Exploring Dye Solubility in Inkjet Inks

Application Note 139

Inkjet manufacturers struggle to achieve the best color saturation with aqueous ink formulations using dyes which have limited solubility in water. Precipitated dye produces poor color saturation. Formulations with more water-soluble dyes suffer from a lack of water-fastness. Increasing the solubility by using organic polar cosolvents works, but at increased cost, and may lead to other problems such as decap (drying ink on the inkjet nozzles). Formulators have many constraints to formulate inkjet inks which meet all performance criteria within cost constraints.

The following data shows a different approach to optimize color saturation by two manufacturers, using relaxation measurements and the Acorn Area. The Area can make measurements on ink formulations as used in the ink cartridge, without dilution. In addition, relaxation measurements are very sensitive to the presence of small particles, such as precipitated dye, as shown in the following results.

The soluble dye inks were MR-05 and MM-08 red inks. The results are listed below:

Water soluble red dye ink	MR-05	MM-08
T_{2a}	1222 ms	426 ms
$\%T_{2a}$	86 %	100 %
T_{2b}	643 ms	none
$\%T_{2b}$	14.1 %	0 %

In a T_2 relaxation experiment, the sample (0.5 mL) is placed in a small tube in a permanent magnetic field, Bo. A temporary magnetic field B1 perpendicular to Bo causes the liquid molecules to align with B1. When B1 is removed, the molecules return to their original orientation with a characteristic time, T_2. For simple liquids and non-porous, noninteracting particles, the process is exponential. Ink with a soluble dye will have a single T_2. In this example, MM-08 has only one T_2 as expected.

If the particles are interacting, porous, or a second phase is present, additional relaxation times may be observed. MR-05 required two relaxation times, T_2a & T_2b, to fit the data. T_2a represents the relaxation time of all the components of the bulk solution. T_2b represents a separate relaxation process within a liquid domain where exchange with the bulk solution is restricted. A part of the bulk solution is “trapped” and exchanges much slower than the bulk solution. Such a condition exists when flocculates are present.

Water has a T_2 relaxation time of about 2300 ms at 25˚C, whereas more polar organic based solvents tend to be much lower, in the hundreds of milliseconds. The MM-08 red ink likely contains one or more polar organic cosolvents (or more of them) than MR-05 ensuring the dye is dissolved. The MR-05 ink probably has

dye crystallites present, and because of the limited solubility, the crystallites flocculate, creating internal surfaces that restrict solvent exchange with the bulk solution. Furthermore, shaking the ink followed by measuring relaxation after a few minutes or after a few hours had a noticeable impact on the T_{2b}. While a thorough study was not done, the T_{2b} varied as much as 25% whereas the T_{2a} only varied by 1.7%. These results suggest a loose flocculate of crystallites is present in the MR-05 ink. Filtering through a 0.2 µ nylon filter did not change the results, but that's to be expected because:

1) the Acorn Area is very sensitive to small particles (down to 0.001 µm)

2) larger particles than 0.2µm will interfere with proper ink-jetting and would have been detected in initial formulation

The inks above were tested "as is" at full concentration. These results would not have been easily obtained with standard dynamic light scattering (DLS) particle size measurements. Opaque inkjet inks require substantial dilution for DLS measurements, which would have solubilized the crystallites and no particles would have been detected. The Acorn Area is marketed for its ability to help and guide formulation and quality control of dispersions. However, these results demonstrate that the Acorn Area can also be useful to determine solubility limits for dye inks, and to find the right mix of water and cosolvents to maximize solubility and improve color saturation performance.