Optimization of UV Curable Inkjet Ink Properties for Jet Stability

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Abstract

UV-curable inkjet inks are rapidly gaining in popularity due to their decreased environmental impact (no VOCs or HAPs), fast cure speeds, and superior end user properties, such as weatherability, excellent film durability, and adhesion to a variety of substrates. In order to fully reap these benefits, however, the ink must have certain physical properties to allow optimum jetting performance to occur. This paper defines what is meant by "optimum jetting" and describes how to create a fluid capable of achieving it.

Introduction

Digital printing will be the main generator of growth for print over the next five years, according to Pira's *Ten-Year Forecast of Disruptive Technologies in Printing and Publishing*[1]*,* and inkjet will be one of the technologies that will dominate and drive this growth, predominantly in the form of piezoelectric drop-on-demand (DOD) printheads.[2] Digital inkjet is ideal for customizable short runs that allow the printer to change graphics at will, making it an attractive option for industrial applications. As the world of digital inkjet expands outside of the traditional realms of graphic arts into the industrial arena, more demands will be placed on the ink in terms of jet stability/reliability as well as cured film properties. Industrial applications will continually push formulators to produce inks that will adhere to more exotic substrates and withstand various stresses from the process line and the environment. However, formulators will be somewhat restricted by the physical properties required to operate reliably within the existing printhead technologies.

Required Properties for Optimal Performance

Optimum performance is achieved not only when nozzles jet reliably at high firing frequencies, but also when the desired jet velocity and drop mass are maintained. This is crucial because fluids that jet with an incorrect velocity or mass will produce very poor quality images, containing satellites, misplaced drops, and blank lines due to missing jets. Some parameters within the printhead itself may be altered to help control these factors. During the printing process, a voltage is applied to the piezoelectric crystals causing them to deflect inward and "squeeze out" a droplet of ink. Obviously, one variable that may be adjusted is this applied voltage. Increasing the drive voltage increases both the drop velocity and the drop mass, all other things being equal. Figure 1 demonstrates the effect of drive voltage on jet velocity for a UV-curable inkjet ink on an SE-128 printhead, manufactured by Spectra, with a pulse width of 5 µs. The increase in velocity is fairly linear with respect to voltage.
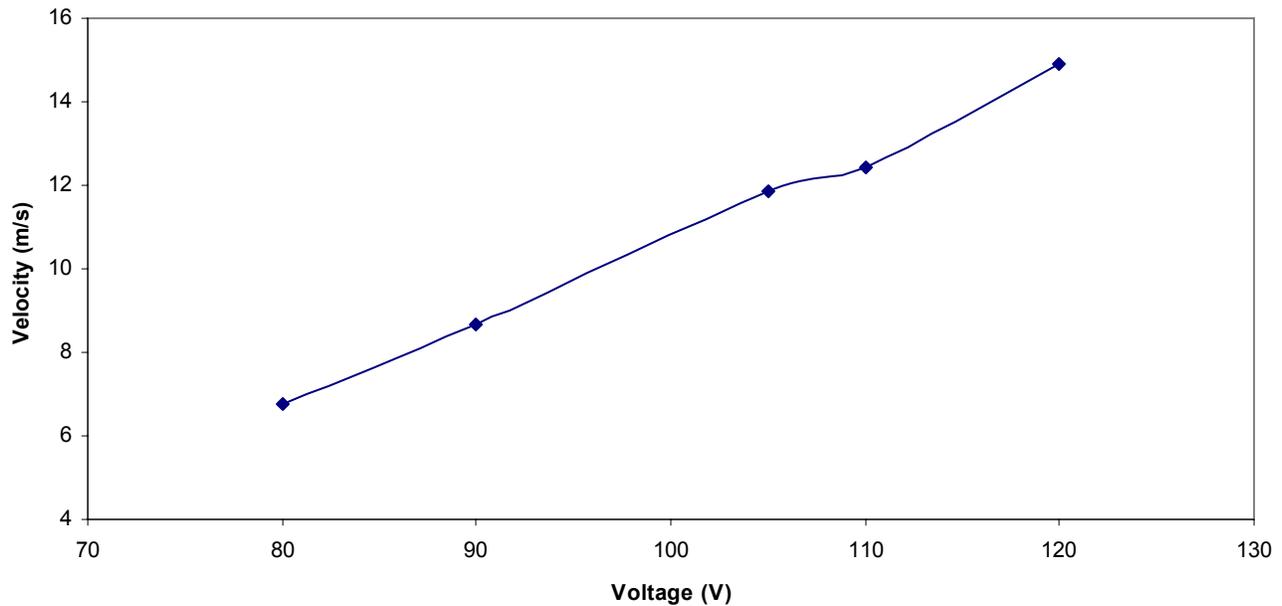
Typical Drive Voltage Response

Figure 1. Typical drive voltage response on an SE-128 printhead (pulse width: 5 µseconds, temperature 45°C, frequency 16 kHz).

Another parameter that may be altered is the pulse width. With each firing event the voltage causes the piezoelectric crystals to deflect inward, hold, and relax back causing a pressure wave. The amount of time that it takes for each step to occur may be altered to produce the best drop mass and velocity. Figure 2 displays the effect of increasing the pulse width while maintaining a drive voltage of 110V. Increasing the pulse width initially increased the drop mass, but at around 9 µs it stabilized. The velocity also initially increased with increasing pulse width, but it eventually began to decrease.
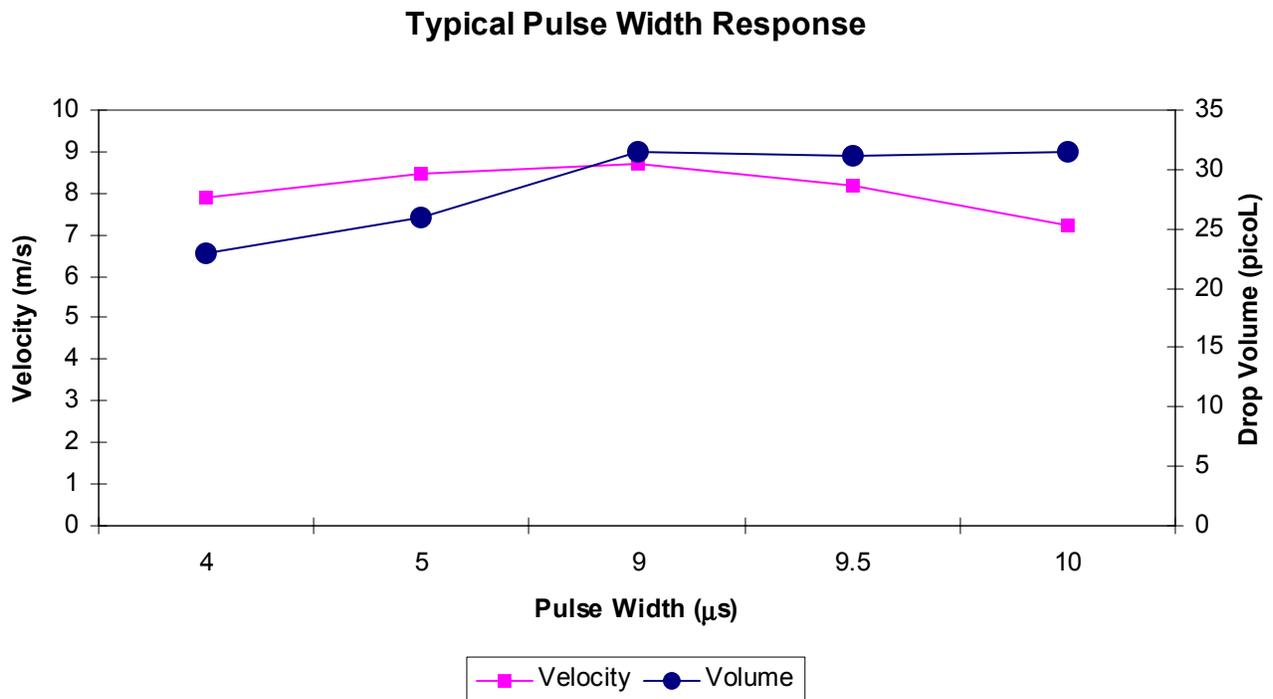
Typical Pulse Width Response

Figure 2. Typical pulse width response on an SE-128 printhead (voltage 110 V, temperature 45$^{\text{o}}$C, frequency 16 kHz).
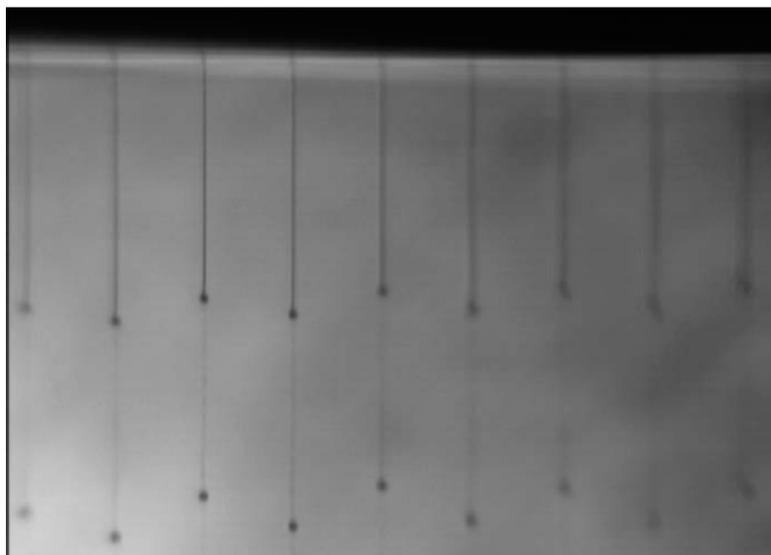

Figure 3. Image of properly jetting ink (SE-128 printhead, 16 kHz, 45$^{\text{o}}$C).

Figure 3 shows an example of ink that is properly emerging from an SE-128 printhead. This ink has the correct jet velocity of 8 m/s as well as the desired drop mass of 30 µL. In addition, it jetted

reliably with no lost nozzles for >10 minutes. This image was collected using a VisionJet OpticaX system made by Xennia in conjunction with Image Xpert software.

Adjusting the aforementioned parameters will help printers achieve the "sweet spots" required for optimum performance, but it cannot correct for fluids with incompatible physical properties. Piezoelectric DOD printheads are designed, in general, to work best with fluids whose viscosity is in the range of 10-16 cps at the jetting temperature. Many printheads have thermal controls that can heat up the internal ink reservoir to achieve the desired viscosity. However, this introduces the added requirement of thermal stability. Additionally, some printheads have the capability of degassing the fluid in the reservoir to remove dissolved air and promote greater jet stability and higher firing frequencies. This can be a detriment to the stability of a UV-curable system since most systems employ stabilizers that require oxygen to function properly. Thus, the design of some printheads necessitates thermal stability in an anaerobic environment.
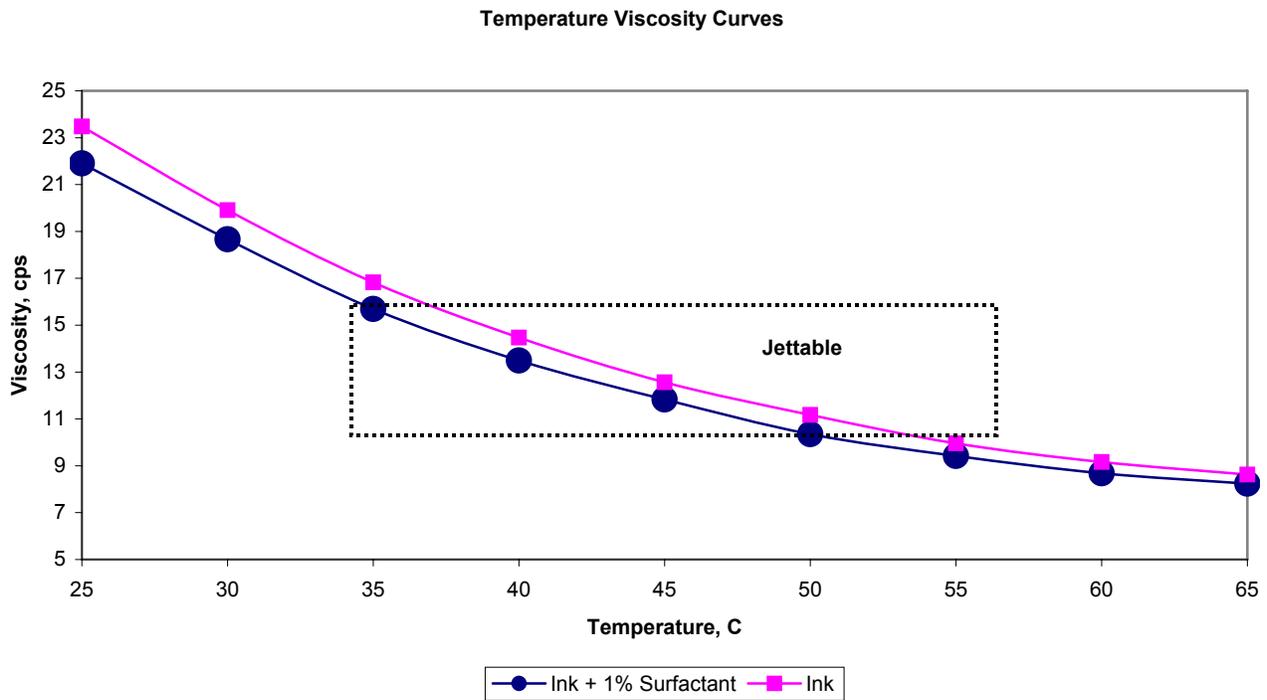
Temperature Viscosity Curves

Figure 4. Plot of Temperature versus Viscosity for two ink formulas (collected on a Haake RV-1 rheometer at a shear rate of 500 s^{-1}).

Another critical factor in how well an ink jets is how the viscosity of the ink relates to temperature. Figure 4 shows the effect of temperature on viscosity for two different ink formulas. The box shows the temperature range where the fluids have an acceptable viscosity to provide optimum jetting – however, it should be noted that various parameters within the printhead as well as properties of the fluid must also be optimized.

The activation energy of fluidization (AEF) may also play a role in the jetting performance of a fluid. High shear rheology on a CMYK ink set provided AEF values at high shear rates. This was

obtained from the viscosity flow curves (viscosity versus shear rate plots) at shear rates of 1 - 165000 sec^{-1} at 25, 40, 50º using an RS300 Haake rheometer equipped with a parallel 35mm plate accessory.

The relationship between the viscosity of an ink and temperature can be illustrated in the form of an Arrhenius equation ln η = ln A + (E/R)*(1/T), where η is viscosity, R is the gas constant (8.3), T is the temperature in degrees K, and E is the activation energy of fluidization (AEF) in kJ/mol. From the viscosity flow curves between 25 to 50°C at shear rates of 1 - 165K sec^{-1}, the AEF was calculated by plotting ln η versus 1 / temperature. The AEF was obtained by multiplying the slope by R. The corresponding viscosity values were extracted from the viscosity flow curves at various shear rates and used to obtain AEF values. The steeper the slope is the higher the AEF is, indicating more variation in the temperature viscosity curve (i.e. the viscosity is highly impacted by the temperature).

The desired magnitude of the AEF depends on the jetting situation of the ink. In terms of viscosity stability a lower activation energy is desirable so that the viscosity is maintained even if the temperature fluctuates or over a wider temperature operating window. However, it could also be argued that a steeper slope (and higher activation energy of fluidization) would result in the ink achieving a jettable viscosity at lower temperatures. Jetting at lower temperatures provides the advantages of reduced energy requirements and potentially improved ink stability in the print head. Either way, additional properties must be investigated to determine if the fluid will have excellent jetting stability. Table 1 shows the AEF for the ink set analyzed at shear rates up to 100K.

Color	AEF Range (kJ/mol)	Shear rates	Temp
Black	27.6	100K	27 to 50C
Cyan	29-22	100K	27 to 50C
Magenta	30-24	100K	27 to 50C
Yellow	30-27	100K	27 to 50C

Table 1. AEF Range for inkjet inks at high shear rates.

It is not only necessary that the fluid has the proper viscosity, it should also display Newtonian behavior under the extreme shear force produced during the printing process, where the shear can reach as high as 1,000,000 sec^{-1} in the nozzle. The viscosity must remain stable to maintain satisfactory jetting.
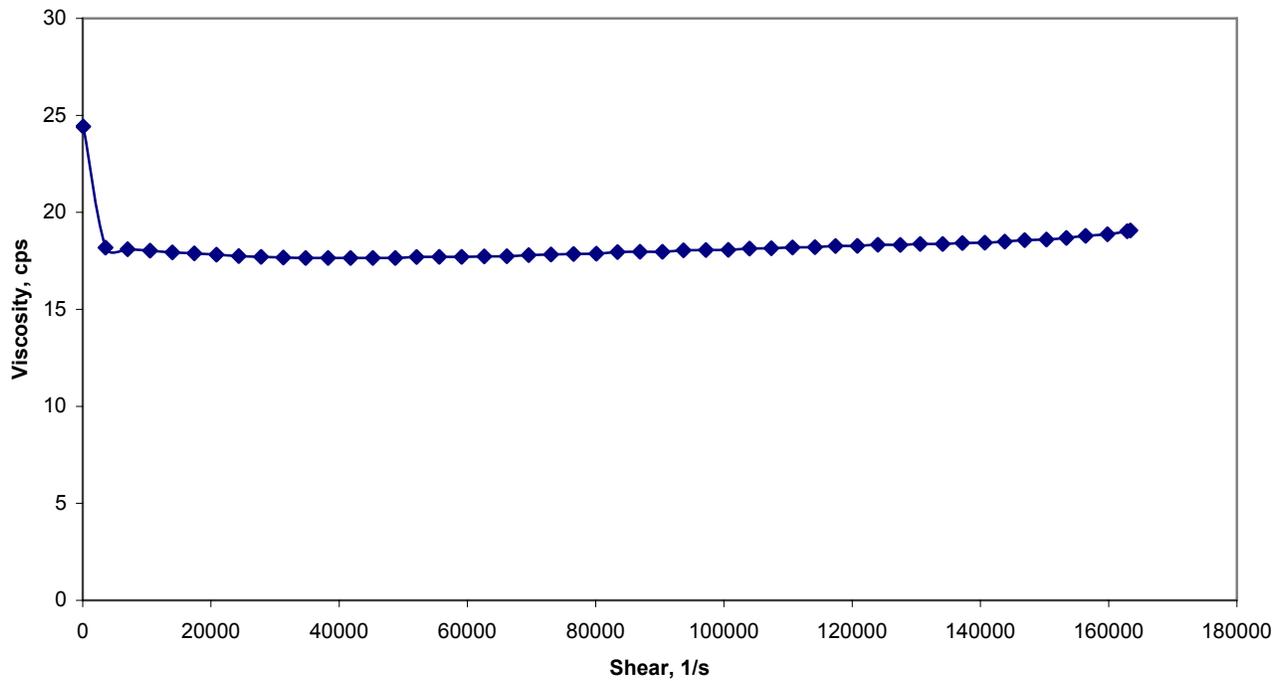
Figure 5. Rheology of a Newtonian inkjet ink.

Figure 5 shows an example of an inkjet ink that undergoes minimal viscosity changes under increasing shear, which is highly desirable for optimum printing. This data was collected on an Haake RS300 rheometer.
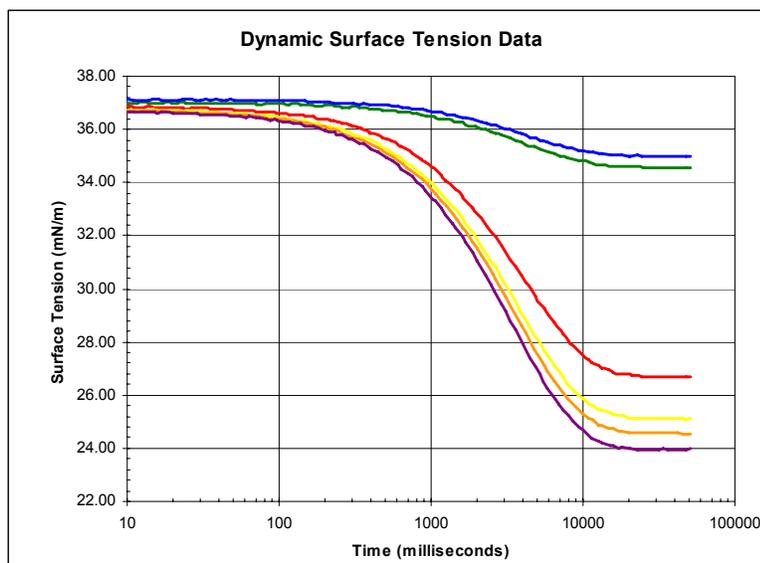

Figure 6. Dynamic Surface Tension Data for inks with varying amounts of surfactant.

Another important property to consider is surface tension. Typical printheads require static surface tensions in the range of mid 20's to low 30's (dynes/cm). Fluids with static surface tensions that are too low may experience excessive nozzle face-plate wet out, which will result in loss of jetting stability. Alternately, fluids with very high surface tensions will not wet out the interior of the printheads adequately, causing a non-homogenous outflow and loss of jetting due to starvation at the nozzle as the meniscus is unable to recover rapidly enough to fire the next drop. Very high surface tensions will also affect the ability of the ink to wet out low surface energy substrates, including many plastics.

It is also important to consider the dynamic surface tension in addition to the static surface tension since the firing frequencies experienced by the fluids are very rapid (up to 40 kHz on some printheads, or 40,000 pulses per second!) and result in a dynamic environment. It has been theorized that an ideal ink would posses a high dynamic surface tension (to promote rapid meniscus recovery at high firing frequencies) and a low static surface tension (to achieve good substrate wet out).[3] Figure 6 displays the dynamic surface tension profile for a series of inks with increasing amounts of surfactant (from 0ppm to 500ppm, increasing in amount from the top plot to the bottom). This data was collected on a Kruss BP2 tensiometer. The parameters may be viewed in Table 2.

Start at Bubble Rate: 5.0 milliseconds
Stop at Bubble Rate: 50,000 milliseconds
Acquistion: Logarithmic
Values: 30
Immersion Depth: 10 mm
Capillary Diameter: 0.282 mm

Table 2. Parameters for Kruss BP2 tensiometer.

The dynamic surface tension curve can be divided into three parts: the first equilibrium state represents values at low surface age (the far left of the graph in Figure 6), a rate limiting state (the middle of the graph in Figure 6), and the second equilibrium state represented by the static surface tension (the far right of the graph in Figure 6). Ideally, the equilibrium state **1** needs to be short followed by a quick drop upon which the ink should reach the static surface tension so that the ink may wet out the substrate upon impact. Figure 6 shows that all of the inks have comparable dynamic surface tensions at low surface ages (this surface age is not low enough to directly mimic the printhead experience; however, it allows for comparison). The surfactant used lowers the static surface tension and also slight shortens the rate limiting stage.

It is also important to ensure that the particle size of any pigment present is well below 1 micron so that it may flow unhindered through the narrow nozzles (typically 25-50 microns in diameter).[4] Figure 7 shows a typical particle size distribution collected on a ZetaSizer from Malvern that uses a dynamic light scattering to measure particle size and distribution. The average particle size for this ink is 164 nm, with a minimum of 91 and a maximum of 342 nm.
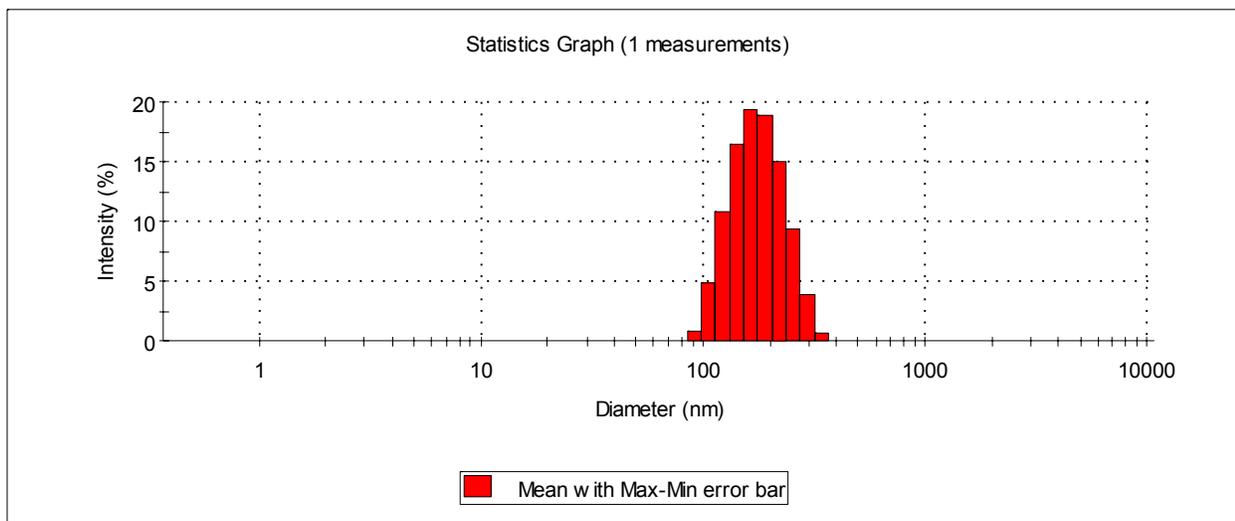
Figure 7. Particle size distribution of an inkjet ink.

Formulating an Optimum Inkjet Ink

There are several components common to most UV-curable inkjet ink formulations. The main properties of the fluid are determined by the choice of reactive monomers and oligomers, which will regulate properties such as flexibility, cross-link density (and therefore solvent resistance, hardness, and elongation), and adhesion, to name a few. However, as mentioned in the previous section, this choice is limited to raw materials with fairly low viscosities, which excludes many desirable oligomers. This presents quite a challenge to the typical ink formulator with experience in the screen or flexo printing fields that are used to working with more viscous fluids.

UV-curable formulations also must contain photoinitiators to promote the polymerization reactions. These are either of the Type 1 or Type II variety. Type I photoinitiators undergo a unimolecular bond cleavage upon irradiation to yield free radicals. Type II photoinitiators undergo a bimolecular reaction where the excited state of the photoinitiator interacts with a second molecule (a coinitiator) to generate free radicals. Both types are quite commonly used in inkjet ink formulations.

Inkjet inks also contain some type of a colorant, typically a pigment or dye (pigments are used most often due to their superior lightfastness). These are often a challenge to incorporate into the system for several reasons. The pigments must be ground to very small particle sizes to flow through the printhead nozzles, as previously mentioned. However, agglomeration and flocculation can occur more readily at these sizes, which can lead to sedimentation and instability. Also, the smaller particle sizes can have a detrimental effect on the weathering ability of the pigment as well as the color gamut and opacity, which are greatly influenced by particle size. Proper dispersing techniques and additives can help alleviate this to some degree.

Finally, various stabilizers and additives are often present to ensure viscosity stability at elevated temperatures and under anaerobic conditions. Surfactants and defoamers are also commonly used to provide the best properties.

Conclusions

Excellent printing in piezoelectric printheads requires that the proper drop mass and velocity be maintained in addition to achieving jet stability. This may be accomplished by formulating the fluid to result in the appropriate physical properties (viscosity, rheology, surface tension, and stability) and also by adjusting the printhead parameters to the correct settings for the particular fluid.

References

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