Investigation of the Physical Properties of Some Pigmented Inks and their Mechanism of Dispersion

Arup K. Basak and Henry M. Dante
Digital Printing Group; Research Development & Engineering
Philip Morris USA; P. O. Box. 26583
Richmond, VA 23261; USA

Abstract

In this study, we investigate the physical properties of some pigment based inks that we have formulated in our laboratory. We have used commercially available specially treated surface modified as well as unmodified dry pigments in these formulations. In both cases we have achieved the stable dispersion of pigment particles by appropriate selection of ingredients of compatible physical properties for ink formulation Furthermore, the influence of ink composition and other physical conditions like temperature, solvent mixture, dielectric constants and surface tension were investigated to study their effects on ink stability as well as print quality. We have shown that by controlling the composition, we can easily achieve the desired physical parameters required for proper ink jet printing operation. Based on these results, and considering the interrelationships of different physical parameters, a plausible mechanism of dispersion will be discussed for the stability and shelf life of pigment based inks.

Introduction

Quality of digital printing depends upon the printer, ink and substrate interactions. According to Fass,[1] media and ink interact in three major ways: wetting, penetration, and spreading. These three factors determine the digital images' durability and appearance. Printer, ink and substrates are three indispensable components for a printing system.

Ink jet images are made up of small drops of inks jetted to the substrates. In liquid ink category, the vehicle is usually organic solvents of high volatility or aqueous based inks. Solvent based inks offer more advantages in high speed printing compared to water based inks. Recent trends are geared to develop an ink vehicle which will provide similar advantages to that of solvent based inks as well as to comply with environmental and health regulations.

In recent years, pigments are widely used in formulating inks due to their unrivaled advantages over dyes because of lightfastness and weather resistance. These properties are the minimum for outdoor application. In Small office home office (SOHO) arena, non - impact ink jet printers are the major consumables. Print quality is dependent upon the printhead, ink and substrate composition. We are reporting here the result of investigation of different inks and their interrelationship of different physicochemical properties of pigmented inks and probable mechanism.

Experimental

Inks: Different black inks were used in this study. Few inks were formulated using carbon black pigment obtained from CABOT Corporation. Because of proprietary reason, detail formulation of in house water based pigmented inks will not be covered. For comparison purposes, we have used other water based pigmented inks with carbon black; CAB-O-JET 200™ & CAB-O-JET 300 ™ (from CABOT Co.). These two inks differ from each other on surface functionality. The physical properties of CAB-O-JET 200 and CAB-O-JET 300 along with their surface functionality are shown in Table 1.

The carbon blacks selected for in - house formulations are produced by CABOT Corporation. For comparison purposes we also picked up another water based pigmented ink from undisclosed vendor, named as Sample 1 (S1). By exercising careful judgement, a couple of carbon black pigments were chosen and one of them one is surface functionalized. Surface treatment of carbon blacks increases the amount of chemisorbed oxygen groups, which in turn facilitates the dispersion through hydrogen bonding in aqueous media.

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Table 1. Physical Properties[**]

Carbon Black	Surface Functionality	pH	Viscocity[1] cP	Surface Tension[2] dynes/cm^2	Particle Size[3] nm
CAB-O-JET 200[a]	sulfonated	7.9	4.27	74.6	128.3
CAB-O-JET 300[a]	carboxylated	8.9	4.8	73.9	138

(Data was provided by CABOT Corp. from their spec sheet).

[1] Shell # 2 Cup

[2] CSC DuNouy Tensiometer

[3] MicroTrack Ultra Fine Particle Analyzer

[a] Joseph E. Johnson & Gaye L. Bok., Proceedings of International Conference on Digital printing Technology , Seattle, 1997.; IS & T's NIP 13: pp. 659 – 663

In this investigation besides CAB-O-JET 200™ and CAB-O-JET 300™, we have used three other different pigment based inks (Sample 2 (S2), Sample 3 (S3), and Sample 4 (S4)) along with one dye based ink as Sample $_{(Dye)}$ (S_d).

The pH and the conductivity of inks were measured by Accumet Research pH meter AR50 with an accumet combination electrode and an accumet dip type conductivity probe from Fisher Scientific. Viscosity measurements were carried out using Rheolyst rheometer AR1000N from TA Instruments and corresponding rheology software. Particle size and zeta potentials were analyzed with a 90PLUS particle sizer and zeta potential analyzer from Brookhaven Instruments Corporation. All other chemicals used were of reagent quality.

The process of ink droplet formation of these experimental inks was observed by in-house developed micro image monitoring system. The inks were jetted through a single nozzle of a printer head and the still images of ink jets were captured. The details of the jetting characteristics will be communicated separately.

Results and Discussions

All physico chemical parameters were determined following standard methods and are listed in Table 2.

Analysis of data represented in Table 2 indicates that though the pH, viscosity and surface tension of ink samples S2, S3 and S4 are in close proximity, there is a wide variation in conductance and particle size. The difference in conductance is attributable to the ingredients, specially additional hyperdispersant used in formulating S4. Viscosity and surface tension parameters of ink samples S2, S3 and S4 are not affected by the ingredients and the grades of carbon blacks used. The increase in viscosity of these three ink samples from pure solvent is obviously due to added components. The particle size of carbon blacks used in formulation of test inks S2, S3 and S4 are 27 nm and 16nm. From particle size analysis of inks S2, S3 and S4 by dynamic light scattering, it was found that added component in formulation has an inhibitory effect on particle dispersion, thus affecting the zeta potential of the suspension. In order to determine the shelf life of S2-S4, we have determined the physical properties after about five months of storage under ambient condition. Those values are shown in Table 3.

Comparison of pH, conductance, viscosity and particle size of inks labeled as S2, S3 and S4 given in Table 2 & 3 unequivocally proves that these inks are stable for at least 4 months of storage. From figure 1 as shown below, the dependence of electrical conductivity on particle size indicates that interfacial conductivity of solute - solvent interface is significant. A general conclusion from above plot is S3 and S4 test inks require additional stabilizing force besides hydration energy of physical wetting for effective stable dispersion.

Table 2. Physico-Chemical Data of Different Inks at Ambient Temperature.

Inks	pH	Conductance, µS / cm.	Viscosity, cP	Surface Tension, dynes / cm	Particle Size, nm
Cab-O-Jet 200	7.0	--------	5.612	73.0	125.8
Cab-O-Jet 300	7.0	-------	5.014	73.0	150.0
S1	8.2	11900	1.165	46.95	80.6
S2	7.2	9590	2.331	39.75	138.0
S3	7.4	3670	2.418	44.62	296.7
S4	7.8	2230	2.676	41.11	489.3
S_d	9.1	11300	1.295	43.30	-------

Table 3. Physical Properties of Inks (S2 - S4) after long storage.

Inks	pH	Conductance, μS / cm.	Viscosity, cP	Particle Size, nm
S2	7.13	9280	2.571	134.2
S3	7.33	3020	2.638	309.0
S4	7.74	1890	3.092	493.6
EPSON Ink	7.00	9377	2.781	------

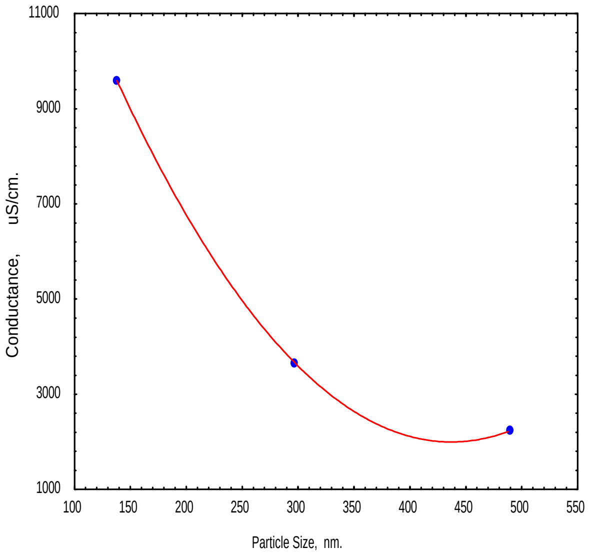

Figure 1. Dependence of Conductance on Particle Size in suspension

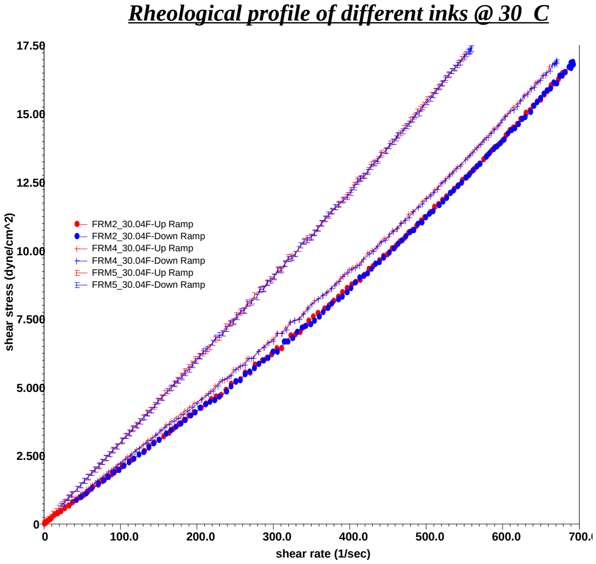

Figure 2. Plot of Shear Stress vs Shear Rate in Low Shear Viscosity of Inks.

The dispersing agents used in these formulation are quite effective to achieve the desired attributes for quality inks.

Figure 2 represents the rheological behavior of inks (S2-S4) at 30 C. It was found that the flow behavior all three inks are Newtonian in nature and no hysteresis was observed. This indicates that the ink systems maintain constant viscosity regardless of shear rate. The flow behavior was modeled and viscosity values were determined in the temperature range 25 ^{o}C - 60 ^{o}C. Viscosity values of three different in-house formulated inks, S2 - S4 were plotted against temperature as shown in Figure 3.

It was observed that viscosity decreases with temperature. This dependency follows an equation η = A exp (Δ E_{vis} / RT) where R is the molar gas constant.

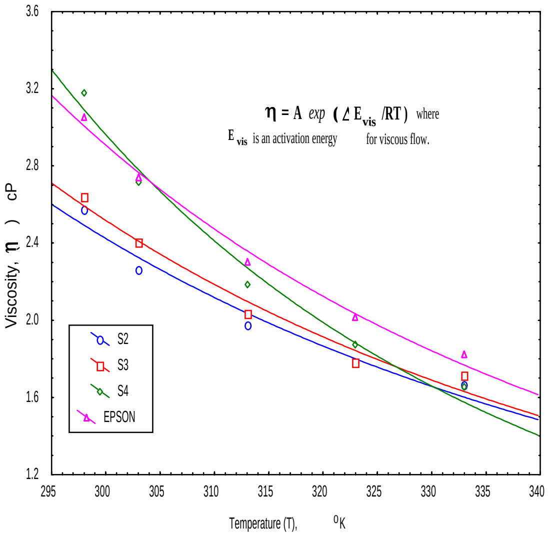

Figure 3. Dependence of Viscosity on Temperature

The value of A and (Δ E_{vis} / R) for S2 , S3 and S4 and EPSON ink are listed in Table 4. The quantity Δ E_{vis} is the energy barrier that must be overcome before the elementary flow process can occur. The term (- Δ E_{vis} / RT) can be explained as a Boltzmann factor giving the fraction of the molecules having the requisite energy to surmount the barrier. Thus Δ E_{vis} is an activation energy for viscous flow. In case of water, hydrogen-bonded structure breaks down with increasing temperature and normally it is about 1/3 to 1/4 the latent heat of vaporization (~ 44 KJ / mol.). In case of Sample 2 (S2), Sample 3 (S3), and Sample 4 (S4) those values are 10.5 KJ/mol, 11.0 KJ/mol, 15.9 KJ/mol respectively, compared to that for EPSON ink is 12.5 KJ/mol.

Table 4. Thermodynamic Parameters for the flow of Ink Fluid

Ink Sample	A	ΔE_{vis} / R
S2	0.037	1255.2
S3	0.031	1315.6
S4	0.005	1912.5
Epson Ink	0.019	1507.4

These values indicate that theoretically ink will evaporate faster than pure water at room temperature. This conclusively proves that added components like resins, surfactant, polymeric dispersant , preservatives, etc. used in formulation are compatible with the ink vehicle and the ingredient's concentration did not adversely affect the pigment dispersion and stability. The added polymeric dispersant in the ink vehicle lowers the energy barrier of flow process by its hydrophilic nature. Besides these additives may also help to achieve faster drying by breaking the hydrogen bond structure in the ink vehicle. Of course, during printing, the media properties will also contribute to accelerate drying by absorption which will be discussed later in separate communication.

From temperature dependency of viscosity for in-house formulated inks, it is plausible to suggest that at about 55 ºC the flow characteristics will be independent of particle size of coloring pigment. This indicates that mobility of charged pigment particle attained an optimum value. This indicate that at temperature ~330 ºK the entropy effect will be responsible for flow. This led us to investigate on dispersion stability of the inks by Freeze - Thaw Cycles.

On a macroscopic basis, it is often predicted, from second law of thermodynamics, that small particles will coalesce into big ones to reduce the surface area. On a microscopic basis, attractive forces are always present pulling the particles together, even in case of completely non polar particles because of their random collision with each other due to diffusion. The dispersion forces are often just as large as any permanent dipole forces of attraction.

Here we are dealing with complex composition of inks, which is neither purely colloid nor simple hydrated ion. Thus a good stable dispersion of pigment particle in the ink vehicle can be achieved with appropriate trade off of the repulsive and attractive force arises from particle media interactions. A solid particle in polar solvent will develop surface charge and mobile in an electric field. Besides this electrophoretic mobility, there are other elctrokinetic phenomena due to elctroosmosis, streaming potential and sedimentation potential.

All three in-house formulated inks are conductive in nature and conductance decreases with increasing particle size in suspension (Figure 1). This can be explained as due to the adsorption of dispersing molecule on pigment surface, each particle acts as a charge carrier and thus contributing to the conductive nature of the ink. Thus higher the sizes of the resultant charge bearing pigment particle, lowern the ionic mobility. This agrees well with the experimental observation as shown in Figure 4.

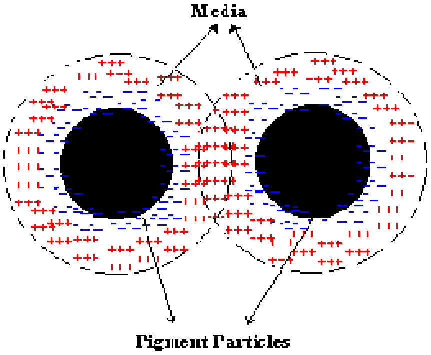

Figure 4. Electrostatic Stabilization

In order to explain the mechanism of the stability of pigment dispersion we need to invoke the electrostatic and steric stabilization mechanism. Electrostatic stabilization of the dispersion can be explained in terms of an electrical double-layer. A charge is generated on the pigment surface, and a more diffuse cloud of oppositely charged ions develop around it.

As two particles approach each other the charge clouds overlap as shown above, and the mutual repulsion of like charges effectively provides a barrier to closer particle interaction. This mechanism is very effective in water and the medium of high dielectric constant.

The charge developed at the solid-liquid interface is the electrical double layer and its thickness will decrease exponentially. The dry pigment particle size is far less than that of the kinetic unit obtained from particle size analysis. The mobility decreases with increase in size of the hydrodynamic unit as is evident from conductance measurement. If the thickness of resultant inner layer of dispersed pigment particles by adsorption of polymers is small, then the pigment particles will aggregate or flocculate. The choices of polymeric chain in these formulations are such that they overcome the Van der Waals forces of attraction between pigment particles and thus enhance the stability of the dispersed inks. The ξ potential is the electrostatic potential at the surface of shear and not the potential at the surface of the particle. The surface of shear extends out from the particle surface. This surface separates the electrokinetic unit from the bulk of the solution, which moves This kinetic unit consists of the particle, ions adsorbed on to the surface, counter ions adsorbed in the layer within the surface of shear, plus the solvent molecules strongly attached to the surface ions and counter ions in the double layer. In addition , the surfactants are attached to the surface along with solvent molecule associated with them constuitute part of the electrokinetic unit, which moves as a single entity through the sorrounding. It is wise not to ignore ξ potential in favor of ionic mobility. Zeta potential measures the optimum repulsive force to counteract the Van der Waals attractive force to maintain the stability of the dispersion. S2 sample ink has more negative zeta potential indicates that electrostatic stabilization predominates over steric stabilization as shown in Figure 5.

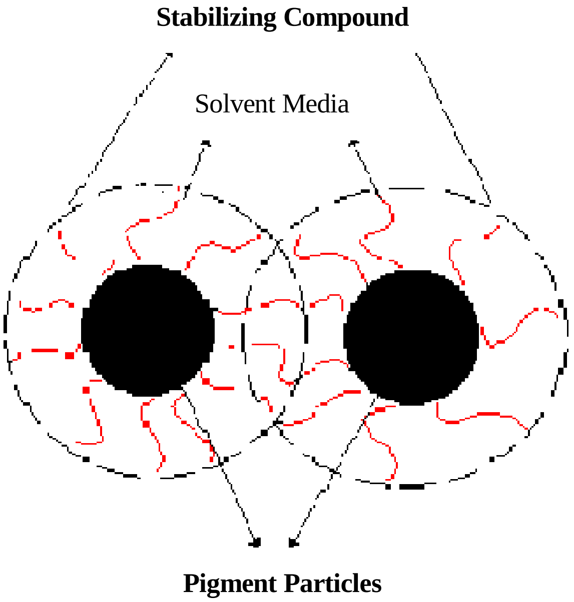

Figure 5. Steric Stabilization

In a complex ink system, we also invoked the steric stabilization theory for greater stability of the dispersion, which is in addition to electrostatic stabilization. The pigment particles adsorbed a layer of resin or polymer chain on their surface. As pigment particles approach each other, these adosrbed layers intermingle as shown below and in doing so, they lose a degree of freedom. These loss of degree of freedom is thermodynamic loss of entropy, which is unfavorable and provides the necessary barrier to prevent further attraction. Mechanistically, it can be viewed as the chains intermingle, solvent is forced out from between particles, which led to an imbalance in solvent concentration. This concentration gradient is resisted by osmotic pressure tending to force solvent back between the particles, thus maintaining their separation.

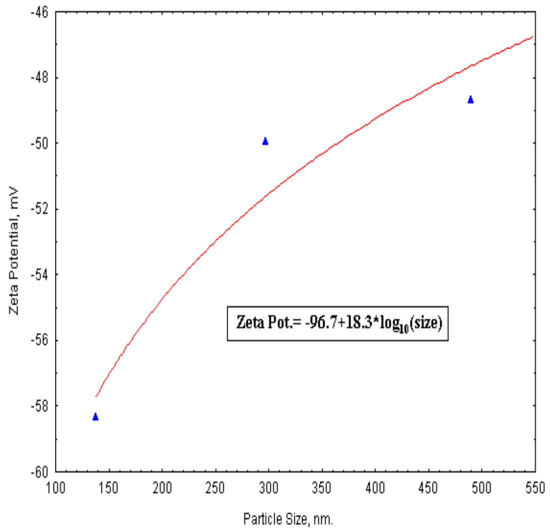

Figure 6. Plot of Zeta Potential vs Particle Size.

Zeta potential measurement will provide some insight on the mechanism of particle dispersion and the stability of these inks. From the dispersion mechanism discussed above, it is quite plausible to suggest that zeta potential will increase with increase in hydrodynamic size of the dispersed particle. Figure 6 represents the correlation of zeta potential for samples S2, S3 and S4 with particle size.

Acknowledgements

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1. Fass, W., Lee, D., Winslow, A., in *Recent Progress in Ink Jet Technologies*, IS&T, Springfield, Virginia, 1996. p. 247

Biography

Arup K. Basak is a research staff member with Digital Printing Group at Philip Morris USA, R & D Center, Richmond, Virginia. His research interests include solution chemistry, reaction mechanisms, chemical synthesis, thermodynamics and physical chemistry.

Henry M. Dante is currently at Philip Morris research and development where he is working on implementing digital printing technologies. He has been with Philip Morris from 1989 where he has worked on developing vision systems, process control, modeling and simulation and implementing new technology.