### Technical Article

### Twenty-six Year Corrosion Study Comparing Decorative Hexavalent and Trivalent Chromium

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The results of a 26-year corrosion study are presented. The study compares the corrosion performance of Service Condition 1 through 4 nickel/chromium plated steel and zinc die-castings. CASS, mobile, industrial and marine exposures are used. Due to the potential increase in regulations on hexavalent chromium electroplating, the study's comparison between decorative hexavalent and trivalent chromium deposits is of particular interest.

### Introduction and background

Decorative trivalent chromium electroplating became available in North America in 1975 after several years of successful use in Europe. This process offered an established method to plate decorative chromium without using hexavalent chromium. Increasingly stringent regulations were making it more difficult and expensive to use hexavalent chromium. Over the 30 plus years since this process was established, several suppliers have introduced their own processes. More regulations have also been introduced governing the use of hexavalent chromium. Due to trivalent chromium's much lower health, environmental and safety (HES) factors, its regulations are much easier to meet.

### Nuts & Bolts: What This Paper Means to You

Despite the fact that real estate developers have gobbled up much of the land around the venerable LaQue Corrosion Center at Kure Beach, NC, the samples of the original corrosion test work on decorative trivalent chromium have been exposed to the marine environment for 26 years. This fortunate survival allows a rare glimpse into true field performance of this important coating system. Of course, its importance is more important in light of the regulatory climate for hexavalent chromium. Initially, electroplaters and their customers were interested in decorative trivalent chromium processes because of their significant HES advantages compared to hexavalent chromium. Some users truly wanted to take advantage of the HES benefits while other platers, as well as some of their customers, just wanted to use trivalent chromium to demonstrate that they were a "green" company. Others chose to spend the time and money to do what was necessary to meet the regulations to continue to use hexavalent chromium.

In recent years, productivity advantages have become the major reason many platers converted to decorative trivalent chromium processes. Product safety became a secondary advantage. However, this might change if OSHA regulates a much lower PEL on hexavalent chromium<sup>1</sup> as planned. No changes in regulations for trivalent chromium are being considered. Decorative trivalent chromium electroplating processes increase productivity through:

- No burning and whitewash
- Complete tolerance to current interruption
- · Increased throwing and covering powers
- Reduction or elimination of the need for auxiliary anodes
- Micro-porous as plated eliminating the need for particle nickel
- · Increased plating rate
- · Less macro-cracking in thicker deposits
- No anode or solution conditioning at startups or shutdowns
- Deposits with physical properties similar to hexavalent deposits.<sup>2</sup>

\* Corresponding author: Dr. Donald L. Snyder Atotech USA 1750 Overview Drive Rock Hill, SC 27930 USA Phone: (803) 817-3639 Fax: (803) 817-3624 E-mail: Don.Snyder@atotech.com By taking advantage of the operational benefits of decorative trivalent chromium electroplating processes, many platers are able to place more parts on their racks while reducing plating rejects. This contributes to increased productivity. Combining the productivity and operating advantages of trivalent chromium processes, many times it is less expensive, per part, to plate from decorative trivalent chromium processes than from hexavalent chromium. This reduced price per part is obtainable even though the price per liter of trivalent chromium operating solution is higher than hexavalent chromium processes.

Some of these operating advantages are:

- Reduced waste treatment no hexavalent chromium and lead salts
  - Reduced drag out due to lower viscosity compared to hexavalent solutions
  - Operates at approximately one-fifth to one-tenth the concentration of chromium
- Reduced ventilation requirements offering lower operating costs with less paperwork and maintenance
- · Consistent bath purity
  - Ion exchange removes metallic impurities
  - · Carbon removes organic impurities, if necessary
  - Complete tolerance to dragged in sulfate, chloride and boric acid
  - Able to return dragged out solution back into operating solution without a buildup of impurities
- "Indefinite life," low cost graphite anodes
- · Reduced health/environmental/safety issues
  - Lower liability potential by eliminating carcinogenic and strongly oxidizing hexavalent chromium ions
  - Solution less aggressive towards operators, equipment and environment

Even though many platers and end users recognize the advantages of using decorative trivalent chromium processes, two concerns are frequently expressed, deposit color and corrosion resistance. The color of the deposits from the original decorative trivalent chromium process is similar in appearance to polished stainless steel or pewter. Even though the deposit color is slightly darker than the standard blue-white color of hexavalent chromium deposits, it has a very eye appealing appearance. The deposit even appears to have depth. Some users prefer this difference in appearance to distinguish their chromium plated parts from others.

The color of commercially obtained electrodeposits can be compared using a colorimetric  $L^*a^*B^*$  analysis (Fig. 1) similar to that used for paints and the like. The original commercial tri-



Figure 1-Color comparison of commercially obtained electrodeposits.

valent chromium deposit, labeled "Pewter Appearance," contains more red and blue than hexavalent chromium deposits. The extra red gives the deposit its darker pewter appearance. The most common North America trivalent chromium deposit used today, labeled "Standard Appearance," has a similar amount of blue as hexavalent chromium deposits but still contains more red, making it slightly darker in appearance. If viewed separately from hexavalent chromium deposits, most people would not recognize that there is a difference in the color between these chromium deposits. However, if hexavalent and trivalent deposits are required to match because they are placed adjoining to each other, deposits such as those labeled "Near Hexavalent Appearance," could be used. Even though the color of the deposits is not identical (Fig. 1), they are close enough that they would be indistinguishable to most people. The processes that produce these different appearing trivalent chromium deposits have different operating conditions that might offer some commercial advantage.3 A "Bright Nickel" deposit is included in Fig. 1 as a reference since most platers are familiar with its yellowish appearance. Thin hexavalent or trivalent chromium deposits over bright nickel tend to have a slight yellow appearance due to the yellow color of nickel showing through the chromium deposit.

Because there are now trivalent chromium deposits that are similar in appearance to hexavalent chromium deposits, there is less concern today regarding the difference in color. However, corrosion resistance continues to be of concern to some. This might be due to the lack of published long-term corrosion data. There might also be a concern that different trivalent chromium processes might offer different levels of corrosion performance. One way to evaluate corrosion resistance is to conduct accelerated corrosion tests. However, most people familiar with CASS testing,<sup>4</sup> the most common accelerated corrosion test used for decorative nickel/ chromium deposits, know that CASS is not necessarily a good predictor of actual in-service corrosion. It is however useful as an indicator of the system's corrosion protection value compared to another or standard deposit system in a CASS environment. The best evidence of in-service corrosion performance is from longterm atmospheric corrosion tests using a variety of corrosive environments. This type of corrosion study is very seldom undertaken today because it requires many years to complete with a major time and expense commitment to the project.

### Long-term corrosion study

When decorative trivalent chromium electroplating became available in North America in 1975, an extensive, long-term corrosion study was undertaken. It was designed to determine if there was a difference in corrosion performance between hexavalent and trivalent chromium deposits when used within a variety of nickel/ chromium plating systems. A major objective of this study was to determine if trivalent chromium deposits would meet decorative automotive corrosion performance requirements. The results could be used as additional information for updating ASTM B 456 and ISO 1456. Both of these international standards address the requirements and performance of decorative copper/nickel/ chromium electroplating systems.

The plating systems for ASTM B 456,<sup>5</sup> Service Conditions 3 (SC 3) and Service Condition 4 (SC 4) were used to represent typical decorative automotive copper/nickel/chromium plating specifications. The deposits used in this corrosion program meet all the requirements specified in the 1975 edition of B 456 including minimum deposit thickness, physical properties and chromium deposits. ASTM B 456 does not distinguish between trivalent and hexavalent chromium deposits. By meeting these requirements, the plating systems should obtain the minimum number of hours of

Table 1 Service Conditions (SC), ASTM B456⁵

SC	Classification	Likely exposure	Typical use	Hours of CASS	Hours of Corrodkote
4	Very severe	Denting, scratching, abrasive wear, salt and water.	Exterior automotive	22	32
3	Severe	Occasionally to frequent wetting (water, rain, dew) and exposure to strong cleaners and saline solution.	Outdoor and hospital furniture; bicycles.	16	16

CASS testing cited in B 456 with zero base metal corrosion (Table 1). In addition to CASS, the study included Corrodkote,<sup>6</sup> mobile, static industrial and static marine corrosion environments.

The deposits were electroplated on flat  $10 \times 15$ -cm (4 × 6-in.) cold-rolled steel panels and zinc die-castings in well worked 760-L (200-gal) tanks. The plating racks held 4 panels at a time and utilized shields and robbers to produce deposits that were uniformly thick within plus or minus 10% of the required thickness. The mobile test was conducted on tractor-trailers exposed to an industrial environment and road salt while traveling around the southern shore of Lake Erie. This area is called the Rust Belt of the northeastern United States. The panels were mounted vertically on the front end of the trailer, directly over the back wheels of the tractor. They were cleaned only when the trailer was cleaned using the same strong cleaning method.

The marine exposure was at Kure Beach, NC, on a site 240 m (800 ft) from the ocean. Many organizations use Kure Beach<sup>7</sup> to investigate marine corrosion because it is a recognized monitored corrosion site on a narrow Atlantic Ocean peninsula. Table 2 lists some of the many corrosion factors that are continuously monitored at Kure Beach. These conditions are for the tenth year of this study but are representative of the conditions over the entire study. The static industrial exposure location was on the roof of a chemical manufacturing site in Cleveland, Ohio, downwind from oil refineries and steel mills. Both the marine and industrial panels were mounted on racks, tilted 60° above the horizontal, facing south. The panels were never washed other than by rain or natural phenomena.

# Table 2Corrosion factors monitored atmarine corrosion site: 1987, Tenth year into study

#### Kure Beach, North Carolina, USA (Recognized corrosion site with monitored environment)

#### **Representative corrosion conditions**

- ✓ 30 g chloride ions /m²/yr
- ✓ Corrosion rate of 54.6  $\mu$ m/yr (2.15 mil/yr) for iron\*
- ✓ Corrosion rate of 2.36  $\mu$ m/yr (0.093 mil/yr) for zinc\*
- ✓ Temperature range of 7.2 to  $25.9^{\circ}$ C (45 to  $79^{\circ}$ F)
- ✓ Relative Humidity range of 62% to 84%
- Average calculated time of wetness, 366 hr/month
  \* using 4 × 6 in. coupons

### Plating systems, 1975 versus present

There are several corrosion inhibiting techniques that are commonplace today that were not normally used in 1975 when this project was started. Experience has shown that if these techniques were used on the deposit systems studied in this project, the corrosion resistance would have been improved. This is particularly true with the improvement obtained in the after corrosion appearance of the surface of the part. Nevertheless, a review of the project data shows that most of the plating systems included in this project surpassed the current ASTM specified minimum hours to substrate corrosion without these techniques. However, the appearance of the deposits after corrosion was not as good as would be available, and expected, today.

Examples of techniques not in the 1975 edition of ASTM B 456 but part of the 2003 edition are:

- Noble nickel deposits between bright nickel and chromium
  - Particle nickel, used to produce micro-porous hexavalent chromium, with STEP measurements<sup>8</sup> more noble than bright nickel.
  - Noble nickel (without particles) with STEP measurements more noble than bright nickel used under trivalent chromium which is micro-porous as plated.
- · Increased nickel thickness
  - Service Condition 5 added to ASTM B 456 for increased corrosion protection of the substrate (66 hr CASS) used on exterior decorative automotive parts, requiring a noble nickel deposit.
- Physical properties of deposits
  - ° Increased emphasis on control of physical properties
  - Introduction of STEP values
  - Elimination of non-microdiscontinuous chromium option for automotive Service Conditions 3, 4 and 5

Other techniques, not mentioned in B 456 but which can be utilized to enhance corrosion resistance, are:

- Post hexavalent or trivalent chromium treatments, mostly used with thin nickel systems or on parts containing unplated surfaces
  - Organic or inorganic corrosion inhibitor immersion coatings
  - Electrolytic chromates; hexavalent, trivalent or non-chromium based.

### Rating of corroded copper/nickel/chromium plating systems

The test panels were rated at least once a year by a group of people experienced in using ASTM's rating procedure for "Electroplated Panels Subjected to Atmospheric Exposure," ASTM B 537.<sup>9</sup> The marine panels were rated during the ASTM B08 annual fall inspection of their corrosion programs at Kure Beach. To help insure a non-biased rating, the panels were rated in a random order without identifying the deposits on the panels. All of the raters had to agree on the corrosion rating within one number. The appearance rating could differ by only two numbers. In almost all cases, the rating team had at least six members. Since the average rating of the team was used, the reported rating could contain non-whole numbers.

The ASTM B 537 corrosion rating system requires some working experience to fully understand. However, for the purpose of this paper, the B 537 rating system can be summarized as follows:

The rating is a two number system, C/A, where

- "C" is the substrate corrosion rating, only substrate corrosion is considered and
- "A" is the appearance rating after corrosion, excluding the loss of appearance due to substrate corrosion.

"C" is determined by the percent of the surface covered by corrosion of the substrate, excluding run-down of corrosion products:

- C = 10, no substrate corrosion
- C = 9, up to 0.1% of the surface has corrosion to the substrate.
- C = 8, between 0.1 and 0.25% of surface has corrosion to the substrate.
- C = 7, between 0.25 and 0.5% of surface has corrosion to the substrate.

"A" reflects the loss of appearance due to corrosion, excluding substrate corrosion. It is calculated by subtracting an appearance penalty from the corrosion number "C," *i.e.*, A = C – appearance penalty:

- Penalty of 0 = no change in surface appearance due to corrosion, excluding substrate corrosion
- Penalty of 1 or 2 = after "car wash" cleaning, only a slight loss of appearance (usually due to surface pitting) which is not easily observed one meter away.
- Penalty of 3 or 4 = after "extra cleaning," a reduction in appearance (reflectivity) is visible one meter away.
- Penalty of 5 or 6 = appearance is no longer commercially acceptable even after cleaning.

The North American automotive industry in 1975 was reported to be working towards a decorative nickel/chromium plated exterior part that does not develop any substrate corrosion for over 10 years. Most automotive companies in 1975 accepted a minimum rating of 10/8 and sometimes a 10/7 after corrosion. Today, corrosion ratings of 10/9 or 10/8 are more common. For some high profile parts, some newer automotive specifications are requiring a 10/10 (no base metal corrosion, no change in appearance) after exposure to their specified corrosion test.

### Long-term corrosion study data, SC 4 and SC 3

The corrosion ratings at the end of the CASS, Corrodkote, industrial and mobile testing of SC 4 and SC 3 deposits are listed in Tables 3, 4 and 5. Two previously published papers<sup>10,11</sup> reviewed this data in detail. Table 3 lists the results for SC 4 nickel/chromium plating systems on flat steel panels without a copper deposit. This was the most common plating system used for exterior decorative automotive applications when this corrosion project started. Today, SC 5 would be used but it was not an option in ASTM B 456 at the start of this study. Table 4 lists the results for SC 4 plating systems on flat steel panels with an acid copper deposit prior to the nickel deposits. This system was used in the 1970s on parts requiring an improved appearance brought about through the superior leveling of acid copper. It is almost never used today on steel substrates. Table 5 lists the results for SC 3 nickel/chromium systems on flat steel substrates without a copper deposit. SC 3 is sometimes used

			unto be i, ste	er substrate,	no coppei		
	Average of	leposit thickness,	, μm	ASTM ratings (B537) after indicated exposure End of corrosion testing for each test condition			
Set	Semi-bright nickel	Bright nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hr	Corrodkote 132 hr
1	30	10	0.3 HC	5/3	6/4	9.7/7.7	8.8/6.7
2	23	7.5	0.3 HC	4/1	6/3	8.8/6.7	7/5
3	20	7.5+3 <sup>b</sup>	0.3 MC	9/5	9/5	10/6	10/6.7
4	23	7.5	0.3 MP	10/6	10/7	10/6	10/8
5	23	7.5	0.3 TC	10/7	10/7	10/6	10/7
6	23	7.5	0.3 TC	10/7	10/7	10/6	10/6

Table 3	
Corrosion test results – SC 4, steel substrate, ne	o copper <sup>10,1</sup>

b = nickel strike to produce MC

HC = Hexavalent Chromium TC = Trivalent Chromium

MC = MicroCracked hexavalent chromium MP = MicroPorous hexavalent chromium for interior and some exterior decorative automotive and motorcycle parts. ASTM B 456 specifies that SC 4 plating systems will have no corrosion of the substrate after 22 hr of CASS or 32 hr of Corrodkote testing. SC 3 should resist 16 hr of either CASS or Corrodkote testing without any corrosion of the substrate (Table 1).

A review of the corrosion ratings in Tables 3 through 5 shows that all MP (hexavalent chromium made micro-porous) and TC (trivalent chromium, micro-porous as-plated) sets have corrosion ratings of 10. This data demonstrates that MP and TC deposits offer equal corrosion protection of the substrate when subjected to CASS, Corrodkote and long term mobile and industrial corrosion conditions. It is also interesting to note that both SC 4 and SC 3 plating systems, with MP and TC, lasted at least 12 years in an industrial atmosphere and 7 years in mobile conditions without any substrate corrosion. The appearance after corrosion, the second number in the rating system (A), was mostly 6 or 7 indicating some loss of appearance/reflectivity. This is predominantly due to surface pitting originating at the micro-pores. The after-corrosion appearance would have been better if a noble nickel deposit was used between the bright nickel and the chromium. This is required

in all current SC 5, SC 4 and SC 3 specifications using microporous chromium. This study shows that MC (micro-cracked hexavalent chromium) offered slightly lower corrosion protection of the substrate and had a lower appearance rating after corrosion. This is consistent with other data that supports the North American automotive company's position not to include micro-cracked chromium in their standards.

Hexavalent chromium deposits (HC) are not micro-porous as plated. Some pre- or post-treatment must be used to make them micro-porous. The HC systems did not perform as well as the micro-discontinuous chromium systems (MC, MP and TC) even when thicker nickel deposits were used (Tables 3, 4 and 5). All HC sets had substrate corrosion by the end of the tests. Some had corrosion ratings as low as 4. A corrosion rating of 4 designates that between 2.5 and 5% of the surface contains corrosion down to the substrate.<sup>9</sup> This data supports the removal of the HC option (designated "r" in B 456) from SC 3 through SC 5 in the 2003 edition of ASTM B 456.

Tables 6 through 8 contain the corrosion data for SC 4 and SC 3 plating systems covering 26 years in a marine environment, at Kure Beach. A previous paper<sup>11</sup> reviewed the first 15 years. During

Table 4
Corrosion test results – SC 4, steel substrate, with copper <sup>10,11</sup>

		Average depo	osit thickness, $\mu$ n	ASTM ratings (B537) after indicated exposure. End of corrosion testing for each test condition				
Set	Copper	opperIndustrial 12 yearsIndustrial 12 yearsIndustrial 12 years				Mobile 7 years	CASS 96 hr	Corrodkote 132 hr
7	18	13	7.5	0.3 HC	5/3	5/2	9.3/6.7	10/8
8	18	10	7.5+3 <sup>b</sup>	0.3 MC	9/5	9/5	10/6	10/6
9	18	13	7.5	0.3 MP	10/7	10/7	10/7	10/8
10	18	13	7.5	0.3 TC	10/7	10/7	10/6	10/7

See footnotes for Table 3.

Table 5Corrosion test results – SC 3, steel substrate, no copper<sup>10,11</sup>

	Average d	eposit thickness,	μm	ASTM ratings (B537) after indicated exposure. End of corrosion testing for each test condition			
Set	Semi-bright nickel Bright nickel Chromium		Industrial 12 years	Mobile 7 years	CASS 96 hr	Corrodkote 132 hr	
11	23	7.5	0.3 HC	5/2	5/2	9.4/7	5.3/3.3
12	18	7.5	0.3 HC	6/3	5/2	9.3/7	5/4
13	15	7.5+3 <sup>b</sup>	0.3 MC	9/5	9/3	10/6	10/6
14	18	7.5	0.3 MP	10/5	10/6	10/6	10/8
15	18	7.5	0.3 TC	10/5	10/6	10/6	10/7

See footnotes for Table 3.

the first 21 years, all of the micro-porous hexavalent chromium (MP) and trivalent chromium (TC) systems were essentially free of substrate corrosion. A few panels had a corrosion rating of 9.5 indicating that there was one corrosion site on one of the panels among the five duplicate panels. However, this is far better than the 10-year, rust free, exterior decorative part desired by the automotive companies. The plating systems had appearance ratings of 6 and 7 (penalties of 4 and 3) mostly due to surface pitting. Fine, fairly uniformly dispersed surface pitting is an indication that the corrosion protection offered by the micro-porosity in the chromium deposit is working.<sup>12</sup> Micro-porous chromium increases the protection of the substrate while sacrificing some of the appearance/reflectivity

of the deposit. Service experience demonstrates that with a noble nickel deposit between the bright nickel and the MP or TC chromium, the appearance after corrosion is much better than what was obtained in this study without noble nickel deposits. The appearance after in-service corrosion is even better than what is observed after most CASS testing.

After 26 years of marine exposure, the corrosion ratings for the MP and TC sets were mostly 8. This indicates that during the last 5 years of marine exposure, the deposits developed substrate corrosion covering between 0.1 to 0.25% of the surface area. Even though there was substrate corrosion, all of the MP and TC plating systems performed almost identically and were also much better

Set	Ni/Cr <sup>a</sup>	Marine Corrosion Study for SC 4 ASTM Ratings (Appearance Penalty)							
	System	1 Year	5 Years	10 Years	15 Years	21 Years	26 Years		
1	30/10/0.3 HC	9.5/7.5 (-2)	6/5 (-1)	6/5 (-1)	5/1 (-4)	Removed	Removed		
2	23/7.5/0.3 HC	9.3/7.3 (-2)	6/4.7 (-1.3)	5/4 (-1)	4/1 (-3)	Removed	Removed		
3	20/7.5+3 <sup>b</sup> /0.3 MC	10/8 (-2)	10/8 (-2)	10/8 (-2)	9/5 (-4)	9/4.5 (-4.5)	8/3.5 (-4.5)		
4	23/7.5/0.3 MP	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/7 (-3)	10/7.5 (-2.5)	8/4 (-4)		
5	23/7.5/0.3 TC	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/7 (-3)	9.5/5.5 (-4)	8/4 (-4)		
6	23/7.5/0.9 TC	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/7 (-3)	10/6.5 (-3.5)	8/4 (-4)		

### Table 6Marine corrosion test results – SC 4, steel substrate, no copper

a = Shorthand nomenclature for micron thickness of semi-bright nickel/bright nickel/chromium. See footnotes for Table 3 for nomenclature for chromium deposits.

Set	Cu/Ni/Cr <sup>a</sup>	Marine Corrosion Study for SC 3 ASTM Ratings (Appearance Penalty)						
	System	1 Year	5 Years	10 Years	15 Years	21 Years	26 Years	
7	18/13/7.5/0.3 HC	10/8 (-2)	6/5 (-1)	6/5 (-1)	4/0 (-4)	Removed	Removed	
8	18/10/7.5+3 <sup>b</sup> /0.3 MC	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/8 (-2)	9/6 (-3)	8/4 (-4)	
9	18/13/7.5/0.3 MP	10/9 (-1)	10/9 (-1)	10/9 (-1)	10/8 (-2)	9.5/7 (-2.5)	8.5/4.5 (-4)	
10	18/13/7.5/0.3 TC	10/9 (-1)	10/9 (-1)	10/9 (-1)	10/8 (-2)	10/6.5 (-3.5)	8/4 (-4)	

### Table 7Marine corrosion test results – SC 3, steel substrate, with copper

a = Shorthand nomenclature for micron thickness of copper/semi-bright nickel/bright nickel/chromium. See footnotes for Table 3 for nomenclature for chromium deposits.

than any of the HC plating systems. Except for the first few years in marine exposure, the use of acid copper under the nickel deposits did not improve the after-corrosion appearance over the entire 26 year period.

All of the hexavalent chromium sets (Tables 6, 7 and 8) that did not have micro-discontinuous chromium (HC) developed substrate corrosion primarily during the first five years of marine exposure. There was also a loss of appearance generally due to large nickel/ chromium corrosion sites, blisters and in some cases, macro-cracking of the chromium deposit. Due to the different corrosion mechanism for plating systems without micro-porous chromium, noble nickel deposits usually did not significantly help reduce the loss of appearance during corrosion of HC plating systems.

Tables 9 and 10 contain the corrosion data for SC 4 deposits on zinc die-castings. The corresponding deposits on a steel substrate are in Tables 3, 4 and 6. Under all corrosion conditions studied, the corrosion performance for SC 4 over zinc die-castings did not perform as well as over steel. Even though the quality of the zinc diecastings appeared to be good prior to plating, they might have been of a lower quality than the steel substrates. The MC and TC plating systems on zinc die-castings performed about the same under all test conditions. They all had a corrosion rating of 10 after 22 hr of CASS as cited in ASTM B 456. They also performed much better than the HC system, especially in the marine test. This is consistent with the SC 4 deposits on steel substrates.

### Long-term corrosion study data, non-automotive plating systems

In the 1970s, many European standards called for bright nickel only when North American standards specified semi-bright and bright nickels. In order to compare single nickel (bright nickel) with Duplex nickel (semi-bright/bright nickels), steel panels were plated with a total nickel thickness of 25  $\mu$ m (0.001 in.), SC3

	Table 8 Marine corrosion test results – SC 3, steel substrate, no copper								
Set	Ni/Cr <sup>a</sup>		Marine Corrosion Study for SC 3 ASTM Ratings (Appearance Penalty)						
	System	1 Year	5 Years	10 Years	15 Years	21 Years	26 Years		
11	23/7.5/0.3 HC	9/7 (-2)	6/5 (-1)	6/5 (-1)	5/1 (-4)	Removed	Removed		
12	18/7.5/0.3 HC	9.7/7.7 (-2)	6/5 (-1)	6/5 (-1)	4/1 (-3)	Removed	Removed		
13	15/7.5+3 <sup>b</sup> /0.3 MC	9.7/7.7 (-2)	9.7/7 (-2.7)	9.7/7 (-2.7)	9/7 (-2)	9/6.5 (-2.5)	8/4 (-4)		
14	18/7.5/0.3 MP	9.8/8 (-1.8)	9.8/8 (-1.8)	9.8/8 (-1.8)	9.7/8 (-1.7)	9.5/7 (-2.5)	9/4.5 (-4.5)		
15	18/7.5/0.3 TC	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/6 (-4)	8.5/4 (-4.5)		

a = Shorthand nomenclature for micron thickness of semi-bright nickel/bright nickel/chromium. See footnotes for Table 3 for nomenclature for chromium deposits.

Table 9 Corrosion test results – SC 4, zinc die-castings<sup>10,11</sup>

		Average depo	<i>u</i> m	ASTM rat End of cor	ings (B537) a rosion testin	after indicat g for each t	ed exposure. est condition	
Set	Copper	Semi-bright nickel	Bright nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hr	Corrodkote 132 hr
33	7.5	30	10	0.3 HC	7/4	8/5	9.2/5	9/7
34	7.5	23	7.5	0.3 HC	6/4	7/4	9.3/6.3	9.5/6.7
35	7.5	20	7.5+3 <sup>b</sup>	0.3 MC	8/5	9/7	9.7/6.3	9.7/5
36	7.5	23	7.5	0.3 TC	8/5	9/7	9.5/6	9.5/5

See footnotes for Table 3 for nomenclature for chromium deposits.

(Tables 11 and 12). This was included in this study because the evaluation would be useful for ISO 1456, which reflects European technology. The test results showed that SC 3 Duplex nickel systems (Tables 5, 7 and 8) outperformed equal thickness single nickel systems (Tables 11 and 12) under all the test conditions in this study.

Almost all the bright nickel-only deposits developed substrate corrosion after the first year in the marine, mobile and industrial test sites.<sup>10,11</sup> Micro-discontinuous chromium (MC, MP, TC) retarded the formation of substrate corrosion but not to the extent that it did with the Duplex nickel systems. This is consistent with the corrosion theory for micro-discontinuous chromium over Duplex nickel.<sup>12</sup> Even though single nickel systems did not impede substrate corrosion for very long, both micro-porous hexavalent (MP) and trivalent (TC) chromium systems performed essentially the same.

Without any post chromium treatments that replace the "chromating" effect of hexavalent chromium ions on nickel and unplated steel, trivalent chromium deposits over thin nickel systems would not be expected to protect the substrate from corrosion as well as plating systems using processes containing hexavalent chromium ions. The 13- $\mu$ m (0.0005-in.) bright nickel plating systems in Table 13 were tested to investigate if increasing the chromium thickness would help overcome this lack of "chromate" formed by hexavalent chromium ions. These plating systems are similar to SC 1 in ASTM B 456, except B 456 only permits standard chromium (HC). Micro-discontinuous chromium is not recommended over thin nickel deposits because the nickel tends to be porous thus exposing the substrate. These plating systems were not exposed to the marine environment in this study because SC 1 is intended for use only in a dry indoor atmosphere.

A review of the data in Table 13 indicates that both the hexavalent and trivalent micro-discontinuous chromium deposits (MC, MP, TC) actually were a little better in retarding substrate corrosion than the standard hexavalent chromium deposits (HC). Also, except for the industrial test, a very slight improvement was obtained in the protection of the substrate with increased chromium thickness. This might be due to the high quality of the steel substrates, which could make the 13  $\mu$ m (0.0005 in.) of nickel pore free. When the nickel is porous or when the substrate is exposed

		Corrosio	n test results	– SC 4, zinc	die-castings				
Set	Cu/Ni/Cr <sup>a</sup>	Marine Corrosion Study for SC 3 ASTM Ratings (Appearance Penalty)							
	System	1 Year	5 Years	10 Years	15 Years	21 Years	26 Years		
33	7.5/30/10/0.3 HC	10/8 (-2)	10/7 (-3)	9/6 (-3)	6/4 (-2)	4/1 (-3)	Removed		
34	7.5/23/7.5/0.3 HC	10/8 (-2)	10/7 (-3)	9/6 (-3)	5/3 (-2)	3/0 (-3)	Removed		
35	7.5/20/7.7+3 <sup>b</sup> /0.3 MC	10/9 (-1)	10/9 (-1)	9.7/7 (-2.7)	8/6 (-2)	8/6 (-2)	8/4 (-4)		
36	7.5/23/7.5/0.3 TC	10/9 (-1)	10/9 (-1)	9/6.3 (-2.7)	9/6 (-3)	9/6 (-3)	9/4.5 (-4.5)		

Table 10

a = Shorthand nomenclature for micron thickness of copper/semi-bright nickel/bright nickel/chromium.

See footnotes for Table 3 for nomenclature for chromium deposits.

Table 11	
Corrosion test results – bright nickel over s	teel <sup>10,1</sup>

	Average deposit	thickness, µm	ASTM ratings (B537) after indicated exposure. End of corrosion testing for each test condition					
Set	Bright nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hr	Corrodkote 132 hr		
19	25	0.3 HC	2/1	1/0	3.7/2.7	3.2/2.3		
20	22+3 <sup>b</sup>	0.3 MC	5/3	2/0	7.7/4.3	9.7/8.7		
21	25	0.3 MP	5/4	5/4	6.7/3.7	8.3/7		
22	25	0.3 TC	5/4	5/4	5.5/2.7	6.3/4.3		

See footnotes for Table 3 for nomenclature for chromium deposits.

for other reasons, such as in the low-current-density areas of a part, industrial experience has demonstrated that a post chromium treatment improves corrosion protection much more than thicker chromium deposits. This is especially true for trivalent chromium systems without the benefit of the "chromating" due to the hexavalent chromium ions.

Even though the data in Table 13 does not definitively demonstrate that thicker chromium deposits help to retard corrosion of the substrate, OEM truck bumpers and some preliminary automotive standards specify 0.45  $\mu$ m (17.7  $\mu$ -in.) of trivalent chromium over noble nickel. This improves the wear without any detrimental corrosion and appearance effects. For hexavalent chromium deposits, North American automotive standards specify a minimum of 0.25  $\mu$ m (9.8  $\mu$ -in.) and sometimes a maximum of 0.4 to 0.5  $\mu$ m (15.7 to 19.7  $\mu$ -in.). The maximum is stipulated so that the chromium deposit does not bridge over the particles in the particle nickel deposit, thus reducing the effect of the micro-porous chromium. Trivalent chromium deposits are plated micro-porous so bridging over of the particles is not a concern. They also do not macro-crack as easily as thick hexavalent chromium deposits, resulting in an improved appearance.

Many truck specifications require Duplex nickel, which was not included in the plating systems reviewed in Table 13. Tables 14 and 15 contain the corrosion data for SC 3 Duplex nickel systems with normal and thick chromium deposits. In contrast to the bright nickel-only data (Table 13), there was no observable difference in base metal protection when using thicker trivalent chromium deposits over Duplex nickel systems. However, 0.9 µm (35.4 µin.) of hexavalent chromium (Set 18, HC) performed much better than 0.3  $\mu$ m (11.8  $\mu$ -in.) by protecting the substrate similar to the micro-porous trivalent chromium deposits. The appearance ratings were also similar. However, the loss of appearance in the trivalent chromium deposits without noble nickel was due to surface pitting while macro-cracking degraded the appearance of the thick hexavalent chromium deposit. This macro-cracking probably permitted the system to develop the same substrate protection corrosion mechanism as micro-cracked chromium systems.

Corrosion test results – bright nickel over steel								
Set	Ni/Cr <sup>a</sup> System	Marine Corrosion Study for SC 2 ASTM Ratings (Appearance Penalty)						
		1 Year	5 Years	10 Years	15 Years	21 Years	26 Years	
19	25/0.3 HC	6.3/4.3 (-2)	2.7/1.7 (-1)	2/1.7 (-0.3)	Removed	Removed	Removed	
20	22+3 <sup>b</sup> /0.3 MC	6/4 (-2)	6.3/4 (-2.3)	5.3/4 (-1.3)	2/0 (-2)	Removed	Removed	
21	25/0.3 MP	7/6 (-1)	5/4 (-1)	4/3 (-1)	2/0 (-2)	Removed	Removed	
22	25/0.3 TC	5.7/4.7 (-1)	4.6/3.6 (-1)	4.3/3.3 (-1)	2/0 (-2)	Removed	Removed	

### Table 12

a = Shorthand nomenclature for micron thickness of bright nickel/chromium. See footnotes for Table 3 for nomenclature for chromium deposits.

#### Table 13

#### Corrosion test results – effect of chromium thickness over thin bright nickel<sup>10,11</sup>

	Average deposit	thickness, $\mu$ m	ASTM ratings (B537) after indicated exposure. End of corrosion testing for each test condition					
Set	Bright nickel	Chromium	Industrial 1 year	Mobile 1 year	CASS 16 hr	CASS 48 hr		
23	13	0.3 HC	6/5	5.7/4	3/3	2/2		
24	10+3 <sup>b</sup>	0.3 MC	7/5	7.7/5.7	7.7/5.7	7/5		
25	13	0.3 MP	7/5	7.7/5.7	7.7/5.7	4/2		
26	13	0.3 TC	5/3	6.7/5.3	5.3/4.3	3.7/0.7		
27	13	0.6 TC	4.3/2.3	6.7/4.7	7.7/6.7	6/3.3		
28	13	0.9 TC	4.3/2.3	8/5.7	9/9	7.7/4.7		

See footnotes for Table 3 for nomenclature for chromium deposits.

### Summary

This long-term corrosion program had two main objectives:

- 1. To determine if SC 4 and maybe even SC 3 nickel/chromium plating systems within ASTM B 456 could be used to produce exterior decorative automotive parts that do not develop any substrate corrosion for at least 10 years of service and
- 2. To determine if there is a performance difference between decorative chromium deposits produced from the hexavalent and trivalent chromium processes used in these plating systems.

The advantage of this type of study is that all of the panels are very uniformly plated to the required thickness at the same time using the same processes. The physical properties of the deposits were well controlled within the requirements of ASTM B 456. The panels were also randomly positioned, tested and rated at the same time. This made it possible to make accurate comparisons between the plating systems. Production parts might not perform identically under different corrosion conditions. Many times they have lower quality substrates and less uniform deposit thickness without all the physical properties that improve the performance of the total plating system.

Both SC 4 and SC 3 (ASTM B 456) plating systems remained essentially free of substrate corrosion throughout the 15 years of marine, 12 years of industrial, 7 years of mobile, 96 hr of CASS and 132 hr of Corrodkote testing if the plating system included micro-porous chromium (MP and TC). Micro-cracked chromium systems (MC) had slightly lower corrosion and appearance ratings. This supports the North American automotive companies' exclusion of micro-cracked plating systems. Standard hexavalent

	Average deposit thickness, $\mu m$			ASTM rat End of cor	ings (B537) ដ rosion testin	ngs (B537) after indicated exposure. osion testing for each test condition		
Set	Semi-bright nickel	Bright nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hr	Corrodkote 132 hr	
12	18	7.5	0.3 HC	5/2	5/2	9.3/7	6/4	
15	18	7.5	0.3 TC	10/7	10/6	10/6	10/7	
16	18	7.5	0.6 TC	10/7	10/7	10/6	10/5	
17	18	7.5	0.9 TC	10/7	10/7	10/6	10/6	
18	18	7.5	0.9 HC	10/7	10/5	9.7/6.7	10/8	

Table 14	
Corrosion test results - effect of chromium thickness over Duplex nicke	10,11

See footnotes for Table 3 for nomenclature for chromium deposits.

Set	Ni/Cr <sup>a</sup> System	test results – effect of chromium thickness over Duplex nickel Marine Corrosion Study – Varying Chromium Thickness ASTM Ratings (Appearance Penalty)						
		1 Year	5 Years	10 Years	15 Years	21 Years	26 Years	
12	18/7.5/0.3 HC	9.7/7.7 (-2)	6/5 (-1)	6/5 (-1)	4/1 (-3)	Removed	Removed	
15	18/7.5/0.3 TC	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/6 (-4)	8.5/4 (-4.5)	
16	18/7.5/0.6 TC	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/6 (-4)	8.5/4.5 (-4)	
17	18/7.5/0.9 TC	10/8 (-2)	10/8 (-2)	10/8 (-2)	10/8 (-2)	9.5/6 (-3.5)	8.5/4.5 (-4)	
18	18/7.5/0.9 HC	10/8 (-2)	10/8 (-2)	10/7 (-3)	10/6 (-4)	10/6 (-4)	8.5/4.5 (-4)	

Table 15 Corrosion test results – effect of chromium thickness over Duplex nickel

See footnotes for Table 3 for nomenclature for chromium deposits

chromium systems (HC) all had substrate corrosion early into all of the different corrosion tests. These systems, which are not microdiscontinuous, are not permitted for exterior decorative automotive applications. They have also been removed as acceptable options for SC 3 and SC 4 in the 2003 edition of ASTM B 456.

Trivalent chromium deposits (micro-porous as plated, TC) and hexavalent chromium deposits (with micro-porosity generated through an additional step, MP) performed almost identically in substrate protection and after corrosion appearance throughout all the tests. Except for the faintly darker color and slightly more surface pitting of the trivalent chromium deposits, both micro-porous systems were equivalent. The difference in color would be less today because of the changes made in the trivalent chromium electroplating technology over the 26 years of this study. Also, recent service experience has shown that this slight increase in surface pitting would most likely have been almost eliminated if a thin, noble nickel deposit was deposited between the bright nickel and the chromium, as required in North American automotive specifications today.

The value of Duplex nickel (semi-bright and bright nickels) versus single nickel (bright nickel) plating systems, both with a total nickel of 25  $\mu$ m (0.001 in.), was dramatically demonstrated in this study. The single nickel systems developed substrate corrosion during the first year of exposure to all of the outdoor sites. They developed an extensive amount of corrosion after five years. There was a slight improvement when micro-discontinuous chromium, trivalent (TC) and hexavalent (MP and MC), was used. Some of the Duplex nickel systems developed one or two small substrate corrosion sites early in the testing but all micro-discontinuous systems, trivalent and hexavalent, were about equal in performance even at the end of the long-term outdoor tests.

### Conclusion

This study demonstrated that SC 4 and possible SC 3 plating systems most likely would last for 10 years without substrate corrosion on decorative exterior automobile parts. The deposits lasted over 10 years when uniformly plated over good quality substrates and micro-discontinuous chromium was utilized. Also, all trivalent chromium deposits performed at least as well as micro-porous hexavalent chromium deposits. This was observed even when plating systems thinner than SC 3 were used. Both trivalent and microporous hexavalent chromium deposits performed much better than standard hexavalent chromium deposits without micro-porosity.

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per 10-mL sample). Place the weighed manganese carbonate into a bucket, add water, stir to make a slurry and pour evenly over the solution surface. Never add to the solution any oxidizing agents such as hydrogen peroxide, potassium permanganate or compressed air to oxidize ferrous iron. When ferrous iron oxidizes to ferric and precipitates as iron-phosphate sludge, free phosphoric acid is formed, reducing the ratio of total to free acid. Severe etching and lower-quality coatings are obtained with an increased consumption of phosphating materials.

An indication that the free acid is too high is the continued gassing during phosphating. In a balanced solution, gassing will normally subside within 8 to 12 min, especially if a grain refiner precedes the phosphating and the ratio of total to free acid is 6.0 to 1 or above.

The secret to consistent, good-quality phosphate coatings, whether manganese or zinc, and trouble-free operation is frequent and regular chemical analysis and additions to maintain solution chemistry and balance. Once the solution is heated, adjusted and ready to operate, process the work continuously without delays between loads. When work is finished reduce the temperature immediately. Do not idle at operating temperature. An excellent source of practical operational information of the phosphating process can be found in MIL-HDBK-205.

Technical Editor's Note: The edited preceding article is based on material compiled and contributed by John Laurilliard, as part of the Finishers' Think Tank series, which began its long run in this journal 25 years ago. It dealt with everyday production plating problems, many of which are still encountered in the opening years of the 21st century. As we have often said, much has changed ... but not that much. The reader may benefit both from the information here and the historical perspective as well. For many, it is fascinating to see the analysis required to troubleshoot problems that might be second nature today. In some cases here, words were altered for context.