

Technical Bulletin

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THE PASSIVE LAYER IN AUSTENITIC CHROME ALLOYS SUCH AS 1.4435

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Georg Henkel, MSE, PhD

Benedikt Henkel, MSE

*The component's
value is assured
by its surface*



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The excellent corrosion resistant properties of austenitic Chrome-Nickel steel alloys lead during its development to the somewhat misleading name of "Edelstahl" in German which lent itself from "Edelmetalle" i.e. precious metals such as Gold and Platinum and was meant to describe the resistance properties of this material. The English name "stainless steel" whilst not associating with precious metals also describes the corrosion resistance of the material.

Whereas "true" precious metals enjoy a so-called saturated valence shell due to their chemical-physical structure, which means that their inertness i.e. inability to form compounds (e.g. with oxygen) has thermodynamic reasons and that this is true for every mass point in the structure; the supposed inertia of austenitic stainless steel alloy to chemical reactions respectively their passive behaviour is attributable to quite different mechanism.

On adding increasing quantities of chrome to steel alloy under laboratory conditions an astonishing discovery was made: the dissolution behaviour of alloys with quantities of up to 12% Chrome showed hardly noticeable differences in a concentrated nitric acid solution. The addition of approx. 13% Chrome showed a sudden non-sequential change in behaviour, in that the dissolution of the material in concentrated nitric acid suddenly no longer took place.

The closer analyses of the reasons behind this phenomenon showed, that the material was apparently coated and protected by a covering chromium-oxide layer which may be explained in the following model:

On an addition to the alloy of, for example 13 % Chrome, statistically every seventh atom on the surface is a chrome atom.

Speaking about thermodynamic chrome has the highest affinity to oxygen compared to Fe (and Ni resp. Mo). The rapidly developing chrome oxide is comparable to the oil film which develops on a water surface from one drop of oil, whereby the 13 % Chrome completely covers the surface and forms a closed layer.

The property of excellent corrosion resistance of austenitic chrome-nickel steels is therefore apparently explained and caused by the formation of a covering chrome oxide layer which itself is thermo-dynamically caused. This chrome-oxide layer is called the passive layer: the oxidation process passivation.

This layer is normally very thin (approx. 10 - 15 molecule) layers which correspond to 0.05 - 0.1 μm) and otherwise behaves like a semiconductor in that electrons can pass through without hindrance whereas ions are blocked, which interrupts the usual corrosion circuit. It is a disadvantage that the layer is very thin and therefore, of course, susceptible to damage.

If for example a local ferrite (or non-metallic) contamination takes place by a steel pin or a similar occurrence, the chromium-oxide layer, which has dynamic properties of composition and decomposition, shows no sandwich effect (i.e. protecting existence under the Fe-particle). On the contrary rapidly destructive corrosion may in the presence of an electrolyte, start from the damaged spot.

This material structure alone explains all the known forms of corrosion in stainless steel alloys, intercrystalline corrosion, stress cracking corrosion, transcrystalline corrosion and above all, pitting.

The objective for a long term material usage must, therefore, be to safely passivate clean pure surface and to avoid troubling corrosion (especially Ferrites and Chlorides), as the consequences of local depassivation can lead to corrosion.

As already mentioned, the properties of the chrome-oxide layer are, speaking chemically, dynamic, both in the composition and decomposition of comparable Redox-processes.

While all oxygen dispensing media support the composition or existence of the layer, reducing media (such as alkaline cleaning agents of the CIP programmes) cause, at last in part, a weakening of the layer or an activation of the surface. Such cleaning programmes require therefore after each alkaline activation a repeated acid neo passivation by means of nitric acid solutions.

Acting on what is known about the electrochemical displacement series as well as the explanation of precious and non-precious metals, the passive condition of the surface is, of course, measurable, whereby the active corrosion resistance may also be expressed. This is achieved by a linear increase of voltage against a platinum electrode in a measuring unit with saline solution.

Perfect passivated stainless steel surfaces attain values of up to 85% of the gold specification. Stainless steel surfaces with local contamination (e.g. discoloration, Re-abrasion etc.) achieve in comparison 20% of the ideal value.

In this context it should be pointed out that it is above all the chlorides, which destroy the passive layer, which always cause pitting, whereby relatively high corrosion current densities cause a rapid pitting-type of destruction of the component. The Ni test is recommended as being helpful in detecting pitting.

Having explained the composition and properties of the corrosion resistant chrome-oxide-passive layer both chemically and chemical-physically, it remains to point out the media behaviour of the passive layer, which may be described as absolutely neutral and non-catalytic, as can be inferred from the chemical properties of chrome-oxide.

In this context it should be pointed out that the uniformity and intact quality of the chrome oxide layer depend on the condition of the surface where process influences should not be underestimated.

Due to the formations properties of the chrome oxide layer described above, it can only form itself completely on surfaces which have been effectively cleaned, This is important for the corrosion resistance. In the same way, a passivation of a stainless steel surface is only meaningful and possible when this surface is metallurgically pure, or chemically pickled or electrochemically polished.

The passivation of a surface which is possibly locally contaminated is not meaningful and cannot ensure the expected result.

In this context it is meaningful to chemically pickle and then passivate in one process or, alternatively, to automatically passivate during electropolishing.

Passivation after chemical pickling takes place due to available oxygen -

e.g.	in pure air	in approx. 48 hours
	rinsing with deionised water	in approx. 5 hours
	rinsing with 3 % HNO ₃	in approx. 60 seconds.

It should be mentioned that especially electrochemically polished surfaces have a distinctly thicker chrome oxide layer (approx. 40-50 molecule layers) than is to be found in other surfaces. The difference in corrosion resistance can be verified by the above mentioned measuring cell trial.

Finally, the formation of annealing colours should be touched on. The thermodynamic relevance of an increase in temperature shows quite clearly a reduction in the affinity barrier for nickel and also for iron that not only Cr but also Ni and Fe increasingly come to O₂ reactions:

straw yellow:	mainly Cr and Cr Ni compound oxides; rarely Fe-Oxides
red, blue, black:	increasingly Fe-Oxides of all three types

These processes are also demonstrable in galvanic measuring cell trials and show a drastic reduction of corrosion resistance of the surface as the discoloration increases.

If, for whatever reasons, stronger oxidation should take place, we recommend the following:

1. Alkaline degreasing on P3 basis, cold, 10 minutes
2. Deionate rinsing 1 µs/cm, cold, 10 minutes ph 7 must be achieved
3. Pickling rinse with POLINOX, cold, 20 minutes
4. Deionate rinsing 1 µs/cm, cold, 10 minutes ph 7 must be achieved
5. Passivation rinsing, POLINOX, cold, 10 minutes
6. Deionate rinsing 1 µs/cm, cold, 10 minutes ph 7 must be achieved
7. Deionate rinsing 0.5 µs/cm 50° C, 20 minutes until ph 7 and 0.5 µs/cm are achieved.

The installation should be conceived as a circular pump rinsing, where the construction should ensure that the system is completely emptied.

Please contact us for further information

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Procedures for the treatment of metal surfaces

- ▶ Electrochemical polishing
- ▶ Electrochemical and chemical deburring
- ▶ Chemical polishing
- ▶ Chemical pickling
- ▶ Passivation
- ▶ Derouging and professional repassivation

All services can be carried out on the premises of the customer

Development and supply of

- ▶ chemicals for pickling, electropolishing and passivation of metal surfaces
- ▶ chemicals for derouging and repassivation of stainless steel surfaces
- ▶ turnkey constructions/equipments for the chemical and electrochemical surface treatment of metals

Technical consultation

- ▶ for the surface treatment of
 - Stainless steel (i.e. 1.4435 / 1.4404 / 316l, 1.4539 / 904l, etc.)
 - Nickel and Nickel Alloys (i.e. Alloy 59, Hastelloy, Inconel)
 - Aluminium
 - Copper
 - Niobium
 - Titanium
 - Zirkonium
 - C-steel
- ▶ for apparatus, tubes and fittings in the food, beverage, chemical, cosmetic and pharmaceutical industries, bio and medical technology, plant, refrigeration and heat technology
- ▶ for surface treatment specifications for apparatus and tube systems
- ▶ concerning corrosion of stainless steel

Further services

- ▶ Colouring of stainless steel
- ▶ Clean room treatment
- ▶ Waste water technology
- ▶ Research & Development

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info@henkel-epol.com
www.henkel-epol.com



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HENKEL Beiz- und Elektropolieretechnik
GmbH & Co. KG
Stoissmühle 2
A – 3830 Waidhofen / Thaya
Tel : + 43 (0) 28 42 / 543 31 - 0*
Fax : + 43 (0) 28 42 / 543 31 - 30
info@henkel-epol.at
www.henkel-epol.com

HENKEL Beiz- und Elektropolieretechnik
GmbH & Co. KG
An der Autobahn 12
D – 19306 Neustadt-Glewe
Tel : + 49 (0) 387 57 / 66 - 0*
Fax : + 49 (0) 387 57 / 66 - 122
info@henkel-epol.com
www.henkel-epol.com

HENKEL Kémiai és Elektrokémiai
Felületkezelő Kft
H – 9172 Györzámoly, Központi Major
Tel : + 36 (0) 96 / 352 - 035
Fax : + 36 (0) 96 / 585 - 035
info@henkel-epol.hu
www.henkel-epol.com

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