

Passivation of Stainless Steel

Stainless Steel

When stainless steel is newly made it is cleaned of oils and greases used in the fabrication process, and acid, usually nitric, is used to remove free iron from the surface. Slowly and naturally a passive layer develops on the surface of the steel as the chromium at the surface reacts with oxygen in the air to produce chromium oxide. The term passive refers to steel now being unreactive.

$4Cr + 3O_2 \rightarrow 2Cr_2O_3$

This layer is invisible and only a few molecules thick but it provides a barrier to prevent oxygen and moisture from reaching the iron underneath. If oxygen got to the iron, the iron would oxidize or rust, producing an unwanted yellow to orange-red color and over the long term, weakening the steel.

Surface Damage

After stainless steel equipment has been installed and is in operation the existing passive layer can be damaged or removed by physical abrasion (welding, brushing, grinding, scraping) or by chemical reactions. It can also be weakened by physical damage due to expansion and contraction caused by heating and cooling. If this damage happens faster than the passive layer can heal itself naturally, rusting will result. The natural reaction of oxygen from the air combining with chromium from the steel to produce chromium oxide may be interfered with by the processing going on or chemicals that are in contact with the surface. The regeneration of the passive oxide layer might not be adequate to provide constant protection. A more effective passive layer can be produced by chemical methods.

What is chemical passivation?

Chemical passivation is a two step process. The first step is to clean the surface of all organic greases and mineral or silicone oils. Specialty cleaners need to be used to dissolve these impurities. The standard alkaline products used to remove organic oils and greases are normally not suitable to remove mineral and silicone oils and greases. The second step is to remove any free iron or iron compound that is on the surface and to form uniform chromium oxide protective layer on the surface. It is important to remove iron impurities prior to chromium oxidation, otherwise this iron will create a localized site where corrosion can continue. Acid is used to dissolve away the iron and its compounds. The surface itself is not affected by this process. Furthermore an oxidizer is used to force the conversion of chromium metal on the surface to the oxide form.



How is it done?

Prior to passivation, a thorough degreasing of the surface to be passivated is essential. If this is not done and grease remains on the surface of the metal, the passivating acid will not be able to reach the metal surface underneath the grease and these parts will not be passivated. After the degreasing step, this step is validated, normally by a camphor test. This test is very sensitive to oil and grease residues. If residues are still present, the degreasing step needs to be repated.

Most common method – Nitric acid. The most commonly used chemical method to passivate a stainless steel surface is to apply nitric acid. Nitric acid is a strong mineral acid so it can quickly dissolve all iron compounds and other trace metals that are on the surface. Nitric acid is also a strong oxidizer so it can generate the chromium oxide layer at the same time. Even though nitric acid is a strong chemical, high temperatures and extended times are used to ensure the reaction is effective and complete. The application condition ranges are:

| Time: | 3-4 hours |
|-------|--------------------------------------|
| Temp: | up to 80°C |
| Conc: | $20\ to\ 50\%$ by volume nitric acid |

Note: Under these conditions nitric acid is very aggressive on gaskets and it may be necessary to replace them after a passivation procedure. If the surface has signs of corrosion (eg. because of contact with sea water) stronger passivation agents based on hydrofluoric acid may be required.

When to passivate

There is no simple rule that says when a piece of equipment must be passivated. The surface should definitely be passivated before being put into use for the first time, or following any modification or repair to the equipment. The need will vary according to how the equipment is being used and whether the surface has been damaged. Some companies will choose to

passivate processing equipment once per year as a scheduled maintenance procedure. Other companies will do it more frequently because they are processing foods that are aggressive on the stainless steel. Aggressive foods are those that contain high chloride levels and are acidic, for example salsa, tomato juice, etc. Plants that use water with a naturally high chloride level may have to passivate more frequently since the chloride will disrupt the protective layer. Pharmaceutical companies that use ultra pure water for injection are known to passivate 4 times per year because the high purity water itself is hard on the surface layer! Many times companies will passivate when they notice iron deposits forming on the stainless steel and the source of iron is not the water. There are test kits available from chemical supply firms that will test for free surface iron. If a high level is found, it could be time to passivate.

Other methods

1. Citric acid is also sometimes used for passivating stainless steel. It is an acid that can effectively remove iron and its compounds from surfaces.

| Time: | 5 h |
|-------|---------------------|
| Temp: | ambient temperature |
| Conc: | 12% by weight |

This method is being promoted because citric acid is safer to use than nitric acid. Citric acid is biodegradable, produces fewer effluent concerns and is also used as a food ingredient. Citric acid does an excellent job of removing iron from surfaces, which is the first step of traditional passivation. It is not an oxidizer and so it cannot chromium oxide which is the second step of classic passivation. It therefore cannot build up the protective layer, so this process depends on natural air oxidation. Citric acid is mostly used on small parts that will not be used in aggressive chemical or physical environments.

2. Dichromate is a very strong oxidizer that is sometimes added to nitric acid solutions to improve the oxidation of chromium. Dichromate is toxic and is not permitted in industrial effluent, so food plants stay away from using it.



Recommended products and protocol

Breltak (FM002145)

Breltak is used for removal of welding fat, shortening, pickling residues, contaminations in general and assembling residues.

Pascal (FM002027)

This is a high concentration nitric acid product suitable for passivation. Ensure complete rinsing after the passivation is done.

Super Dilac (FM002283)

Not as high concentration of nitric acid but can also be used in passivation.

| Equipment | Product & concentration | | Safety equipment | | Frequency | Special precautions |
|-------------------------|-------------------------------------|------------------|---|-------------------------------|---------------------------|---|
| Silos, tanks & lines | Breltak Pascal or Super Dilac | 5% 20% 25% | Goggles/Face shield Rubber boots Rubber apron Gloves Hard hat Respirator | Yes Yes Yes No No | Yearly, or as required | Always wear proper protective clothing. Never add water to chemical always add chemical to water. Report all accidents immediately! |

Theory:

Stainless steel is composed of iron (Fe); nickel (Ni); chromium (Cr) and several other minor components. Stainless steel is not resistant to chemical or physical attack. The corrosion resistance of stainless steel depends on the formation of a passive surface film composed of nickel and chromium oxides (Cr203 & Ni0).

Passivation involves removing free Fe or 'tramp Fe' from the stainless steel surface. This is the purpose of Pascal. The nitric acid in Pascal enriches the stainless steel with Cr & Ni. The oxides (Cr203 & Ni0) then form and a passive surface now is in place.

Steps:

- 1. If the equipment has been used, thoroughly wash the surface with Breltak 5%. The care should be taken that Breltak is dissolved in hot (40 °C) water. The solution should be circulated for 1-2 hours at temperature up to 80 °C. Keep in mind the key to a good passivation is beginning with a SCRUPULOUSLY CLEAN SURFACE.
- 2. Rinse the system with hot water.
- 3. Prepare a 20% solution of Pascal or 25% solution of Super Dilac. Heat the solution to 60-80 °C and circulate for 3-4 hours at temperature.
- 4. Drain the system and rinse with clean water. Check the pH of the water to insure all the acid is removed.
- 5. Allow the system to air-dry overnight.
- 6. Sanitize all surfaces prior to production

Notes:

The concentration of Pascal required to produce a passive surface on stainless steel may also be aggressive against gaskets if they are old or of low quality. Therefore, it is best to perform the passivation just prior to outfitting equipment with new gaskets

When to passivate? This depends on a number of factors, but generally passivation is preformed when:

- New equipment has been installed. Repairs (i.e. welding) have occurred.
- Aggressive products (high salt/low pH) are processed through the equipment.
- Equipment surfaces appear dull and dark.

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