Diblock copolymer dispersants in polyester powder coatings

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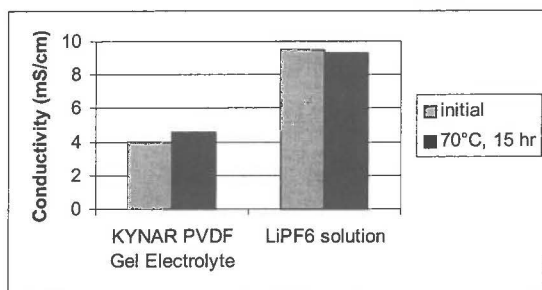
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Figure 11: Comparison of initial ionic conductivity and conductivity after aging at 70 °C for 15 hours.

DIBLOCK COPOLYMER DISPERSANTS IN POLYESTER POWDER COATINGS

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ABSTRACT

Poly(2-vinylpyridine)-b-poly(ε-caprolactone) copolymers have been used as dispersants for TiO_2 pigments in a polyester/TGIC powder coating. In coatings without TGIC, the block copolymer dispersants prevented the flocculation of the TiO_2 pigments at typical curing temperatures, by the formation of a steric barrier around the pigment particles. Consequently, non-crosslinked powder coatings with high gloss and excellent flow were obtained. In the presence of TGIC, the dispersants were found to catalyse the crosslinking reaction, leading to powder coatings with lower gloss and poor levelling. By replacing the basic poly(2-vinylpyridine) anchor block of the dispersants with an acidic or neutral anchor group, this undesired effect may be avoided. Alternatively, the poly(2-vinylpyridine)-b-poly(ε-caprolactone) dispersants are expected to be of special benefit in powder coatings with alternative crosslinking mechanisms, such as UV curable powder coatings.

KEYWORDS

Powder coatings; pigment dispersing; block copolymers; dispersing agents.

INTRODUCTION

Since the development of thermosetting powder coatings in the 1960's, major progress has been made in powder coatings technology [1]. A wide variety of resin systems and crosslinking mechanisms have been developed over the past years; also several additives and pigments have been developed specifically for powder coatings [2-4]. As a result, powder coatings with a variable degree of gloss and special pigment effects (*e.g.* metallic finishes) can be prepared today. Despite the large progress, the application of powder coating layers with sufficient opacity at thicknesses below 25 μm is still difficult [5]. Another well-known difficulty of powder coatings, the dispersing of pigments, has received attention only recently. Thometzek focussed on the influence of inorganic and organic surface modifications of various inorganic pigments on the degree of dispersing in powder coating systems [6], whereas Scott and Walters focussed on the residence time distribution of the powder coating material in a twin screw extruder [7]. Previously we showed that the origin of the poor pigment dispersing is due to the combination of poor (= slow) pigment wetting by the resin and poor deagglomeration during extrusion [8]. The latter is caused by too low shear forces generated in the extruder and short residence times within the extruder, typically 30 seconds or less. Given the current trend of using high speed extruders with enhanced throughput rates it is likely that pigment dispersing remains a problem [9].

Recently, predispersions of pigments in low-molecular weight resins have been developed to optimise the degree of pigment dispersion in powder coatings. These so-called pigment preparations or pigment predispersions can simply be added to the dry blend prior to extrusion. This will lead to powder coatings with improved colour and better reproducibility

between different powder coating batches [10,11]. Their efficiency depends on the miscibility between the powder coating resin and the resin used in these pigment predispersions.

Alternatively, the use of specific pigment dispersing additives, as is common in conventional coatings, may be even more effective. Pigment dispersants improve pigment wetting, prevent pigment flocculation and can facilitate the break-up of pigment agglomerates. The most efficient dispersants are diblock copolymers with a number of pigment-affinic groups (anchor block) and a long, resin-soluble tail (buoy block) [12]. The choice of the anchor and buoy blocks depends on the chemistry of the pigment surface and the coating resin [13]. Usually, the anchor block is shorter than the buoy block.

In earlier publications, we have reported on the design and synthesis of diblock copolymers of 2-vinylpyridine (2VP) and ε-caprolactone (CL) which can be used as dispersants for TiO₂ pigments in polyester powder coatings [14,15]. In this report, the effects of the use of these dispersants on the properties of a standard polyester/TGIC powder coating are discussed. After a general overview of the P2VP-*b*-PCL dispersants used, their application in both crosslinked and non-crosslinked powder coatings is discussed.

EFFECT OF PIGMENT DISPERSION ON COATING APPEARANCE

The degree of pigment dispersion in a coating has a large effect on its appearance after application. A coating with poorly dispersed pigment particles contains large pigment clusters due to either flocculation or incomplete break-up during dispersing. These clusters can, for instance, increase the surface roughness of the coating, which in turn leads to coatings with low gloss and high haze values [16-18]. Usually, haze is more sensitive for changes in surface roughness than gloss.

Another effect of the presence of pigment clusters in the coating is the increase of the viscosity of the resin prior to application. This can be attributed to the immobilisation of the resin material that has been occluded within the flocculates [19]. Additionally, extensive pigment flocculation can lead to the formation of a pigment network through the coating resin, which can give rise to a yield value and to thixotropic behaviour [19]. Only at sufficiently large stresses, the pigment network can be destroyed, allowing the coating resin to flow.

The effect of the degree of pigment dispersion on the viscosity is particularly important for powder coatings, since the flow and levelling of the powder coating surface is largely determined by the resin's viscosity during curing [1,20]. Unlike solvent-based coatings, the flow and levelling of powder coatings is not facilitated by solvents and is purely dependent on the melt viscosity (η) and the surface tension (γ) of the resin. This dependence is given by Orchard's equation (see Figure 1) [21]. Besides the viscosity, also the yield stress determines the extent of surface levelling, since this stress should first be overcome before the powder coating material can flow [20]. In practice, the extent of surface levelling is measured by evaluation of the surface waviness [22,23]. The surface waviness is usually divided into a longterm and shortterm component, L and S, with S correlating best with the actual surface roughness.

In this study, the degree of pigment dispersion was assessed both directly by scanning electron microscopy (SEM) and indirectly by evaluation of gloss, haze and surface levelling.

P2VP-*b*-PCL COPOLYMER DISPERSANTS

Previously we reported on the synthesis of P2VP-*b*-PCL copolymers *via* sequential anionic block copolymerisation [14]. The general synthetic scheme is shown in Figure 2. In this block copolymer, the P2VP block is the anchor block that adsorbs onto the TiO₂ pigment surface, and the PCL block is the buoy block that is miscible with the polyester resin [15]. In Table 1, the characteristics of the block copolymers used as dispersants are listed. The numbers used in the denomination of the dispersants represent the number of monomer units in the anchor and buoy blocks respectively.
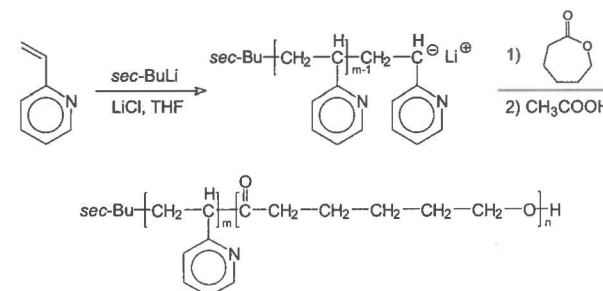

Figure 2. *General reaction scheme of the synthesis of the P2VP-b-PCL copolymers [14].*

Table 1. Characteristics of the P2VP-*b*-PCL dispersants used.

dispersant	P2VP block M_n	(DP)	PCL block[a] M_n	(DP)	M_w/M_n	v_a	Γ_{max}[b] (mg/m²)
9-39	1000	(9)	4400	(39)	1.69	0.19	0.81
15-58	1600	(15)	6600	(58)	1.76	0.21	1.10
27-57	2800	(27)	6500	(58)	2.03	0.32	0.93
22-32	2300	(22)	3600	(32)	1.92	0.41	0.98
22-13	2300	(22)	1400	(13)	1.60	0.63	0.84
39-13	4100	(39)	1500	(13)	1.71	0.75	0.87

[a]molecular weights in g/mol; [b]onto TiO₂ pigments (Kronos 2160).

Poly(2-vinylpyridine) is known for its strong affinity for silica, alumina and titania surfaces [12,13]. Consequently, the P2VP-*b*-PCL dispersants are expected to have a strong affinity for TiO₂ pigments as well. In Figure 3, typical adsorption isotherms from toluene solution are shown for three dispersants. In this plot, the adsorbed amount Γ is shown as a function of the concentration of dispersant in the solution after mixing pigment and dispersant (equilibrium dispersant concentration). The strong affinity of the dispersants for the TiO₂ pigment surface can be easily recognised from the rapid increase of the adsorbed amount Γ as the dispersant concentration in the solution is increased. As the pigment surface becomes saturated with block copolymer chains, the adsorption levels off. When the pigment surface is completely saturated, Γ reaches a maximum value, Γ_{max}. The values of Γ_{max} are included in Table 1. For all dispersants, the plateau value Γ_{max} was reached at dispersant concentrations of *ca.* 1.5-2.0 wt% with respect to TiO₂. This is clearly shown in Figure 4. Here, Γ is plotted as a function of the ratio of the amounts of dispersant and pigment, prior to mixing.

$$\ln \frac{a_t}{a_0} = -\frac{16\pi^4 h^3}{3 \lambda^4} \int_0^t \frac{\gamma}{\eta} dt$$

Figure 1. *Schematic representation of powder coating levelling according to Orchard [21].*
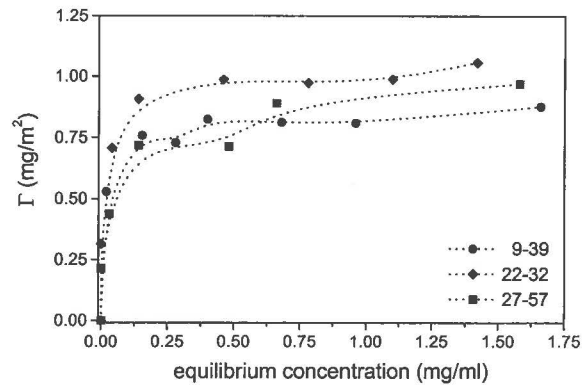
Figure 3. Typical adsorption isotherms of P2VP-b-PCL dispersants onto TiO₂ (Kronos 2160) from toluene. Dotted lines are added to guide the eye.
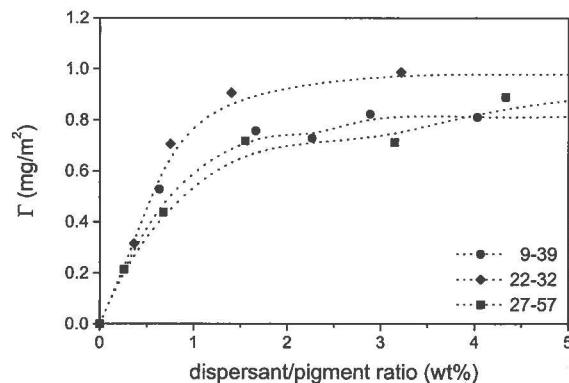

Figure 4. Influence of the dispersant/pigment ratio before adsorption on the adsorbed amount of P2VP-b-PCL copolymers on TiO₂ from toluene.

USE OF DISPERSANTS IN NON-CROSSLINKED POWDER COATINGS

In this section, the use of the P2VP-b-PCL copolymers as dispersants for TiO₂ pigments in a polyester powder coating resin without crosslinker is described. The dispersants were used at concentrations of 0.5, 1.5 and 2.5 wt% relative to the amount of pigment. In our studies, the dispersants were applied in two ways: i) by pre-adsorbing the dispersants onto the TiO₂ pigments in a volatile solvent (see Experimental section), and ii) by pre-mixing the dispersants through the polyester resin *via* extrusion, after which the pigment was mixed through this resin/dispersant pre-mix in a second step. For both methods it could be concluded from SEM analysis that the TiO₂ pigment was perfectly dispersed in the polyester resin after extrusion, both in the absence and in the presence of the dispersants [8]. Moreover, as is shown elsewhere the performance of the dispersants is the same for both methods [24]. Therefore, this paper focuses on the use of the pre-adsorbed dispersants.

The colloidal stability of the TiO₂ dispersions was studied at a temperature of 200 °C. This temperature was chosen, because it is a typical temperature at which curing takes place. Although the dispersions do not contain crosslinkers, the dispersions were treated as 'normal'

powder coatings. In Figure 5, the effect of the dispersants on the colloidal stability of the TiO₂ dispersions in a polyester resin is shown. As can be seen, in the absence of dispersants, flocculated TiO₂ particles were observed after heating the dispersion for 15 minutes. At temperatures below 200 °C, no flocculation was observed within this timescale. In the presence of dispersants at a concentration of 0.5 wt% (*i.e.* < 1.5 wt%), flocculation also occurred, as was expected from the incomplete pigment surface coverage at that low concentration. By applying the dispersants at *ca.* 1.5 wt%, flocculation was significantly reduced by dispersants 22-13 and 39-13 and completely prevented by the other dispersants. By increasing the amount of dispersant to 2.5 wt%, flocculation was prevented completely by all dispersants.
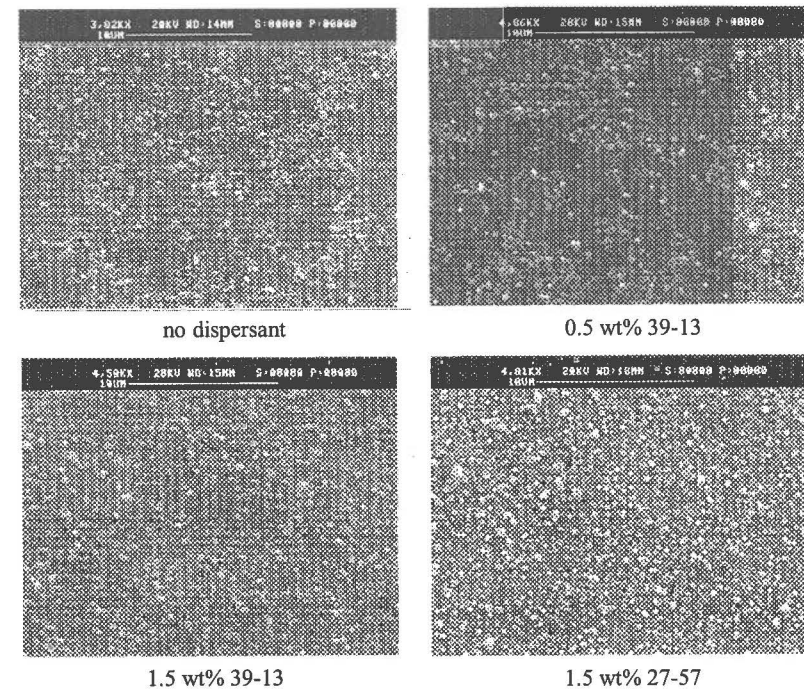

no dispersant   0.5 wt% 39-13

1.5 wt% 39-13   1.5 wt% 27-57

Figure 5. Typical scanning electron micrographs of 30 wt% dispersions of different modified TiO₂ pigment after heating to 200 °C for 15 minutes.

The suppression of the flocculation can be attributed to the PCL chains, forming a steric barrier around the pigment particles. The efficiency of a block copolymer dispersant depends on a number of factors, such as the thickness of the steric barrier and the density of adsorbed buoy chains [12,25,26]. Both of these factors are governed by the projected areas of the anchor and buoy blocks when the block copolymer is adsorbed onto a pigment surface. This is schematically shown in Figure 6. The projected area A of an adsorbed block can be estimated from its radius of gyration, R_g: $A \cong 1/\pi R_g^2$. The ratio of the projected areas of the anchor and buoy blocks, the reduced surface density σ^* ($\sigma^* \cong R_{g,buoy}^2/R_{g,anchor}^2$), influences the thickness of the steric barrier. In the anchor regime, when $\sigma^* < 1$, the adsorbed buoy chains do not touch each other at full surface coverage. The buoy chains then adopt their unperturbed dimensions and the thickness of the adsorbed buoy layer is approximately $2 \times R_{g,buoy}$. In the buoy regime, when $\sigma^* > 1$, the buoy chains do touch and overlap at full surface coverage and

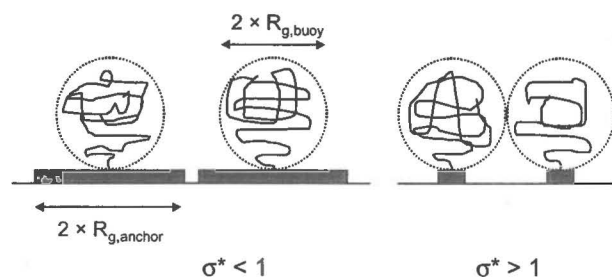the buoy chains will stretch. Significant stretching only occurs at large values of σ*, though [27,28].

Figure 6. *Schematic representation of the adsorption of a block copolymer onto a surface.*

For optimal steric stabilisation to be achieved by the dispersants, the buoy chains must fully cover the pigment surface. In other words, the buoy chains must be stretched to some extent (*i.e.* σ* > 1). In Table 2, the results of the stability tests are summarised and compared with the estimated theoretical values of σ*. In the estimation of σ* it was assumed that all the dispersant mixed with the pigment was indeed adsorbed onto the pigment surface. The radius of gyration $R_{g,PCL}$ of the PCL chains was estimated from $R_{g,PCL} = b \times M_n^{1/2}$, with $b = 0.031$ nm (as calculated from reported data of intrinsic viscosity under theta conditions and using a Flory universal constant of 2.5×10^{21}) [29,30]. Although this is not perfectly correct under the present conditions (dichloromethane is not a theta solvent for PCL), $R_{g,PCL}$ does not change significantly when a correction for the solvent is used (because of the low molecular weights of the block copolymers) and the data presented here give a fair indication of the expected structure of the adsorbed layers in the polyester resin matrix. The projected area of the anchor block was estimated from the adsorbed amount Γ [25,31].

Table 2. Colloidal stability of 30 wt% TiO$_2$ dispersions in the polyester resin at 200 °C or higher.

dispersant	PCL layer thickness $2 \times R_{g,PCL}$ (nm)	0.5 wt% σ*	0.5 wt% stability	1.5 wt% σ*	1.5 wt% stability	2.5 wt% σ*	2.5 wt% stability
39-13	2.4	0.2	-	0.6	+/-	1.0	+
9-39	4.1	0.6	-	1.9	+	3.1	+
22-32	3.8	0.5	-	1.4	+	2.3	+
22-13	2.4	0.3	(-) [a]	0.9	+/-	1.5	(+) [a]
27-57	5.0	0.5	(-) [a]	1.6	+	2.6	(+) [a]
15-58	5.0	0.6	(-) [a]	1.8	+	3.1	(+) [a]

[a] expected result, not determined.

As can be seen in Table 2, at a dispersant concentration of 0.5 wt%, σ* < 1. This explains the observed pigment flocculation at this concentration. The buoy chains do not entirely cover the pigment surface and the pigment particles can flocculate. At 1.5 wt%, σ* is close to 1 or slightly higher, except for 39-13 and 22-13. This agrees with the observed slight flocculation of the dispersions containing these two dispersants. At the highest concentration, σ* > 1 for all dispersants, which is in accordance with the colloidal stability found experimentally.

Based on the results discussed here, a PCL layer thickness of 2.4-5.0 nm is already sufficient for obtaining steric stabilisation. This is lower than minimum required thicknesses reported in literature for pigment dispersions in solvents or polymer melts (*ca.* 10 nm) [12,32].

As was discussed in the beginning of the paper, the degree of pigment dispersion in a coating influences a number of properties, such as the viscosity of the molten coating powder, the gloss and haze of the coating and the extent of levelling of the coating surface. The viscosity is perhaps the most important property that is influenced, since the effect of flocculation on the gloss/haze and the levelling is, at least partly, through the viscosity.

The effect of the TiO$_2$ flocculation on the elastic modulus G' of the polyester resin is shown in Figure 7. The elastic modulus G' was monitored, because it is more sensitive to pigment flocculation than the viscosity [19,33]. As can be seen, G' increases steadily in time in the absence of dispersants when the TiO$_2$ dispersion is heated to 200 °C. For the dispersion of TiO$_2$ with 0.5 wt% 39-13, only a slight increase of G' in time could be observed, whereas in the dispersion containing 1.5 wt% 39-13 G' remained almost zero. The same behaviour was observed for the other dispersants. This behaviour is in agreement with the flocculation results, discussed above. In the absence of dispersants, the TiO$_2$ pigment particles can flocculate leading to an increase of G'. By using the dispersants at a concentration of 0.5 wt%, the tendency to flocculate is reduced, leading to a smaller increase of G'. At concentrations of ≥ 1.5 wt%, no flocculation takes place and G' does not increase in time.
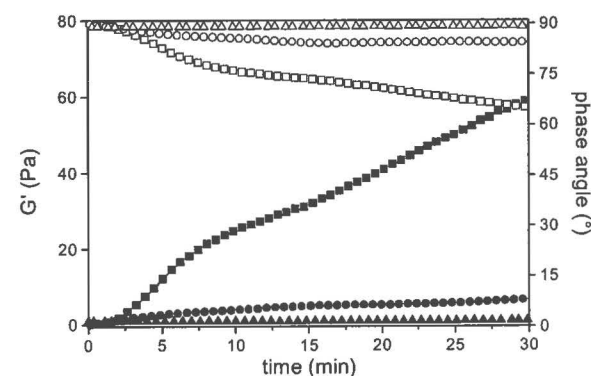

Figure 7. *Elastic modulus G' (filled symbols) and phase angle (open symbols) vs. time for 30 wt% TiO$_2$ dispersions in a polyester resin at 200 °C with: no dispersant (squares); 0.5 wt% 39-13 (circles); 1.5 wt% 39-13 (triangles).*

The improved colloidal stability of the TiO$_2$ dispersion and the constant low viscosity during prolonged heating at 200 °C have a profound effect on the appearance of the powder coatings. The effect of the addition of the P2VP-*b*-PCL dispersants on the gloss and haze of the coating surfaces, as measured at 20°, is shown in Figure 8. Without dispersant poor haze and fairly good gloss values were obtained. The addition of 1.5 and 2.5 wt% of dispersants leads to much lower haze and slightly higher gloss values, as expected. However, at the lowest dispersant concentration of 0.5 wt%, the haze is only slightly reduced, which is consistent with the results described earlier.
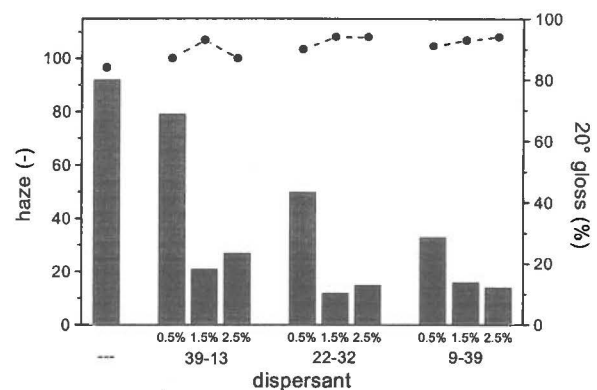
Figure 8. *Effect of dispersants on the 20° gloss and haze of powder coatings, containing 30 wt% TiO₂. Coatings heated to 200 °C for 10 minutes. Circles indicate gloss; bars indicate haze.*

The results for all dispersants used at a concentration of 1.5 wt%, are given in Table 3.

Table 3. Effect of the use of 1.5 wt% of dispersants on the surface waviness, 20° gloss and haze of coatings with 30 wt% TiO₂, after 10 minutes heating to 200 °C.

dispersant (1.5 wt%)	20° gloss (%)	haze (-)	waviness L	S
-	84	92	64	67
22-13	91	25	43	47
9-39	93	16	17	12
39-13	93	21	22	15
22-32	94	12	14	13
27-57	95	11	31	27

The effect of the use of 1.5 wt% dispersants on the levelling of the coating surfaces was studied as well. The results are included in Table 3. Here, the surface waviness was used as a measure of the surface levelling [22]. As can be seen, the levelling of the coatings is significantly improved, as a result of the improved colloidal stability.

The improved gloss and haze of the coatings in the presence of dispersants suggest that the mean surface roughness of the coating surfaces is lowered by the addition of the dispersants. The arithmetic mean surface roughness R_a was measured with atomic force microscopy (AFM). For the coatings without dispersant, $R_a \sim 4.9$ nm, whereas for the coatings with 1.5 wt% of dispersant 27-57 $R_a \sim 1.6$ nm. These values are in agreement with values reported in literature for powder coatings with well-dispersed TiO₂ pigments [6]. In Figure 9, typical AFM micrographs are shown.
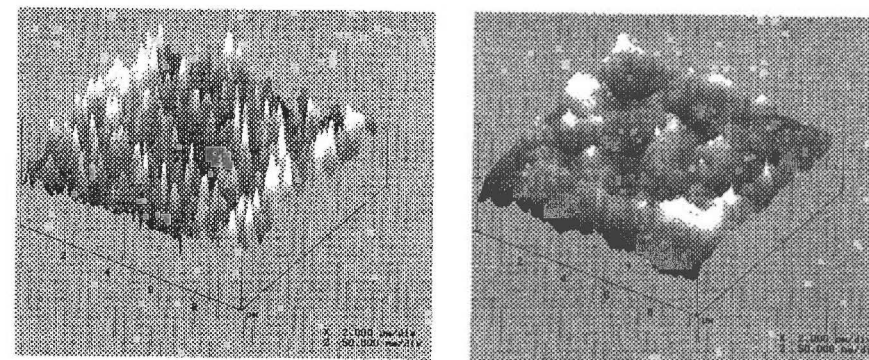

Figure 9. *AFM micrographs of surfaces of coatings with 30 wt% TiO₂ without dispersant (left, $R_a \sim 4.9$) and with 1.5 wt% 27-57 (right, $R_a \sim 1.6$ nm).*

USE OF DISPERSANTS IN POLYESTER/TGIC POWDER COATINGS

In order to investigate the use of the dispersants in fully cured powder coatings, three dispersants were used in polyester/TGIC coatings at a concentration of 1.5 wt%. The coatings were cured isothermally at 200 °C for 10 minutes. As can be seen in Table 4, the addition of dispersant 15-58 had little effect on the gloss and haze, but the addition of dispersants 39-13 and 22-32 had a detrimental effect on the gloss and haze.

Table 4. Gloss and haze of the coatings, cured for 10 minutes at 200 °C.

dispersant (1.5 wt%)	20° gloss (%)	haze (-)	T_{oc}[a] (°C)
-	87	50	155
22-32	63	321	145
39-13	50	422	130
15-58	86	75	[b]

[a]onset temperature of crosslinking (see text); [b]not determined.

Generally speaking, cured powder coatings have lower gloss and higher haze values than non-cured (thermoplastic) coatings. Because of increasing viscosity due to crosslinking, the levelling of the coating surface gradually slows down and eventually stops. This suggests that the dispersant-containing coatings of Table 4 should, due to suppression of flocculation, have better gloss and haze than the one without dispersant. As the results show the opposite trend, it seems that an unexpected factor increases the crosslinking in these samples, leading to a quick rise in viscosity.
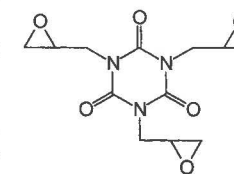
TGIC

Therefore, the rate of crosslinking of the coatings was monitored rheologically while heating the coating material from 110-200 °C at a rate of 2 °C/min. The results are shown in Figure 10. As can be seen, G' decreases at first due to the temperature dependency of the resin viscosity. At a certain temperature, the crosslinking reaction commences and G' starts to increase. At the end of the crosslinking reaction, G' levels off. This is the typical rheological profile for thermosetting powder coatings [34,35]. The temperature at which G' starts to

increase was taken as the onset temperature of crosslinking, T_{oc}. These are included in Table 4. In the absence of dispersants, $T_{oc} \approx 155$ °C. In the presence of 1.5 wt% 22-32, $T_{oc} \approx 145$ °C, whereas with 1.5 wt% 39-13, $T_{oc} \approx 130$ °C. It is known, that TiO_2 pigments have a retarding effect on the crosslinking of polyester/TGIC powder coatings. However, the effect observed here suggests a catalysing effect of the dispersants, because of the enormous shift of the temperature at which crosslinking begins. This is most likely due to the basic pyridine anchoring groups, which can catalyse the carboxylic acid-epoxy reaction.
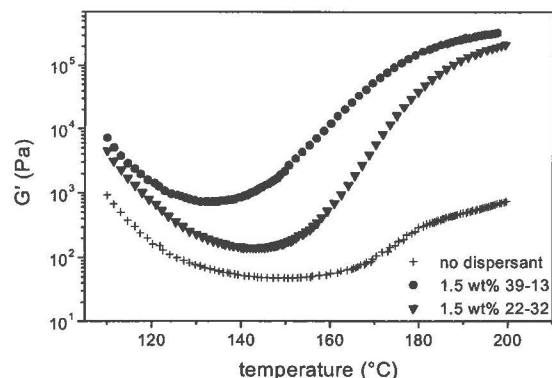

Figure 10. Effect of the P2VP-b-PCL dispersants on the crosslinking of polyester/TGIC coatings containing 30 wt% TiO_2.

In order to confirm this, the polyester resin without TiO_2 was crosslinked with TGIC in the presence of either 0.5 wt% P2VP homopolymer ($M_w/M_n = 2400/1700$) or 0.5 wt% PCL homopolymer ($M_w/M_n = 21900/15800$). The results are shown in Figure 11. For the pure polyester resin, $T_{oc} \approx 145$ °C. In the presence of PCL, crosslinking seems to be somewhat retarded and $T_{oc} \approx 160$ °C. In the presence of P2VP, however, crosslinking readily starts at $T_{oc} \approx 120$ °C. Therefore, the basic pyridine moieties have a catalysing effect on the crosslinking reaction.
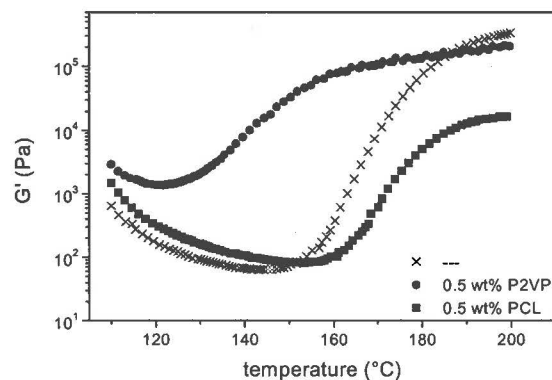

Figure 11. Effect of P2VP and PCL homopolymers on the COOH/TGIC crosslinking reaction.

The mechanism of the catalysing effect of the P2VP groups is schematically shown in Figure 12. The crosslinking reaction involves the nucleophilic attack of a carboxylate anion onto the oxirane ring of TGIC. The formation of the carboxylate anion is facilitated by the basic

pyridine moieties. The catalysing effect of the P2VP block also explains the difference observed between dispersants 39-13 and 22-32. Dispersant 39-13 has the largest P2VP anchor block and will, therefore, have the largest catalysing effect. Especially when free, non-adsorbed block polymer chains are present within the coating, the catalysing effect will be large.
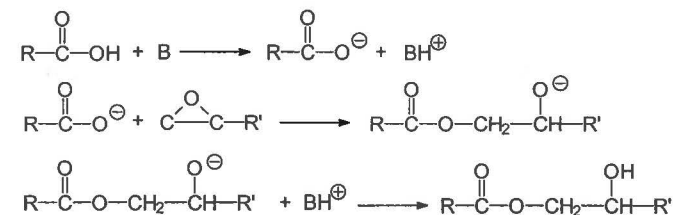

Figure 12. Schematic representation of the catalysing effect of a basic moiety on the COOH/TGIC crosslinking reaction.

As shown in Figure 12, the crosslinking reaction in a polyester/TGIC powder coating is extremely sensitive for basic catalysis. Therefore, a suitable pigment dispersant to be used in this type of powder coating is one with acidic or neutral anchoring groups [13]. For TiO_2 pigments, this poses no problems with the adsorption of the dispersants, because of the amphotheric nature of the TiO_2 pigment surface [36]. Alternatively, the P2VP-b-PCL dispersants can be used in powder coating systems with crosslinking mechanisms which are not base-catalysed. Examples of such powder coating systems are systems based on carboxylic acid functional resins with β-hydroxyalkylamide crosslinking agents (so-called "Primid" crosslinkers) and hydroxyl-functional resins with hexamethoxymethylmelamine (HMMM) crosslinking agent (see Figure 13) [37,38]. Furthermore, the P2VP-b-PCL dispersants will be beneficial especially in powder coating systems which are crosslinked by UV radiation, since in these systems levelling and crosslinking are separated in two steps [39,40].

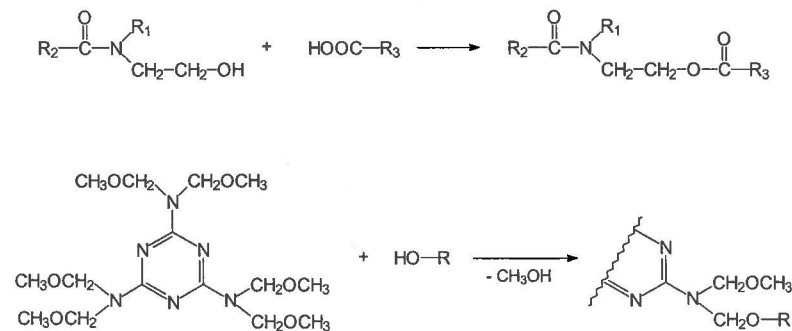*Figure 13. Schematic representation of alternative crosslinking reactions that are not sensitive towards base catalysis.*

CONCLUSIONS

In this paper, the effects of the use of block copolymer dispersants of 2-vinylpyridine and ε-caprolactone on the properties of TiO_2 pigmented polyester/TGIC powder coatings were studied. When the pigment surface was fully covered by the dispersants, pigment flocculation

was prevented completely in coatings without crosslinker. This behaviour can be explained by polymer adsorption theories. A stabilising layer thickness of *ca.* 2.4-5 nm was already enough to obtain a colloidally stable dispersion. As a result, (non-crosslinked) powder coatings with high gloss, very low haze and excellent flow were obtained. In the presence of a TGIC crosslinker, coatings with low gloss, high haze and poor flow were obtained, due to a catalysing effect of the P2VP anchor block on the crosslinking reaction. This can be readily solved by replacing the basic anchor groups by acidic or neutral ones.

The studied dispersants can be especially useful in powder coatings with alternative crosslinking mechanisms, such as the upcoming UV curable powder coating systems, which are not sensitive to base catalysis. Furthermore, because of the prevented pigment flocculation and improved flow, the characteristic orange peel effect may be reduced considerably, and it would make the application of thin layer powder coatings with sufficient opacity more accessible.

EXPERIMENTAL

Materials. A standard carboxyl-functional polyester powder coating resin (Uralac P3400, DSM Resins) was used. A commercial grade TiO_2 was used (Kronos 2160) having an organic modification (0.25% trimethylolpropane) and an inorganic surface treatment (3.3% alumina, 3.8% silica), a specific surface area of 12 m^2/g (BET value) and a number averaged diameter of the primary particles of 210 nm (specified by manufacturer). Flow agent (BYK 360P) was kindly supplied by BYK Chemie (Wesel, Germany). Benzoin (Fluka) was used as degassing agent. Triglycidylisocyanurate (TGIC, Araldite 810, Ciba) was used as crosslinking agent. All materials were used as received. The P2VP-*b*-PCL copolymers were synthesised *via* sequential anionic polymerisation, as described elsewhere [14].

Adsorption isotherms. Adsorption isotherms of the block copolymers on TiO_2 from toluene were determined by analysing the block copolymer concentration in the centrifuged supernatant gravimetrically (depletion method [41]). The adsorbed amount was also determined with thermogravimetric analyses (TGA) of the pigment sediment after centrifugation of the pigment dispersion. With this method, the adsorbed amount was determined from the difference in weight loss between the pigment sediment and the pure untreated pigment after heating to 800 °C at 40 °C/min. The adsorbed amounts determined by both methods agreed within experimental error. It was checked with TGA that the organic modifier TMP remains adsorbed on the pigment when the pigment is dispersed in toluene.

Pre-adsorption of the dispersants onto TiO_2. TiO_2 pigments were dispersed ultrasonically in a solution of the block copolymer in dichloromethane (typically 40 g of TiO_2 in 200 ml of CH_2Cl_2). After removal of the solvent *in vacuo*, the pre-treated pigments (with the pre-adsorbed dispersants) were added to the dry blend. For the reference coatings, the TiO_2 pigment was given the same treatment in pure CH_2Cl_2. It was confirmed that the latter treatment has little effect on the dispersability of the pigment, compared to the dispersing of pure TiO_2 in polyester resin. The polyester resin was used as flakes.

Preparation of powder coatings. In general, powder coatings were prepared by extrusion of dry blends containing 30 wt% TiO_2 (*ca.* 11 vol%), 1 wt% flow agent, 0.5 wt% benzoin and possibly dispersant (pre-adsorbed on TiO_2) with a Prism TSE 16 laboratory scale twin screw extruder at 110 °C with a screw speed of 200 rpm. The coatings that were to be crosslinked contained 5 wt% TGIC (ratio resin/TGIC = 93/7 wt/wt). Dry blends (typically 300 g total weight) were prepared in plastic bags by extensive hand-shaking for at least 1 minute. The conveying zone of the extruder was set at 75 °C and the kneading zone at 110 or 120 °C. After extrusion, the extruded material was powdered with a centrifugal mill (Retsch ZM 100) and sieved through a 100 μm sieve. Subsequently, the powder was sprayed electrostatically onto degreased aluminum panels (Q-Panel A36) with a Gema PG-1B spraying gun at 60 kV and 1 bar air pressure, and placed vertically in an air-circulated oven (Heraeus LUT 6050) for 10 minutes. Coatings with a layer thickness of *ca.* 80 μm were used for analysis.

Colloidal stability. The powdered dispersions were heated in aluminum trays in an air-circulated oven at 200 or 240 °C for 15 minutes, unless stated otherwise. The degree of pigment dispersion was subsequently studied with SEM.

Scanning electron microscopy. Scanning electron microscopy (SEM) was performed using a Cambridge Stereoscan 200 Scanning Electron Microscope operating at 20 kV. The extruded material was broken in liquid nitrogen in order to obtain a smooth cross-cut. The samples were etched with an oxygen plasma for 10 minutes and coated with Pd/Au prior to examination.

Rheology. Rheological measurements were conducted using a stress-controlled rheometer (AR-1000N, TA Instruments) equipped with an extended temperature module. Oscillatory measurements were performed with parallel plates (2 cm diameter, 1 mm gap) at 1% strain (linear viscoelastic conditions) and an angular frequency of 6.28 rad/s. For the crosslinking experiments, the sample was heated from 110-200 °C at a heating rate of 2 °C/min. From the samples containing TGIC, some bubbles of air were released in the rheometer, especially at 200 °C. The rheological data for these experiments should therefore not be used quantitatively.

Analyses. Gloss and haze were measured at 20° with the Micro-haze Plus gloss/haze meter (BYK-Gardner), according to ASTM D523. The waviness of the coatings was measured with the Wave-scan Plus (BYK-Gardner). Atomic force microscopy (AFM) was performed on a Dimension 3100 (Digital Instruments).

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Dynamic wetting properties of different acrylates

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Abstract
Today most of the modern industrial finishing processes for e.g. wood, plastic and metal coatings involve the use of energy curing technology. The limited space requirement, the high curing speed and the absence of volatile solvents are just some of the reasons. Energy curing coating formulations are nowadays available for any kind of application technologies.
Sufficient substrate wetting is always important for good adhesion of the cured coating to the substrate. Measuring the surface tension of a coating formulation gives some information of the wetting performance. Most of the coating technologies are dynamic processes. Therefore the dynamic surface tension gives more reliable information for the wetting properties during the application process than the information given by the static surface tension.

Keywords
Energy curing acrylates; dynamic surface tensimetry, method of the maximum bubble pressure.

Introduction
This paper presents the dynamic surface tension of different energy curing acrylates commonly used in energy curing formulations.
Sufficient substrate wetting is very important for many industrial-coating processes. The surface tension of the liquid coating should be significant lower than that of the substrate to be coated. The different acrylates and the usage of wetting additives influence the surface tension of the liquid coating. These surface-active properties of the formulation are normally measured by the static surface tension method. The influence of a substrate on surface tension has traditionally been measured using static, equilibrium techniques such as the du Nouy ring or the Wilhelmy plate tensiometer. For these equilibriums the surface has to be stable for some seconds – even hours to get the equilibrium between diffusion and orientation onto the surface. However, many applications involve rate-limited effects of surface tension where equilibrium values of surface tension are not reached and where such measurements would not reveal a time factor on the process. At ink-jet printing the time frame is in the range of milli seconds and curtain coating and roller applications are below seconds. Interlayer actions are therefore far beside the equilibrium. In periods of milli-