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# Impact of the Dispersion Quality of $TiO_2$ Pigments in Coatings on Their Optical Properties and Weathering Resistance

*Dr. Peter Gross and Dr. Josef Schmelzer*

KRONOS INTERNATIONAL, INC., Technical Service Department,
Peschstrasse 5, D-51373 Leverkusen, Germany

**Summary:** The dispersion status achievable with different dispersing equipment of an acrylic/MFA stoving enamel was monitored in the conventional way via the Hegman-gauge and gloss, gloss haze and tinting strength measurements. Then the same drawdowns of the cured coating were submitted to diffuse reflectance spectroscopy. Original and normalised remission curves were then compared and the distribution coefficients emerging from these measurements were correlated to the conventional methods for monitoring the dispersion process. The interpretation of the spectra with respect to the particle size, particle size distribution and the concentration of particles of a particular size was achieved on a qualitative and comparative way.

## 1. Introduction

$TiO_2$ pigment powder as delivered to customers consists of a mixture of primary particles, agglomerates and aggregates. During the dispersion process the primary particles and aggregates are merely distributed evenly in the liquid phase, whereas the agglomerates will be broken down to smaller particles to yield as an optimum purely primary particles and aggregates. Commonly, in coatings industry the quality, progress and efficiency of the dispersion process are monitored by the use of a grindometer (for the determination of the coarse particles) as well as by means of optical measurements like gloss, gloss haze and tinting strength. These methods give an overall and average account of the dispersion status in the coating and do not allow a detailed insight.

In the year 2000 J. Schmelzer[1] proved that the use of diffuse reflectance spectroscopy of $TiO_2$ containing coatings allows a deeper insight into the particle distribution of the pigment in the coating. In course of this investigation the dispersion status of an acrylic/MFA stoving enamel as achieved with different dispersing equipment was monitored in the conventional way via the grindometer and gloss, gloss haze and tinting strength measurements. Then the same

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drawdowns of the cured coating were submitted to diffuse reflectance spectroscopy. Original and normalised remission curves were compared with the results of the conventional methods. The interpretation of the spectra with respect to the particle size, particle size distribution and the concentration of particles of a particular size was achieved on a qualitative and comparative way. Based on an earlier work[2], two different $TiO_2$ pigments representing easy (Pigment A) and more difficult (Pigment B) dispersing behaviour were chosen for this investigation (table 1).

**Table 1. Pigments under Investigation**

| | Inorganic Surface Treatment | | | |
|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $ZrO_2$ | Production Process |
| Pigment A | 0.1 | 3.0 | 0.4 | Sulphate Process |
| Pigment B | 2.8 | 3.5 | --- | Chloride Process |

Pigments A and B differ not only by their surfaced treatment and ease of dispersion but also by the way of manufacturing (sulphate and chloride process) which may lead to consequences as described later.

## 2. Experimental

### *2.1 Monitoring the dispersing process with conventional means*

In course of this investigation the dispersing behaviour of pearl mill, high speed stirrer (saw tooth blade) and Skandex® mixer were examined. Earlier laboratory studies proved that under the applied conditions the Skandex® mixer dispersion is the optimum. The dispersing conditions for the pearl mill were chosen with regards to the mildest conditions achieving a good dispersion of Pigment A. Table 2 gives a summary of the dispersing conditions.

**Table 2. Dispersing conditions applied with the different dispersing tools**

| | | |
|---|---|---|
| Skandex | | 60 minutes |
| High speed stirrer | Time | 20 minutes |
| | Circumference speed | 20 m s$^{-1}$ |
| Pearl Mill | Volume of milling chamber: | 125 cm$^3$ |
| | RPM: | 500 |
| | Volume of pearls in milling chamber | 80% |
| | Pearls | ceramic |
| | Diameter of pearls | 1.6 mm |
| | Through put | ~4.0 kg h$^{-1}$ |
| | Temperature | 23-25 °C |
| | Passes | maximum 4 |

Table 3 shows the results achieved with the different dispersing tools monitored with the conventional evaluation tools.

**Table 3. Dispersion status of pigments A and B as achieved with the different dispersing tools**

| | Pigment | Gloss 20° | Gloss Haze | Hegman |
|---|---|---|---|---|
| High Speed Stirrer | A | 80 | 16 | 7.25 |
| | B | 78 | 39 | 7.00 |
| Pearl mill, 1. Pass | A | 80 | 18 | 6.50 |
| Pearl mill, 2. Pass | A | 80 | 18 | 6.75 |
| Pearl mill, 3. Pass | A | 80 | 18 | 7.00 |
| Pearl mill, 4. Pass | A | 80 | 18 | 7.25 |
| Pearl mill, 1. Pass | B | 72 | 99 | 6.00 |
| Pearl mill, 2. Pass | B | 74 | 80 | 6.25 |
| Pearl mill, 3. Pass | B | 75 | 76 | 6.75 |
| Pearl mill, 4. Pass[*3] | B | 75 | 75 | 7.00 |
| Skandex | A | 80 | 16 | 7.25 |
| | B | 78 | 46 | 7.00 |

The results show that Pigment A is indeed easy to disperse in the coating system used. A perfect dispersion of this pigment can be achieved with all dispersing methods, even at circumference speeds as low as 5 m $s^{-1}$ of the high speed stirrer. In the pearl mill dispersion a differentiation of the passes by optical measurements is not possible. Here only the grindometer readings show that there is a progress in dispersing. However, measurements show a readily achieved destruction of the gloss and gloss haze disturbing smaller agglomerates.

The dispersing behaviour of pigment B is noticeably different:

1. Perfect dispersion in all parameters monitored is achieved with the Skandex and the high speed stirrer only.
2. In the pearl mill dispersion process deficiencies in gloss and gloss haze remain even under much more vigorous conditions. The grindometer readings indicate perfect dispersion. Thus, whereas coarse agglomerates of Pigment B are broken down it appears as if the smaller agglomerates resist a break down.

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[*] After 4 passes through the pearl mill noticeable greying of the white coating could be observed with Pigment B which resulted in a diminution of the Brightness L* from 98.1 to 97.9. This was not observed with pigment A, a sulphate process pigment with which the Brightness L* remained unchanged at 97.3. This demonstrates the known higher abrasivity of chloride process pigments compared to sulphate process pigments.

### *2.2 Diffuse reflectance measurements (remission)*

The contribution of a $TiO_2$ containing coating to the remission at a specific wavelength is mainly due to particles of a specific size (approximately half of the wavelength). Thus a spectral comparison of $TiO_2$ containing coatings could reflect the details about the particle size distribution changes occurring during the dispersing process and/or give account of the differences in the dispersing behaviour of the pigments. Figures 1 and 2 show typical remission spectra in the visible light region yielded from white $TiO_2$-pigment containing coatings

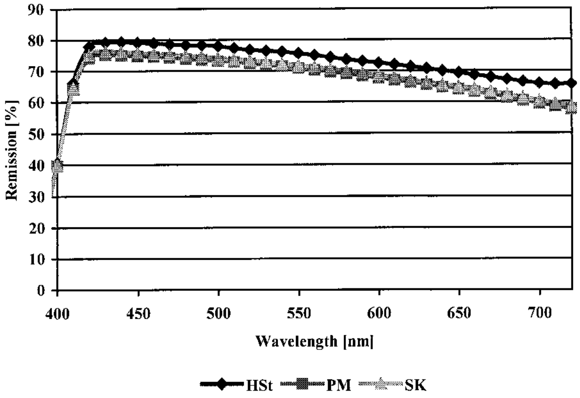


Figure 1. Remission spectra for Pigment A: Comparison Skandex mixer (Sk), pearl mill (PM) and high speed stirrer (HSt)

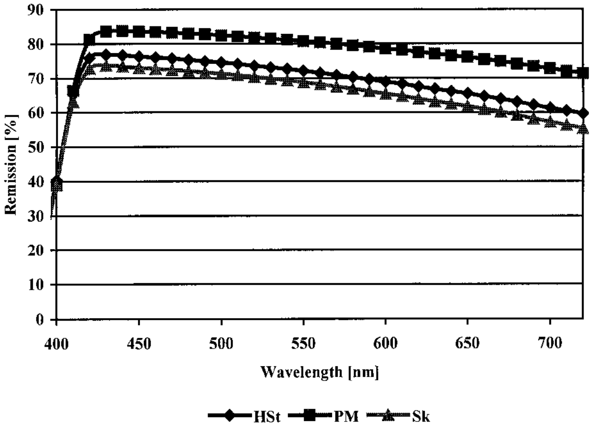


Figure 2. Remission spectra for Pigment B: Comparison Skandex, pearl mill and high speed stirrer

The intensities observed with a coating where the dispersion of the pigment was carried out with a Skandex mixer should be highest since this mixer yields the best dispersion. This is valid for coatings of identical thickness but for drawdowns as measured here the variation of coating thickness appears to be too large.

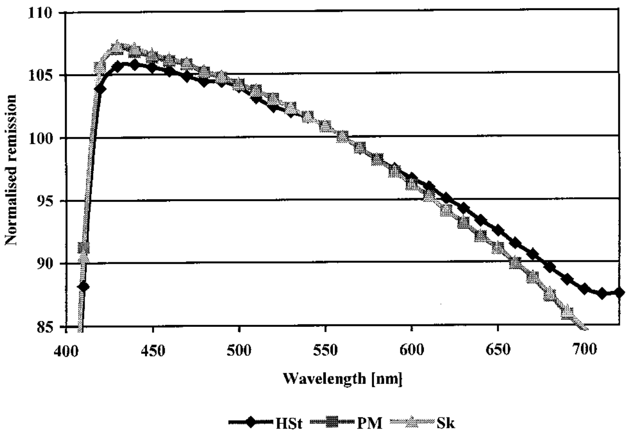


Figure 3. Normalised remission spectra for Pigment A: Comparison Skandex mixer, pearl mill and high speed stirrer

For these reasons normalisation of the spectra was carried out as described by Schmelzer[1] to allow a qualitative discussion of the particle size distribution. Normalisation was carried out by fixing the remission at 560 nm to be 100 % and calculating the "new" remission values at the other wavelengths. This procedure leads to the spectra as shown in figures 3 and 4.

In the following the term "smaller particles" refers to the pigment particles which account for the remission at wavelengths below 560 nm and the term "bigger particles" to the pigment particles accounting for the remission at wavelengths above 560 nm. In the same sense the terms "lower" and "higher" wavelengths are used.

The normalised spectra show that with the Skandex mixer the spectra exhibit highest remission at lower wavelengths and lowest remission at higher wavelengths. In terms of "particle size distribution" the Skandex mixer yields the highest portion of smaller, pigmentary particles. Thus, according to the remission spectra, too, the Skandex mixer is the most effective dispersing tool. For Pigment A the pearl mill dispersion leads to identical results as the Skandex mixer. With the high speed stirrer the portion of "bigger" particles is increased. This different dispersing behaviour is not observed with the conventional methods.

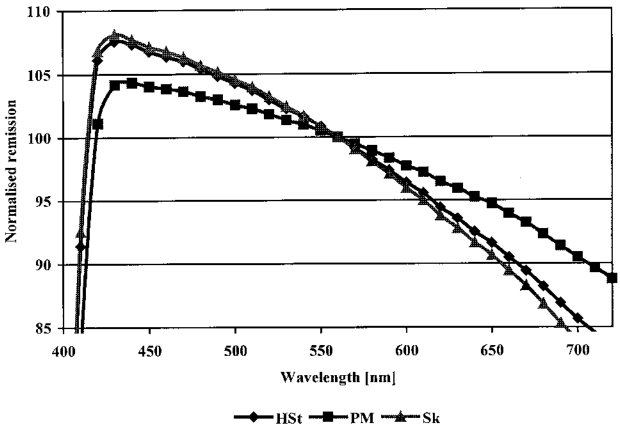


Figure 4. Normalised remission spectra for Pigment B: Comparison Skandex mixer, pearl mill and high speed stirrer

Dispersing with a high speed stirrer occurs to be more effective for Pigment B. Here the pearl mill dispersion is less effective which is in accordance with the "traditional" evaluation of a good dispersion. Figures 5 and 6 show the remission spectra of the progressing dispersion achieved after each pass through the pearl mill for pigment A and B respectively.

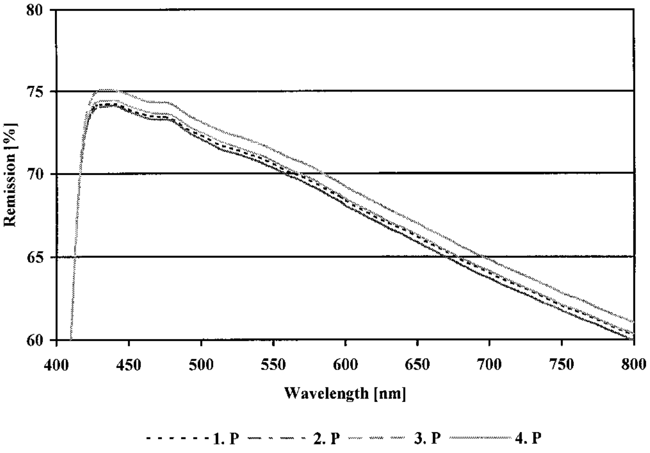


Figure 5. Remission spectra for Pigment A: pearl mill dispersion 1st to 4th pass

Uniformly, the remission level of the chloride grade pigment (B) is on a higher level compared to the sulphate grade pigment (A). This corresponds to normal optical measurements, where the chloride grade pigments exhibit a higher brightness L* (cf. footnote *, page

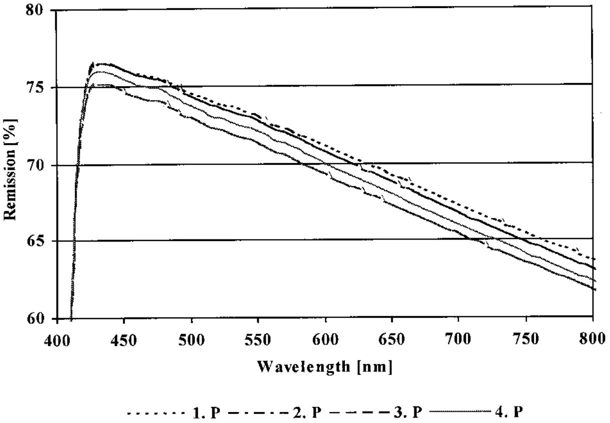


Figure 6. Remission spectra for Pigment B: pearl mill dispersion (1st to 4th pass)

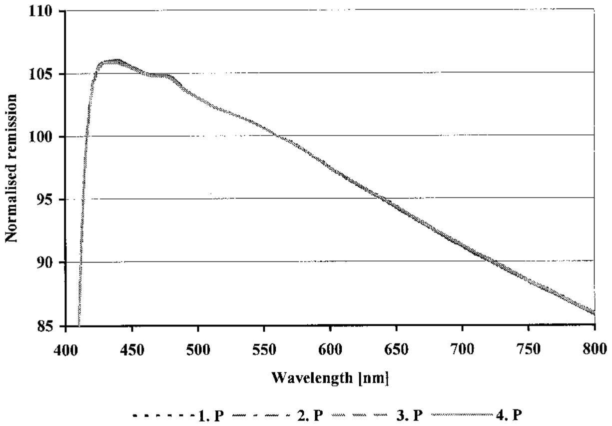


Figure 7. Normalised remission spectra for Pigment A: Comparison pearl mill dispersion (1st to 4th pass)

After normalisation of the spectra (figures 7 and 8) the spectra of the different passes of pigment A are identical. The different grindometer readings find no reflection in the spectra with regards to changing particle size distribution as a result of the progressing break down of coarse agglomerates.

The spectra of pigment B, however, differ noticeably. The biggest change is recorded between the 1st pass and the 2nd pass. Here the ratio bigger pigment particles to smaller pigment particles changes most. The changes between 2nd pass and 4th pass are only marginal. Again, this is found in the measured gloss and gloss haze values as listed in table 2, too. Here the biggest progress in dispersion was observed between pass 1 and pass 2.

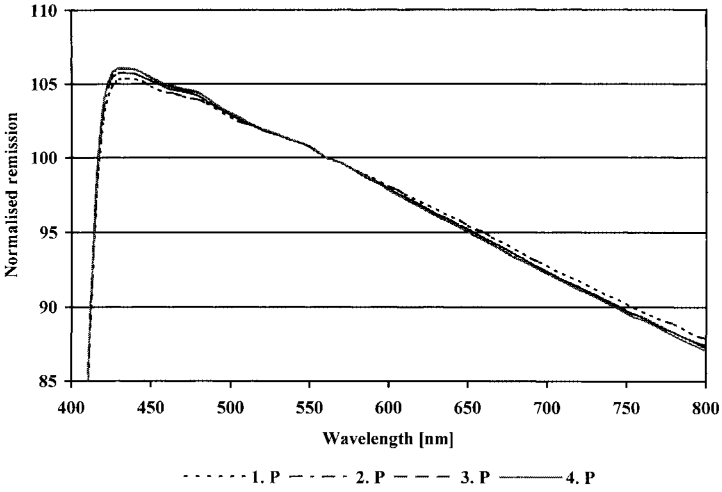
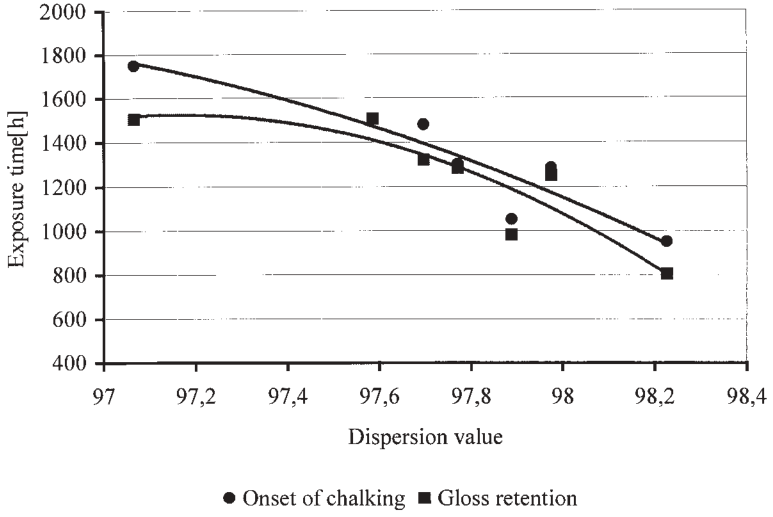


Figure 8. Normalised remission spectra for Pigment B: Comparison pearl mill dispersion (1st to 4th pass)

*Distribution values and weathering*

As seen before, dispersing pigment A with different machines gives different remission spectra although the values for gloss, gloss haze and grindometer do not indicate a difference. A good tool to quantify this difference in the remission spectra is the so called distribution values[4]. The distribution values are determined through the normalised remission curves. From those the ratio of the areas underneath the remission curve from 380 nm to 560 nm and from 560 nm to 720 nm is taken. For pigment A the ratios vary between 112 for the high speed stirrer to 115 for the pearl mill or Skandex mixer respectively.

In an earlier investigation coatings were prepared with pigment A exhibiting different dispersion values in its normalised remission spectra. The coatings were submitted to accelerated weathering. Figure 9 illustrates the correlation between distribution values of the coatings and the exposure time after which the deterioration of gloss to 50 % and the onset of chalking.



The results give the impression that a good dispersion is not desirable, since the weathering results improve up to almost 50 % with a poorer dispersion status. This is expected since with a higher portion of fine particles the surface area of the $TiO_2$ increases considerably and with this its photocatalytic activity. However, a good dispersion leads to a reduction of the amount of $TiO_2$ pigment necessary for the desired UV-protection and the optical properties of the coating and is, therefore, counterbalancing the higher photocatalytic effect.

## 3. Summary

The dispersing process with different dispersing tools was monitored with the common methods like gloss, gloss haze and grindometer readings and compared to the corresponding remission spectra. Differences in the dispersing behaviour of the pigments could be linked to differences in the remission spectra. For pigment A, an easy to disperse pigment in the acrylic-melamine coating system the remission spectra proved, that the pearl mill is the adequate dispersing tool, whereas for pigment B the high speed stirrer proved to be superior. A correlation between remission spectra and gloss and gloss haze measurements were found, whereas the progress in the break down of coarse particles as monitored with the grindometer finds no obvious reflection in the spectra. The different action of the dispersing tools were revealed with pigment A where the traditional evaluation tools for a good dispersion give identical results. Whereas the dispersion of pigment A with a pearl mill gives identical results as the Skandex mixer with regards to the remission profiles (figure 3), the high speed stirrer dispersion results in a lower portion of "smaller" particles. Finally, the accelerated weathering correlates well to the distribution values and demonstrates that the weathering results can be influenced strongly by the dispersion status of the coating.

## References

[1] J. Schmelzer, Farbe & Lack, 2/2001, 37-45, Mit Remissionskurven Pigmentverteilungen bestimmen

[2] P. Gross, APi Konferenz 2001: Untersuchung über das Dispergierverhalten verschiedener Titandioxid- pigmente mit unterschiedlichen Dispergieraggregaten

[3] B. Vielhaber-Kirsch, E. W. Lube, Abrasion characteristics of titanium dioxide pigments, KRONOS INFORMATION 6.30

[4] J. Schmelzer , KRONOS TITAN GmbH & Co. OHG, Charakterisierung der Verteilungsgüte von Weißpigmenten in einer Matrix, Offenlegungsschrift DE 10043038