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POLYMERS PAINT COLOUR JOURNAL

Inside: Egyptian Coatings Show 2017 Catalogue

Inside: Top 25 paint manufacturers in Europe

Small is beautiful –

Nanodiamond composite coatings improve abrasive wear resistance

Loulou Rozek, Borchers, discusses novel dispersants for optimum pigment dispersions.

Developing colour to its full potential

The automotive and performance coatings industries have seen a significant shift from solvent to waterborne systems in recent years. This change has brought challenges to paint formulators. One of those challenges is producing colours to match those of solvent systems in vibrancy and undertones, particularly with low surface functionality pigments such as perylene, phthalocyanine blues and high jet carbon black pigments. To overcome those challenges, novel dispersants with unique structure and chemistry have been developed to produce better colour performance and jetness than ever before in waterborne coatings. Understanding the relations between the dispersant's chemistry, structure and affinity to organic pigment surface will help the formulator not only optimise colour performance but also understand and control other parameters that are key to production efficiency, such as grind time (energy) and grind viscosity (pigment loading).

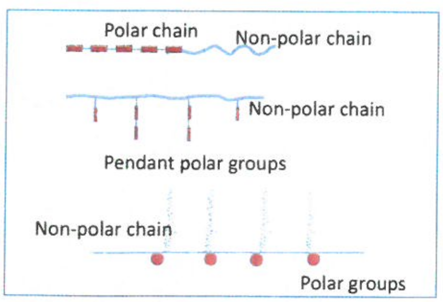


Fig 1. Typical structures of polymeric dispersants

Resin-free pigment concentration	1	2
Disp. 1 (40% active)	18.76	0.00
Disp. 2 (50% active)	0.00	15.00
DI water	50.74	54.50
Defoamer	0.50	0.50
PR 179	30.00	30.00
	100.00	**100.00**

Table 1. Concentrate formulation, benchmark

STRUCTURE OF DISPERSANTS

There are two key properties common to all of the polymeric dispersants, pigment-affinic groups and polymer side chains for sterrical hindrance **(figure 1)**.

The polar groups will interact with pigment surface polar sites through hydrogen bonding or dipole-dipole interactions creating a barrier and providing sterrical hindrance **(figure 2)**.

When pigments particles have few polar sites available on the surface, those interactions will not take place and the dispersant will fail to properly wet the surface of the pigment and provide the necessary stabilisation. Such pigments are carbon black, perylene and phthalocyanine pigments **(figure 3)**.

Waterborne novel dispersants with polyurethane chemistry have been developed to create additional interaction mechanism to the hydrogen bonding and dipole-dipole interactions **(figure 4)**.

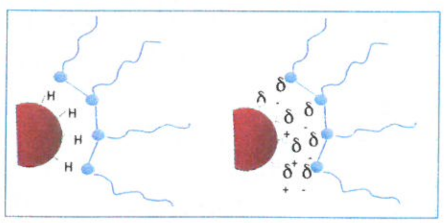


Fig 2. Interactions of dispersant's polar groups with pigment surface polar sites

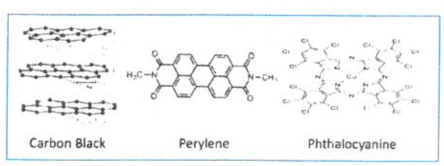
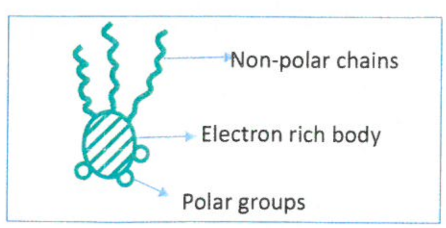


Fig 3. Pigments with low surface functionalities



This additional interaction is the pie-pie interaction between the electron rich aromatic body of the dispersant and the aromatic rings on the surface of the pigment **(figure 5)**.

The difference in pigment surface wetting efficiency between typical polymeric dispersants and novel dispersants and the resulting effect on the particle size, viscosity and viscosity stability of the dispersion was studied. Additionally, colour development or jetness, gloss and haze of the finished paint were analysed for perylene (PR 179) and high jet carbon black (PBk 7) in a 2K waterborne system. The study was done with grind times of half, one, two, four and eight hours for the PR 179 and half, one, two and four hours for PBk 7.

CASE STUDY: PR 179

The following concentrates were made with a benchmark dispersant (Disp. 1) and novel dispersant (Disp. 2) using 2mm glass beads as the grinding media **(Table 1)**. The letdowns in WB 2K system are shown in **Table 2**.

Figure 6 shows the mean particle size evolution over time for both dispersants. It is evident early in the grinding process that the novel dispersant (Disp. 2) exhibits a finer particle size than the benchmark. The difference of around 0.1 micron remains as the dispersion grinds up to eight hours.

Colour strength and hues ($L^*a^*b^*$) for each of the time units were measured **(figure 7)**. As predicted from **figure 6**, the colour development with Disp. 2 is stronger than Disp. 1. The colour over time becomes stronger for both dispersants (L^*). Consequently, the red undertone (a^*) increases with time and is stronger for Disp. 2 than Disp. 1. The yellow undertone (b^*) is stronger with Disp. 2, and is in fact stronger at half an hour than it is at four hours with Disp. 1. As PR 179 is a yellow shade red pigment, it is safe to say that the true colour of the pigment has developed early on in the process with Disp. 2.

The difference in grinding efficiency is reached after two hours of grind-time with the benchmark (Disp. 1) and one hour with the novel dispersant (Disp. 2).

Figure 8 shows the difference in colour development with the two dispersants. Disp. 2 appears more chromatic with no low haze.

Gloss measurements at 20° angle show significantly higher values for the novel dispersant in comparison to the benchmark **(figure 9)**. The gloss at half hour grind with the novel dispersant is two units higher than that of the benchmark at four-hour grind. This indicates that finer particle size of the benchmark at four hours (0.8μm) compared to that at half hour with the novel dispersant (1.27μm) does not necessarily correlate to better gloss. Other factors, such as pigment wetting, stabilisation and compatibility play a key role in achieving high gloss.

VISCOSITY AND VISCOSITY STABILITY

Pigment dispersions that are well stabilised tend to exhibit lower viscosities and maintain it over time. A lower viscosity will allow the formulator to raise the pigment loading, resulting in a more efficient process. Viscosity stability over time is an indicator of how well the dispersion is stabilised, and less stable dispersions may have a low initial viscosity but that tends to increase over time. **Figure 10** shows that dispersion made with novel dispersant remains low in viscosity after one month RT storage while the benchmark shows significant increase in viscosity.

CASE STUDY: PBK7

A similar study was performed with high jet carbon black pigments. Concentrate formulations are given in **Table 3** and let-downs in **Table 4**. The grind times were done at half, one, two and four hours and 0.8mm zirconium beads were used as the grinding media.

Mean particle size, jetness, 20° gloss and haze graphs were evaluated to study the pattern of all the parameters.

Figure 11 shows Disp. 2 (novel dispersant) carbon black dispersion to have half the particle size (0.20μm) compared to 0.4μm with Disp. 1 (benchmark) within the first half hour of grind-time. Although after four hours of grinding, Disp. 1 reduced in particle size to below 0.1μm or slightly less than Disp. 2, the graph on the right shows jetness reduction over time from 298 to 291. The novel dispersant (Disp. 2) on the other hand, produced jetness of 320 within the first half hour and increased to 328 after four hours of grind time.

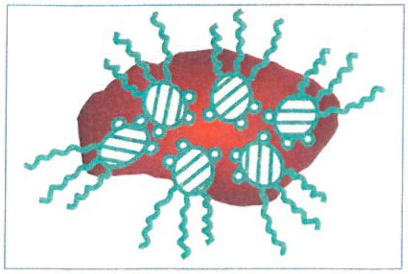


Fig 5. The electron rich body of novel dispersants creates a strong interaction with pigment surface

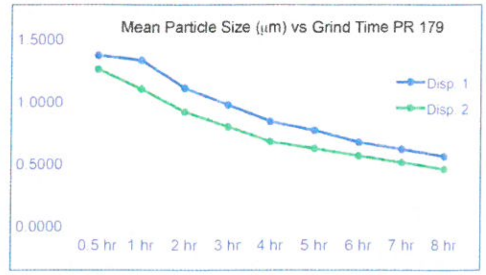


Fig 6. Particle size of novel dispersant against benchmark

System	Concentration	Formulation	Pigment in paint
Clear 2k WB w hardener	1.5	8.5	4.5%
White 2k WB w hardener	0.5	9.5	1.5%

Table 2. Let-down in WB 2K PU systems

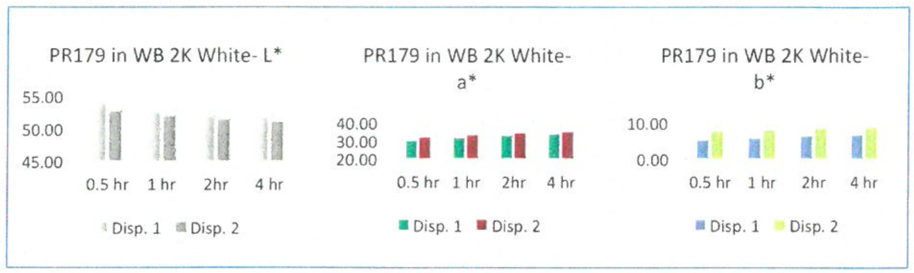


Fig 7. Hunter L*a*b* values novel dispersant and benchmark

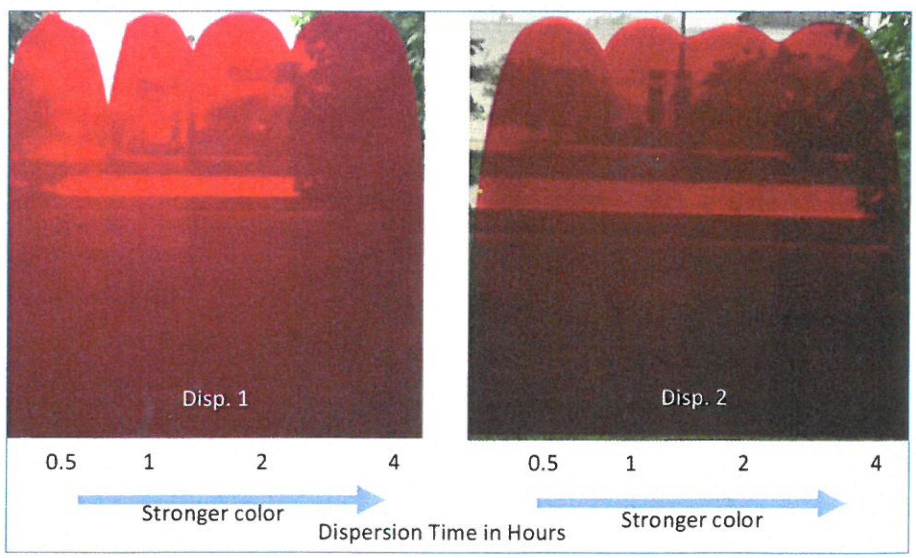


Fig 8. PR 179 colour development over time with Disp. 1 and Disp. 2

The gloss and haze shown in **figure 12** follow the similar pattern, higher gloss and lower haze with the novel dispersant. It is interesting to note that finer particle size with Disp. 1 at two and four hour grinds did not result in higher jetness; in fact the jetness dropped further with more grinding and lower particle size.

When fine pigment particles lack good surface wetting and stabilisation, they tend to re-agglomerate and produce

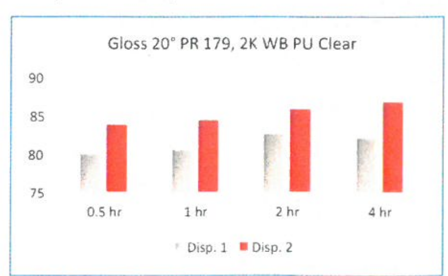


Fig 9. Disp. 2 has higher gloss at 0.5hr than Disp. 1 at four hr

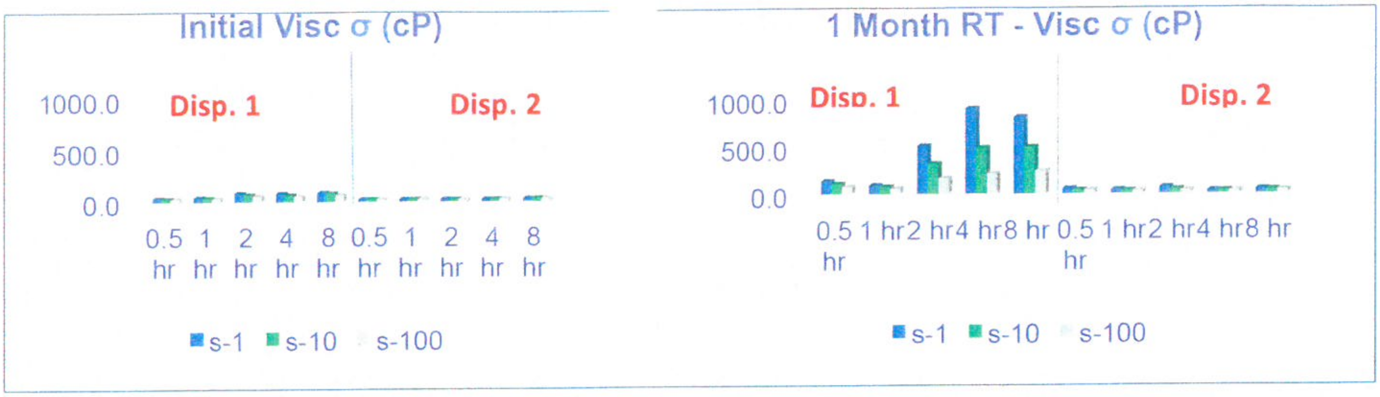


Fig 10. Viscosity initial and one month at RT

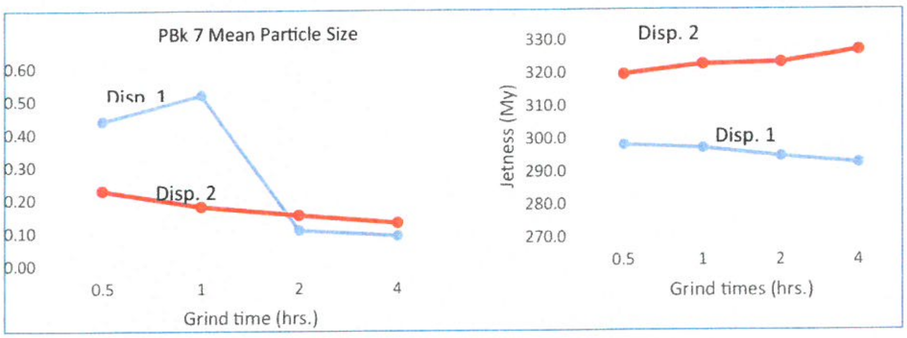


Fig 11. (Left) mean particle size over time and (right) jetness over time

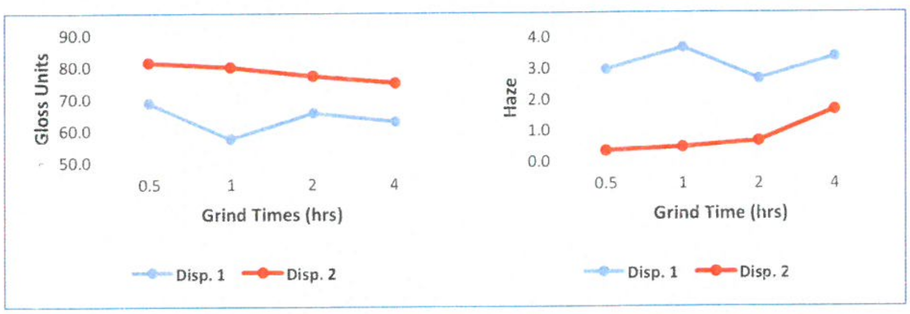


Fig 12. (Left) 20° gloss, (right) haze

Concentrate	1	2
Disp. 1 (40%)	37.50	0
Disp. 2 (50%)	0.00	30.00
DI water	47.00	54.50
Defoamer	0.50	0.50
PBk 7 Grade 1	15.00	15.00
	100.00	100.00
Dispersant on pigment)	100%	100%

Table 3. Concentrate formulation, benchmark (Disp. 1) and novel dispersant (Disp. 2)

Let down		
Clear 2k WB (comp 1 + 2)	13.50	13.50
Concentrate	3.00	3.00
Pigment on total paint	3.33%	3.33%

Table 4. Let-down in WB 2K PU system

larger particles, which in turn impacts colour development or jetness negatively. Additionally, pigment wetting performance impacts the viscosity of the grind. **Figure 13** shows reduced viscosity with Disp. 2.

Jetness was evaluated the previous two black pigments as well as two more known to the automotive industry using the same formulations as in **Tables 3 and 4**. The jetness in all cases was higher with novel dispersant Disp. 2, as shown in **Table 5**.

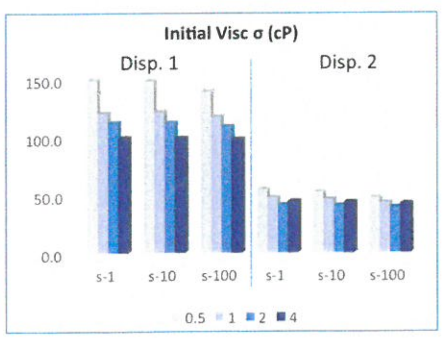


Fig 13. Three step viscosity (cPs)

2K WB 3.33% pigment	Bayhydrol 2470/Bayhydur 304 Dispersant	Jetness
PBk 7 Grade 1	Ref. 3	287
PBk 7 Grade 1	BG0851	309
PBk 7 Grade 2	Ref. 3	303
FW255	BG0851	320
Emperor 2000	Ref. 3	310
Emperor 2000	BG0851	352
Monarch 1300	Ref. 3	290
Monarch 1300	BG0851	313

Table 5. Jetness values for four PBk 7

CONCLUSION

Engineering polymeric dispersants to maximize dispersant-pigment interaction with PR 179 and high jet carbon blacks has proven to positively impact not only the colour development of the pigment but, equally important, the viscosity and viscosity stability of the grind. While reducing the mean particle size of the grind through longer milling process improves colour strength, it is not the only determining factor for good colour development. Pigment surface wetting and stabilisation of the finely dispersed particles are crucial to delivering the desired hues and jetness. Optimising such interaction will enable formulators to create stable dispersions with less milling time allowing for colour and process optimisation.

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