

A Primer on Colorful Additives

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INTRODUCTION

The melt coloring of plastics is one of the most functional value added features a resin producer, compounder, or parts fabricator can impart to their products. It not only provides desired appearance properties that help sell the product, but it can also enhance several other properties, such as stability toward UV light. In addition, melt coloring usually eliminates the need for a separate, off-line, painting step. Overall manufacturing costs can thereby be reduced.

Once the color system is incorporated into the plastic matrix, however, it becomes an integral part of the material and may alter the engineering, performance, and processing properties in ways not considered during the design and formulation of the new material. Coloring, frankly, is usually viewed as the end-users problem, and the ball lands in the court of the color formulator. This specialist (who is usually untrained in the finer points of polymer science) is then left with the task of navigating through what often seems to be an obstacle course of known and unpredicted interactions while trying to give the end-user an economical color package that will meet the product's appearance requirements. The task is even more critical in the case of high performance polymer blends and alloys, whose highly valued engineering and performance properties are often sensitive to small compositional changes.

The objective of this Section is to raise the level of awareness that color needs to be part of any total systems approach to material design. We will survey the major classes of colorants suitable for use in high performance polymer blends and alloys and describe some of the potential chemical and physical colorant/material interactions.

THE MAJOR CLASSES OF COLORANTS

The colorants used in plastics fall into two very broad categories: pigments and dyes. Pigments are defined as colorants which do not dissolve in the plastic matrix of interest, whereas

dyes are colorants that do go into solution. Pigments, therefore reside as a separate phase. Consequently, there are phase boundaries to consider, and these can be crucial to the end-user.

INORGANIC PIGMENTS

Inorganic pigments are metal salts and oxides which can predictably impart color to a substrate. Most of these pigments have an average particle size of about 0.2-1.0 microns. The manufacturers take great pains to eliminate agglomerates with particle sizes above 5 microns. With few exceptions, inorganic pigments are inexpensive raw materials (see tables which follow). Because of their relatively low color strength they are not always the best value. Some good properties which many inorganic pigments share are:

- 1 easy to disperse (relatively little work is required to break down the pigment, coat it with the plastic, and distribute it uniformly);
- 2 good heat and weather resistance;
- 3 little, if any, reactivity.

There are, of course, exceptions, and we will be quick to point these out. For example, reactivity is a potential problem in any polymer system.

Simple Metal Oxides

Several inexpensive colorants compatible with a wide variety of polymers have a simple chemical structure - they are single metal oxides. For convenience, we have listed the four most commonly used examples in Table 1, along with several properties of interest, such as compliance with food contact applications and cost.

Titanium Dioxide (Titania) Titanium dioxide is the least expensive and most widely used white pigment. Nearly all of the titania used in this country is produced from titanium ore (mostly titanium and iron oxides) by the "chloride process", which goes through a $TiCl_4$ intermediate.

Although TiO_2 is viewed as an inert chemical, the crystal is defective - lacking 1 oxygen atom in about 100,000. This defect results in each titania particle (ca. 0.2-0.3 microns) having a small number of reactive $Ti(+)$ sites on or near the surface. In chloride process titania, some of these sites have bound chloride ions. $Ti(+)$ ions and bound $Cl(-)$ ions can be double trouble for some blends and alloys. Titanium ions can react with a variety of organic substances to form organic titanates that can catalyze all kinds of reactions. Polymer chemists, for example, use titanates to catalyze polymerization of polyesters. In addition, the chloride ion promotes the degradation of polycarbonate, PC. Some grades of titania are therefore unsuitable for use in blends or alloys containing PC.

Table 1. Inorganic pigments

Pigment	Strength	Heat stability	Weather resistance	FDA status	Cost \$/lbs
<i>Simple metal oxides</i>					
Titanium dioxide (Pigment White 6)	G	G-E	G-E	yes	1.0
Zinc oxide (Pigment White 4)	P	G-E	G-E	yes	1.0
Iron oxides (Pigment Red 101)	F	G-E	G-E	yes	1.0
Chrome (III) oxide (Pigment Green 17)	F	E	E	yes	2.0
<i>Mixed metal oxides</i>					
Nickel titanate (Pigment Yellow 53)	P	E	E	no	4.0
Nickel chrome titanate (Pigment Brown 24)	P	E	E	no	4.0
Copper chromate (Pigment Black 28)	P	E	E	no	6.0
Cobalt chromite (Pigment Green 26)	F	E	E	no	8.0
Cobalt aluminate (Pigment Blue 28)	F	E	E	yes	15.0
<i>Metal sulfides</i>					
Zinc sulfide (Pigment White 7)	F	G-E	G	yes	1.5
Cadmium sulfide (Pigment Yellow 35,37)	G	E	F	no	12.5
Cadmium sulfoselenide (Pigment Orange 20)	G	E	G	no	17.0
Cadmium sulfoselenide (Pigment Red 108)	G	E	E	no	22.0
<i>Ultramarine pigments</i>					
Ultramarine blue (Pigment Blue 29)	F	E	P-F	yes	2.0
Ultramarine violet (Pigment Violet 15)	P	E	P-F	yes	4.5

To minimize the reactivity of this important white pigment TiO_2 producers process special plastics grade versions in which the reactive sites are masked with alumina, silica, and/or silicone fluid *via* proprietary means.

Both crystal forms of titania, rutile and anatase, have a high Mohs hardness rating and are abrasive. For example, the pigment particles can etch glass fibers and greatly reduce the tensile strength of glass fiber reinforced thermoplastic blends and alloys.

Synthetic Iron Oxide Reds The synthetic iron oxide red pigments are based on Fe_2O_3 chemistry.

These pigments offer a great deal of hiding power (opacity), but are relatively weak and dirty. A wide range of rust colored hues are available. Again, the Fe(+3) acts as a Lewis acid. Even at low concentrations it poses a problem for PVC and is not suitable for blends and alloys containing PVC. At higher concentrations it may adversely affect some PC materials.

Chrome(III) Oxide Chromic oxide is a weak, olive shade green with excellent weathering and heat stability. Because other green pigments with higher color strength and cleaner hues are available, chrome oxide pigments are usually reserved for long-term outdoor applications.

Mixed Metal Oxide Pigments

The mixed metal oxides are a large class of calcined pigments (final step involves a slow heat treatment at about 1000°C) developed originally for ceramics, that have excellent weatherability and heat stability. As a class, they are the least reactive pigments and, for example, have enjoyed wide use in vinyl siding. On the down side, these pigments have low tinting strength and, as a rule, are abrasive toward glass fibers. Properties of some commonly used MMO pigments are listed in Table 1.

Many of the MMO pigments contain significant levels (about 10% by weight) of antimony, which is considered a heavy metal by some regulatory agencies. Antimony free versions are now available from several suppliers, but there is a cost penalty of about 25-50%.

In the past, MMO pigments were found to be hard to disperse and the source of color specks. Recently, however, all of the major suppliers have targeted polyamide fibers as a lucrative new market and have greatly improved the particle size distribution and ease of dispersion. Some combinations of metals and the colors produced are given in Table 1.

Metal Sulfide Pigments

Included among these pigments are zinc sulfide (ZnS) and the cadmium-based pigments. ZnS is a white pigment which has found a niche in coloring glass reinforced resins. The cadmium pigments represent a large class of bright pigments in the yellow-orange-red range of the color spectrum. Some properties of metal sulfide pigments are listed in Table 1.

Zinc Sulfide White ZnS is a white pigment having about one-half the opacifying and tinting strength of titania. Two special features are:

- 1 its low Mohs hardness recommends it for use in glass reinforced resins
- 2 it exhibits much lower light absorption in the near UV region of the spectrum than titania. Because of this, it can be used with some bright fluorescent dyes with minimal quenching of fluorescence.

Zinc(+2), as noted above, is a Lewis acid, and most color formulators avoid the use of ZnS in PC and its blends and alloys.

Cadmium Sulfides and Sulfoselenides Calcined CdS is a bright orange shade yellow with excellent light fastness and heat stability. It does not hold up well in moist atmospheres

and is not necessarily suitable for all outdoor applications. By combining Cd and Zn (up to about 12% Zn) bright primrose and lemon yellow hues can be achieved. Replacing some sulfur with selenium shifts the color toward the red region. Total replacement yields CdSe, a deep maroon pigment.

Traditionally, the cadmium-based pigments have been widely used in engineering resins such as the polyamides 6 and 6/6, PC, thermoplastic polyesters and their blends and alloys.

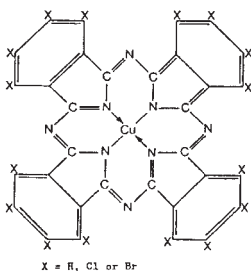
Cadmium, however, is classified as a heavy metal by all regulatory agencies. For example, Cd is one of the four heavy metals cited in the CONEG legislation governing packaging materials. More and more, end-users of engineered materials - including blends and alloys - are specifying heavy metal free formulations, and cadmium-based pigments are slowly, but surely, being replaced.

Although regarded as chemically inert, the cadmium sulfide pigments can react with Cu(+2) during melt processing to yield black CuS. This color contaminant results in yellows shifting green and reds turning brown. One potential source of Cu(+2) ion is copper based heat stabilizer for polyamide.

Ultramarine Pigments

Chemically classified as “Sodium-Aluminum-Sulfo-Silicates”, the ultramarine pigments represent a class of heat stable, light fast pigments. Unfortunately, their chemical resistance is limited - readily attacked by both acids and alkali - and they are therefore not recommended for extended outdoor exposure. A small selection of acid resistant grades protected with a silica coating are available at a slightly higher cost. A natural form of ultramarine is the mineral lapis lazuli.

The ultramarines range in color from a medium shade blue through violet to pink. A household example of an ultramarine blue in full shade is the “Milk of Magnesia” bottle. Standard grades of ultramarine pigments (uncoated) react with polyacetal resins, and I have observed color drift of these pigments in PC and PA 6/6. Some properties of ultramarine pigments are listed in Table 1.



ORGANIC PIGMENTS

Organic pigments range in complexity from simple carbon black to the heme-like structures of the phthalocyanine pigments (Figure 1). The use of organic pigments in polymer blends and alloys has been increasing rapidly as end-users and color formulators move away from heavy metal pigments. Typically, organic pigments have 10-20 times the color strength of inorganics of comparable hue. This is due to their much smaller particles size - in the

Figure 1. The phthalocyanine ring system

range of 0.05 microns. On the one hand, the small particle size affords the possibility of creating transparent colors. On the other, it means that organic pigments are often very hard to disperse. On a per pound basis organic pigments are generally much more expensive than inorganics. However, because of their inherent strength they are sometimes more cost effective. In general, our experience has been that replacing heavy metal pigments with organic pigments leads to higher coloring costs.

Another down side in the use of organic pigments is potential reactivity with the resin. Many organic pigments contain the C = O (carbonyl) group as part of the chromophore (the structure within the molecule which confers absorption in the visible region). Polyamide resins are weak reducing agents which can convert carbonyl groups to hydroxyl groups. This reaction often results in the destruction of the chromophore and a complete loss of color. Care must therefore be taken in the selection of organic pigments (and dyes - see below) when coloring polyamide based blends and alloys.

Carbon Black Carbon black pigments are usually made by either of two processes. Most are produced by the furnace process in which petroleum is reduced to carbon at high temperature. Since there are small quantities of suspected carcinogen polynuclear aromatic hydrocarbons produced as by-products, "furnace black" does not comply with regulations for food contact applications. The natural gas process takes place at much lower temperature and the resulting pigment is found to comply with FDA regulations. The resulting pigment called "Channel Black" is also considerably more expensive.

Carbon black ranges in strength from "low jetness" utility grades (about 0.06 microns) to "high jetness" grades (as low as 0.015 microns), which includes some conductive grades. Several carbon black grades with particle size in the region of 0.02 microns are found to confer excellent weathering properties to just about any plastic material when present at 2 pph. Carbon black properties are summarized in Table 2.

Phthalocyanine Pigments In the blue-green region of the color spectrum the formulator's requirements are well met by the phthalocyanine pigments, which represent some of the best cost for performance values in the industry. As a class, these pigments, which were discovered serendipitously in an ICI research lab, share the following desirable properties:

- low cost
- high strength
- clean, bright hues
- good to excellent heat stability
- excellent light fastness
- good to excellent weathering
- transparency
- meet food contact regulations (with some exceptions)

Table 2. Organic pigments

Pigment	Strength	Heat stability	Weather resistance	FDA status	Cost \$/lbs
<i>Carbon black</i>					
Furnace black (Pigment Black 7)	E	E	G-E	no	0.7
Channel black (Pigment Black 7)	E	E	G-E	yes	4.0
<i>Phthalocyanines</i>					
Red shade phthalo blue (Pigment blue 15:1)	E	G	G-E	yes	12.0
Green shade phthalo blue (Pigment Blue 15:3)	G-E	G	G-E	yes	10.0
Blue shade phthalo green (Pigment Green 7)	G	E	G-E	yes	15.0
Yellow shade phthalo green (Pigment Green 36)	G	E	G-E	no	18.0
<i>Quinacridones</i>					
Quinacridone red (Pigment Violet 19)	G	F	G-E	yes	30.0
Quinacridone violet (Pigment Violet 19)	G	F	G-E	yes	30.0
Quinacridone magenta (Pigment Red 122)	G	G	G-E	no	35.0
Quinacridone (Pigment Red 202)	G	G-E	G-E	no	40.0
<i>Other organic pigments</i>					
Disazo yellow (Pigment Yellow 93,95)	G	G	G-E	PY 95 yes	32.0
Quinophthalone yellow (Pigment Yellow 138)	G	G	F	no	27.0
Disazo red (Pigment Red 220)	G	G	G	yes	45.0
Azoic red (Pigment Red 177)	G	G	G	yes	60.0

These along with other properties of the phthalocyanine pigments are summarized in Table 2.

The structure shown in Figure 1 is the parent compound of the phthalocyanine pigments. The unsubstituted (no halogen atoms) ring system yields a blue pigment which is available in two crystal forms, alpha (red shade) and beta (green shade). The commercial pigments usually have some Cl substitution, which provide additional heat stability.

Chlorination of the ring system yields a blue shade green pigment which, in my experience, has the highest heat stability of any organic pigment (other than carbon black). Replacing some of the chlorine substituents with bromine atoms yields a yellow shade green.

The major problems associated with the use of phthalocyanine pigments in polymer blends and alloys are:

- phthalos blues are slightly soluble in polystyrene and may lead to color control problems in styrene based materials;
- all phthalos pigments may act as nucleators in crystalline resins - leading to uncontrolled shrinkage and warpage - and must be used with care in crystalline materials. (Note: the phthalos green pigments display the largest effects.)

Quinacridone Pigments First commercialized in 1958, the quinacridone, QA, pigments

rapidly gained acceptance in the coatings industry as a replacement for heavy metal pigments due to their high strength, good light fastness and weathering properties, and moderate cost. Figure 2 shows the chemical structures of the three most commonly used QA pigments in plastics. These pigments, whose properties are summarized in Table 2, are in the red and violet range of the color spectrum.

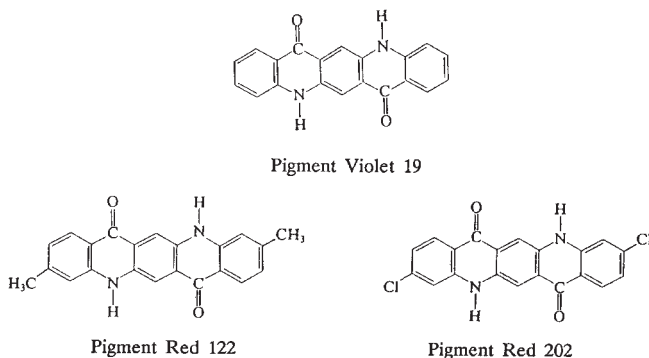


Figure 2. Quinacridone pigments.

Pigment Violet 19 is polymorphic, and can be produced in a blue shade (beta crystal) that is a bright red shade violet and in a yellow shade (gamma form) that is a deep red. By adjusting the particle size QA suppliers can produce a variety of red and violet shades.

The dichloro-QA (Pigment Red 202), a bright magenta pigment appears to have the broadest applicability in engineering resins and their blends and alloys. It has the highest heat stability (over 550F) and has the lowest tendency to solubilize during melt processing. Its one drawback is that it has not been cleared for food contact use. The other QA pigments, especially Pigment Violet 19, will solubilize to various degrees in PS-based materials and result in the appearance of fluorescent green streaks in the part. We have also seen this happen in PET. QA pigments react with polyamides, which are reducing agents, and lose their color. They are therefore not suitable in PA based blends and alloys.

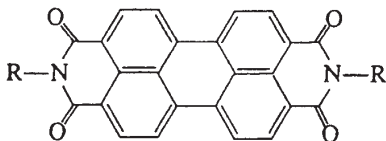


Figure 3. The perylene ring system.

Perylene Pigments Based on the ring structure shown in Figure 3, the perylene pigments represent a class of highly heat and light stable pigments in the red region of the spectrum. In general, these pigments are harder to disperse and more expensive than the QA reds and violets. For the past several decades, perylenes; have been used extensively in automotive coatings. Consequently, they are used more and more in automotive plastics applications.

Because of the increased heat stability, perylenes can be used in a wider variety of blends and alloys than the QA pigments. However, like the QA's, they are not recommended for materials containing polyamide resins.

Other High Performance Organic Pigments Table 2 lists a variety of other high performance organic pigments which have been used successfully in blends and alloys. Of these, the disazo condensation pigments are most noteworthy because of their broad clearance for food contact applications. I have not had success with any of these pigments in polyamide 6/6 or its blends and alloys.

DYES

Because dyes dissolve into the resin matrix during melt processing, dispersion is not an issue. As a rule, dyes have very limited solubility in polyolefin resins. Avoid their use in blends and alloys that have an olefin component. Some desirable properties which most high performance dyes share are:

- transparency
- excellent color strength
- ease of dispersion
- good light fastness in transparent colors

On the other hand, high performance dyes are expensive, have only fair color fastness (tend to migrate from the plastic), and generally have only poor to fair light fastness in opaque colors. In addition, dyes can have adverse effects on the plastic materials themselves. These include

- 1 acting as a plasticizer and reducing thermal properties
- 2 reactions. For example, some grades of the dye Solvent Yellow 163 contain residual chloride ion from an intermediate step and, therefore, cannot be used in polycarbonate (chloride ion promotes the degradation of PC).

The two major classes of dyes used in melt coloring polymeric materials are the anthraquinones and the perinones. Between the two they offer the colorist a complete range of colors from yellow to violet - and many are suitable for use in polyamide blends and alloys.

Table 3. Dyes

Dye	Strength	Heat stability	Weather resistance	FDA status	Cost \$/lbs
<i>Antraquinone dyes</i>					
Solvent Red 111	G	E	E in mass F in tint	no	25.0
Solvent Red 52	G	E	G	no	100.0
Solvent Blue 59	G	F-G	F	no	35.0
Solvent Blue 97	G	E	F	no	55.0
Solvent Yellow 163	G	E	F	no	30.0
Solvent Green 28	G	E	F	no	65.0
Solvent Green 3	G	G	F	no	40.0
Solvent Violet 13	G	F	F	no	45.0
<i>Perinone dyes</i>					
Solvent Red 135	G	G	E in mass F in tint	yes, PET	35.0
Solvent Red 179	G-E	E	F	no	43.0
Solvent Orange 60	G	G	E in mass F in tint	no	40.0
<i>Fluorescent dyes</i>					
Solvent Yellow 160	E	G-E	F	no	100.0
Vat Red 41	E	G	F	no	85.0
Solvent Orange 63	E	G	F	no	115.0

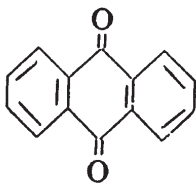


Figure 4. The anthraquinone ring system.

Anthraquinone Dyes

The anthraquinone dyes are based on the structure shown in Figure 4. Key properties are summarized in Table 3. Most commercial anthraquinone dyes have sufficient heat stability to be used in polycarbonate and thermoplastic polyesters. However, as indicated in Table 3, only a handful of these dyes are suitable for polyamide resins and their blends and alloys. Even in these cases caution must be applied. Polyamide materials colored with red anthraquinone

dyes have been observed to slowly shift bluer over time. One hypothesis states the color shift is due to the slow absorption of moisture.

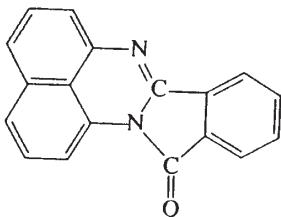


Figure 5. The perinone ring system.

Figure 5 shows the structure of Solvent Orange 60, a perinone dye. The properties of three important perinone dyes are listed in Table I SR 135 and SO 60 have been widely used in engineering resins for decades. Both are used, for example, in automotive lenses. SR 135 is used in both acrylic and PC “tail-light red” formulations, and SO Orange is the familiar “parking light amber”. Because of their heat stability, both are finding use in a variety of engineered alloys and blends. SR 135 reacts with polyamides and is not recommended for NY6 or NY66 applications or in blends and alloys based on this resin. More recently, several producers have been offering SR 179, a perinone with superior heat stability and strength compared to SR 135. It holds up well in both PA6 and PA66, even under high shear injection molding applications.

Fluorescent Dyes

Fluorescent colorants convert energy from the near UV region of the spectrum to visible light. The result is that the colored object reflects more visible light than it receives and appears to glow in daylight. Fluorescent dyes are used widely in the packaging industry to attract the consumer to their products on store shelves. The majority of fluorescent dyes (on a weight basis) goes into the production of fluorescent “pigments”, which are solutions of the dyes at 2-5% concentration in an oligomer carrier. These “pigments” are then compatible with polyolefins such as HDPE (for bottles) and PPRO (for caps). Some grades have sufficient stability for blends and alloys based on olefin and styrenic resins. A small sub-class of these dyes, however, has the heat stability required for engineering resins and their blends and alloys. Again, one cannot use heat stability alone as a guide to which materials can be colored by a given fluorescent dye. Reactivity rears its head. SO 63, e.g., is unsuitable for polyamides.

The structure of Solvent Green 5, a bright primrose yellow dye, is shown in Figure 6, and

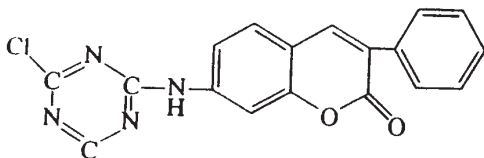


Figure 6. Solvent Green 5 (a fluorescent dye).

the properties of three popularly used high performance fluorescent dyes are given in Table 3. All of the fluorescent dyes suitable for high heat applications share high color and tinting strength, intense chroma, and outrageous pricing. The range is from \$75-125/lb. Some special dyes with extraordinary brilliance are being offered at about \$3000/lb.

What would motivate a colorist to use these expensive dyes in a blend or alloy? Very often the material being colored is very opaque or has an inherent “dirtiness”. Often, fluorescent dyes offer the only means to overcome these inherent characteristics to yield a clean, bright color.

CONCLUDING REMARKS

Make note of this: COLOR SELLS! If you want a new high performance thermoplastic alloy or blend to reach the widest number of appropriate end user markets, you have to be able to color it in a cost effective manner that does not harm its performance properties. Barriers to cost effective coloring include:

- the material's inherent color and opacity;
- chemical incompatibility with one or more polymeric or compatibilizer components;
- physical incompatibility with one or more polymeric components (many materials will not physically accept dyes, e.g.);
- stringent heat stability and/or weathering requirements.

Of these barriers, the one that is most overlooked is the first. Many of the new thermoplastic materials coming into the market place are blends and alloys that are specifically engineered to provide a combination of the properties of the individual polymers. Often these materials combine crystalline and amorphous polymers with an impact modifier. The products of these marriages often contain a maze of phase boundaries that result in light scattering (miliness) equivalent to as much as 0.5% titanium dioxide. Obtaining high chroma colors (e.g., some electrical code colors or even a jet black) in the presence of this inherent miliness becomes an expensive proposition. Often so much color has to be added to the material formulation that critical material properties are affected - a double whammy, cost and performance.