New Pigment Developments for the Plastics Industry: Organic Ultramarine Pigments

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Abstract

Ultramarine blue is a staple pigment of the plastics industry. It is a bright red shade blue pigment offering exceptional performance properties such as being heat stable, light fast, migration resistant and non-warping in poly olefins at a good cost/performance ratio. Despite such exceptional performance properties the ultramarine chemistry is limited in colour breadth or "functionality" to blue, pink and violet. Organic pigments on the other hand can span the total colour space from yellows through to reds, violets, greens and blues. However within the organic chemistry area, each pigment family has performance benefits and negatives. For example, phthalocyanine blue has exceptional light and weathefastness but for the most part has poor warping properties in poly olefins. This paper describes a new family of pigments utilising the lattice structure of ultramarine pigments chemically bound to an organic chromophore. This new family has the broad colour functionality of organic pigments combined with many of the performance benefits of ultramarine pigments.

Introduction

The ultramarine family of pigments span the reddish blue to pink and violet shades of the colour spectrum. Ultramarine is essentially a three-dimensional aluminosilicate lattice with entrapped sodium ions and ionic (negatively charged) sulphur groups within a cage like structure. The nature of the sulphur groups are responsible for the colour. There are two types of sulphur groups in blue ultramarine, S^{3-} and S^{2-}, both being free radicals stabilized by the lattice entrapment (Figure 1)[1].

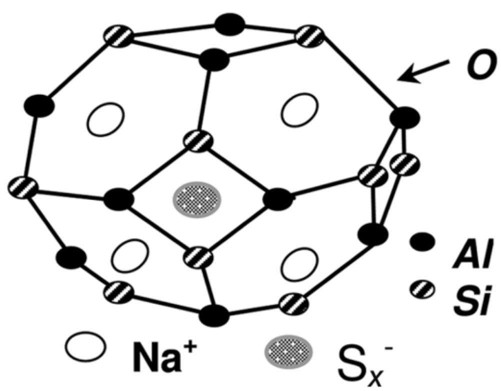

Figure 1 Simplified structure of ultramarine blue

The aluminosilicate lattice provides an excellent environment to entrap the sulphur groups and thus provide a very stable almost inert bright coloured pigment.
The basic ultramarine color is a rich, bright reddish blue, the red–green tone varying with chemical composition. The violet and pink derivatives have weaker, less saturated colours[1].

The major use of ultramarine pigments is in plastics where ultramarine blue can be used in any polymer. Violet ultramarine has a maximum processing temperature of 280 °C, and pink ultramarine has a maximum processing temperature of 220 °C. As such violet and pink ultramarine pigments are limited in scope to essentially poly-olefin based applications.

Some of the major benefits of ultramarine based pigments are:

- Bright shades
- Non-migratory
- High lightfastness
- Non warping in polyolefins
- High heat resistance (for Ultramarine blues)
- Relatively low cost

However there are some limitations within the performance of the chemistry too:

- Poor acid resistance
- Limited in breadth of shade or “functionality” to red shade blues, pink and violet
- The violets and pink shades have limited heat stability.

Organic pigments are also widely used for coloration of plastics. The chemistries used are broad such as:

- Metal azo pigments, e.g. Pigment Yellow 62 (PY.62) and Pigment Red 57:1 (PR.57:1)
- Diarylides pigments, e.g. PY.83
- Dianisidine pigment, e.g. PO.16
- Disazo pigments, e.g. PY.155, PY.93, PR.144
- Phthalocyanine Blues, e.g. PB.15:3, PB.15:1
- Phthalocyanine Greens, e.g. PG.7
- Carbazole violets, e.g. PV.23

Organic pigments are in general bright high chroma pigments with high tinctorial strength. They are synthetically produced from raw materials ultimately stemming from the oil industry. Their performance properties are vast and varied depending on the chemistry used. For example phthalocyanine based pigments have very high heat resistance and weatherfastness but cause warpage in poly-olefin based polymers. Metal azo pigments on the other hand, such as PY.62, have relatively low heat stability (approx.

240C) and lightfastness, and can also cause warpage in poly-olefin based polymers. Diarylide pigments can also cause warpage (e.g. PY.83) and can also suffer from migration or plate out.

Due to their chemical nature, compared to ultramarine blue, almost all organic pigments have a higher cost/performance ratio.

Table 1 below lists selected performance properties of specific organic pigments as selected examples.

Table 1 – Performance Properties of Selected Organic Pigments

Pigment	Chemistry	Shade	Heat Stability (°C)	Relative Lightfastness	Warpage
PB.15:3	Phthalocyanine	GS-blue	>300	High	3
PB.60	Indanthrone	RS-blue	>300	High	3
PG.7	Phthalocyanine	Green	>300	High	3
PY.62	Metal azo	GS-yellow	240	Low	2
PY.83	Diarylide	RS-yellow	200	Low	3
PY.93	Disazo	GS-yellow	>280	High	3
PY.155	Disazo	GS-yellow	260	Medium	3
PY.180	Disazo	GS-yellow	280	High	1
PY.191	Metal azo	RS-yellow	300	Low	1
PR.48:2	Metal azo	BS-red	240	Low	1
PR.57:1	Metal azo	BS-red	260	Low	1
PR.122	Quinacridone	BS-red	300	High	2
PR.254	DPP	YS-red	300	High	3
PV.23	Carbazole	Violet	300	High	3

Key:
GS = Green shade, RS = red shade, YS = Yellow shade, BS = blue shade
Warpage – 1 = minimal warpage, 2 = some warpage, 3 = severe warpage

As can be seen in table 1 many organic pigments can cause warpage in poly-olefins. In addition very few organic pigments can be used in engineering type resins such as polyamide, due to the relatively low heat stability of the organic pigments and the reactive nature of the resins. For example metal azo pigments, benzimidazolone pigments, disazo pigments and even DPP are not recommended for use in polyamide resins.

In an attempt to combine some of the performance attributes of organic based pigments with the performance attributes of ultramarine based pigments research was carried out to incorporate organic chromophores into the lattice structure of ultramarine pigments. The performance of the resultant organo-ultramarine pigments has been assessed and presented in the following sections.

Experimental

Preparation of masterbatches – the pigments were dispersed in HDPE using a high intensity mixer.

Heat stability measurements – the resultant masterbatch samples were letdown to 1% pigmentation in HDPE and injection molded on a Kawaguchi injection molding machine at 20°C intervals starting at 200°C (control) until colour failure.

Lightfastness – plastic colour HDPE chips based on 1% pigment and 1:1 tints were exposed using a carbon arc fadeometer. The colored plastics chips were exposed in the fadometer for 5 cycles of 72 hours, 360 hours. The color change of the exposed versus unexposed colored plastics chips was measured. The assessment is based on delta E data.

Warpage – the pigments were dispersed in a high intensity disperser at 0.1% pigmentation in H.D.P.E. They were granulated and ten plaques were prepared for each pigment using the Kawaguchi Injection Moulding Machine set at 220^{o}C with a dwell time of three minutes and water-cooling. The mould used was specially prepared for the warpage test with a cavity of 60 mm x 60 mm x 2.5 mm.

The warpage of a test plaque is the relationship of vertical to horizontal shrinkages. The vertical and horizontal sides of each plaque were measured using a digital calliper and its warpage in percentage was then calculated according to the following equation.

Equation for determining Warpage:

$$\%\ \text{Warpage} = \left[\frac{\left(\left(\frac{60-Vertical\,(mm)}{60}\right)x100\right)-\left(\left(\frac{60-Horizontal(mm)}{60}\right)x100\right)}{\left(\frac{60-Horizontal(mm)}{60}\right)x100}\right]x100$$

Warpage Rating:

The industrial warpage rating of a pigment in polyolefins was determined according to the percent of warpage induced by the pigment in H.D.P.E. and the rating is described below.

Percent Warpage	Warpage Rating	Degree of Warpage
0 - 10%	1 (good)	minimal warpage
11 - 20%	2 (suitable)	some warpage
21 - 100%	3 (unsuitable)	strong warpage

Results and Discussion

A range of organo-ultramarine based pigments were prepared using a proprietary synthesis technique incorporating an organic chromophore into the ultramarine lattice. The organic chromophore essentially replaces the ionic sulphur groups within the lattice cage. The resultant pigments pigments are bright in colour spanning the complete colour spectrum from yellow to orange to red to violet to blue and finally to green (see figure 2).

Figure 2 – examples of colour range of the new Organo-Ultramarine pigments

Typically all the organo-ultramarine pigments produced exhibited non-migratory properties in polyolefins. No colour transfer or bleed characteristics could be seen. The performance of the pigments for heat stability, light fastness and warpage was compared against traditional organic and ultramarine blue pigments. The comparative results are shown in tables 2 to 6 and figures 3 to 8.

Yellow Pigments (table 2 and figure 3)

The shade of the yellow organo-ultramarine pigments can be varied from green shade yellow to very red shade yellow, as can be seen in figure 3. The greenest shade pigment developed to date, DCC Y 1, is greener than PY.180 and the reddest shade yellow, DCC Y 4, is redder than PY.83. DCC Y 2 and Y 3 are green to mid shade yellows similar to PY.62. As such the pigment family has the potential to expand the yellow colour space.

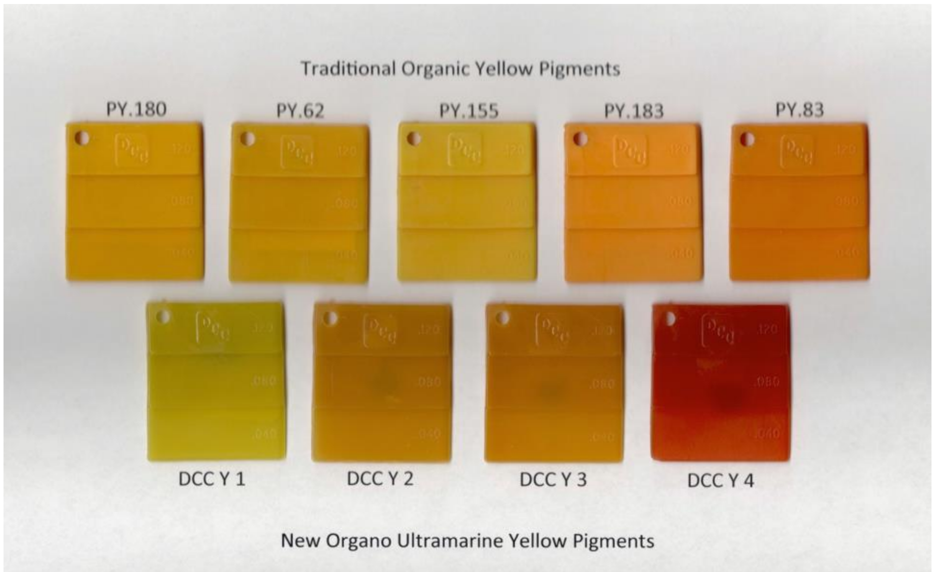

Figure 3 – Shade Comparison of Yellow Organo-Ultramarine Pigments vs Traditional Organic Yellow Pigments

The new yellow organo-ultramarine pigments have a heat stability in the area of 260°C with a lightfastness of medium to low in masstone and tint, similar to PY.62 and PY.155, allowing their use in polyolefin type applications (table 2). All the organo-ultramarine yellow pigments exhibited low/no warpage.

Table 2 – comparison of certain performance properties of yellow pigments

Pigment	Chemistry	Shade	Heat Stability (°C)	Relative Lightfastness		Warpage
				Masstone	Tint	
PY.62	Metal azo	GS-yellow	240	Medium	Low	2
PY.83	Diarylide	RS-yellow	200	Medium	Low	3
PY.155	Disazo	GS-yellow	260	Medium	Low	3
PY.180	Disazo	GS-yellow	280	Medium	Low	1
PY.183	Metal azo	RS-yellow	300	Medium	Low	1
DCC Y 1	Organo Ultramarine	GS-Yellow	260	Low	Low	1
DCC Y 2	Organo Ultramarine	RS-Yellow	TBD	TBD		
DCC Y 3	Organo Ultramarine	RS-Yellow	260	Low	Low	1
DCC Y 4	Organo Ultramarine	RS-Yellow	260	Medium	Low	1

Red Pigments (table 3 and figure 4)

The shade of the new organic-ultramarine red pigments can be seen in Figure 4. Overall they are blue shade pigments approaching that of PR.57:1 and PR.122. DCC R 5 is the bluest of the group, being much bluer in shade than PR.122.

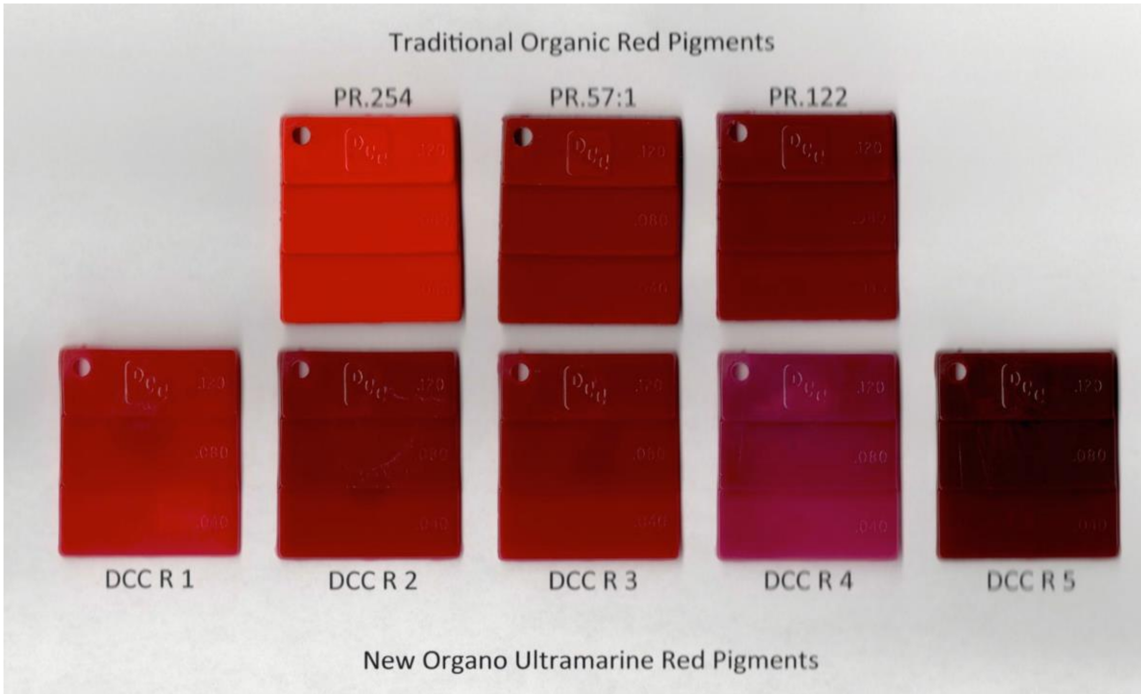

Figure 4 – Shade Comparison of Red Organo-Ultramarine Pigments vs Traditional Organic Red Pigments

The performance of the red organo-ultramarine pigments is higher than that of the yellows with the heat stabilities ranging from a low end of 240°C to a high of 340°C (DCC Red 1) in HDPE allowing for use in high heat applications such as injection molding. In addition, the warpage of the new red pigments is very low. As with the yellow pigments the lightfastness performance of the red organo-ultramarine pigments is similar to that of the standard performance azo pigments, PR.48:2 and PR.57:1, being medium to low lightfastness in masstone and tint.

Table 3 – comparison of certain performance properties of red pigments

Pigment	Chemistry	Shade	Heat Stability (°C)	Relative Lightfastness		Warpage
				Masstone	Tint	
PR.48:2	Metal azo	BS-red	240	Low	Low	1
PR.57:1	Metal azo	BS-red	260	Low	Low	1
PR.122	Quinacridone	BS-red	300	High	High	2
PR.254	DPP	YS-red	300	High	High	3
DCC R1	Organo Ultramarine	BS-red	340	Medium	Low	1
DCC R 2	Organo Ultramarine	BS-red	240	Low	Low	1
DCC R 5	Organo Ultramarine	BS-red	280	Medium	Low	1
DCC R 4	Organo Ultramarine	BS-red	280	Medium	Low	1
DCC R 3	Organo Ultramarine	BS-red	240	Low	Low	1

Blue Pigments (table 4 and figure 5)

Copper phthalocyanine blue (e.g. PB.15:3), ultramarine blue (PB.29) and Indanthrone Blue (PB.60) are the major blue pigments used in the plastics industry. Copper phthalocyanine blue is a green shade blue, PB.29 is redder and purer in shade and PB.60 is a very deep red shade blue pigment. The new blue organo-ultramarine pigments have a broad shade range, from a very green shade, almost turquoise blue (DCC B 1) to a very deep red shade blue (DCC B 4), similar to PB.60. The breadth of shade or shade functionality is broad allowing for some new colour matching potential, in particular in the very green shade area (DCC B 1)

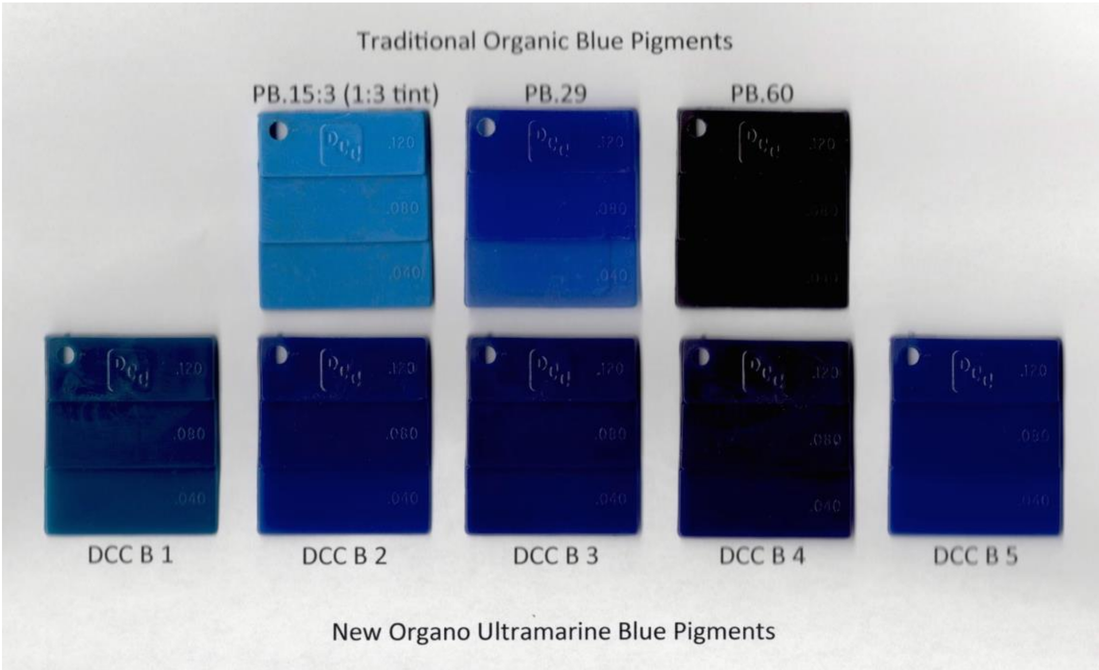

Figure 5 – Shade Comparison of Blue Organo-Ultramarine Pigments vs Traditional Organic Blue Pigments

All the blue organo-ultramarine pigments mirror the warpage rating one expects from ultramarine blue itself, with low/no warpage. The heat stability of the new blue pigments ranges from 240 to 260°C allowing full use in poly-olefin applications. In addition DCC B 3 has high performance light fastness characteristics, not fading even after 1000 hours in a weatherometer. Such a performance allows for use in non warping weatherfast applications, such as garbage bins and other exterior uses.

Table 4 – comparison of certain performance properties of blue pigments

Pigment	**Chemistry**	**Shade**	**Heat Stability (°C)**	**Relative Lightfastness**		**Warpage**
				Masstone	**Tint**	
PB.15:3	Phthalocyanine	GS-blue	>300	High	High	3
PB.29	Ultramarine	RS-blue	>300	High	High	1
PB.60	Indanthrone	RS-blue	>300	High	High	3
DCC B741	Organo Ultramarine	GS-blue	260	TBD		1
DCC B3	Organo Ultramarine	GS-blue	240	TBD		1
DCC B7	Organo Ultramarine	GS-blue	240	TBD		1
DCC B14	Organo Ultramarine	GS blue	240	High	High	1
DCC Blue 45	Organo Ultramarine	RS-blue	240	TBD		1

Violet Pigments (table 5 and figure 6)

The new violet pigments present an interesting potential for new shade matches in the markets. The traditional organic pigment, PV.23, is a strong highly chromatic violet pigment. The new violet pigments have a broad shade range, from very red shades (e.g. DCC V 4) to much bluer shade products (e.g. DCC V 1). With such a variety in shades available new colour matches are possible expanding the colour gamut.

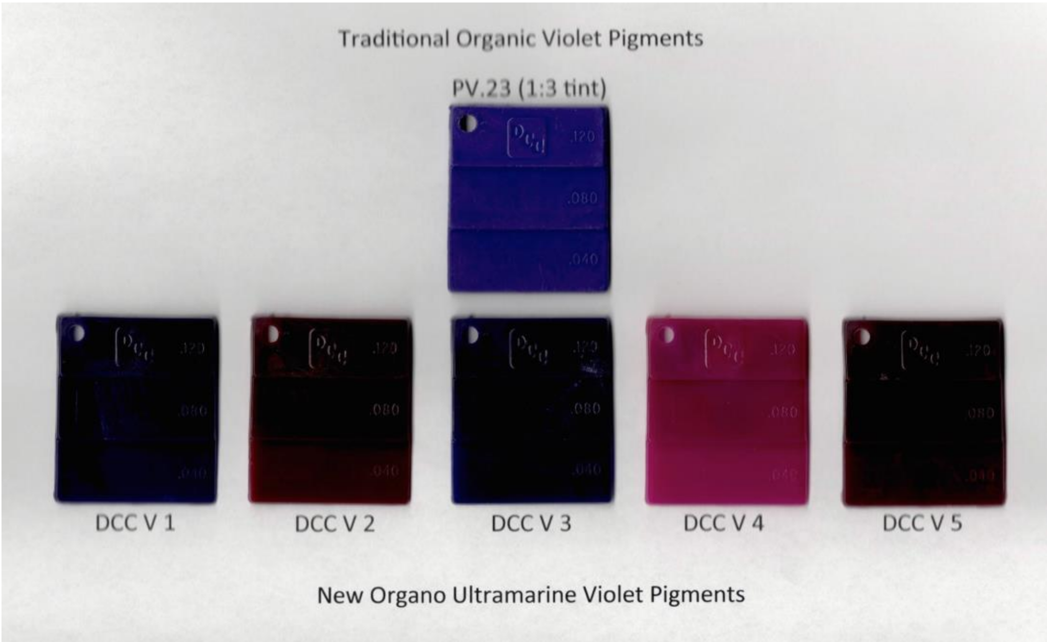

Figure 6 – Shade Comparison of Violet Organo-Ultramarine Pigments vs Pigment Violet 23

The performance of the violet organo-ultramarine pigments is interesting as they start approaching medium to high performance. Overall the heat stability ranges from 260°C to 320°C (DCC V 2 and V 5) with a light fastness rating from high in masstone (DCC V 5) and low in tint. The additional benefit of the new violet pigments is that their warpage is low compared to PV.23 offering new potentials in molding applications.

Table 5 – comparison of certain performance properties of violet pigments

Pigment	Chemistry	Shade	Heat Stability (°C)	Relative Lightfastness		Warpage
				Masstone	Tint	
PV.23	Carbazole	Violet	300	High	Medium	3
DCC V 1	Organic Ultramarine	BS-violet	260	TBD		1
DCC V 2	Organo Ultramarine	RS-violet	320	Medium	Low	1
DCC V 3	Organic Ultramarine	BS-violet	260	TBD		1
DCC V 4	Organo Ultramarine	RS-violet	300	Medium	Low	1
DCC V 5	Organic Ultramarine	RS-violet	320	High	Low	1

Green Pigments (table 6 and figure 7)

The shade of the green organo-ultramarine pigment is similar to the traditionally used green pigment, copper phthalocyanine green (PG.7).

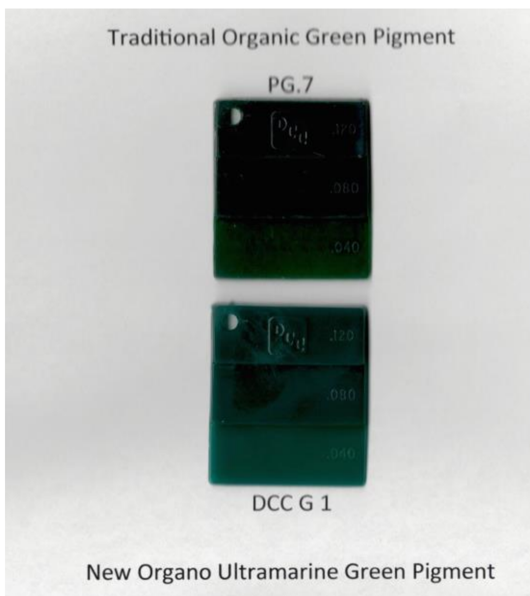

Figure 7 – Shade Comparison of Green Organo-Ultramarine Pigment vs Pigment Green 7

As with the other organo-ultramarine pigments DCC G1 is non warping which is a significant benefit over phthalocyanine green, PG.7, the main pigment used in this colour space. With a heat stability of 260°C the pigment can be used in poly-olefin applications, with the advantage of being non warping for molding uses.

Table 6 – comparison of certain performance properties of violet pigments

Pigment	Chemistry	Shade	Heat Stability (°C)	Relative Lightfastness		Warpage
				Masstone	Tint	
PG.7	Phthalocyanine	Green	>300	High	High	3
DCC G1	Organo Ultramarine	Green	260	Low	Low	1

Conclusions and future work

As has been demonstrated a new range of pigments has been developed by incorporating an organic chromophore, replacing the ionic sulphur groups inside the ultramarine blue lattice. The performance of these new organo-ultramarine pigments, can be summarized as follows:

- A broad shade functionality or range, from yellows, oranges, reds, violets, blues and greens
- Low/no warping
- Depending on the pigment a heat stability range from 240 to 320°C
- Lightfastness from low to high, again depending on the pigment.
- Non-migratory

Future work will be to optimize the dispersion and strength of the pigments and assess their performance in engineering resins such as polyamide and polyester based systems.

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References

1) Industrial Inorganic Pigments third edition, G. Buxbaum and G Pfaff, Printed by Wiley