Coagulation Kinetics of Surface Modified Pigment Particles

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Abstract

Pigment particle coagulation is an important step in the formation of an inkjet image. The size of the formed colorant flocs determines how deeply the colorant penetrates into the substrate and hence has a significant impact on image quality (optical density, gloss, chroma, etc.). Many factors (e.g. charge density) determine the colorant coagulation rate and an in-depth understanding of these factors is needed to assist in the design of advanced colorants for inkjet applications. This study focused on a series of pigment particles that had been chemically modified using Cabot's patented surface modification technology. When the pigment was de-stabilized under various triggering conditions, such as ionic strength and pH, particles started to coagulate. The rate of coagulation was measured by monitoring the time evolution of the floc size as determined by dynamic light scattering (DLS). A characteristic coagulation time, τ, was derived from fitting the DLS data. The impact of trigger condition and surface modification type on the coagulation time, τ, was determined and provides critical insight as to how the pigment coagulation can be controlled to yield optimal print performance.

Introduction

Pigmented inks are widely used in inkjet applications[1-4] with stability and reliability performance reviling dye based inks. The next generation of pigment colorants need to be engineered to provide superior print quality: high optical density (OD), durability, gloss, chroma, and less inter color bleeding. Solving these new challenges requires a fundamental understanding of the image formation process. Particle coagulation or the formation of large flocs is considered to be an important variable controlling colorant penetration into the substrate and hence directly impacts print quality. Colloidally stable pigment particles can be made to coagulate by modulating the repulsive stabilizing forces. The triggering mechanisms can come from the substrate (paper) surface, for example pH, ionic strength (salt from paper surface) or as recent patent literatures indicates that trigger solutions can also be deliberately introduced either prior or after the ink is applied.[5-7] An in-depth understanding of the particle coagulation process and its kinetics will help the design of next generation particles for inkjet inks with optimized coagulation rates.

Nanoparticle coagulation kinetics have been investigated extensively using light scattering techniques (both dynamic and static).[8-10] However, to the best of the authors' knowledge, this paper represents the first coagulation kinetic study of carbon black (CB) particles in an aqueous system. Previous publications on CB coagulation kinetics had focused on non-aqueous system.[11-12] Cabot's proprietary surface modification technology offers an unique opportunity for kinetic study, since all the stabilizing groups are covalently bound to the pigment surface and therefore are not subject to adsorption and desorption kinetics.

Coagulation Theory

There are two regions of coagulation mechanisms: diffusion controlled (fast coagulation) and reaction limited coagula-tion (slow).[13] For the fast coagulation, every collision is effective in forming an aggregate, the collision efficiency is 1. As a result the aggregation rate constant is the same as the collision rate constant. The rate of change of the k-fold aggregate concentration, where k = i + j are expressed by Smoluchowski equation:

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1,i+j=k}^{k-1} k_{ij} n_i n_j - n_k \sum_{i=1}^{\infty} k_{ik} n_i \qquad \text{(Eqn. 1)}$$

where k_{ij} is second-order coagulation rate constant. For continuous particle size distribution, an integral version of Eqn 1 can also be written. The second-order coagulation rate constant (k_{ij}) for diffusion controlled coagulation can be calculated from the collision rate and expressed as follow:

$$k_{ij} \sim k = \frac{8k_B T}{3\mu} \qquad \text{(Eqn. 2)}$$

where, k_B is Boltzmann's constant, T the absolute temperature, and μ the viscosity of the suspending fluid. For an aqueous dispersion at 25 ^{0}C the $k_{ij} = 1.23 \times 10^{-17}$ m^3/s. As indicated in Eqn. 2, the rate constant is nearly independent of particle size. This independence can be rationalized by the fact that larger particles have slower diffusion coefficients but larger capture radius which effectively cancel each other out. The assumption of a constant k_{ij} is a reasonable approximation for particles, which differ in size by a factor of about 2 or less. Eqn 1 can be integrated with the initial condition $n_t = n_0$ (n_0 is the initial concentration of particles) to give Eqn 3.

$$\frac{n_0}{n_T} = 1 + \frac{t}{\tau}, \qquad (\tau = \frac{1}{k_a n_0}, \mathrm{k}_a = \frac{1}{2}\mathrm{k}_{ij}) \quad \textit{(Eqn. 3)}$$

The characteristic time τ is often referred to as the half-life of aggregation. At this time the total number of particles in the dispersion has been reduced by a factor of 2. The ratio on the left hand side of Eqn 3 is a measure of the average aggregate size (number of particles within the floc), and hence a measure of the mean floc volume. This is the basis for data analysis in this paper. For a typical ink with particle radius 50 nm and concentration of 3.5 % by weight, n_o is calculated to be ~ 4×10^{19} $\#/m^3$ and hence the coagulation half life is on the order of 4 ms which is considerably shorter than the ink penetration times (~ 1 sec).

In the region of reaction limited coagulation, the rate of coagulation is reduced due to the additional repulsive force from electrostatic or steric interaction. In this region not every collision results in coagulation. Only a fraction 1/W of collisions is successful. W is commonly defined as stability ratio, which is the ratio of the diffusion limited (fast) coagulation rate to the slow coagulation rate. When W = 1, the coagulation is in the diffusion-limited region.

$$W = \frac{k_{ij}(fast)}{k_{ij}(slow)} \quad or \quad \frac{\tau(slow)}{\tau(fast)} \qquad \textit{(Eqn. 4)}$$

Dynamic Light Scattering (DLS)

In DLS particle size analysis the intensity fluctuations of scattered light is recorded. The decay rate of the scattered light auto-correlation function is then used to calculate the intensity weighted diffusion coefficient (D). From the diffusion coefficient the hydrodynamic particle diameter is calculated using the Stokes-Einstein equation (Eqn 5).

$$d = \frac{k_B T}{3\pi\eta \overline{D}} \qquad \textit{(Eqn. 5)}$$

The measured hydrodynamic particle size of a coagulating dispersion is an average of the individual aggregate particle sizes, weighted by their scattered light intensities. The growth of the aggregates in a coagulation process can thus be monitored using time-resolved DLS measurement.

Experiment and Samples

Material: Black Pearls (BP) 700 with different surface functionality were prepared and purified according to published patent procedures.[2-4,14] Standardized solution of NaOH, HCl, and NaCl were purchased from Aldrich.

Measurement

Trigger solutions of varying ionic strength were prepared by diluting the appropriate 1.0M standardized solution with DI-water. Trigger solutions with different pHs were prepared by adding small quantities of either 10mM HCl or 10mM NaOH to the above solutions with known ionic strength. The ionic strength change resulting from the pH adjustment step was insignificant except for pH >10 and pH <3. All pigment dispersions were made into 100 ppm stock solutions. From the stock solution 30 μL was injected into 3 mL of trigger solution in a 1 cm disposable plastic cuvet to yield a particle concentrations of 1 ppm. After thorough mixing, the cuvet was placed into the DSL instrument and measurement started within 5 seconds. Analysis showed that pH change due to the addition of surface modified CB was small. Measurements were performed at 25 °C. The particle size evolution was then monitored as a function of time. When the pigment concentration was too low, large errors were observed in the auto-correlation function. At high concentrations the scattered signal was too weak due to the absorbing power of carbon black. A consistent data set was obtained in the pigment concentration range 0.5 to 10 ppm.

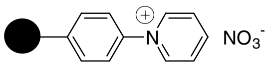
DLS measurements were performed on a BIC ZetaPlus from Brookhaven Instrument Corp. which is equipped with a 30 mW, 670 nm solid state laser. Scattered light at 90 ° was collected by a single mode fiber optic. Autocorrelation was performed with BI-9000AT Digital Autocorrelator with a user selectable channels up to 512. During this study 200 channels were used with BI-PSDW software. The effective hydrodynamic diameter was collected every 10 seconds, followed by a 1-second delay (required for the software to clear its memory). In a typical measurement 100 data points were collected over a period of 19 minutes. Experiments showed that if the data collection time was too short the auto-correlation would be noisy and the baseline was ill defined. If the data collection time was too long, time resolution of the aggregation process was lost.

Data Processing

Time-resolved effective diameters were plotted vs time. By analyzing the plot, we found that the relationship between agglomerate diameter and time approximately follows the power law $(r_t/r_0)^3 = 1 + t/\tau$ (where, r_t is the diameter at time t, and r_0 is the diameter of a stable dispersion). The observed behavior is consistent with assuming that the volume of the aggregate is proportional to the average aggregation number (n_o/n_T) in Eqn 3. The data was therefore analyzed using a linear fit of the relative volume change versus time with a slope 1/τ and intercept 1.

Results and Discussion

A carbon black modified with a permanent quaternary group represents the simplest possible case to study. Such a system should be sensitive to ionic strength but should not be affected by pH. The chemical structure of the attached group is shown below.



(Scheme 1)

As shown in Figure 1 the coagulation kinetics of particles with permanent quaternary groups was studied at different ionic strengths (IS). As expected, the coagulation rate increased with increasing IS. With increasing IS the Debye length (a measure of the double layer thickness) decreases allowing the colliding carbon black aggregates to agglomerate. Figure 1 shows the plot of relative particle volume change $(r_t/t_0)^3$ vs time, and the linear fitting used to calculate the characteristic aggregation time τ. As the degree of aggregation increases, the total number of agglomerates drops, which eventually means that large fluctuations in the measured particle size occurs due to the migration of agglomerates into and out of the laser beam volume.

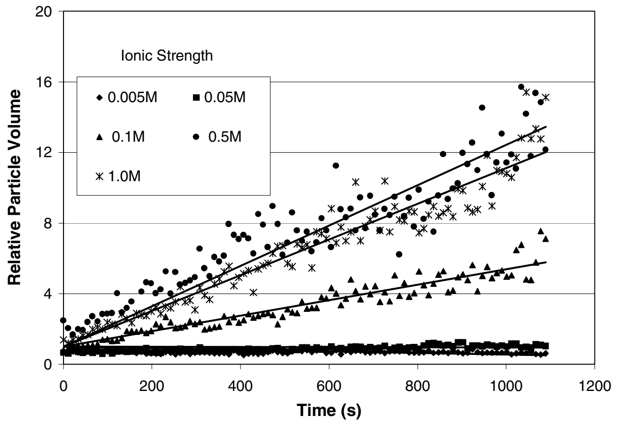


Figure 1. Coagulation of cationic BP700 as a function of ionic strength (NaCl)

From Figure 1, the characteristic time τ can be calculated from the slope of the fitted lines. The stability ratio can then be calculated according to Eqn 4 where the fast aggregation corresponds to ionic strength 0.5 M in Figure 1 (note that a further increase in ionic strength does not increase the rate of agglomeration, hence this limit is defined as τ_{fast}). The stability ratio, W, as function of electrolyte is plotted in Figure 2.

From Figure 2 one can estimate that at a critical electrolyte concentration (~ 0.12 M) all the repulsive forces have been effectively screened and coagulation process was purely controlled by diffusion. It is clear that, even though our kinetic experimental design can not directly yield the absolute coagulation rate constant, it is a valid tool to study the relative coagulation kinetic for a given system.

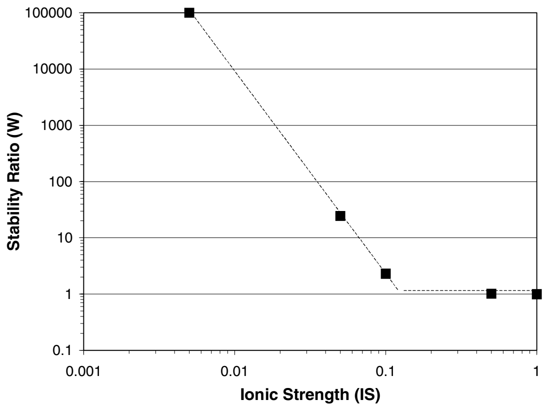
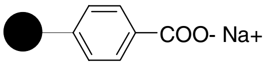


Figure 2. Stability ratio plot

As mentioned before the next generation of pigment particles for inkjet application require a balance between stability within the printhead and instability on the media. The ability of fine tuning surface charge density is one of the key advantages of Cabot's surface modification technology.[1,2,3,4] Table 1 shows three samples that were prepared by the controlled surface modification of BP 700 with carboxylic acid groups to yield various levels of surface charge density.



(Scheme 2)

Treatment level can be varied reproducibly to yield particles having enhanced stability (and hence lower OD) to marginal stability with improved OD.

Table 1. BP 700 with surface carboxylic acid groups at different levels

	Treatment Level (μmol/m^2)	**OD of 4% Draw-Down**
High Level	1.60	1.21
Medium Level	1.15	1.30
Low Level	0.75	1.39

Figure 3 showed the coagulation kinetics of the samples presented in Table 1 in 10 mM of IS as a function of pH. As expected, for all these samples, when more surface carboxylic acid groups were neutralized with increasing pH, coagulation rate decreased as indicated by an increasing τ value. Yet it was also obvious that at the same pH and IS, particles with higher surface attachments were more stable. At lower pH, when the coagulation was diffusion limited the difference between these three samples is small. In the design of pigmented inks, coagulation studies can provide important insight as to what type of triggers will yield the optimal performance.

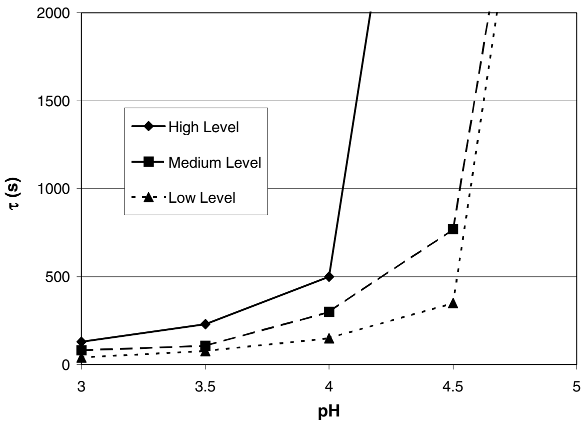


Figure 3. Comparisons of coagulation rate of carboxylic acid modified BP700 in 10 mM of ionic strength

Typical CB dispersions have a broad size distribution, which makes the interpretation of kinetic data in terms of the theoretical models complicated. For example, there will be many different combinations for the formation of dimers, which lead to a distribution of k_{11} values. If the particle size distribution is narrow (within factor of 2), all k_{11} will be similar. Another impact of particle size distributions is that large particles will scatter more light than small particles. All modern light scattering particle size analyzers encounter this problem and some of the venders solve the problem by compensating the scattering power difference among different particle sizes. In BIC-ZetaPlus instrument, the particle size distribution is calculated based on light scattering intensity weighted average, so-called d5 average. Because the instrument measures preferentially the large particles, the measured coagulation rate will be dominated by the aggregation of large particles. According to DLVO theory, at the same surface charge density, electrostatic repulsion is more effective in stabilizing large particles. As a result, if the coagulation rate of large particles contributes more to the overall rate, the measured rate will be slower than theory. In order to validate the above claims, a dispersion of BP700 modified with surface carboxylic acid groups was fractionated using centrifugation. Particle size of each fraction and the original dispersion are shown in Table 2.

Table 2. BP 700 with surface carboxylic acid groups at different particle size distribution

	Mean Volume Particle Size (nm)
Un-fractionated	130
Small	73
Medium	112
Large	155

As shown in Figure 4 the three particle size fractions and the original material were triggered under constant IS (5 mM) at different pHs. At low pH, when most of the carboxylic acid groups were uncharged, the coagulation process was diffusion limited. The observed difference in diffusion limited coagulation rate may be related to number of particles in the 1 ppm of solution. For example, the particle size of the Small fraction was about half of the Large fraction, as a result, in 1 ppm of dispersion, the Small fraction contains about 7 times more particles. Since the rate constant for the diffusion-limited case should be similar for all the cases, smaller particle should coagulate faster at the same weight fraction (since n_o is larger for the smaller particles, hence τ is smaller). At higher pH, when the coagulation process was reaction-limited, large particles were far more stable than small particles as predicated by DLVO theory. The coagulation kinetics of the unfractionated dispersion suggests that coagulation of large particles dominate the measured coagulation rate.

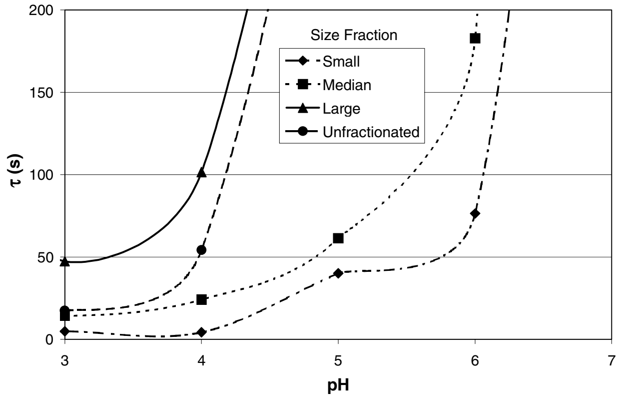
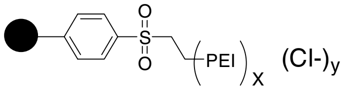


Figure 4. Impact of particle size on coagulation kinetics: 1 ppm solution in 5 mM of NaCl

So far we have examined several cases where the charge groups are very close to the particle surface. In the design of next generation of pigmented inkjet inks, polymer attached particles are a class of very important material for achieving image durability and gloss. Recently Cabot's has extended surface modification technology to include polymer attachment.[15] Scheme 3 shows an example of where a PEI (polyethyleneimine) polymer with molecular weight (MW) of 1200 has been attached to carbon black surface. This material had a surface charge density (fully charged) around 4 μmol/m^2, which is about 3 to 4 times higher than previous small molecule modification.



(Scheme 3)

Figure 5 shows the plot of τ vs pH at different ionic strength.

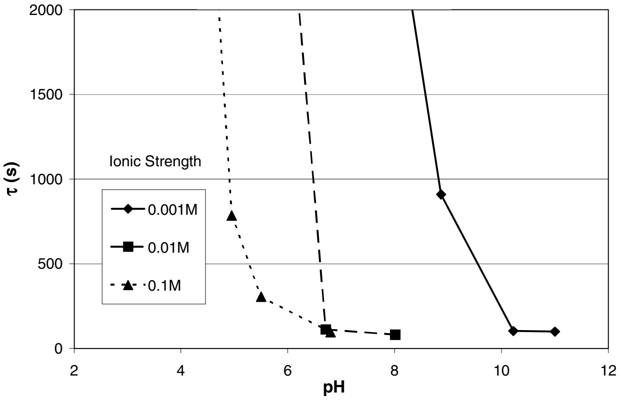


Figure 5. Coagulation of PEI-1200 modified BP700

As expected, particles became less stable with an increase of pH or ionic strength. The limiting coagulation times τ in this example (about 100 s) were about 2 to 4 times longer compared with the non polymer (small molecule) treatments (see Figure 3 and Figure 4) and is indicative of a slight barrier to coagulation. This barrier that is present in the polymer treated pigment, may reflect a slight steric contribution to stability. As particles approach each other, it becomes increasingly difficult to drain solvent molecules from the gaps, which will typically slow down the coagulation process.

Conclusion

The ability to tailor and quantify the aggregation behavior of surface modified pigments was demonstrated. By understanding the flocculation behavior and possible triggers at a fundamental level, the next generation of colorants may be tuned to precipitate out once they come into contact with the paper surface. By controlling where the pigment is retained on the paper, optical properties such as OD, chroma and gloss can be manipulated.

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Biography

Dr. Yuan Yu received his B.S. Degree in Chemistry from the Peking University in China in 1990 and Ph.D. degree in Organic and Material Chemistry from the University of Minnesota in 1996. He joined Cabot Corporation in 1998 and has since focused on the technologies for nano-particle surface modification.

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