Ink Stability During Printing

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Abstract

It was found that particle sizes of ink pigments change after several hours of printing in such a way, that it affects printability properties. This was demonstrated on several gravure and flexo printing trials lasting for several hours. Both rotogravure toluene-based process inks and flexo water-based inks exhibited changes in pigment particle size.

Decrease of rotogravure inks particle size was most obvious in black (from 482nm to 231nm), while the decrease of particle size in all other colors was rather similar: from 257 to 173 (yellow), from 270 to 193nm (magenta) and from 282 to 207nm (cyan). Differences in color, print density, and specular gloss measured on printed substrates at the beginning of trial and after seven hours of printing were found. Color changes were calculated from L*a*b* color coordinates as ΔE values. ΔE was higher than 3.0 for each process color rotogravure ink. Such color difference can be observed by human eye. Further measurements indicate that specular gloss increases with the decrease of the particle size. On the other hand, density mottle decreased with diminished particle size. There was no dot gain change observed. Particle size of Pantone Brown flexo water based spot color decreased from 250nm to 178nm after 270 minutes of printing, producing a change in ΔE value of 3.2.

Keywords: Ink, pigment, colour-difference, gloss

1 Introduction

Each type of printing ink requires a very careful balance of formulation to meet the requirements of the printing process and the end use properties. Many of these properties are controlled by the particle size of the pigments. Small particles provide excellent color strength [1], saturation [2], gloss [1], hiding power [1], dispersion [3], and flow [4,5]. On the other hand, large particles tend to exhibit poor dispersion (plate or cylinder wear, poor ink/water balance, hickeys, printability problems), poor flow, poor hiding power, poor color strength (color fluctuation), and lower ink gloss.

The important characteristics affecting the color of the printing ink are the color strength (the effective concentration of coloring materials per unit weight or volume of ink) and the opacity (the ability of a pigment to cover or obscure the surface to which it was applied) [1]. To achieve the desired visual characteristics, inks need to have varying degrees of opacity and transparency [6]. That can be accomplished by the choice of colorant and degree of its dispersion in the ink [7]. Different colorants behave differently when irradiated with light. The degree of reflectance, absorption and a colorant's refractive index determine its opacity and transparency [8]. Both color strength and opacity depend on pigment particle size. Scattering increases with the pigment particle size increase, until the wavelength of incident light is reached. At higher pigment particle size, the opacity decreases again. Thus, the opacity of an ink pigment is maximum around 350-500 nm (Figure 1). If scattering is so intense that no light passes through the material, the ink is opaque. The smaller the particles in the ink, the more transparent the ink is. The transparent inks require smaller particles than opaque inks. Color strength increases with decreasing particle size because of the larger surface area per unit mass and better bonding among the particles (Figure 1) [9].

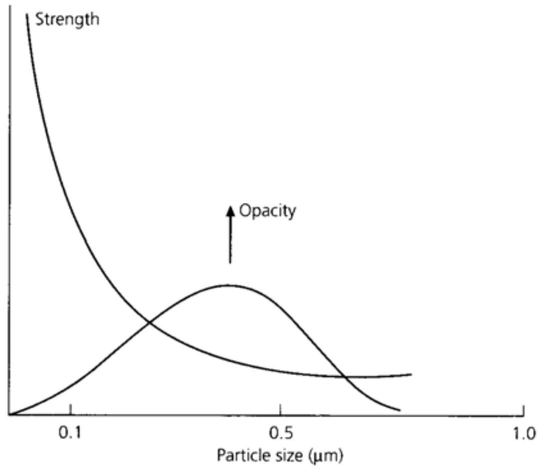

Figure 1: Dependence of Color Strength and Opacity of Pigments on Particle Size [5]

A pigment hides or tints by means of its ability to scatter and absorb light. The ability to scatter the light depends upon several factors, but the primary one for pigments is the index of refraction (n). The ability to absorb light depends upon the pigment's absorption coefficient (k). For colored pigments, light absorption is more important than light scattering in developing opacity, although the latter is not negligible. Consequently, the primary property for colored pigments is the complex index of refraction, m, with m= (n-ik) [10], as a function of wavelength and particle size. The dependency of the hiding power and tinting strength on the particle is shown in Figure 2.

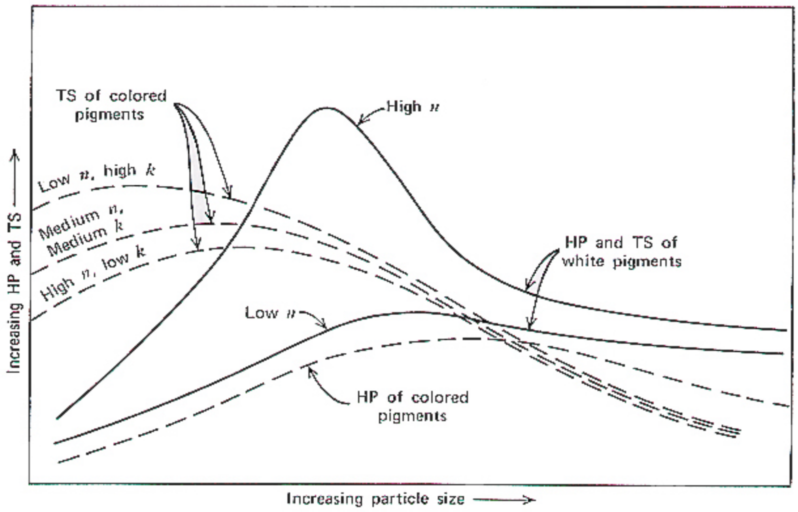

Figure 2: Schematic Diagram Showing Effect of Particle Size on Hiding Power (HP) and on Tinting Strength (TS) for White and Colored Pigments [10]

For colored pigments, the optimum particle size for hiding power is larger than that required for optimum tinting strength since the former property involves both scattering and absorption, whereas the latter is primarily due to absorption. In addition, the hiding power and tinting strength are dependent upon such other factors as the particle size distribution, particle shape, and degree of dispersions [11].

The properties of printing inks are studied and tracked in ink manufacturers' facilities. When the ink reaches its user, its properties are not measured to a great extent. The aim of this work was to study how the ink behaves on the printing press. Therefore, inks particle size was studied during printing trials. In addition, printability properties of job printed with inks staying for several hours in ink sump were compared to those printed with fresh inks.

Particle size analyses of process color inks, commercially available in North America, for flexographic, rotogravure, lithographic, ink-jet and for screen-printing processes have been presented elsewhere [12-16]. The particle size of coated gravure inks was in the range from 247.7 nm (process cyan) to 433.4 nm for process black. The uncoated inks exhibited smaller particles than coated inks [12,13]. This was attributed to the presence of higher amounts of extender in uncoated inks. The average particle size of gravure extender was around 179.3 nm. Preliminary results from this study were presented elsewhere [12,13,17].

2 Experimental

Gravure printing was performed on the Cerutti Rotogravure Press running at 1000'/min for seven hours at the Western Michigan University Printing Pilot Plant. The paper roll was a grade 5, ultra lightweight coated RG sheet with furnish consisting of approximately 25% mechanical pulp and 75% chemical pulp. Its pigment blend was mostly clay with a very small amount of $CaCO_3$ mixed with talc. The GE brightness of that sheet was 71 ^oGE with specular gloss of 50%. The basis weight was 32.0 lb/3300 ft^2 (47.4 g/m^2), and the caliper was 0.0017 inches, resulting in a bulk of 0.91 cm^3/g. All the inks used in the rotogravure printing trial were toluene-based coated process color inks (Yellow, Magenta, Cyan, Black). The ink viscosity was kept at 22 ± 0.3 seconds for yellow, magenta, and cyan inks and 20 ± 0.3 seconds for black ink based on a Shell cup #2, by frequent addition (every 15 minutes) of toluene during the printing process.

Flexo Printing was done on an Evers Flexo Press No. 54, running at 700 ft/min for five hours. The substrate was a liquid packaging board, both sides coated with polyethylene. The basis weight was 186 lb/3000 ft^2, and the caliper was 0.0147 inches. Two kinds of water-based inks were tested: Spot color Pantone Brown 497 that is combination of warm red, green and black. The second ink was Aquapak Process Black.

3 Analytical

3.1 Inks Particle Size

The Particle Sizer Submicron 370 NICOMP analyzer based on DLS (dynamic light scattering) was employed in for the measurements of the particle size (Figure 3).

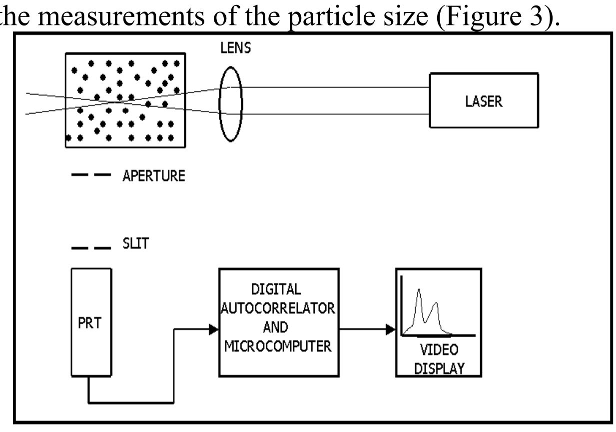

Figure 3: Simplified Block diagram of Photon Correlation Instrument (NICOMP [18], DLS Instrument)

The operating principle of dynamic light scattering is illustrated in Figure 3. Light from a laser is focused into glass tube or cuvette containing a diluted suspension of particles. The temperature of this scattering cell is held constant, for reasons, which will soon become apparent. Each of the particles illuminated by the incident laser beam scatters light in all directions. The intensity of light scattered by a single, isolated particle depends on its molecular weight and overall size and shape, and also difference in refractive indices of the particle and the surrounding solvent. The incident light wave can be thought of as consisting of a very rapidly oscillating electric field, of amplitude E_o. The arrival of this alternating field in the vicinity of a particle causes all of the electrons, which are free to be influenced (polarizable electrons) to oscillate at the same frequency. These oscillating electrons give rise to a new oscillating electric field, which radiates in all directions- the scattered light wave. The quantity of interest in a scattering measurements is the intensity of the scattered wave, I_s, rather than amplitude, E_s. The intensity is given by the square of the amplitude: $I_s = (E_s)^2$.

The dependence of the scattered light intensity I_s on the molecular weight (MW) or volume (V) of the particle is particularly simple when the particle diameter is much smaller than the laser wavelength λ (Rayleigh region). In this case, all of polarizable electrons within a particle oscillate together in phase, because at any given time they all experience the same incident electric field. Hence, the scattered wave amplitude E_s is simply proportional to the number of polarizable electrons, times the incident wave amplitude, E_o. The former quantity is essentially proportional to the overall molecular weight of the particle or its volume. The constants of proportionality, which connect these various physical quantities, depend on the indices of refraction of the particle n_p and solvent n_o. That is, how well a given particle scatters light depends not only on MW or V but also on the polarizability of the particle (related to n_p) relative to that of the solvent (related to n_o). For the very small particles in the Rayleigh region, we arrive at simple expression for the scattered intensity I_s:

$$I_s = f(n_p,n_s)*(MW)^2*I_o \quad (1)$$

$$I_s = g(n_p,n_s)*V^2* I_o \quad (2)$$

where I_o is the incident laser intensity, $f(n_p,n_s)$ and $g(n_p,n_s)$ are functions of the indices of refraction of the particle and solvent, which are fixed for a given system composition. For these small particles in the Rayleigh region, there is negligible angular dependence in the scattered intensity T.

After setting up the appropriate conditions, different for water-based inks and for the solvent (toluene)-based inks, the particle size of each sample was measured. The following conditions were set for the measurements:

- *Refractive Index*: 1.333 (water), 1.494 (toluene)
  This establishes the index of refraction of the solvent, in which the particles are suspended, assuming a dilute dispersion. The ink particle sizes were measured in this case using water or toluene as solvents.

- *Viscosity*: 1.002 cP (water), 0.590 cP (toluene)
  The viscosity of the sample suspension is expressed in units of centipoises (cP). The particle suspension must be very dilute for measurements based on dynamic light scattering, in order to avoid errors due to interparticle interactions and multiple scattering. Therefore, the viscosity is by default as a viscosity of the pure solvent in which the sample particles are suspended.

- *Intensity*: 200-300 kHz
  The average scattered intensity or photopulse rate, expressed in kHz, which is desired for a measurement, can be established by setting this parameter. The

default value was set at 200-300 kHz. This value is typically recommended for most samples, which scatter adequately. It is designed to optimize the efficiency of the autocorrelation process and thereby minimize the time needed to obtain reliable, accurate results for most samples.

- *Temperature:* 20°C
  After measurements, the results obtained from NICOMP Particle Sizing Systems - CW380 Version 1.51a Software were evaluated.

4 Printability Analysis

Printability analyses were done at the beginning and after the trial. Color coordinates, CIE [19] (usually referred to as the CIE 1976 space or CIELAB) L*a*b*, were measured using a datacolor Spectraflash 600 spectrophotometer. ColorTools software was used for data analysis. Specular gloss was measured using a Gardener Glossmeter with 60°geometry. Optical density mottle index measurements were performed using a Tobias Mottle tester and dot gain measurements were determined with a X-Rite 408 (reflection densitometer).

5 Results and Discussion

Distortion of color sometimes occurs during long printing press runs. However, lack of knowledge exists to explain this phenomenon. Therefore, the aim of this work was to focus on behavior of printing inks and look for the possible causes of this problem. Several gravure and flexo runs were executed with duration 5-7 hours. It was found that the particle sizes of the inks diminished during these runs. The change of gravure inks particle size is illustrated on Figure 4. This could be a consequence of the shearing and friction forces developed during the printing process such as interaction of doctor blade and gravure cylinder, ink pumping, and recycling.

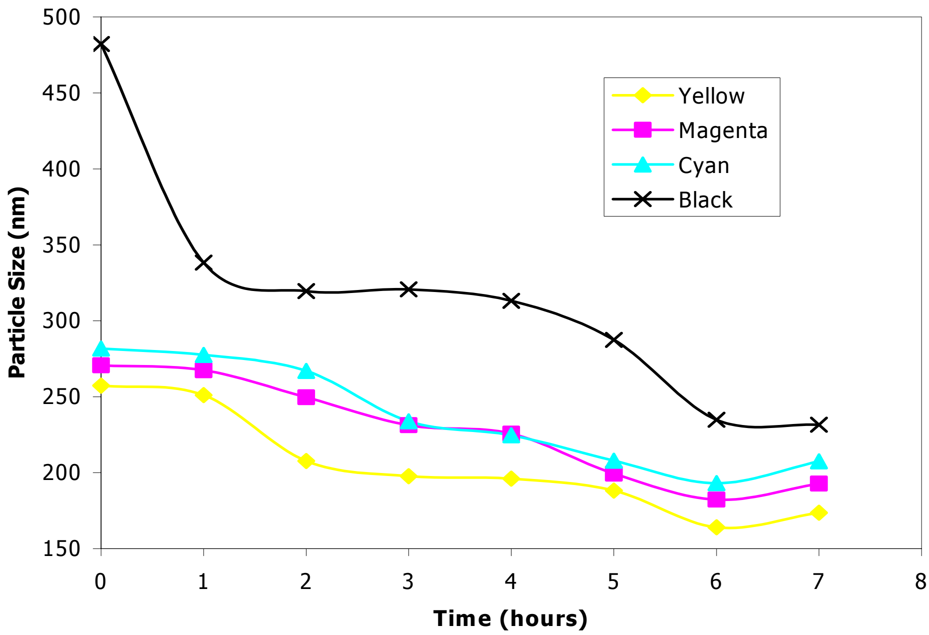

Figure 4: The decrease of the particle size during gravure printing.

During the printing run, each color pigment decreased in particle size (Figure 4), but it was more apparent for black process color ink. Its particle size at the beginning of the trial (482.2 nm) was almost twice the size of other pigments [yellow (257.3 nm), magenta (270.6 nm), and cyan (281.7 nm)]. After seven hours of printing the particle size decreased from 257.3 to 173.6

nm (yellow) from 270.6 nm to 192.8 nm (magenta), from 281.7nm to 207.5 nm (cyan), and from 482.2 nm to 231.6 nm for black, respectively (Figure 4).

It is well known that ink optical properties such as specular gloss, print density, and color characteristics, are controlled by pigment particle size [2,5,20].

One of the most obvious changes in print quality at the end of trial was observed in color characteristic measured as L*a*b* color coordinates. L*a*b* color coordinates were used for the calculation of color difference, ΔE, that indicates color change. Color difference was calculated according to original CIE 1971 color difference equation**:**

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (3)$$

The left hand side of equation 3 is often written as ΔE^*_{ab} to differentiate it from other difference formulas such as ΔE^*_{94} or ΔE^*_{2000} [21,22]

Table 1: Color difference ΔE between the beginning and end of the gravure trial.

Gravure Printing Process				
	Yellow	Magenta	Cyan	Black
ΔE	3.04	6.55	4.07	6.40

The measured ΔE value needed to distinguish a colorimetric difference is still an active area of research [23]. However, a color deviation that is less than ΔE = 1.0 is generally considered very small and cannot be perceived by the naked eye. ΔE = 2.0 is usually only detectable by a trained observer. On the other hand, ΔE values between 2.0 and 3.5 indicate moderate differences. Such color difference can be noticed by an untrained eye. Generally, the higher the ΔE value, the larger the perceived difference will be. The values of ΔE obtained from the gravure printing trial for each process color are presented in the Table 1. Surprisingly, the largest color difference was found for magenta ink (ΔE=6.55), followed by black (ΔE=6.40), cyan (ΔE=4.07), and yellow (ΔE=3.04) knowing, that the largest particle size drop was found with the black ink.

It is well known that the smaller the pigment particles, the higher the gloss [2,5,20]. Small particle size of pigments provide more even, and more uniform films of inks on surfaces, thus better reflection of the incident light. This is verified in this experiment (Figure 5), where values of the specular gloss at the beginning of trial were lower compare to those found after seven hours of printing. The smallest difference in gloss was found for yellow ink, probably as the result of the smallest initial pigment particle size.

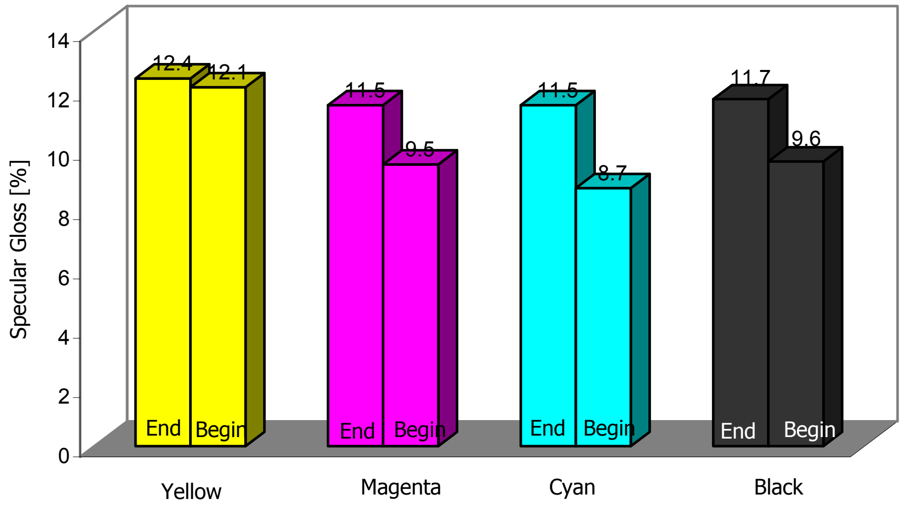

Figure 5. The change in specular gloss for process colors at the beginning of gravure trial and after seven hours of printing.

The observed "grinding" of the pigment on the press had some positive effects, too. It was found that the density mottle for all colors was lower after seven hours of printing than at the beginning of trial (Figure 6). The most significant change was found in process black ink. This could be also caused by the largest decrease in particle size during trial found for this color. Apparently, pigments with smaller particle size have the tendency to impart more consistent ink films. The dot gain was slightly higher after seven hours of printing than at the beginning of the print (Figure 7). The largest dot gain difference was found for magenta ink (Figure 7).

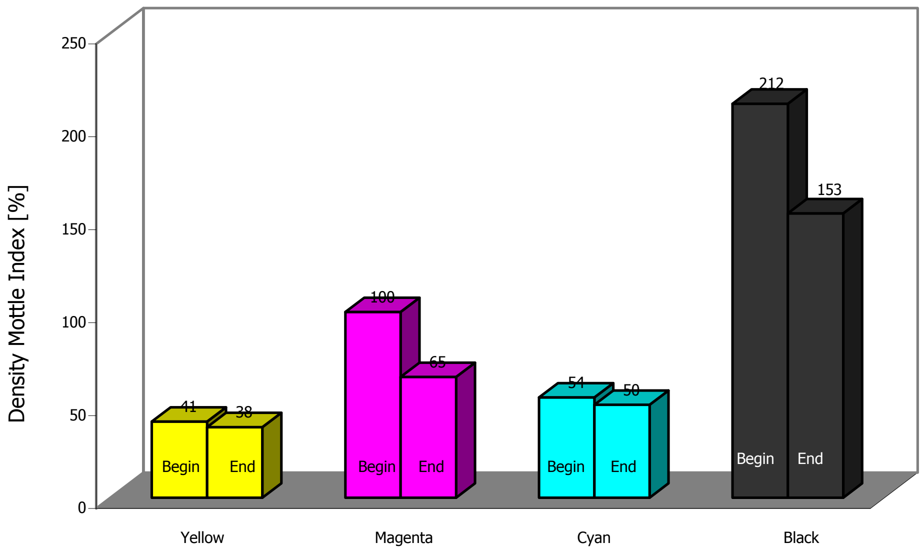

Figure 6: The difference in density mottle index for process colors at the beginning and after seven hours of gravure printing

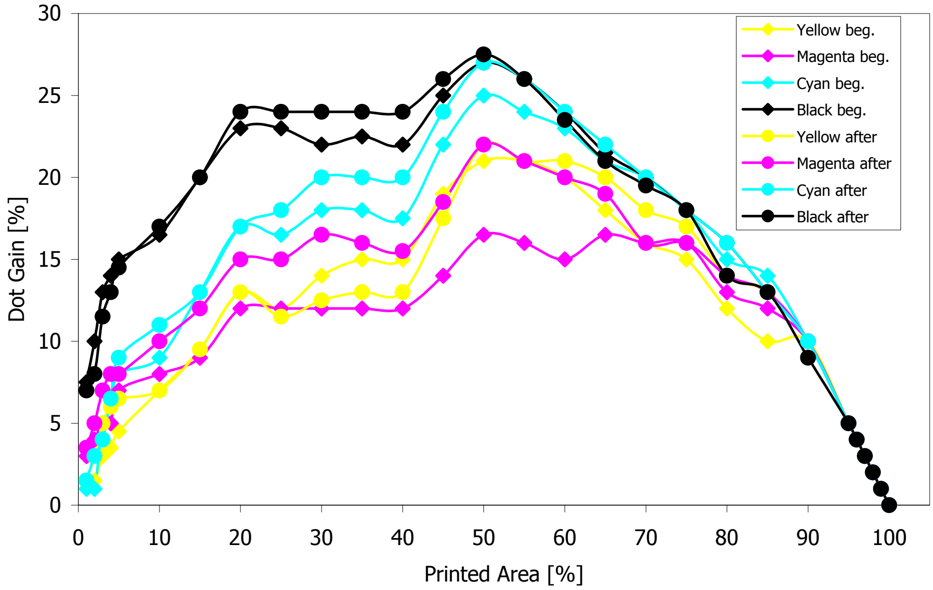

Figure 7: The dot gain at the beginning of gravure trial and after seven hours of printing

The flexo trial was performed with water based spot color brown and process black. A decrease in particle size was observed only for brown spot color. The initial particle size of spot brown was 251.8 nm and it dropped to 178.5 nm (Fig. 8) after 270 min of printing. The change of particle size of brown spot color affected the CIE L*a*b* values as well as ΔE. The color difference ΔE was 3.29. Process black had a very small particle size (190 nm) and it did not change significantly during the trial (Figure 8). Most likely, when the initial particle size of the pigment is sufficiently small at the beginning of the printing process, no significant changes will occur. This was confirmed in the color difference calculation (Table 2), where ΔE value was found very low (ΔE =0.64) for process black.

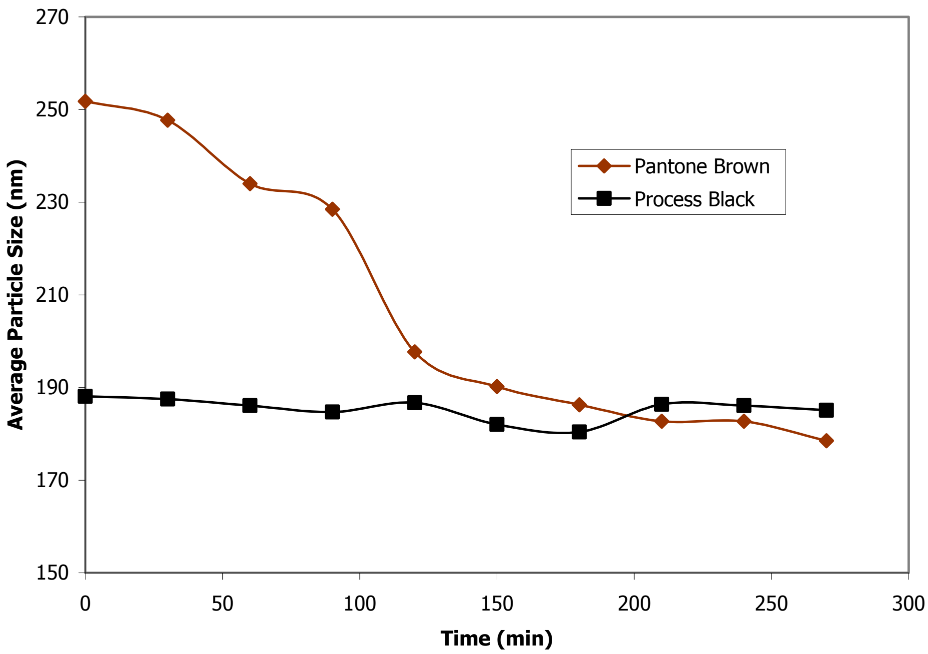

Figure 8: The decrease of the pigment particle size during flexo printing

Table 2: Color difference ΔE between the beginning and at the end of the flexo trial

	Flexo	
	Brown	Black
ΔE	3.29	0.64

6 Conclusion

During printing trails taking several hours, the ink particle size has been found to decrease. These phenomena affect printability of the printed substrate. In gravure printing, the most significant reduction in particle size was observed for black process color ink, from 482.2 nm to 231.6 nm, followed by yellow (from 257.3 to 173.6 nm), magenta (from 270.6 to 192.8), and cyan (from 281.7 to 207.5 nm). This decrease of the particle size caused color difference on the printed substrate between the beginning and the end of the trail. The color difference was determined by ΔE value, calculated from L*a*b* values. For each gravure printing ink, ΔE was higher than 3.0. Even an untrained eye can notice this color change. Surprisingly, the largest color difference was found for magenta (ΔE = 6.55), followed by black (ΔE = 6.40), cyan (ΔE = 4.07), and yellow (ΔE = 3.04). Further printability analysis showed that values of specular gloss were higher at the end of the trial as a result of decreased particle size. One of the positive effects of diminishing particle size, noticed for all the process color inks, is the decrease of the density mottle observed on the printed samples from the end of the trial. In the case of dot gain values, there was no change visible.

Five hours of flexographic printing caused the decrease of the particle size only for Pantone brown ink, where the initial particle size was 251.8 nm and it dropped to 178.5 nm. Measured L*a*b* values, expressed by ΔE, indicated color difference ΔE = 3.29. However, the black ink showed no particle size change (~188 nm) during the printing process. Thus, no significant color changes occurred, ΔE being observed at a negligible value of 0.64.

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