Use of Analytical Techniques to Characterize the Stability of Difficult Ink Jet Pigmented Systems

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Abstract

Pigmented inks are now commonplace in all types of ink jet systems, from industrial to desktop. To achieve robust printer performance in the printheads an understanding of the ink's stability is vital even before testing in a printhead is undertaken. It also provides valuable information regarding settling and shelf life. All of this analytical work highlights the requirement for the correct formulation before printer trials can begin.

Several new analytical techniques are available for determining the stability of pigment dispersions. One of these is sedimentometry using the Turbiscan system. This system involves the scanning of a column of ink using a near infrared monochromatic pulsed LED. The system detects transmitted light through the sample and also backscattered light from particulate material in the ink. The system takes a scan every 40 microns through the sample and multiple scans can be overlaid to give information about stability with time.

Using this system several difficult pigment types have been successfully incorporated into ink jet inks. These include various heavy inorganic pigments of particle sizes up to 2 microns. Metallic powders with particle size distributions in the order of D 50 of 2.0 to 3.5 microns and D 90 of 4.5 to 6.5 have been successfully stabilised and subsequently printed. This level of particle size is unheard of in the desktop market where inks are commonly filtered to below 0.5 microns and often 0.2 microns.

Use of these analytical techniques has highlighted issues such as chemical and physical instability long before conventional techniques and can then allow for the correct choice of dispersants, resins and solvents to be chosen produce a stable ink system that can then be reliably printed through ink jet printers.

Introduction

For the desktop and wide format markets there is a trend towards pigmented inks for durability and lightfastness reasons. This trend is also true for the wide format markets. In addition, the industrial sector is an exciting arena for using novel pigments in ink formulations for a wide variety of applications.

The robust nature and the ability to apply more energy into the ink during firing with industrial printheads allow for an increase in the viscosity and the variety of chemistry and formulations possible for printing. The robustness of the printheads and ink delivery systems allows for the inclusion of larger particle sized pigments, higher viscosity solvents and interesting resins to enable formulations to achieve a wide range of possibilities.

Pigments are not only limited to the traditional process color printing using the standard organic pigments. Inorganic pigments have uses for outdoor applications where their superior lightfastness give them an advantage over organic pigments. Inorganic pigments are also exclusively used in the ceramic industry.

Inorganic phosphors are used in both the production of various display screen technologies and in security applications. Magnetic readable inks containing inorganic materials have a huge market to exploit. Metallic powders are being explored for both decoration and the printing of conducting elements.

In all these cases heavy pigments with typically larger than standard particle size are required to be formulated and then printed. Standard particle sizes have been dictated by the printhead manufacturers and typical values are in below 0.5 microns, preferably below 0.2 microns. In this paper examples will be given for pigments with particles typically over 1 micron and in some cases over 5 microns.

Accelerated Ageing

Conventional techniques for determining the stability of pigmented systems often involves measuring the physical properties of the ink and particle size of the pigments after some form of accelerated ageing trials.

Typical routines will involve raised temperature trials at 40°C or 60°C and freeze / thaw testing. These accelerate any instability in the system and testing normally continues for up to six weeks.

The results gathered from this sort of testing can be very useful in screening purposes to determine differences in inks and effects of formulation changes. For screening a range of additives or resins these tests can begin to show effects within the first few weeks and can be used very effectively to highlight paths to take in formulation work.

Accelerated ageing however is not a quick system for testing. Results generally take a few days if not weeks to be gathered resulting in a slow iterative process to finalize ink formulations.

In addition to the slow working times involved, in accelerated ageing the results are often difficult to interpret. An ink may have good chemical and physical stability and been observed to remain stable at room temperature for up to a year but in elevated temperatures it may show instability within days. In this case there is no reason why the ink cannot be declared to have a years shelf life with the limitations of storage temperatures.

There is always a place for elevated temperature studies for the understanding of the ink during transportation and storage outside of optimal conditions.

Sedimentometry

Typical light scattering methods of particle size analysis require the dilution by several hundred, if not thousand, in the ink solvent. This obviously changes the pigment's environment drastically and can possibly destabilize otherwise stable pigment systems. A method that requires no dilution is sedimentometry.

This method uses the dispersion or ink as received and scans through a vertical column using a near infra-red light. Although using it in the configuration mentioned here does not give rise to particle size information is does show sedimentation, clarification and agglomeration of the pigments.

Backscatter is determined by the size and number of particles present in a given area. An increase in the backscatter indicates a higher concentration in pigment or a change in particle size. Therefore an increase in backscatter would be seen in areas where pigment is likely to settle and there will be a concurrent decrease in backscatter where clarification of the sample takes place.

The technique is very sensitive and scan times of up to two hours can be useful in screening formulation variations whilst 24 and 48 hour scans can give in depth information as to the settling rates and any qualitative information on particle size changes. Additionally the sample can be scanned, removed from the instrument and placed in an oven overnight and re-scanned the next day to gain the same thermal stability information normally achieved through accelerated ageing.

Dispersing Techniques

Conventional techniques for dispersing pigments include high speed, high shear mixing, bead mills and triple roll mills. Typically the manufacture of pigment dispersions with high shear mixing and bead mills is to reduce the pigments to their primary particle size and then to stop re-agglomeration between pigment particles, this involves the optimization of the inter-particle attraction through the dispersant chemistry.

Numerous polymeric and low molecular weight dispersing additives are available to stabilize the pigments once the primary particle has been reached. In addition to the dispersants there are numerous resins to aid in the pigment grind. The grinding media and exact procedures are all areas that need to be optimized to ensure the best possible dispersion.

To ensure a fast and efficient optimization of the dispersion and ink formulations, a screening process needs to be undertaken with a range of dispersants under a variety of milling conditions. The quick analysis and interpretation of each formulation is vital in understanding the improvements that can be made. This is where the sedimentometry data provides a quicker solution to high temperature ageing.

Chemical and Physical Stability

Chemical stability of an ink or dispersion is the assurance that can be given that no agglomeration or particle size increase occurs. This does not always necessitate that the system is free from any settling. Physical stability refers to a system that has observable settling, however if chemical stability is not achieved this system will not have long term stability.

With large and heavy pigment particles the physical stability of a dispersion is not always possible to achieve. The particles are too large and dense to resist the force of gravity. What can be achieved, is very good chemical stability. This means that although the system is observed to settle, the speed of settling being very dependant on the quality of the dispersion, the pigment is very easily re-dispersed under very low shear.

A soft settled system can be easily reincorporated into solution by simple shaking. The pigment particles have been effectively dispersed by the dispersant so that there is no irreversible agglomeration or particle size increase.

This soft settling system is a viable option in the industrial markets where there is a greater flexibility in the ink management systems. Obviously settling in a desktop ink is very unfavorable when no such luxury is possible within the ink cartridges.

The ink management systems can allow for agitation and stirring of the ink reservoir and the flushing of the tubing and printhead. In addition control can be achieved over the head capping mechanism and the priming and wiping requirements.

Using this control over the printhead and ink system allows for the development of a reliable ink jet system that can print difficult pigments observed to soft settle in the inks.

Examples of Difficult to Disperse Materials

For a whole range of applications there are novel and unusual pigments that need to be effectively dispersed into ink systems to allow for reliable printing.

Inorganic pigments for security and ceramic printing, metallic powders for decoration and magnetic readable pigments are just a few of the applications that require the stabilization of pigments not normally considered for ink jet.

In each example described, the pigment size and density means that physical stability over any prolonged period of time at the ink jet ink viscosities is impossible to achieve. Therefore although physical stability cannot be achieved chemical stability must be achieved and then the soft settling issues can be addressed with ink management systems.

Inorganic Pigments

Inorganic pigments are useful in a range of areas including outdoor applications, security phosphors, display phosphors and ceramic colorants. Depending on the density and particle size different levels of dispersion stability can be achieved.

Inorganic phosphors for security and display screens are generally very dense (~5g/cm^3) and of a particle range of between 1 and 5 microns. By varying the choice of dispersant can considerably vary the stability of the ink. Figure 1 shows the sedimentometer scan of an ink containing a heavy inorganic pigment stabilized with a dispersant optimized for ionic stabilization.

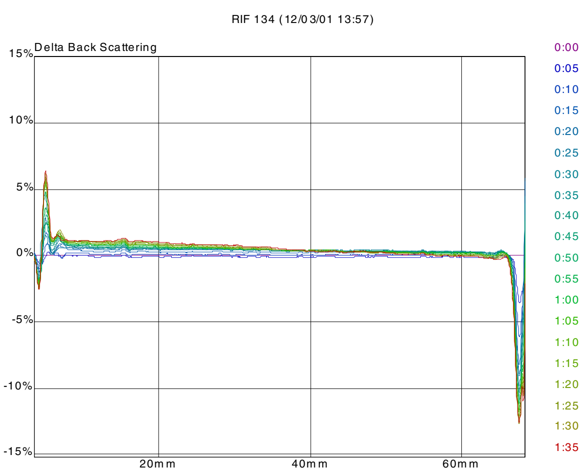

Figure 1. Ionic and Sterically Stabilized Pigment

Figure 2 shows the same formulation with the dispersant replaced with one that relies on 100% steric stabilization rather than a combination of steric and ionic methods.

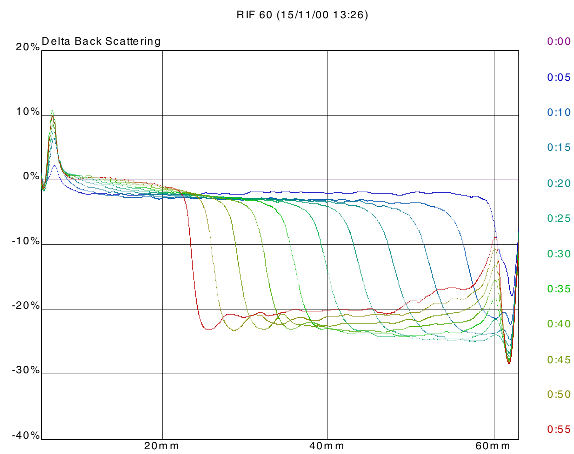

Figure 2. 100% Sterically Stabilized Pigment

The results show that by changing and optimizing the dispersant used the settling rate decreases by two orders of magnitude.

The difference in stability between the two samples is significant and could be detected by the naked eye within a few hours of sitting. However the sedimentometer scans show differences in the inks within the first ten minutes of scanning.

Screening of a large number of possible dispersant candidates is possible with this analysis system and detailed information can be gathered regarding the level of stability with time including valuable information such as the migration rate of the settling particles in the ink.

Metallic Particles

To achieve full, metallic luster the size and shape of the metallic particles is very important. Particles need to be generally above 1 micron and ideally nearer 5 microns. The shape of the particles should be platelet to improve the luster of the finished print. To this end, the particles used for metallic decoration purposes have a mean particle size of 2-3 microns with a D90 of 4.5 to 6.5 microns.

The metallic particles are also dense and so the combination of dense platelets with dimensions in the order of 3 or 4 microns poses a difficult formulation and stability issue.

The screening of a variety of dispersants and resins was again possible using the sedimentometer to quickly determine the path forward to develop the most robust ink possible. Due to the size of the particles involved, preparation of a physically stable ink was impossible, some degree of settling was inevitable.

Due to the correct selection of dispersants and resins the amount of settling can be reduced significantly and Figure 3 shows the sedimentometry scans.

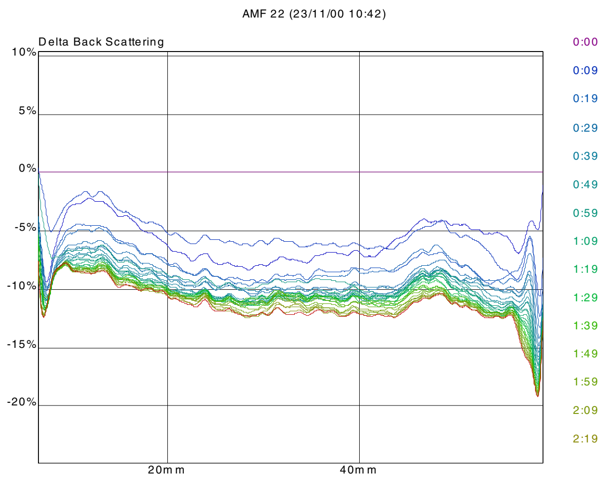

Figure 3. Dispersed Metallic Particles

The results show that there is generally little settling of the pigment within the two-hour scan time. However the decrease in the backscattering across the sample is caused by a particle size increase. This agglomeration was found however to be reversible and on shaking the particles separated, the sedimentometry scan would be identical and the ink would filter to the required level for printing, in this case ten microns.

The redispersibility of the particles indicates chemical stability if not physical stability has been achieved. This chemical stability needs to be understood to develop an effective ink maintenance system to allow for robust printing of these types of ink.

Knowing the sedimentation rates and the agitation required to maintain the ink allows for the development of a maintenance system and program of action to maintain the ink in a printable state. This will include idle and dwell requirements in addition to overnight stops.

Ceramic Inorganic Pigments

If pigments are to be printed prior to the final glaze the pigments to be used must be the standard ceramic pigments. This means that there is little scope for drastically changing particle size or pigment composition. Therefore the particle sizes are in the order of several microns and the loadings must be high to achieve the vibrancy of color.

Again, the required physical stability of the system is achieved through the careful selection of solvents, resin and dispersants with the added complication that the combination of these materials does not affect the firing process and lead to pin holes or cratering effects on the finished article.

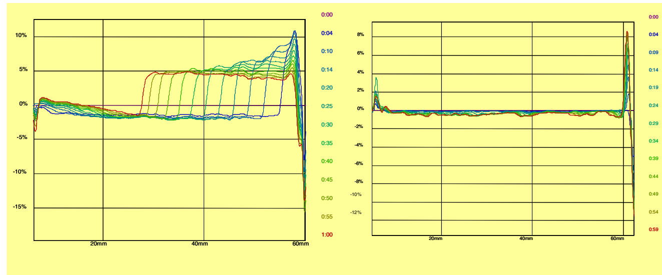

Figure 4. Ceramic Pigmented Ink with and without Stabilizing Agent

Figure 4 shows two sedimentometry scans with and without a silica stabilizing agent and the results show a 300 fold increase in stability with its inclusion. The silica provides the required stability increase without the need for additional resins that can cause imperfections during the firing. The loading of the additive is important and screening of likely formulations is fast with the sedimentometer, as it can start to show differences between formulations within the first twenty minutes.

Conclusion

The use of sedimentometry is important in understanding the differences between physical and chemical stability. The results presented show that a range of difficult to disperse materials can not only be efficiently dispersed into low viscosity ink jet ink but also gives us enough understanding to allow for the robust and reliable printing of these inks in a production environment.

The science that can be bought to bear on the development of stable systems is improving all of the time and understanding the rates and modes of settling and agglomeration allows for a fuller understanding of the effects of the ink components on the stability and allows for faster and more efficient formulation work to be undertaken.

The boundaries of what can be reliably printed with ink jet is expanding daily and being at the forefront of this arena means having to have high levels of understanding of all the chemistry and physical factors involved in the ink stability. Modern analytical techniques are therefore vital it reducing the risks and unknowns in the formulation work and allowing for science to play a part in ink design.

References

1. Drake, J. A. G., Chemical Technology in Printing and Imaging Systems, *The Royal Society of Chemistry*, 1993, pg. 107.
2. Harvey, Robert. A., *Digital Printing Applied to Ceramic Decoration*, IS&T, Vancouver, BC, 2000, pg. 516.
3. Matz, David. J., *Lightfast Ink Jet Images*, IS&T, Vancouver, BC, 2000, pg. 100.

Biography

After completing an analytical chemistry degree at Loughborough University, UK, Kris Sime remained at the institute to undertake a PhD. The subject of this study was the characterization of the polymeric materials used in Dye Diffusion Thermal Transfer printing. Following this research he started at Xennia Technology, where he has worked for the last three years. During this time Kris Sime has established himself in a pivotal role focusing on the management of the research laboratories.