Mark Ryan, The Shepherd Color Co, discusses why high-performance complex inorganic colour pigments make excellent colourants for high-durability resin systems based in fluoropolymers

## High-performance weathering powder coatings colours

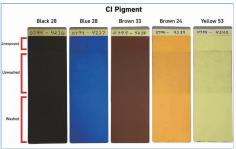
owder coatings are an environmentally friendly way to apply coatings to a wide range of substrates for a number of uses. One of the most demanding applications is for building materials in aggressive environments.

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Organic Red masstone in Kynare 500, 6 years



Figure 1. Titanium dioxide tinted with organic pigments in PVDF/Acrylic in South Florida exposure. Image courtesy of Arkema



re 2. Photos of CICP pigmented PVDF/Acrylic in South Florida (31 years exposure).

All the variables that lead to degradation of coatings – hear, ultraviolet (IV) light, moisture, oxidation agents and chemicals along with simple physical abuse – are present. For these applications, the highest performance components have to be used if specifications, such as those prescribed by American Architectural Manufacturers Association (AAM) 2605 are to be met. Part of the equation is the resin used while the other is the colourant.

The direct UV degradation of polymers is well known and documented. Between the solar UV cut off due to ozone, to the transition between ultraviolet and the visible spectrum, solar radiation is a main driver of degradation. To combat this degradation, resin chemistries were developed that avoided this degradation by reducing the chance of UV breaking carbon bonds or to be transparent and not interacting with the UV light.

The fluoropolymer resins developed in the 1960s followed the transparent/ non-interaction model. For coatings, these resins were typified by the polyvinylidene difluoride (PVDF) chemistries. These thermoplastic polymers, besides being UV transparent, were also highly resistant to acids, bases and solvents. This combination of properties led to their adoption as coatings resins for metal substrates by the coil-coating process, which applies very thin coatings (20µm/0.7mils) at high temperatures. An acrylic resin was included in the coating formulations to facilitate flow, pigment wetting and film formation as the thermoplastic PVDF would melt in the baking cycle, forming a PVDF-Acrylic film that was pigmented.

During initial testing, the coating formulations held up well. An issue arose when colours other than white were formulated and tested in high-UV climates like South Florida. When tints were made with TiO<sub>2</sub> and then current high-performance organics, the tints would lose colour within two years of weathering, often faster than in standard high-performance resins (see Figure 1).

The developers of the PVDF coatings were aware that porcelain enamels were often coloured and retained their colour. Porcelain enamels are essentially glass coatings on metal. The pigments used in these systems must have the high-heat stability and resistance to the effects of molten glass. They are also often used in exterior applications, so colour stability is important. The pigments used for these applications are inorganic instead or organic in nature. To survive the molten glass and high temperatures and have chromatic colours, the pigments are often of a specialised inorganic class called Complex Inorganic Colour Pigments (CICPs), Test panels were prepared with the PVDF/Acrylic resin system and the CICPs. Some of the original panels can be seen in Figure 2. The top area marked by the highest red marker is an unexposed portion, the next area is an unwashed portion and the bottom represents a washed area.

CICPs are the standard colourants used in high-durability coatings applications for liquid and powder coatings for building products. Their robustness stems from the inherent chemical structure that is 'locked-in' by high-temperature calcination up to 2350°F/1300°C. After processing to micron size particles for optimum colour properties, the pigments are basically inert to UV, high-heat, acid/base and chemical attack. They come in a wide range of colours from highly durable blacks, to bright chromatic blues and greens, along with new pigment chemistries that expand the durable colour space in yellow and orange colours.

These CICPs are equally usable in liquid and powder coatings. They are especially useful in powder coatings based on FEVE (fluoroethylene vinyl ether) resin chemistry due to their inherent weathering properties, but they also have excellent opacity and low oil absorption values so that they provide opaque and high-gloss coatings. The FEVE-based powder coatings give inherent processing advantages in that they can be extruded and processed into powder coatings without the need for specialised equipment.

To demonstrate the performance capabilities of FEVE resins with CICP colourants, a number of panels were coated with a FEVE, crosslinked with a blocked-polyisocyanate, processing additives and pigmentation for masstone colours and tints with white.

The panels were electrostatically sprayed to a thickness around 50µm (2mils). The panels were then exposed to a range of accelerated and real-world exposures:

Table 1. QUV-A Testing	q							
Masstone colour change (DE); hours of exposure (QUV-A)								
Pigmentation	500	1000	1500	2000	2500	3000	3500	4000
IR Black PBr29	0.3	0.3	0.4	0.4	0.4	0.4	0.6	0.7
Std. Black PBk28	0.2	0.4	0.6	0.7	0.7	0.7	0.8	0.8
Cobalt Blue PB136	0.9	0.9	1.1	1.0	1.2	1.1	1.4	1.5
Cobalt Green PG50	0.3	0.3	0.5	0.6	0.6	0.6	0.7	0.7
RTZ orange PY216	0.5	0.9	0.8	0.8	0.8	1.1	1.0	1.2
Chrome Titanate PBr24	0.4	0.8	0.8	0.7	0.7	0.9	0.8	0.9
NTP Yellow PY227	0.6	1.1	1.0	1.0	1.0	1.3	1.3	1.4
4:1 Tint colour change (DE); Hours of exposure (QUV-A)								
Pigmentation	500	1000	1500	2000	2500	3000	3500	4000
IR Black PBr29	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Std. Black PBk28	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cobalt Blue PB136	0.3	0.3	0.3	0.3	0.4	0.3	0.3	0.3
Cobalt Green PG50	0.2	0.2	0.3	0.2	0.4	0.3	0.3	0.3
RTZ orange PY216	0.2	0.4	0.4	0.4	0.4	0.5	0.4	0.5
Chrome Titanate PBr24	0.2	0.3	0.4	0.4	0.4	0.5	0.5	0.5
NTP Yellow PY227	0.3	0.5	0.6	0.6	0.7	0.8	0.8	0.9

Table 2. Emmaqua weathering					
Masstone colour change (DE) Emmaqua (MJ exposure					
Pigmentation	290	580	870		
IR Black PBr29	0.7	0.6	1.1		
Std. Black PBk28	0.3	0.4	0.4		
Cobalt Blue PB136	1.1	1.3	1.8		
Cobalt Green PG50	0.4	0.5	0.7		
RTZ orange PY216	0.1	0.1	0.5		
Chrome Titanate PBr24	0.4	0.4	0.2		
NTP Yellow PY227	0.5	0.6	0.4		
4:1 Tint colour change (DE) Emmagua (MJ exposure)					
Pigmentation	290	580	870		
IR Black PBr29	0.3	0.3	0.3		
Std. Black PBk28	0.3	0.3	0.3		
Cobalt Blue PB136	0.5	0.5	0.6		
Cobalt Green PG50	0.2	0.2	0.2		
RTZ orange PY216	0.2	0.3	0.2		
Chrome Titanate PBr24	0.3	0.4	0.4		
NTP Yellow PY227	0.6	0.9	0.9		
290MJ/m² roughly equivalent to one year weathering					

-	QUV-A (ASTM	154)

EmmaquaSouth Florida

A wide range of pigments¹ was exposed to better understand the relationship between accelerated and South Florida exposure. These exposures have started and follow-up testing and analysis will be conducted.

Initial results for colour retention on masstone panels and tints with white (four

Table 3. South Florida weathering				
4:1 Tints colour change (DE) South Florida (months)				
Pigmentation	6	12		
IR Black PBr29	0.1	0.1		
Std. Black PBk28	0.1	0.1		
Cobalt Blue PB136	0.3	0.3		
Cobalt Green PG50	0.2	0.3		
RTZ orange PY216	0.1	0.2		
Chrome Titanate PBr24	0.1	0.5		
NTP Yellow PY227	0.5	1.0		
Masstone colour change (DE) South Florida (months)				
Pigmentation	6	12		
IR Black PBr29	0.4	0.4		
Std. Black PBk28	0.1	0.3		
Cobalt Blue PB136	0.8	1.0		
Cobalt Green PG50	0.5	0.4		
RTZ orange PY216	0.2	0.2		
Chrome Titanate PBr24	0.1	0.4		

parts white: one part colour pigment) display low DE values (see **Tables 1-3**).

NTP Yellow PY227

0.8

A workhorse pigment liake & Dements between the coating is the Pigment Black & Dementsty because of its weathering properties, controllable colour, blue-shade colour and futting properties. Many new formulations are based on infrared (fill) reflective pigments, of which the black is the most impactful. By absorbing in the visible for dark colour, but reflecting away the surivisible IN wedeentshs, building mate as

## **PIGMENTS**

can remain cooler than if made with standard black pigmentation

The cobalt-based blue and green pigments are used because the organic alternative phthalocyamine-based chemistries have been shown to change colour over time. The Pigment Green 50 chemistry is also based on a formula without chromium for applications that are looking for alternatives to Chromium Oxide (PGIAT).

While many powder coating chemists may be familiar with Pigment Brown 24 titanate yellow because of its heat stability for standard powder coatings, the pigment chemistry is also very useful in high durability coatings because of its red-shade yellow tone and excellent weathering properties. Newer pigment chemistries to powder coatings are the NTP Yellow<sup>a</sup> and RTZ Orange. These two pigments together expand the range of durable colours available past standard inorganic pigments, into the range of organic pigments. Bright RAL colours, such as RAL 1003 Safety Yellow can be matched with all inorganic pigments.

High-performance complex inorganic colour pigments make excellent colourants for high-durability resin systems based in fluoropolymers. Continued studies in different weathering protocols will look at using accelerated weathering to better predict real world performance. Real world testing will demonstrate usefulness of the CICP colourants.

## References

- 1. Piaments used in study
  - IR Black PBr29 Shepherd Color Black 10G996 Std. Black PBk28 – Shepherd Color Black 430 Cobalt Blue PBi36 - Shepherd Color Blue 211 Cobalt Green PG50 – Shepherd Color Green 10G655
  - RTZ Orange PY216 Shepherd Color Orange 10P340
  - Chrome Titanate PBr24 Shepherd Color Yellow 10C229
  - NTP Yellow PY227 Shepherd Color Yellow 10P150.
- NTP Yellow Pigment technology is protected under the following patents: US Pat. RE45,382, Australian Pat. 2011 264994, Chinese Pat. 103097299, European Pat. 2580163, Japanese Pat. 5778264. South Korean Pat. 101809028.

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