



April 2006

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### Recommended Citation

Pal, Lokendra and Fleming, Paul D. III (2006) "The Study of Ink Pigment Dispersion Parameters," *The Hilltop Review*: Vol. 2: Iss. 1, Article 9.

Available at: <http://scholarworks.wmich.edu/hilltopreview/vol2/iss1/9>

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# The Study of Ink Pigment Dispersion Parameters

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## ABSTRACT

The purpose of this study was to investigate the influence of rotation speed and milling time on the pigment dispersion quality. The information can be used to obtain a standard laboratory condition at which a wide range of pigments may be dispersed to formulate water-based rotogravure inks. The influence of pigment concentration and shear forces on the pigment dispersion were also studied.

The procedure consisted of dispersing the pigment using a laboratory Dispermat® SL bead mill at various milling times with two different rotation speeds and measuring the particle size and particle size distribution of the milled samples. The pigment was then dispersed at standard laboratory condition with different pigment concentrations.

## INTRODUCTION

As for the future of printing processes, ecology will play a much larger roll, with special attention being paid to eliminating waste, emissions, and reducing energy input. One main focal point will be the reduction of the volatile organic compounds (VOCs) released into the atmosphere. Water-based inks represent a proven solution to reducing VOC emissions. Water-based inks are cheaper, decrease atmospheric pollution, have less solvent, lower fire risks, less print odor, remove the need for recovery plants; and are easier to wash-up on the press.

The manufacture of printing ink is a technologically advanced highly specialized and complex process. The basic formulation of ink involves the grinding of pigment in a vehicle to form the pigment dispersion, then letting down the pigment dispersion with suitable resins to meet rheological and functional properties. The main components of water-based inks are pigment, binding agent, carrier (water) and additives. Binding agents are acrylic resins, which are emulsions or diluted to water with amines. The proportion balance of these types of binding agents is made to fit the printing process and the quality requirements of the final product. Additives used in water-based inks are antifoam, waxes, extenders, pH-controllers and surfactants. Water-based gravure ink formulation contains pigment 6-17%, binding agents 10-30%, solvents 1-12%, and water 45-66% [1]. The surface tensions of the water-based inks are 30-40 dyne/cm. The primary feature of the drying process in water-based inks is evaporation.

The pigment in most printing inks is the most expensive part of the formulation; economics of pigment selection and proper dispersion are of vital importance [2]. The production of ink depends on basic physical processes involving complete wetting of the pigments and their even distribution in the surrounding vehicle. This complex process is called "Dispersion", and has to be clearly differentiated from mixing or stirring [3]. The quality of the final dispersion is dependent on the optimization of many influencing factors.

The dispersion of pigments in printing inks is important for several reasons but the effect of dispersion quality on the rheological behavior of the ink is perhaps the most important criterion. Because of the application methods flow properties are all important in inks and this is certainly the first hurdle that a printing ink must satisfy, in order to be considered for potential use [4]. To achieve the optimum benefits of a pigment, it is necessary to obtain as full a reduction as possible to the primary particle size. The color strength of a pigment depends on its exposed surface area, and the smaller the particle the higher the surface area and thus stronger the color [1,7]. Increasing demands on quality printing inks regarding the optical characteristics such as gloss, transparency or color strength require the use of more effective dispersing techniques [2].

There is a wide variety of printing ink media used in the modern printing processes. Variation in the viscosity of the ink vehicle and the methods of incorporating pigments into such vehicles have considerable effects on the shear that can be applied to pigment particles and agglomerates and therefore on the speed and fineness of the ultimate dispersion [4]. The rheological properties are important in the application of inks and associated phenomena such as tack of the ink. This is important in obtaining an even distribution on the press and proper transfer to the paper. This is also controlled to some extent by the dispersion properties of the material.

### **The Dispersion Process**

The dispersion process involves the breakdown of associated particles into smaller particles and their distribution in a fluid, leading to a colloidal suspension. A colloidal suspension is characterized by the behavior that the finely divided particles do not settle under their own gravitational forces. Pigment particles can be divided into three classes: primary particle, crystallites, aggregates, (primary particles having a surface to surface contact) and agglomerates, (primary particles touching each other via edges and corners) [3,5]. The steps involved in pigment dispersion process as follows.

### **Wetting of the Pigment Particles**

The wetting of the pigment particles is influenced by the following factors (a) geometry of the particles, (b) viscosity of the vehicle, (c) surface tension of the vehicle, and (d) chemical character of the solvents. The Washburn equation describes the wetting process [3,6]:

$$\frac{V}{T} = \frac{\pi * R^3 * \sigma_L * \cos \delta}{2 * l * \eta} \quad 1$$

- V = transported vehicle volume
- T = time
- R = capillary radius
- $\sigma_L$  = surface tension of the vehicle
- $\eta$  = viscosity
- l = length of the capillary

The equation shows that the speed of the wetting increases with the size of the capillary in the pigment powder and with a lower surface tension of the vehicle. Another important factor for the speed of wetting is the viscosity of the vehicle. The Washburn equation states that the low viscosity provides faster wetting. The chemical nature of the solvent plays an important role in the wetting process. The affinity between pigment and solvent must guarantee a sufficient wetting ability.

### **Breakdown of the Pigment Particles**

The breakdown of pigment particles can be described as follows:

(a) spontaneous breakdown, during the wetting process

The pigment particles are wetted by the vehicle, which causes a more or less spontaneous breakdown of the forces holding the smaller agglomerates together;

(b) mechanical breakdown

The remaining agglomerates have to be broken down by transferring mechanical energy into the system; The transfer of energy is performed with special dispersing equipment [3,5].

### **Stabilization of the Dispersion**

The purpose of the stabilization is to maintain a colloidal system during further processing or storage of the dispersion. The stabilization of the finely dispersed particles avoids reagglomeration and flocculation

### **OBJECTIVE**

The objective of this project was to evaluate the effect of rotation speed, milling time, and pigment concentration on pigment dispersion quality, particle size and particle size distribution using different mixing/milling techniques for water-based gravure inks.

### **EXPERIMENTAL DESIGN**

#### **Materials**

Pigment Heuco Blue-15 was used for dispersion supplied by Heucotech limited USA. Joncryl HPD-96 resin solution (34% NV), low VOC colloidal solution, 26 % solids and 1.07 sp. gravity was used as dispersing resin for high solids, gloss, strength and improved shock stability. Surfynol CT-131 grind aid was used as wetting agents to reduce the vehicle surface tension and help the vehicle to penetrate the microscopic air pockets in the pigment agglomerates. DeeFo PI-45 antifoam was used to prevent foam buildup

#### **Dispersing Media- "Dispermat® SL" Bead Mill**

A "Dispermat® SL" bead mill consists of a milling system and separate instrument control case. The milling system exists as a double wall grinding chamber and a motor for the agitator in the chamber. The essential dispersion parameters can be optimally and independently controlled via the control case. Product feeding can be done by air pressure and the dispersion process is completed in several passes. The actual particle size reduction in the grinding chamber of a mill is accomplished by the moving grinding material, which is activated by a high speed and high-energy agitator. There are two types of particle size reductions (a) shear and (b) collision / impact, as the grinding material collides and rolls about each other, the solid particles get caught between them and are gradually reduced in size.

The quality of the dispersion degree is dependent on the following characteristics:

- (1) pigment volume concentration, pigment to vehicle ratio,
- (2) type, size and density of the grinding media,
- (3) residence, or dwell, time,
- (4) milling time or cycle,

- (5) rotation speed,
- (6) energy input, and
- (7) temperature [3,5].

The selection of the grinding media depends upon the nature of the pigment, viscosity, desired particle size of the finished product, color and appearance requirements (gloss, haze, color strength, transparency). The residence time or dwell time is the time required for the product to pass through the mill. If the dwell time is too short, the mill base will not be sufficiently dispersed and if the dwell time is too long the material can be over dispersed resulting in decreasing gloss and increasing haze. The dwell time can be controlled by the amount of applied air pressure. The rotation speed should be independently adjustable from the throughput rate. The dispersion degree depends on the amount of energy input i.e. the highest possible agitator speed and the residence time in the chamber. The agitator speed of the Dispermat SL is variable between 0- 6000 rpm. For optimum dispersion results, the temperature of the mill base has to be controlled. The Dispermat® SL is equipped with a double wall for circulation of cooling water through it.

### **Particle Size Analyzer- NICOMP 370 DLS**

DLS (dynamic light scattering) also called QELS (quasi-elastic light scattering) or PCS (photon correlation spectroscopy) was used for analyzing the size distribution of particles suspended in water. Light from a laser is focused into a glass tube containing a dilute suspension of particles [7]. The intensity of light scattered by a single, isolated particle depends on its molecular weight and overall size and shape [8], and also on the difference in refractive indices of the particle and surrounding solvent. Three different types of weighting systems (a) volume-weighted, display the relative particle volume vs. diameter; (b) intensity-weighted, display the relative intensity of scattered light vs. diameter; (c) number-weighted, display the relative number of particles vs. diameter; may be used for the measurement of particle size and particle size distribution.

### **Particle Size and Particle Size Distribution (PSD)**

The main objective of the dispersion process is to produce a stable colloidal system in which the pigment particle size distribution ranges between 50 and 500 nm. Color strength, purity, gloss, and opacity achieve maxima in this range [1,3,5,7]. The particle size and particle size distribution (PSD) fundamentally affect the ink performance. Small changes in the PSD can often dramatically alter product performance. Small particle size provides excellent dispersion, color strength, saturation, gloss, hiding power and flow properties whereas large particle size provides poor dispersion (plate or cylinder wear, poor ink/water balance, hickeys, printability problems), unstable flows, poor hiding power, poor color strength (color fluctuation), and low gloss properties.

### **Phase 1: Pigment Dispersion at Different Rotation Speed and Milling Time**

The pigment blue-15 powder was mixed in water under low shear for 20 min with different additives as outlined in Table 1. The pigment suspension sample was taken after proper mixing for measuring the particle size and particle size distribution (PSD). This suspension was then added to the mill. A constant air pressure was applied and the milling rotor speed set to 2000 rpm. The operating mode of constant power input was selected and maintained throughout the duration of the experiment. After 5, 10 and 20 passes a pigment suspension samples were taken for observing the particle size reduction. Again the same mixing and milling process was performed using the operative conditions described in the first experiment. In this case the milling rotor speed was increased to 4000 rpm.

In order to determine the particle size distribution of the pigment suspensions, the solution was diluted to get the appropriate intensity i.e. in between 200 to 400 counts, and then the particle size was measured with the NICOM 370 DLS particle sizing systems submicron analyzer. The particle size distribution and the volume mean diameter were determined by interpolating the distribution frequency of all particle size classes and by constructing an undersize cumulative plot, respectively.

### **Phase 2: Dispersion at Different Pigment Concentration**

The pigment was dispersed under standardized laboratory conditions (4000 rpm and 10 pass) at three different concentrations shown in Table 2. Particle size and particle size distribution were measured by using the NICOM 370 DLS particle sizing systems submicron analyzer.

Table 1: Organic Color Pigment Dispersion Formulation

| Ingredient |                             | Amount (%) | Amount (grams) | Purpose          |
|------------|-----------------------------|------------|----------------|------------------|
| Pigment    | Heuco Blue - 15             | 35         | 210.0          | Colorant         |
| Vehicle    | Resin (Joncryl HPD 96)      | 25.7       | 154.2          | Dispersing agent |
|            | Surfactant ( Surfynol T131) | 5.0        | 30.0           | Wetting agent    |
|            | Antifoam                    | 0.5        | 3.0            | Antifoam agent   |
|            | Water                       | 33.8       | 202.8          | Diluent          |

Table 2. Summary of Pigment and Vehicle Ratio

| Ingredients |                                                                                        | By weight (%) |         |          |
|-------------|----------------------------------------------------------------------------------------|---------------|---------|----------|
|             |                                                                                        | Case I        | Case II | Case III |
| Pigment     | Heuco Blue – 15                                                                        | 30            | 35      | 40       |
| Vehicle     | Resin (HPD 96) - 25.7 %<br>Surfactant (T131)- 5 %<br>Antifoam- 0.5 %<br>Water - 33.8 % | 70            | 65      | 60       |

## **RESULTS AND DISCUSSION**

The Chi squared value is very high ranging from 5.48 to 16.2 and therefore the multimodal distribution is appropriate. Hence, based on the NICOMP distribution analysis, a comparison of particle size from Table 3 and Figure 1 shows the intensity mean diameter of the pigment blue decreasing with milling time. The experiment allowed a particle size reduction from 221 nm to 178 nm at 2000 rpm and 200 nm at 4000 rpm after 20 passes. A comparison of particle size shows larger reduction at 2000 rpm with increasing milling time. The lesser decrease in particle size for the 4000 rpm sample probably results from rheological properties of the dispersion. This needs to be confirmed with rheological measurements.

Table 3 shows the particle size distribution at zero passes 0.9 % of particles were found at a mean diameter of 14 nm, the 57.1 % of particles were found at a mean diameter of 140.5 nm and the 42 % of

particles were found at a mean diameter of 337 nm. Figure 2 shows that after 20 passes at 2000 rpm, 2.0 % of particles were found at a mean diameter of 27 nm, the 98.0 % of particles were found at a mean diameter of 180 nm, whereas Figure 3 shows that after 20 passes at 4000 rpm, 17.8 % of particles were found at a mean diameter of 63 nm, and 82.2 % of particles were found at a mean diameter of 225 nm. This shows the particle size distribution narrowing with an increase in milling time. From both the tables and figures it is shown that there is no significant reduction in particle size after 10 passes at 4000 rpm, but that the particle size is reduced at every pass, at least up to 20 passes at 2000 rpm.

In second phase of experiment, a comparison of particle size results at standardized laboratory condition from Table 4 and Figure 4 shows the intensity mean diameter of the pigment blue increasing with pigment concentration as agglomerates can be formed by collisions between particles, and as the probability of such collisions is proportional to the square of the particle concentration.

Table 3. Phase I: Intensity Wt. NICOM Distribution Analysis

| Rotation Speed         |     | 2000 RPM |      |      |     | 4000 RPM |      |      |      |
|------------------------|-----|----------|------|------|-----|----------|------|------|------|
| Milling Time (Passes)  |     | 0        | 5    | 10   | 20  | 0        | 5    | 10   | 20   |
| I.M.D (Int. Mean Dia.) |     | 221      | 209  | 199  | 178 | 221      | 208  | 203  | 200  |
| Peak I                 | M.D | 14       | 0    | 0    | 0   | 14       | 0    | 0    | 0    |
|                        | (%) | 0.9      | 0    | 0    | 0   | 0.9      | 0    | 0    | 0    |
| Peak II                | M.D | 140.5    | 95.3 | 82   | 27  | 140.5    | 98   | 78   | 63   |
|                        | (%) | 57.1     | 29.5 | 21.2 | 2.0 | 57.1     | 23.8 | 18.6 | 17.8 |
| Peak III               | M.D | 337      | 257  | 227  | 180 | 337      | 250  | 225  | 225  |
|                        | (%) | 42.0     | 70.5 | 78.8 | 98  | 42.0     | 76.2 | 81.4 | 82.2 |

Table 4. Phase II: Intensity Wt. NICOM Distribution Analysis

| Case                            |     | I (30 % Pigment) | II (35 % Pigment) | III (40 % Pigment) |
|---------------------------------|-----|------------------|-------------------|--------------------|
| I.M.D (Intensity Mean Diameter) |     | 183              | 203               | 204                |
| Peak I                          | M.D | 12               | 0                 | 29                 |
|                                 | (%) | 0.30             | 0                 | 1.70               |
| Peak II                         | M.D | 136              | 78                | 163                |
|                                 | (%) | 50.70            | 18.60             | 55.0               |
| Peak III                        | M.D | 396              | 225               | 403                |
|                                 | (%) | 49.0             | 81.40             | 43.3               |

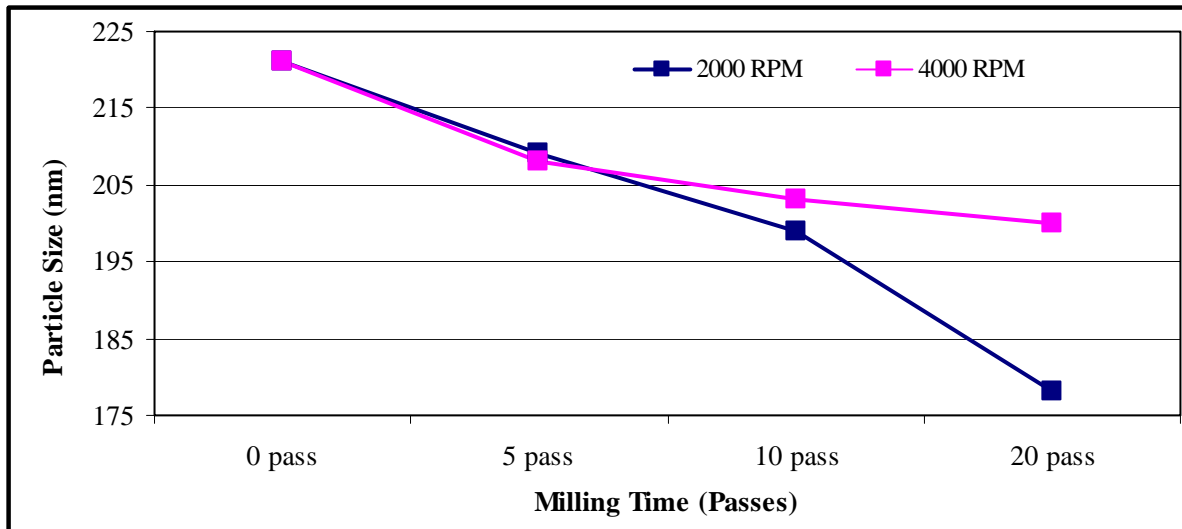


Figure 1. The influence of Rotation Speed and Dispersion Time on Particle Size

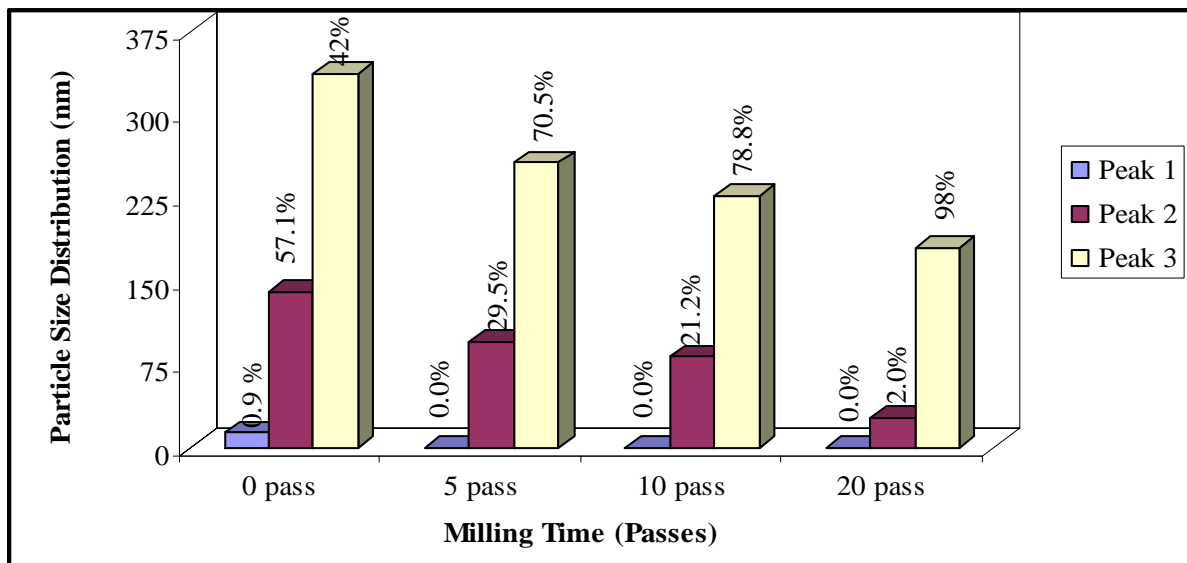


Figure 2. NICOMP Particle Size Distribution Analysis (2000 RPM).



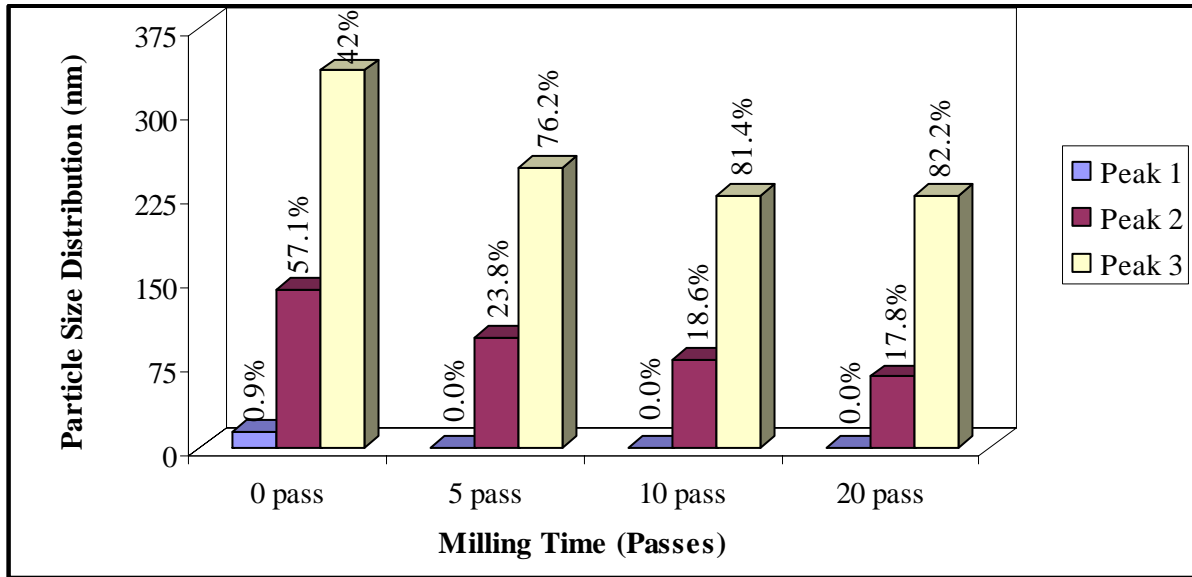


Figure 3. NICOMP Particle Size Distribution Analysis (4000 RPM)

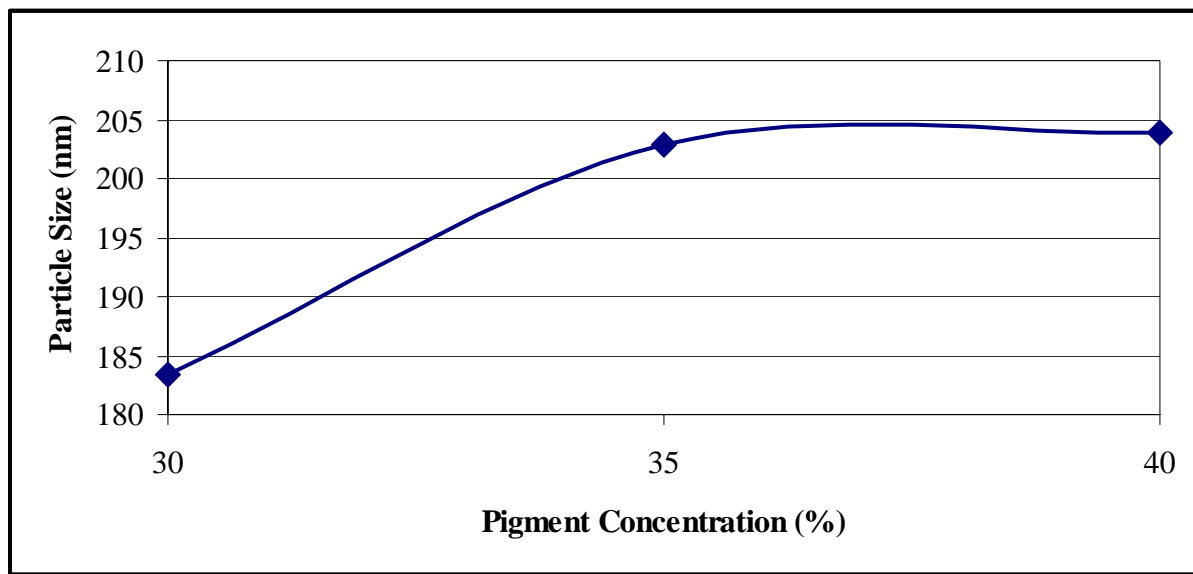


Figure 4. The influence of Pigment Concentration on Particle Size

## CONCLUSIONS

The pigment dispersion at 2000 rpm and 20 passes allowed a particle size reduction of 43 nm (I.M.D) whereas the pigment dispersion at 4000 rpm and 20 passes allowed a particle size reduction of 21 nm (I.M.D). Regardless of speed, there is significant reduction in particle size after every pass. The most effective time and speed seems to be 10 passes at 2000 rpm, since the particle size is reduced to about 200 nm, near to the ideal size for a blue pigment [1]. The particle size increases with pigment concentration because of aggregate formation at higher concentration, but appears to approach an asymptote of about 205 nm.

Because of the apparent effect of rpm on final particle size, rheological properties need to be measured.

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