Over a quarter century ago, lasers were thought of as “tools of destruction.” From cutting through steel to use as weapons, lasers were powerful devices and thought to only be used that way. Of course today’s lasers carry a much tamer connotation and a much broader usage basis that is ever growing. With the technological refinement that has occurred, lasers are now used in delicate surgical procedures, sight lines for alignment, precision grinding and cutting, lithography, communications and for the marking of products. Laser marking on plastics, that is the marking and decorating of plastic parts, is of particular interest.

Laser marking on plastics is growing in use. Bar codes and product lot data can currently be marked with lasers at high speeds on some commodity resins. However, of specific interest is the use of lasers to mark functional or decorative information on engineering resins. Many engineering resins because of their inert surface characteristic have been difficult in the past to mark via printing using ink. It is extremely difficult, for instance, to pad print on acetal without surface treating with very harsh chemicals. And even if the ink “adheres,” the printed markings exhibit very poor wear characteristics and can be easily removed.

Laser marking is an excellent solution when problems in printing occur, or when there is a need for a truly indelible mark. For example, in engineering resins such as polyester or nylon, functional components such as connectors and switches can be laser marked with the functional description without fear of the identification rubbing off. In other applications, decorative marks can be made such as company logos and tradenames. These would include such items as car stereo trim plates, electrical component housings and other miscellaneous goods where the part supplier requires an indelible mark.

This paper focuses on the development of specialty grades of engineering resins that yield excellent sharp, clear images when laser marked. Specifically grades have been developed for laser marking on general purpose parts including electronic components. Additional grades have been developed for laser marking on those applications requiring the utmost in ultra-violet (UV) light stabilization for both automotive and non-automotive applications.
Lasermarkable Engineering Resins (continued)

pads required for design changes, speed of design change, and no hazardous waste generation for emissions or disposal, will generally favor laser marking depending on the number of components to be labeled. Even at somewhat higher per part costs, laser marking offers significant advantages that include:

- Indelible marks
- Non-contact to surface
- Extremely sharp images without smudging
- No pre- or post-treatments typically required
- No solvent use and no associated disposal
- Precision placement of marks and letters, even on irregular or curved surfaces
- Quick design changes via programmable software
- 2-D-Symbology potential (ultra dense data capability)
- No adverse effect from part surface moisture
- Low operating cost (no consumable supplies to purchase such as ink)
- Low maintenance

Laser Marking on Plastics

The word laser is an acronym that stands for Light Amplification by Stimulated Emission of Radiation. The device itself emits a concentrated, precisely focused parallel beam of light. Lasers typically generate this light using an energy source, a lasing medium that allows the light to concentrate, and reflecting mirrors to direct the energy within the lasing medium. There are three types of lasers currently used to laser mark on plastics. They differ primarily in the wavelength of the resulting light energy. This is determined by the lasing medium used in the construction of the laser as described below.

TEA-CO₂ Laser

As the name implies, this laser uses carbon dioxide as the lasing medium (the acronym TEA stands for Transversal Excited Atmospheric pressure). The TEA-CO₂ laser operates at a relatively long wavelength of 10,600 nm. Images are typically produced using a mask that has the information etched into it. The laser fires its intense light through the mask. The resulting image is focused and redirected onto the object. The actual mark is achieved by the partial carbonization of the polymer due to the intense energy and creates an etch into the polymer with a depth typically in the range of 100 to 500 microns. The quality of mark is comparable to a dot matrix printer especially when marking at high speeds. TEA-CO₂ lasers are typically effective for simple coding such as lot numbering. However, high resolution graphics for appearance applications are better served by either of the other types of lasers. For acetal resins in particular, the major portion of the TEA-CO₂ laser energy is absorbed by the polymer matrix. This causes engraving of the surface without significant contrast.

Nd:YAG Laser

In contrast to the carbon dioxide laser, the Nd:YAG laser uses a solid state medium of Neodymium Doped Yttrium Aluminum Garnet. The YAG laser, for short, can be operated either at 1064 nm or doubled frequency at 532 nm. The doubled frequency gives rise to sharper images. YAG lasers are typically interfaced with a computer to generate the graphics using a vector process achieved with focusing mirrors (see Figure 1). The YAG laser in a sense writes on the surface of the plastic part. Since no masks are required, design change and flexibility are improved versus the TEA-CO₂ laser. And with the higher frequency, the distinctness of image is also far superior compared to the TEA-CO₂ laser.

![Figure 1 - Nd:YAG Laser Schematic](image-url)
Lasermarkable Engineering Resins (continued)

Frequency doubled Nd:YAG lasers operate with a wavelength in the visible region at 532 nm (green light) and typically effect pigments and other additives that absorb at that wavelength. The resulting color change is due to a photochemical process occurring to these pigments and additives rather than from melting and foaming of the polymer. However, if very high peak laser output is used, localized heating of the polymer can still occur resulting in melting and foaming.

YAG lasers are becoming increasingly popular for laser marking appearance applications. They are particularly suited for developing a light mark on a dark plastic part. To this end, lasermarkable engineering resins were specially formulated to enhance the contrast of a white mark on a black part using the YAG laser. These resins include acetal copolymer, polyester (PBT) and polyester elastomers, and nylon 6,6 including filled and impact modified grades.

**Excimer Laser**

The Excimer laser generates UV light in the wavelength range of 193 nm to 351 nm. Here the laser marks totally by a photochemical process and the polymer matrix is not thermally loaded. Excimer lasers typically act on titanium dioxide or other mineral fillers to generate a dark mark on a white or light colored substrate. Relatively high levels of pigment or filler are necessary to achieve acceptable contrast. Since the process is photochemical, little to no etching occurs on the polymer surface. Marks penetrate to depths typically less than 40 microns. Excimer lasers have limited use for marking plastics today primarily due to being more expensive than Nd:YAG lasers and their limited ability to only produce a dark mark on a light substrate.

**Lasermarkable Acetal Copolymer Resin**

Because the Nd:YAG laser is the preferred marking device for developing high contrast marks on a dark substrate, development of a specialty lasermarkable grade of acetal copolymer was focused on that laser type. In particular, the objective was to develop a lasermarkable black formulation that yields the highest possible contrast when marked with the Nd:YAG laser. To that end, black lasermarkable acetal copolymer was developed using patented technology. This resin yields extremely white, high contrasting marks as shown in Figure 2. Conventional black grades show little to no contrast as pictured in Figure 3. Typical applications for general purpose lasermarkable resins include appliance buttons and knobs, keypad keys, miscellaneous switches and incremented thumb wheels, and floppy disk shutters. An application such as functional and decorative markings on an electric razor take advantage of the wear and chemical resistance of the laser mark, as well as those same properties of the base acetal copolymer resin.

Building upon this patented technology, a UV stable, lasermarkable resin was developed for interior automotive and other applications. This resin combines the laser marking ability with the world-class ultra-violet light stability and can be laser marked with the Nd:YAG laser to produce excellent white marks with no yellowing caused by the UV stabilizer system. The mark produced on this UV grade is of the same high contrast as depicted in Figure 2.

UV stabilized, lasermarkable acetal copolymer meets all current automotive interior weathering requirements including the 1240.8 kJ/m² exposure requirement which is the highest standard in the industry. This resin is designed to be used in automotive interior functional components such as cassette stereo buttons, hood and trunk release levers, or cruise control buttons. In these applications, the parts can be laser marked with the functional description without fear of the identification rubbing off as currently can occur with ink printed components. In other applications, decorative marks can be made such as company logos and tradenames. An example is a car stereo trim plate marked with either the logo of the automaker or the stereo manufacturer.
Lasermarkable Engineering Resins (continued)

**Lasermarkable Nylon Resins**
Nylon 6,6 can be modified using proprietary technology to achieve high contrast white marks on a black substrate. These grades can include one or more combinations of modifiers including heat stabilizers, impact modifiers, fiberglass reinforcement or mineral fillers. A general rule, however, is as the amount of modifier increases, the lower the contrast achieved in the resulting mark. For example, a nylon containing 13% glass will achieve higher contrast marks (whiter looking marks) compared to a 43% glass reinforced product. UV stabilized nylon for automotive interior can also be customized to be lasermarkable as well. Applications for lasermarkable nylon include turn signal stalks, tool housings and various under the hood parts where the mark is required to withstand harsh environmental conditions.

**Lasermarkable Polyester Resins**
Polyester (PBT) resins can also be modified using proprietary technology to achieve contrasting white marks on a black substrate. However, it must be understood that since PBT has higher intrinsic whiteness than other resins mentioned so far, the whiteness of the mark is not as bright as achieved with acetal or nylon. Also, the black substrate color is not as black as in these other resins. This results in the overall effect not having as much contrast as acetal or nylon. While the contrast may not be suitable for decorative finishes, it is clearly legible for use in functional marks or for identification purposes on such items as electrical connectors or components. Here, where product traceability is required more and more, bar codes or 2-D symbology may be employed. Capture such information as product and date codes, lot information, manufacture date, manufacturing plant, and so on.

Polyester resins may include unfilled, glass filled, impact modified or mineral filled resins. These may also include polyester elastomers and alloys and blends. As in the case for nylon, the general rule is as the filler content increases, the apparent contrast decreases.

Polyester resins also generally include flame retardant versions. Depending on the laser type, flame retardant polyester resins can be inherently lasermarkable for functional markings. For example, flame retardant PBT natural and light colored grades generally exhibit a black mark when marked with the Nd:YAG laser. The contrasting dark mark is generally acceptable for identification marking as long as the base color is not too dark. Darker colors including black, in flame retardant resins, will generally require modification to allow a contrasting lighter colored mark.

**Lasermarkable PPS and LCP Resins**
Both polyphenylene sulfide and liquid crystal polymer are very opaque resins. As a result, lasermarking on black substrates modified to enhance lasermarkability will achieve marks with reasonable contrast, but not as high in contrast as achieved with other resins like acetal or nylon. Again, the marks are of acceptable contrast for functional or informative marks, but may not have enough contrast to be considered for decorative marks. Since these resins find applications in computer systems and other electronic systems, indelible traceability and identification marking is extremely important, particularly for the automotive and aerospace industries. Both PPS and LCP resins are generally lasermarkable in their natural state depending on the laser employed. In particular, both PPS and LCP resins generally exhibit a contrasting dark mark on natural and light colored resin using a Nd:YAG laser. As the color of the substrate moves darker, the less contrast will be observed unless the formulation is specifically modified to enhance lasermarkability.

**The Future in Color**
While the initial focus of laser marking has been on developing a high contrast white mark on a black substrate, the possibility of developing a colored mark is intriguing, but challenging. A colored mark would no doubt expand the usage of laser marking and allow greater design flexibility for the customer.

Currently, the Excimer laser will yield a grayish to black mark on a light colored substrate. That is one option for color other than the white mark, albeit a limited one. The Nd:YAG laser offers seemingly more potential for marking colors. In acetal resin for example, laser marking with the YAG laser on a medium to dark color will yield a mark which is lighter in color and similar in hue. For instance, marking on a dark blue acetal part with the YAG laser will yield a light blue mark.

Building on this lasermarking technology, it may be possible in the future to expand the palette of colors when marking with the YAG laser. Possibilities include high contrast colored markings on a black substrate. Our initial successes in this area have included blue, green, yellow, or red marks on a black acetal substrate. What’s more, it may be possible in the future to expand on this
Lasermarkable Engineering Resins (continued)

by developing technology which creates a colored mark on a colored substrate of different hue.

Conclusion
In conclusion, if your application calls for indelible, high contrast marks, combining lasermarkable engineering resins with the Nd:YAG laser will produce the brightest, highest contrasting white marks on black molded parts, that can be achieved in industry today. Equally important, this combination truly eliminates any problems associated with ink printing adhering onto acetal and other resins, and removes any worry concerning the mark wearing off.

References


World-Class Engineered Materials

- Celanex® thermoplastic polyester (PBT)
- Hostaform® and Celcon® acetal copolymer (POM)
- Celstran®, Compel® and Factor® long fiber reinforced thermoplastic (LFRT)
- Celstran® continuous fiber reinforced thermoplastic (CFR-TP)
- Fortron® polyphenylene sulfide (PPS)
- GUR® ultra-high molecular weight polyethylene (UHMW-PE)
- Impet® thermoplastic polyester (PET)
- Riteflex® thermoplastic polyester elastomer (TPC-ET)
- Thermx® polycyclohexylene-dimethylene terephthalate (PCT)
- Vandar® thermoplastic polyester alloy (PBT)
- Vectra® and Zenite® liquid crystal polymer (LCP)

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