

TECHNICALLY speaking

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Determination of Hexavalent Chromium in NAVAIR Trivalent Chromium Process (TCP) Coatings and Process Solutions

Military weapon systems are coated for a variety of reasons. In addition to aesthetic appearance, the coating system must provide characteristics designed to meet demanding military mission requirements such as camouflage, chemical warfare agent resistance, electrical grounding, and electromagnetic shielding. Clearly the most important contribution of the coatings system is protection of these assets from environmental degradation, including corrosion.

A typical protective military coating system consists of an inorganic pretreatment, an epoxy primer, and a polyurethane topcoat. The pretreatment is applied directly to the metallic substrate to provide corrosion protection and adhesion to primers and topcoats. The majority of military applications typically use various chromate chemistries in some part of the finishing process.

Chromate conversion coatings are routinely applied to substrates of aluminum, titanium, magnesium, zinc, cadmium, and ferrous alloys. These coatings enhance adhesion as well as provide protection to the metal when the paint system becomes damaged. Chromates are chemically defined as hexavalent chromium species. During the conversion process, Cr⁶⁺ is reduced to Cr³⁺, with the exception of

approximately 5–15% remaining as Cr⁶⁺ as an integral part of the layer. This amount retains the solubility properties of Cr⁶⁺ compounds and will leach out of the layer under humid or wet conditions.

However, hexavalent chromium is an EPA priority pollutant and a known carcinogen. New local and international regulations and directives have significantly restricted the use of processes based on hexavalent chromium, in addition to banning its use in coatings. Consequently, a search for a safer, yet effective, hexavalent chromium substitute became an industry priority.

Recently, a conversion coating process, designated “trivalent chromium process,” or TCP, has been developed and patented by NAVAIR. It should be emphasized that trivalent chrome compounds by definition are not chromates, which specifically describe chromium in the +6 oxidation state. The new technology is based on low levels of Cr³⁺. The process solution and the coating it produces are totally free of Cr⁶⁺. It provides a total replacement for traditional hexavalent chromium conversion coatings. Whereas hexavalent chromium is a carcinogen, trivalent chromium is defined as non-hazardous and much safer to use by regulatory and occupational health agencies.

The TCP process was extensively evaluated and became commercially available through NAVAIR licensees in North America and internationally.* It can be used as a dip, spray, or brush-on application. It is essentially a drop-in replacement for conventional chromate-based conversion coatings, sealers, and post-treatments, and it is widely used in many applications for DoD and non-military industries. A concern voiced as this technology was introduced was the stability of Cr³⁺ in the coating and whether any Cr⁶⁺ formed in the protective layer or in the TCP process solution.

A cooperative study was undertaken between NAVAIR, the U.S. Army Research Lab, the University of Connecticut, and TCP licensees to investigate the stability of the TCP process.

The focus of this work was to analyze and determine the speciation of chromium in the TCP, and determine whether hexavalent chromium is present in the process solution or the coating, or if any is formed on standing and during corrosive environmental exposure. These coatings find applications for military spacecrafts where the body of the craft needs to be highly resistant to corrosive environments and free of toxic leachable Cr⁶⁺ species.

Experimental work: All experimental results reported here were obtained using commercially licensed TCP from either SurTec International or Henkel Surface Technologies to

* NAVAIR approved TCP licensees: **(North America) CST-SurTec:** SurTec 650 chromital TCP; **Henkel Surface Technologies:** Alodine T5900; **Metalast International:** TCP-HF; **Luster-On Products:** Aluminescents; **(International) SurTec International, GmbH:** 650 chromital TCP.

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establish the following:

(A) Determination of hexavalent chromium in coatings produced by TCP and Alodine 1200S systems as treated, and exposed to accelerated corrosion conditions, and TCP coatings on exposure to the environment for extended periods.

(B) Determination of hexavalent chromium in the TCP and Alodine 1200S process solutions under use conditions.

COATING EVALUATION

Effect of Exposure to Accelerated Corrosion. Sample Preparation: TCP and Henkel's Alodine 1200S were used as a dip solution to treat 3 × 10-inch panels of Al 2024 T3 alloy. The panels were dipped for 5 minutes, rinsed, and air dried. Coated panels were exposed to accelerated corrosion treatment for 24, 72, 148, and 744 hours in neutral salt spray (NSS), and in salt spray with periodic infusion of SO₂ gas in accordance with ASTM G85. Panels were identified by process used, type, and time of corrosion exposure. Untreated blanks were used as a baseline. The panels were positioned inside the chamber in such a way that they are tilted at a 6° angle from the vertical.

Treated and corroded panels are designated as follows:

Designation	Description
2024 Blank	Not treated, not corroded
2024 TCP	Treated only, not corroded
2024 TCP SO ₂ 24 hrs	Treated—corroded with SO ₂ for 24 hrs
2024 TCP SO ₂ 72 hrs	Treated—corroded with SO ₂ for 72 hrs
2024 TCP SO ₂ 148 hrs	Treated—corroded with SO ₂ for 148 hrs
2024 TCP NSS 744 hrs	Treated—corroded with NSS for 744 hrs

A similar nomenclature as the one shown in the table above has been used for Alodine 1200S samples by simply replacing "TCP" with "Alodine 1200S."

Test Methods: Determination of Cr⁶⁺

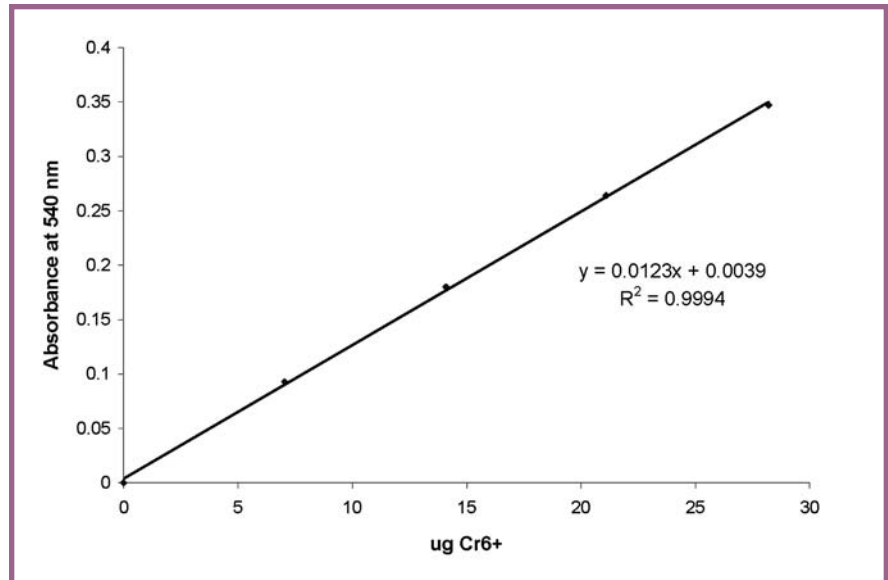


Figure 1: Calibration curve for hexavalent chromium in treated and treated-corroded samples.

Sample	Cr ⁶⁺ level (µg/cm ²)
2024 Acetone wiped (BLANK)	n.d.*
2024 TCP	n.d.*
2024 TCP SO ₂ 24 hrs	n.d.*
2024 TCP SO ₂ 72 hrs	n.d.*
2024 TCP SO ₂ 148 hrs	n.d.*
2024 TCP NSS 744 hrs	n.d.*
2024 Alodine 1200S	0.81
2024 Alodine 1200S SO ₂ 24 hrs	n.d.*
2024 Alodine 1200S SO ₂ 72 hrs	n.d.*
2024 Alodine 1200S SO ₂ 148 hrs	0.03
2024 Alodine 1200S NSS 744 hrs	0.09
*Not detected	

Table 1: Results of Surface Cr⁶⁺ Analysis on Treated and Treated-Corroded Samples

time. A method for determining hexavalent (only) chromium on the surface or as a coating in Al alloys was used. The method is based on diphenylcarbazide chemistry.¹

A solution of 1,5-diphenylcarbazide was prepared by dissolving 0.50 g of the carbazide in 50 ml of acetone and 50 ml of water. Boiling deionized water (25 ml) was added to a set of sample stubs (1.9 × 2.5 cm) placed in a wide-mouth beaker. Typically, 16 pieces of stubs were used at a time. The beaker was placed on a hot plate for five minutes to keep the water hot or just at the boiling point to avoid bumping and sample loss. The stubs were then rinsed with deionized water,

in the coating of treated and treated-corroded samples: This test analyzed the Cr⁶⁺ in the coating before and after exposure to corrosion. A set of stubs (1.9 × 2.5 cm) cut from the previously treated panels were tested in batches of 16 pieces of stubs at a

making sure that the rinse was conserved in the beaker. The solution was then acidified with 1 ml of ~ 4.5 M H₂SO₄ solution. After cooling down, the solution was transferred to a 50-ml volumetric flask.

An aliquot of the diphenylcarbazide (600 µl) was added to the solution and incubated for two minutes, after which the reaction between Cr⁶⁺ and diphenylcarbazide was stopped by the addition of a phosphate buffer solution (55 g NaH₂PO₄·H₂O in 100 ml of deionized water). The solution was then diluted to the 50-ml mark and the absorbance of the solution at 540 nm was obtained using an HP 8452A Diode Array UV-Vis Spectrophotometer.

A calibration curve was obtained by preparing a series of standard K₂Cr₂O₇ solutions in order to interpolate the concentration of hexavalent chromium in a sample. The same addition of diphenylcarbazide and stopping with the phosphate buffer was carried out. Absorbance of the standard solutions was similarly obtained at 540 nm. As a rule, the absorbance of prepared solutions was obtained in less than 30 minutes after final dilution to 50 ml. Results are expressed as µg Cr⁶⁺ per area (cm²) of sample. Each experiment was done in duplicate.

Verification of hexavalent chromium detection method: To verify the method used to detect hexavalent chromium, the surface of Al 2024 blank stubs (1.9 × 2.5 cm) was spiked with 500 µL each of TCP and Alodine 1200S solutions. The stubs were then air dried without rinsing. The same Cr⁶⁺ analysis technique was used as detailed in the previous section. This was done in order to confirm that any Cr⁶⁺ detected was coming from the treated panels and not from an oxidation process of Cr³⁺ during the test. It can also be used, if desired, to correlate between the Cr⁶⁺ content in the process solution in contact with the surface—in this case the Alodine

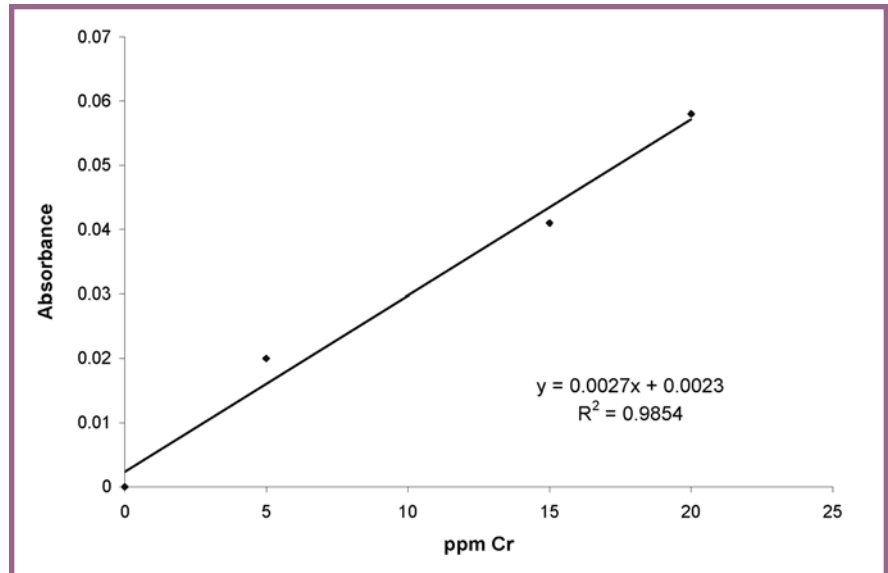


Figure 2: Calibration curve for total chromium analysis by AAS.

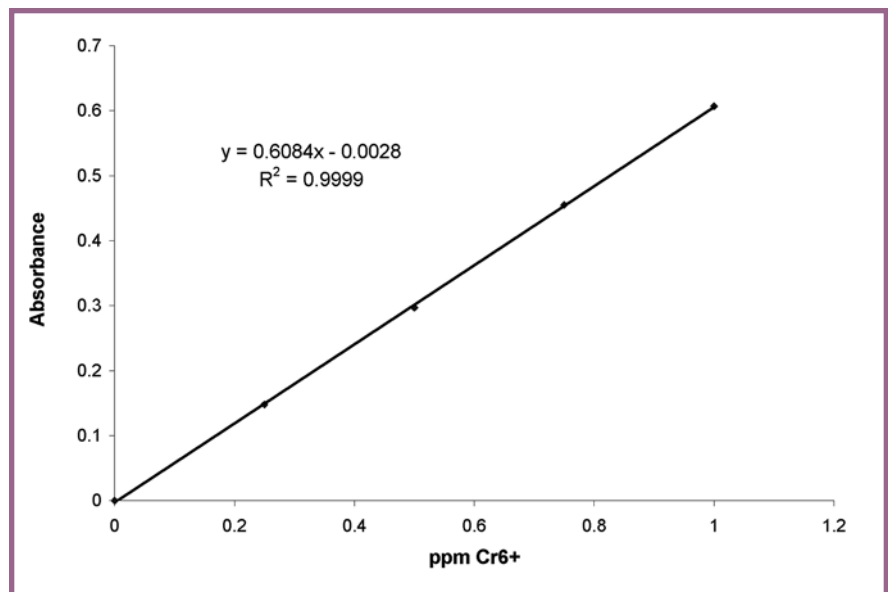


Figure 3: Calibration curve for the Cr⁶⁺ analysis of pretreatment solutions.

1200S—and the content in the resulting coating.

Determination of total chromium using atomic absorption spectroscopy (AAS): AA2024T3-treated panels were cut into stubs (1.27 × 1.27 cm) weighing around 0.37 g. The stubs were placed in a 50-ml beaker and digested in aqua regia.² A blank digestate was also made (no Al stub). Samples were digested in duplicate. A calibration curve was prepared from standard Cr solutions. The digestate and standard solutions were analyzed for Cr content using a Perkin Elmer Atomic Absorption Spectrometer

3100 and an air-acetylene flame. Results are reported as ppm Cr.

Effect of Environmental Exposure.³ Panels of known surface area were processed in TCP at various temperatures (20–50°C) and various treatment times (0.5–10 min), then they were rinsed and dried. The coating on the panels was tested for Cr⁶⁺ after they were exposed to environmental conditions as follows:

- Directly after processing in TCP
- After 6 weeks of storage indoors
- After 6 weeks of outdoor exposure

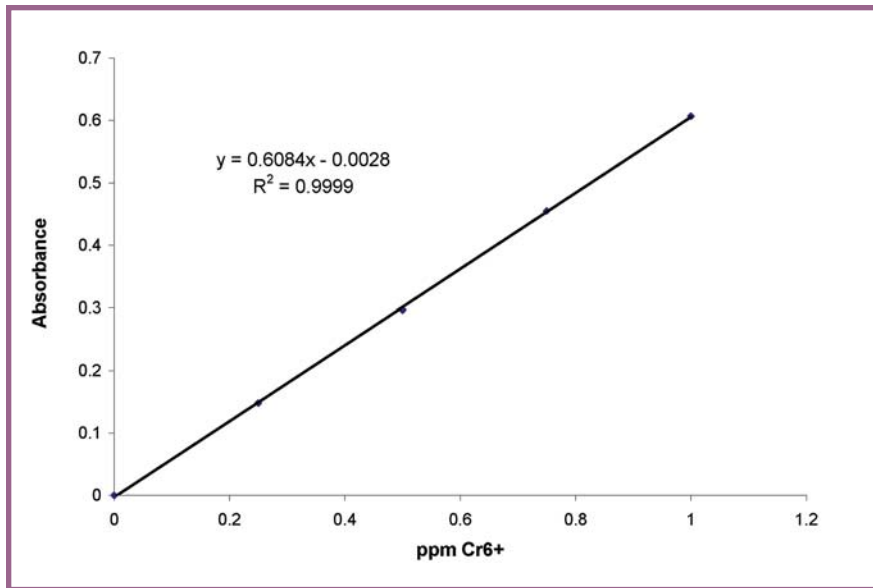


Figure 4: Calibration curve for the Cr⁶⁺ analysis of pretreatment solutions.

• After 384-hour neutral salt spray test (ASTM B-117)

The test panels were then leached in boiling DI-water, and the Cr⁶⁺ content in the leachate was determined according to DIN 38405 (color reaction with diphenyl carbazide and photometric analysis at 540 nm).

THE PROCESS SOLUTION

This test was used for the determination of hexavalent chromium content of the TCP and Alodine 1200S process solutions. The analysis was performed on the solutions before and after dip coating two (3 × 10-inch) AA2024T3 panels in each solution. They were diluted and analyzed according to the EPA 7196A method of determining dissolved hexavalent chromium in ground water or industrial wastes.¹

RESULTS

Hexavalent Chromium in the Coating of Treated and Treated-Corroded Samples. Figure 1 gives the calibration curve for the analysis of hexavalent chromium on treated samples. Table 1 gives the results of the analysis. No Cr⁶⁺ was detected on any of the TCP samples, including the blank. These data confirm that the TCP treatments do not contain, nor do they produce, hexavalent chrome

under all tested conditions. The Alodine 1200S-treated samples showed 0.81 µg Cr⁶⁺/cm² directly after treatment and drying, while none was detectable after exposure to ASTM G85 Annex 4 acidified salt spray for 24 and 72 hours.

Verification of Hexavalent Chromium Detection Method. No Cr⁶⁺ was detected for the stubs spiked with the TCP solution. This is in agreement with the results described earlier. A level of 238 µg Cr⁶⁺ was detected in the Alodine 1200S spiked stub. It was noted that not all the chromium was extracted from the stub by the 5-minute leaching in the analysis method described in the experimental section. The dry-in-place conversion coating on the spiked stub was much heavier than the coating on the panels.

Total Chromium Detection on Treated Samples Using AAS. Figure 2 gives the calibration curve for the total Cr analysis using AAS. Samples 2024 Blank and 2024 TCP were analyzed for total chromium content showing levels of 480 ppm and 540 ppm Cr, respectively. As expected, the total chromium content of 2024 TCP was

slightly higher than 2024 Blank. The TCP process is based on low levels of trivalent chrome. The amount found in the coating will vary depending on the alloy. Using this method, the different Cr uptake upon treatment of different types of Al alloys can be assessed. None of this Cr, however, was present in the hexavalent form in the TCP process as shown earlier.

Hexavalent Chromium Content in Treatment Solutions. Figure 4 gives the calibration curve for the Cr⁶⁺ analysis on treatment solutions before and after coating two 3 × 10-inch Al 2024 panels. No Cr⁶⁺ was detected in the TCP solutions before or after coating the panels. A level of 1,678 ppm Cr⁶⁺ was measured in the fresh Alodine 1200S solution and 960 ppm on the used Alodine 1200S treatment solution.

Environmental Exposure. All the panels exposed to indoor and outdoor exposure for up to six weeks, including panels exposed to 336 hours of ASTM B117 neutral salt spray, showed values <0.02 µg/cm² (i.e., in the non-detectable range for Cr⁶⁺).

DISCUSSION OF RESULTS

TCP. From the hexavalent chromium analysis it is clear that TCP-coated and corroded panels do not show any Cr⁶⁺. Nor was any detected as a result of environmental exposure. Furthermore, no Cr⁶⁺ was detected in the TCP treatment solutions before or after coating of the panels. In practice, samples of TCP-coated parts and solution taken from the tanks in production plants after 6, 12, and 18 months of continuous operation show no detectable Cr⁶⁺. No changeover of process solution took place during that time.

Alodine 1200S. Table 1 lists the hexavalent chrome values in the coating. As formed, the Cr⁶⁺ level was 0.81 µg Cr⁶⁺/cm². There was no detectable Cr⁶⁺ after 24- and 48-hour exposure to NSS-SO₂. The last two samples, NSS-SO₂-treated for 148 hours and NSS-treated for 744 hours, gave Cr⁶⁺ levels of 0.03 and 0.09 µg Cr⁶⁺/cm², respectively.

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One explanation is the loss of the coating through corrosion in the aggressive medium used in the first few hours. Panels inspected after 24 hours show widespread pitting. As corrosion proceeds deeper into the panel at 148 hours and beyond, Cr as an alloy component may be the source of detected Cr⁶⁺. Panels treated with TCP showed far less corrosion, which may explain the lack of detectable Cr⁶⁺ after 148 and 744 hours in this test. A parallel evaluation of a blank panel is needed to confirm this conclusion.

Another explanation may be based on the mechanism of corrosion observed by Kendig et al.⁴ After 24 hours of ASTM G 85 SO₂ salt spray exposure, most of the soluble, hexavalent chromium species could have been washed away. The coating, however, remains uncorroded due to the formation of compounds between the oxy-anion of Cr⁶⁺ and copper in the alloy at localized sites.⁵ But after 148 hours, these hexavalent chromium containing compounds may no longer be stable and hence get completely stripped from the alloy surface, becoming part of the surface corrosion and thereby detected. The analysis of hexavalent chromium-type coatings in corrosive atmospheres is beyond the scope of this study. Further investigation is needed to confirm the related corrosion mechanism.

CONCLUSIONS

Two methods were used in this study to determine presence and quantities of hexavalent chromium produced by the TCP process when applied to AA2024T3. A hexavalent chrome-containing process, Alodine 1200S, was used as the reference. One method analyzed for surface Cr⁶⁺ on coated panels and the other for its presence in treatment solutions. In TCP-coated samples, no hexavalent chromium was detected even after exposure of coated samples to ASTM G 85 SO₂ salt spray for up to 744 hours. Similarly, none was detected after exposure to indoor or outdoor environments. It was also

confirmed that no hexavalent chromium is produced in the TCP treatment solution or in treated parts under production conditions. This is corroborated by analyzing parts and solutions from production plants treating various Al alloys in excess of 18 months with no solution changeover.

Surface analysis of Alodine 1200S-coated panels shows 0.81 µg/cm² of Cr⁶⁺. Amounts detected during accelerated corrosion vary depending on the corrosive environment and length of treatment time. These ranged from non-detectable after short but aggressive corrosion exposure, to detectable low levels after extended exposure. Further investigation may be needed to accurately explain this behavior.

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REFERENCES

1. *Methods for Chemical Analysis of Water and Wastes*. EPA-600/4-82-055, December 1982.
2. Zhang XM. *Yejin Fenxi*. 2001, 21, 67.
3. SurTec International, P.Volk. *Evaluation of Cr6+ in SurTec 650 chromitAL TCP*, 2007
4. Kendig M, Jeanjaquet S, Addison R, Waldrop J. *Surface and Coatings Technology*, 2001, 140, 58–66.
5. Grilli R, Baker M, Dunn B, Watts J. *Surface and Interface Analysis*, 2008, 40, 132–136
6. Alodine 1200S-Technical Process Bulletin, Henkel, Surface Technologies, 1999.

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