

The star performer

Star-shaped molecule produces pigment concentrates with very low VOC content

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Three wetting and dispersing additives were compared for their ability to produce high solids pigment concentrates. In most formulations, a new star-shaped dispersant provided exceptional viscosity reduction, thus allowing VOC levels to be reduced in mixing paints, concentrates and direct grinds. It is also shown that binder-free concentrates are not always more expensive than those using a grinding resin.

The need to reduce VOC contents poses a particular challenge to formulators of coatings. The coatings must satisfy environmental guidelines, but also meet performance criteria.

Alongside waterborne formulations, high-solids and ultra-high solids systems are an important alternative to conventional solventbased coatings. In such systems, the low organic solvent content is achieved by using tailored binders of low molecular weight and thus low viscosity. However, there are natural limits to this way of reducing solvent levels and in many cases further reduction of the VOC content is not possible.

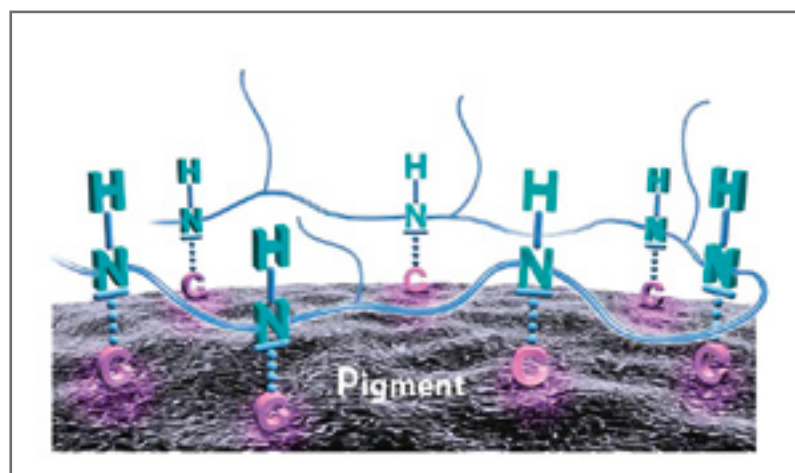


Figure 1: Adsorption of a dispersing additive on a pigment surface

Advantages	Disadvantages
Cost of raw materials	Moderate colour strength
High solids content	Limited degree of pigmentation because of high viscosity
Little effect on mechanical properties	Limited application range because of limited compatibility

Table 1: Advantages and disadvantages of pigment concentrates containing binder

This article shows further options for reducing the VOC content of solventborne coatings using modern wetting and dispersing additives with outstanding viscosity reduction characteristics, and compares binder-based with binder-free pigment concentrates.

Resins limit scope of solventborne pigment concentrates

The most costly step in manufacturing a coloured coating is dispersion of the pigment. Large volume products are usually manufactured by direct grinding, in which various pigments are dispersed in one step in the main binder, which is commonly also used in the letdown. Pigment concentrates are used here to adjust the final colour [1].

In the case of special colours or small batches, pigment concentrates allow cost-effective, flexible production. The base paints are coloured simply by mixing.

Traditionally, pigment concentrates containing binders are used in solventborne industrial coatings. Grinding resins such as ketone or urea-aldehyde resins ensure broad compatibility and hence applicability of the concentrates.

In addition to their good price/performance ratio, these resins stabilise the pigments and promote colour strength. The lowest possible amount of wetting and dispersing additives is used to reduce viscosity and increase colour strength. In spite of this, the compatibility of concentrates containing binders is limited.

On the whole, these concentrates with their binders have little effect on the mechanical properties of the coating. The arguments to date for and against binder-based pigment concentrates are summarised in Table 1.

Because of more stringent environmental legislation, the VOC content of pigment concentrates must be reduced. As the ketone or urea-aldehyde resins used are already of low molecular weight (under 2000 g/mol (M_n)) it is almost impossible to lower the viscosity of the solution by further decreasing the molecular weight of such resins. Dispersing additives that provide exceptional viscosity reduction are thus becoming increasingly important.

Novel additives reduce viscosity

Wetting and dispersing additives are polymers which contain functional groups such as carboxyl, amino or phenyl with an affinity for pigments and also a side-chain soluble in the medium (Figure 1) [2]. The pigment-affinic group should align quickly and permanently to the surface of the pigment. The side chain should be well solubilised by the coating matrix and – looked at simply – keep the pigment particles separated.

The reduction of interactions between the coated pigment particles means that the viscosity is low (Figure 2).

From a thermodynamic point of view, the resulting free movement leads to a high entropy and low energy. Both factors change unfavourably if pigment particles approach each other. This principle is indispensable for long-term storage stability and achieving a good reduction in viscosity.

Stabilisation can be further improved if additive and binder associate together so that the polymer coat around the pigment particle is thicker [3]. This is the reason behind the use of grinding resins. However, a high viscosity is not consistent with high stability. The binder molecules either do not effectively reduce the interactions between the pigment particles or interact with each other. The result is a lower pigment loading in the pigment concentrate and a simultaneous need for more organic solvent. To achieve higher pigment loading, grinding resins are therefore combined with dispersing agents.

Very efficient wetting and dispersing agents have block structures. A statistical distribution of different building blocks in the polymer is not advantageous. The polymers can be linear, comb-like or star-shaped. The pigment-affinic area is in the linear chain, on the backbone of a comb-like molecule or in the centre of a star-like structure.

In star-shaped structures, many groups of high pigment affinity can be concentrated in a small space and

Results at a glance

- »» The need to reduce VOC levels while still meeting performance demands poses ever-greater challenges for formulators. In the case of high-solids systems, there are limits to how far VOC can be reduced by the use of tailored binders with low viscosity.
- »» Three wetting and dispersing additives have been compared in relation to their ability to produce high-solids pigment concentrates, with or without the use of a binder resin.
- »» In most formulations tested, the use of a new star-shaped dispersant molecule provided exceptional viscosity reduction, which allows VOC levels to be reduced in mixing paints, concentrates and direct grinds.
- »» Although binder-free concentrates are normally considered to be more expensive, due to the high cost of the extra dispersant, the tests carried out here showed that this is not always the case.



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Figure 2: Schematic representation of viscosity reduction due to reduction of interactions between the pigment particles

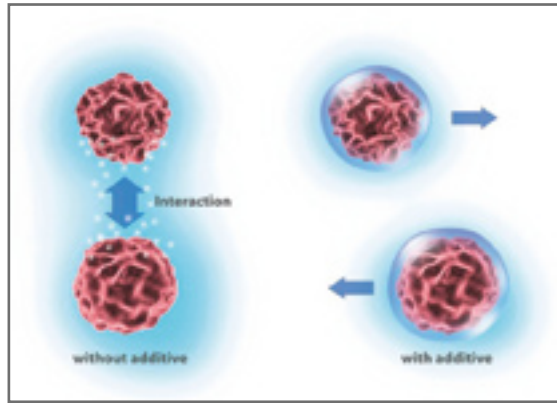
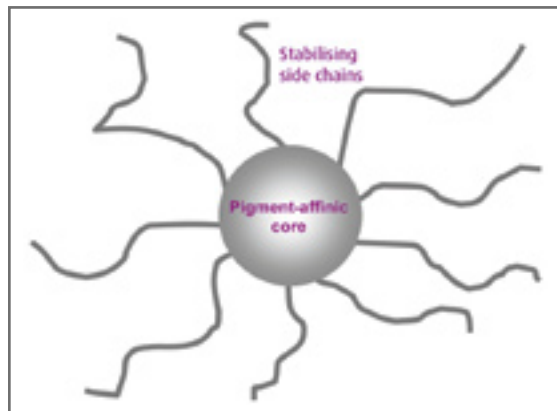


Figure 3: Schematic representation of star-shaped wetting and dispersing agent



modification with stabilising side chains is easy. Such polymers have a very high molecular weight with compact spatial arrangement and thus low solution viscosity. Interactions between the coated pigment particles are reduced.

The polarity of the stabilising side chains can be varied over a wide range and thus made suitable for any particular coating. Compact, star-shaped dispersing agents are therefore very efficient for formulating easy-flowing millbases with high pigment content.

Taking these aspects into account has led to the manufacture of new, star-shaped wetting and dispersing additives with excellent viscosity reduction (Figure 3).

Dispersants compared in pigment concentrates

Pigment concentrates with and without binder based on one of the new wetting and dispersing additives were produced and compared. Priority was given to optimising the VOC content; costs were only a secondary consideration. By definition, binder-free formulations do not contain any grinding resin.

In the following discussion, pigment concentrates based on phthalocyanine blue (PB 15:4), iron oxide red (PR 101) and titanium dioxide (PW 6) are used as examples (see Table 2). A commercial urea-aldehyde resin was used as the grinding resin.

The new star-shaped dispersing additive was compared with commercial benchmarks which had viscosity-reduc-

Table 2: Formulations for pigment concentrates with and without binder

Raw material	Phthalocyanine blue (PB 15:4)		Iron oxide red (PR 101)		Titanium dioxide (PW 6)	
	Binder-free	With binder	Binder-free	With binder	Binder-free	With binder
Grinding resin (60 % in MPA)	-	25.0	-	19.0	-	20.6
Methoxypropyl acetate (MPA)	67.5	42.5	9	7.8	7.7	11.1
Bentone paste	-	-	-	-	0.3	-
Dispersing additive	12.5	12.5	21	8.2	12.0	3.3
Pigment	20.0	20.0	70.0	65.0	80.0	65.0
Total	100.0	100.0	100.0	100.0	100.0	100.0
Dispersing additive solids relative to pigment [%]	25	25	12	5	6	2
Grinding resin solids relative to pigment [%]	-	75	-	17.5	-	19
Density [kg/l]	1.2	1.2	2.6	2.4	2.5	2.0
VOC content [g/l] when using star-shaped additive	855	675	398	430	283	407
Non-volatiles [%]	28.75	43.75	84.7	82.1	88.5	79.7



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tion characteristics considered by formulators to be very good. According to the manufacturers, the statistically branched polyurethane is recommended for systems containing binder and the block polymer polyacrylate especially for binder-free systems. These two additives chosen for comparison represent established chemical classes.

The formulations are different. In the case of PB 15:4 the concentrate containing a binder uses the same amount of dispersing agent as the binder-free variant to maintain the viscosity as low as is compatible with a high pigment loading and the highest stability. The pigment content is the same in both cases.

In contrast, the iron oxide red concentrates with binder contained less additive but also 5% less pigment. The binder-free concentrate with 80% titanium dioxide was thickened with bentone paste to control the precipitation of the pigment.

The rheological properties were investigated in accordance with DIN EN ISO 3219 (using a "RotoVisco1" cone and plate viscometer from Thermo Electron, with CP 35/2°, D = 0 - 1000 s⁻¹).

To determine colour intensity, the pigment concentrates were added to unpigmented 2-pack PU or polyester/melamine paints (at pigment loadings of PR 101: 8%, or PB 15:4: 4%). The test paints were applied to Leneta cards (wet film thickness: 150 µm). The colour properties were determined spectrophotometrically (using an X-Rite type "SP62" spectrophotometer).

Lower viscosity achieved in most cases

Viscosity reduction is a good criterion for the quality of a dispersing additive. The more pronounced the viscosity reduction, the higher the pigment loading can be and the less organic solvent is required. A high pigment loading is desirable on economic grounds in order to disperse as much pigment as possible in a single grinding operation.

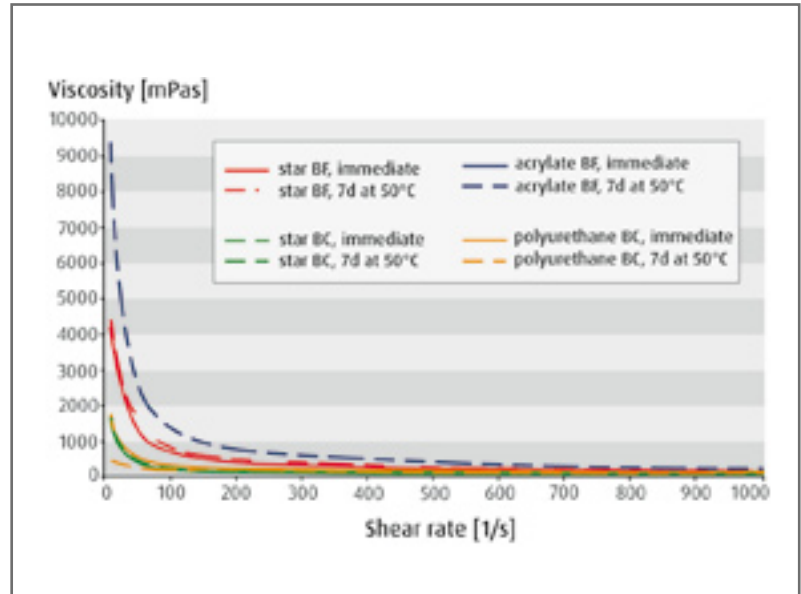


Figure 4: Comparison of the viscosities of the PB 15:4 concentrates before and after storage: BC: binder-containing; BF: binder-free

It is clear from Figures 4 and 5 that the benchmarks based on polyacrylate and polyurethane dispersants do not provide extremely low viscosities. Although in the case of PB 15:4 the polyurethane performed similarly to the star-shaped additive, significantly higher viscosity values resulted with PR 101. The viscosity of the polyacrylate-based concentrates was always higher than that of those based on the star-shaped additive.

By and large, differentiation must be based on the type of pigment. With inorganic pigments, the binder-free technology leads to lower viscosities despite unusually high pigment loadings. This advantage is not discernable in the organic pigment PB 15:4. The viscosity of the binder-based concentrates is somewhat lower for the same pigment loading.

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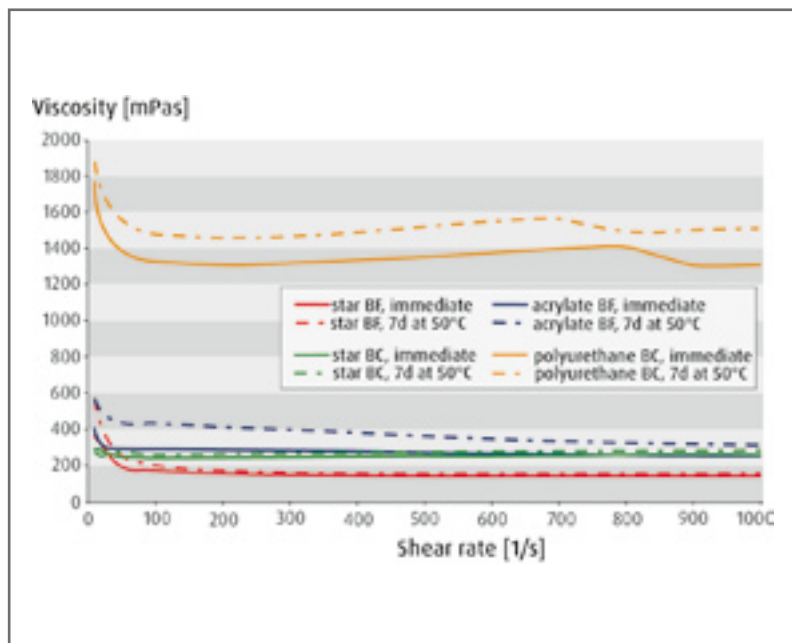


Figure 5: Comparison of the viscosities of the PR 101 concentrates before and after storage: BC: binder-containing; BF: binder-free

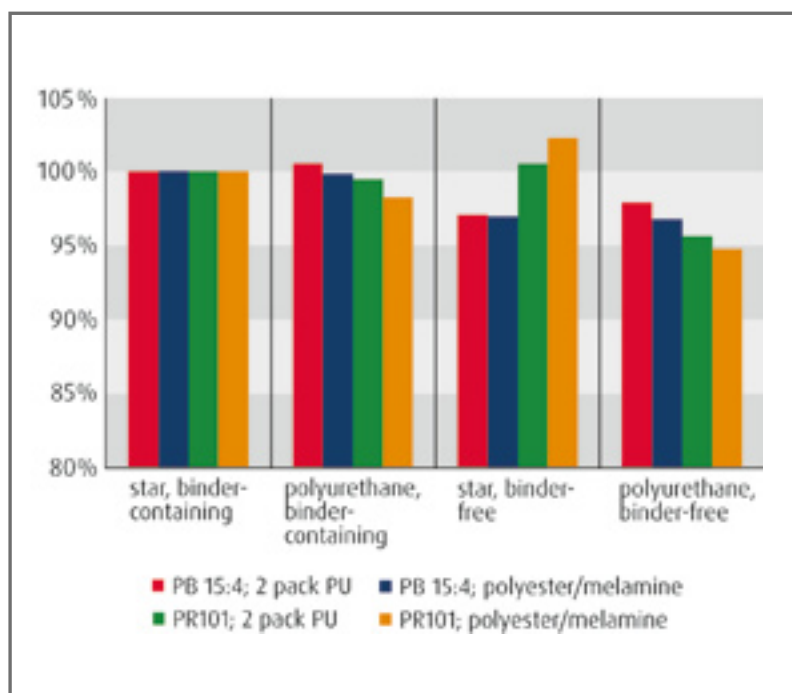


Figure 6: Relative colour strength of the pigment concentrates after letdown (star shaped additive, formulation containing binder = 100 %)

In all cases stability was adequate, although that of the PR 101 formulations based on the comparison additives was at the limit. In the case of PW 6, the formulation of a free-flowing, binder-free concentrate was only possible using the star-shaped additive. Use of the comparison additives resulted in paste-like products.

Star-shaped additive shows gains in colour strength

For better comparison, the unpigmented test coatings were treated with the same amount of pigment, so that the amount of each concentrate used in the coating varied. Figure 6 shows the colour strength of the concentrates in the various paints relative to the colour strength of the concentrates containing binder made with the star-shaped additive. With PR 101, the star-shaped additive increased the colour strength compared to the benchmarks; with PB 15:4, a similar level was always achieved.

The colour strength of the binder-free concentrate with the star-shaped additive is slightly greater (by about 2%) than that of the variant with binder. The pigment loading is also higher, so that the same colour strength can be achieved using 10% less pigment concentrate. With PB 15:4, the combination of the grinding resin with the dispersing additive results in approximately 3% higher colour strength.

Lowest VOC levels with star-shaped dispersant

With PB 15:4, the star-shaped additive provides pigment concentrates with binder with the lowest possible viscosity at equal pigment loadings. This variant thus offers significant advantages in terms of solids content and VOC content (see Table 2).

The results of the grinds of the inorganic pigments using the star-shaped additive were truly remarkable. Despite the high density of the inorganic pigments, the VOC content of the binder-free PR 101 concentrate and PW 6 grind are lower (by approximately 8% and 31% respectively) because of the greater pigment concentration. The formulation of binder-free pigment concentrates with a VOC content below the limiting value of 400 g/l was therefore successful.

Similar costs for concentrates with or without binder

Up till now, the main argument against using binder-free pigment concentrates in solvent-based coatings has been cost, because the price of an additive is frequently higher than that of a grinding resin.

Raw material costs relative to colour strength were calculated for the various pigment concentrates, using manufacturers' standard prices (averaged in the case of the dispersing additives).

In the case of PB 15:4 and PW 6, the raw material costs of the two variants were comparable, at about € 750/100 kg for PB 15:4 and € 300/100 kg for PW 6. Taking into account the production costs (time/kg of pigment dispersed), the binder-free technology offers advantages because of its higher pigment loading.

In the case of PR 101, there is a definite link between price and VOC content. The raw material costs of the binder-free variant are some 22% above those of the binder-based variant (€ 380 and € 310 respectively). The reduction in production costs due to higher pigment loading shifts the relationship only slightly.

However, the emphasis during development of the concentrates was on achieving the lowest possible VOC content. Binder-free PR 101 concentrates with raw material costs considerably lower than those of the binder-containing variants can easily be formulated with the new additive since the concentration of the inexpensive PR 101 can be increased to $\geq 75\%$. Because of the high density of PR 101, the VOC content is then, however, above 400 g/l.

The influence of the concentrates on typical properties, such as drying rate, gloss, pendulum hardness and weathering resistance, was evaluated in various coatings after letdown. Contrary to initial assumptions, the values of the binder-based and binder-free concentrates were comparable. The grinding resin had no positive effect.

New dispersant has a starring role in VOC reduction

The use of the new technology described above enables binder-free pigment dispersions of inorganic pigments to be formulated with lower VOC content than that of counterparts containing binder.

If raw material and production costs are based on the amount of pigment dispersed, binder-free technology can offer an alternative to the established practice of us-

ing highly compatible grinding resins, although costs and VOC content can be diametrically opposing factors.

The outstanding characteristic of the star-shaped wetting and dispersing additive described here is its powerful viscosity reduction effect. Compared to dispersing additives based on different chemistry, it results in significant advantages in terms of reducing the viscosity of binder-based and binder-free pigment concentrates, mixing paints and direct grinds while other properties are at a level similar to this best performer.

The viscosity reduction effect of the new dispersing additive will help to keep coatings below the further reduced limits specified in impending VOC regulations. Liquid grinding resins such as polyether ketones will become increasingly important here. Formulations with a VOC content below 250 g/l already provide an indication of what lies ahead [4]. ◀

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