What is Passivation vs. Pickling?

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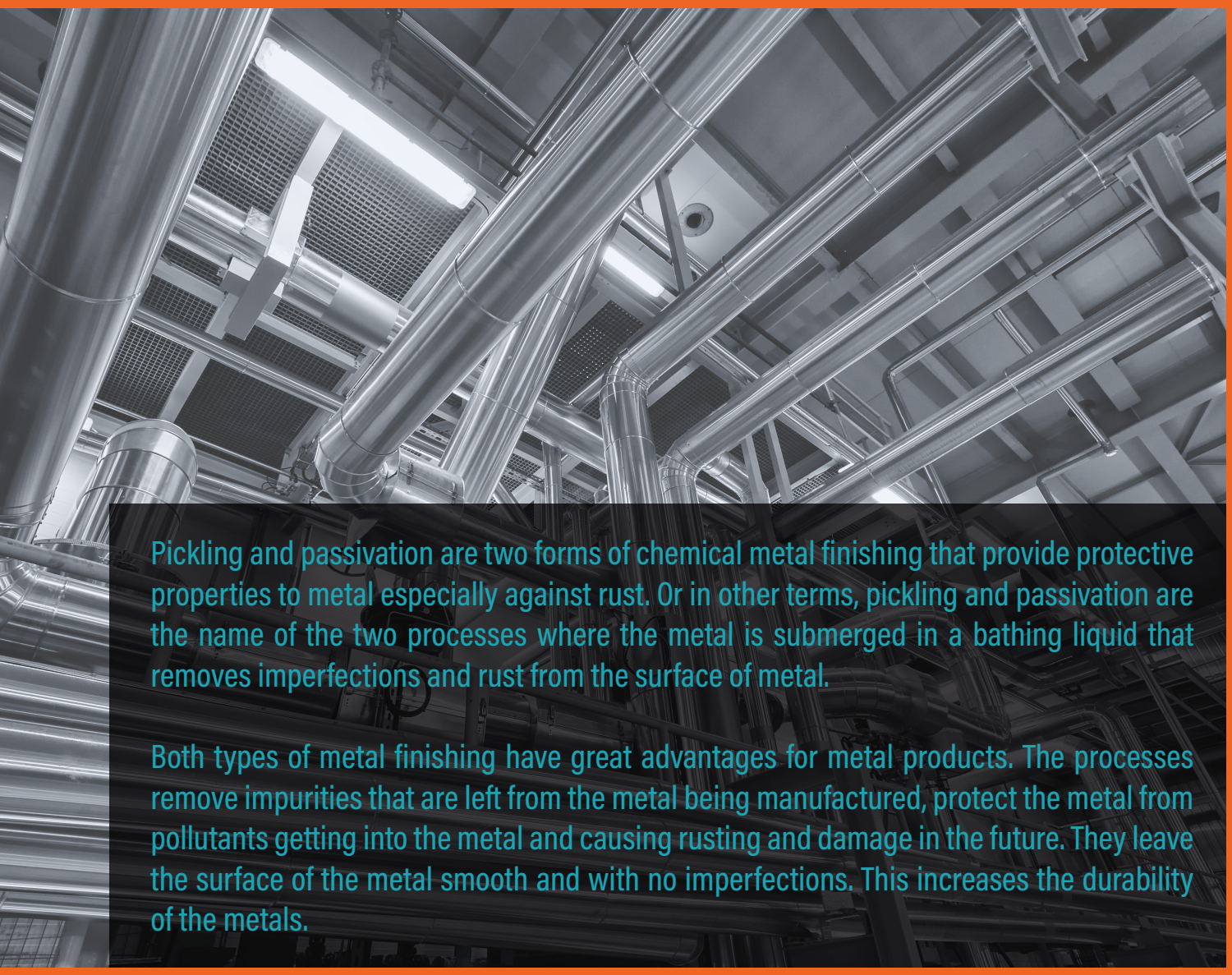
CONTENT

ABSTRACT



Pickling and passivation are two forms of chemical metal finishing that provide protective properties to metal especially against rust. Or in other terms, pickling and passivation are the name of the two processes where the metal is submerged in a bathing liquid that removes imperfections and rust from the surface of metal.

Both types of metal finishing have great advantages for metal products. The processes remove impurities that are left from the metal being manufactured, protect the metal from pollutants getting into the metal and causing rusting and damage in the future. They leave the surface of the metal smooth and with no imperfections. This increases the durability of the metals.

METAL FINISHING

Stainless steel forms its own layer of iron-chromium oxide as a deterrent against corrosion. This layer protects the metal. However, harsh chemicals, salt-laden environments such as constant exposure to saltwater, and damage to the surface by a mechanical action such as cutting will create openings in the layer. Fabrication, machining and welding leave behind contaminants such as metal oxides, inclusions, fabrication debris, and tramp iron, thereby compromising the metal's natural ability to resist corrosion. Although passivation occurs naturally in corrosion resistant and chromium-rich alloys, given the proper conditions, a new stainless steel vessel or part needs to be passivated prior to being placed into service.

This metal, unlike other metals, is unique in that it attempts to repair the surface naturally through a chemical interaction between oxygen in the environment and the stainless steel. In a perfect world, this natural reaction would form a new bond with the same protection. Because some environments are filled with contaminants, the result is far from perfect. These contaminants settle in areas where the original iron-chromium oxide was disrupted.

The contaminants prevent the complete interaction of the oxygen and the stainless steel. Instead of forming a corrosion resistant barrier, the barrier formed traps the contaminants creating the potential for corrosion.

The cost for repairing damage from corrosion is extremely expensive. This is why companies dedicate so much effort in finding methods to clean and maintain metals. Proper cleaning plays an important role in stainless steel maintenance.

PICKLING

Pickling is a method of impurities removal from the surface of stainless steel. A pickling agent is usually made from nitric acid and hydrofluoric acid. The agent is applied to a surface to remove contaminants. The hydrofluoric acid removes the contaminants while the nitric acid aids in activating the stainless steel surface to promote passivation. Pickling has a long history of use for cleaning the corrosion from stainless steel. The process is somewhat flexible.

Application of the pickling agent varies depending on the size of the surface. Common methods include brushing or spraying. However, dipping larger parts or surfaces in a large bath filled with the pickling solution has use in some applications. The benefits of dipping are that it allows the pickling solution to reach everywhere on the part/surface and covering hard to reach areas.

Several pickling pastes have been developed to allow for application to larger surfaces and containment of the acids regardless of the surface orientation. However, the pickling paste is quite ineffective under low temperatures so it cannot be used outside during cold weather.

Pickling as a means of cleaning does come with significant hazards.

- The chemicals used in pickling pose hazards to workers and the environment.
- Workers exposed to the nitric and hydrofluoric acids in pickling agents risk damage to tissue and bone.
- Burns are painful and common.
- The eyes, heart, digestive and respiratory systems may experience significant damage.

Most companies using pickling agents require workers in contact with pickling wear respiratory masks, full-face shields along with acid resistant clothing including gloves, overalls and footwear.

Pickling agents also pose a hazard to the environment.

- If exposed to fresh waterways such as rivers without pretreatment, the pickling agent alters the pH balance, which can deplete the oxygen levels in the water.
- Fish and other wildlife along with plant life exposed to the chemicals not only die, but also could pass the toxins on to animals including humans if consumed.

Despite the obvious shortcomings, pickling was often preferred when cleaning larger surfaces since it provided faster results than other methods.

PASSIVATION

To understand passivation of stainless steel, it is critical to look at stainless steel itself. All stainless steels are alloys of iron, nickel, and chromium. Chromium makes up at least 10% - 30% of the metal. It is this element that gives stainless steel its resistance to corrosion. Often steelmakers add molybdenum to enhance chromium's protective characteristics for highly corrosive or high-temperature applications.

As defined in MIL-STD-753C, the passivation process is the final treatment/cleaning process used to remove iron from the surface of corrosion resistant steel parts such that a more uniform formation of a passive surface is obtained thus enhancing corrosion resistance. Stainless steel is different from other metals in that as you get closer to the surface the composition of the metal actually changes. In the passivation process, free iron is removed from the surface into solution, leaving behind a higher chromium level. A good chrome to iron ratio is usually considered to be 1.5 to 1 or higher.

When the surface iron is removed, the other components of the alloy (primarily chromium, often nickel as well) are left behind as a surface layer over the underlying steel. Upon exposure to air, these elements react with oxygen to form an oxide layer that protects the rest of the steel from corrosion. This corrosion-resistant surface can be damaged through mechanical means or heat or chemical damage. When that happens, iron is exposed, and the item is once again subject to rusting. For this reason, passivation may need to be performed on a regular basis.

Historically nitric acid has been used to passivate stainless steel, but recently a safer and more effective means using citric acid has been introduced.

Beyond the chemical makeup of the metal, the composition varies in the different layers that make up stainless steel. At the surface is the passive layer, sometimes referred to as the passive film, is responsible for providing corrosion resistance. It is a very thin layer of highly stable metal atoms that do not easily corrode or rust. It is only a few atomic layers in thickness where the ratio of chromium to iron (Cr/Fe) is at least 1.5-to-1. The chromium binds with oxygen to create a chemically inert, "passive" surface. The oxide layer left by passivation is only .0000001 inch thick.

Below the passive layer is the transition area where nickel is in higher concentrations. Like the passive film, it is only 3 to 4 atomic layers in thickness. The nickel in this section protects the passive film by preventing chemical reactions with the iron in the layer below. It also acts as a protective barrier to the base metal which makes up the majority of the stainless steel. The percentages of chromium, nickel and iron vary by the intended use of the item.

There are many benefits of passivated equipment and systems:

- Passivation removes surface iron contamination
- Passivation increases corrosion resistance
- Passivation reduces the risk of product contamination
- Passivation allows to extend system maintenance intervals

ADVANTAGES & DISADVANTAGES

On the surface there does not seem to be a big difference between the two processes. The differences come down to the intensity of the treatments.

Pickling is typically a cleaning process -often even before doing any fabrication.	Pickling is typically a cleaning process -often even before doing any fabrication.
Pickling uses acids that take off the surface of the metal to treat impurities as a sublevel basis.	Passivation uses either nitric acid or citric acid that are not recognized as being as aggressive as the acids used in pickling. Can also use chelating agents (better than citric, not as good as Nitric, but less hazardous).
Pickling leaves a greater change to the metal.	Passivation does not typically go below the surface of the metal and does not change the properties of the metal.

SUMMARY

Pickling process is used where there is a need of deeper cleaning of the contaminated or deactivated surface. It uses harsher, stronger acids and will change the appearance of the metal. The type of the contamination that is slated for pickling process is more than just a surface rust removal. Weld discoloration, carbon precipitation, deactivated layer of corrosion protection due to heat or deep impurities penetration are the typical uses.

Passivation is typically used with weaker acids or pastes that only used to change the Cr content in the surface layer and does not remove the original metal.

The decontaminated Chromium layer gets oxidized and the corrosion protection is reestablished in both cases.

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