

# Pickling and Passivation

The chemicals used in pickling and passivation are acidic and must be handled with due OHS and environmental precautions as well as neutralisation and suitable disposal of waste. In addition, hydrofluoric acid (HF) is a schedule 7 poison. Stainless steel can corrode in service if there is contamination of the surface. Chemical treatments can be used to improve the corrosion performance of the steel, and hence its appearance in service.

Both pickling and passivation are chemical treatments applied to the surface of stainless steel to remove contaminants and assist the formation of a continuous chromium-oxide, passive film. Surfaces must be free of grease and dirt before using these acid treatments.

Stainless steels resist corrosion best if they are clean and smooth. Clean means being free of contaminants on or in the surface that can either react with the steel (like carbon steel or salt) or that create crevices or other initiation points where corrosion can start. Smooth means having a low surface profile at the 'micro' level. Mechanically abrading the surface can roughen the steel's surface and may also embed unwanted particles. After mechanical cleaning, passivation is required for maximum corrosion resistance.

The common feature of chemical treatments is that they all clean the surface of the steel. They may also smooth or roughen the steel surface, or leave it unaffected depending on which process is chosen. But if carried out properly, they all increase the corrosion resistance.

ASTM A380 Standard Practice for Cleaning, Descaling and Passivation of Stainless Steel Parts, Equipment and Systems is a valuable source of information on pickling and passivation treatments. Other sources of information may be obtained by contacting ASSDA.

## Stainless Steel Products

During steel making, sulphur in the steel is controlled to very low levels. But even at these levels sulphide particles are left in the steel, and can become points of corrosion attack. They can be removed by chemical surface treatment.

Most bar products are slightly higher in sulphur for easier machining, so chemical treatment to remove

inclusions in the surface of these products becomes more important.

Generally mill finishes for flat products (sheet, plate and strip) will be smoother as their thickness decreases.

A No. 1 (HRAP) finish on a thick plate may have dimples or other imperfections and a surface roughness of 5 to 6 micrometres  $R_a$ .

A typical 2B cold rolled finish on 1.7mm thick sheet might have a surface roughness of 0.2 micrometres  $R_a$  or better.

New surfaces will be created during fabrication processes (eg. cutting, bending, welding and polishing).

The corrosion performance of the new surfaces will generally be lower than the mill supplied product for a number of reasons: the surface is rougher; sulphide inclusions sitting just under the surface have been exposed; or mild steel tooling contamination may have occurred.

Chemical treatments that are correctly performed can clean the surface and ensure the best possible corrosion performance.

## Chemical Surface Treatments

These can be grouped into four categories:

**Pickling** - acids that remove impurities (including high temperature scale from welding or heat treatment) and etch the steel surface. 'Pickling' means some of the stainless steel surface is removed.

**Passivation** - oxidising acids or chemicals which remove impurities and enhance the chromium level on the surface.

**Chelating agents** - chemicals that can remove surface contaminants.

**Electropolishing** - electrochemical treatments that remove impurities and have the added benefit of smoothing and brightening the surfaces.

Electropolishing is also an electrochemical process. It removes gross weld scale and heat tint but is not intended to brighten or smooth the surface.

Both pickling and passivation solutions can employ dangerous acids that can damage both the operator and the environment if not handled correctly. Pickling acids for stainless steel are highly corrosive to carbon steel.

It is essential that all acids are thoroughly removed by rinsing the component after completing the process. Residual hydrofluoric acid will initiate pitting corrosion.

If there are crevices, it may be of benefit to neutralise the acid with an alkali before the final rinsing step.

## Pickling

Pickling is the removal of any high temperature scale and any adjacent low chromium layer of metal from the surface of stainless steel by chemical means.

Where the steel has been heated by welding, heat treatment or grinding to the point where a coloured oxide layer can be seen, there is a chromium depleted layer on the surface of the steel underneath the oxide layer.

The lower chromium content causes lower corrosion resistance. To restore the best corrosion resistant performance, the damaged metal layer must be removed, exposing a fully alloyed stainless steel surface.

Pickling time is longer with higher grades, lower temperatures or more severe heat tint, which is usually caused by poor gas purging.



*Example of a good post-weld practice.*

Mechanical removal alone may leave abrasive or other particles embedded (interfering with corrosion performance) or may be impractical. If mechanical means are used, chemical passivation will be required for maximum corrosion resistance.

Procedures incorporating pickling solutions, such as a mixture of hydrofluoric (HF) and nitric ( $\text{HNO}_3$ ) acids, remove the scale and the underlying chromium depleted layer and restore the corrosion resistance.

Mixtures of HF and  $\text{HNO}_3$  are the most common and are generally the most effective. Acids are available as a bath, a gel or a paste.

Commercially available mixtures contain up to about 25%  $\text{HNO}_3$  and 8% HF. These chemicals etch the stainless steel which can roughen and dull the surface.

Pickling solutions also remove embedded contaminants such as carbon steel and ferrous and ferric oxide particles. Pickling solutions other than mixtures of  $\text{HNO}_3$  and HF acids exist and can be used for specialised applications. They tend to be slower.

Pickling pastes, where the solution is mixed with an inert carrier, are commonly used to treat selected areas such as welds. Pickling involves metal removal and a change or dulling in the visual brightness of the metal.

Procedures involving electropolishing are a useful alternative or additional treatment following pickling. Metal removal is achieved and usually results in a bright, smooth and more highly corrosion resistant finish.

### **Passivation**

Passivation is the treatment of the surface of stainless steels, often with acid solutions (or gels), to remove contaminants and promote the formation of the passive film on a surface that was freshly created, eg. through grinding, machining or mechanical damage.

Passivation works by dissolving any carbon steel contamination from the surface of the stainless steel, and by dissolving out sulphide inclusions breaking the surface. Nitric acid ( $\text{HNO}_3$ ) may also enrich the proportion of chromium at the surface. Some chelants also claim to do this.

Common passivation treatments include HNO<sub>3</sub> solutions or pastes which will clean the steel surface free of iron contaminants.

Formulations contain up to about 30% HNO<sub>3</sub> and may also contain other oxidisers such as sodium dichromate. When used correctly, an HNO<sub>3</sub> treatment should not affect the appearance of the steel.

Passivation does not usually result in a marked change in appearance of the steel surface, although mirror polished surfaces should be tested first.

The corrosion resistance of the stainless steel is affected by the roughness of the surface after polishing, with a marked decrease in the corrosion resistance as the surface roughness increases above a R<sub>a</sub> value of about 0.5 micrometres. This roughly corresponds to the surface produced by grinding with 320 grit abrasives as discussed below.

Either passivation or electropolishing can be used to improve the corrosion resistance of polished surfaces.

**Chelants**

Chelants have chemical 'claws' designed to selectively clean the surface.

The carboxylic acid group -COOH is the basis for many chelants which are used in cleaners, water softening and lubricants. The pH and temperature must be correct for the chelant to do its job. Chemicals containing these COOH 'claws' include citric and oxalic acids and EDTA. Citric based formulators are most used as they are not toxic.

Turbulent rinsing of pipes and vessels afterwards is important.

Cleaning by chelating agents tends to be based on proprietary knowledge and systems, and is less standardised than the other methods described. The successful use of these systems needs to be established on a case-by-case basis.

**Chemical vs Mechanical Treatment**

The figure below shows the relative importance of the surface smoothness and chemical treatment on corrosion

resistance. Note that a pickled or passivated rough, matt 36 grit finish could have better corrosion resistance than an untreated 220 grit finish. The study reported by G.Coates (Materials Performance, August 1990) showed the effect of mechanical and chemical treatments of furnace generated heat tint on a high molybdenum grade of 316.

**Electropolishing**

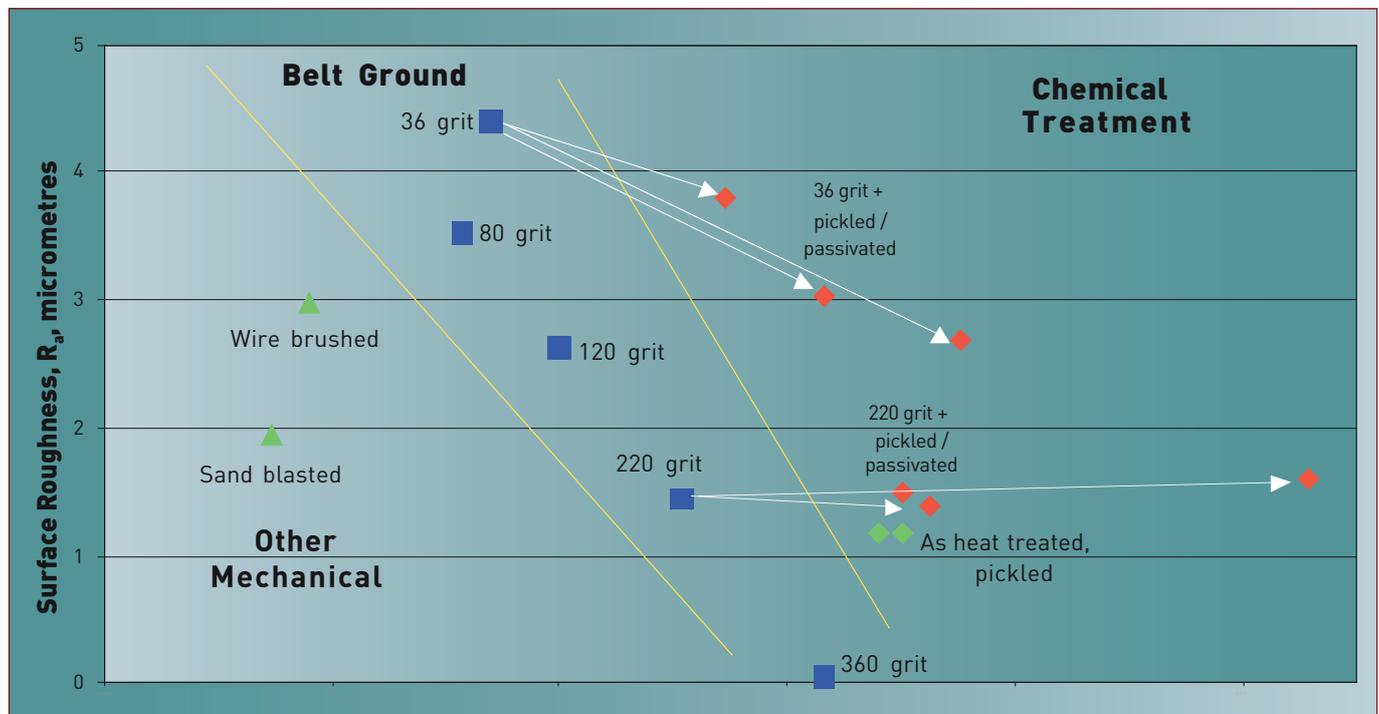
Electropolishing of stainless steel is a method of imparting brilliance to its surface by removal of a thin surface layer, especially the peaks.

Studies have also shown that electropolishing benefits corrosion resistance. The work to be polished is the anode in an electrochemical cell containing a suitable electrolyte.

The process may be considered the opposite of electroplating and is an important production tool in the fabrication of the stainless steels, along with mechanical polishing processes.

Generally speaking, electropolishing supplements the mechanical polishing

Effect of chemical and mechanical treatments on corrosion resistance



Corrosion resistance improves as you go to the right of this graph. The graph shows the relative importance of the smoothness of the surface and chemical treatment of the surface. They can be used together to get the best corrosion resistance.

The study reported by G.Coates (Materials Performance August 1990) looked at the effect of various methods of treating an artificial welding heat tint on a 2B surface.

*Contrasting features of pickling and passivation*

Pickling	Passivation
Removes both weld oxide and stainless steel	Does not remove weld oxides not attack stainless steel
Typically hydrofluoric, sulphuric (or in steel mills, hydrochloric) acid	Nitric acid or electropolishing. Chelating formulations can have similar effects to nitric acid
Removes surface breaking sulphides and carbon steel	Removes surface breaking sulphides and, less rapidly, carbon steel smears
Changes appearance as it lowers gloss by etching	Nitric and chelating treatments should not change appearance. Electropolishing will brighten and slightly smooth it
Usually mixed with nitric acid – and with rinsing leaves a passive surface	Will improve the passive film over a simply pickled one.

methods by providing an economical means of brightening many shapes or forms that cannot readily be finished mechanically.

Electrolytic methods should not be specified to remove surface blemishes such as scratches, burrs, pits, scale patterns, forging marks, etc. although they will do so if such defects are very shallow. It is important to realise that defects initially present on surfaces may be greatly accentuated if not treated appropriately.

Surface condition before electropolishing governs the finished appearance. These processes are also applicable to cast stainless steels. However, the resulting surfaces will not be as smooth as those on wrought materials, unless they are mechanically prepared beforehand.

Most commonly, phosphoric and sulphuric acids are used in conjunction with a high current density to clean and smooth (by metal removal) the surface of the steel. The process preferentially attacks peaks and rounds valleys on the surface and raises the proportion of chromium at the surface.

The technique can have a substantial effect on the appearance, increasing lustre and brightness while only reducing the measured roughness by about 30%.

**Standards**

The four categories of chemical treatment are detailed in a number of standards, but the most commonly used are:

ASTM A380 Standard Practice for Cleaning, Descaling and Passivation of

Stainless Steel Parts, Equipment and Systems.

ASTM A967 Standard Practice for Chemical Passivation Treatments for Stainless Steel Parts.

ASTM B912 Standard Practice for Passivation of Stainless Steels using Electropolishing.

These very useful documents give detailed recommendations on many aspects of selection, application and evaluation of these treatments and are highly recommended.

**Precautions**

Pickling and passivation use strong acids, and normal precautions for safety should be followed. Consult the Materials Safety Data Sheets and product packaging for detailed advice.

Note that hydrofluoric acid is a schedule 7 poison and in concentrations greater than 1% requires a specific licence for use.

For chemical processes that etch the stainless steel, reaction times will increase with increasing grade.

More care is required with 'free machining' grades and these will usually require substantially less aggressive chemicals. The sulphur addition in these steels means they are readily attacked by chemical treatments. Care is also required when treating martensitic or low chromium ferritic stainless steels.

Detailed recommendations for each grade of stainless steel are given in the ASTM Standards.

Bath composition (acid strength and iron concentration) must be checked as extended pickling times or old solutions tend not to give as good a result.

Dirt and grease will mask the surface from treatments outlined above. Therefore, the steel surfaces must be free of these agents before applying chemical treatments.

Many of the chemical treatments described contain strong acids and both handling and PPE requirements must be followed. Before disposal they will require neutralisation. Check with your local authority concerning the requirements for trade waste, neutralisation and disposal.

Many of the chemicals described above will be classified as hazardous substances under State OHS legislation, with implications for purchasing, transport, storage and handling.

Chemical treatments are useful tools in cost effectively achieving peak performance with stainless steels. With appropriate training, hazards associated with their use can be managed.

More details on chemical handling and disposal are given in suppliers' datasheets and Trade Waste and/or Environmental legislation and/or regulations.

*Extract from the Pickling and Passivation section of the Australian Stainless Reference Manual (2012) published by Australian Stainless Steel Development Association (ASSDA)*