha crystal. It has a strong red shade and finds use in low temperature applications like rubber and PVC. Heat stability becomes a problem above 230°C.

**Pigment Blue 15:1** is a stabilized or noncrystallizing alpha or red shade. Because of differing types and qualities of additives, heat stability can range from 275 to 300°C. Red shade blues are stabilized by additives or by the
addition of up to one molecule of chlorine. The chlorinated version is slightly greener in a tint and has a jet masstone as compared with the additive-stabilized Pigment Blue 15:1. In recent years, a semi-Cl version has become popular. It is a midshade and has good heat stability. Pigment Blue 15:2 is a noncrystallizing, nonflocculating red shade. It does not find much use in typical thermoplastics. Its design is for resistance to flocculation and is used in some plastisol, acrylic, and liquid color application. Heat stability is equal to that of Pigment Blue 15:1.

Pigment Blue 15:3 is a nonstabilized beta shade or green shade blue. The more stable beta phase crystal does not require an additive to stabilize it for heat resistance. It has heat stability up to 290°C. It is applicable for and used in almost all thermoplastics.

Pigment Blue 15:4 is a noncrystallizing, nonflocculating beta or green shade blue. Its original design was for coatings application. In spite of this, the additive used for flocculation provides excellent heat stability and accordingly Pigment Blue 15:4 finds use in very high temperature applications. Pigment Blue 15:4 often finds use in place of Pigment Blue 15:3 in engineering polymers.

Phthalocyanine Green Pigment. Phthalocyanine green demonstrates the good overall properties of phthalo blue, differing from blue in that it is not a polymorph (4). Pigment Green 7 is recognized as being more stable than its phthalo blue counterpart. This is largely due to the stabilizing factor of chlorine or bromine or both. Heat stability is the area of most improvement over blue. Pigment Green 7 is offered in medium to blue shades of green. Pigment Green 36 is much yellower than Pigment Green 7.

Quinacridone Pigment. Quinacridone pigments fill an important need in the coloring of plastics. They are the high performance counterparts to azo red pigments. They cover a key color space, from bright red to violet. They are exceptionally strong but can be difficult to disperse because of its especially small particle size. A few suppliers offer predispersion that limits loss through dusting and provide additional dispersion and strength, as a result, increasing their value in use. They have excellent fastness properties. They can be used in olefins for everything from packaging to fiber applications. They are also used in acrylonitrile, nylon-6, and polyester fiber. Some varieties find use in engineering resins. Quinacridones are also the pigment of choice for automotive interior and vinyl applications. Most have some FDA approval. Pigment Violet 19 is polymorphic and has two basic crystals. The beta crystal is a violet whereas the gamma crystal is a yellow shade red. The beta crystal is most stable.

Quinacridone pigments are made by the use of two different but similar processes. They involve either the oxidation of dihydroquinacridone or the cyclization of 2,5-diarylaminoterephthalic acid. Both processes require a condensation of diethyl succinylsuccinate with an aromatic amine to form the 2,5-diarylamino-3,6-dihydroterephthalic acid diester. The diester is converted to dihydroquinacridone during ring closure at high temperatures. Subsequent conditioning leads to a quinacridone with the desired morphology. Use of 2,5-dianilinoterephthalic acid yields Pigment Violet 19 (29). Use of 2,5-ditoluidinoterephthalic acid yields the 2,9-dimethylquinacridone, Pigment Red 122. Use of 2,5-diparachloroanilinoterephthalic acid yields the dichloroquinacridone, Pigment Red 202 (4).
Pigment Violet 19 (Violet) (29) can have a variety of shades and properties. This diversity is largely dependent on the particle size and manufacturing processes. The beta crystal provides a clean violet shade. Most have FDA approval and can find use in FDA applications using extrusion coating, injection molding, and film processes. Its excellent lightfastness and heat stability make it useful in most melt-dyed fiber. Some solubility issues exist when used at very low loadings in engineering resins.

Pigment Violet 19 (Red) is also offered with variety of properties and comes in a variety of shades and opacities. The more opaque have better lightfastness and heat stability and the more transparent have excellent tinting strength. Some recently developed products can offer both. The particle size and particle size distribution are mainly responsible for the variety of products offered. Most grades are FDA approved.

Pigment Red 122 (30) is the dimethylquinacridone. It is a magenta shade and is typically thought of as having better fastness properties than of the unsubstituted types. It is used in all of the above-mentioned plastic applications. Some grades are FDA approved.
Pigment Red 202 (31) is a dichloroquinacridone. It is also a magenta shade and is similar in properties and uses to Pigment Red 122. Pigment Red 202 was typically offered in a hard to disperse and opaque coatings grade. New, easy dispersing, high tinting strength grades are now available. Red 202 is unique in that it is the least soluble of the quinacridones. Therefore, the majority of its use is in engineering resins and other high performance applications.

Perylene Pigments.

The chemical structure of Perylene Pigments.

Perylene pigments are similar to quinacridones, given that they find use in high performance applications. Of perylenes, only three types are actively used for coloring plastics. They are Pigment Red 179 (32) (R=methyl), Pigment Red 149, and Pigment Violet 29 (32) (R=H). They are unique as compared with quinacridones in that the majority of the pigment not consumed in automotive coatings is used to color fiber. Caution should be exercised when perylenes are used in olefins that are stabilized with HALS (Hindered Amine Light Stabilizers) UV Stabilizers. At high pigment levels the stabilizers can be inactivated upon exposure to light. Perylenes are used to a lesser degree in PVC for automotive interiors.

Perylenes are chemically diimides of perylene tetracarboxylic acid. The shade change is dependent on the substitution of the imide nitrogen (4).

Pigment Red 149 is a clean, medium shade red. It exhibits high tinting strength and is very transparent. Its small particle size can cause shrinkage in large molded parts. Interestingly, its influence on shrinkage decreases with increasing temperatures. Superior migration resistance in plasticizers allows use of all types of vinyl. Pigment Red 149 can endure processing in polycarbonate because of its heat stability of 320°C. Pigment Red 149 is also used to color unsaturated polyester and other cast resins (1). Pigment Red 179 is perylene maroon. It is a very blue shade that is very dirty and brown looking at high loadings. Most common usage is in fiber as tinted and low percentage masstone colors. At these levels it is a clean, reddish-maroon color. It is thermochromic and will change color during processing only to return to original color as it cools. Pigment Violet 29, a very blue shade violet, appears black at high pigment concentration. Pigment Violet 29 finds use in fiber; however, volumes are much lower than those for Pigment Red 179.
Dioxazine Pigment.

Dioxazine violet or *Pigment Violet 23* (33) can be used in most plastics excluding engineering resins. It is very strong in tint and can look black in masstones at normal levels. It finds most use in olefins and PVC. It is often used at low levels with TiO₂ to provide a clean pastel violet. In fiber, carbazole is often added in small quantities to blue to provide a clean red shade blue. Another use is in combination with blue as a bluing agent for whites. Use caution as decomposition can occur if processing above 250°C. Pigment Violet 23 has also exhibited solubility issues when used at very low levels. Lightfastness also requires attention since it can swing from 8 (excellent) to 3 (poor) on the blue-wool scale as pigment loadings are decreased. Carbazole dioxazine violet is manufactured by reacting chloranil with 2 mol of aminoethylcarbazole followed by oxidative cyclization.

**Diketopyrrolo Pyrrole Pigment.** *Pigment Red 254* is a new arrival when compared with most of the other pigments mentioned. It is offered in several different shades of medium red. The tint reductions are somewhat bluish red. Pigment Red 254 offers good color strength and has excellent fastness properties. For economic reasons it is often combined with less expensive napthols and quinacridones. This provides both a variety of shades and properties while reducing the expense of the formula.

**FD&C Food Lakes.** FD&C lake pigments are vital to the plastics industry. They are certified by U.S. Government specifications to be of a purity and composition that allow their use as a direct food additive and colorant for certain drug and cosmetic applications. This certification makes them the pigment of choice for medical or food packaging applications (5,6). They have heat stability in the area of 250°C. Limited light stability and poor tinting strength excludes them from use in areas where their certification is not required.
Manufacture of the food lakes requires the precipitation of food-certified dyes onto the surface of aluminum hydrate. The water of hydration present is to some extent driven off during incorporation into the plastic. Vented equipment is recommended. Over 90% of their use in plastics is in olefins for food-packaging applications. The colors available are FD&C Red 40 (34), FD&C Blue 1 (35), FD&C Yellow 5, and FD&C Yellow 6 (36).

**Dyes.** Dyes similar to pigments are listed according to their class, generic name, and Color Index (CI) name and number. The dyes are essential; without them, many transparent effects in plastics could not be achieved. Dyes are soluble in plastic, and therefore more transparent by nature than pigments. Dyes are known for poor lightfastness in tinted application. This is not as great a concern in masstone or transparent parts as failure occurs on the surface, and the color beneath is unaffected.

Dyes should be avoided in plasticized PVC and olefins because they tend to migrate. Plasticizers solubilize the dyes making them fugitive. In olefins, the dyes lack an affinity for aliphatic hydrocarbons and consequently migrate to the surface. Migration testing is a standard procedure unless the dye is proven in the polymer system.

**Azo Dyes.** Azo dyes contain the structure \(-\text{N}=\text{N}\) similar as referred to in the Azo Pigment section. They are available in a wide range of colors. Their main uses are coloring transparent, rigid PVC, polystyrene, phenolics, and poly(methyl methacrylate). The most commonly used azo dyes are Solvent Reds 1, 24, and 26,
Solvent Yellows 14 and 72, and Solvent Black 3. Acid Orange 7 and 8, and Acid Yellow 36 find most use in phenolic resins (7) (37, 38).

**Anthraquinone Dyes.** Anthraquinone dyes have much better heat and light stability when compared with azos. This does not come without a cost. In spite of this, it greatly expands the potential for use in exterior application. The most commonly used are *Solvent Red 111, Solvent Violet 13 and 3, Solvent Blue 12 and 59, and Solvent Green 3*. Usage is expanded to ABS and polycarbonate. Most recognize Solvent Red 111 for its use in automobile taillights made with poly(methyl methacrylate). Again, the acid types are mainly for phenolics. They are *Acid Blue 24 and Acid Green 25*.

**Xanthene Dyes.** Xanthene dyes are an important class since they offer brilliant and fluorescent colors. Conversely they are only fair to good in heat and light stability. Useful xanthene dyes are Basic Violet 10, a fluorescent, Solvent Green 4, Acid Red 52, Basic Red 1, and Solvent Orange 63.

**Azine Dyes.** Azine dyes include nigrosine and induline. They have excellent heat and lightfastness. They produce very jet blacks, which are not achievable with carbon black. Nigrosens, Solvent Black 5, and Solvent Black 7 are the largest volume dyes used in the plastics industry. *Solvent Black 5* is alcohol soluble and can be used in coloring ABS, phenolics, and polypropylene. Solvent Black 7 has higher tint strength than Black 5. Its low electrical transmission properties make it very desirable for coloring phenolic resin often used in electrical components (7).

**BIBLIOGRAPHY**


**GENERAL REFERENCES**


*Society of Plastics Engineers, Color and Appearance Division*, RETEC Papers 1998.


SCOTT HEITZMAN
Sun Chemical Corporation