

Designed for selective adsorption

Dispersants based on core/shell structures stabilize pigments in reactive systems

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Dispersing additives with a hyperbranched core/shell structure have been developed with encapsulated aminic pigment-affinitive groups. These can be used in solvent-borne and solvent-free coating systems. They provide highly effective stabilisation of various types of pigment while avoiding any undesirable interactions with reactive coating systems.

The property profile and the associated fields of application of a coating material are essentially determined by the resin that is used. The origins of these resins are diverse and can basically be divided into natural substances, modified natural substances and synthetics [1]. In modern coating systems, synthetically produced oligomeric substances used as resins play a primary role in satisfying the considerable mechanical requirements and providing the necessary chemical and physical resistance of high-performance coating materials. Reactive multicomponent resins, which crosslink through chemical reactions, are of special importance. These include, in particular, the classic two-component systems (2-pack epoxy and 2-pack polyurethane systems), which crosslink by a polyaddition reaction at room temperature, as well as stoving systems based on a primary resin and a crosslinking resin (usually melamine or phenolic resins), which crosslink at higher temperatures with an acidic catalyst [2].

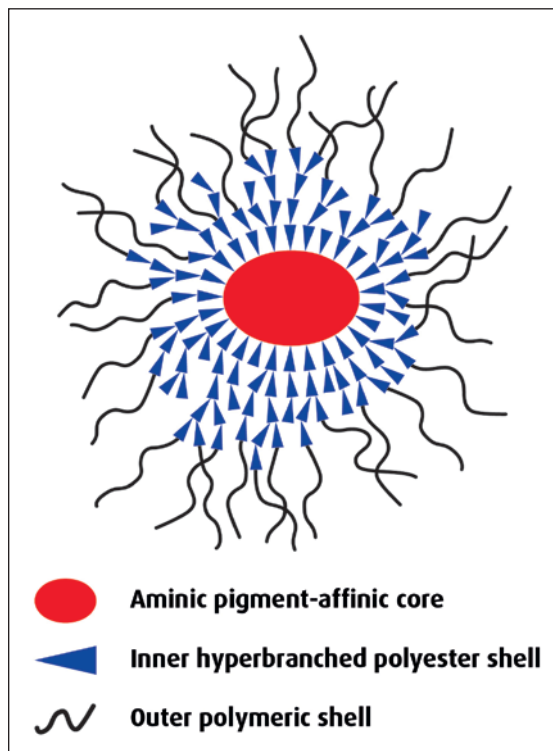


Figure 1: Schematic representation of dispersing additives based on hyperbranched core/shell structures

The nature of pigment dispersants

Polymeric dispersing additives are now widely used in order to meet the demand for high-quality visual properties such as high transparency or hiding power, to ensure that colours have long-term shade stability with enhanced gloss and minimum haze, and to meet the mechanical and chemical requirements in pigmented reactive coating materials. These amphiphilic surface-active additives use either steric or electrostatic hindrance to stabilise the pigments and fillers that have been used in the coating material [3]. Generally speaking, all dispersing additives are composed of low-molecular to high-molecular weight chain segments that have a stabilising effect, combined with at least one pigment-affinitive anchoring group. The interactions with the pigments enable the additive to be adsorbed onto the pigment surface by means of these anchoring groups. This is the prerequisite for effective and long-lasting stabilisation of a pigment. As most pigments used in coating applications carry an acidic surface treatment, dispersing additives with aminic

Table 1: Possible interactions between the coating system and the aminic dispersing additive

System reference	Component A	Component B	Possible system/additive interactions	Effect on coating properties
1	Epoxy	Poly(amido) amine	Interaction with epoxy part	Major effect on storage stability
2	Polyol	Polyisocyanate	Catalysis of curing	Shorter pot-life
3	Alkyd	Oxygen	Complexation of metallic dryers	Longer drying time
4.1	Acrylate/melamine	Acid catalyst	Partial catalyst deactivation	Incomplete curing reaction
4.2	Polyester/melamine	Acid catalyst	Partial catalyst deactivation	Incomplete curing reaction

pigment-affinitive groups, in particular, are considered to be very effective additive structures because they can undergo stable acid/base interactions with the pigment surface. These aminic dispersing additives significantly improve pigment stabilisation; however, in various reactive systems they can cause some undesirable side-effects, leading to adverse effects on the property profile of the formulated systems. *Table 1* provides an overview of the possible interactions between the aminic additives and various reactive coating systems.

Three structurally different additives compared

This application technology study compares innovative aminic dispersing additives based on the hyperbranched core/shell structures shown in *Figure 1* with established structural types to investigate whether a high degree of pigment stabilisation can be achieved in representative reactive systems, while at the same time preventing possible interactions between the coating system and the additive. Three structure types were compared in this study. In each case, these possess both aminic pigment-affinitive groups of a similar chemical nature and basicity as well as polymeric side chains of a similar polarity. As shown in *Figure 2*, these structure types differ in terms of their basic skeleton:

- » Structure type 1: linear copolymer with freely accessible aminic anchoring groups;
- » Structure type 2: branched polymer with sterically shielded aminic anchoring groups;
- » Structure type 3: core/shell polymer with sterically encapsulated aminic core.

Three different coating chemistries studied

These three differently structured dispersing additives were first used to produce solvent-borne pigment con-

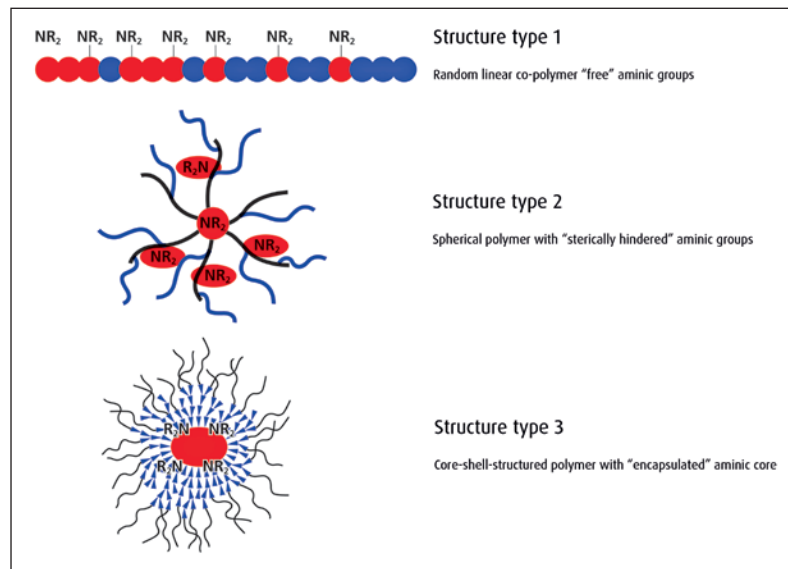


Figure 2: Comparison of structural types of dispersants tested

centrates based on a universal grinding resin and different pigments (Colour Index references P.R. 122; P.R.170; P.G.7; P.B.15:4, and P.Bl.7, fine-sized). The same pigment concentrates without the dispersing additive served as a reference. After 24 hours, the viscosity of the individual pigment concentrates was measured (cone/plate geometry, cone diameter = 25 mm, angle = 1°, temperature = 23 °C (73 °F), shear rate = 1 s⁻¹).

In a second step, these pigment concentrates were used in different solvent-borne reactive coating systems. A 2-pack epoxy system (bisphenol A/polyamide curing agent), a 2-pack polyurethane system (OH-functionalised acrylate with aliphatic-aromatic and/or pure aliphatic polyisocyanate), and an acid-catalysed stoving system (acrylate/melamine) served as let-down systems.

The test systems formulated in this manner were poured onto a Polyester foil which was fixed at a 65° angle. The

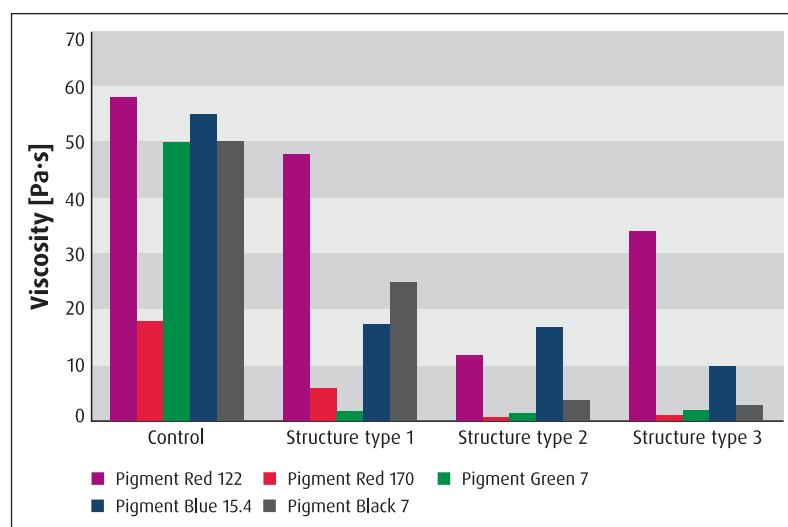


Figure 3: Influence of the various structural types of dispersant on the viscosity of the pigment concentrates

Results at a glance

- » Hyperbranched core/shell structures with aminic pigment-affinitive anchoring groups were used as the basis for new dispersing additives for solvent-borne and solvent-free reactive systems.
- » The specially designed hyperbranched core/shell structure can prevent undesirable interactions between reactive coating systems and the additive.
- » Practical tests confirmed that the use of this type of additive gave effective viscosity reduction and improved stability on storage in both epoxy and 2-pack polyurethane systems.
- » Tests in a stoving system showed that the new structure performed well, whereas a linear copolymer dispersant appeared to interfere with the curing mechanism.

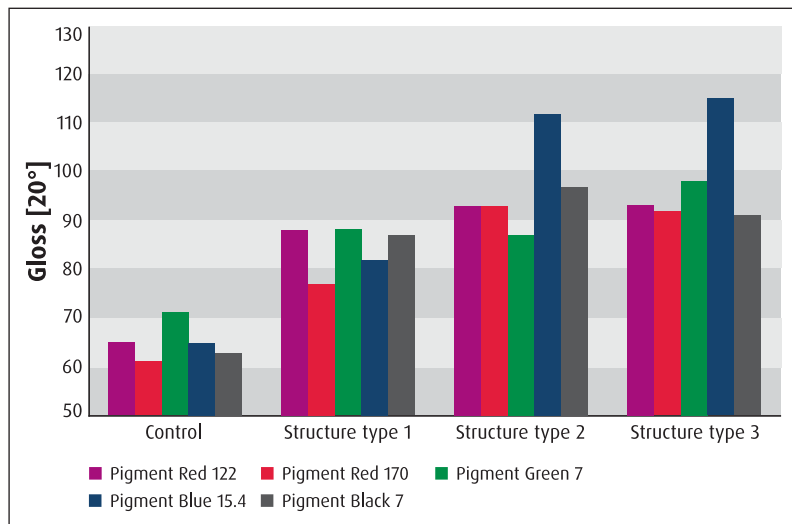


Figure 4: Influence of the different structure types on the gloss of the pigmented 2-pack polyurethane system (OH-functionalised acrylate/pure aliphatic polyisocyanate)

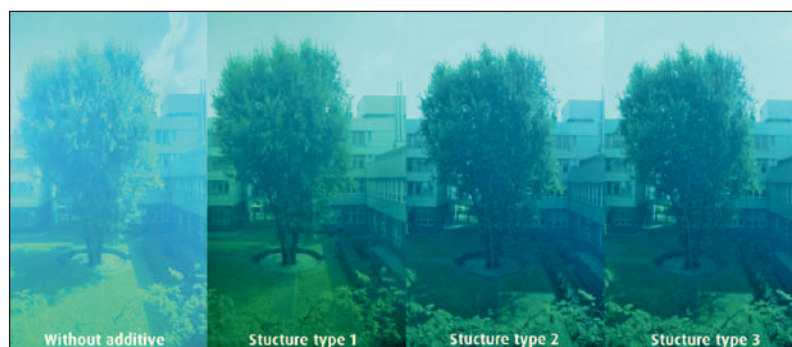


Figure 5: Influence of the different structure types on the transparency of the pigmented 2-pack polyurethane system (OH-functionalised acrylate/pure aliphatic polyisocyanate), here using P.G. 7

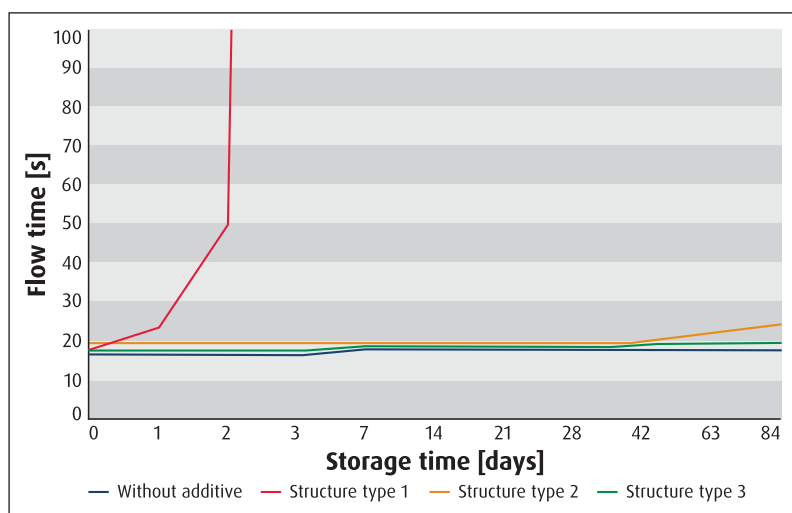


Figure 6: Influence of the structure types on the storage stability of the epoxy base component

qualities of the pigment stabilisation in terms of optical properties were then established by measuring the gloss (at a 20 ° angle) and haze, and by visually assessing the transparency, colour strength and colour shift under both transmitted and incident lighting conditions.

In addition to this, measurements were made with respect to the influence of the different structure types on the undesirable interactions (listed in Table 1) with each coating system. In the case of the 2-pack epoxy system, the pigmented base coating (epoxy component) was stored for twelve weeks at 50 °C (122 °F) and the flow time was measured at regular intervals.

For the pigmented 2-pack polyurethane system, the resulting flow times were measured during the curing reaction between the acrylate and the aliphatic-aromatic and/or pure aliphatic polyisocyanate curing agent. In the case of the acid-catalysed stoving systems, the influence of the various structure types on the mechanical properties was determined by the König pendulum hardness test (in accordance with DIN EN ISO 1522).

Two dispersants effectively reduce viscosity

The reduction of the millbase viscosity by the different dispersing additives gives a rough indication of their efficiency. As shown in Figure 3, when compared with the reference, all three structural types significantly reduced the viscosity, regardless of which pigment was dispersed. Structure types 2 and 3 in particular showed a significant reduction in the paste viscosities, for which structure type 2 was especially good with P.R.122, P.R.170 and P.G.7, whereas structure type 3 gave the best results with P.R.170, P.B.15:4 and P.B.I.7. For all pigments tested, these two structure types gave higher efficiency than structure type 1 – quite considerably in some cases.

Gloss and transparency differences are considerable

In addition to the viscosity reduction of the pigment concentrates, the three structural types were also tested in terms of their influence on the visual properties of the selected coating systems. Figure 4 shows the influence of the three structural types on the gloss of the 2-pack polyurethane system based on the pure aliphatic polyisocyanate curing agent.

In this case again, both the branched polymer with sterically shielded aminic anchoring groups (type 2 structure) and the additive based on the hyperbranched core/shell structure (type 3 structure) gave the best results. For all pigments tested, these two structural types produced a significant increase in gloss compared with the reference. Structural type 1 also tended to significantly improve the gloss; however, this did not always occur, particularly for stabilisation of P.R.170 and P.B.15:4.

This trend in results is also evident in the transparency of the pigmented coating systems. For example, in the 2-pack polyurethane system coloured with the pigment concentrate based on P.G. 7, structure types 2 and 3 produced an outstanding transparency in conjunction with a bluish/greenish colour shade (Figure 5), which is yet another indicator of very effective pigment stabilisation.

In this case, structure type 1 with a more yellowish/greenish colour shade did not match the good results of the other two dispersing additives.

The results shown for the example of the 2-pack polyurethane system were also confirmed in the tests with the 2-pack epoxy and the acid-catalysed stoving system. They can therefore be considered essentially representative for the performance specification of the three different structure types.

How structure correlates to viscosity stability

Figure 6 provides an even clearer picture of the influence of the three types of structure on the storage stability of the epoxy base component. After just a few days, the epoxy base component containing the additive with structure type 1, which has freely accessible aminic anchoring groups, showed a drastically increased flow time, finally resulting in a gelling of the system. Structure type 2, which has sterically shielded aminic anchoring groups, had no medium-term influence on the storage stability of the epoxy base component. However, the viscosity did start to increase after a storage period of six weeks.

Only structure type 3, which has an encapsulated core, showed no viscosity increase across the entire storage period of twelve weeks. Indeed, it provided the same storage stability as the system that did not contain any wetting and dispersing additives.

In the case of the 2-pack polyurethane system, the influence of the structures on the pot-life (period of time until the initial viscosity has doubled after the two components have been mixed) the results were more variable, depending on the curing agent that was used.

As shown in Figure 7, none of the additives shortened the pot-life of the pure aliphatic polyisocyanate. However, compared to a system with no additives and in the case of the reactive aliphatic-aromatic curing agent, the pot-life was considerably shortened with structure type 1 and at least slightly shortened with structure type 2.

Structure type 3 did not shorten the pot life. This different behaviour can be attributed to the exposed aminic functionalities in structure type 1 that catalyse the formation of polyurethane and thus shorten the pot life.

Stoving system shows differences in hardness

The differing influence of the various structure types on system properties was also confirmed by the mechanical tests on the acid-catalysed stoving system (Figure 8). Structure types 2 and 3 showed a damping of the pendulum swing comparable to that of the reference system with no additives. Because of the significant differences in results during testing of the mechanical properties, it is assumed that structure type 1 led to incomplete curing of the system - an assumption based on the interaction of the acid catalyst with the freely accessible aminic functionalities in this molecular structure.

How the hyperbranched core/shell structures function

The selective interaction of the aminic pigment-affinitive core of structure type 3, characterised by efficient adsorption on various pigment surfaces, and the minimised interactions



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Figure 7: Influence of the structure types on the pot-life of the 2-pack polyurethane system. Left: OH-functionalised acrylate + aliphatic-aromatic polyisocyanate. Right: OH-functionalised acrylate + pure aliphatic polyisocyanate

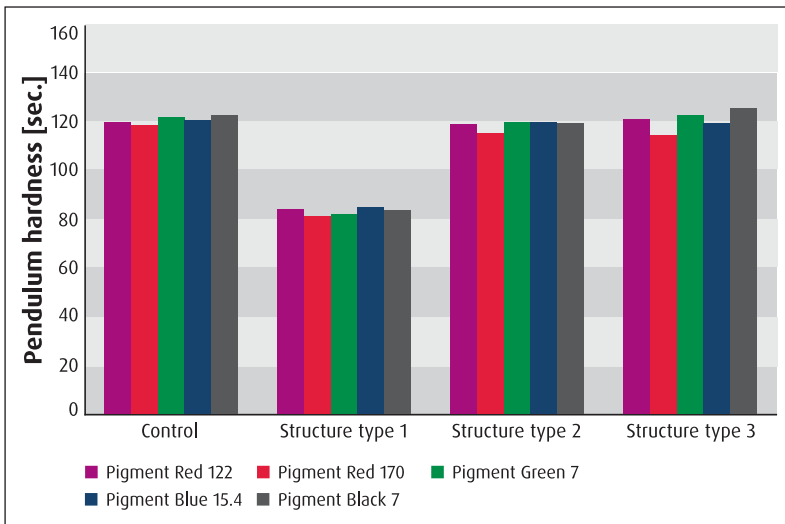
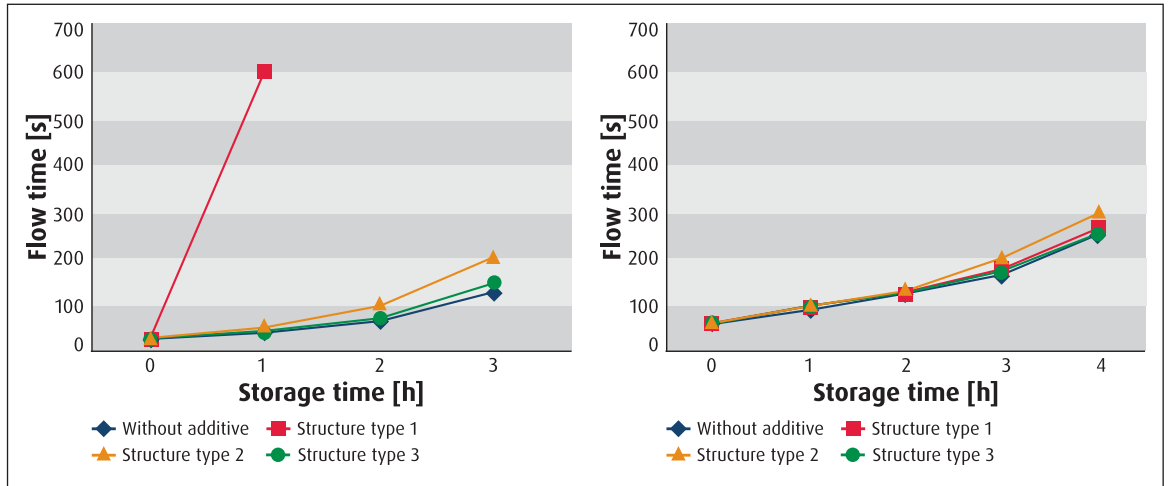


Figure 8: Influence of the structure types on pendulum hardness of the acid-catalysed stoving system

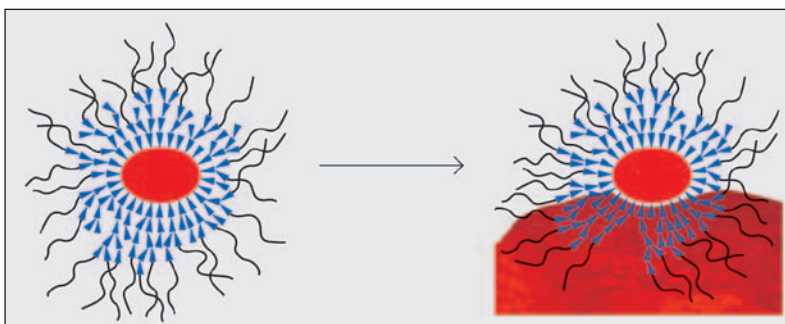


Figure 9: Schematic representation of the working mechanism of the hyperbranched core/shell structures

with reactive coating systems are attributed to the hyperbranched core/shell structure.

The prevailing mechanical shear forces in the pigment grinding process deform the flexible polymer shell of the dispersing additive, which makes the pigment-affinitive core temporarily accessible, allowing it to be adsorbed on the pigment surface. After the pigment has been ground, the polymer shell returns to its original state, thus re-shielding the amine core that was temporarily accessible to the surrounding liquid matrix during the grinding procedure (Figure 9). This then prevents any undesirable interactions.

Effective pigment stabilisation in solvent-borne and solvent-free reactive coating systems imposes great demands on the dispersing additives used. The amine pigment-affinitive groups required for sustained adsorption on pigment surfaces can cause undesirable interactions with these reactive systems.

Innovative dispersing additives based on hyperbranched core/shell structures can thus provide very effective stabilisation of the different pigment types without causing any undesirable interactions with the reactive coating systems. This structure shows superior performance overall to established linear copolymers with freely accessible amine anchoring groups as well as to polymers with sterically hindered amine anchoring groups. ◀

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