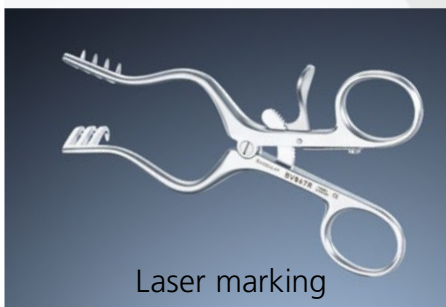




White paper

Novel spray passivation process for corrosion-free UDI laser marking



Laser marking



Spray passivation



Lab testing

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Bernd Block

Industry Manager Medical Technology

Phone: +49 (0)7156 303-32927

E-mail: contact.laser@trumpf.com

Summary

One challenge in the laser marking of medical-grade steels is that the high dose of energy delivered by the laser may cause damage to the protective passive film on the surface of the steel. Restoring a homogeneous passivation layer is essential for two reasons: firstly, to ensure that the surfaces of laser-marked medical devices retain their corrosion-resistant properties and, secondly, to guarantee that the UDI marking meets the regulatory requirements for traceability over the device's service life. Achieving these two goals requires permanent marking solutions that do not negatively impact the corrosion resistance of the base material. It also requires careful planning and coordination of the individual machining operations performed on medical devices prior to, during and subsequent to laser marking in order to create a permanent, corrosion-free marking. For example, it is important to choose the right laser marking method to ensure that secondary passivation will not subsequently reduce the contrast of the mark. Equally important is preventing micro-cracks from forming in the laser-induced dark oxide film, since these could cause the material to corrode. There are a number of parameters which can be optimized to achieve the best combination of excellent contrast and corrosion resistance.

In this white paper, we present an alternative to the conventional method outlined in ASTM A967 of passivation by immersion in an acid bath containing a high concentration of nitric acid. The novel method described in this paper is based on spray passivation with a highly diluted passivation solution (deconex® MT 41, Borer Chemie AG). The advantage of passivation with deconex® MT 41 is its ability to generate a highly protective passive film on medical devices that have been laser-marked using annealing or black-marking processes. Key benefits of the spray passivation system include low chemical consumption, low chemical concentrations, minimal maintenance requirements and a compact set-up. To verify the successful passivation of laser markings with deconex® MT 41, tests were run to check for the presence of free iron on stainless steel 1.4112, which is susceptible to corrosion. Corrosion resistance was also demonstrated by means of a simulated-use extraction study as specified in ISO 10993-12 and 10993-18. The tests were carried out in an accredited laboratory (Niutec AG).

Conventional passivation techniques

Laser marking of medical-grade stainless steels is followed by acid-based passivation treatments to restore the protective passive film. The ASTM A967 standard recommends two acids for secondary passivation. The first option is nitric acid, with a concentration of 20 to 45% by volume, a temperature of 20 to 60°C, and a soak time of 20 to 30 minutes, depending on the exact treatment method in each case. The second option is citric acid passivation. In both cases, treatment is performed by means of immersion in an acid bath.

Industrial companies often favor passivation with nitric acid, since it has the advantage of being an oxidizing acid. This means the acid has an extra oxygen atom available after the dissociation of the acid molecule into water, which helps to oxidize the chromium that is already present at the surface of the metal. This extra oxygen atom does not come from the acid molecule itself, but rather from the ion of the acid residue. This additional oxygen makes nitric acid highly suitable for forming a protective passive film.

However, nitric acid passivation also has a disadvantage: although the passivation process starts out by reducing the amount of free iron on the surface, it subsequently also reduces the amount of other alloying elements. The removal of these elements from the surface introduces heavy metals such as chromium, iron, copper and nickel into the solution. This contaminates the solution, which must then be properly disposed of as hazardous waste.

Passivation with citric acid is more environmentally friendly. The oxidation required to form the passivation layer can only occur with the help of oxygen from the air. Citric acid attacks the free iron and chelates it, while the other alloying elements remain on the surface. Removing the iron oxide increases the content of chromium and chromium oxides in the surface film. However, in-house studies indicate that the passive film formed by citric acid passivation is thinner than that formed by nitric acid passivation.

Passivation with deconex® MT 41

Deconex® MT 41 is a passivation solution consisting of phosphoric acid (15–20% by weight) and nitric acid (< 5% by weight) components as well as non-ionic surfactants (< 5% by weight). The solution falls under the “Nitric 5” category of nitric acid passivation in ASTM A967. Deconex® MT 41 is a strongly acidic passivating agent with a pH value of 2.2. The advantage of this passivation solution is that it can be used in far lower concentrations than those required for Nitric 1, 2, 3 and 4 acid baths. This lower concentration of between 0.02 and 0.08% by volume means that deconex® MT 41 can be used not only for immersion passivation, but also, in particular, for the more economical option of spray passivation. Process temperatures in this case range from 20 to 85°C. High temperatures play a key role in boosting the efficiency of the passivation process,

because chemical activity increases at higher temperatures. Conventional nitric acid passivation would generate hazardous vapors at such high temperatures, making it extremely difficult to perform such a process safely.

The ability to use this novel passivation solution in such low concentrations makes it an excellent choice for both passivation techniques (immersion and spraying). Compared to the conventional Nitric 1, 2, 3 and 4 categories of acid bath passivation, the passivation process with deconex® MT 41 described in this white paper is not only more economical, but also more environmentally friendly and user-friendly. The solution is readily biodegradable and can be disposed of through the standard sewerage system thanks to its low concentrations.

Material, surface finish

The marking and passivation tests were performed on cylindrical steel bar (martensitic steel grade 1.4112; X90CrMoV18) with a diameter of 10 mm. Cylindrical metal bar stock was chosen deliberately since it is more challenging to mark than steel plate. Prior to laser marking, the surface of the steel was subjected to barrel finishing, vapor blasting and electropolishing treatments. The average post-treat-

ment roughness of $R_a = 0.9 \mu\text{m}$ corresponds to normal roughness standards for medical instruments. We chose this particular material as it is a medical grade stainless steel that is known to corrode very quickly after marking, despite its relatively high chromium content. This makes it an ideal “worst case” test material.

Process chain

The process chain of our test series is shown in figure 1. We began with the surface treatment steps of barrel finishing, vapor blasting and electropolishing. Next, the test parts were laser-marked. No primary passivation was carried out; this was regarded as unnecessary for such a simple cylindrical shape. Performing such a step after electropolishing would only make sense if the parts included special geometries such as blind drill holes, where electropolishing might struggle to generate an adequate passive film. Once the TRUMPF TruMark laser had completed the marking process (nanosecond laser for annealing, femtosecond laser for black-marking), the sample parts were cleaned with an alkaline cleaning agent (deconex® MT 19) to remove any grease residue

and then treated with deconex® MT 41 using the two methods of immersion passivation and spray passivation.

After the passivation process, the samples were stored for 24 hours to allow the passive film to continue forming. The parts were then checked for free iron by the accredited Niutec laboratory in accordance with ASTM A967 (Practice F: Free Iron Test). In addition, the test parts underwent a simulated-use extraction study based on ISO 10993-12, in which inductively coupled plasma mass spectrometry (ICP-MS) according to ISO 10993-18 was used to analyze the alloying elements that may leach out as a result of corrosion.

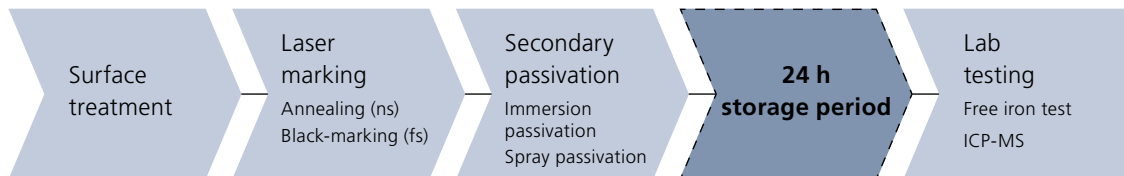


Figure 1: Process chain of the test series using steel 1.4112.

Comparison between spray system and immersion bath

The spray chamber system used in the tests (Miele PLW 8616) offers some notable advantages over a conventional acid bath when it comes to passivation (fig. 2). Immersion systems are often constructed as linear installations that require a considerable amount of space, while spray systems typically come in a more compact design. Spray systems also require far less maintenance and consume significantly less water as well as smaller amounts of chemicals.

Compared to passivation by immersion, spray passivation has the advantage of being able to rely on oxygen from the air to facilitate passivation. This leads to reliable passivation results even when spray passivation is performed with the lowest concentration of 0.02% by volume. Our tests showed that immersion passivation in deconex® MT 41 is an equally reliable process, but only when using higher concentrations (recommended: 0.08% by volume).



Figure 2: Spray passivation system (left), conventional passivation immersion tank (right) as part of a linear system.

Laser marking technology

Markings were applied to the medical-grade stainless steel 1.4112 using two different laser technologies (fig. 3). Firstly, a 25-watt nanosecond laser (TruMark 6030-G2, 200 kHz), was used for annealing. Secondly, a 20-watt femtosecond laser (TruMicro Mark 2000, 1 MHz), was used for high-contrast black-marking. Due to their excellent beam quality and, in particular, their regulated linear power curves, both systems achieve consistently high processing

quality and reproducible results. Their external power control capabilities enable users to configure precise and reproducible settings for the absolute laser power at each operating point on the workpiece and to run an extremely reliable marking process. Combined with modular image processing and automated process sequences, these lasers offer complete turnkey solutions for corrosion-free UDI marking.



TruMicro Mark 2000:
Black-marking with femtosecond laser pulses.



TruMark 6030:
Annealing with nanosecond pulses.

Figure 3a: The TruMicro Mark 2000 (900 fs) was used for black-marking.
Figure 3b: The TruMark 6030 was used for annealing marking.

Test matrix

Our series of tests was based on a test matrix that covered a wide range of parameters (fig. 4). It was based on the two laser technologies described above: the TruMark 6030 nanosecond laser for annealing marking, and the TruMicro Mark 2000 femtosecond laser for black-marking. All possible combinations of the following parameters were then taken into account for each marking:

- Different concentrations of immersion passivation (0.02%, 0.04%, 0.08%) and spray passivation chemicals (0.02%)
- Different passivation times (30 seconds, 10 minutes, 30 minutes)
- Different temperatures of the passivation solution (room temperature, 55–65°C, 80–85°C)

Piecing together all these parameters produced a test matrix with a total of 72 different combinations, which we analyzed in our study. We applied the same marking to all the sample parts. This consisted of a black square, a data matrix code, a symbol and a line of human-readable text – in other words, the typical array of markings used for medical devices (see below).

Passivation	Laser	Concentration	Time	Temperature
Immersion (deconex® MT 41)	TruMark 6030 (ns)	0.02%	30 s	room temperature
	TruMicro Mark 2000 (fs)	0.04%	10 min	55–65°C
		0.08%	30 min	80–85°C
Spray (deconex® MT 41)	TruMark 6030 (ns)	0.02%	30 s	room temperature
	TruMicro Mark 2000 (fs)		10 min	55–65°C
			30 min	80–85°C

Figure 4: Test matrix for the test series with TRUMPF marking lasers and the novel passivating agent deconex® MT 41.

Corrosion resistance of laser markings

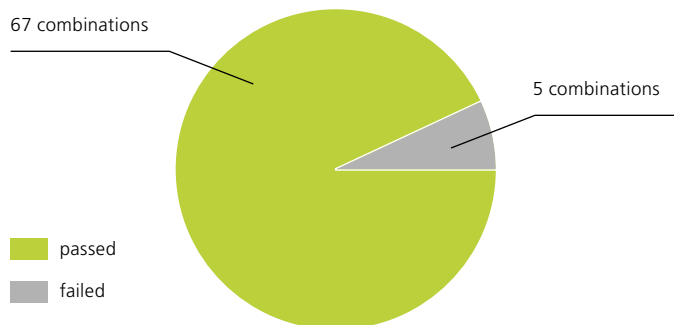
Corrosion testing of the laser-marked sample parts made of medical-grade stainless steel 1.4112 was carried out in accordance with ASTM A967 (Practice F:

Free Iron Test). The results of these tests are shown in figure 5. A total of 67 of the 72 parameter combinations successfully passed the corrosion test.

Passivation	Laser	Concentration	Temperature	Time	Free iron test passed?
Immersion	ns	0.02% /	room temperature	30 s	□ ⁽¹⁾
		0.04% /	55–65°C	10 min	■
		0.08%	80–85°C	30 min	■
Spray	ns	0.02%	room temperature	30 s	□
			55–65°C	10 min	■
			80–85°C	30 min	■
Immersion	fs	0.02% /	room temperature	30 s	■
		0.04% /	55–65°C	10 min	■
		0.08%	80–85°C	30 min	■
Spray	fs	0.02%	room temperature	30 s	■
			55–65°C	10 min	■
			80–85°C	30 min	■

Figure 5: Results of corrosion testing of stainless steel 1.4112 based on ASTM A967 (Practice F: Free Iron Test). Out of a total of 72 combinations, 67 passed the free iron test.

⁽¹⁾For C = 0.04%



The test results in figure 5 include some notable findings. Black-markings applied by the femtosecond laser do not exhibit any corrosion after immersion or spray passivation with deconex® MT 41, regardless of the concentration and temperature of the passivating agent. Particularly noteworthy is the fact that the gentlest form of passivation – spray passivation with a 0.02% concentration at room tempera-

ture for 30 seconds – results in a stable passivation process and no detection of free iron. The concentration in this case is approximately one thousand times lower than that used in conventional nitric acid immersion passivation. This makes the process an extremely economical alternative to conventional nitric acid passivation. The sample parts marked by the nanosecond laser were also passivated by

means of immersion in deconex® MT 41. Observations showed that immersion passivation can only be performed reliably at temperatures substantially above room temperature. Spray passivation can also be used to generate a corrosion-resistant passive film in the case of annealing marking. However, our study showed that spray passivation at room temperature requires a somewhat longer exposure time (10 min, 30 min) to achieve a reliable passivation process. It is also worth noting that passivation with deconex® MT 41 – even at the low concentration of 0.02% – forms a protective passive film that meets

the corrosion resistance standards specified in ASTM A967.

To ensure maximum process reliability, we therefore recommend performing immersion passivation with a higher concentration (0.08%), at a higher temperature ($\geq 55^{\circ}\text{C}$) and with a longer exposure time (≥ 10 min). In the case of spray passivation, the passivation process is facilitated by the additional oxygen from the air. As a result, it is possible to apply similar recommended temperatures and exposure times, but at a significantly lower concentration (0.02%).

Legibility and contrast

Legibility of the markings is maintained in both passivation methods, with a comparable level of

contrast retained after both immersion passivation and spray passivation (fig. 6).



Figure 6: Comparison of annealing markings and black-markings subject to immersion and spray passivation. There are essentially no observable differences in legibility and contrast between the two passivation methods.

Part no.	Passivation	Laser	Concentration	Temperature	Time
V029	immersion	fs	2%	room temperature	10 min
V065	spray	fs	2%	room temperature	10 min
V017	immersion	ns	4%	80°C	10 min
V062	spray	ns	2%	80°C	10 min

The study also included a comparison of the contrast before and after immersion passivation (fig. 7). The

contrast of the black-marking remained completely unchanged even after passivation.

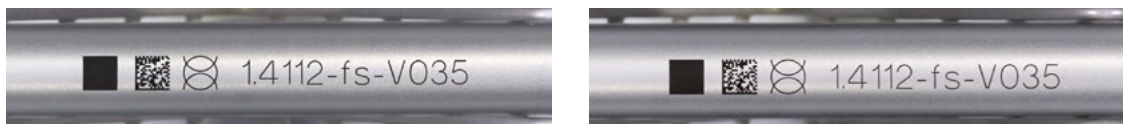


Figure 7: Black-marking before (left) and after (right) immersion passivation in deconex® MT 41 (0.02%, 10 min, 80°C).

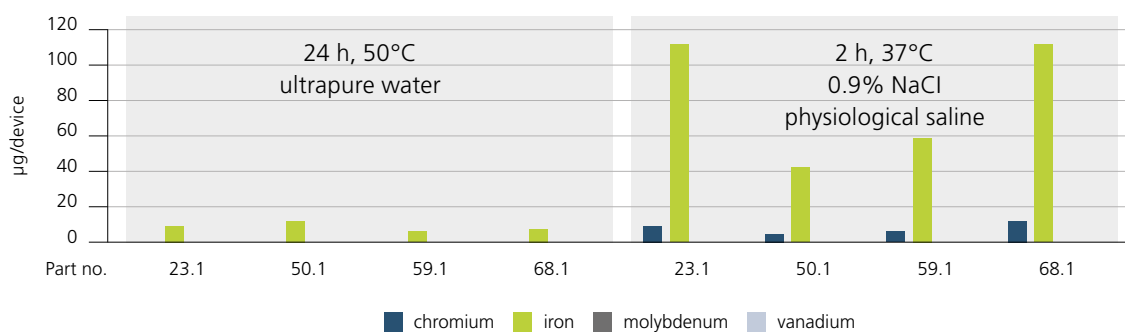
Mass spectrometry (ICP-MS)

To complete our study, we performed a chemical analysis of the alloying elements released into solution by the sample parts. To do this, we applied the method of inductively coupled plasma mass spectrometry (ICP-MS) and performed measurements in accordance with ISO 10993-12 and ISO 10993-18. Release of the alloying elements took place in ultrapure water (24 h, 50°C) and in physiological saline solution (2 h, 37°C), extracts of which were then analyzed by ICP-MS. A total of four sample parts were analyzed, marked either by a nanosecond or a femtosecond laser and passivated either by immersion or spray treatment. The table in figure 8 shows the exact exposure times, concentrations and temperatures in each case.

As expected, small amounts of iron atoms were found in all the samples of ultrapure water. However, the sample parts treated using spray passivation tended to show slightly lower levels of extractables than those treated using immersion passivation. We also found that extraction tended to be somewhat higher for the black-markings than for the annealing markings applied by the nanosecond laser. One explanation for this could be that the microstructuring that occurs during black-marking creates a larger net surface area, allowing more iron to be extracted. Nevertheless, this remains within a perfectly acceptable range with a total extraction measurement of 11 µg/device.

Part no.	Passivation	Laser	Concentration	Temperature	Time
V023.1	immersion	ns	0.08%	55–65°C	10 min
V050.1	immersion	fs	0.08%	55–65°C	10 min
V059.1	spray	ns	0.02%	55–65°C	10 min
V068.1	spray	fs	0.02%	55–65°C	10 min

Release of alloying metals



The alloying elements iron and chromium were found in the physiological saline solution. Quantitative analysis indicated that the maximum amount

of extracted chromium was significantly below the parenteral limit of 1,070 µg/day for both annealing (ns) and black-marking (fs).

Figure 8: Alloying elements of four different sample parts treated with different laser markings (annealing, black-marking) and passivation methods (immersion, spray).

Conclusion

The main purpose of this study was to demonstrate that the combination of TruMark marking lasers and the novel passivation method delivers excellent results in terms of marking quality and corrosion resistance – even using a “worst-case material” in the form of stainless steel 1.4112, which is particularly prone to corrosion. The new deconex® MT 41 solution, which is based on heavily diluted nitric and phosphoric acid, proved to be an economical and environmentally friendly choice for performing passivation of laser-marked medical-grade steels in both immersion and spray treatments. The passivation process did not alter the contrast or legibility of the symbols and lettering applied by means of annealing and black-marking. In the case of black-

markings, even the gentlest spray passivation treatment resulted in a passive surface film on which no free iron could be detected by the ASTM A967 free iron test method. Spray passivation has several advantages over conventional nitric acid-based immersion passivation. Thanks to the low concentration of chemicals, the passivation process can be performed successfully and very efficiently at temperatures of up to 85°C. The low dose of chemicals means that the marking remains clearly legible. Spray passivation even works well for passivating complex geometries such as blind drill holes – and its low chemical consumption makes this method more economical and environmentally friendly than conventional passivation methods based on high doses of nitric acid.

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The following partners supported TRUMPF Switzerland in carrying out this study:

Borer Chemie AG
Gewerbstrasse 13
CH-4528 Zuchwil

Martin Leuenberger
Product Manger Industrial Division
martin.leuenberger@borer.ch

Miele AG
Limmatstrasse 4
CH-8957 Spreitenbach

Thomas Raether
Regional Sales Director
Miele Professional LMD
thomas.raether@miele.com

Niutec AG
Else-Züblin-Strasse 11
CH-8404 Winterthur

Lucio D'Ambrosio
Business Unit Manager Medical Devices
lucio.dambrosio@niutec.ch

TRUMPF



TRUMPF Schweiz AG,
TRUMPF Strasse 8, 7214 Grüşch, Switzerland