Mark-it™

Laser marking pigment

BASF
The Chemical Company

Technical Bulletin

Marking polymer materials using laser energy has been commonplace for many years, and has evolved to produce better marks, more rapidly. This has spurred a desire to mark laser-inactive materials even faster and to produce intricate high-contrast marks, propelling the development of new additives. With the development of Mark-it™ laser marking pigment, the technology is even more versatile.

Laser Marking Processes

The basic technology of laser marking is to irradiate the polymer with a high-energy radiation source such as a laser. The radiant energy is then absorbed locally by the material and converted to thermal energy. The thermal energy induces reactions to occur in the material.

Figure 1a. 22x image of LLDPE laser marked to produce charring.

Figure 1b. Cut-away view of laser marked surface (22x) showing charring to 10 mil depth.

Several types of reactions are possible. Among these are charring, ablation and foaming. The charring process occurs when the energy absorbed raises the local temperature of the material surrounding the absorption site high enough to cause thermal degradation of the polymer. While this can result in burning of the polymer in the presence of oxygen, the limited supply of oxygen in the interior of the work piece results in charring of the polymer to form a black mark as shown in Figures 1a and 1b.

Foaming occurs when the local polymer temperature surrounding the absorption site is sufficiently high that the polymer degrades to gases via burning or evaporation. The hot gases are themselves surrounded by molten polymer and expand to form bubbles.

Figure 2a. Foaming of polymer to create a light image on a dark background.

Figure 2b. Ablation resulting in an etched surface.

The bubbles may break out to the surface of the material resulting in cratering or trenching. If the energy of the laser is controlled, foaming can result in bubbles that scatter light in a way that results in a light mark. This is especially useful to produce a light, high contrast mark when the work piece is dark (Figure 2a).

Ablation is the process whereby the absorbed energy is very high, resulting in the total evaporation of the polymer to produce a depression with little residual char or cratering. Material is removed from the work piece often resulting in an engraved look with little or no change in coloration (Figure 2b). This type of interaction is often found when carbon black is used for coloration due to the high laser energy absorption and heat generation.

Laser Energy Sources

Early laser marking systems utilized CO_2 lasers with a radiation frequency of 10.6 microns – well into the IR region. These systems passed the laser light through a mask to shape the image, then focused the image onto the work piece. The CO_2 laser is pulsed onto the work piece, resulting in an instantaneous energy buildup in the polymer. “Dot matrix” CO_2 laser marking systems are also used where the beam is formed into dots that generate the image similar to a dot matrix printer. Continuous beam CO_2 lasers are now being used as light pens to laser mark, but they suffer from less system energy flexibility.

Currently YAG lasers at 1064 nm wavelength are popular in the laser marking industry due to their variable power and flexibility. This results in greater marking speeds and higher turnaround times for the end user relative to the CO_2 laser marking systems. A fast growing technology is that of fiber lasers, which operate at 1064 nm but require less power/cooling, provide high power density, and long operating lifetimes. The ability to change numerous laser parameters provides these laser systems with the ability to draw with greater finesse than CO_2 laser systems.

A beam steered laser marking system configuration is shown in Figure 3. It consists of a laser that is focused onto the material to be marked with a large field lens. The beam is steered across the surface to generate the mark by independent computer controlled mirrors. A substantial part of the system, (not shown), is the material handling unit that moves the pieces to be marked with precision at high speeds. This system must position the material and retain it in the focal plane of the laser beam for optimum marking speed and quality.

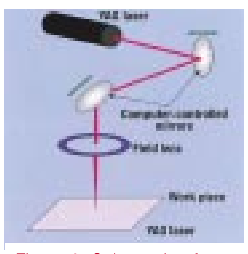

Figure 3. Schematic of YAG laser marking system.

Additives

Polymers that can be marked by laser are those that absorb laser light and convert it from light energy to thermal energy. For a laser marking system at 1064 nm, these materials will typically be either a grey or greenish color for efficient marking. Therefore, most polymers do not mark well. To achieve a good mark, additives that absorb the laser energy are employed.

Requirements for laser marking additives are that they must not change the appearance or the physical aspects of the work piece. They must absorb enough laser energy to raise the local temperature of the polymer to a sufficiently high level to achieve charring or foaming of the polymer, thus creating the mark. This temperature will vary for different polymers, even within a polymer family. Figure 4 shows a thermal gravimetric analyses (TGA) plot for two polypropylenes. The two polymers exhibit different temperatures of thermal degradation – the process that creates the laser mark. The higher temperature polymer will require more laser energy, lower marking speeds, or more absorbing additive to achieve the same mark appearance. This points to the need to understand the material used and the parameters affecting the marking process. Marking parameters and material composition need to be adjusted for optimal results.

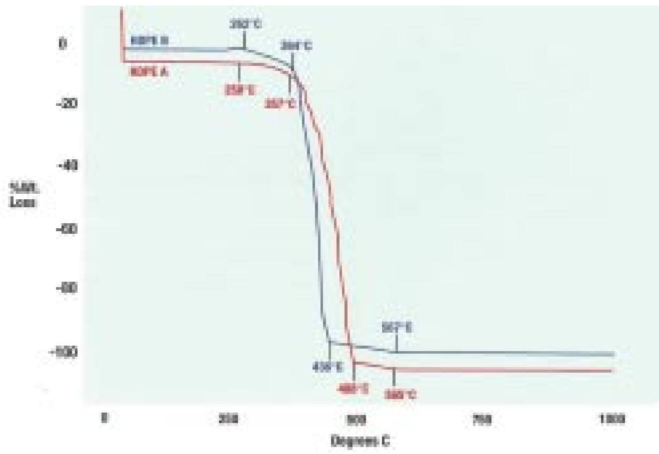

Figure 4. Thermal gravimetric analyses (TGA) from ambient to 1000 C of two HDPE samples showing differences in thermal degradation temperatures. HDPE B will mark more easily than HDPE A.

Mark-it™ Laser Marking Pigment

Mark-it laser marking pigment provides the necessary conversion of laser light energy to thermal energy for 1064 nm laser marking applications, which facilitates faster marking speeds at low loadings in many polymer systems. Marking speeds as high as 190 inches per second have been achieved in some polymer systems.

Mark-it is an antimony-doped tin oxide pigment. It is easily dispersed in polymers as well as liquid colorant systems. Particle size is on the order of 2-3 microns (D(50)). The appearance of the materials incorporating Mark-it are affected minimally by this low chroma pigment. Typically, Mark-it pigment loading is 0.1% in polyolefins to obtain a high quality mark (Figure 5). Mark-it is not based on mica or another substrate and, therefore, does not impart a pearlescent, grainy, or reflective appearance.

Figure 5. YAG laser marked HDPE, 0.2% TiO_2 (left) and with 0.1% Mark-it (right).

Mark-it™ is FDA approved for use at loadings up to 0.5% in polyolefins in contact with food under conditions A-H of 21 CFR 178.3297 ***Colorants for Polymers***. In addition, the U.S. Food and Drug Administration (FDA) approve Mark-it laser marking pigment, for use in the laser marking process using a laser to generate black marks. ***This is the first approval of its kind in the laser marking industry.***

Light colored marks are achievable through the use of Mark-it in conjunction with other additives. By using Mark-it as the laser energy absorber, and $Al(OH)_3$ as a gas-generating agent, light marks can be developed. The process is shown below.

$$\textbf{Mark-it} + h\upsilon \Rrightarrow \textbf{Mark-it*}$$

$$\textbf{Mark-it*} + 2Al(OH)_3 \Rrightarrow \textbf{Mark-it} + Al_2O_3 + 3H_2O_{(g)}$$

*Thermally hot state

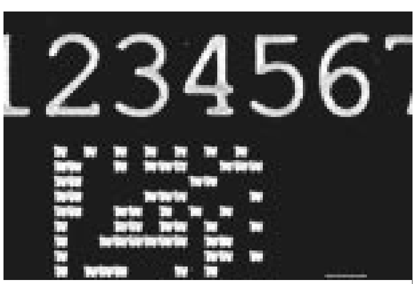

Figure 6. Light marks can be achieved using Mark-it laser marking pigment and $Al(OH)_3$ to generate sub-surface gas bubbles.

The steam released into the molten polymer forms bubbles that scatter light resulting in a light mark (Figure 6). Requirements for using this type of additive are that it be sufficiently stable to survive the molding of the polymer, and that it degrades at temperatures below the thermal decomposition temperature of the polymer, thus avoiding the formation of black spots due to char formation.

Light marks on a dark background can also be achieved by increasing the laser energy delivered to the work piece. This moves the thermal reaction beyond charring to subsurface evaporation of the polymer, resulting in the formation of gas bubbles within the polymer. Again, the bubbles scatter light and produce a light mark. However, regions in the material that do not achieve sufficient temperature to evaporate will char, leaving black spots. Therefore, this technique is best used with black-pigmented materials. Caution should be exercised to avoid forming large bubbles, which protrude from the surface. These can often be easily removed by abrasion.

Mark-it laser marking pigment has been shown to be an optimum solution for laser marking applications when a high contrast mark is desired. Polyolefins, styrenics, nylons, polyesters, polycarbonates, PVC, TPU, ABS, and silicone-based polymers have all been marked successfully. Additionally, coatings based on epoxy and polyesters have been marked with good results. Different effects can be generated with the use of additional additives. The final result will depend on the polymer, laser marking system, and additives used.

Laser marking already has widespread use in such industries as packaging, automotive and consumer goods. The technology offers indelible, fast and programmable marking of dates, codes, numbers and letters on a wide variety of plastic products. It is also considered environmentally friendly since the laser marking process does not require the use of solvents typically required in printing ink processes.

Laser marking for aesthetic applications is experiencing rapid market growth. These applications include company logos and other markings for product differentiation. These marks are usually white markings on darker engineering resins. The primary market for laser marking, however, remains non-aesthetic applications, which include part number, bar codes, dates of manufacture, and expiration dates on plastics. The marks are usually dark letters and numbers on transparent or light-color backgrounds or off-white marks on dark backgrounds. Mark-it may also prove to be a valuable anti-counterfeiting tool.

BASF pigments, performance minerals and additives, decorative and functional coatings, conductive materials and special effect films are used by a wide range of industries to extend product life, improve processing, impart color, create special effects and optimize product performance. We enable our customers to market enhanced appearance and performance in their products. Mark-it™ laser marking pigment is just one of the many ways BASF brings value to our customers.

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