Systematic Considerations for the Thermodynamic Stability of Pigmented Inkjet Dispersions and Inks

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Abstract

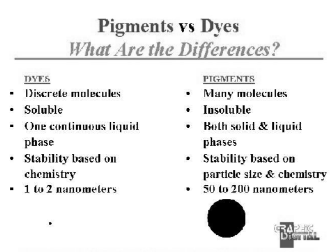
From the thermodynamic point of view, all pigmented inks including dispersions are thermodynamically unstable systems in nature. They are only meta-stable systems, or called kinetically stable systems due to some factors affected, such as electrostatic charge, viscosity, and interfacial potential difference. Therefore, for a well-performed pigmented inkjet ink system, a comprehensive thermodynamic stability (including particle size, viscosity, surface tension, pH etc.) is very important and required, which means the finished pigmented inkjet ink must possess the physical properties as follows, *i.e.* settle free and clog free, for a considerably long period. This paper attempts to provide a deep theoretic analysis and a comprehensive thermodynamic and kinetic consideration for inkjet inks and their dispersions by using quasi- (or pseudo-) equilibrium theory based on the experimental results. Under the guidance of the above theory, the paper finds that a proper dispersion for inkjet ink is a key for manufacturing excellent finished inkjet ink. There is a "gold cut" existing between conventional flexography and gravure dispersions and inkjet ink dispersions. Both inkjet dispersions and finished inkjet inks are superior in stability over the period of three years without obvious settling in the projected shelf life based on accelerating evaluations. Also, a critical particle size for the super stability of digital dispersions and inkjet inks has been found. The finished inkjet inks with ultra-fine particle size (< 0.3 μm) and narrow distribution provide a full range of color gamut, good water bleeding resistance and high UV light fading resistance. They can be utilized in both thermal and piezo drop-on-demand printing systems, including desk-jets, wide-formats, and industrial printers with high-performance printing quality. The invented dispersions and inks are currently in application for US patents and commercially available.

Introduction

Digital printing has become more and more important in printing industrials as computer technology develops. Digital inks or inkjet inks, as one of the most important parts in digital printing,[1] have received more attention than ever before. According to Ink World[2] and American Ink Maker[3] estimated, digital inks sales have been projected to increase at least 10% annually. This data suggests that digital printing will occupy up to 25% of all printing and the total ink sales will be 6 billion US dollars by 2010, which means that at that time, at least **1.5 billion** US dollars of total ink sales will go to the digital ink field. This will be a huge increase in comparison with the 200-250 million[2,3] US dollars in digital ink sales currently.

As the demand of digital printing increases, inkjet inks, especially pigmented inkjet inks, play a more important role than before. This is because pigmented inks possess several superior characteristics in water-bleeding resistance, outdoor UV light fastness resistance, and gas (Ozone) fastness resistance in comparison to dye colorants. However, pigmented inks including their dispersions are unstable systems from the thermodynamic view point. There are still some serious problems existing in the clogging of the nozzles of digital printers, sediments founded on a certain shelf life, and relatively poor color gamut vs. dye colorants. These might be caused by one reason, i.e., too large of pigment particles. The difference between dyes and pigments is shown in the following:

Table 1 Difference of Dyes and Pigments



As we know, pigmented dispersion and ink is a system of many solid particles isolated or surrounded by liquid but insoluble and dispersed in a continuous bulk liquid phase. From the angle of thermodynamics, the system is absolutely unstable. Suspended particles, especially larger ones, will settle down to bottom due to their gravity and separate out of the liquid phase eventually. It is a normal phenomenon for any thermodynamically unstable system. This inherent thermodynamic instability could be postponed or delayed by introducing some kinetic factors or effects into the system to obtain a very "stable" or meta-stable pigmented ink or dispersion system. Referred literature[4-10] shows us several ways to approach that. Figure 1 presents the difficulty of the pigment system.

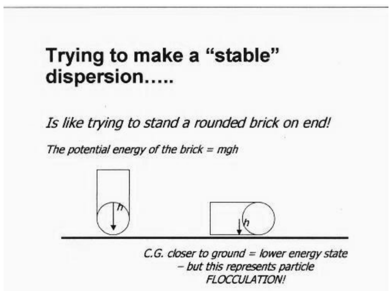


Figure 1. "Stability" in an Unstable System[11]

Generally, adding polymeric materials (dispersant) into the system to assist solid pigments (disperse phase) suspended or dispersed in bulk liquid (dispersion media) is a common way to stabilize the system, which is the steric effect method. Applying surfactants with a certain electrical charge function groups to form micelles and to change the potential of the electrical double-layer to prevent particles from aggregation or agglomeration to maintain the stability is another mean, which is the electrostatic effect method. In actuality, most ink chemists utilize both methods to approach the thermodynamic stability of pigmented dispersions and inks. In the case of traditional pigmented ink, it is easily done by applying polymers and surfactants to the system.

Table 2. Physical Properties of Inkjet vs Conventional Pigmented Ink

	Inkjet Ink	Conventional Ink
% Pigment	< 10	10-20
Viscosity	< 15 cPs	> 50 cPs
Particle Size	< 1 µm	< 50 µm
Stability	> 2 years	6-9 months
Surface Tension	35-50 dyn/cm	30-40 dyn/cm

However, for inkjet pigmented ink, shown in Table 2, the physical properties are much different from those of conventional pigmented ink. Due to the much lower viscosity requirement of inkjet pigmented ink, the utilization of polymers that are often used in conventional pigmented ink to help the ink thermodynamic stability is limited. Additionally, the dilute system means more Brown motions that would cause pigment particles to impact with each other and aggregate together to cause the instability of pigmented ink. Therefore, the best way to maintain the thermodynamic stability of pigmented inkjet ink is to grind the pigments into smaller particles to reduce their gravity affected properties. If small particles are obtained, then they will remain in thermodynamic stability for a longer period of time.

This paper, based on the previous research works,[12,13] presents physical chemistry fundamental concepts and experimental results based on the quasi- (or pseudo-) thermodynamic equilibrium theory regarding pigmented inkjet dispersions and inks to try to set up a theoretical guidance to pigmented inkjet ink formulations.

Background

From the principle of thermodynamics, two pigment particles approach each other due to attraction and repulsion. Their potential energy curves are described as in Figure 2. Of course, this is an energy curve of an ideal formula. Different formulations will give different potential curves. What we try to do is pushing the "ball" up on the hill and let it "stay" there (this is "meta-stable"), but, we have to prevent the "ball" over the energy "hill" from falling into the energy "well" (which is the "flocculation"). If we can successfully keep pigmented inkjet dispersions and inks in this meta-stable state, the formula will provide a very stable thermodynamic stability for this particular system.

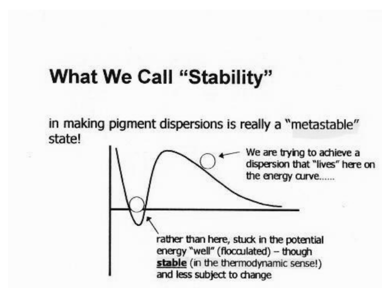


Figure 2. Potential Curves of Two Particles Approaching[11]

Attraction and repulsion among particles have always existed in pigmented systems as a thermodynamic equilibrium, shown in Figure 3. From a pigmented dispersion to a finished inkjet ink, we need to dilute the system. There is a driving force (or energy change ΔE) in the process between these two equilibriums. If we are able to keep driving force $\Delta E = 0$, it will be a true equilibrium process between dispersion and finished ink, which will take an infinitely long time to reach. In fact, what we could do is reduce ΔE close to zero (zero can never be reached) in a limited time. This process will only be taken at a quasi-(or pseudo-) equilibrium ($\Delta E \rightarrow 0$). Under the guidance of this quasi-(or pseudo-)equilibrium theory, we are able to make a super "stable" inkjet pigmented ink from a relatively stable pigmented dispersion.

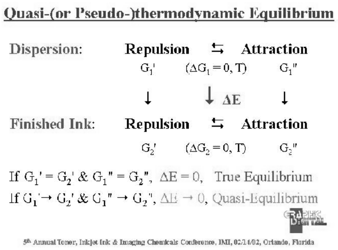


Figure 3. Thermodynamic Equilibriums of Pigmented Systems

Methodology

To grind the pigments into a sub-micrometer or a hundred nanometer scale, a higher pigment loading and polymer content is necessary. In the case of inkjet pigmented finished ink, a relatively lower pigment loading and polymer content is necessary due to the requirement of its much lower viscosity and much higher jetting ability (or flowing ability). So, there is a big difference in rheology properties between dispersion and finished inkjet ink. If we directly dilute the high concentration dispersion into finished inkjet ink, the system would lose the balance due to too much driving force ($\Delta E >> 0$) and result in the loss of thermodynamic stability. Therefore, we have to take this procedure into multiple steps to keep the driving force at a minimum ($\Delta E \rightarrow 0$).

The next question is the number of steps needed to maintain the inkjet ink stability. Theoretically, as many multiple-steps as required to ensure the process is thermodynamic equilibrium. However, this is time consuming and not realistic. For time-saving purposes, one step is more ideal, efficient, and realistic. Is it possible for a stable pigmented inkjet ink from the high concentrated dispersion to be made in just one additional step? The answer from the experimental results is yes if the "0.618 optimal methods"[14] or "Gold Cut" (Coefficient ~ 2/3)[14] is introduced to set that "critical point" or "critical range". For example, the pigment loading of conventional dispersion is usually 30 ~ 40 % and the colorant concentration of inkjet inks is usually ~ 5%. If the coefficient 0.618 is multiplied by the difference between 30 ~ 40 % and ~ 5%, it is found as the following:

$$0.618 \times [(30 \sim 40\%) - 5\%] + 5\% = 20.5 \sim 26.5\%$$

which means the optimal concentration of pigmented inkjet dispersion should be located within this range. By using this methodology, we could obtain a very stable inkjet pigmented dispersion suitable for the finished pigmented inkjet inks.

Results and Discussions

I. Optimized Pigmented Inkjet Dispersions:[15]

Based on the theory of quasi-equilibrium and under the guidance of the optimal method, we are able to target the optimized pigmented inkjet dispersions. They are ultra fine in their particle size with lower and moderate viscosity, neutral to weak alkali pH value, and have a very long shelf-life. The patented pigmented inkjet dispersions manufactured by Graphic Digital possess the following characteristics:

Particle Size:	<< 0.5 µm
Lower & Moderate Viscosity:	100 – 200 cPs
pH:	7.5 – 9.0 (Neutral to Weak Alkali)
Thermodynamic Stability:	2 years (Shelf Life)

Due to their sub-micrometer or hundred nanometer scale of particle size, they are able to overcome the gravity aggregation to be easily suspended in a relatively lower viscous and pH system for a long time with good flow ability and great shelf life to be ready for various inkjet inks. This is a very important key to successfully making super-stable pigmented inkjet inks.

II. High-Performance Pigmented Inkjet Inks:[16]

On the basis of Graphic Digital inkjet dispersions, we have manufactured a variety of water-based pigmented inkjet inks, including CMYK, CcMmYK, CMYKOG, and CMYKOGV etc, which are available for the market. Their largest measurable particle sizes are all less than 0.4 µm (UPA 150), some even less than 0.2 µm, which offers the settle-free and clog-free properties. What we found in laboratory experiments is the particle size in pigmented inkjet inks plays a critical role for ink thermodynamic stability and color gamut. The smaller particles not only ensure longer stability, but also provide the better color gamut. It seems that the half micrometer (0.5 µm) scale of the largest measurable particle size in pigmented inkjet ink is very critical. Graphic Digital pigmented inkjet inks have been tested, under oven conditions (70 ^{o}C), to be able to last at least 12 months without obvious particle size growth and settling phenomenon. Many of pigmented inkjet inks from our competitors only last less than 3 months under the same testing conditions. The pigments settle out to the bottom or separate into two layers of inks, whose upper layer is transparent liquid and the lower layer is settled pigments. Their original largest measurable particle size are greater than 0.5 um. This shows that there is a critical particle size for pigmented inkjet ink thermodynamic stability, which is a half micrometer (0.5 um) in the largest measurable particle size by UPA 150. The result is shown in Figure 4.

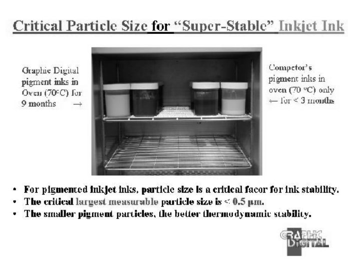


Figure 4. The Critical Particle Size for Pigmented Inkjet Inks

The viscosity is in 2 – 4 cPs, which provides good jet ability and ink running ability with high-performance in various inkjet printers, including both desk jets and wide-format printers. Of course, rheological properties of inkjet ink play an important role in ink performance in printer heads. This is more related to the particular individual printer and its printing technology. Due to the limited length of this paper, it will be discussed further on other papers.

Because of the small particle size of Graphic Digital pigmented inkjet inks, they provide much better color gamut than other pigmented inkjet inks under certain printing settings and on suitable medias. They are comparable to dye inkjet inks with an at least 90% of dye color gamut (See Figure 5). Moreover, they still possess an excellent water bleeding resistant and lightfastness or UV resistant (up to 2 years for outdoor applications), which means the pigmented dispersions and inkjet inks that we invented have a comprehensive advantage in the following:

Ultra fine particle size (Clogging-free)
Super stable thermodynamic shelf life (3 years of settling-free)
High performance (Good running ability on different printers)
Excellent color gamut (Super colorful)
Great water bleeding and UV lights resistant

Figure 5. Print with Graphic Digital Pigmented Inkjet Inks

Conclusion

Based on the understanding to ink chemistry and physics, this paper has proposed a novel quasi-equilibrium theory for making pigmented inkjet dispersion and inks. The results from both Graphic Digital inkjet dispersions and ink products have proved the theory is successful. The adapted optimal method is helpful to the process and feasibility of the theory. For the super thermodynamic stability, the particle size of pigment is playing a very important role in the ink system, and the found critical size is 0.5 micrometer in the largest measurable particle size. It will be very meaningful for pigmented inkjet ink formulations.

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Biography

Dr. Jie Wang currently is a general manager and director of technical & research of Graphic Digital Division, Graphic Sciences, Inc. He graduated from SUNY- College of Environmental Science and Forest, Syracuse University with his Ph.D. degree in polymer science, Syracuse, New York in 1996, graduated from Zhejiang University, Hangzhou, China, with his Master of Science and Bachelor of Science degrees in physical chemistry and polymer chemistry in 1984 and 1982, respectively. Dr. Jie Wang is a recognized, experienced (over 20 years) scientist in polymer science, physical chemistry, analytical chemistry, and organic chemistry. He contributed over 20 publications and multiple patents in pigmented inkjet inks and dispersions, novel organic polymeric semi-conductors included monomers, super-high strength polymeric materials, and instrumental analysis.