Investigations into the Performance of Multi-layer Nickel Coatings in Both CASS and Exhaust Gas Corrosion Testing

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Decorative coatings used in exterior automotive applications are typically comprised of multiple layers of nickel and chromium. Generally, three or four layers of nickel are applied prior to the chromium plating for exterior automotive applications. The properties of these nickel layers have a tremendous impact on the corrosion performance of the deposit and the subsequent service life of the part. The most widely used accelerated corrosion test to evaluate exterior automotive parts is the Copper Accelerated Acetic Acid Salt Spray (CASS) test. Certain areas on the exterior of a vehicle, such as bumpers, are also exposed to exhaust fumes. These fumes can degrade decorative coatings prematurely. A test method has been developed which can simulate prolonged exposure to these exhaust gases. This paper will review the results of experiments focused on the optimization of one of these layers, specifically by reviewing modifications made to the microporous nickel layer and the subsequent impact on the corrosion performance of the parts in both standard CASS testing and after exposure to cyclic corrosion simulating exposure to exhaust gases.

Keywords: *Automotive finishing, decorative finishing, nickel-chromium, CASS test, exhaust fume simulation, corrosion testing.*

Multi-layer nickel plating

For exterior grade automotive applications, most automotive manufacturers specify three or four layers of nickel applied to the part prior to chromium plating. This is because multi-layer nickel coatings have been proven to provide significantly improved corrosion performance compared to single layer nickel of comparable thickness. The multi-layer nickel coatings provide both dramatically increased corrosion protection to the part, and maintain the cosmetic appearance of the part for a much longer time. It is important to understand how the various layers of nickel work together as a system to protect the part.

Plating a steel part in one layer of nickel followed by chromium plating will provide a barrier coating to the steel part, a similar concept to painting the part. However, like paint, once the plated nickel layer is compromised by a chip or crack in the coating, corrosion of the basis steel will occur. A look at the galvanic series (Table 1) shows that both mild steel and nickel are more active than passive (oxidized) chromium. The corrosion will largely be driven by the chromium layer acting as the cathode in the corrosion cell, and the nickel and/or steel acting as the sacrificial anode. This would cause the nickel and steel to be dissolved preferentially to the chromium. Generally, thicker layers give better protection than thinner layers, since there is a thicker, less porous barrier, and there is also more nickel to dissolve.

In order to improve the substrate protection, duplex nickel plating was developed. Duplex nickel involves plating bright nickel over a sulfur-free semi-bright nickel layer. Since bright nickel is normally applied as a base for chromium plating, it needs to be smooth and reflective to provide the best finish. To accomplish this, bright nickels contain organic additives, and portions of these additives are incorporated in the deposit. This in turn increases the sulfur content of the deposit, and causes the deposit to be electrochemically more active than a deposit from a sulfur-free semi-bright process. This means that the bright nickel deposit will dissolve preferentially to the semi-bright nickel deposit. Any corrosion which penetrates to the semi-bright layer will spread laterally into the more active bright nickel layer. Before corrosion will penetrate to the substrate a significant portion of the bright nickel layer must be removed. This would result in much better substrate protection, but the visual appearance of the part will suffer due to the attack of the bright nickel. Generally a duplex nickel coating will be composed of 60 to 70% of the total

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Table 1
Galvanic series

MORE ACTIVE
Magnesium
Zinc
Aluminum
Cadmium
Chromium (active)
Iron & Mild Steel
Stainless Steel (Active)
Titanium (Active)
Lead
Tin
Nickel (Active)
Brass
Nickel (Passive)
Chromium (Passive)
Stainless Steel (Passive)
Copper
Silver
Titanium (Passive)
Gold
Platinum
LESS ACTIVE

deposit thickness being semi-bright nickel, and 30 to 40% of the total thickness being bright nickel.

The above examples illustrate two of the fundamental drivers for the performance of the multi-layer nickel coatings. The deposit thickness and the relative electrochemical potentials of each layer of nickel will have a major impact on the performance of the coating in service. These properties are normally tested using the STEP test. "STEP" stands for "Simultaneous Thickness and Electrochemical Potential." The STEP test measures the thickness and the electrochemical potential of the different nickel layers, and records each layer on a graph, as shown in Fig. 1.

The relative electrochemical potential differences in the nickel layers are what help keep the corrosion from the surface of the plated part and protects the basis metal from corrosion. These values are normally specified by the automotive manufacturers. For example, GM4374M, "Decorative Chromium Plating - Copper, Nickel, Chromium Type" specifies the following:

3.2.2.1.1 *The bright (or satin) nickel layer shall exhibit an anodic electrochemical potential difference of 100-200 mV to semi bright nickel on all significant surfaces. Conformance to this requirement shall be determined using appropriate statistical charting techniques on a routine quality control basis.*

3.2.2.1.2 *The microparticulate nickel layer shall exhibit a cathodic electrochemical potential difference of 10 - 40 mV to the bright nickel on all significant surfaces of all substrates.*

3.2.2.1.3 *The optional "high activity nickel strike" layer shall exhibit an anodic electrochemical potential difference of 15 - 40 mV to the bright nickel layer.*

Triple nickel refers to a three-layer system comprised of semi-bright, bright and microporous nickel layers. Conventional chromium deposits are fairly pore-free. If the coating is compromised in isolated areas, a large amount of corrosion will occur in these few areas. Microporous nickel is a thin layer over the bright nickel where intentionally created pores are formed. These pores aid in spreading the corrosion current into many small pores, opposed to a few large sites. This reduces the current seen at each site, thus slowing the

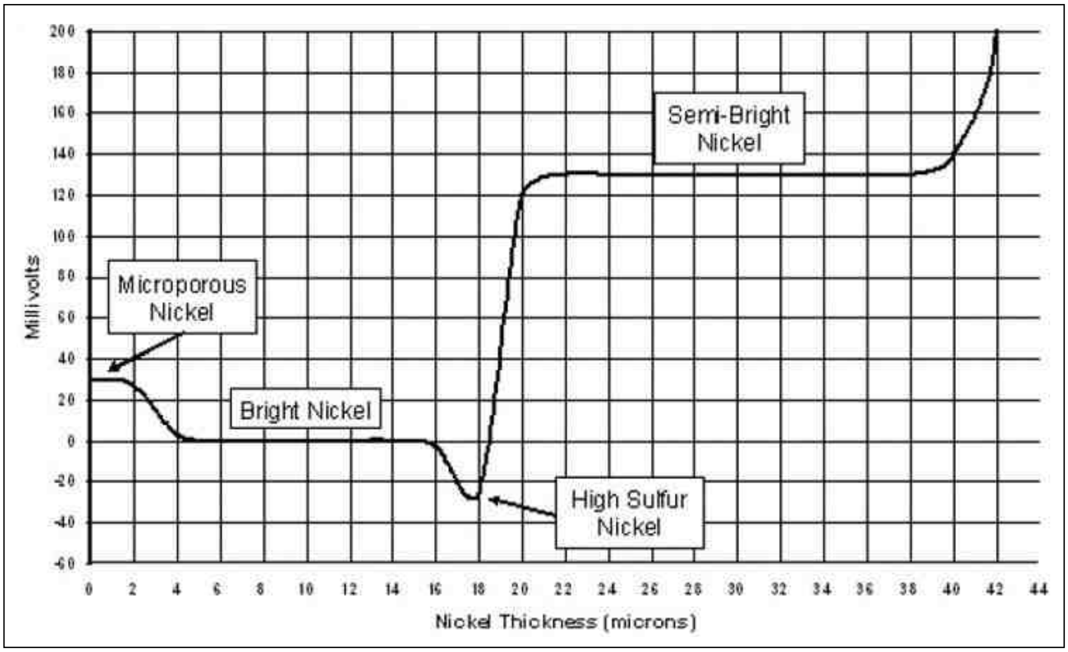


Figure 1—*STEP graph of a four-layer nickel deposit.*

corrosion. Since the current is spread over a large number of very small corrosion cells, the overall appearance remains relatively free of cosmetic defects, due to the greatly reduced size of corrosion sites (Fig. 2). The microporous layer must be less active than bright nickel so that the bright nickel layer corrodes preferentially to the microporous strike layer. If the microporous layer corrodes preferentially to the bright nickel layer, the result will be visible corrosion and a general dulling of the surface.

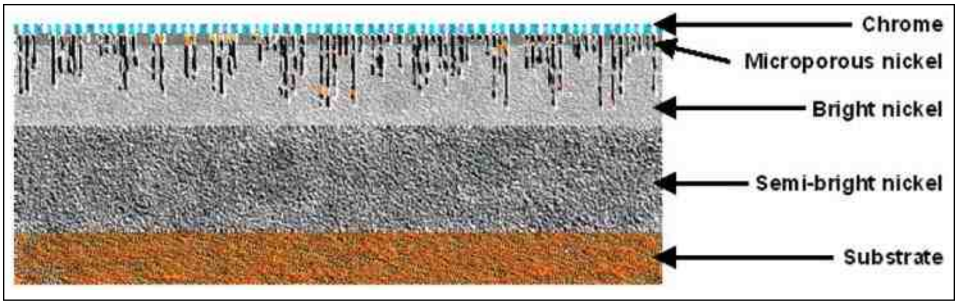


Figure 2—*Triple-layer nickel corrosion mechanism.*

The number of pores is a third major control factor in multi-layer nickel plating (along with the thickness and the relative electrochemical potential). A typical minimum figure for exterior automotive applications is 10,000 pores per cm^2 as measured by the copper deposition (Dubpernell) method, and 2,000 pores per cm^2 as measured by the active site method. Additional control factors for the porosity include pore distribution on the part, the pore size and the thickness of the microporous layer. These factors were controlled in the following tests by using the same inert particles for each set, and measuring a panel from the same rack location.

The fourth layer used in a quad-layer nickel system is a high activity layer plated between the semi-bright and the bright layers. This deposit contains a high level of sulfur, and is a very active deposit. The function of this layer is to dissolve preferentially to all other nickel layers. A photograph of the corrosion mechanism of a high sulfur nickel layer is shown in Fig. 3.

Experimental design

A series of steel panels were plated through multi-layer nickel using eight different levels of inert solids in the microporous bath, which gave a range of porosity in the chromium layer of the plated panels. The sets of panels were designated "Level 0" indicating no solids added, to "Level 7," representing the highest level of solids added (Table 2). The panels were all from the same source, and processed on the same plating line using the same process. The panels were plated in a multi-layer system comprised of semi-bright nickel, high sulfur nickel, bright nickel, microporous nickel and hexavalent chromium. These panels were then subjected to testing to verify the deposit properties, and then performance tested in both CASS (copper accelerated acetic acid salt spray) and a cyclic corrosion test utilizing simulated gas condensate to replicate exposure to exhaust gases. The goal of this series of tests was to determine if an optimal level of porosity exists which maximizes the performance of quad-layer nickel specifically in terms of protecting the substrate. The specific test procedures used were designed to measure the following:

1. Correlation of Dubpernell results vs. active sites at varying degrees of porosity, including active sites generated via CASS and via cyclic corrosion testing.
2. CASS performance vs. various levels of porosity.
3. Performance in cyclic corrosion with exhaust gas condensate vs. various levels of porosity.

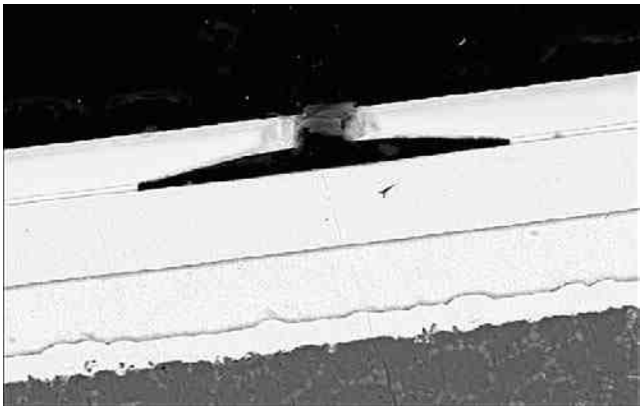
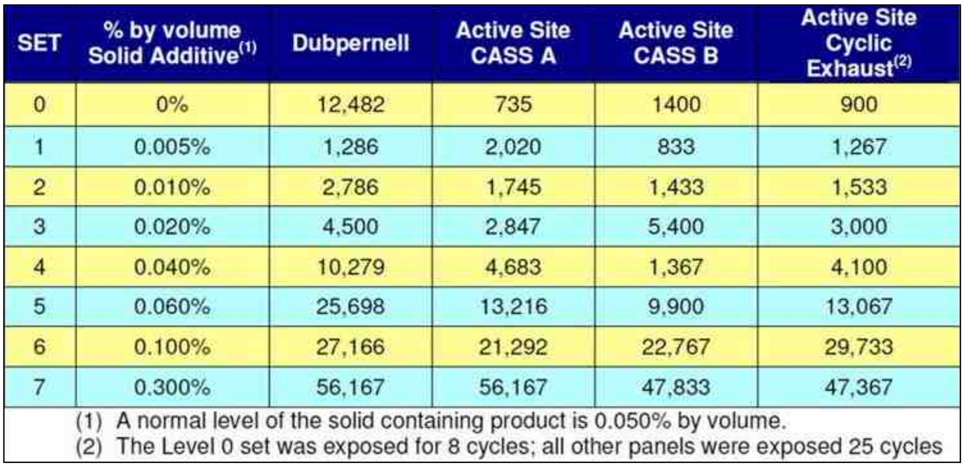


Figure 3—*Corrosion of the sacrificial high-sulfur nickel layer.*

Table 2

Pore count results of various procedures (Pores per cm^2)



SET	% by volume Solid Additive(1)	Dubpernell	Active Site CASS A	Active Site CASS B	Active Site Cyclic Exhaust(2)
0	0%	12,482	735	1400	900
1	0.005%	1,286	2,020	833	1,267
2	0.010%	2,786	1,745	1,433	1,533
3	0.020%	4,500	2,847	5,400	3,000
4	0.040%	10,279	4,683	1,367	4,100
5	0.060%	25,698	13,216	9,900	13,067
6	0.100%	27,166	21,292	22,767	29,733
7	0.300%	56,167	56,167	47,833	47,367

(1) A normal level of the solid containing product is 0.050% by volume.
(2) The Level 0 set was exposed for 8 cycles; all other panels were exposed 25 cycles

Pore count test methods and results

Each set of the eight microporous test runs was tested for pore count using the Dubpernell method per ASTM B-456 Appendix X4. A second set was tested for active sites per ASTM B-456 Appendix X5. These panels were exposed for 66 hr of CASS per ASTM B-368 prior to active site analysis. A third set was tested via the active site method above after 66 hr CASS in a second laboratory. These panels were exposed for 66 hr of CASS per GMW-14458 prior to active site analysis. The fourth set was tested for active sites after exposure to cyclic corrosion testing using GMW-14872 with exhaust gas condensate as an addition. In this fourth set, the Level 0 panels received eight cycles, while all other panels received 25 cycles. The porosity reported for each set is the average of three readings. The results are summarized in Table 2.

A graph of the porosity of each set as determined by the different methods is shown as Fig. 4. CASS B porosity results for Set #4 is significantly lower than either CASS A or the cyclic exhaust tested panels. The active site measurement from cyclic corrosion Set #6 showed a significantly higher pore count than either CASS A or B. Aside from these two anomalous readings, the general correlation of the porosity values as measured by active site after CASS A, CASS B and after cyclic corrosion testing with exhaust condensate is fairly consistent. Future experiments will repeat this testing to verify that the initial correlation consistently holds true.

The porosity as measured by the Dubpernell test shows three significant deviations from the other testing methods (Sets #0, #4, and #5). On Set #0, the Dubpernell method measured more than 12,000 pores/cm^2 while the other three methods all measured 1,400 pores/cm^2 or lower. This is a significant deviation, and highlights the potential unreliability of the Dubpernell method. The fact that pores measured by Dubpernell do not all become active sites is compensated for in most exterior automotive specifications, which require a minimum of 10,000 pores per cm^2, as measured by Dubpernell, but only 2,000 pores cm^2 as measured by active site. One interesting aspect of the result is the fairly good correlation seen in Sets #1 through #3, all fairly low porosity values. More testing needs to be done on this, but one initial theory to explain these results is that at lower porosity, a greater percentage of potentially active sites do in fact become active, due to a greater tendency for electrochemical attack in these areas. In the photos shown in Figs. 5a and b, for each of the seven levels of insert solids in the microporous bath, the pictures on the left are after Dubpernell testing, while the ones on the right are active sites after 66 hr CASS (CASS A). All photos are at 100× magnification.

Corrosion results

Sixteen panels were exposed to CASS corrosion testing, representing two panels from each porosity Level 0 thru 7. The corrosion test used was performed per GMW-14458, described below:

GMW-14458 Procedure for Copper-Accelerated Acetic Acid Salt Spray (CASS) Test
(Issue/Revision Date 5/06):
The procedure for Copper-Accelerated Acetic Acid Salt Spray (CASS) Test is a non-cyclic exposure in a fog environment produced by atomizing a solution, consisting of a base 5% NaCl solution mixed with copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) and acetic acid, in an environmental chamber at 50 ± 2°C (pH = 3.1 - 3.3, specific gravity = 1.0255 - 1.0400 @ 25°C).

The parts were run in CASS until red rust was observed on the panel face, to a maximum of 720 hr. The results are summarized in Table 3.

With the exception of one panel, all parts tested went the full 720 hr without forming red rust. The substrate protection offered by the four-layer nickel system therefore gave outstanding protection to the steel substrate. There was no effective difference seen in substrate protection from the CASS samples.

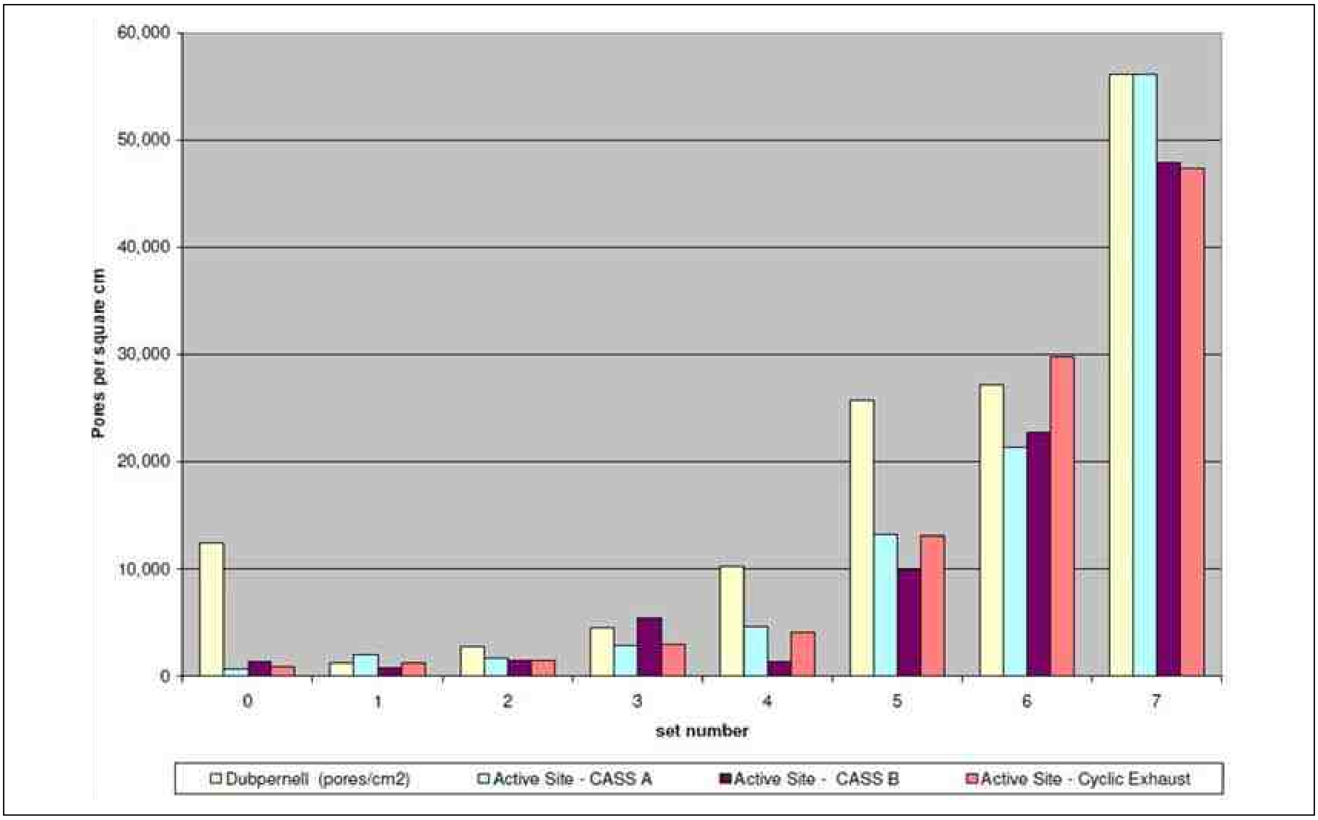


Figure 4—*Comparison of porosity results by test method.*

Sixteen samples were tested using GMW-14872 Cyclic Corrosion Laboratory Test (11/06). The testing was for a total of 25 cycles by means of GMW-14872 Cyclic Corrosion Laboratory Test, Exposure C, Option 5 - Exhaust Condensate Addition. The condensate solution consists mainly of ammonium compounds, chloride and activated carbon (Reference SAE 2001-01-0640). The evaluation points for the test were selected to approximate three- and five-year exposures to severe field automotive corrosion environments (15 and 25 cycles respectively). Note that with the addition of simulated exhaust condensate, the field-to-test correlation has not yet been firmly established. The test method is described below:

8 hours:
Ambient stage: Temperature: 25 ± 3°C; Humidity: 45 ± 10% RH with 1% complex salt sprays (three per cycle) + exhaust condensate sprays (one per cycle).

8 hours:
Humid stage: Temperature: 49 ± 2°C; Humidity: ~100% RH.

8 hours:
Dry-off stage: Temperature: 60 ± 2°C; Humidity: = 30% RH

The panels were rated using the GMW-15357 Component Corrosion Rating Scale specification. The rating scale includes:

10 = no visible corrosion,
9 = trace of corrosion (one or two small red rust spots),
8 = slight corrosion (some small red rust spots),
7 = light corrosion (many small red rust spots, approx. 10% of area),
6 = moderate corrosion (medium size rust spots, 10-40% of area),
5, 4, 3, 2, 1 = progressively more corrosion.

All panels passed the 15-cycle exposure with the exception of the Level 0 samples, which failed after eight cycles. The remaining 14 samples were evaluated after 15 and 25 exposure cycles, at which point the test was discontinued in order to provide surfaces on which active sites porosity could be measured. The results of the testing are summarized in Table 4.

The performance of the parts in the GMW-14872 cyclic corrosion test utilizing exhaust condensate is significantly different than the CASS performance. The most immediately apparent difference is the failure of the Level 0 parts at eight cycles, while the rest of the panels all passed 15 cycles with no evidence of attack. Figure 6 shows the condition of the Level 0 parts after eight cycles. Figure 7 shows examples of three panels illustrating the visual difference in ratings 6, 7 and 8 per the GMW-15357 Component Corrosion Rating scale. The Level 0 parts exposed for eight cycles shown in Fig. 6 are in significantly worse condition than the 25-cycle Level 4 parts with an "8" rating in Fig. 7.

In addition to the very poor performance of the Level 0 parts, the higher porosity panels in Sets 5 thru 7 outperformed the low porosity samples in Sets 0 thru 2. The indication is that increasing porosity beyond what is normally specified may be beneficial for parts exposed to exhaust gas.

Conclusion

Multi-layer nickel coatings have been in use for decades, and have been the subject of many previous studies. The conclusive evidence is that triple- and quad-layer nickel coating systems offer vastly improved performance over single- and double-layer nickel systems for protecting the substrate from corrosion. On any given substrate,

Figure 5a—*Dubpernell porosity (L) and CASS A (R) test results for each of the seven levels of insert solids in the microporous bath (100×): Levels 0 thru 3.*

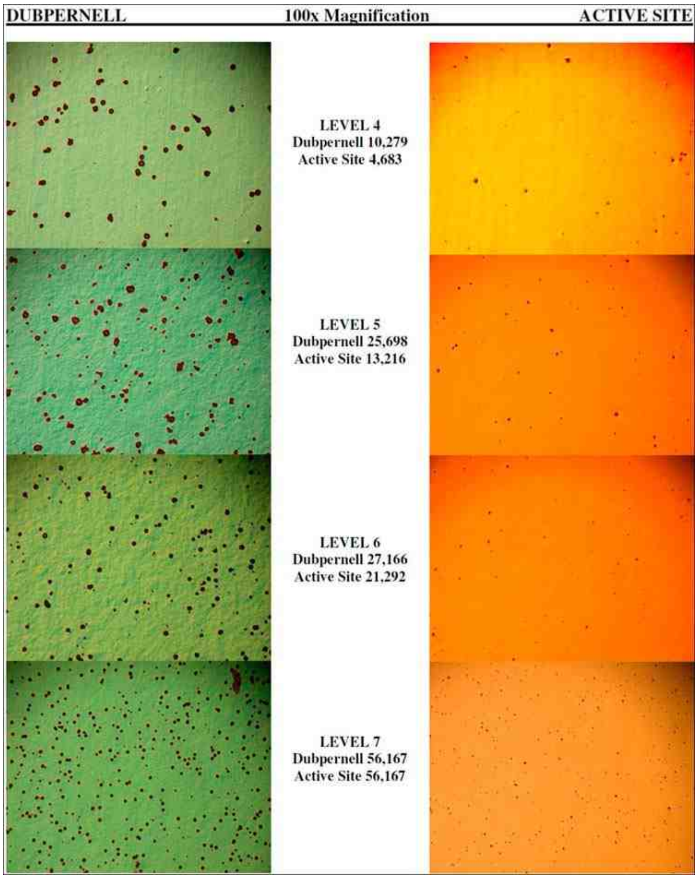
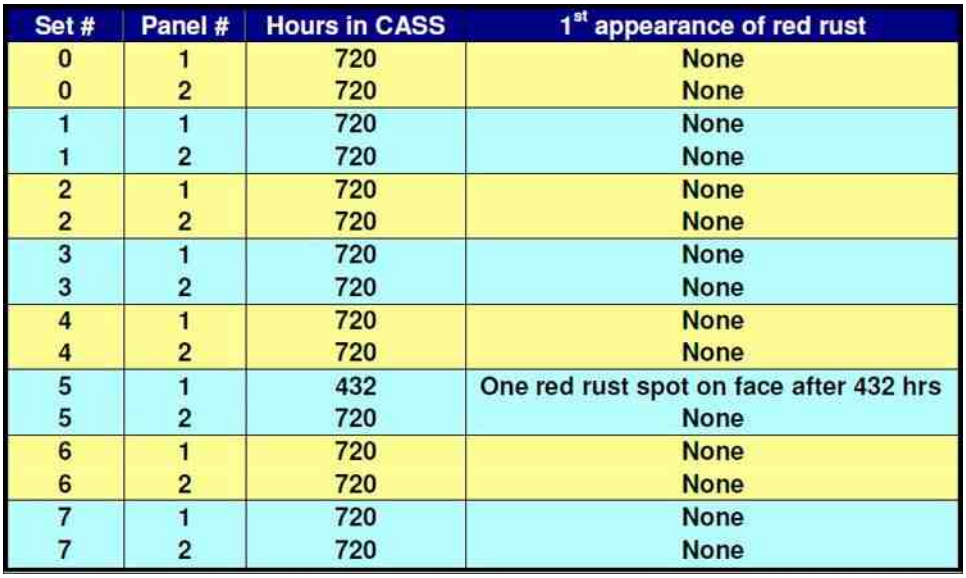


Figure 5b—*Dubpernell porosity (L) and CASS A (R) test results for each of the seven levels of insert solids in the microporous bath (100×): Levels 4 thru 7.*

Table 3

720 hr CASS results



Set #	Panel #	Hours in CASS	1st appearance of red rust
0	1	720	None
0	2	720	None
1	1	720	None
1	2	720	None
2	1	720	None
2	2	720	None
3	1	720	None
3	2	720	None
4	1	720	None
4	2	720	None
5	1	432	One red rust spot on face after 432 hrs
5	2	720	None
6	1	720	None
6	2	720	None
7	1	720	None
7	2	720	None

Table 4

GMW-14872 cyclic corrosion exposure results

Set	Panel #	15 Cycle Rating	15 Cycle Observation	25 Cycle Rating(2)	25 Cycle Observation
0(1)	Panel 1	5	Red rust after 8 cycles		
0(1)	Panel 2	5	Red rust after 8 cycles		
1	Panel 1	10	No red rust	7	Spotty red rust
1	Panel 2	10	No red rust	10	No red rust
2	Panel 1	10	No red rust	6	Spotty red rust
2	Panel 2	10	No red rust	9	Trace, spotty red rust
3	Panel 1	10	No red rust	9	Trace, spotty red rust
3	Panel 2	10	No red rust	10	No red rust
4	Panel 1	10	No red rust	8	Spotty red rust
4	Panel 2	10	No red rust	8	Spotty red rust
5	Panel 1	10	No red rust	10	No red rust
5	Panel 2	10	No red rust	10	No red rust
6	Panel 1	10	No red rust	10	No red rust
6	Panel 2	10	No red rust	10	No red rust
7	Panel 1	10	No red rust	9	Trace, spotty red rust
7	Panel 2	10	No red rust	10	No red rust

(1) The two panels from sample group "0" were removed from test after 8 cycles, with a bare steel control coupon mass loss of 1.07 grams (versus a specified end-of-test mass loss range of 3.66 – 4.22 grams)

(2) All panels, with the exception of the two panels from sample group "0", were exposed for 25 cycles with end-of-test bare steel control coupon mass loss of 3.99 grams (versus a specified end-of-test mass loss range of 3.66 – 4.22 grams)

the performance of the system is dependent on many simultaneous factors, such as total deposit thickness, electrochemical potential, undercoats, chromium type, chromium thickness and many other factors. These factors are the subject of an ongoing extensive joint testing matrix to optimize the performance of these systems.

One fundamental aspect of controlling the performance of the coatings is measuring and maintaining the deposit porosity. While active site measurements are generally considered to be the most accurate, it is not a method that is very useful for in-process checks on a production line. The Dubpernell method is much faster, and is commonly used as a process control check, but the results do not indicate which of the potentially active sites actually become active. The fact that the Dubpernell test results showed a high pore count when active pores actually were low is not reassuring for the Dubpernell technique, and casts doubt on the reliability of the test method in these conditions. The correlation of the results between the Dubpernell and active site methods over a wide range of porosity levels warrants further testing.

This preliminary study looked at how the level of microporosity in a quad-layer nickel system impacts the corrosion performance of the coating system. While CASS testing showed little impact of the porosity in terms of substrate protection, there were significant differences seen in performance on samples tested using GMW-14872 cyclic corrosion testing. In the latter test, the degree of substrate protection had very good correlation to the degree of porosity. The higher porosity levels in series 5 - 7 resulted in less red rust evident on plated steel panels. The most catastrophic failures seen in the GMW-14872 cyclic corrosion test were the samples which exhibited the lowest porosity as measured by active site. These results suggest that in areas exposed to exhaust gases, the higher porosity seen in series 5 through 7 would be beneficial.

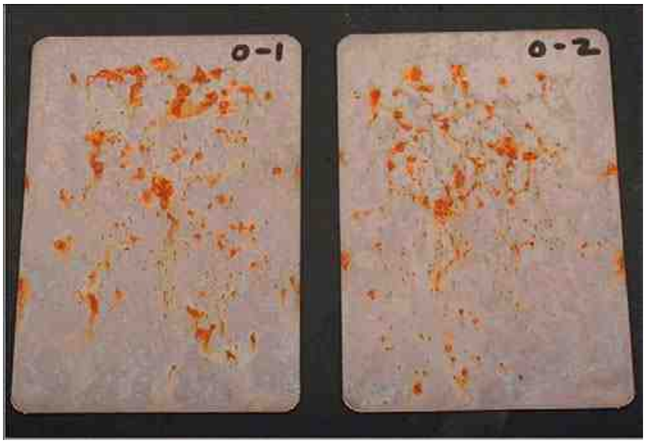


Figure 6—*Sample group "0" panels after eight cycles of GMW-14872 exposure.*

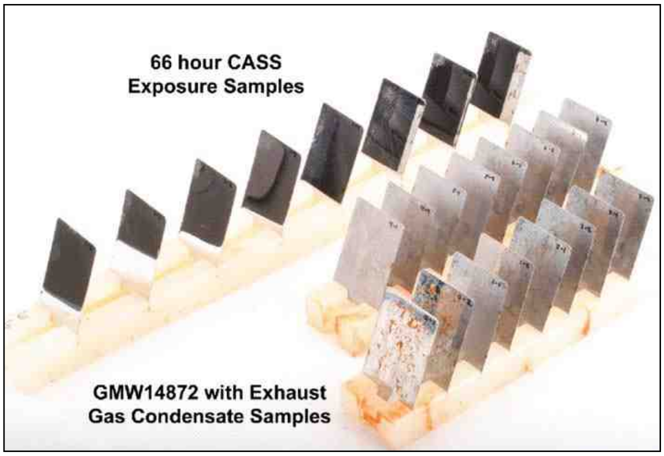


Figure 8—*All sets after CASS and GMW-14872 cyclic corrosion testing.*

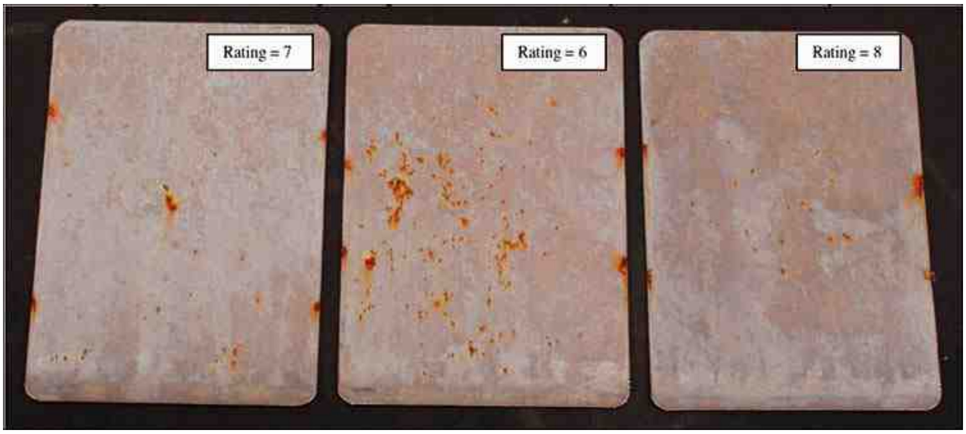


Figure 7—*Panels showing ratings 6, 7 and 8 after 25 cycles of GMW-14872 exposure.*

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Will Schumacher has worked for General Motors his entire career, beginning in 1970 as a forensic metallurgical analyst at Chevrolet Central Lab in Detroit. Much time was spent later at the Milford Proving ground where he was responsible for developing corrosion testing procedures and facilities based on real-world vehicle exposure. Most recently he is with GM's Global Materials Engineering organization, responsible for exterior/interior and electrical systems metals, finishes and corrosion. Also at this time, he is highly involved with hybrid batteries and alternate propulsion systems. Will holds B.S. and M.S. degrees in Metallurgical Engineering from Michigan Technological University.