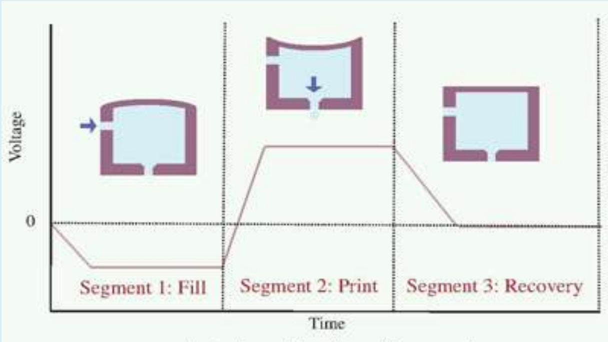
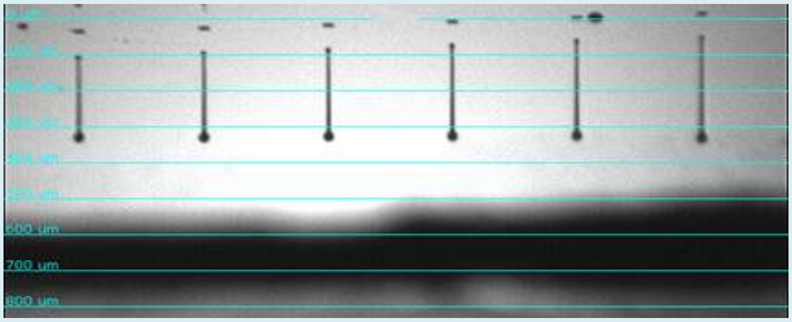
FUJIFILM Dimatix Ink Tutorial

The printer is suited to print fluids (inks) containing proteins, nucleic acids, nanoparticles, conductive polymers, etc. The inks are filled into a disposable cartridge that has 16 individually tunable, piezo-actuated nozzles. Cartridges are available to dispense 10-pL or 1-pL drops. Drops are printed by voltage-driven deformations of a membrane wall of a chamber behind each nozzle. The segments of this action make up a waveform (.CSV file) that is optimized for each ink as well as the intended print job. The waveform, in combination with settings for print height, nozzle firing voltage, meniscus volume, and cartridge temperature make up a cartridge jetting (.JST) file.



Actuation of the piezo-driven nozzle.

Camera view of ink drops jetting from a printhead.



<u>What Inks are Jettable?</u>

Fluids (inks) should have the following physical characteristics for jetting:

- Viscosity = 10-12 cPs at jetting temperature. As a comparison, the viscosity of water is 1cPs. The ideal viscosity enables an ink to be pulled into and pushed out of the nozzle chamber. Viscosity can be altered by heat or additives such as the humectants ethylene glycol or glycerol.
- Surface Tension = 32-42 dynes/cm at jetting temperature. This is high enough to hold the ink in the nozzle without dripping. Surface tension can be adjusted by surfactants. For organic solvents, try toluene or ethanol since there are successful waveforms.
- Low Volatility - Boiling point >100°C. Inks should not dry so quickly that they block the nozzles.
- Density - Specific gravity >1 is optimal.
- Degassing –Inks, especially aqueous ones should be degassed and allowed to rest in the cartridges for a couple of hours before printing. Air bubbles that form in nozzles will block jetting.
- Filtration – Filter particulate inks though a 0.2 μm filter. Optimal inks are composed of solutes that are completely dissolved in the solvent system. Particles > 0.2 microns (100X smaller than the opeinings for the 10-pL cartridges) will block nozzles.
- pH - pH between 4 - 9 is recommended.

How to adjust Ink Parameters

Viscosity: If the viscosity of the fluid is too high (> 30 cPs at room temperature), it's simple to adjust. Use the built-in print cartridge heater to raise the temperature of the ink as it prints. When you heat the ink, you may affect other performance characteristics.

If the ink's viscosity is too low**,** adjust the waveform or add low-volatility water-miscible humectants like ethylene glycol or glycerol (to aqueous inks) at 10-20%.

Some common reference points for viscosity
- Ethyl Alcohol ~.5 cps
- De-ionized water ~1 cps
- Olive Oil ~ 84 cps
- Glycerol ~1490 cps

The NBTC has a viscometer that requires a minimal 10-ml volume.

Surface Tension: If the surface tension is too high, the jetting mechanism can't be primed (all the air removed) and it won't jet. If the surface tension is too low, the ink will stream out of the nozzles or form unstable drops. The quantitative effects of surface tension are complex such that the surface tension of a mixture is **not** proportional to the molar fraction of each component in solution. Surface tension will be lowered slightly by an increase in temperature.

If the surface tension is too high, add a surfactant. For example, adding 1.34% of P103 (BASF, USA) decreases the surface tension of water from 69.5 dynes/cm to 33 dynes/cm at 20°C. Surfactants have a concentration threshold, after which they no longer alter the surface tension. So increasing the surfactant to 5% has no effect on surface tension; the measured value was still 33 dynes/cm.

If the surface tension is too low, use a different solvent system for the ink.

Some common reference points for surface tension
- Mercury ~ 464 dynes/cm
- De-ionized water ~ 73 dynes/cm
- Ethylene Glycol ~ 47 dynes/cm
- Isopropyl Alcohol ~ 22 dynes/cm
- Acetone ~ 24 dynes/cm
- Toluene ~ 28 dynes/cm

The NBTC has a goniometer to measure surface tension.

Dissolved Gases: Inks must not have dissolved air or other gases. Care should be taken when mixing the fluid to prevent air from being introduced into the solution. Typical degassing can be achieved by vacuum (-2 psi for 1 hour), sonicating water bath for 1 hour, or by centrifuging (fully miscible solutions only). Spinning should be used cautiously since it may cause the ink components to separate. Vacuum should not be used with volatile fluids since they may evaporate and alter the concentration. After filling the ink cartridge, the ink should rest for 2 – 24 hours for optimal jetting.

Particle Suspension: Colloidal suspensions or inks with particles >0.2 - 2 μm will clog the nozzles and partially dry, especially at the start of printing.

Colloidal fluids are common inks with a polymer or a metallic nanoparticle (one phase) that is distributed in a non-polymer, non-nanoparticulate phase (solvent phase). These fluids are stabilized by the addition of charged molecules such that the polymers do not aggregate. These inks should be filtered to remove any aggregated material s. Use syringe filters for aqueous or non-aqueous inks.

Volatility: It is better to have an ink with a high boiling point. The effect a fluid's volatility is that evaporation occurring at the nozzle can cause a build-up of molecules or particles around the nozzle and interfere with jetting. This is often referred to as a "skinning" effect where a hardened film develops over the nozzle, or "crusting' which is a build-up of particles around the nozzle.

Jetting a "New" Ink

A) Buy an ink that is specifically formulated for jetting in Dimatix printers. See the list on the tool page for suggestions. Commercial inks that have been printed at the CNF include:

- Nanoparticles (Silver CCI-300 by Cabot)
- PEDOT (Clevios™ P Jet HC by Heraeus)

B) Design an ink that falls within jetting parameters if none is available commercially.

- Know the particle concentration that is required for your application.
- Choose a solvent system that works with your solute/particle and fits viscosity and surface tension parameters.
- Determine the solute/particle solubility in the selected solvent system.

Typical solvent systems include:
- Aliphatic alcohols *(high boiling point better than low in all cases)*
- Aromatic hydrocarbons such as anisole, trimethylbenzene
- Aliphatic hydrocarbons such as hexane, dodecane
- Cellusolves
- Glycols, glycol ethers
- Lactate and similar esters
- Aliphatic and aromatic ketones including tetrahydrofuran *(this evaporates fast)*
- Polyethylene glycols, polypropylene glycols. NMP dries too slowly. *Solvent systems that evaporate slower than acetone and are less aggressive than NMP work best.*

C) Fine-tune the ink.

1. Measure the overall particle size distribution (The NBTC Zetasizer may be helpful).
2. Measure the viscosity (NBTC viscometer) and surface tension (NBTC goniometer). Add modifiers to adjust the viscosity first; then adjust the surface tension.
3. Degas and filter the ink, if necessary. Load a cassette, and (ideally) allow it to degas for 1 -24 hrs.
4. On the printer, set the cartridge angle to 0 degrees, and load a clean blotting pad. Cover the pad with a clean beta wipe. Load the cartridge.
5. Purge the cartridge in 1-4 s bursts until ink appears on the beta wipe. If repeated tries fail, observe the print head using the drop watcher camera. Remove the wetted beta wipe.
    - Fouling of the print head and blocked nozzles indicates that the ink is too far out of the jetting parameters.

- A clean print head and non-firing nozzles that are not pulsing slightly indicate the nozzles are blocked or dried out or that the ink is too far out of the jetting parameters.

6. Open the drop watcher window. Create a jetting file (.JST) with baseline settings: 16 mV nozzle voltages, room temperature nozzle head, 4-inch water meniscus. Embed an existing waveform (.CSV file) that most closely fits the solvent system.

7. Run a few cleaning cycles (Spit-Purge-Blot) to stabilize the ink in the nozzles.

8. Calibrate the nozzle view. The nozzles should be pulsing when not firing. Turn on all of the nozzles. If there's not good jetting, run more cleaning cycles. The 10-pL cartridges have nozzles with 21.5 μm openings, and they are easier to jet from than the 1-pL nozzles.

9. Optimize the jetting for single drops, no tails, traveling straight down. Adjust the speed to place the drops between 600-1000 μm in 100 microseconds. Ensure it is reproducible by running intermittent cleaning cycles (spit-purge-blot). If the jetting file needs to be adjusted, try adjustments in the following order. After all of the adjustments have been made, save the new jetting file, and reload it in the control panel.

    - First, increase the firing voltages to get drops to fire initially and to increase speed.

    - Increase the cartridge temperature for a similar effect (decreases viscosity).

    - Run cleaning cycles (Spit-Purge-Blot) frequently to prime or clean the nozzles.

    - Apply different waveforms or adjust the current one in the Waveform Editor. Try changing the duration of segment 1 and the duration and slew rate of segment 2. *See the waveform basics section for more information.*

10. Load a test pattern, specify the drop spacing, and change the cartridge angle to evaluate single printed drops. A drop spread pattern will print drops far enough apart (typically >100 μm) to measure the spread of a single drop. Calculate the desired final drop spacing to define the smallest attainable feature with closely-spaced drops. Apply the spacing, and change the cartridge angle.

11. Print a converging test pattern with closely-spaced drops to evaluate how the drops interact with each other and the substrate.

Effects of various cartridge settings

Frequency can be changed for different ink uses (and ink quality)

- High-performance inks – jet 20-40 kHz for discrete drops, smaller features, printed electronics.
- Mid-performance inks – jet ≥ 10 kHz for biosensor patterns.
- Low-performance inks – jet < 5 kHz for coatings.

Nozzle firing voltages control drop velocity. Increasing voltages increases velocity. Often there is a critical threshold for jetting. Voltages set too high will fragment the drops.

Waveform Basics

There are several standard waveforms provided for model inks or common solvents. These can be used as a starting point for your ink, or you can build a waveform from scratch. The typical waveform is divided into four segments, each with adjustable settings: duration, level and slew rate. The applied voltage (amplitude) is related to bending the fluid chamber membrane. The slew rate is controls how fast you are bending it, and the duration is how long it stays in that position. The applied voltage and the first two segments have the most impact on jetting. Try changing the duration and slew rate of the first segment as well as the duration of the second segment.

Thicker liquids with high viscosities need higher jetting voltages and steeper slew rates. In general higher viscosity fluids are less sensitive and you may get higher frequency performance with them. Low viscosity inks generally require lower voltages, slower slew rates and are more sensitive to pulse formation. They usually don't perform as well at high frequency.

High surface tension inhibits the fluid from separating, so the firing frequency may need to be lowered, but most importantly, the voltage may need to be increased and the slew rate should be steep.

The basic tactic to get to good drop velocity and good drop formation is to set the voltage to a relatively high level. Still make sure drop formation is somewhat ok, and whether the drops from different nozzles look similar. Then start adjusting the first two segments. The goal is to achieve higher drop velocities, without sacrificing drop quality. Ultimately, the voltage can be reduced, and the drop formation will become better. Finally, slight adjustments of segments 3 & 4 may improve drop formation.