Effects on the Pigment Distribution in Paint Formulations

F. Tiarks[1*], *T. Frechen*[1], *S. Kirsch*[2], *J. Leuninger*[1], *M. Melan*[2], *A. Pfau*[1], *F. Richter*[3], *B. Schuler*[1], *C.-L. Zhao*[4]

[1] BASF Aktiengesellschaft, Emulsion Polymers, 67056 Ludwigshafen, Germany
[2] BASF AG, Product Development Adhesives and Construction, 67056 Ludwigshafen, Germany
[3] BASF AG, New Business Development, 67065 Ludwigshafen, Germany
[4] BASF Corporation, Charlotte Technical Center, 11501 Steele Creek Rd. Charlotte, NC 28273, USA

Summary: Modern water-borne paints are applied in different areas ranging from high-gloss lacquers to flat, scrub-resistant interior paints. The pigment volume concentration (PVC) is one key-parameter adjusting the application properties. In this work formulations differing in the type of binder and dispersing agent were investigated by various techniques concerning the distribution of pigments in the liquid paints and films. The structure of the paints was analyzed by Remission Light Spectroscopy (RLS), Disc Centrifugation, Cryo-Replica Transmission Electron Microscopy (Cryo-TEM) and Cryo-Scanning Electron Microscopy (Cryo-SEM). The pigment distribution in the films was examined by means of Atomic Force Microscopy (AFM), TEM and RLS.
The tendency of the pigments to form aggregates was found to depend on both: the type of binder and the dispersing agent. Only by adjusting the properties of the binder in combination with common dispersants it is possible to get well distributed TiO_2 particles within the paint. Correlation of application properties e.g. gloss and blocking to the microscopic structure is presented.

Keywords: coatings, pigments, gloss, films, emulsion polymerization, dispersion

Introduction

The composition of modern water-borne coatings strongly depends on the desired application properties and therefore on the PVC. In general paints consist of water, a binder, pigments and filler particles. Additives like coalescents, thickeners, dispersants and defoamers are added to guarantee a sufficient stability and good application properties. The PVC is one key-parameter for describing paints: the higher the PVC the lower is the content of binder within the paint and the higher the portion of pigments and fillers. The PVC strongly determines application properties such as gloss, scrub resistance and tensile strength. Besides the PVC the pigment

CCC 1022-1360/00/$ 17.50+.50/0

distribution in a paint is critical and influences the properties: gloss and hiding power at low PVC as well as scrub resistance at high PVC. Whereas in flat paints the high PVC is reached by a combination of cheap filler material and small amounts of TiO_2 (to achieve sufficient hiding power), one is limited to the solely use of TiO_2 in low PVC paints: a high portion of filler would not contribute to the opacity but increases the surface roughness and hence reduces the gloss.

To obtain maximum hiding power with a minimum amount of TiO_2 a homogeneous distribution of the pigments is essential and one of the main requirements for the formulation. The pigment distribution is determined by the colloidal interaction of the TiO_2 particles, which tend to aggregate in the paint. These clusters result in a higher surface roughness as well as a decreased hiding power due to reduced light scattering efficiency. The influence of the surface roughness on the gloss is obvious and has been described in [1]. As PVCs below 20 % are typical for gloss paints the scattering efficiency of the pigment is crucial to achieve a fully opaque coating.

TiO_2 is the favored pigment for producing opacity due to its high refractive index ($n_D \approx 2.6$). Light scattering is maximized when the particle size ranges about 250 nm. However, if the particles form clusters the scattering efficiency decreases because each cluster scatters approx. like a single, larger particle. Accordingly the scattering efficiency strongly depends on the dispergation state of the TiO_2 particles. In the process of paint formulation the break-down of agglomerates into fine particles is important as well as the stabilization of this state.[2] However, it has been shown that most clumps are dispersed in a short time by the milling process.[3] Due to this, pigment clustering in emulsion paints must involve other factors.[4]

In this work we elucidate the influence of the binder and the dispersing agent onto the pigment distribution and identify appropriate analytical tools for characterization of the dispergation state. Another crucial question to be answered is, whether the pigment distribution in the final film is predetermined in the liquid paint or whether additional agglomeration occurs during film formation and loss of water. The following samples were formulated and examined:

	Binder 1	Binder 2	Binder 3
Paste 1		**P 2**	
Paste 2			**P 3**
Paste 3			**P 4**
Paste 4			**P 5**

Table 1. Survey of the different formulations (P 1 – P 5) to examine the influence of either binder or dispersing agent onto the pigment distribution.

The difference between paste 1 and pastes 2 - 4 is the higher PVC (40 % vs. 18 %) and the dispersant. Paste 2, 3 and 4 differ in the type of dispersing agent and are optimized for high-gloss formulations. Binder 1 and 2 are straight acrylics and differ only in their comonomer system. Binder 3 is a styrene-acrylic developed for high-gloss paints. Concerning the dispersants, paste 1 contains pigment dispersant A®, a low molecular polyacrylic acid ammonium salt. Paste 2 comprises pigment dispersant MD 20®, a copolymer of diisobutene and maleic anhydride and paste 3 pigment dispersant Collacral LR 8954®, a solution polymer consisting of an acrylate and acrylic acid ammonium salt. The fourth dispersant Orotan 681® consists of an acrylate-methacrylic acid copolymer and is added to paste 4. Overall the dispersants differ in their hydrophilicity and functional groups.

Results and Discussion

The effect of (i) binder and (ii) dispersing agent on the distribution of TiO_2-particles was investigated. The latter was studied on the liquid paint formulation and the dried film. Via Cryo-Replica TEM and Cryo-SEM it was possible to characterize the pigment distribution in the formulation. The samples of the films were investigated by means of AFM and RLS. By comparing the results gained from analysis of the wet and dried state it is possible to get an insight into the effect of film formation on the clustering of TiO_2.

Distribution of titanium dioxide pigments in the liquid state

The Cryo-Replica-technique enables to measure directly in the undiluted paint. As a reference the structure of a pigment paste with a PVC of 40 % without addition of a polymeric binder was investigated. Already in the pigment paste large aggregates of TiO_2 are formed. The dilution of the sample by different amounts of water affects the pigment distribution: with increasing dilution the size of TiO_2 agglomerates decreased. However, it is clear from this study that even at high dilution clusters are formed. In order to further separate the clusters additional interactions have to be introduced. By formulating a paint from a paste both, the dilution effect and specific interactions are introduced by the binder. Thus a good dispersion should not only break up agglomerates by quasi-diluting but additionally stabilize the small clusters by electrostatic forces against re-agglomeration. It became apparent that fast and easy analytical tools like dynamic light scattering relying on dilution of a sample are restricted in their information, as the dilution affects the cluster size. Therefore it was a major task to identify analytical tools, which enable us to detect pigment clusters in the undiluted samples.

Influence of the binder onto the pigment distribution in the liquid paint

As we concentrate on the pigment distribution in gloss lacquers PVC was not much varied. Pigment distribution at high PVC (> 40 %) is described elsewhere.[5] The focus of this work is the effect of different types of binders and the influence of additives used in the formulation.

For the first, two straight-acrylic binders were compared: binder 1 and 2 differ only concerning their comonomer compositions. Figure 1 displays results from Cryo-TEM (PVC 40 %). TiO_2 is due to its electron density of high contrast (black). The binder is removed by the sample preparation and the Pt/C that was deposited on the sample under a certain angle induces the topology contrast. These areas appear as gray to white regions. The replica of individual latex particles is detectable and indicates that no film formation occurred. As is apparent from this preliminary testing the nature of the binder has an influence on the pigment distribution. Whereas P 1 shows only small and well distributed TiO_2-clusters, P 2 shows bigger aggregates in the paint. Apparently the differences in the comonomers of the binder are essential. Similar results were obtained by Zhao et al. analyzing the effect of functional groups onto the dispergation state.[6]

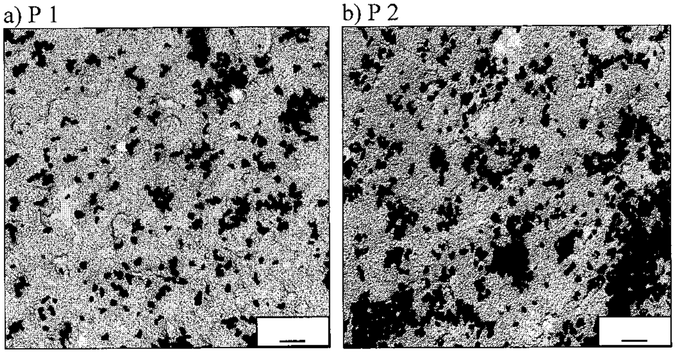

Figure 1. Use of different dispersions as binders in paint formulations and their influence on the pigment distribution analyzed by Cryo-Replica TEM. a) binder 1 leading to a fairly good TiO_2 dispergation, b) binder 2 resulting in highly agglomerated pigment particles.

Another conclusion drawn from this tests is, that the dispersing agent alone is not able to provide complete separation of all TiO_2 particles. As an effect of water-soluble oligomers on the pigment distribution is unlikely, as being shown by [5], it is the latex itself strongly interacting with the surface of the pigment resulting in differences in the pigment distribution.

After confirming that the binder influences the dispergation state, the effect of different dispersants was examined. A similar latex but optimized for high-gloss application was employed in the following testing (binder 3).

Effect of dispersing agent on the pigment distribution

The binder used in this testing was kept constant and the type of dispersant was varied. Figure 2 displays the results by Cryo-SEM (upper row) and Cryo-Replica TEM (bottom line). The difference in contrast (TiO_2 as white or black dots) is due to the different imaging techniques. In the SEM the electron-rich TiO_2 appears as white dot due to the analysis via imaging the back-scattered electrons, in the TEM micrographs TiO_2 is of high contrast (black) due to its electron density. For these samples with low PVC sophisticated Cryo-techniques have to be used. Whereas in flat paints the large $CaCO_3$ particles behave like spacers and hinder structural changes caused by water crystallization these lowly pigmented paints are more sensitive towards ice-crystals. Therefore crystallization has to be avoided which is realized by shock-freezing. A highly reliable method to avoid ice-crystal formation even by shock-freezing is the high pressure technique.[7]

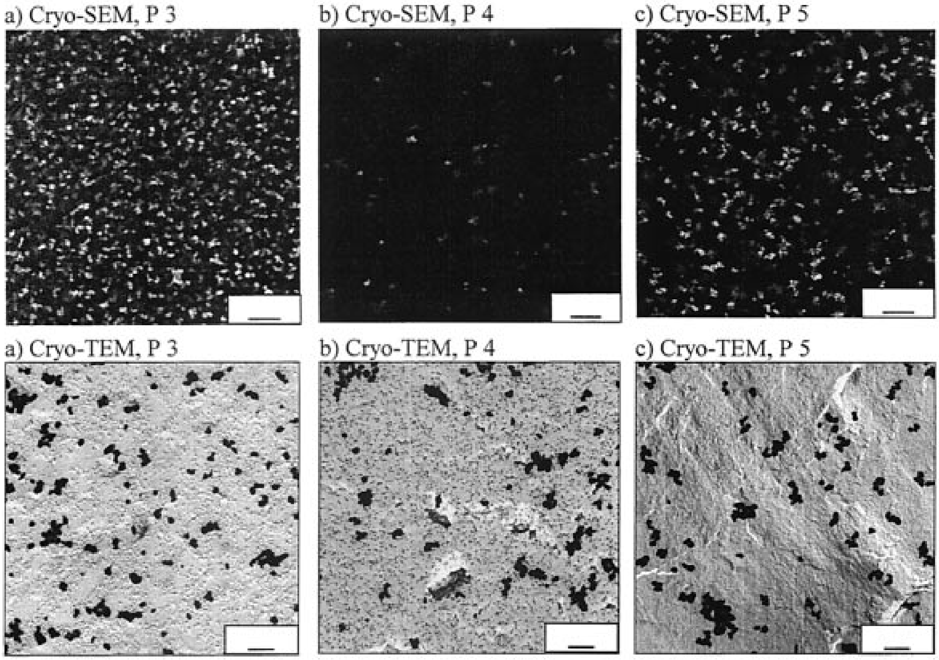

Figure 2. Cryo-Replica TEM and Cryo-SEM micrographs of formulations with the same type of binder but different dispersing agents. a) dispersing agent MD 20® (P 3), b) Collacral LR 8954® (P 4), c) Orotan 681® (P 5). The use of different dispersants influences the dispergation state of titanium dioxide.

As is maintained from the Cryo-Replica TEM and Cryo-SEM measurements the samples exhibit differences in the dispergation state of the TiO_2. Whereas the dispergation by use of pigment dispersant MD 20® (P 3) is relatively homogeneous and only with small clusters, the use of Orotan 681® (P 5) leads to pronounced clustering. Assuming a better interaction of the maleic acid groups in MD 20® as compared to acrylic acid in Orotan 681®, the effect of a better pigment distribution is understandable. This positive interaction enables the de-agglomeration of the clusters. The Cryo-micrographs of P 4, especially the SEM, display small agglomerates but compared to the other samples the number of detected clusters is too small, as all samples possess the same PVC. Large pigment clusters should be observed somewhere else in the sample, but were not visualized in this image.

Imaging techniques via EM are a nice tool to get an impression of the pigment distribution in the paint. However, these techniques are rather complicated, cost and time consuming and give only images of small volumes. These are not necessarily representative for the whole sample and might be misleading. An integral testing method, which allows the measurement of larger volumes is therefore important.

Consequently the paints are compared by disc centrifugation and RLS. Employing disc centrifugation the hard sphere diameter of the pigment pastes as well as the paints were determined. The formulations and pastes were diluted to a pigment concentration of 0.025 % and conditioned by ultrasound for 30 sec (Figure 3).

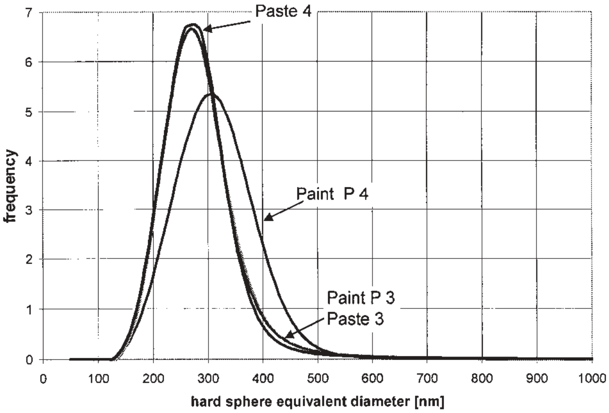

Figure 3. Results of disc centrifugation of the diluted pigment pastes and paint samples P 3 and P 4 possessing different dispersants (MD 20® and Collacral LR 8954®). The shift of the curve of P 4 to larger diameters indicates the formation of clusters.

Pastes 3 and 4 and paint P 3 exhibit an almost identical particle size distribution (approx.

270 nm) close to the primary grain size of the pigment particles (ca. 0.26 μm). Yet paint P 4 exhibits a reproducible and thereby significant shift to larger diameters (ca. 310 nm). This shift can be explained by partly agglomerated TiO_2 particles. The agglomeration did not occur in the paste, which already contains the dispersant, but happens after adding the binder. This demonstrates, that dispersant *and* binder influence the dispergation state of TiO_2 and supports the assumption of better specific interactions of functional groups in P 3 with the pigments.

This result corroborates the hypothesis that P 4 contains larger TiO_2 clusters that were not detected by imaging techniques due to the small picture area. However, disc centrifugation is based on diluted samples and therefore we have to backup this assertion by a second method like RLS. Advantageously RLS works in concentrated opaque samples. The qualitative extent of different particle sizes onto the remission spectrum can be drawn from the scattering factor according to Mie-Theory as the wavelength of monochromatic light and the particle size leading to optimal back-scattering depend on each other.[8]

Thus, for a given particle size distribution a large extent of small particles leads to a high remission in the short-wave region and a high extent of clusters yields to pronounced remission in the long-wave region. The remission spectrum is a distorted image of the original grain size distribution of the pigments. Concerning the spectra one has to keep in mind that in a pigment suspension the back-scattering decreases with an increasing pigment concentration. Paints P 3 and P 4 exhibit the same PVC and consequently their remission behavior can be compared.

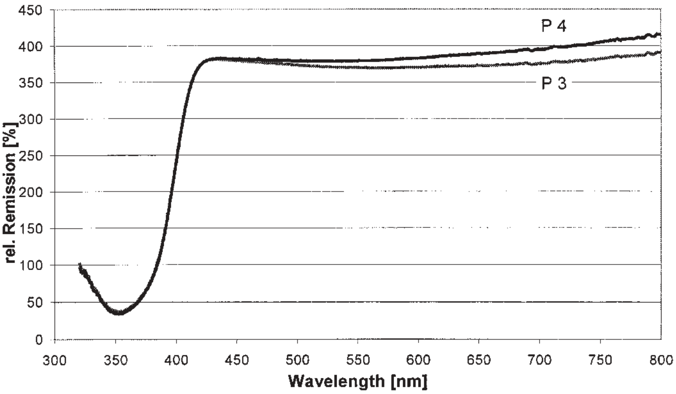

Figure 4. RLS of undiluted paints P 3 and P 4. P 4 displays more remission in the long-wave region of the spectrum, which can be seen as a hint for weakly agglomerated particles.

P 4 displays more remission in the long-wave region of the spectrum than in the short-wave compared to P 3. This effect is small but reproducible and hints to a higher content of agglomerates in the undiluted paint, analogous to the results of disc centrifugation within the diluted state. As both methods give only qualitative information, no information about the size and the volume fraction of the agglomerates can yet be provided. As can be concluded, it is the PVC of a formulation and the binder that influences the dispergation state of the pigment. Furthermore the type of dispersing agent is critical for the aggregation behavior and therefore has to be chosen carefully.

Using sophisticated imaging techniques as Cryo-EM and relatively easy methods as RLS a broad insight into the undiluted liquid state of a paint is gained. The question arises if the observed clustering is also found in the dried film and if so, how does the dispergation state influence the macroscopic paint properties.

Pigment distribution in the dried paint film

Coming from the fluid paint formulation to the dried film, suitable characterization methods determining the pigment distribution have to be evaluated. Again, one of them is RLS. Films of P 3 and P 4 were measured with this technique. The films were obtained by doctor bladeing the paints (thickness of 50 µm wet on acetate foil) and drying at ambient temperature. Regarding Figure 5 one recognizes, that the shape of the remission spectra of the paint films is much different than for the liquid paint.

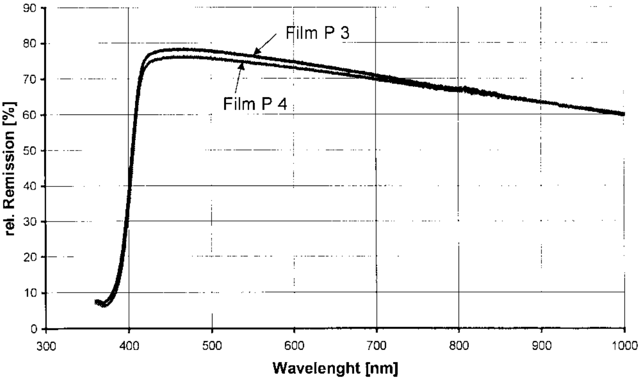

Figure 5. Analysis of the dried paint films of P 3 and P 4 by RLS. The stronger remission of P 3 in the short-wave region compared to P 4 assumes a larger amount of smaller clusters.

Whereas in the wet paint an increase in remission in the long-wave region is observed, this behavior is not detected in the spectra of the films. One possible explanation is that in the film the measurement only reflects the pigment distribution of the film surface, whereas in the paint the bulk is detected. During film formation larger aggregates tend to settle down and hence only smaller clusters or isolated pigments stay at the surface. This would explain the overall lower remission in the long-wave region of both paint films versus their liquid state. In the short-wave region the remission of P 3 is higher than that of P 4, indicating a higher amount of small clusters or single TiO_2 particles at the surface.

However this finding has to be proven by an imaging technique. One well established method for surface analysis is AFM. This technique has been employed to study the surface properties of P 3 and P 4 (Figure 6 a and b). As one clearly sees none of the paint films possesses a completely smooth surface but strong differences in the pigment clustering. Whereas P 3 displays at least pigment particles that are relatively homogeneously distributed on the surface, the analysis of P 5 reflects the inhomogeneity as revealed by Cryo-techniques. One also finds clustered particles leading to a more disturbed surface of the film.

The surface analysis by AFM of a film of P 4 displays only a small amount of pigment particles. One possible explanation could be the already mentioned tendency for aggregation leading to a pronounced segregation process meanwhile the film drying. The pigment particles gather at the bottom side of the paint film due to their higher density whereas the less dense binder particles form a polymer film on top.

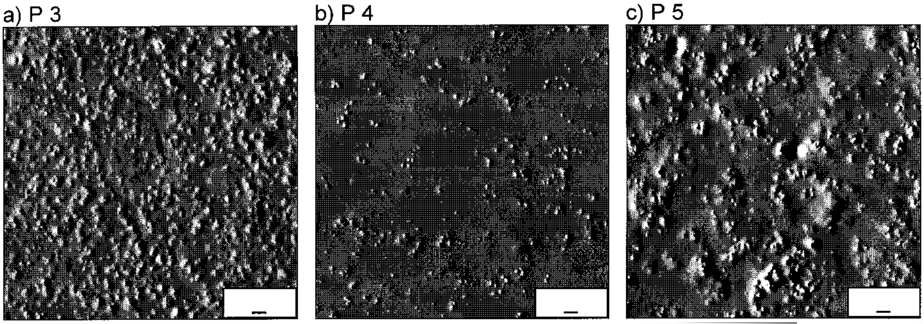

Figure 6. AFM of the paint films in the amplitude mode (20 x 20 μm). a) P 3, b) P 4 and c) P 5. The differences of the surface smoothness affected by TiO_2-clustering are obvious.

It can be concluded that the surface analysis by AFM fits very well the data obtained by RLS and also mirrors the image obtained by Cryo-techniques. Sample P 5 contains strongly agglomerated TiO_2 clusters due to insufficient stabilization. The large clusters of P 4 observed by RLS and disc centrifugation have not necessarily to be detected by imaging techniques. Whereas AFM analysis gives an impression of the surface of the paint samples, cross-cuts of dried paint films and subsequent analysis by TEM enables a view into the bulk structure.

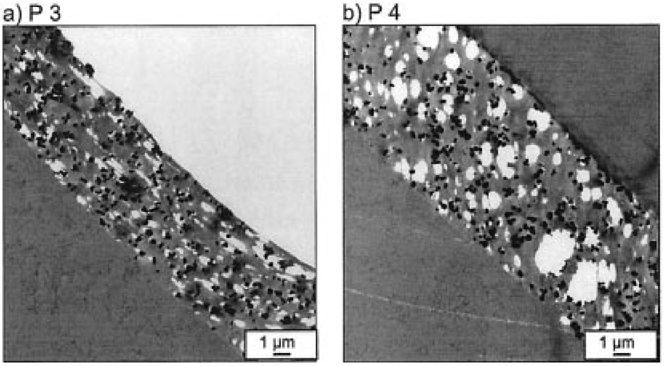

Figure 7. TEM of cross-cuts of the dried films of P 3 (a) and P 4 (b). The size of holes created by the cutting reflects the original size of pigment clusters in the polymeric matrix.

The cross sections of the film reveal the diversity of the particle distribution: P 3 contains relatively well distributed particles, whereas P 4 displays larger clusters or holes that resulted from the cutting process by clusters that fell out of the matrix. However, from the image it is quite obvious that these large clusters have not necessarily to be located at the interface to air. Due to this, surface analysis techniques alone are not sufficient to get all information about the dispergation state.

After proving that both binder and dispersing agent strongly affect the clustering of TiO_2 in paint formulations and after demonstrating that the agglomeration in the liquid state is also seen in the dried paint film, it remains to ascertain if these microscopic findings correlate to macroscopic paint properties.

Correlation to macroscopic paint properties

The correspondence to macroscopic paint properties is gained by correlation of the dispergation state and the gloss measured under an observation angle of 20° and 60° (see Table 2).

By comparing the paints the difference within the dispergation state is reflected by a lower gloss of P 4. The surface roughness of P 3 and P 4 were determined by AFM, showing that P 3 has a much higher roughness than P 4. As P 3 has a higher gloss, the surface roughness is not the only parameter being responsible for this application property. It is in addition the pigment distribution as a result of the high refractive index of TiO_2 compared to the polymer.

The haze of a film, which is often evoked by microstructures due to a bad dispergation of pigments, of P 4 is much higher than of a P 3-film and might only partly be due to a larger surface roughness. Similar is valid for P 5, as its agglomeration was established by Cryo-techniques and is seen again in the gloss and haze values.

Table 2. Application properties of the presented high-gloss formulations: gloss values (observation angle 20° and 60°) and haze, blocking after 1 day drying at room temperature and stressing with 10 kg for 24 h. Defects means film defects noticed after testing the blocking resistance. Marks for blocking and defects ranging from: 0 = excellent to 5 = poor.

sample	Gloss 20°	Gloss 60°	Haze	Blocking	Defects
P 3	62	84	81	1	0
P 4	43	76	191	4	4
P 5	47	80	124	2	0

Another important paint property is blocking. Comparing the results one has to note, that P 4 fails the blocking test and shows defects in the paint film afterwards. The blocking of P 3 and 5 was without failure and can be attributed to the more homogeneous pigment particle distribution at the film surface. The dispergation state strongly affects the macroscopic paint properties. Therefore binder and dispersant of a high-gloss formulation should always be chosen carefully.

Controlling the dispergation state by tailored dispersants and binders

The question arose, whether it would be possible to tailor the polymeric binder in order to overcome the aggregation phenomenon of pigments completely. Figure 8 displays Cryo-SEM images of paints with tailored binders by using surfactants differing in their functional groups.

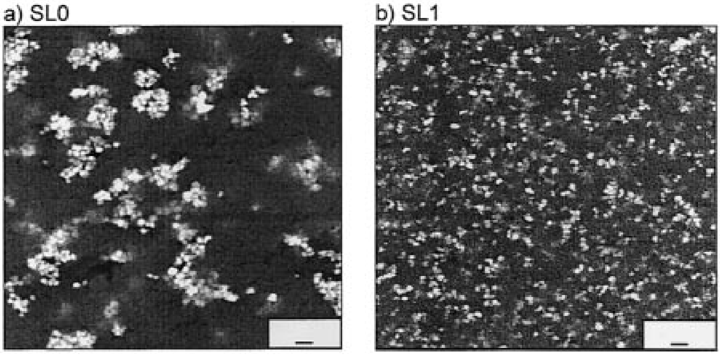

Figure 8. Cryo-SEM micrographs of model latex SL0 (a) and the latex SL1 (b) with a special surfactant. The difference in TiO_2 distribution depending on the surfactant system is obvious.

The distribution of TiO_2 in Figure 8 a) is relatively homogeneous but the pigment particles agglomerated and clusters are detected by Cryo-SEM. This means that the binder was not able to guarantee specific interactions needed for the break-up of agglomerates. The system failed to stabilize smaller clusters or even single pigment particles.

In contrast to this the addition of a special surfactant leads to the absence of pigment clusters. The TiO_2 particles are finely divided within the paint and no agglomerates are detected. This diversity in pigment distribution is again reflected by macroscopic paint properties. The gloss of SL0 is lower than that of SL1 supporting our findings in the previous chapter.

sample	Gloss 20°	Gloss 60°
SL0	10	55
SL1	27	74

Table 3. Gloss values of the formulations under an observation angle of 20° and 60°.

Apart from tailoring the binders by the use of special surfactants the copolymerization with functionalized comonomers is another suitable tool to break up pigment clusters. The obvious improvement caused by optimizing the binder was reflected in the Cryo-SEM micrographs. The dispergation state of TiO_2 as perfectly homogeneously distributed pigments throughout the whole sample can be achieved by choosing an appropriate comonomer. The dependence of the TiO_2 distribution on the binder functionalization is clearly seen in this chapter. In the best case the tailored binder completely eliminates TiO_2 clusters, which is even possible without any change of formulation additives.

Summary and conclusion

To conclude, one can state that the aggregation behavior of pigments in wet and dried paints displays parallels. Pigment agglomeration caused either by binder properties or the functionality or the dispersing agent is already visible in the liquid state and subsequently found in the dried film. The influence of the dispersing agent is obvious and an effect of clustering on corresponding macroscopic parameters as e.g. gloss was established.

The structure of paint films and liquid paints has been investigated by different techniques. The distribution of TiO_2 particles in the paint was analyzed for example by Cryo-SEM, Cryo-Replica TEM, RLS and disc centrifugation respectively. By AFM and RLS the pigment distribution on the surface of the dried paint films was examined. Cross-cuts allowed the visualization of pigment distribution in the bulk via TEM.

With this knowledge we are able to design our binders specifically, which allows the formulation of high-performance paints.

Acknowledgement

The support of L. E. Scriven (University of Minnesota, Dept. Chemical Engineering and Materials Science) regarding the Cryo-SEM measurements is gratefully acknowledged. The authors would also like to thank V. Koch, T. Frey and A. Rennig (BASF AG, Performance Chemicals Physics) for their help concerning RLS and disc centrifugation.

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