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Adhesion

With the emphasis on production schedules and keeping the plating bath in optimum condition, the hydrochloric acid pickle is an often-ignored step in the plating line. However, it becomes a vital step when plating parts such as high-carbon, heat-treated fasteners. Adhesion issues can be common when plating high-carbon, heat-treated steel and one of the primary areas to focus on when addressing this issue is the acid pickling stage of the process. High-carbon steel can generally be classified as an iron-carbon alloy ranging from 0.55-1.40% carbon in the steel. High-carbon steel has an increased hardness and strength compared to regular mild steel. In addition, high-carbon steel is often heat-treated to change properties such as impact resistance, hardness, ductility, and various other properties depending on the type of heat treatment. The resulting makeup of the substrate has a direct bearing on the acid pickle performance.

From a plating standpoint, it is important to know more about the acid pickle bath and the necessary balance and control. Weak pickle baths do not sufficiently remove scale and rust from parts. On the other hand, over-pickling etches parts, making it more difficult to achieve brightly plated work, and increasing the chance for hydrogen embrittlement to occur. The goal of the acid pickle is to remove scale and metal oxides from the surface which generally form during the heat treatment process. The oxide layer is attacked by the acid pickle solution producing a metallic salt and water. A problem arises if the entire oxide layer is removed because the base metal would begin to dissolve, producing a metal salt that liberates hydrogen in the acid pickle. This is where the true challenge lies in plating heat treated, high-carbon fasteners. It often takes higher concentrations of hydrochloric acid or alternatives such as ammonium bi-fluoride to remove the metal-oxide scale or smut. If the oxide layer is entirely removed and the base steel is attacked, it causes dissolution of the steel substrate, creating a carbon-rich surface. The above-mentioned adhesion issues are due to the inability to initiate plating over top of this carbon-rich surface. Furthermore, the liberation of hydrogen can also cause issues with hydrogen embrittlement which is a major concern in the fastener industry. The unique makeup and requirements of high-carbon, heat-treated fasteners present an extremely challenging scenario to strike the perfect balance between over and under-pickling.

Iron is a major contaminant in pickle solutions. While some of the iron is the result of dissolving rust and scale, a large portion comes from the attack by the acid on the base metal. The most common fix for this problem is the implementation of an acid pickle inhibitor. Acid pickle inhibitors work by creating a protective film through methods of adsorption, which protects the steel substrate but allows the oxide layer to be dissolved regularly. It is generally accepted that the inhibitor is attracted to the metal surface and adsorbed there. It is important that the inhibitor not adsorb on the surface of the rust and scale or the acid will not be able to do its cleaning job. The table below shows how the addition of an acid inhibitor considerably reduces the rate of iron buildup in the pickle. An additional benefit is that hydrogen formation in the surface of the part is reduced, minimizing the chance of hydrogen embrittlement from this source.

TABLE 1. Effect of an Acid Inhibitor in a Hydrochloric Acid Pickle Bath for a High-Volume Automatic Hoist Barrel Line[a]

	After 1 Day (*ppm*)	*After 4 Days* (*ppm*)
Dissolved iron in pickle with no inhibitor	7,600	9,310
Dissolved iron in pickle with 1% acid inhibitor[b]	4,080	4,420

[a] Plating bath volume 3,500 gal with 7% drag-out per 22-hr day, plating 14 barrels/hr. Pickle bath volume 550 gal with 42% drag-out per 22-hr day with an average acid concentration of 45%.

[b] Proprietary acid inhibitor manufactured by Columbia Chemical Corp.

When plating high-carbon, heat-treated fasteners without the use of an inhibitor, the steel substrate becomes vulnerable to attack, as carbon is drawn from the steel onto the surface of the part, resulting in adhesion issues. The photo in Figure 1, from left to right, shows a typical 10.9 bolt as-is, then followed by the piece after pickling with no inhibitor, and finally using an acid inhibitor. The as-is bolt in Figure 1 gives a fair representation of a heat-treated fastener and the amount of heat-treated scale present. The bolt after pickling with no inhibitor demonstrates the effect of a typical pretreatment cycle utilizing a pickle with no inhibitor – the bolt is extremely black and smutty due to a carbon-rich surface. Finally, the bolt with the acid inhibitor is a perfect gun-metal grey because the metal oxide layer was dissolved but the substrate was left unaffected. This leads to the bolt being plated effectively. Acid pickle inhibitors offer a myriad of benefits in many different plating applications. Specifically, regarding high-carbon, heat-treated steel, they are designed to inhibit the attack of the steel substrate but allow the speed at which they remove scale or other compounds to remain similar. This permits the substrate to stay relatively unaltered by the acid pickling while still maintaining the necessary cleaning functions of the pickling process. In addition, the acid pickle life is generally extended because less metal is being dissolved into the pickle solution, reducing drag-down of any metallic contamination. Acid pickle inhibitors often contain other types of surfactants which help build a foam blanket designed to reduce acidic misting in the workplace.

Adhesion issues with high-carbon, heat-treated fasteners are often due to parts coming out of the pickle process with a carbon-rich surface because of the base steel being attacked. Careful attention to the acid pickling stage of the process and the addition of an acid pickle inhibitor may help alleviate this problem. Recent developments in acid pickle inhibitors have also reduced excessive film formation or hard to remove substances which were prevalent in older generation inhibitors causing staining and blistering issues. It is worth noting, however, that not all acid inhibitors are created equal and they may not work for the same substrate in the same manner. Qualities that a good acid inhibitor should exhibit are: an inhibition rate of $\geq$95% based on a 24-hour test of carbon steel in 30% hydrochloric acid (percentage is derived by comparing the amount by weight of steel dissolved with and without the presence of the inhibitor), no interference with removal of rust and scale and non-foaming or produces only a slight amount of unstable foam. It is important to rely on a trusted chemical supplier for specific applications or questions.

FIGURE 1