Methods to Improve The Corrosion Performance Of Microporous Nickel Deposits

By Robert A. Tremmel

During the last several years, microporous nickel-chromium coatings have been critically scrutinized by the automotive industry. Today these coatings must be free of all surface defects, even after long-term exposure to accelerated tests and in real-life service. While proper control of all the multi-layer nickel deposits is important, blemish-free surfaces can only be obtained when the microdiscontinuity and the activity of the post-nickel strike are properly achieved and maintained. This edited version of a paper presented at SUR/FIN® '96—Cleveland shows that research indicates that the most important factor is the electrochemical potential of the microporous nickel strike deposit.

Decorative nickel-chromium has been used as a protective coating on a variety of substrates for more than 70 years. During this time, significant improvements have been in the corrosion resistance of these platings. This is especially true for multi-layer coatings developed for highly corrosive environments. The corrosion mechanisms of multi-layer coatings are very well understood. The literature, however, has often been inconsistent with respect to the recommendation of specific operating parameters and the use of additives to obtain the desired conditions required for maximum corrosion performance.

In the past, the main requirement of nickel-chromium coatings was the prevention of base metal corrosion. Surface blemishes and a certain amount of surface dulling was allowed. These surface defects usually occurred because of the deterioration of the microdiscontinuous deposit(s). Today, multi-layer nickel-chromium coatings must provide very long-term base metal corrosion resistance and also be free of surface defects[1]. Simply meeting porosity specifications is not enough. The size of the pores is important, as well as the electrochemical potential of the microporous nickel strike. This latter factor could be the most important.

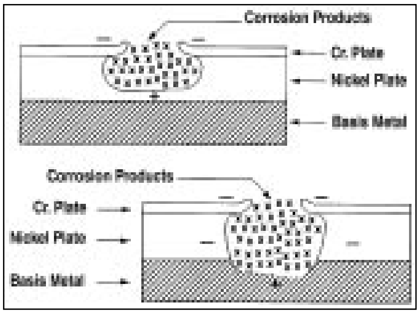

Fig. 1—Corrosion mechanism of decorative nickel-chromium deposits.

Corrosion Mechanisms

Bright Nickel-Chromium

The corrosion of decorative nickel-chromium coatings is electrochemical in nature. A solution of salt, and especially acidic salt solutions encountered in industrial winter atmospheres, sets up a galvanic cell whereby the chromium deposit becomes cathodic while the underlying nickel layer, exposed in the cracks and pores of the chromium layer, becomes anodic. The large cathodic areas of the surface of the chromium and the very small anodic areas of the exposed nickel are precisely the conditions that favor rapid corrosion pitting of the nickel deposit. Very little nickel is corroded but, because the electrochemical attack is concentrated at a small point, there is rapid penetration to the basis metal. Figure 1 illustrates this corrosion cell.

Duplex Nickel-Chromium

Duplex nickel, currently required for all exterior coatings by the automotive industry, was developed in the 1950s. It consists of a layer of semi-bright nickel, which is essentially sulfur-free, plus a thinner layer of bright nickel. Duplex nickel provides corrosion protection that is far superior to single layer systems. In these duplex systems, when corrosion occurs through a pore in the chromium plate, the bright nickel is rapidly penetrated until the semi-bright nickel is reached. Because the electrochemical potential of the semi-bright deposit is greater than that of the bright nickel deposit, thereby making it more noble, the bright nickel layer will corrode preferentially to the semi-bright nickel layer. As the pit widens, however, some attack will eventually occur in the semi-bright nickel layer and ultimately penetrate the basis metal. Figure 2 illustrates the corrosion cell.

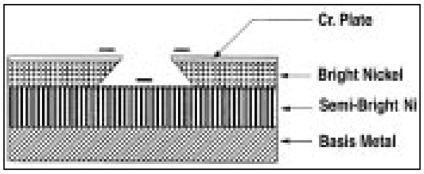

Fig. 2—Corrosion mechanism of duplex nickel deposits.

High Sulfur Nickel

Attack on the basis metal can be further delayed by either increasing the sulfur content of the bright nickel layer (making it more active) or by incorporating the use of a very high sulfur nickel strike between the semi-bright and bright nickel layers. As the potential difference between the bright and semi-bright layers is increased, the rate of penetration to the basis metal will be decreased. Figure 3 illustrates the corrosion mechanism of a high sulfur nickel strike.

Note that the use of a thin high sulfur nickel strike [0.050 µm(0.000020 in.)] can double corrosion protection of the basis metal. This is especially true in

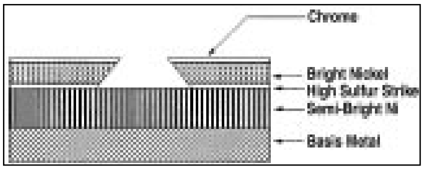

Fig. 3—Corrosion mechanism of high sulfur nickel deposits.

areas where the nickel thickness is low.

Microdiscontinuous Chromium

The advantages of microdiscontinuous chromium with respect to the overall corrosion protection of single and multi-layer nickel coatings was discovered in the late 1950s.[2] It was initially believed that the use of crack-free chromium would provide a completely corrosion resistant surface as there would be no exposed nickel to set up corrosion cells. While crack-free chromium can be plated, internal stresses develop in relatively short periods of time causing cracks to form. This results in corrosion sites developing in the same manner as on normal chromium.

Microdiscontinuous chromium provides unique corrosion mechanisms that significantly improve overall corrosion protection. Microdiscontinuity in the chromium layer decreases the cathode area (the chromium) and increases the anode area (the nickel). As a result, the amount of current supplied to the nickel at a given corrosion site is substantially less, and penetration through the bright nickel layer is reduced. Figure 4 illustrates the corrosion mechanism of microdiscontinuous chromium.

Fig. 4—Corrosion mechanism of microdiscontinuous chromium.

Ways To Achieve Microdiscontinuity

Microdiscontinuity can be produced by several techniques. These include:

1. Highly stressed chromium deposits that provide up to 1500 microcracks per linear inch.
2. A microcracked nickel strike that induces microcracking in the subsequent chromium layer. This is achieved by highly stressing a thin nickel layer that is plated over the bright nickel prior to plating chromium.
3. A microporous nickel strike that induces microporosity in the subsequent chromium layer. This is achieved by either co-depositing or trapping inert particles in the nickel strike deposit. Generally, microporosity from this deposit can be as high as 155,000 pores/cm^2 (1,000,000/in^2)*
4. Impinging the chromium deposit with sand or other fine, hard particles to produce micro porosity. This method can produce microporosity as high as 100,000 pores/cm^2 (650,000 pores/in^2).

Of the four methods, only the last two are used extensively in the plating industry. Microcracked chromium, whether produced in the chromium deposit itself or by a stressed nickel strike, has some serious limitations. These include low crack density in the low current density areas and a tendency to flake off in the extreme high current density areas.

Microporous Nickel Strike

Microporous chromium, which is obtained by impingement, provides excellent porosity but its use is generally limited to simple shapes. It also requires a relatively high capital investment. The most widely used method is the incorporation of a microporous nickel strike prior to chromium plating. This method, however, has some limitations. Because the particles are inert, for example, they do not readily migrate to the cathode surface, especially to the under-shelf areas that are usually the most important surfaces on the part. Furthermore, if the particles are too large, the subsequent corrosion sites will be large and highly undesirable from the standpoint of appearance.

The electrochemical potential of the microporous nickel strike layer also plays a significant role in relation to the size of the corrosion sites. If the nickel strike layer is more active than the bright nickel layer below it, it will corrode preferentially to that layer and cause significantly larger corrosion sites than if less active than the bright nickel.

Microporosity & Electrochemical Potential

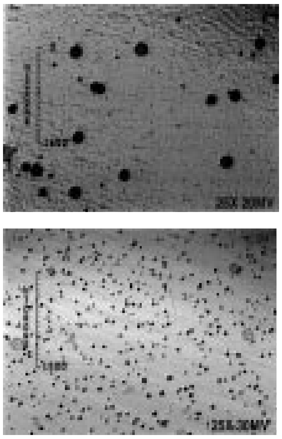

Fig. 5—Effect of electrochemical potential on number and size of corrosion sites. The potential between the microdiscontinuous nickel and the bright nickel in the top photo is a minus 20 mv. The difference in the bottom photo is a plus 30 mv.

Test results have shown that if the microporosity exceeds 10,000 pores/cm^2 (64,000/in^2) and if the potential of the nickel strike is less electronegative (more noble) than the bright nickel underlayer, outstanding corrosion protection can be achieved when used over standard duplex nickel coatings. Within certain prescribed limits, increasing the micro-porosity will decrease the size of the corrosion sites and improve the overall corrosion protection. Ideally, for optimum cosmetic and base metal protection, the microporosity should be between 16,000 and 48,000 pores/cm^2(100,000 and 300,000/in^2). When the porosity is in this range and the desired potential of the nickel strike is met, plated parts can withstand up to 10 cycles of CASS* without any base metal or cosmetic defects. Figure 5 illustrates the effect of electrochemical potential on the size of the corrosion sites.

Additives

Historically, the major problems with microporous nickel strikes have been the inconsistent maintenance of the desired porosity and achieving the desired electrochemical potential. Recently, however, improvements have been made to overcome these limitations. Some of these improvements have been made through the revision of process parameters and the rest by new and improved addition agents.

Very fine powders have been developed that co-deposit much more readily than previous powders. Liquid suspensions are now being supplied to facilitate additions. While the older powders required peroxide additions and electrolysis to activate them, the newer powders are activated immediately and require no break-in period.

---

* Copper Accelerated Salt Spray. The benchmark test currently used to evaluate nickel-chromium-plated automotive trim for exterior exposure. See ASTM Standard B 368-85 for details.

The co-deposition rate of these very fine powders is much higher than with previous solids. Consequently, much less material is required in the bath to achieve desired porosity. In fact, as little as 0.5 gal/L is often sufficient. Older formulations required solid concentrations as high as 7.5 gal/L. Consequently, the new powders are easily removed by filtration, which facilitates bath purification procedures and reduces treatment time and cost.

Other special additives enhance the co-deposition of the inert powder. It is believed that these "activators" cause electro-osmotic effects in the cathode film that make the particles cling to the cathode surface and facilitate co-deposition.[5] They work particularly well with the new, improved powders to enhance under-shelf ("A Surface") porosity. Small additions can double or even triple microporosity.

Agitation

Agitation plays a major role with respect to particle co-deposition. Air agitation is important to keep the particles suspended, however, it tends to blow the particles away from the surface of the cathode, which reduces co-deposition. Pulsing the air has been recommended by Manquen and has provided some improvement.[6] In this case, the air is turned on and off for specific periods of time. A typical cycle might be 15 sec on, 30 sec off. Ideally, the use of air agitation should be minimal — only enough to keep the solids uniformly suspended. The majority of the plating time should be without agitation.

The use of the proper additives, coupled with properly managed agitation, can provide pore densities up to 50,000/cm^2(312,500/in^2) on significant surfaces and up to 160,000/cm^2 (1,000,000/in^2) on top shelf areas.

Pore Size

High porosity, within limits, is important, as it not only reduces corrosion penetration, but also reduces the initial size of the pores. In general, the smaller the initial size of the pore, the smaller the eventual corrosion site. This is important because the smaller the corrosion sites, the clearer the deposit will be, even after long-term exposure to severely corrosive environments.

Chrysler Specification PS 8908 states that the corrosion sites, as examined after CASS, must be no larger than 63µm (0.0026-in.) with an average size of about 31µm (0.0013-in.).

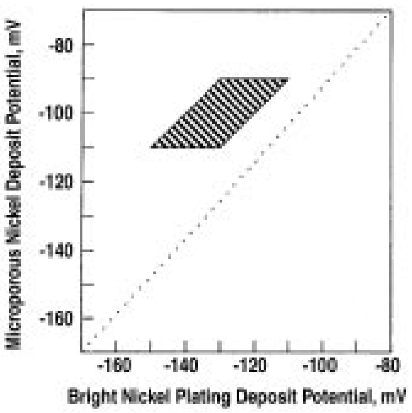

Fig. 6- Shaded area indicates desired potential for optimum cosmetic and base metal corrosion protection.

Electrochemical Potential

The size of the corrosion pit is mainly determined by the electrochemical potential of the microporous nickel deposit, especially with respect to its relationship to the bright nickel deposit. For example, when corrosion takes place in the micropores, if the strike is more active than the bright nickel underlayer, the strike deposit will be anodic to the underlying nickel deposit and corrode preferentially to said nickel layer. This will substantially increase the size of the corrosion sites, which can cause highly visible and unsightly blemishes and/or stains to occur on the surface of the electrocoating. Conversely, if the strike layer is less active than the bright nickel underlayer, said underlayer will corrode preferentially, leaving the corrosion site at the surface almost invisible. As a result, the plated surface will be virtually free of blemishes, even after extensive exposure to severely corrosive environments.

Many automotive industry standards specify that in order to minimize pore size after CASS, the electrochemical potential (measured by a STEP tester) of the microdiscontinous nickel layer should be within plus or minus 20 millivolts of the bright nickel.[7,8] A difference of zero was considered to be ideal. We find, however, that in order to ensure blemish-free surfaces, the microdiscontinuous nickel layer must be substantially more noble than the bright nickel underlayer.

Joint tests made by Ebara-Udylite and Toyota in Japan indicate that there are relative potentials between the microporous strike layer and the bright nickel that will guarantee virtually blemish-free surfaces, even after 200 hours CASS.[9] Using an electrolytic film thickness meter and a multi-layer Ni corrosion resistance meter, absolute potentials were measured on various bright nickel and microporous nickel strike deposits. Results were compared to their corrosion performance in CASS. Fig. 6 indicates that the strike deposits must be 20 to 40 mv more noble than the bright nickel underlayer to achieve the desired corrosion protection and appearance.[10]

Special Addition Agents

In the past, platers tried to minimize potential differences between the two layers by frequent pump-outs and treatments—sometimes as often as weekly. The solids that can be deactivated by the adsorption of impurities were usually changed after pump-outs. Often the solids were filtered off and the strike bath mixed with the bright nickel in order to equalize the potential. While these methods helped, they would rarely, if ever, produce a microporous nickel strike deposit that was more noble than the bright nickel coating.

Test results indicate that the composition and concentrations of the organic addition agents used in the strike bath can have a significant effect on the electrochemical potential of the subsequent deposit.[11] Usually, the activity of a nickel deposit is determined by the amount of sulfur included in the deposit during electrodeposition — the higher the sulfur the more active the deposit. This means that the deposit potential is more electronegative.

Class I brighteners such as saccharin, benzene sulfonic acid, benzene sulfonamide and benzene or toluene sulfinic acids provide sulfur that is co-deposited with the nickel. The amount of sulfur included in the deposit varies depending on the additive(s) used. Of the ones listed, saccharin, which is widely used in bright nickel plating, provides the least amount of sulfur. Benzene sulfinate provides the most.

Class II Brighteners, when used in combination with Class I Brighteners to produce brightness and leveling, also help to increase the sulfur content of the bright nickel deposit. Because they usually contain no active sulfur, they do this by causing the Class I Brightener to plate more sulfur into the electrodeposit.Organic degradation products that tend to build up in a bath over a period of time can also increase the activity of the deposit. These are generally controlled with continuous carbon purification or batch treatments.

Because the bright nickel bath is usually dragged directly into the microporous nickel strike, it is often difficult to maintain the desirable potential difference. Usually, the microporous strike deposit is more active than the bright nickel deposit because the bath cannot be continuously purified. This, in turn, allows degradents to build up. This creates the need to batch-carbon treat on a regular basis.

Certain additives can be used in decorative nickel plating baths to control their electrochemical potential. An example of the effect of carbon and sulfur inclusion on electrochemical potential can be seen in Table 1. The data indicate that the inclusion of sulfur into the electrodeposit makes the deposit more active, electrochemically. Conversely, the inclusion of carbon into the electrodeposit makes it more noble. In practice, before the addition of desired additives, the potential of a microdiscontinuous nickel strike is generally more electronegative than the bright nickel deposit. After the desired materials are added, the deposit becomes much less electronegative. These results demonstrate that by carefully controlling the types and the amounts of certain additives in both the bright nickel and the microporous strike baths, the desired potentials can be achieved.

Multi-layer Nickel Coatings Can Improve Performance

In conclusion, when using multi-layer nickel coatings, outstanding cosmetic and base metal corrosion protection can be achieved when the electrochemical potential of the microporous nickel strike is 20 to 40 mv more noble than the underlying bright nickel deposit. This can be achieved by minimizing the sulfur inclusion in the strike, adding the supplier's recommended additives to facilitate carbon co-deposition and low pH, carbon treating the strike as required (usually every four to six weeks). The desired porosity in the nickel strike is now more easily obtained through the use of finer, more active powders, pulsed air agitation and the addition of special activating agents. Assuming that the STEP between the semi-bright and the bright nickel deposits is in the desired range, and thickness specifications are met, multi-layer deposits with a noble microporous strike can provide rust and blemish-free surfaces even after exposure to 200 hours CASS. ***P&SF***

References

1. R. J. Clauss, R. Tremmel, R. E. Fischer and E. Hoover, *Products Finishing,* 60 (March 1983)
2. G.A. Dibari, *Metal Finishing,* **75**, 3 (June 1977)
3. Standard Specification B456-85, Appendix 4, ASTM, Philadelphia, PA.
4. E. P. Harbulak and E. W. Romanowski, *Plating & Surface Finishing,* **76**, 58 (March 1989)

Effect of Sulfur and Carbon on Electrochemical Potential Of Nickel Deposits

Test No.	% Sulfur	% Carbon	Potential (mV)
1	0.001	0.017	0
2	0.004	0.007	-60
3	0.032	0.003	-180
4	0.033	0.031	-110
5	0.036	0.220	0
6	0.053	0.067	-90
7	0.088	0.240	-40
8	0.172	0.005	-200
9	0.172	0.013	-190

Test Matrix: Standard WATTS Nickel Plus Various Addition Agents.

Plating Conditions:

T	60 °C (140 °F)
pH	4.0
CD	4.3 A/dm^2 (40Amps/ft^2)

5. T. W. Tomaszewski, L. C. Tomaszewski and H. Brown, *Plating*, **56**, 1237 (Nov. 1969)

6. J. W. Manquen, *Plating & Surface Finishing*, **66**, 47 (April 1979)

7. Engineering Standard, “Chromium Plating—Decorative- Zinc Base Alloys—Interior and Exterior,” Process Standard 8893, Chrysler Motors, Auburn Hills, MI (1991)

8. Engineering Standard, “Decorative Nickel Plating On Stainless Steel,” GM 4255M, General Motors, Warren, MI (1988)

9. A. Fukada, M. Ozawa, M. Kamitani, T. Fukushime, T. Hatanaka, H. Wada, “Improvement of the Corrosion Resistance of Decorative Chrome Plating.” Presented at the *Surface Finishing Society of Japan, 87th Conference*, p. 253 (March 1993)

10. *Ibid.*

11. A. Fukada, N. Ozawa, T. Fukushime, M. Kamitani, M. Ohgane, “Effects of Sulfur and Carbon in Nickel Plating Deposits on Corrosion Potentials.” Presented at the *Surface Finishing Society of Japan, 87th Conference*, p. 253 (March 1993).

About the Author

Robert Tremmel manages the R&D facility of the Udylite Division of Enthone OMI Inc., 21441 Hoover Rd., Warren, MI 48089. He joined Udylite in 1962 and has been part of the Research staff since 1964. He is a graduate of the University of Detroit and an established member of the AESF Detroit Branch. Robert has authored numerous publications and claims more than 25 U.S. patents.