Analytical strategies for ink formulation

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PARTICLE SIZE

RHEOLOGY AND VISCOSITY

Controlling the performance of an ink is a complex optimization challenge. Understanding how features of the system, the dispersed particle size in particular, impact stability and behavior during each stage of the printing process is crucial for effective formulation. This white paper offers practical guidance on using a range of analytical techniques, including rheology, and particle size and zeta potential measurement to generate the required knowledge.

Over the past 30 years the use of commercial and industrial inks has changed substantially. In particular, the maturation of inkjet technology has revolutionized printing. From office printers through to industrial coding and marking systems, inks are now required to meet demanding performance targets, for a wide range of different applications.

Inks are complex dispersions or emulsions consisting of dyes or pigments, and other components, suspended within a continuous phase. Formulation is complicated by the fact that the properties of these components impact multiple aspects of ink performance. For example, the particle size of a suspended pigment determines the hue, gloss and weatherability of the finished coating. At the same time it also affects the stability of the ink and its flow properties (viscosity). Ink formulation is an exacting science and relies on gathering relevant data from multiple analytical techniques to achieve an optimal solution.

In this white paper, experts from Malvern Instruments explore analytical strategies that support formulation and provide practical guidance on gathering data to:

- characterize ink components
- quantify performance characteristics such as jetability and tendency to drip
- engineer formulation stability
- control manufacture.
- Case studies are presented to illustrate the value of different analytical techniques in accelerating formulation to a successful conclusion.

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Innovations in inks

Every advance in printing requires an associated advance in ink formulation. The invention of the printing press, for instance, called for thick oil-based formulations to cling to the metal type face, in place of the high viscosity water-based inks that were prevalent at the time. Today, modern developers face the challenge of developing high performance inks that produce a consistently high quality finish, for every type of printing technology.

There is no universal ink formulation that will perform well in all types of printing process. For example, inks are required to flow more quickly through an inkjet printer head than when applied via screen-based techniques, so the preferred viscosity characteristics are different in each case. In addition, advances in technology have extended printing to a diversity of substrates, from thin films and vinyl sheets through to ceramic tiles and objects with three-dimensional features. For success, performance-defining characteristics of the ink must be engineered for compatibility with the printer and the substrate, as well as delivering a desirable finish.

Components of modern inks include:

- a carrier fluid – either aqueous or organic
- colorants – pigments or dyes
- surfactants – to control the surface tension of the ink droplets
- binders – to control the elasticity of the ink and the way in which it breaks up when shear is applied
- dispersants – to improve the dispersion of colorants in the carrier fluid.

The formulation of high performance, stable products relies on the optimal inclusion of each of these constituent components.

Controlling performance during the printing process

A good starting point for formulation is to consider the requirements of the printing process and how to make an ink compatible with these. Here rheology has an important role to play, since rheological characteristics impact the way in which an ink jet, atomizes, drips and spreads.

Figure 1 shows two inks being used in a 'drop-on-demand' inkjet printing process. The first behaves properly, producing a single discrete drop following actuation, while the second behaves improperly, producing double droplets. This disruptive dripping behavior is typical of inks with poorly optimized rheology and it compromises printing performance.
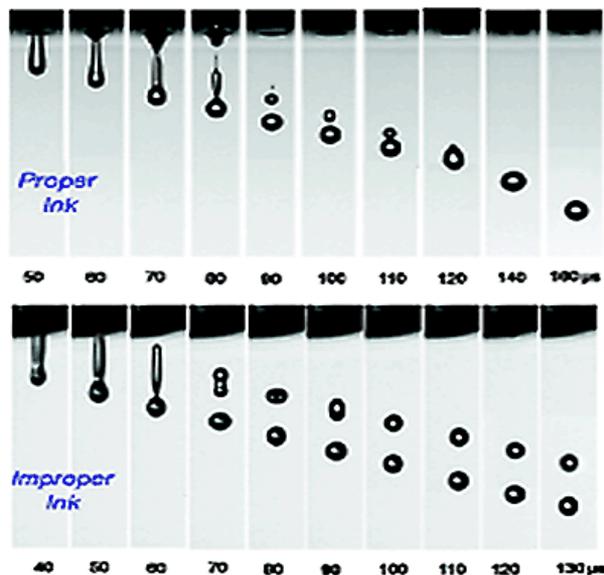
Figure 1: Comparison between a proper (top) and improper (bottom) ink within a 'drop on demand' print head illustrates the importance of controlling formulation rheology

The rheology of an ink is directly influenced by properties of the suspended components, such as particle size. However, particle size specifications for a suspended pigment are often dictated by formulation goals relating to the finish. For any given carrier fluid/pigment combination, the rheology of the continuous phase is more practically manipulated through the use of polymers, surfactants and binders. Polymeric additives can be used to control the viscosity of the continuous phase, and to impart sophisticated characteristics such as elasticity or shear thinning behavior.

Viscosity

Simple viscosity measurements quantify how an ink will flow through the print head, and to some extent how it will atomize. Successfully incorporating additives designed to control viscosity requires an understanding of the structure-function relationship between additive characteristics, such as molecular weight and molecular weight distribution, and ink performance. Techniques such as multi-detector gel permeation chromatography/size exclusion chromatography (GPC/SEC) enable the detailed characterization of polymeric additives. Rheological measurements quantify viscosity and, by extension, ink performance.

To be relevant and useful, viscosity values must be measured under conditions that simulate those at the print head. This can be challenging when designing for modern printers, which typically apply shear rates as high as 10^5 to 10^6 s^{-1}. These shear rates are not achievable with even the most highly specified rotational rheometers because of the inherent mechanical limitations of the technology. The following case study demonstrates how microfluidic rheometry, a relative new technique, more efficiently meets the need for high shear viscosity measurement.

Case Study 1: Using microfluidic rheometry to assess performance at the print head1

Research suggests that for a ceramic inkjet ink a viscosity of between 5 and 25 mPa.s is optimal for good performance at the print head. Figure 2 shows viscosity measurements made to assess how the viscosity of two commercial ceramic inkjet inks vary as function of temperature, in the range 20°C and 40°C. This range reflects typical operating temperatures during printer use. The measurements were made using an m-VROCi microfluidic rheometer at an ultra-high shear rate of $30,000s^{-1}$.

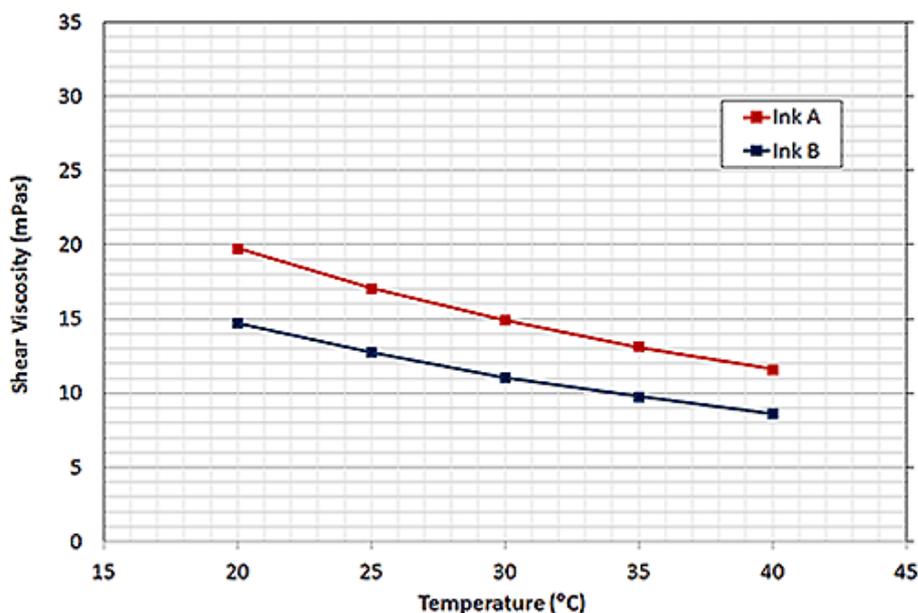Figure 2: Measurements at high shear ($30,000 \ s^{-1}$), made with a microfluidic rheometer, confirm that viscosity remains within the target range of 5 to 25 mPa.s across an operating temperature range of 20 to 40°C

The results show that the viscosity of both inks decreases with increasing temperature, as expected. However, the shear viscosity of both inks remains within the desirable range across the test temperature range. This suggests that both inks will flow well through the print head, under normal operating conditions.

Viscoelasticity

The rheological characteristic of viscoelasticity also directly influences performance at the print head. Suspensions exhibit behavior that lies along a spectrum ranging from viscous, liquid-like behavior to the elastic response to shear associated with solids. Measuring and controlling viscoelasticity supports the development an ink that successfully breaks up into discrete, well-defined droplets, during printing and holds its desired structure on application to the substrate. Referring back to the poor jetting performance illustrated in figure 1, this is indicative of an ink with sub-optimal viscoelasticity. The ability of the elongated droplet to break from the bulk liquid and re-form into a single sphere is linked directly to the property of viscoelasticity, and also to the surface tension of the ink.

Developing structure-performance relationships to enable the successful incorporation of additives to control viscoelasticity relies on quantifying this more complex aspect of rheological performance. Here rotational rheometry is a valued technique.

However, because inks are so weakly structured, alternative strategies can be helpful. Microrheology is an emerging technique that is useful for probing viscoelasticity under conditions that give valuable insight into performance at the print head.

Engineering stability

Formulating for successful printing is crucial but it is equally important to look at how to maintain that performance over time. Engineering a robustly stable formulation ensures that ink quality does not degrade with time and relies on maintaining discrete particles in suspension, under the conditions encountered during use and in storage. This can be one of the most challenging aspects of ink formulation.

The general strategy for achieving stability is to avoid particle aggregation since this produces larger particles that are more prone to sedimentation or settling and can block the print head. In addition, the presence of aggregated particles in a finish can adversely affect quality. The mechanisms that give rise to stability can be classified as kinetic or thermodynamic. Kinetic stability is associated with particle movement. Slowing particles down induces kinetic stability by reducing the risk of aggregation and sedimentation. Achieving thermodynamic stability on the other hand, depends on discouraging aggregation by increasing the strength of repulsive forces between fine particles, usually through electrostatic or steric means. These forces are a function of particle size, shape and electrostatic charge or steric forces.

The likelihood of sedimentation in a suspension can be predicted from the ratio of gravitational to Brownian forces, see equation 1[2]

$$(1)\ a^4 \Delta\rho g / k_B T$$

[where a is the particle radius, $\Delta\rho$ is the density difference between the dispersed and continuous phases, g is acceleration due to gravity, k_B is the Boltzmann constant and T is the temperature]

In a sub-micron suspension Brownian motion is usually significant and this ratio has a value of less than 1. For these systems thermodynamic stabilization is usually required to prevent aggregation. A ratio in excess of 1 is indicative of a system prone to sedimentation as a result of gravity driven kinetic instability.

When it comes to the practicalities of controlling the ink stability, formulators can manipulate one or more of the following three variables:

- Particle size of the dispersed phase. Larger particles are more prone to sedimentation than those that are finer. However, small dense particles, as exemplified by many pigments, will settle because of the large density difference between the dispersed and continuous phases (see equation 1).
- Viscosity of the continuous phase or the suspension. Increasing viscosity slows down particle movement and tends to decrease the risk of sedimentation.
- Zeta potential of the system. Zeta potential is a measure of the charge between particles at the slippage plane1. In systems containing sub-micron particles, a zeta potential with a magnitude of greater than 30 mV, either negative or positive, is associated with a high degree of repulsion between particles, and thermodynamic stability. Steric repulsion through the adsorption of macromolecules or surfactant provides an alternative route for stabilization particularly for non-aqueous systems.

The case study below illustrates a systematic strategy for assessing and improving stability in a suspension of particles of defined particle size.

Case study 2: Inducing stability in a suspension of fine particles.2

Figure 3 shows the effect of pH on the zeta potential of a suspension of particles with an average size of 3.7 µm. These data were gathered using a Zetasizer Nano S in conjunction with an MPT2 autotitrator. Zeta potential drops below -30 mV at around pH 2 indicating the system is thermodynamically stable at all pH values higher than this.
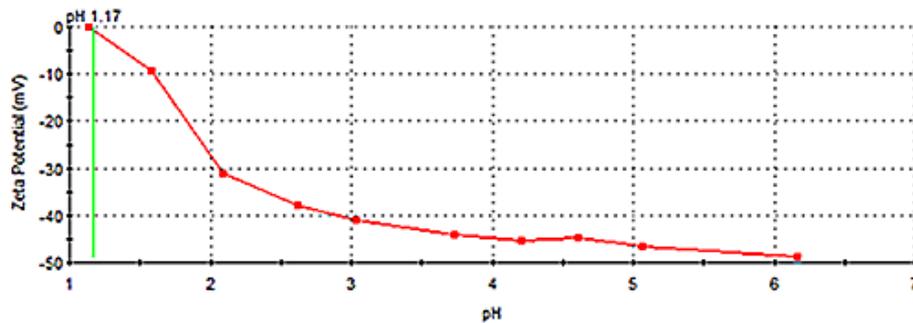

Figure 3: Varying the pH of a system can help to control the zeta potential to achieve thermodynamic stability

During these tests a compact sediment layer appeared in samples that were left to stand, even in those with a pH higher than 2, which had been shown to have a large negative zeta potential. Inputting system parameters into equation 1 reveals why. The ratio of gravitational forces to Brownian forces is around 45, which suggests that thermodynamic stabilization will have little effect on this system. Kinetic stabilization strategies are likely to be far more effective.

One way of inducing kinetic stability is to increase the viscosity of the continuous phase, potentially through the inclusion of viscosity modifying polymeric additives. An alternative, less intuitive, approach is to reduce the repulsive forces between particles so that they can approach one another and form a network structure. Such structure can give an ink a yield stress. Systems with a yield stress remain stationary and solid-like until the applied shear exceeds a certain value, and tend to have relatively high viscosity under low shear conditions.
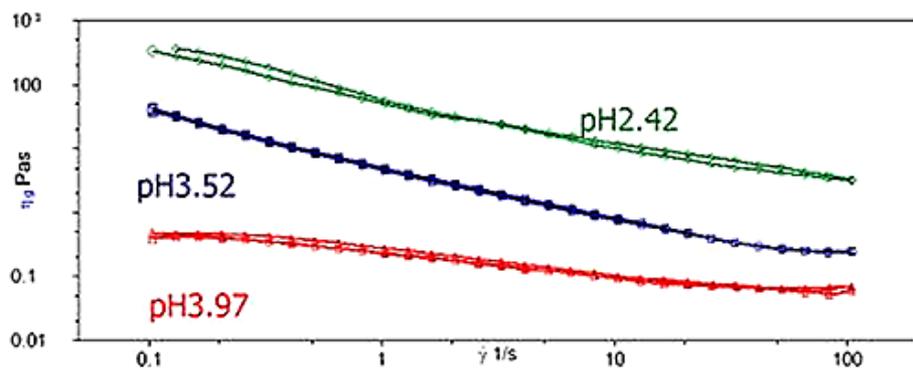

Figure 4: Flow curves for the suspension reveal that the system has a yield stress at a pH of 2.42 and 3.52 which has been induced by encouraging flocculation/aggregation

The data displayed in figure 3 suggest that this system will be more prone to aggregation as pH values become smaller. The effect of pH on suspension viscosity profiles is shown in figure 4, which displays shear viscosity as a function of shear rate

for concentrated dispersions. All rheological data were measured using Kinexus Pro and Gemini 2 rotational rheometers.

At a pH of 3.9, a zero shear viscosity plateau is observed, meaning at low shear rates, viscosity attains a constant value. This shape of curve is associated with a sample that is liquid-like under low shear conditions. In contrast, no zero shear viscosity plateaux are observed (in the measured range) when measurements are made at a pH or 2.42 and 3.52. Rather viscosity continues to rise as shear rate is reduced. This suggests that at very low shear these suspensions may become more solid- or gel-like.

In summary, for this system, increasing pH reduces zeta potential and encourages the particles to interact. This produces a network structure in the suspension that induces stability at low shear, in the form of an apparent yield stress.

Squaring the circle – rationalizing performance and stability targets

In the preceding discussions, performance and stability have been treated as discrete goals but in reality formulators must meet performance and stability targets, rather than one or the other. This calls for the reconciliation of conflicting formulation demands, most especially the preference for high viscosity at low shear rates, for stability, with the need for low viscosity at higher shear, for good performance. To be successful, inks must exhibit a rheological profile that meets both of these requirements. Engineering a formulation that has a suitable yield stress is one way to meet this goal, as outlined in the preceding case study but such a system must be shear thinning so as to break down any aggregates and give the correct viscosity at the point of printing.

Shear thinning

Materials that shear thin have a viscosity that is dependent on the magnitude of applied stress; viscosity decreases as shear stress and hence shear rate is increased. For inks, shear thinning must occur over several decades of applied shear since under storage conditions shear rates are very low, while at the print head applied shear is ultra-high. This creates a requirement for viscosity measurement across a wide range of conditions which can be met by applying rotational and microfluidic rheometry, together.

Case study 3: Combining rotational and microfluidic rheometry to generate complete flow curves for ink formulation1

The viscosities of the commercial ceramic inkjet inks characterized in case study 1 were measured across an applied shear rate of 0.5 s-1 to 100,000 s-1, using a Kinexus, rotational rheometer and an m-VROCi microfluidic rheometer. Figure 5 presents a single flow curve for each ink, generated from the combined measurements.
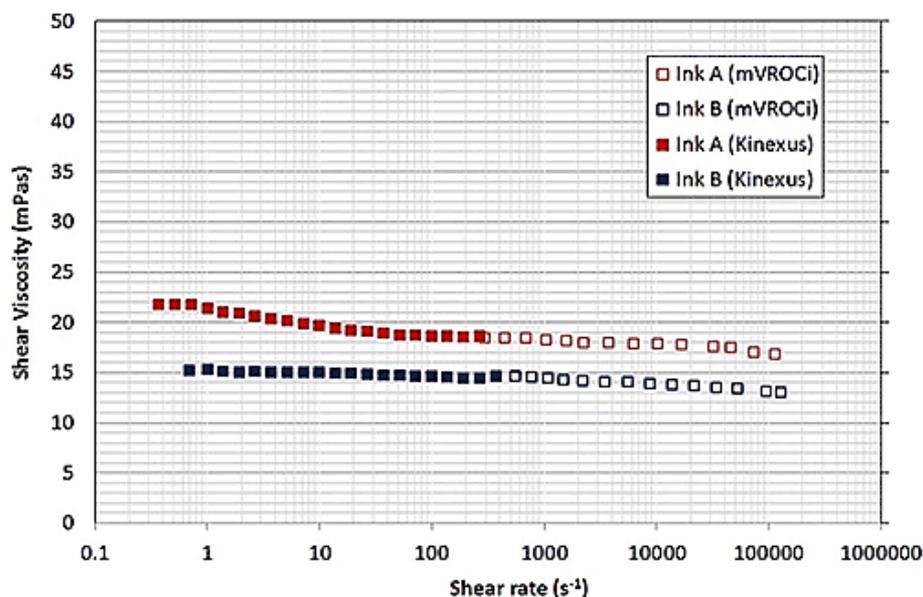
Figure 5: Flow curves can be produced over a very wide range of shear rates by combining rotational (solid squares) and microfluidic (outlined squares) rheometry

For both samples, viscosity remains relatively constant across the shear range investigated. However, there is some evidence of slight non-Newtonian shear thinning behavior, especially with Ink A. This formulation has a measured viscosity of approximately 22 mPa.s at $1s^{-1}$ compared with 17 mPa.s at 100,000 s^{-1}. This is a small but significant drop in viscosity that suggests that the ink has a certain degree of microstructure which breaks down as applied shear is increased.

Thixotropy

Ensuring that an ink transitions from one optimal viscosity to another is critical, but it is also important to consider the timescale over which such transition occurs. A formulation becomes less viscous because structure within it is breaking down. In many systems this structure rebuilds, over a finite timescale, once shear is reduced, increasing viscosity back to a higher value. Thixotropy is a measure of this rebuild time. Formulations that are more thixotropic take longer to rebuild than those that are less so.

The transition from low shear to high shear occurs as an ink passes through the ink head. But there is a reverse transition, back to low shear, once the ink hits the substrate. Thixotropy is important in both instances. Fast rebuild times ensure that the ink quickly attains high viscosity on the substrate, resisting dripping and maintaining high print definition.

Case study 4: Assessing thixotropy2

Figure 6 shows the results from tests designed to assess thixotropy in one of the weakly structured suspensions produced in case study 2. These tests were carried out using a Kinexus Pro and Gemini 2 rotational rheometer. At the start of the test a relatively low shear rate is applied. Shear is then increased and the resulting drop in viscosity is recorded. Returning to low shear allows the structure in the sample to rebuild and viscosity returns to a relatively high value.
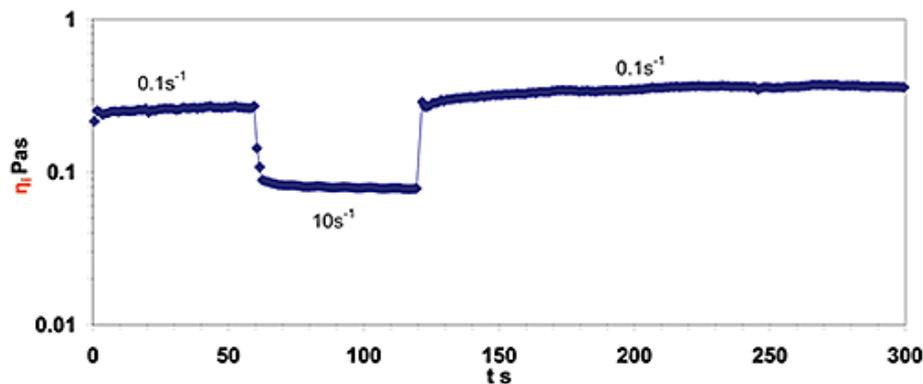
Figure 6: An ink that rapidly transitions between high and low viscosity helps to ensure optimal performance on the substrate

These results indicate that the structure in this sample rebuilds rapidly once shear is reduced, a positive feature for ink performance.

Controlling manufacture

Once a formulation has been optimized the focus shifts to consistent manufacture. Here there is a need for analytical techniques that can be applied to control the characteristics of individual components to meet the defined specifications. For polymeric additives, such as binders and dispersants, GPC/SEC is an important QC tool since molecular weight and molecular weight distribution define performance. For pigments, particle size impacts every aspect of ink performance and must be closely controlled during manufacture.

Dynamic light scattering (DLS) provides particle sizing in the range < 1 nm to 10 µm and is useful for inks containing relatively fine pigment particles. Laser diffraction is a complementary technique that spans the measurement range 0.01 µm to 3500 µm and can be used to measure pigments in either the wet or dry state. Both techniques are relatively easy to use, and are highly automated. Laser diffraction technology has matured to the point of established on-line implementation, which means that particle size measurements can be made in real-time, to control, for example, a milling process. The implementation of on-line DLS is less established but advancing rapidly.

The following case study shows the use of off-line laser diffraction measurements to monitor the milling of inkjet ink components.

Case study 5: Monitoring inkjet ink milling using laser diffraction particle size measurement3

The production of inkjet inks is a two-stage process that begins with dispersion of the pigment in a suitable mobile phase, via mechanical stirring. This 'pre-mix' is then wet milled to reduce particles to the required size and break-up any strongly bound agglomerates.

Figure 7 shows particle size distributions measured using a Mastersizer 2000 laser diffraction particle size analyzer, during the milling of an inkjet ink premix. The premix was known to contain large aggregates at the beginning of the mill run and these can be clearly seen in the particle size distribution data. Measuring particle size data as a function of time tracks the break up of these aggregates to the conclusion of the process. After 180 minutes a narrow particle size distribution is attained, centered on

a Dv50 (the particle size below which 50% of the particle population lies, on the basis of volume) of around 137 nm. At this particle size, the risk of jet-blockage and defect formation during printing is minimized.
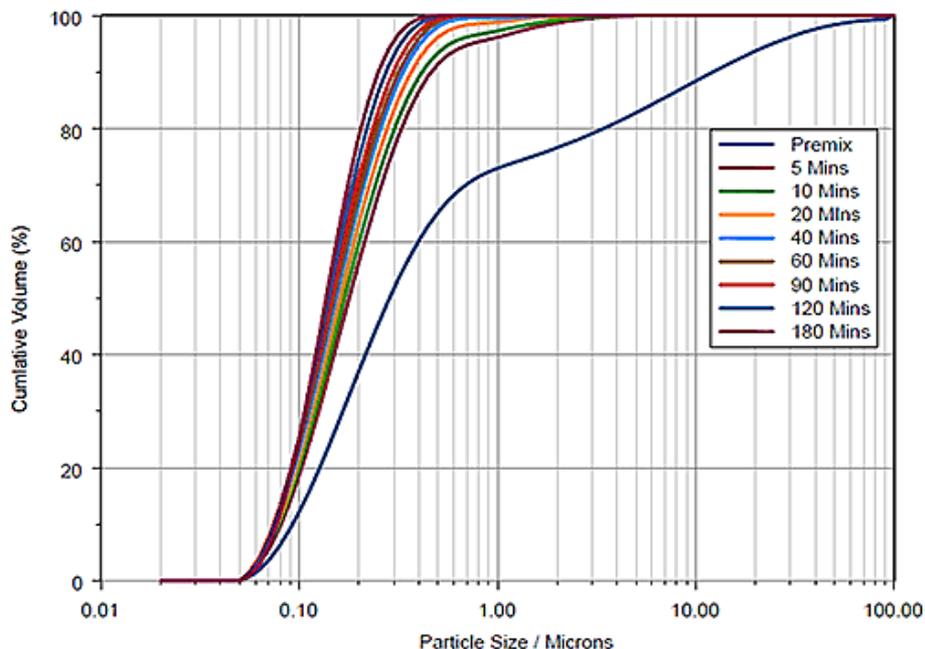

Figure 7: Particle size distributions measured for different milling times in the production of inkjet inks

Figure 8 shows the change in Dv10, Dv50 and Dv90 as a function of milling time. At the start of the process particle size is relatively large, as is distribution width, the range bounded by the Dv10 and the Dv90. Initially there is a rapid decrease in particle size, which corresponds to the break up of loosely agglomerated material. As milling progresses, the rate of particle size decrease becomes much slower as size reduction requires the break up of large, primary particles. This is evident by the fact that only the Dv90 changes significantly during the latter part of the milling process. The results clearly demonstrate the ability of laser diffraction to track the milling process to a successful conclusion. A constant, sufficiently fine particle size distribution is attained after around 100 minutes of milling.
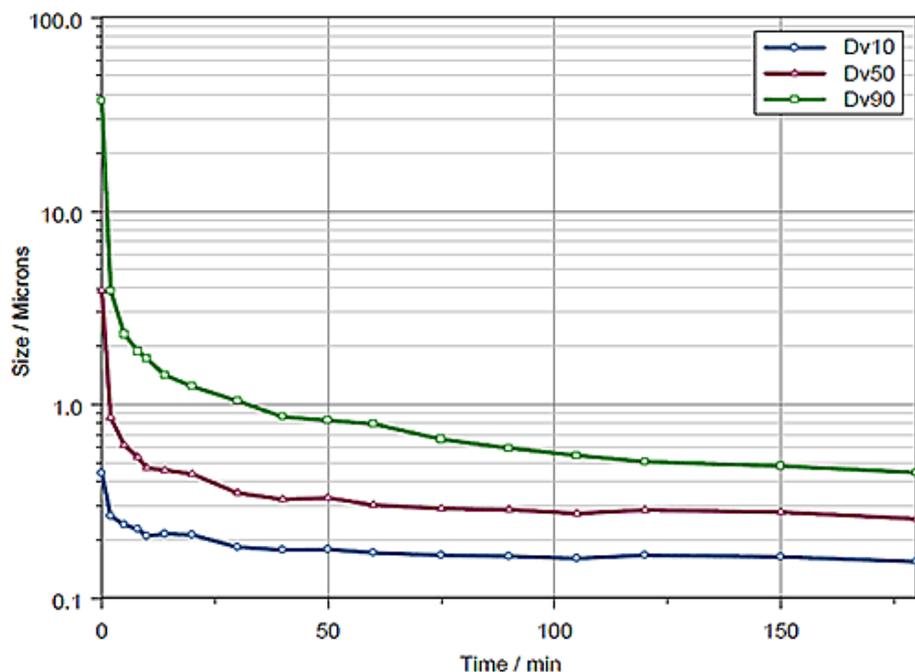
Figure 8: Laser diffraction particle size data show that milling of this inkjet ink is complete in around 100 minutes

In summary

The need for high performance inks that work well in modern and emerging printing technology makes ink formulation an exacting science. At one time formulation involved trial and error processes, whereas today an advanced knowledge-led approach provides greater product control and faster commercialization. Gathering the information required to support this approach relies on the application of comprehensive and effective analytical strategies. Particle sizing, rheological analysis, polymer characterization and measurements of zeta potential all have an important role to play.

For further reading on inks go to any of the references in this paper or view our on-demand webinars on this subject at Inkjet ink webinars

1. Optimizing Rheology for Ceramic Inkjet Inks – Malvern Instruments application note http://www.malvern.com/en/support/resource-center/application-notes/AN140408OptimizeRheologyCeramicInkjet.aspx
2. Suspension Stability – Malvern Instruments application note http://www.malvern.com/en/support/resource-center/application-notes/AN101130SuspensionStability.aspx
3. The measurement of ink jet inks using laser diffraction particle size analysis - Malvern Instruments application note http://www.malvern.com/en/support/resource-center/application-notes/AN101104MeasurementInkJetInksLaserDiffraction.aspx

Formulation Tool Box 1: Particle characterization

Laser diffraction

Laser diffraction is used across industry to measure the particle size of sprays, emulsions, suspensions and dry powders with particles in the size range 0.01 to 3500 µm. A sample passing through a collimated laser beam scatters light over a range of angles. Large particles generate a high scattering intensity at relatively narrow angles to the incident beam, while smaller particles produce a lower intensity signal but at much wider angles. Laser diffraction analyzers record the angular dependence of the intensity of light scattered light and from it determine a particle size distribution for the sample using the Mie theory of light.

Dynamic Light Scattering

Dynamic light scattering (DLS) systems determine particle size from measurements of the Brownian motion of particles within a suspension, using the Stokes-Einstein relationship. The measurement range of the technique is 0.3nm – 10.0 microns. The optical components needed for DLS particle sizing are closely similar to those required for measuring zeta potential using the technique of electrophoretic light scattering (ELS). An investment in a modern system may therefore deliver both particle size and zeta potential measurement, from a single instrument.

Multi-detector Gel Permeation Chromatography/Size Exclusion Chromatography (GPC/SEC)

GPC/SEC separates polymers and macromolecules in solution into discrete size fractions, on the basis of hydrodynamic radius. Each fraction is then analyzed using one or more detectors. A multi-detector array that includes a light scattering, refractive index and/or UV detector, and a viscometer maximizes the informational productivity of GPC/SEC. Such arrays provide absolute molecular weight and molecular weight distribution data, and structural information about such as chain linking and/or the degree of cross branching. These capabilities bring clarity in the development of the structure-function relationships needed for successful polymer use.

Formulation Toolbox 2: Rheological characterization

Rotational rheology

Rotational rheometers measure how a material responds to applied shear over an extremely broad range of shear rates, from less than 1 s-1 through to over 1000 s-1. Samples are loaded between two plates, or other similar geometry such as cone and plate or alternatively a cup and bob system. Measurements are then made by applying a torque to the top plate and recording the resulting strain or strain rate. Subjecting samples to programmed shear regimes enables the assessment of a range of useful rheological properties, such as viscosity, yield stress or shear thinning behaviour.

Microfluidic rheology

Microfluidic rheometers measure fluid viscosity at ultra-high shear rates, in excess of 100,000s-1. Sample is pushed through a narrow microfluidic channel and the resulting pressure drop is measured using embedded fixed point Micro Electro Mechanical System (MEMS) pressure sensors (MEMS). Sample viscosity values are generated by correlating pressure drop measurements with volumetric flow rate. The unique ability to access ultra-high shear rates allows formulators to directly simulate conditions that are not accessible with rotational rheology.

DLS Microrheology

Microrheology describes a range of techniques that involve extracting rheological data from measurements of the movement of colloidal tracer particles in a sample. Dynamic light scattering is one of the techniques that can be successfully used to track this motion. With DLS microrheology it is possible to probe the rheological behavior of very weakly structured samples, under very high frequencies and at very low applied stresses. In this way microrheology extends rheological characterization into areas not accessible with other techniques.

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