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Understanding Immersion Deposits

Dear Advice & Counsel,

Our company conducts reel-to-reel plating on wire made from steel, copper clad steel and a nickel-iron alloy. Over the years, personnel have changed and “brain drain” has caused us to lose much of the detailed information about our process. We have discovered that the adhesion of our nickel deposit plated over the ferrous based alloy wire is not as great as we would like it to be. The adhesion of nickel plated from the same process line is more than sufficient. All our efforts to date to determine the cause and improve our process have not resolved the issue. Can you provide some insight?

Signed,
Enzo Ropa

Dear Mr. Ropa,

We conducted an on-site investigation of your process and offered a number of observations and suggestions. The primary problem is believed to be immersion deposits which typically yield adhesion that is less than the desired level.

This base metal made from a nickel-iron alloy typically requires a low pH nickel strike, usually a Wood's formulation or a sulfamic acid formulation. This is because these alloys form an oxide film that yields poor adhesion if not removed, yet forms instantly when the surface is exposed to air.

Woods and sulfamic acid strikes yield excellent adhesion on such alloys by simultaneously removing oxides from the surface and depositing a relatively pure and adherent nickel film over the alloy.

You are employing a Watts formulation at low pH (about 2.0), which may provide sufficient adhesion in most cases, and most of the time, but this is not the way it is typically done. Further, since the Watts



solution at low pH plates mostly gas, the efficiency (productivity) of the plating line is impacted.

One possible change that can improve adhesion is to employ a sulfamic acid strike followed by a Watts solution at somewhat higher pH. This may also speed up production. Since the wire requires a ductile nickel deposit, you will need to keep the pH in the range of 2.5 to 3.0.

Key to the Problem

We believe that the biggest key to your problem is the fact that the same line is used to plate nickel onto copper clad wire and onto the nickel-iron alloy.

In your reel-to-reel plating line the wire is processed through a dilute solution of phosphoric acid, immediately prior to nickel plating. When processing copper clad wire, there is no DC power applied in this acid. When steel or nickel-iron alloy wire is processed, DC power is applied

so that hydrogen gas is generated over the surface of the wire (wire is the cathode), thereby reducing surface oxides to water (hydrogen plus oxygen produces water).

The over-all purpose of this acidic process is to:

- Neutralize any residual alkali remaining on the wire after the electroclean rinse.
- Remove any surface oxides that remain on the wire after the electrocleaning step.

Surface oxides are produced by anodically electrocleaning and are naturally produced whenever clean wire is exposed to air. Oxides that are bonded to the surface of the wire prevent a strong atomic bond from forming between the wire and the nickel electroplate. Failure to remove surface oxides can result in weak adhesion or no adhesion.

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reaching as the effect of human activity on the planet didn't drive some species to extinction. Whether the rate of extinction is truly unprecedented, however, is not so clear. I have to confess that I have this sneaking suspicion that animals have probably been becoming extinct at a high rate for hundreds of millions of years. After all, an animal so specialized that it can only survive on one part of one kind of tree is not a good bet to win the Darwinian sweepstakes. And, of course, since we have no idea how fast they became extinct in the past, we have no way of knowing whether their extinction rate is going up or down today."¹¹

The 'lungs of the planet' claim is also mythical. Lomborg explains that plants produce oxygen by means of photosynthesis, but when they die and decompose, precisely the same amount of oxygen is consumed. Therefore, forests in equilibrium neither produce nor consume oxygen in net terms.¹⁰

More from Stott; "The Northern environmentalists conception of the tropical rain forest is far removed from the ecological realities of the places it purports to denote. Most of the 'million year old forest' to which environmentalists senti-

mentally refer turns out to have existed for less than 20,000 years. During the last ice age the tropics were colder and drier than today and probably more closely resembled the savanna grasslands of East Africa."⁹

Yet, here's an example where the statement about "millions of years old forest" is used. It's from a 1992 textbook by Chris Park, *Tropical Rainforests*, which is widely employed in schools and colleges throughout the UK.

"Tropical rainforests are the most complex ecosystems on earth. Rainforests (better known to many people as jungles) have been the dominant form of vegetation in the tropics for literally millions of years and beneath their high canopy lives a diversity of species which is unrivaled anywhere else on earth."¹²

E.F. Bruenig, Emeritus Professor of Forestry, Hamburg University, says this, "Knowledge of ecology and forestry is poor among the public and understanding of ecosystem properties is almost absent, while myths abound especially with respect to tropical rain forests and their peoples. There is a certain unwillingness to bridge the knowledge gap and abandon inherited or newly developed myths, if they serve self-interests."¹³

References

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We noted that when copper clad wire is plated, the stainless steel electrodes used to apply DC voltage to the nickel-iron wire are not removed from the acid tank. With the power off, if stainless steel is immersed in any acid containing copper ions, copper metal will galvanically deposit out of the acid and onto the stainless steel (the accompanying photo illustrates the heavy amount copper deposited over the stainless steel).

When the nickel-iron alloy is processed, DC voltage is applied to these copper coated electrodes. We suspect that under DC power some of the copper on the electrodes re-dissolves and is "plated" onto the wire in the acid tank, or may be galvanically deposited over the steel.

Since the acid tank is not designed to be a copper plating tank, the nickel plated over this undesired copper deposit may not have the level of adhesion required, and the copper between the nickel and the surface of the nickel-iron alloy may de-laminate.

Immersion Deposits

When any metal is immersed into a water based solution containing free (un-com-

plexed) ions of other metals, an immersion deposit will result of those free ions in the solution are more noble than the base metal you are processing. Coatings of metals produced by immersion deposition (also known as cementation) are notoriously in-adherent, unless the solution producing the immersion deposit is specifically formulated to contain complexing agents that control the population of free ions in the solution. Immersion deposits produced from commercially available solutions (example: silver, gold, and zincate) are typically very adherent because of the presence of such complexing agents. Strike solutions are typically formulated to contain low concentrations of metal ions, complexing agents (example: cyanide in a copper strike) or very high levels of acidity (to favor deposition of hydrogen instead of metal ions) to control the population of free ions.

Nickel and iron are both less noble than copper. Your phosphoric acid does not contain any complexers that will prevent the copper from acting as free ions. The acid may be high enough in acidity to favor hydrogen production when it is fresh (2%

volume), but as it ages, we suspect the acidity is too low to prevent copper deposition. Then an immersion deposit of copper over the nickel-iron alloy is highly likely.

Whether the immersion deposited copper has sufficient adhesion depends upon a number of factors including concentration of copper ions, temperature and the strength of the acid. As the acid gets older, the copper concentration increases and the temperature goes up, less adherent immersion deposits result, possibly leading to your sporadic adhesion problems.

In a recent "Advice & Counsel" article (see "Galvanic and Other Corrosion Mechanisms" March 2006 *P&SF*, page 24), we published a galvanic series. Any metal that is below another metal in that table will act as the more noble metal. The further apart the two metals are on this table, the higher the likelihood that an in-adherent immersion deposit will be produced when you immerse the less noble metal into a solution containing un-complexed ions of the more noble metal. A basic knowledge of the positions of various metals on this table is very valuable in avoiding adhesion problems related to immersion deposits. *P&SF*