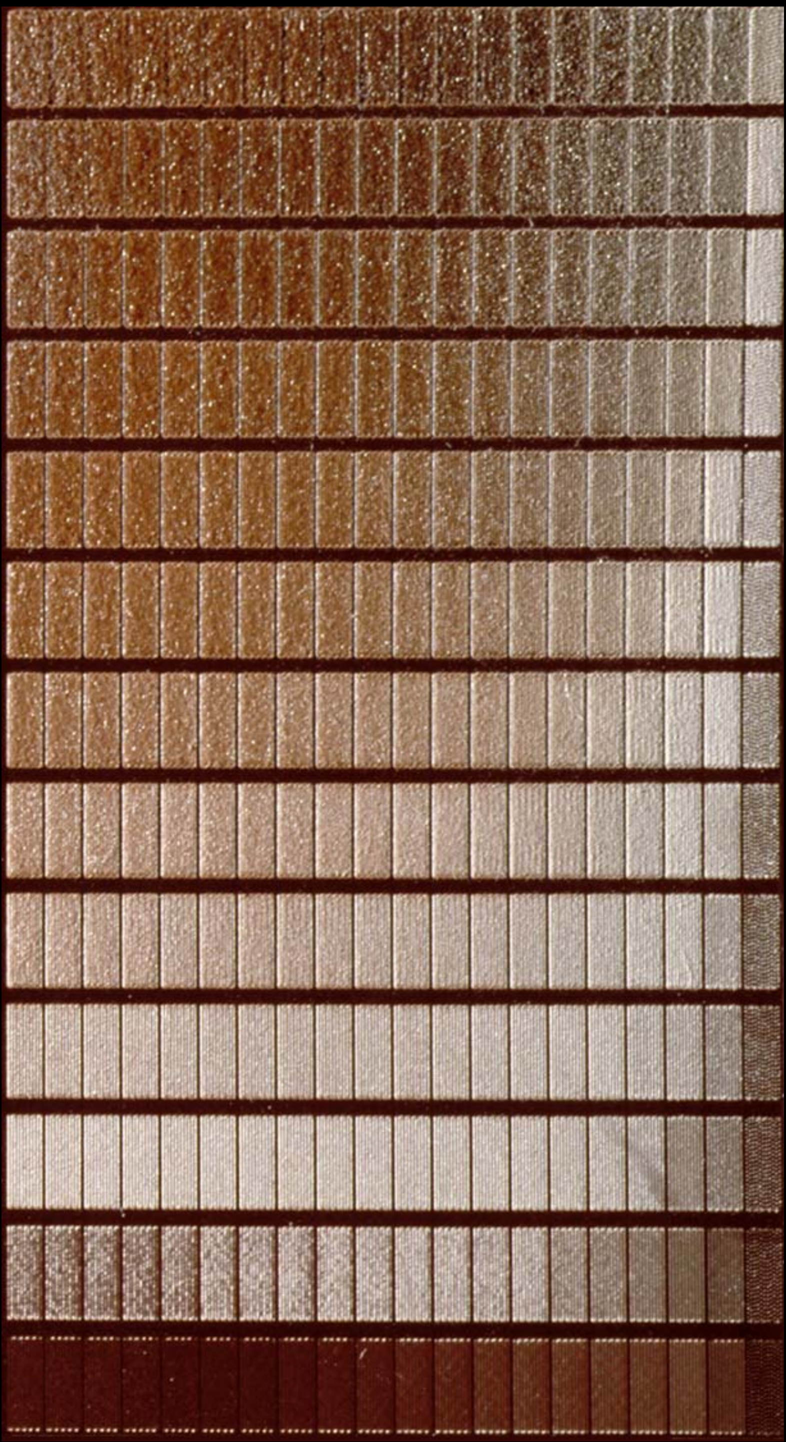
LATI HIGH PERFORMANCE THERMOPLASTICS



LATI THERMOPLASTICS LASER MARKING

LASER MARKING

- *Definition of "Laser"*
- *Laser Marking Techniques*
- *Laser Beam Sources*
- *Characteristics of the Beam-steered Laser Systems*
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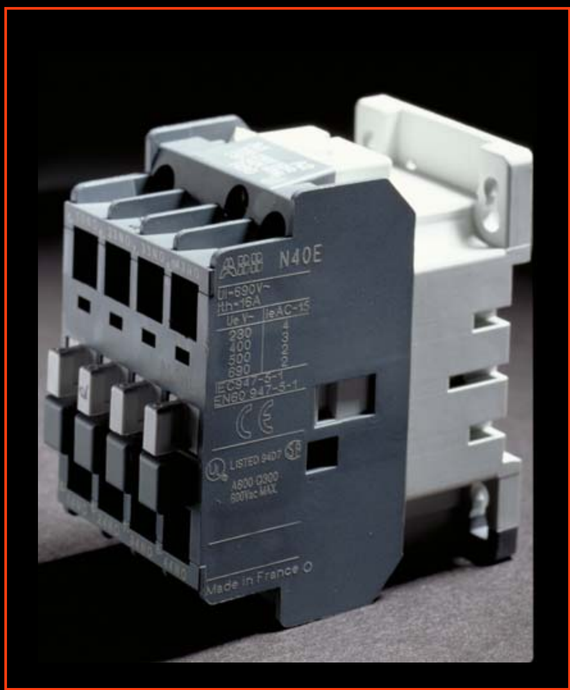
- *Marking Quality and Technical Specifications*
- *Marking Effects*
- *Troubles and Poor Marking Performances*
- *Thermoplastic Materials Markability*
- *Examples of Laser Marking Effects on Various Lati Engineering Thermoplastic Compounds*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WHAT IS A LASER?

Laser **is an acronym** for "Light Amplification by Stimulated Emission of Radiation".

A laser can be considered as a system which stores light energy and releases it in a very localised area. In this way the emitted energy has a very high–density energy.

The laser is based on the stimulated photon emission phenomenon. When a photon hits an atom it can excite the electron to move to a higher orbital. As the electron moves back to its original orbital it releases a photon having an energy given by the difference between the energy level of the two orbitals. This mechanism is known as photon spontaneous emission (Fig.1).

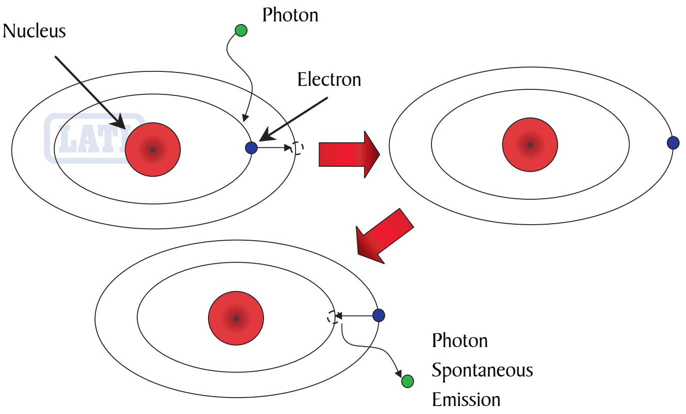

Fig.1 Photon Spontaneous Emission. The excited electron releases a photon spontaneously.

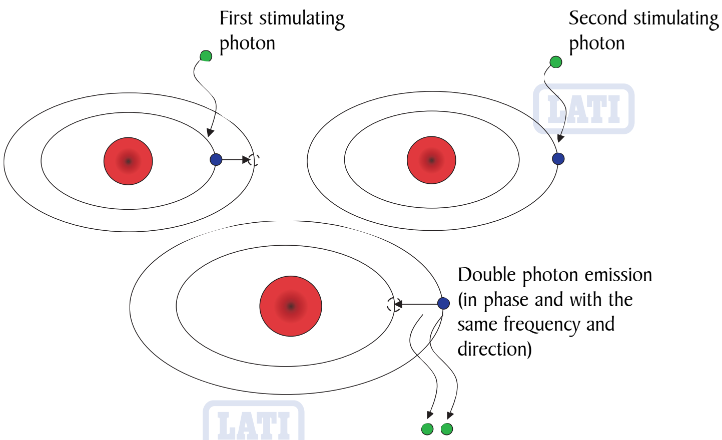

Fig.2 Stimulated Photon Emission.

The stimulated photon emission (Fig.2) is a bit different. Briefly, the phenomenon is the following: first an atom is excited by a photon, and then, before it spontaneously releases a photon, it is hit by another photon (the so called passing photon) having a frequency corresponding to the energy difference between the electron's upper and lower levels. As a consequence of this the atom releases "its" photon (by moving the excited electron to the lower orbital), in the same direction as the passing photon which will continue its motion. Therefore, at the end, two photons will travel in phase, with the same frequency (fixed by the difference between the levels' energy) and in the same direction.

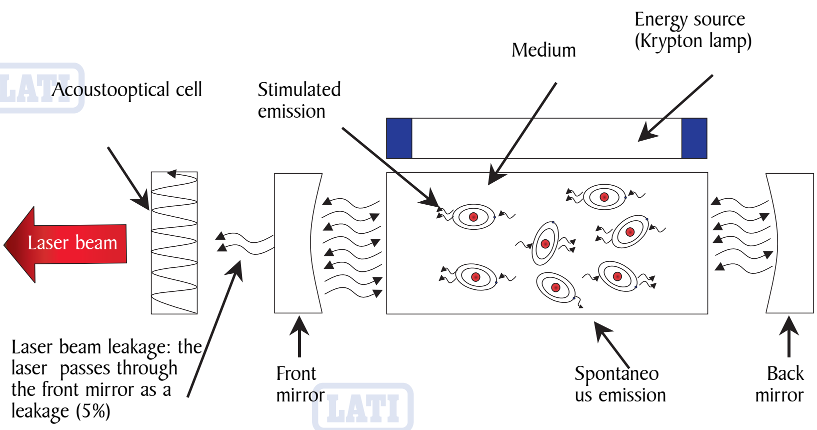

Fig.3 Laser beam generation

The incident photon (or passing photon) having the same frequency as the atom's emitted one is generated by means of a mirror system that reflects the photons spontaneously emitted. In a laser equipment (Fig. 3) the spontaneously and stimulated emitted photons are continually forced by means of mirrors, to move across a Neodymium doped crystal; in this way the energy is stored in form of light at a fixed frequency. The front mirror is able to leak part of the incoming photons and these create the laser beam. A storing system, the acoustooptical cell, is then used to store the laser energy and releases it as a pulse with high power. The laser beam is then "expanded" by means of an optical system, the beam expander, and then sent to a focusing system for the photo masking technique, or to the movable mirrors in the beam steered technique.

TYPES OF LASER MARKING TECHNIQUE

There are different types of marking techniques, mainly the **photo masking** and the **beam steering**. In the photo masking techniques (Fig. 4) the expanded beam outgoing from the laser source is projected against a template representing the picture/text that has to be written on plastic. Then the filtered beam passes through an optical lens which concentrates the laser beam on a very localised area; in this way the picture/text is projected with a high energy density onto the plastic part and produces the reaction of the plastic material, resulting in the marking. The laser has a pulse frequency generally higher than 100 Hz and an exposure time lower than 50 ns. This system is very rapid but at the same time it is not very flexible because the marking is dependent on the template picture. Therefore, photo masking is most suitable for repeated labels, nameplates, logos etc. The beam steering technique (Fig. 5) is more flexible than the photo masking, but with a lower speed. As flexibility is one of the key

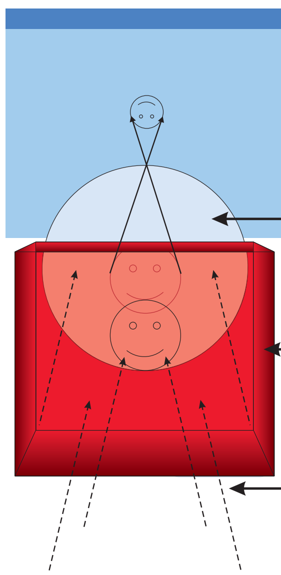

Fig.4 Photo masking process.

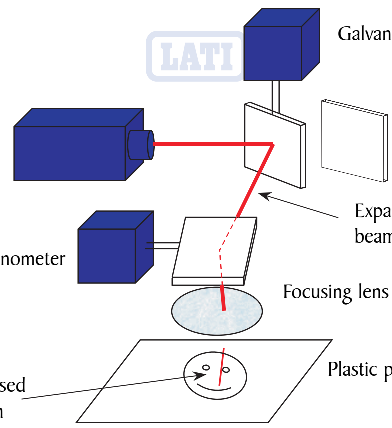

Fig.5 Beam steered laser marking

points of laser marking, this technique is the most commonly used. Two galvanometer-operated mirrors deflect the expanded laser beam; the mirrors steer the laser beam onto an optical lens which focuses the steered beam onto the plastic surface, following the pattern that needs to be created. The motion of the mirror is very precise and accurate, and therefore the quality of the picture/text produced is very high. The flexibility is also high as the computer controlling the system can store many possible patterns, and switching from one to the other is a very simple and quick operation. With this technique it is also possible to vary parameters such as the laser power, the pulse frequency and the beam speed in order to obtain the best possible quality of the image. The marking field is dependent on the system used, and generally ranges from 80 to 500 mm (sometimes it can reach 1000 mm).

LASER SOURCES

There are different types of laser sources. For the photo masking technique are typically used:

- CO_2 with a wavelength of 10600 nm.
- Excimer lasers, with lower wavelength (175-483 nm) resulting in thinner and sharp per marking.

For the beam steering technique the primary sources are the Nd:YAG (Neodymium doped Yttrium Aluminium Garnet), with a wavelength of 1064 nm (infrared light) and the doubled Nd:YAG with a wavelength of 532 nm (green light); in this way it is possible to achieve a smaller beam diameter and sharper images (however, the marking speed will be lower for thick patterns).

The different lasers used for marking thermoplastics are summarised in the following table. It can be observed that the best compromise in terms of speed, flexibility and marking quality is offered by the Nd:YAG.

Type of laser	Wavelength (nanometers)	Power
CO_2	10600 nm	10-200W max, 6J/pulse when marking
Excimer	175 - 483 nm	Max 2 J/pulse when marking
Nd:YAG	1064 nm	25-10W, 0.2 J/pulse when marking
Doubled Nd:YAG	532 nm	1 - 3W

BEAM-STEERED LASER CHARACTERISTICS

As the beam steered laser is the most commonly used, we will now discuss the parameters that can affect the quality of the laser marking. These are mainly the wavelength, the output power, the energy-density, the incident spot size, the pulse rate, the pulse power-peak and the beam velocity. The combination of these parameters has a decisive influence on the marking results.

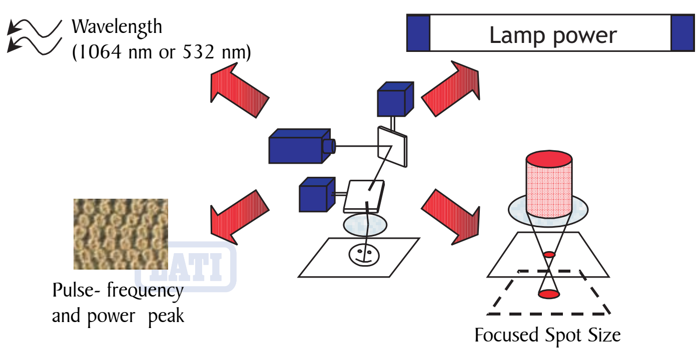

Fig.6 Beam-steered laser characteristics.

Wavelength

The wavelength is important because the material has to absorb the laser energy if a good marking effect is to occur. The majority of plastic materials are able to absorb the laser energy at a wavelength of 1064 nm (the wavelength of the Nd:YAG, which falls in the infrared band); for those requiring a lower wavelength the 532 nm, doubled Nd:YAG could be used.

Lamp power

The power of the outgoing beam is dependent on the energy of the light source (for a Nd:YAG, the Krypton arc lamp is usually used). By increasing or decreasing the input energy (lamp power), the output laser beam energy increases or decreases accordingly.

Pulse Rate and Pulse Power Peak

Generally the laser beam is not continuous, but it is pulsing at medium-high frequencies. In this way the energy stored in the acousto-optic cell is released in a very short time. The laser beam generator may be thought of as a capacitor that releases the stored charge instantaneously, thus producing high energy. The lower the frequency at which this energy is released the higher will be the pulse power and the consequent effect. It can be observed that when low frequencies are used the effect on the plastic surface is material vaporisation, due to the very rapid temperature increase and the low heat transmission inside the part. With high frequencies the material vaporisation still occurs, but less than before, and the laser's released energy results in a temperature rise in the neighbourhood of the exposed area. Typically the frequency of the pulse varies from 1 to 50 kHz.

Focused Spot Size and Energy Density

The output power alone is not enough to assure good laser marking. In fact, it is essential that this power is directed against a localised area. The device that controls the spot size direction is called the focusing system. The diameter of the focused laser beam on the work surface determines both the marking line width and the real marking efficiency. This diameter is a function of the focal length of the lens and the divergence of the laser beam. Simply stated, when the focal length is increased, the focusing spot size is correspondingly enlarged. The setting of the focal length affects two properties: first the incident spot size, and hence the energy density (the lower the focal length the higher the energy density) , and second the marking field area (the higher the focal length the larger the marking field).

It should be noted that the size of the focused spot is sometimes smaller than the line width required for plastic marking. Therefore, the characters or logos have to be "written" more than once, to give the proper appearance and readability, by placing several lines one close to the other or by using a spiral trace to fill the thick patterns.

Beam Velocity (Marking Speed)

The result of the combination of the pulse rate and the beam displacement velocity is the mark point overlap (or mark point density). A good overlap results in a continuous high quality marking, whereas a low density of mark-points produces a poor overlap. Too high the beam displacement speed on the part surface produces a non continuous marked line, and the marking appears as a series of spots. Too low a marking speed however, may result in an excessive mark depth or burning particularly nearby the etched area.

Fig.7 shows a correlation between the pulse rate, the mark-point density (ratio between the spot size and the distance to the closest spot) and the beam displacement velocity. It clearly shows that the mark-point density can vary according to the pulse rate and beam velocity.

The typical marking line width for a 1064 nm Nd:YAG is 100 µm. However, this value is influenced not only by the incident beam size, but also by the power density and by the plastic material to be marked. Typical beam velocity values range from 300 mm/s to 400 mm/s, and in some cases up to 6000 mm/s. As a conclusion we could state that there are many parameters that affect the quality of the marking on plastics ; the most important ones, in the process setting, are the lamp current intensity and the pulse frequency.

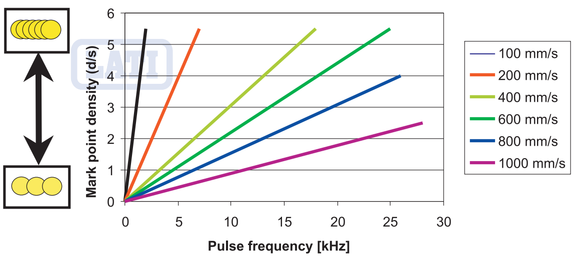

Fig.7 Mark-point density vs. pulse rate at various beam velocity.

PARAMETER SETTING FOR THE Nd:YAG LASER MARKING

The laser marking parameters have to be optimised for each polymer type, grade and colour being marked. The following parameter ranges are typical of a beam-steered Nd:YAG laser:

	Typical values for LATI thermoplastics with a Nd:YAG laser
Out-put power (arc-lamp; 3.5 kW)	20 - 25 A
Pulse rate	5000 - 6000 Hz
Beam velocity	300 - 400 mm / s
Etched spot size (diameter)	1.5 - 2mm (smaller values for fine details; higher values for thicker marks)

The goal of the laser parameters setting is to match the specific energy absorption requirement for each plastic material. All the parameters previously listed are important, but the most utilised, and the easiest to set, are the laser beam power (lamp energy density) and the pulse frequency.

For some materials it may be necessary to proceed with a low pulse frequency and low lamp energy density, for another one with higher frequency and still low lamp energy. There are many possible combinations available, and it takes some experimentations (usually easy and quick) to find the best setting.

It should be noted that because the process is not continuous, but pulsing, and because the mark-spot size is quite small, the value of the energy density can reach values up to 10^{13} W/cm^2.

DIFFERENT LASER MARKING EFFECTS

When a laser beam strikes a thermoplastic material several types of reaction occur, some of which are not completely understood. What is known is that the interaction between the laser beam and the thermoplastic is dependent on many factors, and so the consequent results are different. For example, a grey colored PA66 could be laser markable in its natural/unfilled version, but may be unmarkable in its flame retardant version.

We will now describe the various types of reactions that have been observed.

Foaming

The first effect shown is “foaming”. This phenomenon indicates that something in the compound absorbs the laser energy turning it as heat in the part. It could be produced by pigments, flame retardants or other additives. In order to obtain this type of result the laser needs to be set to high pulse frequencies, resulting in high heat transmission to the compound. This effect is observed on dark colours and the foam is generated around the area exposed to the beam.

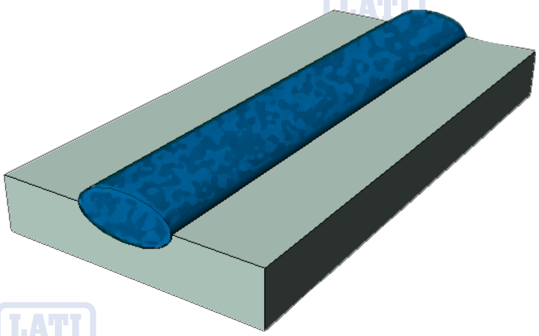

Fig.8 Foaming effect

The foam structure, having a depth of up to 100 µm into the material and up to 50 µm in height, is able to scatter light efficiently, resulting in a lighter appearance. This effect, alone or in combination with other effects, results in a good marking appearance. The drawback is the poor scratch resistance of the marking.

Engraving without colour change

This effect is based on the removal of material by vaporisation. It is usually seen on thermoplastics that absorb most of the laser

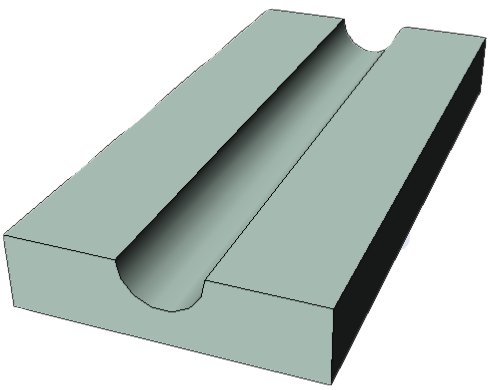

Fig.9 Engraving without colour change

energy or those containing pigments unsuitable for the laser marking or when operating with a high powered CO_2 laser. This effect usually gives low contrast marking, but performs good wear resistance.

Engraving with surface carbonisation

Material removal and carbonisation of the surface are the characteristic features for this effect and are normally seen when using light colour pigmented plastics. This effect is capable of yielding images/text with a high and sharp contrast. In addition to the engraving and carbonising, there is also a "damming" effect along the edges of the line.

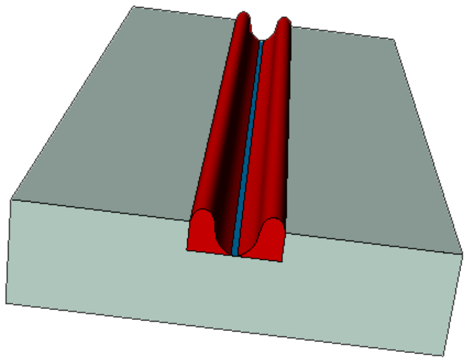

Fig.10 Engraving with colour change

Colour change or internal blackening

What happens in this effect is a reaction of one (or more) of the pigments used in the compound that is sensitive to the absorbed laser beam energy; this pigment is destroyed or changes colour, thus giving the marking effect. This effect is the ideal method for marking up to a depth of 100 µm without significant damage to the surface. However, it is possible in only a few plastic-pigment systems due to the limitations in current pigment technology. The contrast with the colour change effect is generally not as sharp as with foaming or engraving. When using different pigments, each one characterised by specific sensitivity to different laser colours (red and green) it is possible to achieve multicoloured marking. The development of both the laser marking systems and the plastic compounds is still under research.

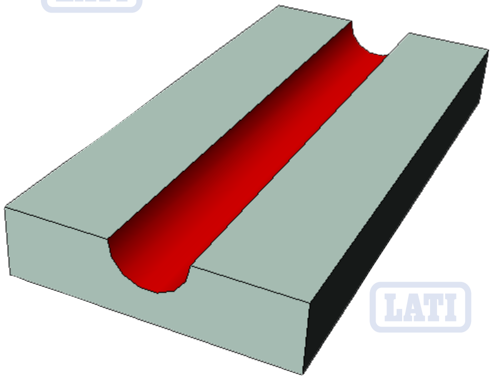

Fig.11 Colour change or internal blackening

Laser marking by coating removal

Special coloured or translucent markings are made possible by removing one or more layers of a preapplied coating. The coating removal process can also be used on plastics that do not react well to the standard laser marking methods.

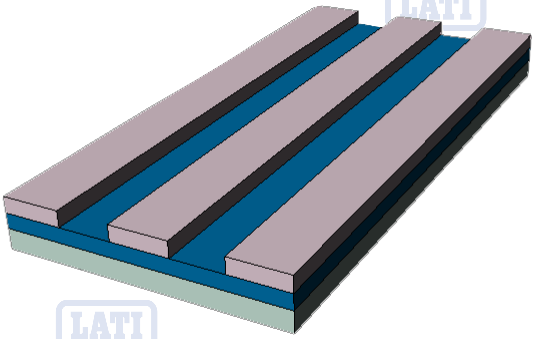

Fig.12 Coating removal

This process is popular for the production of “Day and Night” or “Back Lit” buttons, knobs, and other dashboard components in the automotive industry. This special effect is created when a transparent plastic is first coated with a thin white coating and then a subsequent dark coating. The dark coating is then removed by the laser, thus producing the shape of the desired image. This process allows for image/text to be visible both in reflected day-light, and when it is illuminated from behind in transmitted light.

LASER MARKING PROBLEMS

Laser marking may also result in poor quality marking or side effects. The most common ones will now be discussed.

Pearl-chain structure (discontinuous marking)

This undesirable laser effect is the result of inconsistent energy absorption, causing spotting or moderate darkening along the marking line. This effect is mainly seen on natural coloured (non pigmented) plastics.

This negative effect can be obviated by means of the addition of a well-dispersed, suitable pigmenting system.

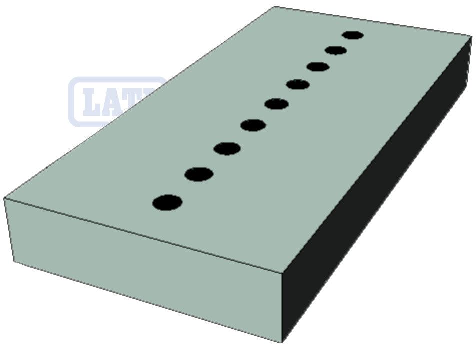

Fig.13 Pearl-chain structure

Side effects

Under certain circumstances, laser marking can give-off vapour residue or cause a dust/debris build-up. This is usually the result of left-over degraded polymer coming out of the “engraved trench”. These by-products should be removed by evacuating the dust and venting the vapours. In certain cases, laser marking can slightly lower the impact strength of some notch-sensitive polymers. It may also reduce surface the resistivity of some specific polymers/compounds.

No visible effect

Certain polymers do not absorb the Nd:YAG laser beam and therefore are not markable. With suitable well-dispersed pigments or other additives, these polymers can be made laser markable.

MARKING QUALITY AND SPECIFICATIONS

Optical Evaluation

Independing whether the marking is to be decorative or functional, high demands are often required for the image quality. The quality of the lines and of the image "filling" capacity are optimised and evaluated according to the four most important characteristics: contrast, uniformity, sharpness of lines, and surface.

The most important of these is usually the contrast. Contrast is the relationship between the brightness of the surface background and that of the marking. The best contrast is obtained with a dark background and light marking, or with a light background and a dark marking. "Contrast" is very subjective; it is dependent not only on the quality of the laser mark but also on other aspects (i.e., the surface finish of the part).

Abrasion Resistance of Laser Marking

The various marking effects, can produce a line depth over 100 µm, assuring therefore a readable text even in case of moderate wear. In comparison with other marking technologies, such as ink-pad printing, the laser marks are significantly more resistant to abrasion thanks to the higher thickness of the imprinted image.

Weatherability of Laser Marking

Some plastic and plastic/pigment combinations can change colour, fade or can yellow when exposed to UV light. This applies also to laser-marked surfaces. The largest factor in the mark alteration of a laser treated part surface is the weathering stability of the polymer-pigment combination. Accelerated weathering tests have shown that a darker background colour normally fades faster than the lighter laser marking; notwithstanding that the contrast ratio undergoes a slight decrease only. Generally speaking it can be assumed that the laser marking effects are not badly affected by the weathering/ageing processes.

LASER MARKABILITY OF THERMOPLASTICS

The necessary condition for laser marking is the absorption of the laser beam energy resulting in a colour change or similar effect. This may be achieved by the polymer alone or through the addition of pigments and/or additives.

Most non-pigmented thermoplastics (in their natural colour) are not readily laser markable, or are only slightly markable, because they are not absorbent to the laser light (the wavelength of the standard Nd:YAG laser is 1064 nm).

Thermoplastics in their natural color can be roughly divided into three categories according to their laser markability:

1. Thermoplastics with good absorption and consequent carbonisation, resulting in an extensive darkening of the laser-exposed areas. Examples include PES, PSU. PC.
2. Thermoplastics with inconsistent absorption and carbonisation, resulting in an uneven marking (pearl-chain effect). Examples include PS, SAN, ABS.

Besides the styrenic polymers, this group includes also the polyesters (PET, PBT). By adding a suitable pigment/additive combination, the marking effect can be made more uniform resulting in a high quality imprint.

For both these groups, the proper selection of the pigment/additive package for the dark backgrounds, can yield a light marking usually off-white in colour.

3. Thermoplastics with little or no absorption, resulting in poor or unreadable marks

   This group includes PA, POM, PP, PE, PPS. In their natural, uncoloured state, they are not laser markable. With the addition of a specific dark pigment system, an almost white marking results. Some of these plastics, when pigmented in light colours yield only a light marking. But with special additives, a dark print may also be obtained.

   In short, every polymer/compound and every colour needs to be carefully evaluated.

Laser markability can be greatly influenced by mineral fillers, reinforcements, processing aids, flame retardants, and other additives. Contrary to popular belief, the addition of glass fibres to a polymer reduces its markability only slightly. In addition, some mineral fillers and/or flame retardants may reduce the laser markability due to their inherent colour. On the other hand, the additives contained in some flame retardant packages can have a positive effect on the contrast of the marking.

Critic material formulations

It is rarely possible to predict whether a given formulation will give a good contrast with laser marking. We at LATI are regularly testing our various formulations to better understand which additives are more effective for laser marking, and which formulations result in better laser markability. For those formulations which do not give satisfactory results, we continue to try and research ways to improve the contrast while maintaining the properties and characteristics of the original material.

These tests have been largely carried out particularly on self-extinguishing Polyamide formulations.

From our tests and experiences the following considerations flow:

1. Uncoloured (natural) PA and PP/PE, whether unfilled, impact modified, glass filled, or combinations of the above, do not laser mark.
2. Some colours are inherently "difficult" to laser mark. It is difficult (or impossible) to obtain a good contrast with red, yellow and green base colours, especially in resins like PA that are not inherently laser markable.
3. It is difficult to obtain a "good" contrast with some material/colour combinations, not because they are not laser markable, but because, as an example, the background colour itself is too dark to show good contrast with a dark mark. At the same time the background may be too light to show a good contrast with a light mark. This

has been noticed on certain "medium grey" colours.

4. Moreover just because a material is laser markable in one specific colour, it is not possible to pre dict whether any other formula tion (even only slightly modified) with the same colour, is also markable.

5. It is often possible to improve the laser contrast of a formulation (apart from natural PA, PP, PE, POM). This is achieved by modifying the additive and pigment formulation (selecting the pigments that are more responsive to laser light).However there could be a negative effect on the properties of the resulting compound, such that it is no longer suitable for the end-use. For example, formulations that are self-extinguishing may have some properties (including the flame resistance) negatively affected by the incorporation of additives for laser marking.

EXAMPLES OF LASER MARKING EFFECTS ON ENGINEERING THERMOPLASTIC MATERIALS

In this section some examples of laser marking on LATI's engineering compounds are reported. It is possible to observe, in detail, the effect of the laser on the part surface. For completeness purpose, examples of poor quality marking are also reported.

Fig.14 **KELON B FR H2 CET/30-V0** (PA6, mineral filled, FR with halogens): engraving + colour change. Visible engraved points at low magnification. At a normal distance the marking appears good readable.

Fig. 15 **LASULF white** (PSU): darkening + slight foaming effect

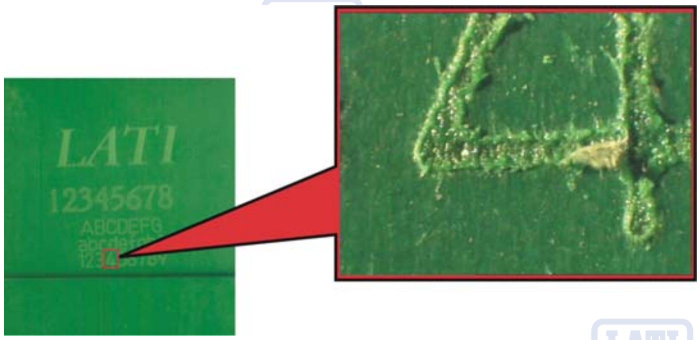

Fig. 16 **LATAMID 66 H2 G/25-V0CT1** green (PA66, glass fibres, FR with halogens): engraving without colour change (poor marking effect)

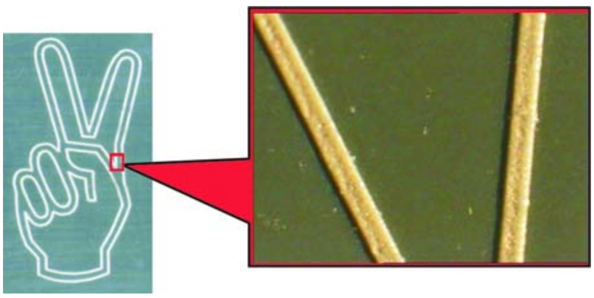

Fig. 17 **LATAMID 68 H2-V0 grey** (PA 66/6, FR halogen-free): foaming, with excellent contrast

Fig. 18 **LATER 4 G/15 yellow** (PBT, Glass fibres): different quality of laser marking as a function of the pigment type used in the formulation

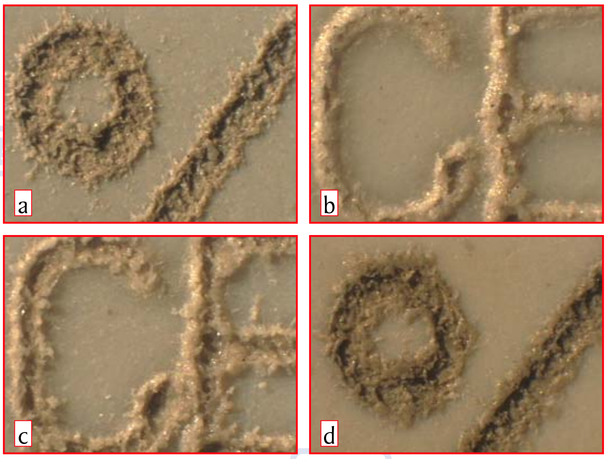

Fig. 19 Different types of marking on **KELON A FR H2 CET/35-V2 grey** (PA 66, mineral filled, FR with halogens):
a) Engraving
b) Foaming
c) Engraving and foaming
d) Engraving with colour change

Fig. 20 Effect of laser beam velocity on **LATAMID 66 H2 G/25-V0 HF grey** (PA66, glass fibres, FR halogen-free):
a) High beam velocity (green mark)
b) Low beam velocity (whitish mark)

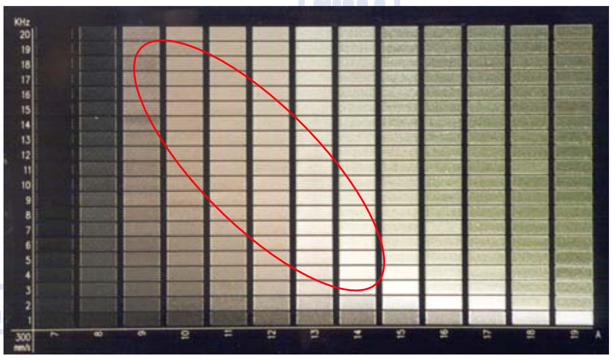

Fig. 21 Matrix of the laser marking process parameter conditions on **LATAMID 66 (PA66) grey**. This system enables to identify the ideal range (in the green area) for the lamp current intensity and the pulse frequency in order to get the best marking result. You can also observe the different laser marking colours depending on the different marking parameters used (frequency and amperage).


VRSRA1DA1 25758.319
3(1)A 250Vac 5E4
T125


VRSN01AC1 28056.339
16(4)A 250Vac 1E4
T125


VRSR96A1A 25613.248
16(4)A 250Vac 1E4 µ
T125

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