FDA-Approved Additives Boost Inline Plastics Laser Marking

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F ast speed, superior contrast and cost-savings are among the significant benefits of incorporating novel FDA-approved additives into polymers for laser marking. Chemical additive breakthroughs produce jet black and light-colored contrast on molded and extruded products, both "on-the-fly" and during secondary operations. Designed for affordable fiber lasers, inline inkless laser marking now replaces rotary gravure and pad printing. ▶

Product applications

Many clear, semi-transparent and opaque colored polymers, including nylons, PET, polycarbonates, polyolefins, PVC, styrenics, TPU/TPE (for wearables) are uniquely formulated using non-heavy metal, FDA-/EFSA- (European Food Safety Authority) approved additives to achieve high-contrast marking quality. Polymer clarity, spectral transmission and base physical properties are not affected. Non-contact, digital laser marking replaces expensive adhesive labels and ink-chemical printing processes. The result is a cost-effective, environmentally friendly, superior aesthetic appeal in the application.

"On-the-fly" laser marking is performed on molded and extruded products, such as wire/cable, tubes and pipes. Marking speeds for polyolefin synthetic wine corks and undercap promotions on linerless beverage closures are capable of 2,000 pieces per minute for alphanumeric text and graphics. Marking speed is a function of many variables, including polymer type, substrate color, laser additive type and loading level, cable size (weight), laser type and power, software, number of alphanumeric characters, text height, length of text string, space between characters, bar code/data matrix, logos/graphics, single-stroke or true-type filled fonts, fill direction and continuous or repeating text. Use of the proper formulated additive-colorant will ensure that "power density" at the mark surface is not the limiting factor. Rather, the beam-steered galvanometers will be operating at maximum speed.

Due to the complexity of factors influencing on-the-fly production marking capability, every application must be precisely examined. There are few, if any, rules that can be extrapolated. However, for general purposes, consider the following nylon polymer example: 50-watt fiber laser, 254mm flat field lens, 100 alphanumeric characters, 2mm height, comprising a repeating text string length of 14.68 inches with a marking time of 0.232 seconds. The calculated speed is approximately 315 linear-feet per minute.

Polymeric laser marking reaction mechanisms

The advancements achieved in formulating laser additives for use with near infrared lasers (1060-1080nm wavelength) are their compatibility with Ytterbium fiber, Vanadate and predecessor Nd:YAG lasers. Most polymers do not possess near infrared absorption properties without chemical additives. 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. Vastly different formulation chemistries and laser optics/setup parameters are used, depending upon the desired marking contrast and functionality.

The most common surface reaction mechanism is termed thermal chemical "carbonization" or "charring," whereby 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 polymer. 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 setup, there will be minimal surface carbonization residue.

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A second surface reaction is chemical change through use of additives that release steam during degradation, resulting in foaming of the polymer. 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. 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 easily can be scratched (poor durability).

Third, laser energy is used to heat/degrade one colorant in a colorant mixture, resulting in a color change. 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.

Laser additives

Laser additives improve the degree of contrast, which can be further intensified by changing the laser setup parameters. Polymers possess inherent characteristics to yield "dark-colored" or "light-colored" marking contrast. Some colorant compounds containing low amounts of Titanium dioxide (TiO_2) and carbon black also may 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, physical or functional properties.

Compared to ink printing processes (pad/screen printing and inkjet), laser additives are cost-saving and demonstrate 15-percent (or greater) faster marking speeds versus non-optimized material formulations. Laser additives are supplied in pellet granulate and powder form. Granulate products can be blended directly with the polymer resin, while powder forms are con-

verted to masterbatch. Most easily are dispersed in polymers. Based upon the additive and polymer, the loading concentration level by weight (in the final part) ranges from 0.01 percent to 4.0 percent.

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 polymer composition, substrate color, desired marking contrast color and end use certification requirements. Some additives contain mixtures of antimony-doped tin oxide and antimony trioxide that can impart a "grayish" tint to the natural (uncolored) substrate opacity. Other additives can contain aluminum particles, mixed metal oxides and proprietary compounds. Color adjustments are made using pigments and dyes to achieve the final colormatch appearance. As commercially supplied, specific additives (also used for laser welding) have received FDA approval for food contact and food packaging use under conditions A-H of 21 CFR 178.3297 Colorant for Polymers. For the European Union, there are similar compliance statements. Certification conditions are specific for polymer type, loading level threshold and direct or indirect contact. Further qualification of FDA-approved additives blended into a "final part" can achieve biocompatibility of medical devices (reference International Standard ISO-10993).

Processing considerations

During the laser additive loading/colormatch chemistry, it is not uncommon for a finished product to contain less laser additive than the calculated amount. This problem almost always relates to non-uniform distribution during extrusion or molding. Simple adjustments to the molding machine, such as increasing the back pressure and screw rotation speed, will resolve most issues. Homogeneous distribution/dispersion of laser additives throughout each part is critical to achieve optimal marking performance. For extrusion, injection molding and thermoforming operations, precolor compounded materials versus color concentrate yields better uniformity. Hand-mixing should be avoided. Mold flow and gate type/location are important factors.

Laser technology

The advancements in laser technology have been instrumental to 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 solid state 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 fiber optic cable all the way to the beam delivery optics.

Fiber lasers yield superior beam quality and brightness compared to Nd:YAG lasers. One metric for beam quality is M2. The smaller the M2 value, the better the beam quality, whereas M2 = 1 is the ideal Gaussian laser beam. A laser with superior

beam quality can be focused to a small spot size, which leads to high energy density. Fixed and variable pulse (MOPA) fiber lasers with pulse energy up to 1 mJ 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(er) pulse width can be advantageous for sensitive polymeric applications.

IPG Photonics, a leading developer and manufacturer of high-performance fiber lasers, offers both fixed pulse (sometimes referred to as "Q-switch") and variable short pulse (MOPA) lasers. Application development is highly specific. The selection of which laser type to integrate is determined by the output characterisics of the laser interacting with the optimized polymer material. Reference the graphs below, representing Temporal Pulse Shapes of Fixed and Variable (MOPA) Pulse Length Ytterbium Fiber Lasers – IPG Photonics.
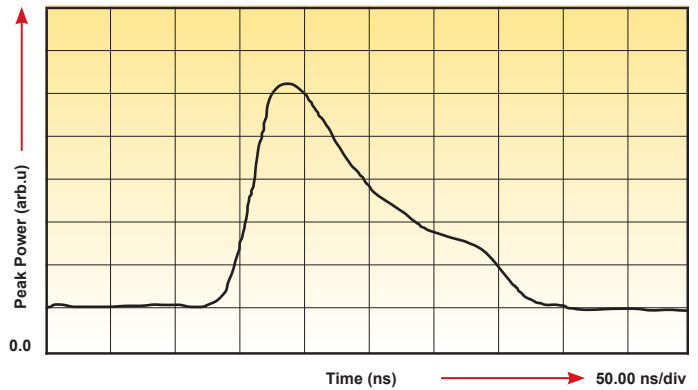

Illustration 1. Temporal pulse shape IPG fixed pulse length laser at 100 ns pulse length

When setting up a fixed pulse length fiber laser for marking, two inputs must be set.

1) Pulse repetition rate (often referred to as pulse frequency)
2) Pump power in percent (100 percent refers to the maximum possible electrical input to the pump diodes)
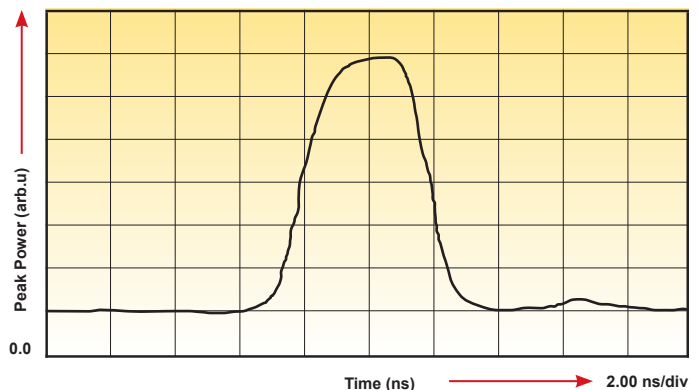

Illustration 2. Temporal pulse shape IPG MOPA laser at 4 ns pulse length

When setting up a variable short pulse MOPA fiber laser for marking, three inputs are set.

1) Pulse duration (often referred to as pulse length)
2) Pulse repetition rate (pulse frequency)
3) Pump power in percent (100 percent refers to the maximum possible electrical input to pump diodes)

For both graphs on the previous page, the particular combination of parameter inputs controls the output properties of the laser beam, namely the pulse energy, the peak power (the highest instantaneous peak of the pulse energy, J/pulse duration) and the average power (average power in Watts = pulse energy in joules x pulse repetition rate in Hz).

All beam-steered Fiber, Vanadate and YAG lasers are not created equal. The hardware and software components incorporated into a laser manufacturer's systems makes significant difference in marking contrast, quality and speed. A primary attribute is the power density (watts/cm^2) 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. The arithmetic curves of power versus pulse repetition rate are inversely proportional. 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. Additional contributing factors that influence the marking contrast and quality are, of course, beam velocity and the vector line separation distance.

Conclusion

The newest generation of FDA-approved laser additives incorporated into polymers yields superior marking contrast, line edge detail and speed. Inline, on-the-fly laser marking now replaces rotary gravure and pad printing. Advancements in affordable fiber laser technology have been instrumental. These benefits rapidly offset the incremental material additive cost. Optimized material-science chemistry for plastics laser marking requires expertise in polymers, colorants, pigments and dyes relative to solubility, particle sizes, threshold concentration limits, color match and regulatory certifications (GRAS, FDA Direct/Indirect Food Contact). All lasers are not created equal. ■

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