

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

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The results of a 26-year corrosion study will be 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 were used. Due to the potential increase in regulations on hexavalent chromium electroplating, the study's comparison between hexavalent and trivalent chromium deposits is of particular interest.

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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.

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 have physical properties similar to hexavalent deposits<sup>2</sup>.

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
  - o reduced drag out due to lower viscosity compared to hexavalent solutions
  - o 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
  - o ion exchange removes metallic impurities
  - o carbon removes organic impurities, if necessary
  - o complete tolerance to dragged in sulfate, chloride and boric acid
  - o able to return dragged out solution back into operating solution without a build up of impurities
- “indefinite life”, low cost graphite anodes
- reduced health/environmental/safety issues
  - o lower liability potential by eliminating carcinogenic and strong oxidizer hexavalent chromium ions
  - o 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's 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, etc. The original commercial trivalent 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<sup>3</sup>. A Bright Nickel deposit is included in Figure 1 as a reference since most platers are familiar with its yellowish appearance. Thin hexavalent or trivalent chromium deposits over bright nickel tends to have a slight yellow appearance due to the nickel's yellow color showing through the chromium deposit.

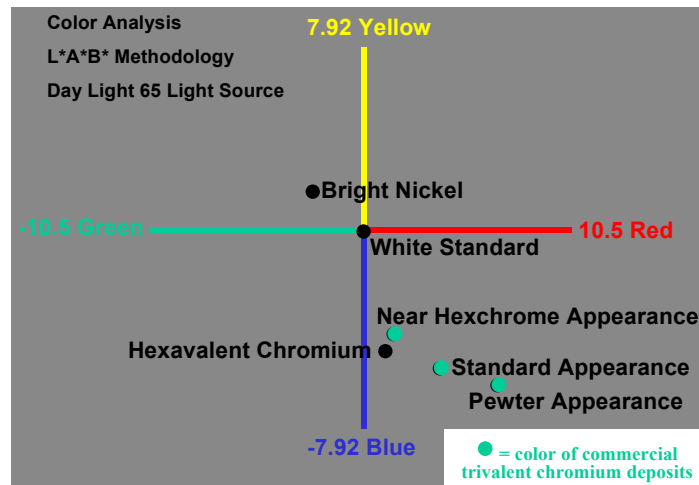


Fig. 1 - Color comparison of commercially obtained electrodeposits

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<sup>4</sup> testing, 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 to conduct long-term 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 B456 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 B456<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 B456 including minimum deposit thickness, physical properties and chromium deposits. ASTM B456 does not distinguish between trivalent and hexavalent chromium deposits. By meeting these requirements, the plating systems should obtain the minimum number of hours of CASS testing cited in B 456 with zero base metal corrosion (Table 1). In addition to CASS, the study included Corrodokote<sup>6</sup>, mobile, static industrial, and static marine corrosion environments.

Table 1 – Service Conditions (SC), ASTM B456<sup>5</sup>

SC	Classification	Likely Exposure	Typical Use	Hours of CASS	Hours of Corrodokote
4	Very Severe	Denting, scratching, abrasive wear, salt and water	Exterior automotive	22	32
3	Severe	Occasional to frequent wetting (water, rain, dew) and exposure to strong cleaners and saline solution	Outdoor and hospital furniture and bicycle	16	16

The deposits were electroplated on flat 10 x 15 cm (4 x 6 inch) cold-rolled steel panels and zinc die-castings in well worked 760 liter 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 Lake Erie area. This area is called the Rust Belt of 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, down-wind from oil refineries and steel mills. Both the marine and industrial panels were mounted on racks, tilted sixty degrees above the horizontal, facing south. The panels were never washed other than by rain etc.

Table 2 – Examples of monitored corrosion factors at marine corrosion site

<p align="center"><b>Kure Beach, North Carolina, USA</b> (Recognized corrosion site with monitored environment)</p>	
<p><b>Representative corrosion conditions – 1987 (year 10)</b></p>	
✓	30 g chloride ions per square meter per year
✓	Corrosion rate of 2.15 mil per year for iron*
✓	Corrosion rate of 0.093 mil per year for zinc*
✓	Temperature range of 7.2 °C to 25.9 °C
✓	Relative Humidity range of 62 % to 84 %
✓	Average calculated time of wetness, 366 hours per month
	* using 4 inch by 6 inch 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 is not as good as would be available, and expected, today.

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

- noble nickel deposits between bright nickel and chromium
  - o particle nickel, used to produce micro-porous hexavalent chromium, with STEP more noble than bright nickel
  - o noble nickel (without particles) with STEP more noble than bright nickel used under trivalent chromium which is micro-porous as plated
- increase nickel thickness
  - o Service Condition 5 (66 hours CASS) added to ASTM B456 for increased corrosion protection of the substrate used on exterior decorative automotive parts – requiring noble nickel deposit
- physical properties of deposits
  - o increased emphasis on control of physical properties
  - o introduction of STEP values
  - o elimination of non-microdiscontinuous chromium option for automotive Service Conditions (SC 3, 4, and 5)

Other techniques, not mentioned in B 456 but 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

- o organic or inorganic corrosion inhibitor immersion coatings
- o 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 B537<sup>8</sup>. The marine panels were rated during ASTM B08's 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 2 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.

ASTM's B537 corrosion rating system requires some working experience to fully understand. However, for the purpose of this paper, B537's rating system can be summarized as:

- rating is a two number system, C/A, where
  - o "C" is the substrate corrosion rating, only substrate corrosion is considered
  - o "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
  - o C = 10, no substrate corrosion
  - o C = 9, up to 0.1 % of the surface has corrosion to the substrate
  - o C = 8, between 0.1 and 0.25 % of surface has corrosion to the substrate
  - o 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.*  $A = C - \text{appearance penalty}$ 
  - o penalty of 0 = no change in surface appearance due to corrosion
  - o penalty of 1 or 2 = after "car wash" cleaning, only slight loss of appearance (usually due to surface pitting) which is not easily observed 1 meter away
  - o penalty of 3 or 4 = after "extra cleaning" reduction in appearance (reflectivity) is visible 1 meter away
  - o penalty of 5 or 6 = appearance is no longer commercially acceptable even after cleaning

The North American automotive industry is 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>9</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 B456 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 70s 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 for interior and some exterior decorative automotive and motorcycle parts. ASTM B456 specifies that SC 4 plating systems will have no corrosion of the substrate after 22 hours of CASS or 32 hours of Corrodkote testing. SC 3 should resist 16 hours 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), is mostly 6 or 7 indicating some loss of appearance/reflectivity. This is predominately due to surface pitting originating at the micro-pores. These ratings 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 micro-porous chromium. This study shows that MC (micro-cracked hexavalent chromium) offered slightly lower corrosion protection of the substrate and has a lower appearance rating after corrosion. This is consistent with other data that supports the North American automotive company's position to not 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 in this study as the micro-discontinuous chromium systems (MC, MP, and TC) even when thicker nickel deposits are 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>8</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.

Table 3- Corrosion test results – SC4, steel substrate, no copper<sup>9</sup>

Set	Average Deposit Thickness (µm)			ASTM Ratings (B537) after Indicated Exposure End of Corrosion Testing for each Test Condition			
	Semi-Bright Nickel	Bright Nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hours	Corrodokote 132 hours
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

b = nickel strike to produce MC

MC = MicroCracked hexavalent chromium

MP = MicroPorous hexavalent chromium

HC = Hexavalent Chromium

TC = Trivalent Chromium

Table 4- Corrosion test results – SC4, steel substrate, with copper<sup>9</sup>

Set	Average Deposit Thickness (µm)				ASTM Ratings (B537) after Indicated Exposure End of Corrosion Testing for each Test Condition			
	Copper	Semi-Bright Nickel	Bright Nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hours	Corrodokote 132 hours
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

Tables 6 through 8 contain the corrosion data for SC 4 and SC 3 plating systems covering 26 years in a marine environment, Kure Beach. A previous paper<sup>9</sup> reviewed the first 15 years. During 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 5 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>10</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.

Table 5- Corrosion test results – SC3, steel substrate, no copper<sup>9</sup>

Set	Average Deposit Thickness (µm)			ASTM Ratings (B537) after Indicated Exposure End of Corrosion Testing for each Test Condition			
	Semi-Bright Nickel	Bright Nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hours	Corrodokote 132 hours
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

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

Set	Ni/Cr <sup>a</sup> System	Marine Corrosion Study for SC 4 ASTM Ratings (Appearance Penalty)					
		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)

<sup>a</sup> = Shorthand nomenclature for micron thickness of semi-bright nickel/bright nickel/chromium

See footnotes for Table 3 for nomenclature for chromium deposits

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 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 do not significantly help reduce the loss of appearance during corrosion of HC plating systems.

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

Set	Cu/Ni/Cr <sup>a</sup> System	Marine Corrosion Study for SC 3 ASTM Ratings (Appearance Penalty)					
		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)

<sup>a</sup> = Shorthand nomenclature for micron thickness of copper/semi-bright nickel/bright nickel/chromium

See footnotes for Table 3 for nomenclature for chromium deposits

Table 8- Marine corrosion test results – SC 3, steel substrate, no copper

Set	Cu/Ni/Cr <sup>a</sup> System	Marine Corrosion Study for SC 3 ASTM Ratings (Appearance Penalty)					
		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	18/7.5+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 (-2.8)	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)

<sup>a</sup> = Shorthand nomenclature for micron thickness of semi-bright nickel/bright nickel/chromium

See footnotes for Table 3 for nomenclature for chromium deposits

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 die-castings appeared to be good prior to plating, they might have been of lower quality than the steel substrate. 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 hours of CASS as cited in ASTM B456. 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.

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

Set	Average Deposit Thickness (µm)				ASTM Ratings (B537) after Indicated Exposure End of Corrosion Testing for each Test Condition			
	Copper	Semi-Bright Nickel	Bright Nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hours	Corrodokote 132 hours
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

Table 10 – Corrosion test results – SC 4, zinc die-castings

Set	Cu/Ni/Cr <sup>a</sup> System	Marine Corrosion Study for Zinc Diecasts, SC 4 ASTM Ratings (Appearance Penalty)					
		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)

<sup>a</sup> = Shorthand nomenclature for micron thickness of copper/semi-bright nickel/bright nickel/chromium

See footnotes for Table 3 for nomenclature for chromium deposits

### 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 microns, SC3 (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>9</sup>. Micro-discontinuous chromium (MC, MP, TC) retarded the formation of substrate corrosion but not to the extent that it does with Duplex nickel systems. This is consistent with the corrosion theory for micro-discontinuous chromium over Duplex nickel<sup>10</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 micron 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.

Table 11 – Corrosion test results – bright nickel over steel<sup>9</sup>

Set	Average Deposit Thickness (µm)		ASTM Ratings (B537) after Indicated Exposure Corrosion Testing under Different Test Condition			
	Bright Nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 64 hours	Corrodokote 88 hours
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

Table 12 – 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 + 3b/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

<sup>a</sup> = Shorthand nomenclature for micron thickness of bright nickel/chromium

See footnotes for Table 3 for nomenclature for chromium deposits

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 microns of nickel pore free. When the nickel is porous or when the substrate is exposed 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.

Table 13 – Corrosion test results – effect of chromium thickness over thin bright nickel<sup>9</sup>

Set	Average Deposit Thickness (µm)		ASTM Ratings (B537) after Indicated Exposure Corrosion Testing under Different Test Condition			
	Bright Nickel	Chromium	Industrial 1 year	Mobile 1 year	CASS 16 hours	Corrodokote 48 hours
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	3.7/07
27	13	0.6 TC	4.3/2.03	6.7/4.7	7.7/5.7	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

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 microns 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 microns and sometimes a maximum of 0.4 microns. 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 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 is no observable difference in base metal protection when using thicker trivalent chromium deposits over Duplex nickel systems. However, 0.9 microns of hexavalent chromium (Set 18, HC) performed much better than 0.3 microns by protecting the substrate similar to the micro-porous trivalent chromium deposits. The appearance ratings are 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.

Table 14 – Corrosion test results – effect of chromium thickness over Duplex nickel<sup>9</sup>

Set	Average Deposit Thickness (µm)			ASTM Ratings (B537) after Indicated Exposure End of Corrosion Testing for each Test Condition			
	Semi-Bright Nickel	Bright Nickel	Chromium	Industrial 12 years	Mobile 7 years	CASS 96 hours	Corrodokote 132 hours
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

See footnotes for Table 3 for nomenclature for chromium deposits

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

Set	Ni/Cr <sup>a</sup> System	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)

See footnotes for Table 3 for nomenclature for chromium deposits

### Summary

This long-term corrosion program had two main objectives:

- 1) Determine if SC 4 and maybe even SC 3 nickel/chromium plating systems within ASTM B456 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) Determine if there is a performance difference between 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 makes 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 B456) plating systems remained essentially free of substrate corrosion throughout the 15 years of marine, 12 years of industrial, 7 years of mobile, 96 hours of CASS and 132 hours of Corrodokote 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 company's exclusion of micro-cracked plating systems. Standard hexavalent chromium systems (HC) all had substrate corrosion early into all of the different corrosion tests. These systems, which are not micro-discontinuous, 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, PM) 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 microns, was dramatically demonstrated within 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 micro-porous hexavalent chromium deposits performed much better than standard hexavalent chromium deposits without micro-porosity.

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