

Color Inkjet Printing and Laser Marking for Plastics

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Digital printing technologies, such as inkjet and laser on plastics, offer monumental advantages for manufacturers compared to traditional analog methods, e.g., pad printing, hot stamping, screen printing, etc. Digital printing allows for full product customization, unique alphanumeric part identification, product security, serialization, barcode/2D codes, logos, graphics and more. These capabilities are essential for today's digital interactive universe. A tangential benefit is the capability to print assembled products at the end of manufacturing operations, which offers cost savings and better inventory control management. This article examines two types of digital printing/marking process methods: full color piezoelectric drop-on-demand inkjet printing and beam-steered fiber laser marking. Piezoelectric drop-on-demand (DOD) inkjet and fiber laser are modern technologies that offer countless advantages for product (and mass) customization.

Piezoelectric DOD inkjet printing and beam-steered fiber laser marking are both digital, noncontact processes. Many manufacturers already recognize the value of offering both technologies to meet custom printing requirements on diverse polymeric substrates. One cannot accurately characterize either technology as better or worse than the other because of the diversity of application requirements. The decision as to which process is preferred (inkjet or laser) for any given application may appear easy. For example, if one or more (custom) colors are needed for printing on white glass-filled nylon, select inkjet. Or, if indelible jet-black contrast on white nylon is needed, select laser marking. Now then, in reality inkjet inks do not adhere readily to nylon (or most low-surface-energy polymers) without specialized ink and pretreatment. Laser enhancing additives are needed to achieve black contrast on white nylon (and many other light-colored polymers).

Robust marking/printing solutions require precise engineering of ink/laser chemistries, polymeric surface science, process design and equipment. Too often, companies choose to purchase "off-the-shelf" generic equipment that fails to produce the

required results. As a result, the "total solutions" aspects of inkjet printing and laser marking technologies as a guide for systems procurement and process optimization become very important.

Piezoelectric "drop-on-demand" UV LED inkjet technology

Inkjet is noncontact, computer-to-print process where droplets of ink are propelled toward a substrate in a regular x-y pixel pattern derived from a digital file. Major system components consist of a printhead assembly, printhead drive electronic controllers, UV inks, curing irradiator and motion-controlled parts handling.

The basic component is the printhead (Figure 2). It has a supply of ink and a multiplicity of small volume ink chambers with circular nozzles from which the droplets are ejected. The nozzles are arranged linearly orthogonal to the direction of movement. Each head may hold from one to five rows of nozzles – each row having 128, 256, 512 or 768 nozzles. Each color has its own ink supply and printhead(s). In the contemplated printer, the printheads scan back and forth (x direction) with the items stepping (y direction) with each pass. Steps and nozzle spacing are matched (Figure 1). With more frequent firing and smaller steps, equivalent pixel spacings can be much closer than the nozzle spacing. For example, a 300 dpi head can print at 300x300, 300x600 and so on to as high as 2400x2400 dots per inch. Normal printing is

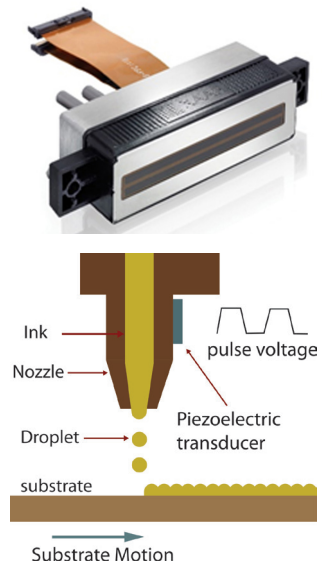


Figure 2. Top to bottom, a piezoelectric "drop-on-demand" printhead and a printhead schematic.



Figure 1. Piezoelectric "drop-on-demand" UV LED inkjet printing on contoured writing pen

binary – at each position there is either a droplet or no droplet. High-end technology offers grayscale, which means ink volume for each dot can be deliberately varied.

Piezoelectric DOD printhead design

In the piezoelectric drop-on-demand inkjet, deformation of the piezoceramic material causes the ink volume change in the pressure chamber to generate a pressure wave that propagates toward the nozzle. This acoustic pressure wave overcomes the viscous pressure loss in a small nozzle and the surface tension force from ink meniscus so that an ink drop can begin to form at the nozzle. When the drop is formed, the pressure must be sufficient to expel the droplet toward a recording media (Figure 2). Viscosity between 10 and 20 mPa-s ensures the fluid moves rapidly. In general, the deformation of a piezoelectric driver is on the submicron scale. To have large enough ink volume displacement for drop formation, the physical size of a piezoelectric driver is often much larger than the ink orifice. Each pixel on the substrate is either covered with ink or not – a binary choice. Grayscale inkjet differs in that the print head can eject multiple small drops extremely rapidly – fast enough for them to print as a single dot. Advanced printheads have eight levels – zero to seven droplets. The result is significantly higher apparent resolution using the same native resolution as binary.

UV-curable inks

Ultraviolet (UV)-curable inks and coatings are preferred for industrial and outdoor applications because, when cured, they are tough and durable. They have a full color gamut and, with fine resolution, yield outstanding print quality. UV-curable formulations include photoinitiators, monomers, oligomers, colorants and additives. The monomers and oligomers are about 85 percent of the formulation, colorants may be 10 percent, photoinitiators about five percent and surfactants and stabilizers one to two percent.

UV exposure induces the photoinitiator bonds to fracture, giving two free radical entities. These begin a chain reaction through the monomers and oligomers, resulting in extensive but not complete cross-linking (curing) of the resins. The reaction is exothermic, and UV sources also emit heat. The temperature rise can help with both adhesion and degree of cure, which contributes to the abrasion, mar and scratch resistance of the cured fluids¹. A challenge with UV cure ink formulating is meeting the requirement for very low viscosity while also forming useful polymers. However, by heating the ink, print heads and ink delivery system to about 50°C viscosities useful for piezoelectric printheads are obtained, albeit with significantly higher cost than for room temperature systems.

Ink – plastic substrate compatibility

All ink printing processes require the liquid ink chemistry (UV, solids, thermal, etc.) to be compatible with the plastic substrate to achieve proper surface wetting. UV inks are typically lower in viscosity (approximately 25 dynes/cm) than

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pad or screen printing inks. A major contributing factor to ink-substrate compatibility is that many plastics are chemically inert, nonporous surfaces with low surface energy. Surface pretreatments on today's high-performance engineering resins will solve most ink adhesion. As a rule, acceptable ink adhesion is achieved when the surface energy of a substrate (measured in dynes/cm) is approximately 10 dynes/cm greater than the surface tension of the liquid. In this situation, the liquid is said to “wet out” or adhere to the surface.

Surface tension, which is a measurement of surface energy, is the property (due to molecular forces) by which all liquids, through contraction of the surface, tend to bring the contained volume onto a shape having the least surface area. Therefore, the higher the surface energy of the solid substrate relative to the surface tension of a liquid, the better will be its “wettability” and the smaller the contact angle. (For detailed information pertaining to surface pretreatments, see “Plasma Surface Pretreatment of Polymers for Improved Adhesion” on pages 44-51 of the April/May 2018 issue of *Plastics Decorating*.)

Surface pretreatments are used to increase surface energy and improve the wetting and adhesive properties of polymer materials. A variety of gas-phase surface oxidation pretreatment processes are used in the industry, including low-pressure, cold-gas plasma (Microwave/RF), electrical (corona discharge), flame plasma and low-temperature, voltage-free atmospheric plasma. Each method is application-specific and possesses unique advantages and potential limitations. Each of these processes is characterized by its ability to generate “gas plasma” – an extremely reactive gas consisting of free electrons, positive ions and other chemical species. In the science of physics, the mechanisms in which these plasmas are generated are different but their effects on surface wettability are similar. Chemical primers can sometimes be used instead of gas plasma processes.

UV LED curing

Until recently all cure was initiated with mercury discharge lamps. Mercury has a very broad emission spectrum with more energy emitted as heat than as UV. Low efficiency is one

drawback. Another is heating of the ink and substrate, preventing the use of UV cure for a great number of applications. (Mercury lamps produce ozone at levels dangerous to health, a further complication.) UV LED lamps (Figure 3) are now displacing mercury bulbs. UV LED curing uses light-emitting diodes that emit a narrow band of UV, delivering a peak of UV energy – typically centered on 400nm – so most energy is useful for photoinitiation. A modest amount is visible, but very little is infrared (IR).



Figure 3. UV LED curing

Another advantage is that they are almost instant on-off, reducing downtime as well as energy and material waste, as when mercury lamps are coming to full power. UV LED curing has further advantages over traditional mercury (Hg) vapor lamps. Small profile semiconductor devices are designed to last beyond 20,000 hours operating time, about 10 times longer than UV lamps. Output is extremely consistent for long periods. UV LED emits pure UV without IR, making it process friendly to heat-sensitive plastic substrates. Without the very short wavelength light, much less ozone is generated.

Inkjet equipment systems

The inkjet printing process departs from conventional ink printing techniques in that engineering is required in many distinct disciplines for turnkey systems integration. In contrast, manufacturers of pad and screen printing equipment almost always can provide turnkey systems including inks, printing consumables, curing equipment, automation and chemical clean-up equipment. Inkjet system components consist of the printhead, drive electronics, inks, parts-handling and motion control hardware, and curing irradiator. Further, digital information needs to be communicated to the printhead through hardware/software file protocol including the main controller drive software. No single manufacturer provides all of the mentioned components for every custom application. A high degree of engineering knowledge of all the inkjet components and piece-part compatibility is critical to achieving robust manufacturing operations.

Ytterbium fiber laser marking technology

Beam-steered laser markers utilize mirrors that are mounted on high-speed, computer-controlled galvanometers to direct the laser beam across the surface to be marked, much like writing with pencil and paper. Each galvanometer, one on the Y-axis and one on the X-axis, provides the beam motion within the marking field. A flat-field lens assembly focuses the laser light to achieve high-power density on the substrate surface. Figure 4 shows an optical beam delivery system using computer-controlled galvanometers.

Polymeric laser marking reaction mechanisms

Most polymers do not possess NIR absorption properties without chemical additives, thus are difficult or impossible to laser mark. Novel chemical additives can produce jet-black, light-colored and custom color contrast, using both on-the-fly and secondary operations. Polymer clarity, spectral transmission and base physical properties are not affected.

Polymers that can be marked by lasers are those that absorb laser light and convert it from light energy to thermal energy. Experts utilize additives, fillers, pigments and dyes to enhance the absorption of laser energy for localized color changes. Contrary to popular belief, a single laser additive that solves all marking problems does not exist. Vastly different formulation chemistries, laser type (fiber, YAG, vanadate) and laser optics/setup parameters are used depending upon the desired marking contrast and functionality.

Near-infrared laser additives improve the degree of contrast, which can be further intensified by changing the laser setup parameters. Both granulate and powder form can be blended into precompounded color material or color concentrate. The selection of which additive to incorporate depends upon the

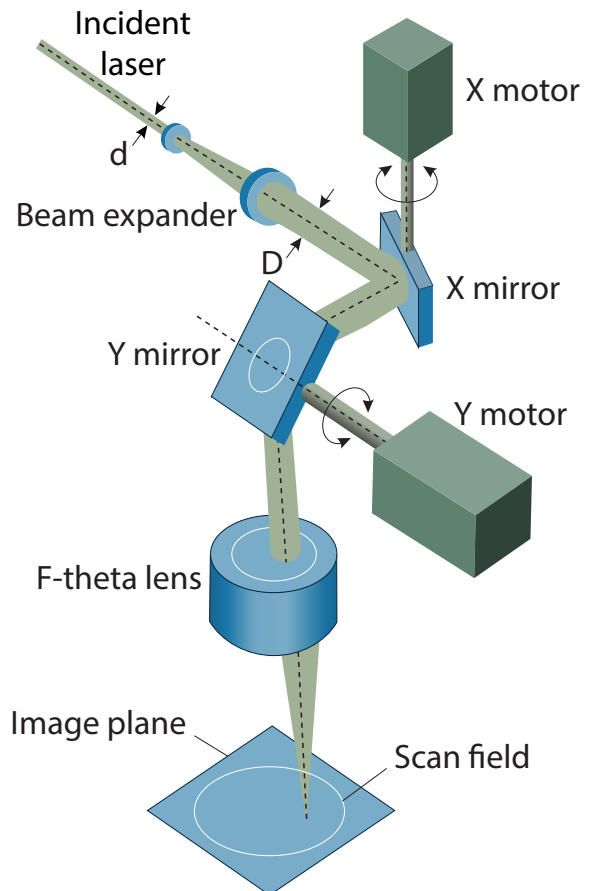
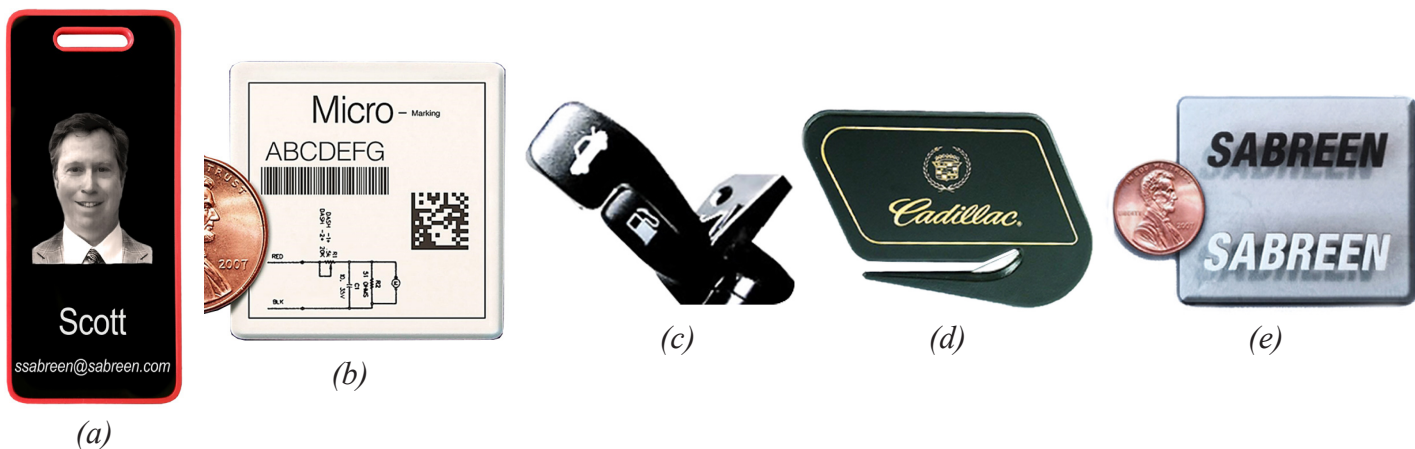


Figure 4. Beam-steered laser marking technology schematic



Figures 5(a)-(e). From left, various polymeric laser marking reaction mechanisms

polymer composition, substrate color, desired marking contrast color and end-use certification requirements.

Polymers possess inherent characteristics to yield dark-colored or light-colored marking contrast. Some colorant compounds containing low amounts of titanium dioxide (TiO₂) and carbon black may also absorb laser light and, in some instances, improve the marking contrast. Each polymer grade, even within the same polymeric family, can produce different results. Additive formulations cannot be toxic or adversely affect the products' appearance or physical or functional properties.

The most common surface reaction mechanism is termed thermal chemical carbonization, or "charring," where the energy absorbed in the substrate raises the local temperature of the material surrounding the absorption site high enough to cause thermal degradation of the polymer² (Figure 5 [b]). The darkness or lightness of the mark is dependent on the energy absorbed as well as the material's unique thermal degradation pathway. By optimizing the laser set-up, there is minimal surface carbonization residue.

Additives that – when blended into the resin colorant matrix – yield dark marking contrast often contain mixtures of either antimony-doped tin oxide, antimony trioxide or aluminum particles. All are easily dispersed in polymers. Typical loading concentration levels by weight are 0.01 to 3.0 percent. Many of the final formulations have received FDA approval for use under conditions A-H of 21 CFR 178.3297 Colorant for Polymers.

A second surface reaction is chemical change, through use of additives that release steam during degradation, which results in foaming of the polymer (Figure 5(c)). During the foaming process, the laser energy is absorbed by an additive that is in close proximity to the foaming agent. The heat from the absorber causes the foaming agent to degrade, releasing steam. Examples of foaming agents are aluminum hydroxide

or various carbonates. To prevent charring, the mechanism requires the polymer to degrade at a temperature higher than that of the foaming additive. Through tight control of the laser-operating parameters, high quality and durable light marks can be generated on dark substrates. Poor laser control can result in generation of a friable or low-contrast mark, which can be easily scratched (poor durability). Figure 5(e), recently developed, demonstrates both jet-black and opaque-white contrast within the same formulation (FDA-approved). This breakthrough is ideal for transparent (amorphous) polymers.

Third, laser energy is used to heat/degrade one colorant in a colorant mixture resulting in a color change (Figure 5 [d]). An example is a mixture of carbon black and a stable inorganic colorant. When heated, the carbon black is removed, leaving behind the inorganic colorant. These mixed colorant systems are dependent on specific colorant stabilities, and not all color changes are possible.³

Another specialized surface reaction shown in Figure 5 (a) incorporates laser additives into a multi-laminate layer structure for a photo identification badge. Unique high-resolution marking features, overt and covert, and RFID provide strong anticounterfeit security.

Compared to ink printing processes (pad/screen printing and inkjet), laser additives are cost-saving and can demonstrate 20 percent and faster marking speeds vs. non-optimized materials. Laser additives are supplied in pellet granulate and powder form. Granulate products can be blended directly with the polymer resin, while powder forms are converted to masterbatch. Most are easily dispersed in polymers. Based upon the additive and polymer, the loading concentration level by weight (in the final part) ranges between 0.01 and 4.0 percent.

Nanosecond ytterbium fiber laser technology

Improvements in laser technology have been instrumental in the rapid development of the newest generation of FDA-approved laser additives. The emergence of nanosecond ytterbium fiber lasers is one of the most significant advancements for marking, welding and cutting. Fundamentally, fiber lasers are different than other diode-pumped solid-state (DPSS) marking lasers. With fiber lasers, the active medium that generates the laser beam is dispersed within a specialized fiber optic cable. In contrast to fiber-delivered lasers, the entire path of the beam is within the fiber optic cable all the way to the beam delivery optics. This all-fiber structure is largely responsible for the reliability and ruggedness of these lasers, which accounts for their rapid growth.

Fiber lasers yield superior beam quality (M2) and brightness compared to Nd:YAG lasers. A laser with superior beam quality can be focused to a small spot size, which leads to high energy density. Fixed- and variable-pulse master oscillator power amplifier (MOPA) fiber lasers with pulse energy up to 1mJ and high-power density can mark many historically difficult polymers. Vanadate lasers also possess a small M2 value, with shorter pulse width than fixed fiber and YAG lasers. Pulse duration influences the degree of heat and carbonization into the material. Short pulses, typically <40ns, enable more controlled energy input when processing sensitive polymeric materials. These pulses still have the peak power to overcome material thresholds but have lower pulse energy to reduce localized thermal damage.

All beam-steered fiber lasers are not created equal. The hardware and software components a laser manufacturer incorporates into their systems makes significant difference in marking contrast, quality and speed. A primary attribute is the power density (watts/cm²) at the mark surface – which is different than the raw output power of the laser. The output mode of the laser beam is critical to the marking performance. These output modes relate to factors including the beam divergence and power distribution across the diameter of the laser beam.

Power density is a function of focused laser spot size. Focused laser spot size for any given focal length lens and laser wavelength is a function of laser beam divergence, which is controlled by laser configuration, mode selecting aperture size and upcollimator (beam expander) magnification. Pulse repetition rate and peak power density are critical parameters in forming the mark and achieving the optimal contrast and speed. High peak power at low frequency increases the surface temperature rapidly, vaporizing the material while conducting minimal heat into the substrate. As the pulse repetition increases, a lower peak power produces minimal vaporization but conducts more heat.

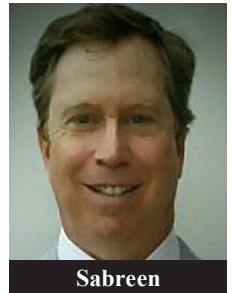
Conclusion

Digital piezoelectric DOD inkjet and fiber laser technologies offer countless advantages for product customization. Robust

marking/printing solutions require precise engineering of ink/laser chemistries, polymeric surface science, process design and equipment. Frequently, companies that choose to purchase cheap, off-the-shelf equipment fail to integrate robust systems due to a lack of process understanding. Each process offers advantages and potential limitations. Many manufacturers already recognize the value of offering both technologies. A tangential benefit is the capability to print fully assembled products at the end of manufacturing operations, offering cost savings and better inventory control management. ■

The Sabreen Group offers comprehensive onsite education and training on adhesion bonding processes, plasma pretreatment and advanced manufacturing techniques. Pretreatment equipment demonstration is conducted in-house, using actual production parts and real-time testing. Guaranteed Results.

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