



Necessity of Removal of Heat Tints on Stainless Steels to Avoid or Minimize Corrosion

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Preface

This paper, prepared by Giel Notten of NTT Consultancy is covering the subject Heat Tints on Stainless Steels. This part covers the general principals and a theoretical background and is part of Giel's Corrosion Engineering Guide.

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1. Introduction

During welding of stainless steels coloured surface oxide films may be developed in case a perfect inert gas protection is missing. Of course these coloured surface oxides may be formed also during other heat treatments of stainless steels in presence of oxygen.

The presence of these coloured metal oxide films, referred to as heat tints, makes the stainless steels vulnerable to several types of local forms of corrosion.

To avoid these forms of corrosion it is essential that heat tints are properly removed before the stainless steel equipment or piping is exposed to aggressive environments.

2. Heat tints on stainless steels

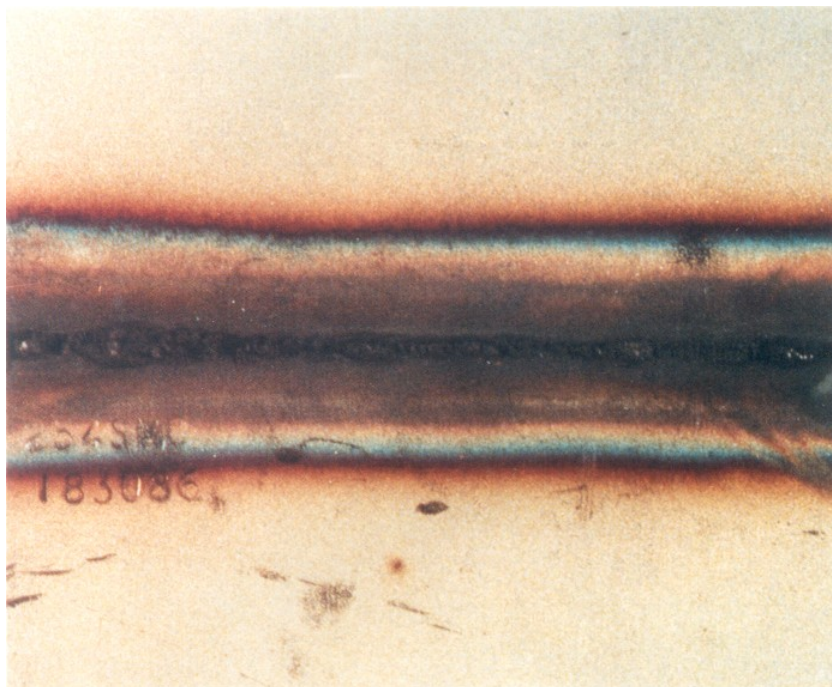
Stainless steel welds made with inadequate inert gas protection develop coloured metal oxide films. In literature this surface discolouration is referred to as heat tint although the term weld discolouration is also used.

As a result of the heat input from welding (or other heat treatment), chromium diffuses outward from the base metal into the surface oxide film, leaving a thin chromium-reduced layer in the underlying base metal. Photo 1 shows a heat tint at the root side of a GTAW weld in duplex stainless steel X2CrNiMoN22-5-3.

Lack of back purge Argon gas shielding has led to the formation of an unacceptable heat tint. First of all these heat tints may lead to an unacceptable appearance of the equipment. Secondly, during operation of the equipment the porous oxide layer may lead to contamination of the process media.

A third, and generally the most serious consequence of thick, porous metal oxide films is a higher susceptibility to corrosion when exposed to aqueous environments.

Photo 1: Heat tint at the root side of a GTAW weld in duplex stainless steel X2CrNiMoN22-5-3 due to lack of back purge Argon gas shielding



3. Effect of presence of heat tints on corrosion resistance of stainless steels

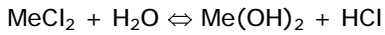
The corrosion resistance of stainless steels is dependent on the presence of a thin, protective, passive oxide layer on the metal surface.

An important reason of the diminished corrosion resistance is the chromium-reduced layer in the underlying base metal at locations of heat tints. Additionally, in the porous heat tints chlorides are selectively adsorbed resulting in higher chloride concentrations and lower pH values. The formation of a more aggressive micro-climate in the porosities of a heat tint can be explained according to the mechanism of pitting.

A corrosion pit is a unique type of anodic reaction. It is an autocatalytic process. That is, the corrosion processes within a pit produce conditions, which are both stimulating and necessary for the continuing activity of the pit. This is illustrated schematically in figure1.

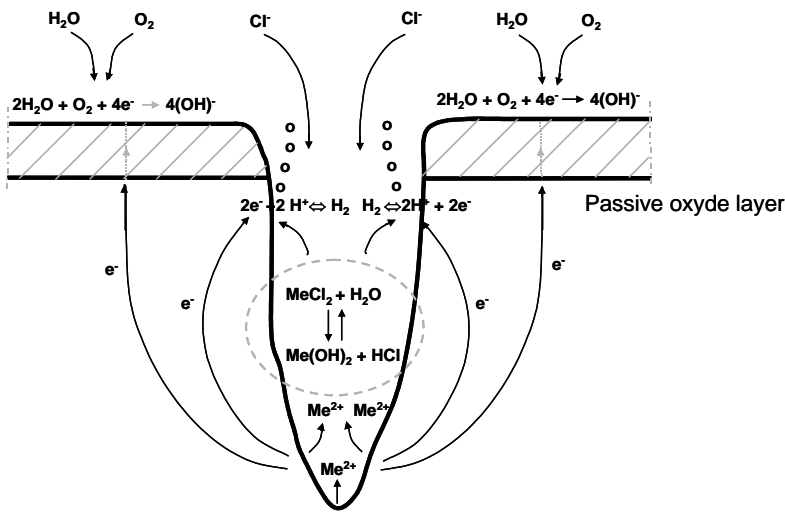
In this figure a metal Me is being pitted by an aerated solution containing some chlorides. Rapid dissolution of the metal occurs within the pit, while oxygen reduction takes place on adjacent surfaces. This process is self-stimulating and self propagating.

The dissolution of the metal within the pit tends to produce an excess of positive charge in the pit, resulting in the migration of chloride ions to maintain electro-neutrality. As a result of hydrolysis of MeCl_2 according to equation:



a high concentration of hydrogen ions exists in the pit and decrease of pH will occur. Both hydrogen ions and chloride ions stimulate the dissolution of most metals and alloys, and the corrosion process accelerates with time.

Figure 1: Schematic illustration of mechanism of pitting.

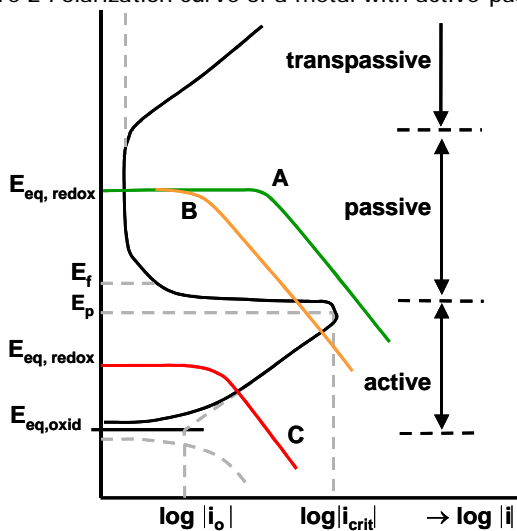


The solubility of oxygen is very low in concentrated solutions, so hardly any oxygen reduction occurs within a pit. This model describes the propagation of pitting as an autocatalytic process.

To understand the mechanism of the diminished corrosion resistance of heat tinted stainless steel one should understand the active/passive behaviour of stainless steel.

Figure 2 shows a typical anodic polarization curve for a metal undergoing an active-passive transition.

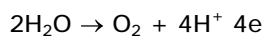
Figure 2 Polarization curve of a metal with active-passive behaviour.



Starting from the equilibrium potential $E_{eq,oxid}$ of the anodic (oxidation) reaction Me/Me^{n+} (black curve), the metal initially demonstrates behaviour similar to non-passivating metals.

That is, as electrode potential is made more positive and dissolution rate increases exponentially. This is the active region. At more noble potentials E_p , the dissolution rate decreases to a very small value and remains essentially independent of potential over a considerable potential region. This is termed the passive region. Finally at very noble potentials, dissolution rate again increases with increasing potential in the transpassive region.

At this high potential a new anodic reaction occurs, namely oxidation of water:



Important characteristics are:

- E_p : (primary) passivating potential
- I_{crit} : critical anodic current density
- E_f : Flade potential, close to the passivating potential, indicates the transition from passive to active behaviour at a decrease of the electrode potential.

Figure 2 shows beside the anodic polarization curve, three different cathodic polarization curves with different consequences on the corrosion behaviour of the metal. In case A (green curve) there is only one stable intersection point which is in the passive region. For such a system, the metal or alloy will spontaneously passivate and remain passive with a very low corrosion rate. This system cannot be made active and always demonstrates a low corrosion rate. This system is typical of e.g. stainless steels in acid solutions containing oxidizers.

Case B (orange curve) is particularly interesting since there are three possible intersection points at which the total rate of oxidation and total rate of reduction are equal. Although all three of these points meet the basic requirements of the mixed-potential theory, the point in between E_f and E_p is electrically unstable and, as a consequence, the system cannot exist at this point. Hence both other points are stable, one point in the active region corresponding to a high corrosion rate and the other point in the passive region with a low corrosion rate. This system may exist in either the active or passive state. In case C (red curve) there is only one stable intersection point which is in the active region, and a high corrosion rate will occur. From a corrosion point of view it is obvious that case A is most desirable.

With an external rectifier the electrode potential of a passivating metal can be brought at the wished positive value and maintaining on this value. Another possibility is the application of a redox-system. To obtain a stable passive situation this redox system has to meet the following requirements:

- the equilibrium potential of the redox-system must be more positive than the Flade-potential of the metal which must be passivated: $E_{eq, redox} > E_f$,
- the cathodic current density of the redox system must have a higher value than the critical current density of the metal: $|i_{c,redox}|_{E_p} > i_{crit}$

Provided that the potential can be maintained in the passive area of the anodic polarization curve, the current required to maintain passivity is very small. This current, I_{pass} , is the current just necessary to plug the "weak spots" where passivity has broken down.

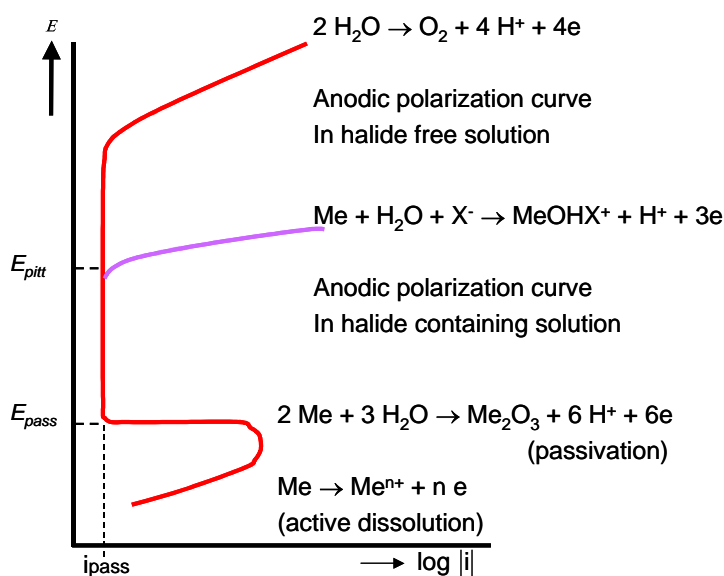
The presence of chlorides has a deleterious effect on the passivation process and favours conditioning for pitting, crevice corrosion and stress corrosion cracking.

Initiation of pitting and stress corrosion cracking is expected to occur at particular locations where, for any reason, the rate of metal dissolution is momentarily high. Chloride ions will migrate to this point and since chlorides stimulate metal dissolution, this charge tends to produce conditions which are favourable

to further rapid dissolution at this particular point. Besides that halides like chlorides have the property to adsorb and settle down in the oxide layer of stainless steel and cause weak spots. Pitting will occur if the corrosion potential is above the so called pitting potential E_{pitt} , which is in most cases more positive than the passivation potential E_{pass} .

This is indicated schematically in figure 3. An increase of chloride content results in a decrease of the pitting potential and as a consequence in an increase of susceptibility for pitting.

Figure 3 Anodic polarisation curves of material with active/passive behaviour in a halide free and halide containing environment.



As more positive is the pitting potential as more pitting resistant is the material

Most pitting is associated with halide ions, with chlorides, bromides and hypochlorites being the most aggressive. Fluorides and iodides have comparatively little pitting tendencies. From a practical point, most pitting failures are caused by chlorides. Chlorides are present in varying degrees in most waters.

Oxidizing metal ions with chlorides are aggressive pitters. Cupric, ferric, and mercuric halides are extremely aggressive. Even very corrosion resistant alloys can be pitted by $CuCl_2$ and $FeCl_3$. Cupric and ferric ions do not require the presence of oxygen to promote attack because their cations can be cathodically reduced; these ions are electron acceptors. This is the reason why $FeCl_3$ is widely used in pitting studies.

Another disadvantageous effect of ferric and cupric ions is the increase of the redox potential in presence of these ions. This indicates that the risk of trespassing the pitting potential will be increased.

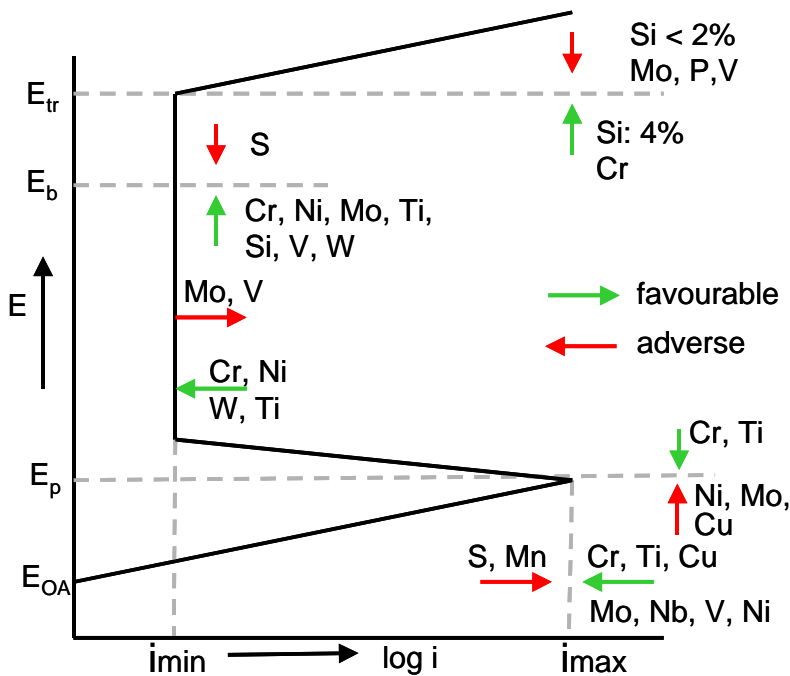
Out of this it can be concluded that the increase of chlorides in the porous oxide layer (heat tints), especially in presence of oxidising components, will increase the risk of pitting.

Beside the environment the pitting potential will also be influenced by alloying components like Cr and Mo.

All different kinds of alloying elements and impurities have different influence on the corrosion behaviour of (austenitic) stainless steels. Figure 4 illustrates the influence of the different alloying elements and impurities on the anodic polarization curve of stainless steel.

Figure 4 Influence of alloying elements and impurities on anodic polarization curve of stainless steel.

E_{OA} : equilibrium potential for anodic process
 E_p : passivating potential
 E_b : pitting potential
 E_{tr} : transpassive potential
 i_{max} : passivating current
 i_{min} : leakage current in the passive state



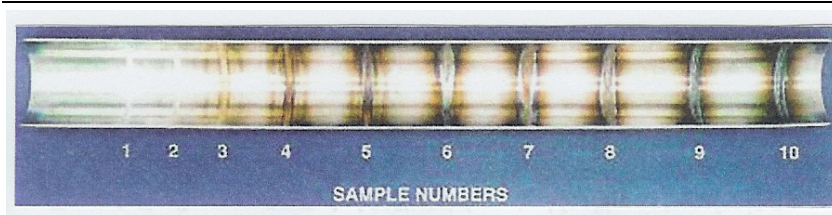
The important influence of Cr is quite clear. One can imagine that the Cr depletion in the upper layer of the stainless steel base metal beneath the heat tint has a disastrous effect on the resistance to localized forms of corrosion like pitting, crevice corrosion and stress corrosion cracking.

It is obvious that presence of heat tints on stainless steel has a harmful effect on the corrosion resistance of stainless steel.

First of all it is a challenge to the stainless steel industry to avoid harmful conditions during welding. However, it is not always possible to avoid these harmful conditions and heat tints will be present.

The American Welding Society (AWS) did perform quite some examinations on the influence of heat tints on corrosion resistance and provided a reference colour chart as shown in Figure 5. This figure shows different degrees of weld heat tinting. The sample numbers refer to the amount of oxygen in the purging gas varying from 10 ppm in No.1 to 25000 ppm in No. 10. The reference chart should be used to identify the degree of heat tint oxide by a number and not to specify the maximum oxide content in the purge/backing gas.

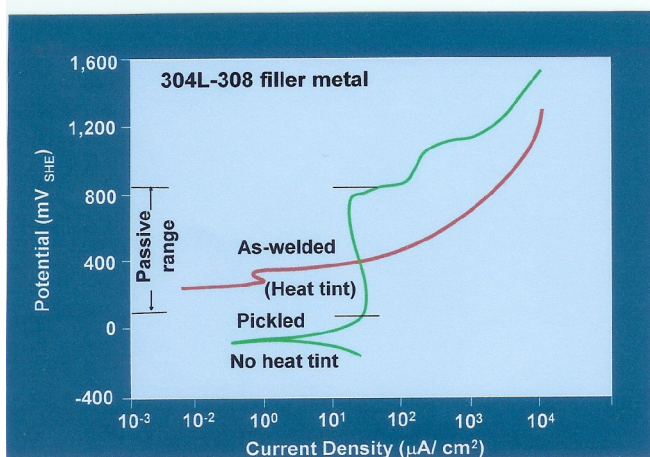
Figure 5 AWS D18.2: Heat tint levels on the inside of 316L austenitic stainless steel tube



The acceptable degree of heat tint will vary with different service environments. In a chloride containing cooling water with micro biological activity the presence of heat tint No.3 can be more harmful than a heat tint No. 10 in nitric acid.

The reduced corrosion resistance of a heat tinted stainless steel is shown in Figure 6. The as-welded stainless steel surface with heat tint shows a seriously diminished passive range compared to the pickled weld surface exposed to fresh water containing 100 ppm chloride. This will result in deleterious effect on the corrosion resistance.

Figure 6 Polarization curves for 304L stainless steel welds with type 308 filler metal in water containing 100 ppm chloride



The presence of heat tints makes stainless steels vulnerable to several types of localized forms of corrosion due to lack of a coherent passive oxide film.

Possible forms of localized attack are:

- Pitting corrosion
- Stress corrosion cracking
- Crevice corrosion
- Microbiologically induced corrosion (MIC)

4. Removal of heat tints

To avoid or minimize the risk of these forms of localized attack the heat tints have to be removed in case the stainless steels are exposed in environments in which these forms of corrosion are likely to occur. An exception here are stainless steel equipment and piping applied in fluids that have a pickling effect, such as HNO_3 .

In case of doubt the decision to allow or to reject the presence of heat tints has to be taken in consultancy with a corrosion specialist.

Of course, there also might be an esthetic reason to remove heat tints.

Removal of heat tints can be performed by means of mechanical or chemical methods or combinations thereof.

Mechanical cleaning methods

Stainless steels may be mechanically cleaned as follows:

- by sanding with 360 grit or higher (rotary disk) or
- by brushing with a 3M nylon or stainless steel rotary brush or
- by sandblasting

During sanding, overheating of the stainless steel must be avoided. Sand blasting, manual stainless steel wire brushing and sanding with grit No. 80 does not give any significant improvement in corrosion resistance over the original condition with oxide scaling. The fact that sanding with grit No. 80 does not give satisfactory results does not mean that insufficient material is removed but is due rather to deformation of the material. Coarse sanding causes material overlaps on a microscale whereby impurities are entrapped.

Experience indicates that sanding is better than brushing or sand blasting and that the critical pitting temperature (CPT) increases with increasing grit numbers.

Always be sure the blasting grit does not contain any alloyed or unalloyed steel. Otherwise, entrapped less noble steel particles will have an adverse effect on the corrosion resistance of stainless steel. The adverse effects of any mechanical treatment can be overcome by subsequent pickling. This will remove the chromium-depleted layer and the surface deformations brought about by the mechanical treatment.

Chemical cleaning methods

Before starting the pickling procedure the material shall be free of impurities such as dirt, grease, paint, self-adhesive tape, etc. Removal of non-metallic and non-oxide bearing impurities shall be removed by means of alkaline cleaning agents or by means of solvents. Chloride-containing cleaning agents and solvents are not allowed.

Next to the removal of non-metallic and non-oxide bearing impurities the oxide scales (heat tints) resulting from a heat treatment (annealing or welding) shall be removed.

Solutions and compounds used for pickling of stainless steels should:

- be capable of dissolving or soaking off the oxide scale;
- leave the metal intact; however, the chromium-depleted layer must be removed from the metal surface.

Suitable compounds are those commercially available, containing less than 200 ppm chlorides.

Particularly suitable solutions are mixtures of HNO_3 and HF.

In view of the wide variety of steel grades and differences in the properties and thickness of oxide scaling, only indications of the optimum pickling time can be given. For the austenitic Types AISI 304 and AISI 316 the following treatment will usually give satisfactory results:

Pickling agent: aqueous solution of 20 % HNO_3 + 4 % HF

Pickling temperature: 20/50°C, pickling time e.g. 4 hours/1 hour.

Normally, a higher temperature results in a shorter pickling time whereas a higher chromium or molybdenum content results in a longer pickling time. Pickling times can be shortened by mechanical cleaning prior to the chemical treatment.

If the regular pickling agent performs inadequately, a stronger agent may be used, consisting of 10-15 % sulphuric acid, 3 % nitric acid, 1.5 % hydrofluoric acid in water at 20-50°C. Such treatment should be closely monitored.

Steel producers commonly apply electrochemical pickling (and polishing) processes, because these processes operate more quickly than bathing; salt baths are also employed.

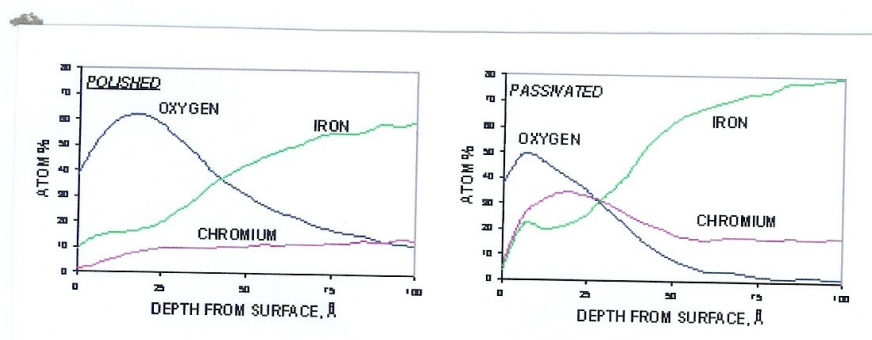
For environmental reasons nowadays also other pickling solutions are used, like: 6% H_2SO_4 + 5 % HF + 0,1 % H_2O_2

It is experienced that from point of view of corrosion a chemical cleaning has to be preferred above mechanical cleaning. This improved corrosion behaviour is explained by an increase of chromium content in the outer layer of the stainless steel.

To avoid over pickling in case of presence of a thick oxide layer a mechanical cleaning followed by chemical cleaning can be performed. The resultant corrosion resistance is equivalent to that obtained by 'regular' pickling.

Material Interface Inc. did perform examinations on mechanically polished and passivated stainless steel by means of Auger and XPS (ESCA) analyses techniques. The surface composition is obtained in metal oxide ratios for chromium and iron. To measure the level of passivation, the composition as a function of depth can be determined for the major elements as shown in Figure 7. The left figure shows the concentration of O, Cr, and Fe as a function of depth of a mechanically polished 316L; the right figure illustrates the effect of passivation on the near-surface Cr/Fe ratio.

Figure 7 Concentration as a function of depth of O, Cr and Fe of mechanically polished 316L (left) and passivated 316L (right)



The metal need not be passivated after pickling provided the pickling agent is one based on HNO_3 . In that case, passivation will not give any significant improvement in corrosion resistance; it will only require more chemicals to be used and disposed of, so adding to the environmental impact. A literature search and a Dutch research project "Verwerking en gebruik van roestvast staal" (Processing and use of stainless steel), performed from 1991-1993, indicate that the need for post-pickling passivation is questionable, to say the least. It is often found that the passive layer formed during rinsing (with formation of dilute nitric acid) and next in the air provide adequate protection of the base metal.

5. Conclusions and recommendations

- Presence of heat tints accelerates initiation of localised types of corrosion like stress corrosion cracking, pitting and MIC.
- To minimize the risk of localised types of corrosion heat tints have to be removed.
- From point of view of corrosion a chemical cleaning by means of pickling with 20% HNO_3 + 4% HF or 6% H_2SO_4 + 5% HF + 0.1% H_2O_2 has to be preferred above a mechanical cleaning.

6. Literature

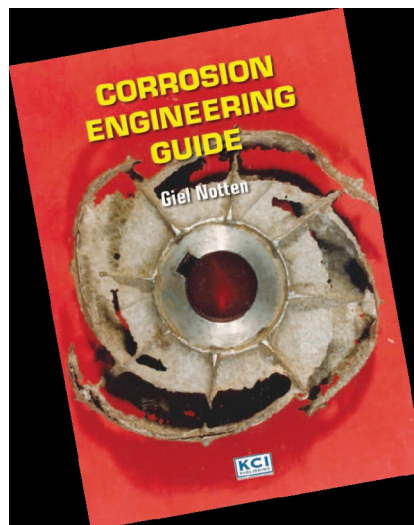
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Oberflächenbeschaffenheit ist entscheidend.
Beizen verbessert Korrosionsverhalten austenitischer Stähle.

This paper is part of Giel's Corrosion Engineering Guide, a valuable asset for any engineer working in a urea plant.

This guide is available via:

<http://www.stainless-steel-world.com/>

Please find the Table of Content of this Corrosion Engineering Guide herebelow.



About Giel Notten

Giel is a true materials and corrosion expert who, before his retirement in 2004, spent thirtyeight years working with DSM in The Netherlands. After gaining his Engineering degree at the Higher Technical School of Heerlen, The Netherlands, he joined DSM's central laboratory.

He was to remain with the company for the rest of his career and held several positions as a materials and corrosion expert there.

For the last twenty years before he retired, Giel worked in the Corrosion Department

as Managing Senior Corrosion Engineer. He has further participated in numerous conferences spreading the word about his broad experiences as a corrosion and materials specialist in chemical process plants.

For Stamicarbon, a subsidiary company of DSM, and licensing DSM's know-how, he set up programmes for lifetime extension studies in urea and ammonia plants and supervised them. He was also involved in the development of Safurex[®], the super-duplex stainless steel grade (developed by Sandvik in cooperation with Stamicarbon) for application in Stamicarbon urea plants.

Giel has always enjoyed teaching so, after only five years working in the field at DSM, he already began to develop a Corrosion Engineering course. Since then he has taught many young engineers from both inside and outside DSM about the ins and outs of corrosion control in chemical plants. He was also a board member of NACE Benelux and a member of the Contact Group Corrosion of the Dutch Chemical Process Industry and the Studiekern Corrosion of the Dutch Corrosion Society (NCC).

Since his retirement from DSM, Giel Notten has remained active as a corrosion engineering consultant. He has devoted much of his time to passing on his extensive knowledge and experience on the complicated topic of corrosion engineering to a new generation of engineers. He has done this in the form of numerous corrosion courses and workshops.

Alongside his professional career, Giel has been very active in local societies and has been a Rabobank board member for about thirty-five years, twenty-five years of which as Chairman of the Board. Furthermore, he is an active cyclist. Together with his wife, Lianne, he has made trips up to 2500 km by bicycle to Santiago de Compostela, Spain and Rome, Italy.



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