Determination of the Colloidal Stability of Concentrated Pigment Dispersions

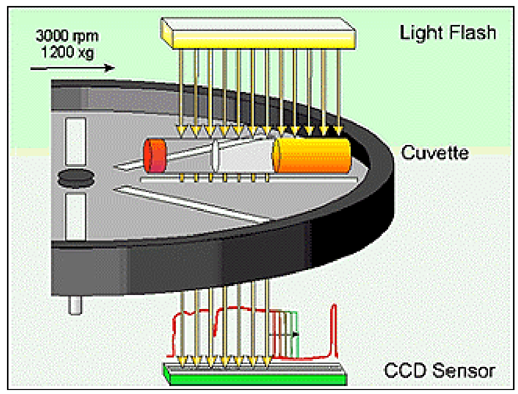
Yuan Yu, Richard Hall, and Ervina Halim, Inkjet Colorant Division, Cabot Corporation, Billerica, MA, USA

Abstract

Pigment dispersions are playing an increasingly important role in high performance inkjet inks. Colloidal stability of pigment particles can have a profound effect on print head and paper printing performance. Reliable and quick analytical methods to assess colloidal stability are essential in any development effort. Commonly accepted practice calls for aging the sample under accelerated conditions and then measuring the changes in particle size distribution. Widely applied particle sizing techniques require samples to be diluted. Dilution can disturb the system and the results may not reflect the concentrated state. In this report we explored the possibility of using an accelerated centrifugation method to evaluate colloidal stability without dilution. The instrument for this study is LUMiFuge®. In this study, the colloidal stability of pigment dispersions as function of pH and ionic strength were successfully determined without dilution and aging. Particularly intriguing, the LUMiFuge method can discern the difference among samples that the traditional methods had failed. This manuscript will also discuss the limitation of LUMiFuge®. Our study strongly indicated that this is an extremely sensitive method to evaluate colloidal stability of dispersions at their original concentration. When LUMiFuge® results are correlated to the performance of pigmented inkjet inks, it can serve as a valuable tool for both research development and quality control and assurance.

Introduction

Pigmented inkjet inks are becoming increasingly important due to their inherent permanent properties.[1] On the other hand, they pose a challenge to the ink formulator particularly in the area of reliability performance. Lengthy and costly print head tests will yield the most direct and relevant information, but it is highly desirable to identify indirect measurement methods. Pigmented inkjet inks are colloidal systems and are subject to particle settling and particle aggregation. Particle growth and settling due to a variety of factors represent the most prevailing mechanisms for the reliability failure. Many techniques have been developed to study the colloidal stability of pigmented inkjet inks. Typically, pigment dispersions or inkjet inks are aged at elevated temperature to assess the long-term room temperature storage stability. Then those dispersions or inks are tested for any changes in colloidal parameters. Those parameters normally consist of particle size, large particle counts, pH, surface tension, and viscosity.[1] Particle size and large particle count are considered to be the most relevant. The most common technique for particle sizing is dynamic light scattering, which requires the dispersions and ink to be diluted. Large particle count measurement (particle size greater than 0.5 µm), which is determined by AccuSizer®, also requires the sample to be diluted. Sample dilution alters the environment of the colloidal system. It has become obvious that an analytical method to evaluate the colloidal stability of pigment dispersions and ink at their original concentration is needed. Particle sizing using acoustic method is one of the choices.[2] This paper focuses on a new technique that has been introduced recently using centrifugation and photo detector to monitor the settling behavior of a concentrated colloidal dispersion. The instrument is LUMiFuge®.[3,4]



LUMiFuge® is a bench top analytical centrifuge that studies the settling behavior of colloidal systems under accelerated conditions without dilution. Scheme below illustrates the working principle of LUMiFuge®. Sample in cuvette is rotating horizontally at high speed. At predetermined time interval, light shines at the cuvette and the transmittance profile along the sample cuvette length is collected by CCD sensor. The line resolution of the CCD sensor is 0.1 mm. As particles settle or float the transmittance profile will change. Analysis of profile changes yields colloidal stability information.

Table 1 summarizes some of the key machine features. The design and usage of this instrument are simple, however, particle settling in confined spaces and light extinction of colloidal particles are complex. Comparative data can be easily acquired, in depth data analysis demands more fundamental understanding of settling and light extinction. The objective of this report is to explore LUMiFuge® as an analytical tool to assess the colloidal stability of surface modified pigment dispersions at their application concentrations.

Table 1: Machine Parameters of LUMiFuge® 116.

Light source	880 nm
Speed (rpm)	300 to 3000
G force (g)	12 to 1200
Temperature Range	28 to 65 °C
Sample Volume	0.1 to 2 mL
Measurement Range	25 mm
Position Resolution	100 μm
Time Interval (S)	10 to 600
Longest Continues Run	40 hrs

Experiment

Material

Dispersion for this study is CAB-O-JET™ 300, which is surface modified Black Pearls ™ 700 carbon black. Surfaces of this carbon black have been modified with carboxylic acid groups. As a result, the dispersion is stabilized by electro-static stabilization. Original concentration of CAB-O-JET™ 300 dispersion is 15% and it has been diluted to 10 and 5% for this study. In order to check the sensitivity of LUMiFuge®, CAB-O-JET™ 300 was also intentionally de-stabilized by adjusting pH with acid and by adding additional electrolyte ($NaNO_3$). Table 2 summarizes different samples for this investigation.

Table 2: Samples

Samples	pH	% Solid	Additional Ionic Strength
A: CAB-O-JET™ 300	8	5	0
B: CAB-O-JET™ 300	8	10	0
C: pH adjusted	6	5	5.4 mM
D: pH adjusted	6	10	8.9 mM
E: Added electrolyte	8	10	20 mM
F: Added electrolyte	8	10	40 mM

Particle sizes of these samples were measured using Microtrac® Ultrafine Particle Analyzer (UPA150), a dynamic light scattering method. Particle size of these samples were identical immediately and 1 week (at room temperature) after they had been prepared. Thus, it is important to note that UPA can not tell the difference among these samples. LUMiFuge® experiments were carried out less than 1 week from the time those dispersions were prepared.

Results and Discussions

Figure 1 shows typical transmittance profiles of 5% CAB-O-JET™ 300 performed at 3000 RPM. Time interval for profile collection during the run is 4 minutes. For better illustration, the interval in Figure 1 is 20 minutes. As the dispersion being centrifuged, the transmittance profile moved to the bottom of the cell. However, we have observed a peculiar effect and we refer it as "back folding". When the sedimentation proceeded to a certain degree the top layer actually got more opaque, which indicates that some of the settled particles returned. This can be cleared seen in Figure 1. We are currently investigating the nature and method to avoid "back folding" and they will be a subject of a separate report. There are couples of ways the LUMiFuge® profile data can be processed. One is to track the movement of a certain transmittance front as function of time. As illustrated in Figure 1, 10% transmittance can be tracked, this analysis is refereed to as Front Tracking (FT). The other method is to plot the transmittance integration of each profile as function of time. Since the "back folding" affects the integration, this report will only apply FT method.

Figure 2 shows 10% FT profile of samples A, B, C, and D. As predicated, at low % solid the front will move faster than at higher % solid. Dispersions, which had been intentionally de-stabilized, settled at a higher rate. As mentioned in the previous section, normal analytical method (e.g. UPA) can not tell the difference among those 4 samples. Additionally, differences among those samples were detected without aging. There is another feature in Figure 2 worth noting. There seems to be two distinctive regions of front movement, the front first hardly moved or moved extremely slow and then sped up after an "induction" period. This can be rationalized because carbon black not only scatters but also absorbs at the incident wavelength of 880 nm. Even though the path length of the cuvette is small (2 mm), a certain amount of particles still need to settle out before light can penetrate the cuvette and be detected.

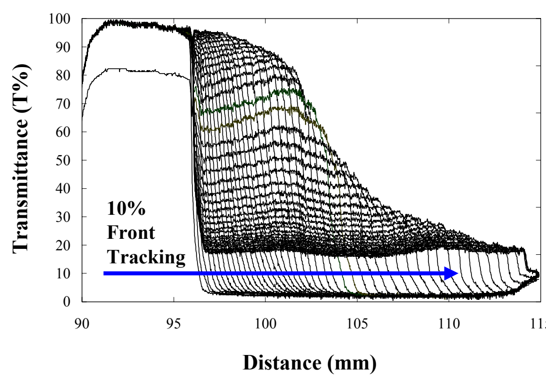


Figure 1. LUMiFuge Profiles of 5% Dispersion

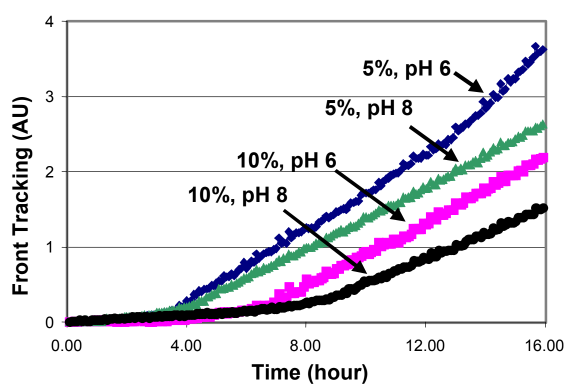


Figure 2. 10% Front Tracking of CAB-O-JET™ 300 at Different pH and Solid Level: 1500 RPM

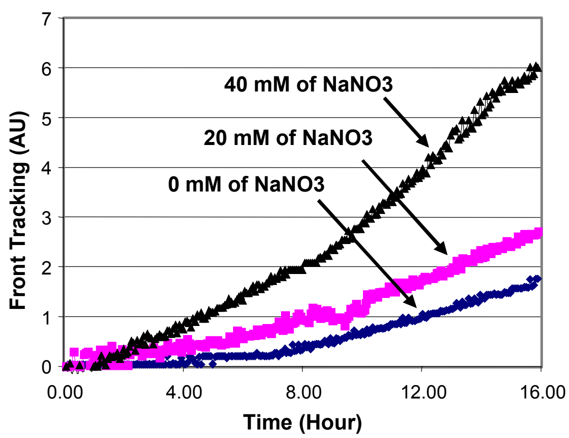


Figure 3. 5% Front Tracking of CAB-O-JET™ 300 at Different Electrolyte Level

CAB-O-JET™ 300 can also be destabilized with addition of electrolyte. Figure 3 shows the 5% FT profile of sample B, E, and F. As expected, the dispersions were de-stabilized and resulted in a faster settling rate. When the same dispersions were analyzed by UPA and large particle count, no particle size growth can be detected. The induction period for those samples were also different, as the electrolyte level increased, the induction period reduced. This is consistence with the formation of large aggregates, which will settle out quicker for the light to go through cuvette.

Conclusions

LUMiFuge® is a new analytical tool that allows dispersion manufactures and inkjet ink formulators to study their system at high concentration. Time and effort are needed to understand the application and limitation of this instrument. During one of our studies we have found an apparent correlation between large particle count (by Accusizer®) and the slope of FT by LUMiFuge®. Dispersions with larger number of particles above 0.5 µm also gave a faster settling rate. Since the particle above 0.5 µm only counts for an extremely small fraction of the total particle distribution, LUMiFuge® is unable to detect them. But there is a correlation. As demonstrated in this report, LUMiFuge® can discern the difference that other techniques had failed. Furthermore, differences among samples can be detected without aging. However, there are several phenomena need to be understood before the full potential and limitations of this instrument can be realized.

References

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Author Biographies

Dr. Yuan Yu received his B.S. Degree in Chemistry from 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 and characterization.

Dr. Richard Hall joined Cabot Corporation in 2001 and his research interests have been using existing or novel characterization methods to investigate colloidal systems.

Ms Ervina Halim received his B.S. Degree in Chemistry from Regis College in 2002. She joined Cabot Corporation in 2002 and her experience has been the characterization of surface modified colloidal dispersions.