



**Damstahl**  
stainless steel solutions

# **Chemical Surface Treatment of Stainless Steel**

Types of Process, how they work and their Limitations

## Chemical Surface Treatment of Stainless Steel Types of Process, how they work and their Limitations

Any manufacturing or handling of stainless steel implies the potential risk of weakening the corrosion resistance. Should this weakening be larger than the built-in safety margin for the steel, as compared to the corrosivity of the environment, one has to reestablish the original corrosion resistance of the steel. In most cases, the cheapest and safest way to do this is by performing a chemical surface treatment.



*Bluish heat tinting around welds in a 4301 stainless steel tank. If kept un-treated, the risk of pitting corrosion in the bluish zone is significant, and therefore, the heat tinting must be removed. The easiest way to do this is a pickling.*

### Pickling

By far the most important chemical treatment, the pickling consists of an aqueous solution containing in between 10 and 20 % nitric acid (HNO<sub>3</sub>) and between 1 and 8 % hydrofluoric acid (HF). High-alloy stainless steel types require an aggressive pickle containing a high concentration of HF, while the “normal” 4301 and 4401 grade steels should be pickled in a milder acid with a lower content of HF. Instead of HF, some pickles contain hydrochloric acid (HCl) as “activator”; however, using such aqua regia pickles implies a serious risk of pitting corrosion during the pickling process. HCl-based pickles are not recommended!

At room temperature, the pickling time may be anything from 30 minutes to several hours, depending upon the pickle itself as well as the darkness of the heat tinting to be removed (the darker, the longer time required) and the concentration of metal contaminations in the bath.

After pickling, all contaminations and inclusions in the steel surface have been dissolved, along with the heat tinting and the critical de-chromed layer underneath. After the pickling, all the weak spots have been removed efficiently, and (after repassivation) the steel has reestablished its excellent passive layer and thereby its original corrosion resistance.

The main drawback with the pickling process is the fact that it is a powerful etching of the steel. Apart from losing a few microns of thickness (affecting fine tolerances), the surface roughness will usually increase, in particular for very smooth specimens, an effect which may be unwanted in the dairy and medical industry. Here, the surface roughness should be kept low in order to make life difficult for micro organisms, and frequently, a limit of 0.6 µm for Ra is used as the upper limit.

In additions, even small variations in the surface roughness may affect the visual appearance of the specimen; however, this is mainly a cosmetic problem.



*Pickled weld on a 4404 specimen. Please note that the specimen appears slightly mat – almost like after a glass blasting. This is because of the increased surface roughness due to the etching of the steel.*

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Applying the pickle can be done in two ways. The easiest one is to simply immerse the specimen into the pickling bath. However, if this is not possible, the pickle can be applied as a paste. In this case, one has to use a pickle in which a “thickener” has been added, so that the product resembles a paste. Thereby, one can “paint” the pickle onto selected parts of the specimens.

Note that the lowest alloyed ferritic types (such as 4003 or 4512) are suitable for pickling, and neither are the sulphur alloyed fine machining steel types (such as 4305) or any of the martensitic ones. Higher alloyed ferritics (4509, 4521) may be pickled, but require a milder pickle than the austenites. In Denmark, using hydrofluoric acid pickles require a special permit which can be obtained at a police station.

### Passivation

The purpose of a passivation is to strengthen the natural protective oxide film of the steel, and in addition, non-metallic inclusions are largely dissolved. Normally, the bath consists of pure 18-25 % nitric acid (HNO<sub>3</sub>), and typically the process time is about one hour. As above, sulphur alloyed steels and low-alloyed ferritics need special treatment, i.e. di-dichromate inhibited nitric acid.

A significant advantage of the passivation is the fact that the surface roughness is not affected (measurably) by the process. A passivation is therefore an excellent treatment after a grinding or glass blasting. A major disadvantage is the lack of effect on the heat tinting. To remove these and the dechromed layer underneath, a pickling is required – or a gentle grinding followed by a passivation.



*Left: Using pickling paste on a weld on the inside of a 4436 steel pipe.*

*Right: Steel-Tech “Pickle Gel 122”, a nitric acid + hydrofluoric acid based paste, useful for normal stainless steel. Applied by using a special, acid resistant brush.*

### Decontamination

Literally, decontamination means de-poisoning, and that is exactly what is happening. It's a semi-advanced dish-washing where all impurities are removed, while the stainless steel is hardly affected at all; neither heat tinting, nor the natural passive layer, and therefore decontamination does not affect the surface roughness. In addition, decontamination does not affect most rubber and plastic types, all of which make the process very useful in i.e. the medical industry and other super-critical equipment where etching of the steel itself or damage of the gaskets are unacceptable. Many polymers do not like nitric acid or other strongly acidic oxidants.

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Decontamination is typically performed in a solution of 2-10 % of a weak acid, such as phosphoric acid, nitric acid, citric acid, formic acid, oxalic acid or so. The temperature can be anything from 20 to 90 °C, and the process time may exceed many hours if the impurities are very sticky.

Iron contamination is a particular problem, but frequently, one can get away with decontamination as compared to a pickling. Rust (iron oxides and hydroxides) is generally slowly soluble in nitric acid, but much easier to cope with in a hot mixture of citric acid and phosphoric acid. Metallic iron, on the other hand, is easier soluble in nitric acid.

### Electro Polishing

Electro polishing is the only surface treatment process using an external current source. Typically, the bath is a strong mixture of sulphuric acid and phosphoric acid, the temperature is above 50 °C, and using a rectifier, the specimen is connected to the anodic pole. As cathodes, stainless steel is normally used.

During the process, the steel is slowly dissolved and, as the etching primarily takes place from the tops of the micro-roughness, the process minimizes the difference in between the top and the bottom of the surface profile. This “leveling” process reduces the surface roughness, and the surface becomes gradually brighter.

Apart from producing a very bright surface, the corrosion resistance of an electro polished stainless steel is better than any other surface (of the same type of steel, of course!). This is linked to the low surface roughness, making it increasingly difficult to form harmful local environments. Above the water-line, the main benefit is the inability of salts and water to stick to the bright surface, causing an electro polished 4301 to perform almost as well as a 4401, 2b.

In theory, electro polishing is able to remove heat tinting. However, this may not always be the case. If heat tinting is the problem, a pickling should be performed prior to the electro polishing.

The drawback of electro polishing is mainly the price. It is a complicated and expensive process, partly due to the equipment and partly due to the trouble mounting the cathodes and performing the process. Consequently, electro polishing is a process which is most widely used within critical appliances, such as the medical business where the ultra-low surface roughness is essential for hygienic reasons.

### Chemical Surface Treatment, Overview:

	Bath	Heat Tinting	Cr Oxides	Roughness
Pickling	10-20 % HNO <sub>3</sub> + 1-8 % HF	Removed	Removed	0,30-1,00
Passivation	18-25 % HNO <sub>3</sub>	No effect	Strengthened	No effect
Decontamination	2-10 % "semi-weak acids"	No effect	No effect	No effect
Electro Polishing	60-70 % H <sub>2</sub> SO <sub>4</sub> + H <sub>3</sub> PO <sub>4</sub>	Some effect	(Removed)	Decrease