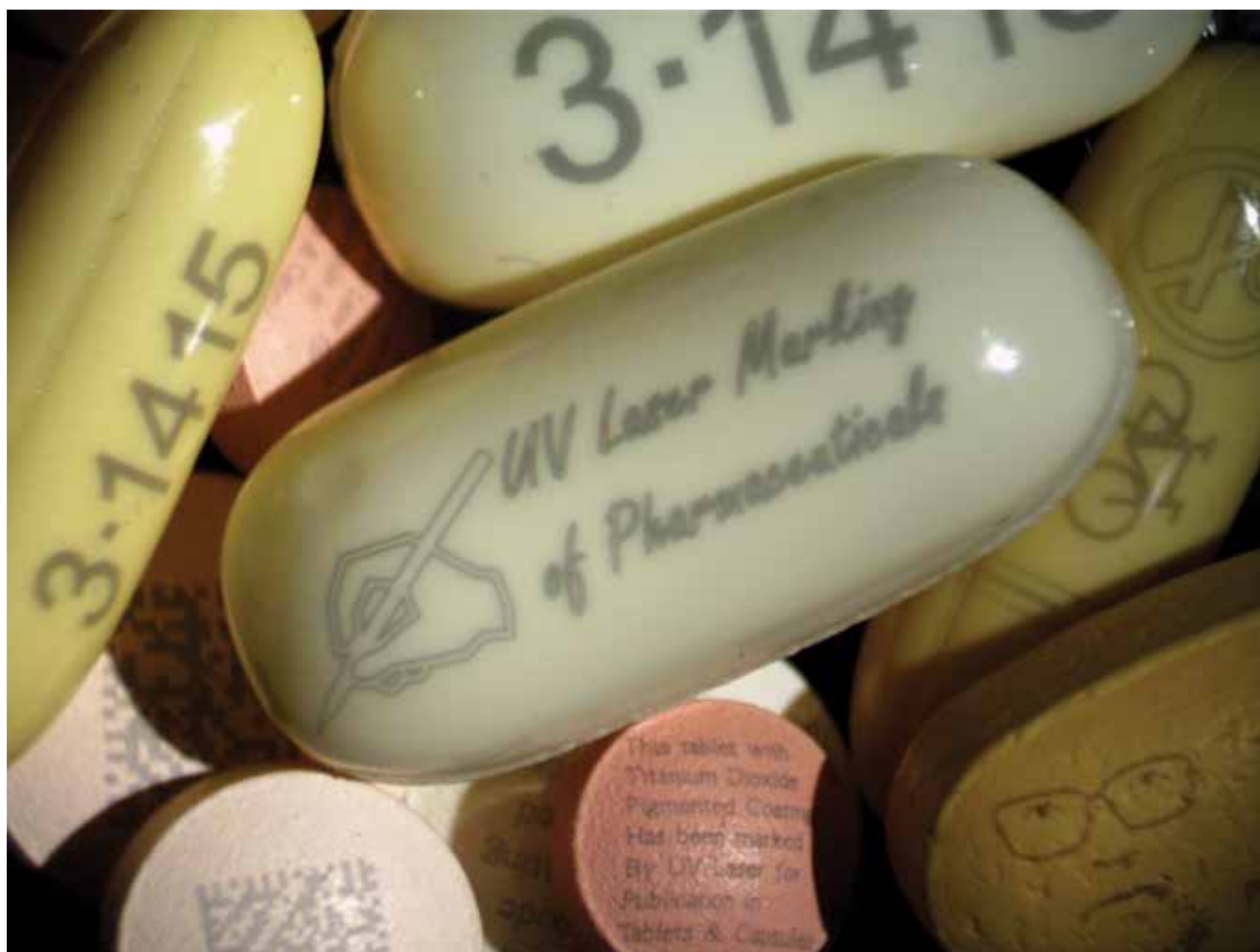# tablet and capsule marking

DIRECT UV LASER MARKING OF TABLETS AND CAPSULES

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This article describes the basic principles of UV laser marking and its applicability to solid oral dosage forms. It focuses on laser-surface interactions with emphasis on the role of titanium dioxide exposed to intensive UV laser pulses in the process of marking. Topics covered include experimental data and theory, advantages and limitations, and practical implementations.

In 2016, the global market for laser marking machines was estimated at $2.21 billion [1], yet only a handful of lasers are currently used for direct identification of pharmaceuticals. For decades, every major component required for direct laser marking of pharmaceuticals has been in place. Twenty years ago, approximately 22,000 laser marking machines were in use in various industries worldwide, some of which were using carbon dioxide (CO_2) lasers to imprint lot numbers on the aluminum backing of pharmaceutical blister packs [2]. CO_2 lasers were not suitable for marking individual tablets or capsules through the clear plastic of a blister pack, however, because CO_2 radiation melts the plastic and destroys the package. Ultraviolet (UV) radiation, on the other hand, safely passes through a transparent blister and can be used to mark tablets or capsules pigmented with titanium dioxide (TiO_2) [3].

US pharmacies filled close to 4 billion retail drug prescriptions in 2017 [4]. This does not include over-the-counter drug products or products sold outside the US. At least 10 percent of the formulations for these drug products contain TiO_2.

TiO_2 is added to thousands of different formulations of paints, coatings, and plastics to modify optical, physical, and other material properties and is FDA-approved for use in foods and pharmaceutical products. For most industrial applications, it is produced as a powder or slurry with white, submicron particles, but it may also be grown as a single crystal for research and other purposes. Because of its bright white color, TiO_2 is primarily used as a pigment.

An optical band gap around 3.1 electron volts accounts for TiO_2's intense absorption of UV radiation with wavelengths shorter than 380 nanometers [5,6]. Irradiation with a UV laser permanently turns TiO_2 particles from white to blue/black without altering the material properties of the pigmented surface.

This article describes UV laser marking of TiO_2-pigmented solid oral dosage forms, focusing on laser-surface interactions, and specifically on the color-changing mechanism of TiO_2 exposed to intensive UV laser pulses.

Basic considerations

A laser marking system consists of a laser coupled with a beam-delivery system synchronized with a parts-handling mechanism. Lasers and beam-delivery systems for material processing are the subject of many comprehensive reviews and a variety of reference sources and textbooks [7-10]. The basic principles and challenges of laser marking of plastics are given in Hoffman et al. [11].

The reaction of a solid surface to laser irradiation depends on many factors including laser wavelength and power, exposure time, and optical properties. For example, a laser beam can be completely reflected from a surface, as a ray of sunlight from a mirror, or propagate unaffected, as a ray of sunlight through a transparent window. The laser does not change or mark either the mirror or the window. To mark a material, at least part of the laser radiation must be absorbed directly on or near the material's surface.

Laser radiation can mark a material surface via several different mechanisms, as shown in Figure 1:

• *Ablation.* The irradiated material evaporates, leaving relatively sharp border trenches on the surface.

• *Melting.* The irradiated material melts and spills from the inside out, creating hills and valleys in the middle of a plain.

• *Burning.* The irradiated material heats up and produces gaseous components that react with atmospheric oxygen, depositing a product of combustion (such as soot) on the surface.

• *Color change.* The material changes color without any other visible surface modifications.
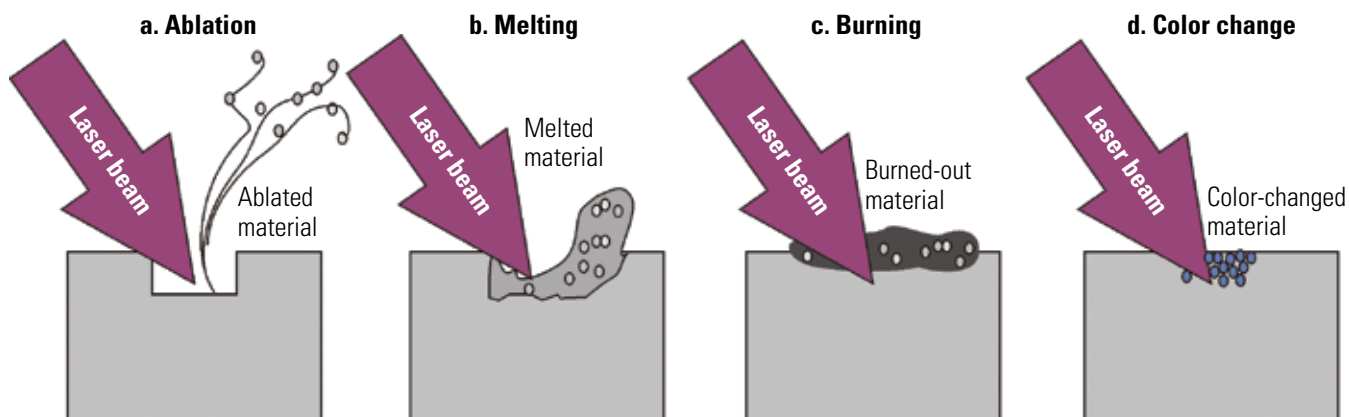
• *All of the above.*

Ablation is the cleanest way to inscribe pharmaceuticals but provides low marking contrast because the marked area does not change color. Making deeper and wider marks improves legibility but reduces material integrity. One approach is to apply at least one coating layer in a color that contrasts with the tablet color then use a laser to selectively remove the coating and expose the tablet beneath. This leaves a legible mark without destroying the actual tablet. The disadvantage of this method is the requirement for an additional coating layer and a potential problem with long-term durability, since part of the coating—especially around and within the imprint—can chip off and destroy the mark. This may happen when tablets collide with one another during transportation, dispensation, and other processes. The higher the resolution of the mark—a 2D barcode, for example—the weaker the marking integrity, as the remaining coated area becomes smaller and more vulnerable to any structural defect.

Melting and burning marking processes are subject to long-term durability problems because the melted material and burned out deposit may not stick well to the unaffected area. Other issues include tablet integrity and the possible formation of new substances not recommended for human consumption.

Color-change marking can be an excellent solution on the condition that it provides sufficient contrast, good

FIGURE 1

Types of laser-surface interaction

a. Ablation — Laser beam — Ablated material

b. Melting — Laser beam — Melted material

c. Burning — Laser beam — Burned-out material

d. Color change — Laser beam — Color-changed material

durability and long-term stability; does not affect the efficacy of the medicine; and does not create unwanted chemical components. UV laser marking of TiO_2-pigmented tablets and capsules satisfies all these requirements.

Experimental data and theoretical estimates

Some commonly used pharmaceutical additives such as titanium oxide change color upon intensive short-pulse UV laser exposure. The same effect occurs when those additives are embedded into a substrate. Ideally, laser radiation does not react with the outer material and passes freely through to the substrate surface. The pigment particles distributed in the substrate absorb the laser energy, which modifies the particles' structure and appearance, including color.

This practically irreversible change provides a mark with both chemical and mechanical permanency. Due to strong absorption, most of the beam's energy dissipates within a few surface layers, so only a small fraction of pigment is modified. Typically, the concentration of such additives is minimal, so the total amount of modified material in the substrate is extremely low. The depth of marking is inversely proportional to the additive concentration and usually does not exceed 100 microns. Short nanosecond laser pulses prevent regular heat exchange between the additives and the surrounding material, limiting any structural and/or chemical modifications to the pigment particles themselves.

Figure 2 shows UV laser marking of a soft gelatin capsule under different magnifications. The marking depth is less than 100 microns, while the thickness of gelatin film is about 600 microns. Even though the mark has spread "under the skin," the structural properties of the gelatin remain unaffected, guaranteeing the mechanical durability of the print. It can only be "erased" by cutting the surface layer. Importantly, the marking penetration ends far away from the border with the API, assuring no interference with the capsule's medical efficacy.

One can also make a rough estimate of how much material is involved in color transformation. The total area of the letter E in the figure is about 1 mm². Accounting for 0.1 mm penetration results in 0.1 mm³ volume for the E and 0.6 mm³ for the entire mark. The volume of gelatin in the capsule is about 200 mm³, so less than 0.3 percent of the gelatin is affected.

The color change may be explained by the transformation of laser-irradiated TiO_2 particles into other oxygen-deficient forms of titanium oxide that have assorted colors, varying from nearly transparent off-white to a dark blue/black.

Specific colors depend on material structure and composition. Titanium-oxygen (T-O) solid solutions have many stable phases and crystal structures [12]. The T-O phase diagram [13] in the composition range between Ti_2O_3 and TiO_2 shows Ti_3O_5, Ti_4O_7, Ti_5O_9, other so-called Magnéli [14] phases (Ti_nO_{2n-1}, n<21), and intermediate TiO_{2-x} structures. Some physical properties of these compounds are described in Bartolomew and Frankl [15].

Examples of changing color by vacuum annealing of solid crystals and powders

Oxygen-deficient or reduced phases (suboxides) can be created by vacuum annealing of rutile TiO_2 and, in addition to apparent color change, are characterized by the formation of oxygen vacancies and titanium interstitials [16]. Oxygen vacancy defects in nonstoichiometric rutile are described in Bursill and Blanchin [17]. Partial losses of oxygen from the TiO_2 lattice upon annealing in a vacuum or in hydrogen at 600°C for an hour were observed [18]. The crystal became blue. A paramagnetic resonance study showed the presence of Ti^{3+} species. Keeping the reduced crystal in an oxygen atmosphere at 600°C for another hour restored both color and oxygen concentration. The annealing temperature is the major factor determining the color of the suboxides. Heating single rutile crystals in a furnace at 1,273°, 1,350°, and 1,450°K resulted in light blue, blue, and dark blue stains respectively. Reoxidation in the air at 1,450°K again changed the dark blue crystals back to their originally transparent state [19]. Similar transformations occur in powders. For example, different blue-grey suboxides were produced by the solid-state reaction between TiO_2 powders and silicon used as reducing agents at temperatures below 1,000°C in an inert atmosphere [20].

How long does it take to get the color back?

The reversible process of changing color at elevated temperatures becomes irreversible under normal conditions. In thermodynamic equilibrium, titanium oxides are quite stable and have a specific structure and composition determined by the temperature and pressure. Oxygen

FIGURE 2

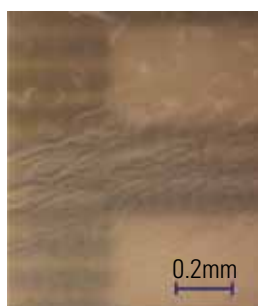**Typical UV laser imprint on a soft gelatin capsule**

a. Entire capsule
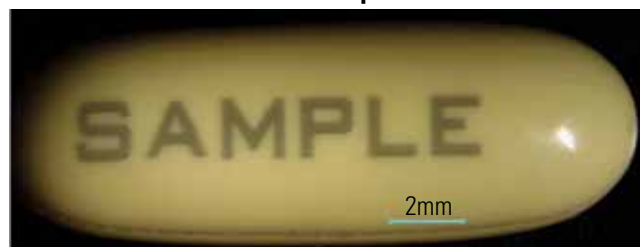
2mm

| **b. Imprint cross section** | **c. Magnified image of letter E** | **d. Further-magnified image of portion of letter E** |

0.5mm   0.5mm   0.2mm

concentration on the surface follows the changes in the surrounding atmosphere. However, the thermodynamic equilibrium in the bulk can only be achieved in time, depending on diffusion rates from the surface to the bulk and from the bulk to the surface if the conditions at the interface remain the same.

The diffusion rate itself depends on factors such as the temperature, pressure, stoichiometry, and structure. In general, activation energies for oxygen transport across the surface are considerably less than for oxygen diffusion in the bulk [21]. That makes the latter a limiting factor. Detailed studies on defect chemistry, diffusion, and oxygen self-diffusion in rutile are presented in Hoshino et al. [22] and Dennis and Freer [23]. It follows that, once modified crystal cools down to a normal temperature, it will never return to its normal equilibrium state and will therefore retain its new color.

The math behind the permanent color change

The time of diffusion t_d through a solid layer Z can be estimated as:

$$t_d = Z^2/D$$

Despite the wide spread, most of the experimental data fits into the standard Arrhenius plot, showing a sharp decline with a temperature decrease:

$$D \sim exp(-E/RT)$$

D, E, R, and T are the diffusion coefficient, activation energy, universal gas constant and absolute temperature, respectively [24].

The coefficient of chemical diffusion in rutile for both oxidation and reduction reactions at 600°C is about 10^{-6} (cm²/s) [25]. Therefore, it takes about 10,000 seconds before new conditions on the gas/solid interface produce a new equilibrium state 1 millimeter below the surface. This explains how TiO₂ crystal "sitting" in a vacuum sauna at 600°C for a few hours loses its oxygen and changes color. But once it "steps out" to the room with normal conditions, it cannot get the oxygen back because the temperature drops, and oxygen can barely move inside the crystal. Extensive studies on the reduced rutile surface detected no diffusion between the surface and bulk at temperatures below 127°C and very low diffusion rates for both oxygen and titanium at temperatures below 427°C [26].

In other words, when D is close to zero, t_d is close to infinity. This means that, at normal conditions, the process of reoxidation is extremely slow, and reduced TiO₂ crystal "freezes" in the non-equilibrium state, keeping its stoichiometry and color.

Examples of changing color by direct UV laser exposure

A number of studies found similar discoloration and restructuring in the TiO₂ surface after direct exposure to a pulsed, frequency-tripled (UV, 355 nanometers) Nd:YAG laser. A visible change in color from white to dark blue is reported for both dry powder and a 0.1-percent aqueous suspension [27]. Laser-treated powder converted back to white by annealing at 500°C for 2 hours. Intense laser exposure created oxygen vacancies and blue color traces on the surface of thin rutile films [28]. The microstructure of the resulting Magnéli-oxide films had been determined using X-ray diffraction and Raman spectroscopy. Surface melting and evaporation, changing color from white to blue, and an eight-order-of-magnitude increase in conductivity of the samples were observed [29]. Blue color at the surface of the laser-irradiated sample was strongly attenuated after one hour of exposure to air at 420°C. EPR and XPS analysis confirmed significant loss of oxygen and formation of Ti^{3+} and Ti^{2+} ions. The depth of modification was limited to a few thousand angstroms. The diffuse reflectance and EPR spectra of laser-irradiated TiO₂ were similar to titanium suboxides (Ti_nO_{2n-1}, n>15).

What happens inside a TiO₂-pigmented substrate under UV laser exposure?

The same color-changing mechanism seems to occur when the laser beam interacts with TiO₂ particles distributed in the bulk of a solid substrate. Since particles have submicron sizes, their entire volume might be modified. Solid media surrounding each particle significantly restrains its distraction and dispersion during the laser impact. This also prevents contact of the modified particle with open air and makes reoxidation and, therefore, discoloration practically impossible. UV laser irradiation of TiO₂-doped PET emulsion and PTFE tape resulted in contrast darkening without any visible degradation of the polymers [30]. The changes were identical to the changes in the pure TiO₂. Long-term stability of UV laser marking on TiO₂-doped ETFE films was investigated in Wolf et al. [31]. The marking showed little change during either thermal aging (770 hours at 229°C) or simulated solar irradiation (equivalent to 17 years of UV exposure in the Arizona desert).

Figure 3 shows TiO₂-pigmented silicone marked under the same conditions as the TiO₂-pigmented gelatin in Figure 2. The marks look very similar, suggesting the same color-changing process independently on the jacket material.

Figure 4 shows transmission electron microscopy (TEM) micrographs of a 70-nanometer layer of TiO₂ powder mixed with epoxy. Black particles appear only in laser-exposed areas. Darker areas relate to higher absorption/scattering of the electron beam passing through. This corresponds to more condensed matter and indicates a structural rearrangement and/or changes in the ratio between titanium and oxygen within originally undetectable TiO₂ particles.

The physics of determining the laser parameters

1. The material must absorb at least part of the beam. TiO₂ strongly absorbs light below 400 nanometers, making a UV laser suitable.

2. Most of the laser energy absorbed by embedded TiO₂ particles should be spent on modifications of the

particle itself rather than dissipating into surrounding media. For example, warming up matzo-ball soup in a microwave oven raises the broth temperature faster than the temperature of the matzo balls. Keeping the soup in the oven for a few more minutes equalizes the temperatures. The UV-marking process is the reverse. The temperature of TiO_2 particles increases much faster than that of the surrounding matter. The trick is to turn the laser off when the particles are hot enough but the adjacent material is still cold. In other words, energy accumulation during the exposure period and the corresponding temperature increase must be completed at a much faster pace than loss of the energy on the particle border due to heat and mass exchange with the environment.

The characteristic time τ_h of heat transfer across a particle is determined by the thermal conductivity and can be estimated as:

$$\tau_h = d^2 \rho C_p / \lambda$$

d, ρ, C_p, and λ are the diameter, density, heat capacity, and conductivity of the pigment particle, respectively.

Substitution for the typical TiO_2 values listed in Table 1 results in about 100 nanoseconds. This means that laser pulse duration less than 100 nanoseconds ensures that most of the pulse energy is spent on color-changing modifications of the TiO_2 particle.

3. The color changing within the particle requires some energy. A fraction of the energy, H, is used on the structural modifications and can be estimated as the difference in enthalpies of formation between the original and modified materials. The rest, E, is used on raising the temperature to the melting point, at which such modifications are possible. Then,

$$FS = E + H,$$
$$E = \rho C_p V (T_m - T_a)$$
$$H = \rho V (h_o - h_m)$$

Here, applied fluence F is the amount of incident beam energy per unit of area, S is the effective cross-section of the particle for UV light absorption; V is the particle volume; T_m and T_a are the melting and ambient temperatures; h_o and h_m are the mass enthalpies of formation for the original and modified compounds.

Calculations with typical data for TiO_2 pigments and some of the suboxides result in minimum fluence of approximately 0.3 J/cm².

This simple phenomenological model defines a range of applicable laser fluences and pulse durations, and also demonstrates the influence of particle size and agglomeration. For example, it suggests that bigger particles require higher fluence. Consequently, smaller particles require lower fluence, which would make laser marking much more effective and reduce unwanted side effects. For practical purposes laser fluences around 1 J/cm² are used to achieve a legible marking. A higher setting has

little or no effect on the marking contrast and in some cases causes degradation of the substrate surface.

Practical implementations

Figures 5 and 6 show UV laser marking on solid tablets, soft and hard gelatin capsules, and chewing gums. As the images illustrate, this high-resolution, chemically stable, and mechanically inerasable marking clearly satisfies the most stringent requirements for the pharmaceutical industry.

In addition to the laser printer, a regular capsule/tablet marking machine consists of tablet feeding and transporting systems, inspection cameras, and rejection and collection stations. During the system manufacturing process, most of the time and effort is spent on fine tuning the feeding, transporting, and rejecting mechanisms, as they

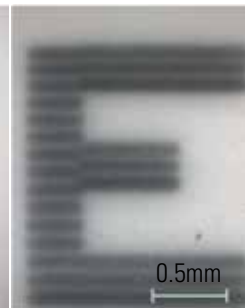### FIGURE 3

Typical UV laser imprint on silicone insulation

a. Entire imprint

2mm

b. Imprint cross section	**c. Magnified image of letter E**	**d. Further-magnified image of portion of letter E**

0.5mm   0.5mm   0.2mm
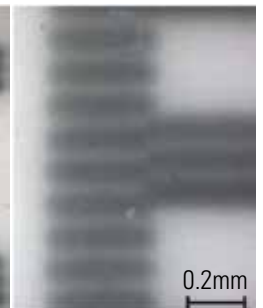
FIGURE 4

TEM micrographs of UV-laser-irradiated TiO_2 particles inside epoxy

White area

Beginning of second dark line
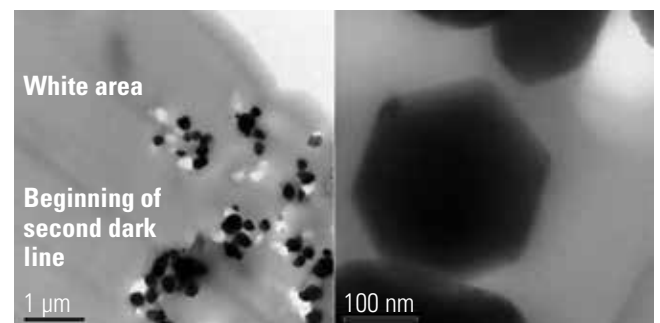
1 µm   100 nm

TABLE 1

TiO$_2$ properties [32]

Density (kg/m³)	Melting temperature (°K)	Heat capacity (J/kg°K)	Thermal conductivity (W/m°K)	Enthalpy of formation at 298°K (10⁶ J/kg)			
				TiO$_2$	Ti$_4$O$_7$	Ti$_3$O$_5$	Ti$_2$O$_3$
4,000	2,116	620-1,000	6.55	-11.73	-11.19	-10.97	-10.56

are highly dependent upon the tablet shape, size, hardness, and other physical properties. The tablet inspection station includes multiple cameras, special lighting, and elaborate software algorithms. All of this results in an expensive system where the marking station itself accounts for only a fraction of the cost.

On the other hand, the pharmaceutical industry is already equipped with many thousands of automated lines for sorting, counting, dispensing, and packaging. For example, blister machines have dedicated tablet-handling mechanisms coupled with inspection and rejection systems. A modular laser printer can be installed and adapted to work on most existing packaging and encapsulation lines and could be relatively easily moved from one line to another in accordance with production needs.

Another laser marking application is a scaled-down version of an industrial laser printer for use at points of sale such as dispensaries, pharmacies, and health clinics. Specific identifying information (such as names of patients and physicians, prescription number, 2D barcode, and photo ID) can be imprinted directly onto each tablet or capsule with high resolution. If necessary, the information can be encrypted or imprinted using lines so thin that they are invisible to the naked eye, adding another layer of security and safety.

Advantages and limitations

The numerous advantages of laser marking compared to conventional printing methods, such as inkjet or offset printing, are summarized in Table 2.

The primary limitation for the marking technology described in this article is the requirement of having TiO$_2$ in the outermost layer of the tablet or capsule. In most applications, TiO$_2$ is used as a white pigmenting agent and normally turns grayish-blue upon laser irradiation. Therefore, only light-colored products can be legibly imprinted. Despite this limitation, UV lasing of TiO$_2$-pigmented tablets and capsules can be a significant step toward implementing user- and environmentally friendly, clean, precise, reliable, and permanent laser-marking technology in the pharmaceutical industry.   *T&C*

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FIGURE 5

Examples of UV laser marking

a. Solid tablets

b. Soft gelatin capsules

c. Hard gelatin capsules

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FIGURE 6

UV laser marking through blister packaging

a. Tablet and chewing gum UV laser marked through blister

b. Same tablet and chewing gum removed from blister

c. Similar tablet and chewing gum with direct UV marking

TABLE 2

Comparison between ink marking and laser marking of tablets and capsules

Ink marking	Laser marking
• Capsules must be dried and cleaned prior to printing, as ink does not stick to oily surfaces.	• Eliminates capsule drying and cleaning stages prior to marking. • Eliminates ink curing and drying stages after marking.
• The cleaning process takes time and chemicals, especially for commonly used soft gelatin capsules.	• Eliminates chemical waste associated with capsule cleaning. • Eliminates inks, make-up fluids and other consumables associated with ink transfer. • Does not require any additional chemicals or pigments, as TiO_2 is already present in most coating and/or gelatin formulations.
• Even after drying and cleaning, the oil from the bulk will diffuse back to the surface in a matter of days, if not hours. This imposes strict timing requirements and reduces marking reliability.	• Streamlines the marking process. • The marking does not depend on the capsule surface properties (wet, dry, oily, etc.) or storage conditions.
• Inadequate printing results in a huge waste of otherwise legitimate and sometimes quite-expensive product.	• The marking is much more accurate, as it is controlled by a precise laser-beam scanning system.
• The marking resolution is limited by the size of the nozzle in the case of the non-contact inkjet printing or stencil in the case of direct-contact gravure marking.	• The technique can produce high-resolution images, including 2D barcodes, as the laser beam can be focused on a very small area.
• The ink marking deteriorates over time depending on the storage and shipping conditions.	• The marks are permanent and chemically inert. The marks are contained within a few micron layers "under the skin" and are therefore protected from any mechanical deformations.

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