Evaluating Novel Digital Methods for Jetting Large Particle High Viscosity Materials

Vince Cahill, Dene Taylor, and Patrice Giraud, The Solutions Group (USA)

Abstract

Refinements in established digital methods and the arrival of novel deposition and printing technologies are expanding the range of materials that can be effectively jetted, even without the imposition of heat. Also some novel methods have obviated the dimensional restrictions of nozzles for the passage of large particles and complex polymers. These advances enable the deposition of temperature sensitive and large cell biologic and highly viscous polymeric materials.

Inkjet printing has typically required the use of less than 50 mPas low viscosity fluids for jetting. Most inkjet print heads fire fluids in the 3 to 20 mPas range. Inkjet systems have been able to convert waxes and many highly viscous materials to the lower viscosity fluids necessary for jetting through the use of heaters and thermistors. As a rule of thumb, viscosity decreases by 2% for each degree Celsius rise for non-Newtonian fluids, including most inkjet inks.

Large particles in fluids can block inkjet nozzles. As a general rule, the longest dimension of the largest particles in a fluid should be no greater than one-fiftieth (0.02) the diameter of the nozzle in order to avoid log jamming of pigment particles at the nozzle and prevention of drop generation.

Analog printing methods typically deposit chemistry with viscosities that significantly exceed those possible with inkjet. Screen process printing uses chemistry ranging from about 500 to 50,000 mPas in viscosity. Flexography and gravure chemistry ranges from about 50 to 500 mPas. Offset lithography is very viscous ranging from 40,000 to 100,000 mPas. Higher viscosity than inkjet inks and larger pigment particle size characterize all of these analog ink chemistries. They are also significantly less expensive by volume as compared with inkjet inks. Analog print processes typically waste a higher proportion of their inks than inkjet production for print preparation and printer cleaning. When considering all factors including waste, however, inkjet materials and processes can still cost significantly more per print than analog processes.

Most monomeric and oligomeric materials, which form polymers, have viscosities exceeding 20 mPas at 25^{o}C. Monomers with very low viscosity (in the range of 2 mPas at 25^{o}C) are used to lower viscosity for inkjet application. A primary example of such is V-Pyrol/RC a.k.a. 2-Pyrrolidinone, 1-Ethenyl- (CAS: 88-12-0) reactive monomer, which accelerates UV curing rates as a reactive diluent imparting viscosity reduction when formulated with acrylate oligomers and enhanced adhesion to non-polar substrates[1]. It is listed as a Class 9 Transportation Hazard, an identified hazardous substance if contacted with skin or eyes or inhaled. Animal studies indicate that it can cause liver and nasal damage and is a possible cancer hazard. Recommended exposure limit for its vapor is 0.1 ppm. The widespread use of 2-Pyrrolidinone, 1-Ethenyl- and related and similarly hazardous viscosity reducers in UV curable inkjet inks raises worker and environmental safety concerns and prompts formulators to investigate alternative methods to either configure the inkjet process with less hazardous chemistry or to identify alternatives to inkjet that can utilize less hazardous chemistry.

The use of inkjet deposited free-radical UV cure photo polymer chemistry, which constitutes "the vast majority"[2] of inkjet UV cure materials, faces another challenge in that typical curing processes do not result in total polymerization and also potentially suffer from migration of its photo-initiators. Also, "The degree of polymerization has a dramatic effect on the mechanical properties of a polymer. As chain length increases, mechanical properties such as ductility, tensile strength, and hardness rise sharply and eventually level off. … However, in polymer melts, for example, the flow viscosity at a given temperature rises rapidly with increasing DP (Degree of Polymerization) for all polymers".[3]

This paper and subsequent presentation preliminarily examines and evaluates digital jetting alternatives to the low viscosity small particle deposition. It describes some of the available non-contact jetting deposition technologies and innovations and our presentation will evaluate their use and performance characteristics for applications, for which traditional inkjet technologies capabilities are inadequate to satisfy requirements. Systems we consider include:

- MicroFab[4] & MicroDrop[5] Type Inkjet
- Valve-Jets including Liquidyne P-Dot CT, Essemtec CDS-Jet-D32, Techcon Jet Tech Valve TS9200D, (also Techcon TS5400 Needle Valve, TS1200 Pinch Valve, TS 500& 7000 Rotary Valve Series, TS5322 & TS941 Spool Valve, and TS5520 & TS5540 Spray Valve), Nordson Asymtek DJ-9500 Jet and DJ-2100 DispenseJet, Fritz Gyger SMLD valve jets
- Nordson EFD PicoDot Jet [6, 7]
- Ultrasonic Droplet Generation
- Electrostatic Inkjet
- Optomec Aerosol Jet[8]
- TNO's Direct Metal & Pyrome Printers[9]
- Laser Induced Forward Transfer (LIFT)
- Photon-Jet, "Donor less LIFT"

The presentation will review and compare these technologies used for depositing high viscosity, large particle and cellular materials against inkjet's XAAR 1002 – GS12 print head[10], which has found use for demanding ceramic applications. Other factors to consider in evaluating deposition technology performance include the precision with which they place their drops and the minimum feature size they can deliver accurately. Here we present, due to space limitations, only some of the data on these deposition devices and our basic comparison device. We will provide an expanded and detailed version to Conference participant upon request.

Applications that would benefit from jetting deposition of materials with larger particles and greater viscosity than available from most TIJ, PIJ and CIJ technologies include:

- 3D builds of polymeric materials to equal or exceed the performance characteristics of injection molding
- Deposition of biologic materials and 3D builds of scaffolds and organs
- Printing of electronic and photonic circuitry
- Printing and building of electronic and photonic components and systems
- Deposition of LCD display filters, LED and OLED display components
- Printing of long-term outdoor durable signage, such as traffic and directional signs

A brief overview of available non-contact deposition technologies for higher viscosity and/or large sized particles that these applications can employ follows:

MicroFab, located in Plano, Texas, USA, offers print heads that are piezo actuated inkjet dispensers. Jetting head assemblies include: PH-47, 41, 46, 03, 43, 04a, 05a. Orifices are available in diameters ranging from 10 to 80µm. Using the rule of thumb for maximum particle size per nozzle diameter, particles fired through MicroFab's available range of nozzle sizes would be not greater than 0.2 µm for 10 µm diameter nozzles and 1.6 µm for 80 µm diameter nozzles.

MicroFab offers the ability to heat dispensing fluids to elevated temperatures with a number of its heads, thereby enabling the dispensing of highly viscous materials. The PH-05a and MJ-SF drop-on-demand print heads offer the ability to flow and fire fluids up to 240°C. The PH-05a is designed for dispensing oxygen and/or water sensitive materials. "Integrated heated inert gas injection is used to creating a local inert environment at the orifice of the dispensing device and around the drop in flight."[11] MicroFab lists 20 mPas as the maximum viscosity for fluids at the point of firing for most of it heads.

Applications using MicroFab dispensing systems include electronics, displays, medical diagnostics, biomedical and photonics. MicroFab print heads can produce a range of drop volumes from 5 to 500 pl.

Microdrop, located in Norderstedt, Germany, offers a number of inkjet type print head with similarities to MicroFab's heads with a number of notable exceptions. Its print heads include: MD-K-130, MD-K-140, MD-K-801, MJ-K-303, MJ-K-103, NJ-K-4..., and piezo actuated pipettes AD-K-901 and AD-K-501. The following table cites data about these heads.

Microdrop offers heads with some larger nozzle diameters than MicroFab. Its nozzles with 100µm diameters can fire 2µm particles and its 500µm nozzle diameters can fire 10µm particles.

Microdrop Dispensing Heads

	Actuator type	Viscosity (mPas)	Nozzle Diameters (µm)	Dispensed Unit Volume (pl)	Heat at Nozzle Tip (°C)	Heat at Hose and Storage Bin (°C)
MD-K-130	Piezo	0.4 to 100	50, 70, 100	90 to 380	25 to 100	NA
MD-K-140	Piezo	0.4 to 10000	70, 100	180 to 380	25 to 80	25 to 100
MD-K-801	Piezo	0.4 to 10000	70, 100	180 to 380	25 to 100	25 to 160
MJ-K-303	Solenoid	0.4 to 20	50 to 500	300000	-	-
MJ-K-103	Solenoid	0.4 to 50	50 to 500	50000	-	-
NJ- K-4…	Piezo valve	0.4 to 2000	70 to 200	8000 to 10000000	-	-
AD-K-901	Piezo pipette	0.4 to 20	30, 50, 70	20 to 180	-	-
AD-K-501	Piezo pipette	0.4 to 20	30, 50, 70	20 to 180	-	-

Liquidyne Dispensing Heads

	Actuator type	Viscosity (mPas)	Nozzle Diameters (µm)	Dispensed Unit Volume	Frequency (Hz)	Applications
P-Dot	Electropneumatic	50-200,000	300-500	10-200 nl	150	Oil, grease, glue, silicon, paint, flux, medical products
P-Dot AN	Electropneumatic	50-3000	300-500	30-200 nl	50	Anaerobic adhesives, acids, corrosives
P-Dot CT	Electropneumatic	50-200,000	300-500	3-200 nl	Up to 150	Oil, grease, glue, silicon, paint, flux, medical products
P-Dot HM	Electropneumatic	50-200,000	300-500	10-200 nl	Up to 150	Hot-melt adhesives 180°C
P-Jet	Electropneumatic	0.5-10000	-	=>10 nl	150	Oil, grease, glue, silicon, paint, flux, medical products
P-Jet AN	Electropneumatic	50-3000	-	30 nl	50	Anaerobic adhesives, acids, corrosives
P-Jet CT	Electropneumatic	0.5-10000	-	3 nl +	Up to 280	Oil, grease, glue, silicon, paint, flux, medical products
P-Jet HM	Electropneumatic	50-200,000	-	10-200 nl	150	Hot-melt adhesives 180°C

Liquidyne, located at Wheat Ridge, Colorado, USA, offers eight dispensing models: P-Dot, P-Dot AN. P-Dot CT, P-Dot HM, P-Jet, P-Jet AN, P-Jet CT, P-Jet HM.

Liquidyne 300µm nozzles can jet particles as large as 6µm in the longest dimension and its 500µm nozzles can jet particles up to 10 µm in length.

Essemtec, a Swiss company**,** manufactures the following dispensing valves: Solder Jet Valve, Jet Dispensing Valve, Time/Pressure Valve, Archimedean Screw Valve and Piezo Flow Valve. The Solder Jet Valve operates at a frequency of 22.2 Hz. It can deposit viscous solder pastes including types T4, T5, T6 and T7. It uses a pneumatic actuator. The Jet Dispensing Valve shots with each actuation volumes from 2 to 10,000 nl at frequencies up to 1,000 Hertz. It uses a piezo actuator. The Time/Pressure Valve is, as the Company describes, "time/pressure controlled dispensing system. The medium is fed by a pressure pulse of programmable time."[12] It has no moving parts and reportedly does not require maintenance. Its applications include depositing glue dots, solder paste, conductive glue, dam & fill, glob top/blob top functions. The Archimedean Screw Valve is a high precision valve using the same application materials as the Time/Pressure Valve. The Piezo Flow Valve is a sliding valve with piezoelectric actuator. The Company developed this valve for silver-filled epoxies and solder pastes. The valve's sealing mechanism enables the dispensing of small dots of thick fluids. It deposits materials as small as 10nl and can meter fluids at frequencies up to 10 Hertz. It features integrated valve heating.

EFD PicoDot Jet Valves come in three types, LV, MV, HV. EFD PicoDot is a Nordson Company headquartered Dunstable, Bedfordshire, UK. All EPD PicoDot Jet Valves use piezoelectric actuation to generate drops as small as 2nl depending on the fluid jetted. They are available with the following nozzle sizes: 0.15 mm, 0.2 mm, 0.3 mm, and 0.4 mm. The standard diameters for the LV are 0.15 mm and 0.3 mm, for the MV is 0.3 mm, and for the HV 0.4 mm. EFD reports that the valve can operate for short periods at a maximum frequency of 1000 Hz, but are limited to a maximum frequency of 150 Hz for continuous operation. One can order MV and HV Jet Valves with heated fluid paths operating at temperatures up to 100°C. Recommended fluids for use in the LV are octane and organic solutions; in the MV and HV include lubricants (oils and greases), varnishes and colors, hydrous solutions, organic solvents, adhesives and adhesive components, liquid polymers and polymeric solutions and many other fluids.[13] Filler materials for these fluids used in MV and HV models may include quartz powder, iron oxide, aluminum oxide, aluminum nitrite, nickel, silver, glass and polymeric particles up to a fill ratio of maximum 50 percent. Maximum recommended particle size is 50 **µ**m. PicoDot Jet viscosity ranges for each type are:

LV: Approx. 50 – 1,000 mPas (thixotropic)
MV: Approx. 50 – 200,000 mPas (thixotropic)
HV: Approx. 1,000 – 500,000 mPas (thixotropic)

Nordson, headquartered at Westlake, Ohio, USA, also offers other dispensing systems under its main corporate brand. These include Nordson Asymtek DJ-9500 Jet and DJ-2100 DispenseJet.

Fritz Gyger AG, located at Gwatt (Thun), Switzerland, specializes in developing and manufacturing, “precision fluid handling devices, with a focus on micro solenoid valves and pumping systems for HPLC (*High Performance Liquid Chromatography*) analysis.”[14] Its SMLD (Sub Micro Liquid Dispenser) can deposit water, reagents, oils, UV-adhesives, and various pastes. It dispenses volumes per actuation less than 10nl. It can deposit volumes at a maximum frequency of 4kHz.

Techcon Systems, headquartered at Garden Grove, California, USA, is part of OK International. It offers a range of valve type dispensers including Techcon Jet Tech Valve TS9000, TS9200D, TS5400 Needle Valve, TS1200 Pinch Valve, TS 500& 7000 Rotary Valve Series, TS5322 & TS941 Spool Valve, and TS5520 and TS5540 Spray Valve. Our cited example, Jet Tech Valve TS9200D, deposits a minimum of 10nl per actuation at frequencies up to 300 Hz. It can flow viscosities up to 400,000 mPas. The Company offers the series with a choice of two diaphragms, EPDM (ethylene propylene diene monomer) and silicone, and three nozzle diameters, 125µm, 150µm and 200µm.

Optomec, headquartered in Albuquerque, New Mexico, USA, produced its Aerosol Jet[15] in six model series: 200 Series, 300 Series, Marathon II Wide Feature Module, Micro Dispense 300/470 Systems, Mid Print Engine, and 3MM Wide Feature Print Head. The Aerosol Jet atomizes liquids with standard ultrasonic or optional pneumatic atomizers. The ultrasonic atomizer requires the use of fluids that have a viscosity less than 7mPas at room temperature. It can produce drops with diameters ranging from 1 to 5 µm and print features ranging from 10 to 200µm. The pneumatic atomizer can use fluids with viscosities in the range from 1 to 1000 mPas using its inline heater and stirrer. Aerosol Jet uses a columnar sheath of nitrogen gas to focus the aerosol spray. The virtually chemically inert gas sheath also isolates deposit materials that are vulnerable to exposure to oxygen and moisture during the deposition process. Optomec Aerosol Jet based systems are used for printing silver and other conductors, EMI shielding, and depositing biologic materials. Aerosol Jet prints circuits, antennae with nanoparticle silver for mobile devices, and 3D printed electronics for use as part of 3D Additive Manufacturing builds.

TNO is located at Eindhoven, the Netherlands. It has developed two methods for printing and potentially building objects with inkjet printed metal, TNO's Direct Metal and Pyrome Printers[16]. TNO's MetalPrint/GoldPrint is, “able to inkjet metals with melting temperatures up to 1400 °C with 50 micron droplets, the technology is able to manufacture highly conductive tracks.” “Contrary to the Metalprint/Goldprint technology, where molten material is printed, the pyrome process uses an inkjet technology where a precursor is printed. After pyrolysis and melting of the metal, a droplet is generated of approximately 5 micron. This may be used to prints highly conductive tracks with a very narrow width.”[17]

Laser Induced Forward Transfer (LIFT) method came to light in a 1986 paper form J. Bohandy et al[18]. LIFT has been proven to be a feasible means for printing electronics and electronic circuits.[19] LIFT focuses energy through an optically transparent material carrier, such as a clear polyester film, on to the material the film is carrying. The laser energy forms a bubble that moves through the material and generates a drop of the material, which then travels to the intended receiver substrate. LIFT can print metals, polymers and highly viscous substances for electronics, micro-power systems such as super capacitors, micro-batteries and dye-sensitized solar cells. As a nozzle-less technology, LIFT does not suffer the limitations nozzles present, but its transfer material carrier is not readily rechargeable and can result in considerable material waste.

Photon-Jet is located in Israel. The Company describes its technology as “Donor less LIFT”. It does not employ nozzles, but, unlike LIFT, its process does not employ a coated static carrier and can recharge its material flow without interrupting the deposition process. Its developers have proven its feasibility and have constructed a functioning prototype. The Company has demonstrated it printing thixotropic materials in the 30,000 mPas range. It reports operating at 1,000 Hz.

We review Ultrasonic Droplet Generation and Electrostatic Inkjet in our expanded paper available to Conference participants upon request.

Our presentation includes greater detail on the listed technologies and compares them to the Xaar 1002 ink jet print head capabilities. We will demonstrate our evaluation method measuring the capabilities of the above mentioned deposition systems for use in bio and printed electronics applications.

We will also make available a more comprehensive evaluation including accuracy and cost-effectiveness parameters.

References

1 http://www.ashland.com/products/v-pyrol-rc-reactive-monomer
2 http://h20195.www2.hp.com/v2/GetPDF.aspx/4AA3-6972ENUC.pdf
3 http://plc.cwru.edu/tutorial/enhanced/files/polymers/synth/Synth.htm
4 www.microfab.com/index.php?option=com_content&view=article&id=109&Itemid=157
5 Accurate High-Speed Liquid Handling of Very Small Biological Samples, A. Schober, R. Günther[1], A. Schwienhorst, M. Döring[2] and B. F. Lindemann, Max-Planck-Institut für Biophysikalische Chemie, [1]LURE, France, [2]Microdrop GmbH
6 High Viscosity Jetting System For 3D Reactive Inkjet Printing, H. Yang, Y. He, C. Tuck, R. Wildman, I. Ashcroft, P. Dickens, R. Hague, Additive Manufacturing and 3D printing group, University of Nottingham, NG7 2RD, UK
7 www.efd-inc.com/NR/rdonlyres/8E79F1BF-F807-45BE-B16F-4FB2C941F9AD/0/PicoDotJetValveManual7..
8 www.optomec.com/.../Optomec_Organic_and_PrintedElectronics.pdf
9 www.tno.nl/content.cfm?context=thema&content=prop_case&laag1=892&laag2=906&laag3=124&item_id=624
10www.xaar.com/
11 www.microfab.com/index.php?option=com_content&view=article&id=91&Itemid=152
12 www.essemtec.ch/products.aspx/High-Speed-Jetting/Dispensing-Valves/?n=02.04.05
13 www.efd-inc.com/NR/rdonlyres/8E79F1BF-F807-45BE-B16F-4FB2C941F9AD/0/PicoDotJetValveManual7..
14 www.fgyger.ch/index.php?article_id=3&clang=1
15 www.optomec.com/.../Optomec_Organic_and_PrintedElectronics.pdf
16 www.tno.nl/content.cfm?context=thema&content=prop_case&laag1=892&laag2=906&laag3=124&item_id=624
17 ibid
18 Bohandy, J., Kim, B., and Adrian, F. (1986). Metal deposition from a supported metal using an excimer laser., J. Appl. Phys., 60(1): 1538-1539
19 www.princeton.edu/~spikelab/papers/book01.pdf

