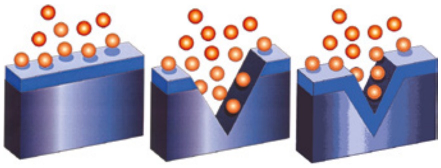
Post-fabrication surface treatment of stainless steels

Why surface finishing is important



The passive layer of stainless steel is only a few millionths of a millimetre.

In terms of surface quality, the food and beverage industry is among the most demanding end-use sectors because good cleanability is essential.

Stainless steel is shielded from the environment by a thin, protective and invisible surface layer – the passive film – that consists mainly of chromium oxide. The oxygen content in the air or in water is usually sufficient to create this passive film and repair it if damaged. However, some fabrication procedures and imperfections may disturb this self-healing process and reduce the corrosion resistance of stainless steel. In this case, post-fabrication treatments are necessary to restore the corrosion resistance, the hygienic and aesthetic qualities of the stainless steel's surface. The procedures used are usually determined by the corrosivity of the environment, the application, the corrosion resistance of the steel grade selected and the size of parts or fabrications. There are both mechanical and chemical cleaning methods that can be used – sometimes in combination – to obtain the required properties [1].

The level of cleanliness required on a stainless steel surface depends on the end-use. In some cases only degreasing and removal of visible contamination is needed. General cleaning should be done by mechanical and/or chemical cleaning methods. Materials must be degreased before acid treatment and vigorously scrubbed with hot water and bristle brushes – or at least by high-pressure water jet, where appropriate. In applications such as those found in the pharmaceutical industry, food and beverage industry, medical products or the nuclear industry, a very high level of cleanliness is required, which can only be achieved by dedicated procedures, including electropolishing[1].

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[1] *Electropolishing Stainless Steels, Materials and Application Series, Volume 11, Euro Inox, 2010, http://www.euro-inox.org/pdf/map/Electropolishing_EN.pdf*

Mechanical methods

Photo: *3M, Brussels (B)*

Grinding and polishing are particularly cost-effective when surfaces have to be treated locally. Photo: CIBO, Tildonk (B)

Grinding and polishing

Grinding and polishing are common methods of removing surface defects, heat tint and scratches. It is important to use a method that avoids unnecessary roughening. When grinding is used on stainless steel, it is advisable to start with rough grinding (such as 40–60 grit), followed by several stages of finer abrasive treatments (180 grit and higher). The last stage should produce a surface as close as possible to the original surface or the surface desired. Additional polishing may also be necessary, if surface requirements are exacting.
A flapper wheel is often sufficient to remove heat tint from welding or surface contamination. Discs, wheels and belts should not contain iron, iron oxide, zinc or other undesirable materials that can contaminate the metal surface. Abrasives used on other metals should not be used on stainless steel [2]. In the event that grinding is not followed by any other technique (for example, pickling), the surface should be completely free of defects, heat tints and scale [3].

Blasting

Blasting can remove high-temperature oxides as well as iron contamination. Clean, previously unused abrasives, such as glass beads, iron-free silica or alumina sand are recommended for abrasive blasting. Steel shot or grit is not recommended for blasting stainless steel surfaces, since their use can induce embedding of iron particles. The use of stainless steel shot or grit reduces the danger of rusting and iron contamination but cannot completely eliminate the possibility of embedding residues of iron-oxide scale [2]. Blasting material must not have been previously used for carbon steel. Similarly, since they become increasingly polluted (even if only used for blasting contaminated stainless steel surfaces), abrasives should not be used too many times [3].

Blasting can be a dry or wet process. In the dry process pressurised air is used as a bead carrier. In the wet process the liquid is tap water. There are several advantages over chemical surface treatments:

- No previous de-greasing is required.
- No aggressive or toxic chemical is used in the process (the mineral shot is considered inert).
- Personal protective-equipment requirements are minimal.
- No process-water treatment is required for disposal.

Blasting is often preferred to produce uniform finishes on larger assemblies Photo: Centro Inox, Milan (I)

In cases where a totally iron-free, scale-free surface is required, abrasive blasting may be followed by a short pickling treatment [2].

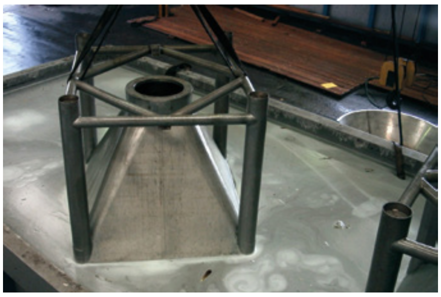
Brushing

Brushing can remove heat tint quickly and efficiently. Nylon brushes usually provide a satisfactory result. These methods cause no significant roughening of the surface. However, they do not guarantee complete removal of the chromium-depleted zone. The rule of using clean tools which have not been used on carbon steels should also be applied in brushing [3].

Water jetting

Cleaning with water pressure up to 70 MPa is recommended for the removal of grease, oils, chemical deposits (except adsorbed chemicals), dirt and even moderately adherent scale. It has proved effective for various contaminants, when they are not actually bonded to the surface. It is mostly used for cleaning piping assemblies that can withstand the pressures involved [2].

Chemical methods



Chemical surface treatment by immersion creates optimal conditions for consistent results. Photos: Edward Uittenbroek, Gouda (NL)

Acid pickling by immersion

Acid descaling or pickling is the removal of heavy, tightly adherent oxide films resulting from hot-forming operations, heat treatments (such as annealing or hardening) or welding. Because most stainless steel products received from the producing mill have been pickled, descaling is required only when material has been exposed to high temperatures in fabrication [1].

Pickling is the most common chemical procedure used to remove oxides and iron contamination. If suitable equipment is available, it can be a convenient method. Pickling normally involves an acid mixture containing nitric acid (HNO_3), hydrofluoric acid (HF) and, sometimes, sulphuric acid (H_2SO_4). Hydrochloric acid (HCl), which is often used in the chemical surface treatment of carbon steels, is not suitable for stainless steels, due to the risk of pitting corrosion [3]. Details of acid-pickling solutions and process conditions are to be found in the Appendix.

Exposure to a pickling solution for more than 30 minutes is not recommended. The product should be drained, thoroughly washed with water and checked for the effectiveness of the treatment. Additional treatment can follow. Most picking solutions will loosen weld and heat-treatment scale, but may not remove them completely. Intermittent scrubbing with a stainless steel brush or fibre-bristle brush may facilitate the removal of scale particles and products of chemical reaction (i.e. pickling smut). Materials must be water-rinsed after pickling and the pH of the final rinse water should be between 6 and 8 for most applications or 6.5 and 7.5 for critical applications. To minimize staining, surfaces must not be permitted to dry between successive steps of the acid cleaning or passivation and rinsing procedure. Thorough drying should follow the final water-rinse [2].

Thorough rinsing prevents staining.
Photo: Edward Uittenbroek, Gouda (NL)

Contamination on the surface can impair the pickling process and make it ineffective. Stainless steel surfaces should be degreased before acid treatment and must be scrubbed with hot water and bristle brushes – or with a high-pressure water jet in less severe cases. The use of suitable chlorine-free and chloride-free degreasing agents is highly effective [4].

The disposal of pickle liquor is a growing problem, tending to limit immersion pickling to those fabricators and chemical cleaning contractors who have pickling tanks and approved disposal arrangements [1].

Swabbing – pickling with paste

For localized pickling or if the fabricated component is too large to be immersed, commercial pickling paste can be very effective. It is recommended to pre-treat oxides, slag and weld defects mechanically. Best results are achieved when welds are still warm and the weld oxides less hard. After mechanical treatment, the area to be pickled should be cooled to below 40 °C. Organic decontamination and degreasing should be carried out before pickling [3]. Pickling paste can be applied with a paint roller or nylon brush. Paste must be washed off within 15–30 minutes of application [1], before the paste dries. At high temperatures and when prolonged pickling times are required, it may be necessary to apply more pickling paste, to prevent it drying out. Pickling should not be done in direct sunlight. Even if, for environmental and practical reasons, neutralisation of the pickling paste is carried out on the metal surface, thorough rinsing with water is vital. High-pressure water jet and cleaning with clean tap water is preferable. Deionised water is used for the final rinsing of sensitive surfaces [3].

For occasional use, smaller parts or local treatment, pickling paste is a practical solution.
Photo: Edward Uittenbroek, Gouda (NL)

Spray pickling is an option for components that are too large for immersion treatment. Photo: Vecom, Maassluis (NL)

Only clean metallic surfaces create the necessary conditions for the passive layer to form properly on stainless steel.

Personnel must wear protective clothing and be trained in safe-handling procedures, as in the case of acid pickling by immersion. Waste water must be neutralised.

Spraying

Spraying with pickling solution or pickling gel is suitable for pickling large surfaces, for example when the removal of iron contamination is also desired. This can be done by alkaline, emulsion, chelate, acid, solvent, detergent cleaners or a combination of these. Safety precautions should be followed [3].

Cleaning with passivation

The term “passivation”can have two distinct meanings:

- It can describe the natural process by which a thin, transparent and strongly adherent layer forms automatically on the surface of stainless steel when oxygen is present.
- It can also refer to dedicated chemical processes, which accelerate the buildup of the passive layer and create optimal conditions for its formation.

The latter has a welcome side-effect: it efficiently removes contaminants such as shop dirt, iron particles from cutting tools and machining lubricants from fabrication operations. Some manufacturers and end-users of food and pharmaceutical processing equipment demand passivation as a final surface-treatment stage [5].

Passivation by chemical treatment with a mild oxidant such as nitric acid solution can be performed in cases where enhancement of the spontaneous formation of the protective passive film is required. Cleaning treatments using other chemicals are also described in ASTM A380 [2]. However, the most common treatment is a 20–40 % solution of HNO_3 at 50–60 °C. The complete passivation treatment includes degreasing, immersion and rinsing. Degreasing, preferably in a non-chlorinated solvent, removes organic contaminants from the surface. Different grades of stainless steel should not be mixed in the same passivating bath, as this can initiate corrosion where surfaces come in contact [1].

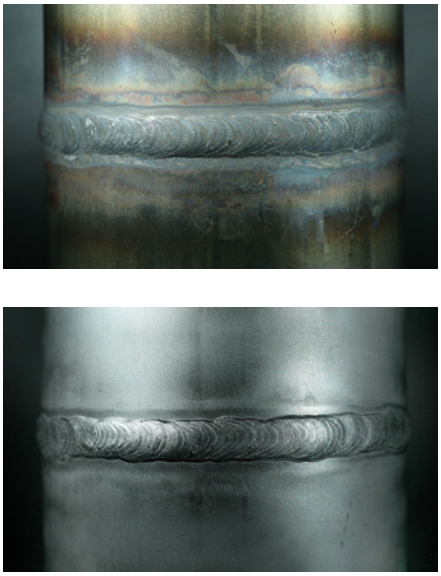
Nitric acid has the disadvantage of being hazardous, from a health and environment point of view. Another option is passivation with

There are suitable chemical treatment techniques for components of any size. Photo: Edelstahl-Oberflächen-Technik, Wedemark (D)

citric acid, a milder alternative to nitric acid. While milder to stainless steel, citric acid nevertheless creates acidic waste and therefore still needs to be disposed of properly.

Another passivation solution is the use of chelating agents. These are extremely versatile, highly effective compounds, which bond to and remove a variety of metallic ions that would otherwise adversely affect the corrosion resistance of the alloy. Commonly used chelates are polyfunctional organic carboxylic acid, such as EDTA and citric acid, with salts containing hydroxyl and amine constituents. However, the problem with at least some chelate agents is that wastewater treatment plants are unable to decompose these sequestering agents, which means that heavy metals are transported through the wastewater plant untreated, directly into nature [5].

Some alternative and proprietary solutions contain no nitric acid and are both user-friendly and environment-friendly. These are usually based on hydrogen peroxide with additions of stabilising agents [6]. Tests with acceptance criteria to demonstrate that the passivation procedures are effective can be found in ASTM A967 [7].

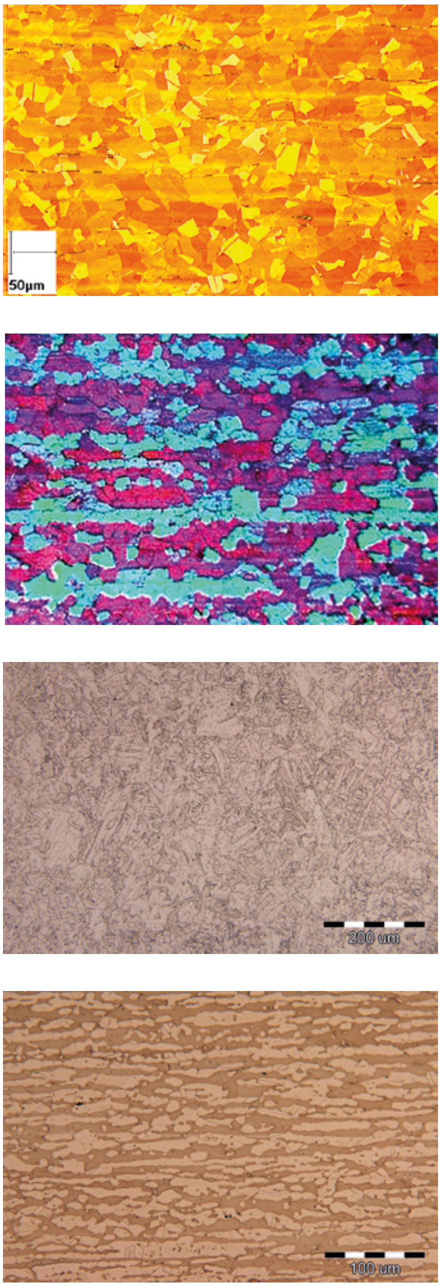


Tube weld before and after pickling

Pickling different stainless steel grades

The pickling behaviour of a stainless steel grade depends on its alloying content, but also on fabrication factors. For this reason, there is no single process effective for all stainless steel grades and fabrication techniques. Part size and the number of parts to be treated are additional criteria for choosing the appropriate pickling agent and application method.

Austenitic stainless steels such as 1.4301/304, 1.4307/304L, 1.4401/316, 1.4404/316L are considered fairly easy to pickle. Mixtures of nitric and hydrofluoric acid in water are still the most widely used pickling solutions. The effectiveness of these mixed-acid solutions can be adjusted within very wide limits by varying acid concentration, temperature and time. The concentration of mixed acids in a water solution is always best determined by actual testing. Conditions are adjusted by the surface conditions of the material and very often vary from 5 % up to 25 % nitric acid and from 0.5 % to 3 % hydrofluoric acid (both by volume). For light scale on the surface, 12–15 % nitric acid and 1 % hydrofluoric acid are usually satisfactory [8].



The composition of a pickling agent, process time and temperature must be adapted to the the microstructure and allying content of a stainless steel grade. From above to below: austenitic, ferritic, martensitic and austenitic-ferritic (duplex) microstructures. Photos: Aperam, Luxembourg (L), Acroni, Jesenice (SLO)

High-alloyed austenitic stainless steels and duplex stainless steels are more corrosion resistant and need a more aggressive mixture of acids, higher temperatures and/or longer times. The risk of over-pickling these grades is low. Steel grades in this group are super-austenitic and duplex grades. When pickling high-alloyed grades, mechanical pre-treatment to break or remove oxides may be advisable [3]. The scale on duplex stainless steels tends to be thin, adherent and more resistant to chemical removal than that on austenitic stainless steels of comparable corrosion resistance. Weld discolouration can be removed chemically by pickling – for example, pickling of 1.4462/2205 with a 20 % HNO_3 and 5 % HF solution. This solution both dissolves the chromium oxide and attacks the stainless steel, so the chromium-depleted layer is removed [9].

Ferritic and martensitic stainless steels such as 1.4016/430, 1.4006/410 and 1.4313 have a lower chromium content than austenitic stainless steels. In general, this means they have lower corrosion resistance and are “easier” to pickle. Pickling conditions usually involve less aggressive pickling solutions and/or shorter pickling times [3]. Pickling under the same conditions as for austenitic stainless steels will not usually give a satisfactory result.

Martensitic stainless steels in hardened condition are subject to hydrogen embrittlement or intergranular attack when exposed to acids that cause hydrogen to be generated on the item being cleaned. Cleaning by mechanical methods or other chemical methods is recommended. If acid treatment is unavoidable, parts should be heated at 120–150 °C for 24 h immediately following acid cleaning, to drive off hydrogen and reduce susceptibility to embrittlement. The cleaning methods given in the Appendix will not lead to hydrogen generation. Post-cleaning thermal treatment is therefore not required when these solutions are used for cleaning [2].

Finishing treatments for welds, oxide scale and heat tint

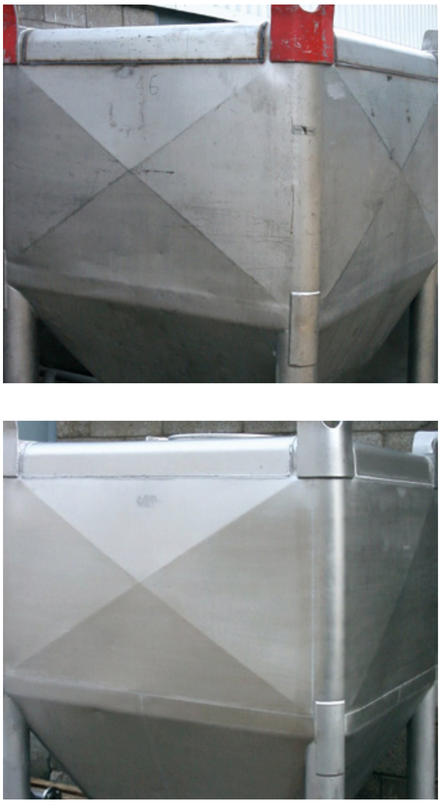
Oxide scale and heat tint form on the surface of stainless steel when the steel is exposed to high temperatures – as in heat treatment or welding. With heating, the passive layer is destroyed or damaged and its protective properties impaired. In addition to a damaged passive film, the surface adjacent to oxide scale suffers chromium depletion. Here, the oxide scale, heat tint and chromium depleted zone must be fully removed, to restore the steel’s corrosion resistance.

Free iron, iron contamination

Iron particles can originate from machining, cold-forming and cutting tools, blasting sand or grit, grinding discs contaminated with lower-alloyed materials, transport or handling in mixed manufacture, conveyer belts, forklift manipulation, etc. Small iron particles will corrode when exposed to humidity in the air and leave rusty spots on the stainless steel surface. Larger particles may also cause crevices. In both cases, corrosion resistance is reduced [3].

The citric acid - sodium nitrate treatment is considered the least hazardous option for removing free iron and other light surface contamination. Spraying the solution, as opposed to immersion, can reduce cleaning time [2].

Precautions must always be taken to minimize iron contamination in the reuse of cleaning and pickling solution, in water rinsing, in circulating cleaning solution and rinse water and in protecting cleaned surfaces.



Passivation also has a cleaning effect and removes iron contamination which may have occurred in a mixed-material workshop. Photo: Edward Uittenbroek, Gouda (NL)

Neutralisation and waste treatment

Waste water from post-pickling rinsing is acidic and contaminated with heavy metals (mainly chromium and nickel that have been dissolved from the steel). This waste water must be treated in accordance with local regulations. Neutralisation with an alkaline agent, such as slaked lime or soda, in combination with settling agent should be carried out. Adjusting the pH value of the waste water causes heavy metals to be precipitated as metal hydroxides. Precipitation is optimal at a pH of 9.5. The heavy metals form a sludge, which must be treated as heavy-metal waste and disposed of accordingly [3].

Transportable modular units create a safe, enclosed environment for the chemical surface treatment of metals.Photo: Poligrat, Munich (D)

Safety rules

The supplier's instructions for personal protective equipment should be followed carefully. Photo: Edelstahl-Oberflächen-Technik, Wedemark (D)

Proper protection for personnel, including face shields, rubber gloves and rubber protective clothing, must always be worn when working with pickling acids. Since noxious gases evaporate from the areas where these chemicals are used, covering the basins with a mixture of acids and adequate ventilation of the space must be maintained. Personnel should be trained on what to do in the case of an accident. Used solutions and process water must be disposed of safely.

Appendix

Table 1. Acid descaling (pickling) of stainless steel [2]

Alloy^{A}	Condition^{B}	Treatment			
		Code	**Solution** *Volume %*^{C}	**Temperature** *°C*	**Time** *minutes*
200, 300 and 400 series, precipitation hardening and maraging alloys (except free-machining alloys)	Fully annealed only	A	8–11 % H_2SO_4^{D} Follow by treatment D or F as appropriate	65–80	5–45 max^{E}
200 and 300 series, 400 series containing 16% Cr or more, precipitation-hardening alloys (except free-machining alloys)	Fully annealed only	B	15–25 % HNO_3 plus 1–8 % HF$^{F, G}$	20–60	5–30^{E}
All free-machining alloys and 400 series containing less than 16 % Cr	Fully annealed only	C	10–15% HNO_3 plus 0.5–1.5 % HF$^{F, G}$	20 (up to 60 with caution)	5–30^{E}

A *This table is also applicable to the cast grades equivalent to the families of wrought materials listed.*

B *Other heat treatments may be acceptable, if proven by experience, see also: acid pickling on page 3 and martensitic stainless steels in hardened condition on page 7*

C *Solution prepared from reagents of the following weight %: H_2SO_4, 98; HNO_3, 67; HF, 70*

D *Tight scale may be removed by dipping in this solution for a few minutes, followed by water rinsing and nitric-hydrofluoric acid treatment.*

E *Contact time should be the minimum necessary to obtain the desired surface, to prevent over-pickling. Tests should be carried out to establish correct procedures for specific applications.*

F *For reasons of convenience and handling safety, commercial formulations containing fluoride salts may be useful in place of HF for preparing nitric-hydrofluoric acid solutions.*

G *After pickling and water rinsing, an aqueous, caustic, permanganate solution containing NaOH, 10 weight % and $KMnO_4$, 4 weight %, at 71 to 82 °C, 5–60 min, may be used as a final dip for removal of smut, followed by thorough water rinsing and drying.*

Table 2. Acid cleaning conditions for stainless steel [2]

		Treatment			
		Code	**Solution** *Volume %^{C}*	**Temperature** *°C*	**Time** *minutes*

Cleaning with HNO3 - HF

Purpose: for use after descaling by mechanical or chemical methods, as a further treatment to remove residual particles of scale or products of chemical action (i.e. smut), and to produce a uniform “white-pickled” finish.					
200 and 300 series alloys, 400 series alloys containing 16 % Cr or more, and precipitation-hardening alloys (except free-machining grades)	Fully annealed only	D	6–25 % HNO_3 plus 0.5–8 % $HF^{B, C}$	20–60	As necessary
Free-machining alloys, maraging alloys and 400 series alloys containing less than 16 % Cr	Fully annealed only	E	10 % HNO_3 plus 0.5–1.5 % $HF^{B, C}$	20 (up to 60 with caution)	1–2

Cleaning-passivating with HNO_3

Purpose: the removal of soluble salts, corrosion products, free iron and other metallic contamination resulting from handling, fabrication or exposure to contaminated atmospheres.					
200 and 300 series alloys, 400 series, precipitation hardening and maraging alloys containing 16 % Cr or more (except free-machining alloys)	Annealed, cold-rolled, thermally hardened or work hardened, with a dull or non-reflective finish	F	20–50 % HNO_3	50–70 20–40	10–30 30–60

Cleaning with other chemical solutions

Purpose: general cleaning					
200 and 300 series alloys, 400 series alloys (except free-machining grades), precipitation-hardening and maraging alloys	Fully annealed only	N	1 wt % citric acid plus 1 wt % $NaNO_3$	20	60

B For reasons of convenience and handling safety, commercial formulations containing fluoride salts may be found useful in place of HF for preparing nitric-hydrofluoric acid solutions.

C After pickling and water rinsing, an aqueous, caustic, permanganate solution containing NaOH, 10 weight % and $KMnO_4$, 4 weight %, at 71 to 82 °C, 5–60 min, may be used as a final dip for removal of smut, followed by thorough water rinsing and drying.

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