What is Acid Pickling?

Several weeks ago, I was teaching a class on basic fastener technology. As part of the class, we had the opportunity to visit a local steel mill where they cast billets and hot rolled them into cold heading quality rod. Hot rolled rod was the end product at this site and I found myself searching for a way to explain to the class that this was just an interim step in the process of converting raw iron and steel scrap into steel wire that is usable in a cold header. I explained that hot rolled rod must be further processed to make it feasible to use. One of the more important changes, I explained, is addressing the surface condition of the rod so that it is free of scale, clean , and lubricated. This metamorphosis begins with acid pickling.

When steel is heated to elevated temperatures in a normal industrial environment such as the open-air conditions in a hot rolling mill or the unprotected environment of a normal tempering furnace, oxides and scale can form on the surface of steel. Those substances stubbornly adhere to the surface and can be extremely difficult to remove. Thus, they require a powerful process to remove them. One such process is acid pickling. **Acid pickling is a process that employs the strength of strong acids to remove stubborn oxides, scale, and stains from the surface of steels and other metals.**

The acid pickling process is straight forward. It involves the following process steps:

- Pre-cleaning
- Pickling
- Rinsing
- Neutralization and Rust Inhibitor Application
- Drying

The process begins with pre-cleaning. Many times, steels or parts have picked up dirt, oil, grease, or a conglomeration of these substances commonly referred to as "smut." These contaminants can normally be removed without abnormal heroic efforts by immersing the items in a caustic, soap-like solution. A simple dip or electrocleaning immersion in a caustic solution is normally successful in removing these types of contaminants. However, these methods are not strong enough to remove the oxides, scale, and rust. Even though this pre-cleaning does not remove these more stubborn contaminants, its role is crucial because removing the smut and related contaminants prevents the acid pickling bath from becoming contaminated with these substances. In doing so the acid can exclusively target removing the more stubborn oxides and scale.

Following the pre-cleaning, raw steel items or parts are immersed into an acidic solution known as the "pickling liquor." Although this sounds simple, it is a delicate procedural balance that requires good understanding and control of the process. In fact, there are multiple variables that determine the outcome of the process, with the primary ones being the type of acid utilized, acid concentration, operating temperature, and immersion time. Secondary variables may include factors like the addition of buffering agents and age or efficacy of the bath.

The most common pickling acids are either hydrochloric (*Fig. 1*) or sulfuric acids. However, there is an extensive list of acids that can be utilized for pickling, particularly for the use with select, non-carbon steel metals. Other acids that may be utilized for pickling include nitric, phosphoric, hydrofluoric, oxalic, tartaric, citric, acetic, and formic acids. For use as pickling agents these acids are diluted to a concentration somewhere between about 15 and 20 percent acid content. There does not seem to be any one definitive norm on this, but it is understood that these values represent a balance between where the pickling medium works effectively without needlessly risking hydrogen embrittlement potential and fuming (the corrosive fumes emitted by the pickling bath). Temperature also plays a vital role. **When the acid is warmed it is more effective, but like acid concentration, a delicate balance must be struck between warmer temperatures and the degree of fuming the bath emits.**

Today hydrochloric acid is the most common pickling agent, although in the past sulfuric acid was more common because it was more affordable. However, sulfuric acid requires more contact time than hydrochloric acid to successfully remove oxides and scale which can be detrimental to processes where production rates require a faster response.

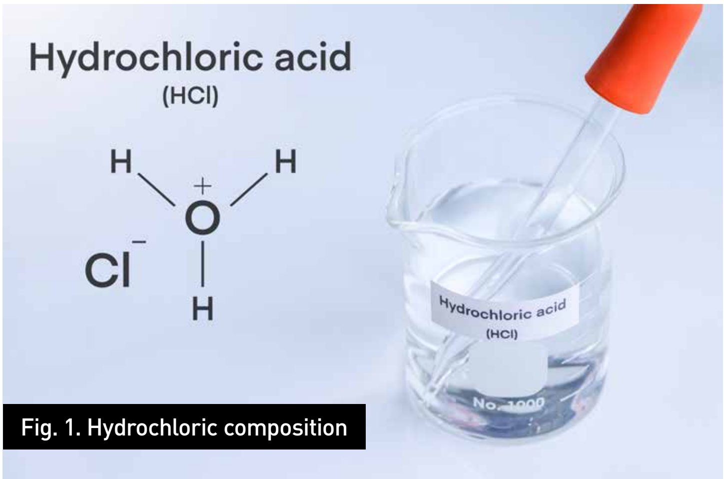

Fig. 1. Hydrochloric composition

Hydrochloric acid more efficiently removes scale and oxides and can do so without having to heat the pickling bath. In fact, a hydrochloric acid pickling bath can be operated at room temperature. Pickling with hydrochloric acid may slightly reduce the amount of hydrogen penetration as compared to other acid types, particularly sulfuric acid. Unfortunately, hydrochloric acid begins to fume at slightly elevated temperatures. Fuming is a problem because it is corrosive to the surrounding exposed areas and presents a health risk to nearby workers. Hydrochloric acid is more corrosive to exposed areas and difficult to recycle and dispose of than sulfuric acid.

Sulfuric acid is less expensive, and pickling efficiency is easily influenced by changing the bath temperature. Unfortunately, sulfuric acid attacks the base metal more aggressively, generates greater hydrogen penetration than hydrochloric acid and experiences greater fuming when higher bath temperatures are employed to raise pickling efficiency.

Cast irons are typically initially pickled with phosphoric acid, nitric acid, or hydrofluoric acid and then with either hydrochloric or sulfuric acid. Corrosion resistant and Chromium-Nickel steels are pickled with nitric or hydrofluoric acid.

In addition to bath temperature and acid concentration, time is an important control factor. This process removes as much as one to three percent of steel mass. On the other hand, steel and parts that are highly oxidized or have a large amount of scale may require longer pickling times. Therefore, processors must be mindful of the time that items remain immersed in the pickling bath.

Immediately following immersion in the pickling bath, parts must receive a rinse. This is important because rinsing in clean water will remove any residual acid from the surface of the item being pickled and halt any further pickling action.

Following the rinse, items may undergo a neutralizing process to eliminate any residual acid on the surface. Items may also receive some form of rust inhibitor to improve corrosion resistance.

In the case of acid pickling utilized in the electroplating process, pickling serves to remove stubborn scale and oxides which would inhibit proper deposition of the plating metal. It also serves as a means of "roughing" up the surface to allow for better adhesion of the plated metal. In the electroplating (***Fig. 2***) process parts are immediately transferred from the pickling to the plating operation.

Fig. 2. Electroplating

One of the significant drawbacks of the pickling process is the part exposure to hydrogen. This is less of a concern on raw steel where there is no barrier to prevent the hydrogen from escaping, but a heightened concern on parts receiving an electroplated surface. Of special concern is electroplated zinc since the zinc layer is non-porous making it more difficult for the hydrogen to escape. Therefore, there are other processes that accomplish the same thing. The most common, at least for the further processing of fasteners, is some form of mechanical abrasive blasting. This includes shot peening, bead blasting, and grit blasting. These processes are commonly employed as cleaning and activation steps for surface finishes and coatings that are designed to be hydrogen embrittlement risk free.

In summary, pickling is a vital component of a number of fastener related processes. It is one of the critical steps in converting hot drawn steel rod into cold heading quality wire. It is also a crucial step in the electroplating process of fasteners, as caustic pre-cleaning and electrocleaning do not always sufficiently produce a clean enough surface to effectively electroplate parts. As beneficial as the process is, however, acid pickling must be carefully controlled and monitored to provide the outcomes necessary to benefit the end user. ■