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# Optical Behaviour of Copper Phthalocyanine Preparations for Inkjet Inks

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## Abstract

The present study investigates the preparation of the copper phthalocyanine pigment for inkjet printing inks. The pigment particle size distribution was measured with laser diffraction at different times of wet milling. Simultaneously, the absorbance spectra in a visible-near infrared spectral region of the corresponding diluted pigment dispersions were measured. At the beginning of the milling process, the particle size distribution is bimodal, showing the presence of aggregates and agglomerates. During the second hour of milling, the particle size distribution changes to unimodal due to the breaking of agglomerates, and the corresponding absorbance spectra change accordingly. Further milling diminishes the size of pigment aggregates up to the steady state value of around 130 nm, where also the absorbance in the corresponding spectra does not increase. A detailed analysis of intensity and position of the absorbance peak at 340 nm in dependence on the milling time and pigment concentration confirms the idea that an optical spectroscopy could be used for the assessment of optimal milling time required for the preparation of pigments with the maximum absorption ability.

**Keywords:** Inkjet, phthalocyanine blue, particle size distribution, optical spectroscopy

## 1. Introduction

With the recent development of inkjet technology, water-based pigmented inks have become more interesting in this field, especially due to their better resistance to fading when compared to dyes. Pigmented inks are treated as aqueous dispersions. Apart from their chemical nature, their properties are also influenced by the physical parameters. Therefore, the size and shape of particles together with the degree of dispersion and the tendency to reagglomeration/flocculation are important parameters for ink manufacturing.

The effect of the pigment particle size in pigmented inkjet inks has been addressed in several studies.[1–4] The requirements on the pigment particle size in inkjet applications depend on the print head parameters, and generally is about 100 nm.[5] Inks with a considerably higher average particle size exhibit low colour strength, chroma and transparency, and are prone to nozzle clogging. Alt-hough small particles overcome these drawbacks, they do suffer from lower light fastness and have a greater tendency to reagglomeration.[2]

Several methods have been in use to monitor the particle size distribution, each of them with its advantages and limitations at different costs. Scanning Electron Microscopy (SEM) has been successfully used in many applications; however, for the evaluation of organic pigments dispersed in organic media, a preceding selective oxygen plasma etching is required.[6] An alternative to SEM is Transmission Electron Microscopy (TEM). In comparison with SEM, TEM micrographs lack the topography information, and it may thus be hard to distinguish individual particles in aggregates or evaluate the particles of irregular shape. Another commonly used technique in the particle size analysis is the laser diffraction measurement, and the calculation of corresponding particle sizes based on the obtained intensity and angle of scattered light with the Mie theory.[7] This measurement, however,

assumes the spherical particles with the defined refractive indices.[8] Moreover, surfactants may be added to the sample to prevent the reagglomeration in the wet measurement. Such additives can cause bubbles that act for the light as a new particle and cause a misreading in the particle size distribution. The latest investigation in the pigment particle morphology also includes Atomic Force Microscopy (AFM).[9] Furthermore, other methods are available, e.g. sedimentation analysis, ultra centrifuge or sieve analysis for larger particles.[10] Such a wide array of analytical methods for small particle sizes at our disposal makes the choice for the most suitable one more difficult.

The aim of this study was to investigate the applicability of the VIS-NIR spectroscopy in monitoring of the pigment size distribution changes during the preparation of concentrated pigment dispersions for inkjet printing inks. The relation between the absorbance spectra at different milling time and the possibility to calculate the spectrum at desired milling from the available data is evaluated.

## 2. Materials and Methods

A concentrated pigment dispersion for milling (pigment preparation) was prepared by premixing 20 wt.% of commercial phthalocyanine blue pigment C.I. Pigment Blue 15 : 3 (Synthesia)[11] with 20 wt.% of Disperbyk 190 (ALTANA Group, BYK Additives & Instruments),[12–13] 15 wt.% of monopropylene glycol, 0.4 wt.% of biocides, 0.4 wt.% of silicone defoamer BYK 019 (ALTANA Group, BYK Additives & Instruments)[14–15] and 44.2 wt.% of demineralised water for about 1 hour in a dissolver. The stabilisation of pigments is achieved through a dispersant steric repulsion.[12–13]

The mixture was further processed with a DYNO-MILL Multilab lab-scale mill by applying 240 ml of glass beads with 0.1–0.2 mm in diameter. The samples for the measurements were withdrawn as follows: initially after the premixing, i.e. before employing the bead milling, after the first passage through the mill (i.e. after 10 minutes) and then after each milling hour up to 7 hours. In consequence, 9 specimens of pigment preparation were obtained for a further analysis. They are denoted here as PP$x$, where $x$ represents the milling time in hours.

For a spectroscopic analysis, the samples PP$x$ were extensively diluted to the concentration $x$ being 2, 4, 6 and 8 mg of pigment per 1 litre. For the dilution, demineralised water enriched with 1 g of dispersant per litre was used; hence, dispersions with four different pigment concentrations were prepared for every PP$x$. They are denoted as $y$PD$x$, where $x$ represents the milling time in hours and $y$ the pigment concentration in mg/L. The absorbance spectra were measured on a Specord 210 double beam UV-VIS spectrophotometer in the spectral range 300–1100 nm. The water solution used for the dilution of PP$x$ samples to prepare the $y$PD$x$ samples was used as a reference.

The particle size distribution of the aqueous dispersion was determined by laser diffraction, using a Horiba LA-950 laser scattering particle size distribution analyser. For these measurements, the PP$x$ samples were diluted to the transmittance of about 80% at the wavelength 405 nm. During the measurement, the samples were subjected to an ultrasonic treatment to prevent sedimentation. In the analysis, refractive indices of 1.33 for water and complex values 1.480–0.300i (at $\lambda = 650$ nm) and 1.660–0.100i (at $\lambda = 405$ nm) for the phthalocyanine pigment were applied.[8] The obtained particle size distributions were characterized by mode, kurtosis and skewness. Mode describes the most frequently occurring size, i.e. the peak position. The kurtosis $k$ and skewness $s$ describe the shape of the distribution peak, $k$ being the measure of whether the data have a peak or are flat relative to a normal distribution, and $s$ being the measure of symmetry, or more precisely, the lack of symmetry. They are defined as follows:

$$k = \frac{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^4}{\sigma^4} \tag{1}$$

$$s = \frac{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^3}{\sigma^3} \tag{2}$$

where $n$ is the number of data points, $x_i$ denotes data values, $\bar{x}$ is the average value and $\sigma$ is a standard deviation of $x$. For a normal distribution, the parameters take values $k = 3$ and $s = 0$.

## 3. Results and Discussion

### 3. 1. Laser Scattering Analysis

The spline approximation of the particle size distribution obtained by laser diffraction for selected samples is presented in Figure 2. Only the samples from the pigment dispersions during the first hour of milling, and after 6 and 7 hours are shown. At the beginning of the milling process, the particle size distribution is bimodal, showing that both aggregates and agglomerates are present. As the milling time increases, agglomerates break up – the corresponding peak at larger particle sizes disappears and the distribution becomes unimodal. All distributions were characterized by mode, standard deviation, kurtosis and skewness of the main peak, while the second peak of the bimodal distribution was not taken into account. The changes of these parameters with milling time are presented in Table 1. They show that the particle size reduces very rapidly in the first hour of milling and then approaches a steady value. The limiting value of mode approaches 100 nm, which is the required value for a good inkjet ink.

At the same time, the distribution becomes narrower as demonstrated by the kurtosis value. However, the size distribution obtained from the diluted PP6 sample does not reveal the shape of a normal distribution. Its kurtosis remains above five and skewness does not drop below one. It shows that more particles are larger than mode.
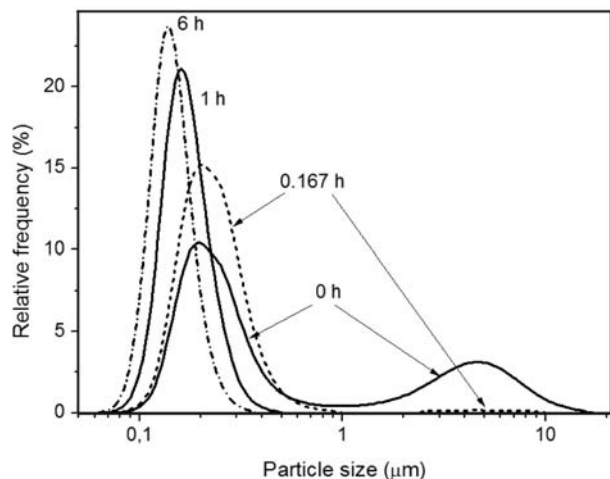


**Figure 1.** Particle size distribution of pigments after 0, 0.17, 1 and 6 hours of milling measured by laser diffraction. Samples were prepared by diluting PPx specimens. After 7 hours of milling, particle size distribution is practically the same as it is after 6 hours.

**Table 1.** Characteristics of the main peak of particle size distribution (cf. Figure 1) in dependence on milling time.

| Milling time (h) | Mode (μm) | Standard deviation | Kurtosis | Skewness |
|---|---|---|---|---|
| 0 | 0.197 | 0.132 | 12.63 | 2.67 |
| 0.17 | 0.197 | 0.095 | 9.25 | 1.89 |
| 1 | 0.150 | 0.051 | 5.69 | 1.28 |
| 6 | 0.131 | 0.037 | 5.41 | 1.17 |
| 7 | 0.131 | 0.037 | 5.46 | 1.17 |

## 3. 2. VIS-NIR Spectroscopy

The VIS-NIR absorbance spectra were measured for all series of pigment dispersion $y$PD$x$, where $x$ = 0, 0.16, 1, 2, 3, 4, 5, 6, 7 hours, and $y$ = 2, 4, 6, 8 mg/L. The absorbance spectra depend on milling time ($x$) and on pigment concentration ($y$). The spectra are typical of copper phthalocyanine with three main bands at approximate wavelengths of 340, 615, and 700 nm (cf. Figures 2a and 2b). The three absorption bands reveal the characteristic properties of copper phthalocyanine: the B- or Soret band at 340 nm, and the two Q-bands at 615 and 700 nm. They are assigned to $\pi \rightarrow \pi^*$ transitions of the system. However, the metal d-band which corresponds to d orbitals of the central Cu atom, falls to somewhat shorter wavelengths outside the measured region.[16–17]

In the experiment, the pigment concentration influences only the absorption intensity, while the milling time also influences the band shapes and their intensity ratio. A typical result of the VIS-NIR measurement in relation to the milling time (i.e. particle size) at a constant pigment concentration is shown in Figure 2. The results reveal two groups of spectra with similar behaviour. In the first group of spectra (cf. Figure 2a), the spectra change both in the line shape, which can be best seen in the wings of the absorbance band, as well as substantially in intensity. According to the laser diffraction analysis, the samples in this group exhibit a bimodal particle size distribution. In the second group (cf. Figure 2b), the absorbance spectra differ only in intensity with only a mild development when the milling time is increased. This group is characterised with a unimodal particle size distribution.
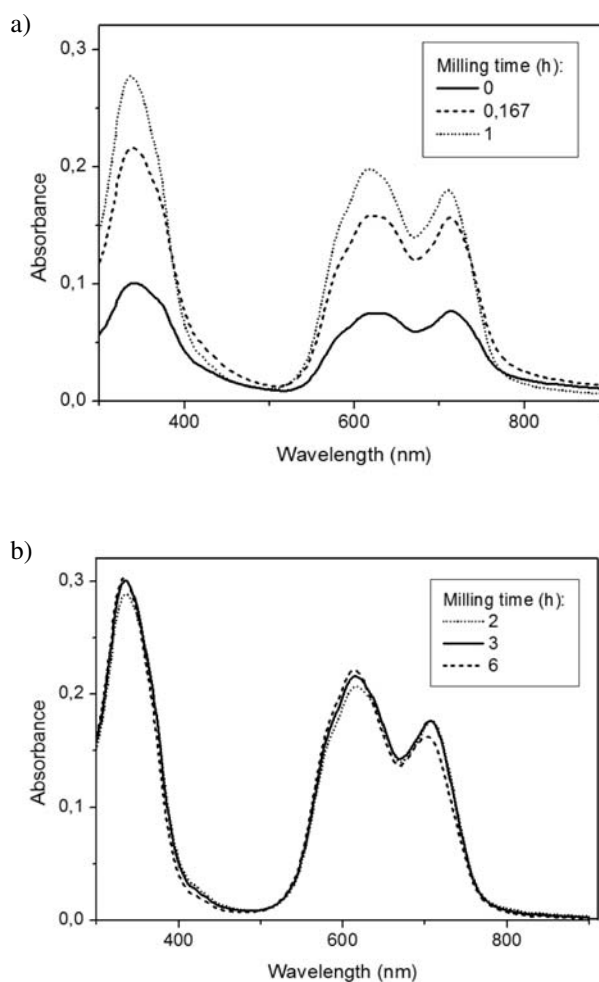
a)



b)



**Figure 2.** Absorbance spectra of diluted pigment dispersion 4PD$x$ (pigment concentration 4 mg/L) in relation to milling time. Samples with bimodal (a) and unimodal (b) particle size distribution.

A better description of the absorbance spectra was obtained by the analysis of the Soret band at around 340 nm. The dependence of the position of the Soret band and

the intensity on the milling time and pigment concentration was analysed. At the beginning of the milling process, the intensity quickly increases and reaches a more-or-less steady value between the first and the second hour of the milling (cf. Figure 3). With further milling, no significant increase in the absorbance peak occurs. Therefore, when the particle size decreases to the limiting value (cf. Figure 1 and Table 1), a further reduction in size does not influence the absorbance. This dependence might be applied to estimate the particle size that gives the highest ink absorbance, and as it cannot be increased – further milling thus not being necessary, it also enables the determination of the optimal milling time.

The resultant steady-state intensity grows linearly with the pigment concentration (cf. Figure 3 and Table 2).
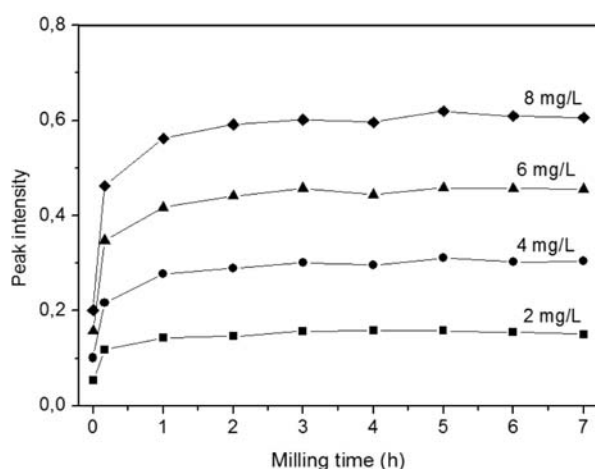


**Figure 3.** Intensity of Soret absorbance band in dependence on milling time for prepared pigment dispersion.

**Table 2.** Intensity of Soret absorbance band reached at 3 hours of milling (cf. also Figure 3).

| Pigment concentration (mg/L) | Peak intensity (absorbance units) |
|---|---|
| 2 | 0.142 |
| 4 | 0.278 |
| 6 | 0.417 |
| 8 | 0.563 |

At the beginning of milling, the Soret band is located at 341 nm and shifts with milling time to shorter wavelengths (cf. Figure 4). At very short milling times, the shift is large and gradually diminishes between the first and the second hour. After the third hour of milling, the shift becomes very small. The two rates of change in the peak position as a function of milling time indicate that two processes occur during the milling. The first one is characterized by a larger shift of the peak and the second by an almost negligible one. The two processes are characteristic of short (up to 2 hours) and longer (more than 2 hours)

milling times. This observation agrees with the milling kinetics suggested for the nano-milling of pigments using a wet stirred media mill.[18–19]
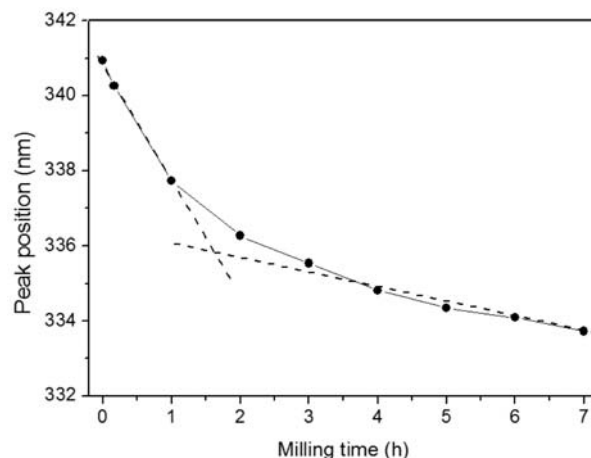


**Figure 4.** Position of Soret band in 2PD*x* samples dependence on milling time.

## 4. Conclusions

The degree of pigment dispersion is an important factor in ink manufacturing, where it affects the application and optical properties of the final ink. It can be studied with the help of various methods of different accessibility in the production laboratory and at different costs. Nevertheless, the determination of the optimal milling time with a minimum energy input and maximum performance is desired.

The changes in the particle size distribution of the commercial phthalocyanine pigment during the wet-bead milling were studied by means of laser diffraction and VIS-NIR spectroscopy. The absorbance spectra were phenomenologically grouped into two groups, i.e. one with different shapes of the peak, esp. in wings, and the other with the same peak shapes (cf. Figure 2). The first group is characterized by a bimodal particle size distribution, showing the presence of aggregates and agglomerates, while the second group shows a unimodal size distribution, which confirms a complete breaking of the agglomerates of pigment particles. A detailed analysis was performed on the band located close to 340 nm with a non-composed nature. Its intensity and position depends on the milling time. For the samples of the first group, the intensity and position change rapidly with milling time. After the complete breaking of agglomerates, the intensity and position of the selected peak becomes nearly constant. These results support the phenomenological dividing of the absorbance spectra into two groups, presenting the two processes which occur during the milling of pigments. The first is characterized by a larger peak shift and intensity increase, and the second by an almost negligible

change in the peak position and intensity. The two processes are characteristic of short (up to 2 hours) and longer (more than 2 hours) milling times, respectively.

The results obtained in this study led to the conclusion that the milling time should be at least 2 hours to break the agglomerate and get the unimodal particle size distribution. Further milling only slightly influences the studied optical properties of the pigment dispersion in the VIS-NIR spectral region. These results confirm that the VIS-NIR spectroscopy can be a useful tool in monitoring the efficiency of the milling process. Although it does not provide absolute values, the advantage of the VIS-NIR spectroscopy lies in the low demand for laboratory equipment and in uncomplicated sample preparation.

# 5. Acknowledgments

# 6. References

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# Povzetek

Raziskali smo pripravo bakrovega ftalocianinskega pigmenta za tiskarske barve, ki so primerne za kapljični (ink-jet) tisk. Porazdelitev velikosti delcev v odvisnosti od časih mletja pigmentne paste smo merili z uklonom laserske svetlobe. Za vse vzorce smo izmerili tudi absorbančne spektre v vidnem in bližnjem infrardečem spektralnem področju. Za začetek mletja je značilna bimodalna porazdelitev velikosti delcev, kar dokazuje prisotnost agregatov in aglomeratov. Med drugo uro mletja se razbijejo aglomerati, porazdelitev velikosti delcev postane unimodalna, oblika absorbančnih spektrov pa se spremeni zlasti v repih absorpcijskih vrhov. Nadaljevanje mletja zmanjša agregate do stabilne velikosti okoli 130 nm, intenziteta pripadajočih absorbančnih spektrov pa postane konstantna. Podrobna analiza intenzitete in položaja absorbančnega pika pri 340 nm v odvisnosti od časa mletja potrjuje, da je mogoče z merjenjem spektrov v vidnem spektralnem področju določiti optimalni čas mletja pigmenta, ki daje maksimalno absorpcijsko sposobnost pigmentne disperzije.