Characterization of NAVAIR Trivalent Chromium Process (TCP) Coatings and Solutions

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The Trivalent Chromium Process (TCP) developed by the Naval Air Systems Command (NAVAIR) is used for the coating of metallic substrates, including high strength aluminum alloys. These coatings find applications for military systems where the structure needs to be highly resistant to environmental corrosion but must be free of toxic Cr(VI) species. In this paper, we present characterization studies of NAVAIR TCP coated substrates focused on the determination of Cr(VI) levels. For the sake of comparison with TCP, we also evaluated a commercial formulation based on Cr(VI). We have conducted tests on bare aluminum substrates, as-deposited coated aluminum panels, corroded panels, and both new and depleted coating solutions. The techniques used in this study include Auger electron spectroscopy for surface analysis, diphenylcarbazide chemistry for spot testing and UV-visible spectroscopy for Cr(VI) detection on coated panels, corroded panels and treatment solutions. All of our tests reveal that no detectable Cr(VI) is present on TCP coated aluminum alloys. Cr(VI) species were not detected in TCP solutions. No Cr(VI) is used in the base solution hence no Cr(VI) formed in the used solution or deposited coating.

Keywords: *aluminum alloy 2024, corrosion, trivalent chromium process, hexavalent chromium detection, Auger electron spectroscopy, diphenylcarbazide test.*

Introduction

Military weapon systems are coated for protection against environmental corrosion. A baseline protective military coating system typically consists of an inorganic conversion coating, an epoxy primer and a polyurethane topcoat. The conversion coating is applied directly to the substrate to provide corrosion protection and promote adhesion of the subsequent primer coating to the substrate. In current metal finishing coatings, processes are available in which Cr(VI) is a key component of the conversion coating.[1,2] Hexavalent chromium has a self-healing property and provides a good base of adhesion for organic coatings.[3,4] Furthermore, Cr(VI) coatings provide excellent corrosion protection across a wide range of substrates, due to their ability to inhibit both the anodic and cathodic corrosion reactions. Chromate coatings also provide good corrosion protection throughout a broad range of pH and chemical environments. Hence, chromate coatings find a wide range of applications in the metal finishing industry.[5]

However, Cr(VI) is an EPA priority pollutant and a known carcinogen.[6,7] Cr(VI) is highly soluble in water, and can exist in several forms such as the hydrochromate ($HCrO_4^-$), chromate (CrO_4^{-2}) and dichromate ($Cr_2O_7^-$) ions. Due to its widespread industrial use, Cr(VI) is often found in waste streams and needs to be removed from them using various adsorbents.[8] New regulations have imposed significant restrictions on the use of Cr(VI).[9] In the United States, the Occupational Safety and Health Administration (OSHA) reduced the occupational exposure limit for Cr(VI) from 52 μg/m^3 to 5 μg/m^3 in 2006.[10] Such restrictions can increase the cost of utilization of Cr(VI) for conversion coatings and the cost of subsequent waste treatment.

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Due to these restrictions, a great deal of effort has been focused on developing coatings that still offer effective corrosion protection but are free of Cr(VI). Trivalent chromium [Cr(III)], which forms insoluble precipitates and is less toxic than Cr(VI), is one such alternative that has been explored.[11-13] NAVAIR has developed a series of zirconium fluoride and trivalent chromium-based compositions and processes (TCP) which are intended to be drop-in replacements for Cr(VI)-containing sealers, post-treatments and conversion coatings.[14] TCP contains a fluorozirconate salt and a Cr(III) salt which form an oxide coating when deposited on an aluminum substrate.[13,14] The majority of work thus far has focused on the use of TCP on aluminum alloys, sacrificial coatings and as a sealant for anodized coatings, all with extremely promising results. Further development is underway for using TCP chemistries to replace chromates on steels, phosphates, zinc and magnesium alloys.

In order for NAVAIR's TCP to be a viable alternative to Cr(VI)-based coatings and processes, it must be ensured that no Cr(VI) is present in the initial TCP solution, the coating formed on the metal substrate being protected, and the waste TCP solution that remains following use.

The objective of this paper is to determine if any Cr(VI) is present in the unused and waste TCP coating solutions and if any Cr(VI) forms after coating on AA 2024 substrates and whether Cr(VI) forms on TCP-coated AA 2024 after subsequent salt spray corrosion. Leachates obtained after corroding TCP-coated AA2024 with salt or harsh acid solutions were also analyzed for Cr(VI) content. For comparison, we chose to test a proprietary hexavalent chromate solution. Apart from these tests, surface elemental analysis of coated and corroded substrates is also presented in this paper.

Experimental

Two proprietary trivalent chromium processes were obtained from two different metal finishing process suppliers.** For the purposes of this work the two products were considered equivalent, and are referred to as "TCP" in this work. A hexavalent chromium process was also obtained*** and is referred to as "1200S" in this paper. Aluminum AA 2024-T3 was used as the primary test substrates for all coating experiments, which are referred to as "aluminum panels" in this work.

Pre-treatment and corrosion of coated AA 2024 alloy

Aluminum panels with dimensions of 7.6 × 25.4 cm were acetone washed, cleaned and deoxidized prior to being immersion coated with either TCP or 1200S. These steps were performed by NAVAIR according to standard procedures.

TCP and 1200S treated aluminum panels were subjected to accelerated corrosion treatment. Two types of corrosion treatments were used: (a) ASTM B117 neutral salt spray[15] (NSS) and ASTM G85-02 Annex A4 modified salt spray[16] (SO_2; exposure time for 24, 72 and 148 hr). The panels were positioned inside the corrosion treatment chambers in such a way that they were tilted at a 6° angle from the vertical.

Samples of relevance to this work are described below. Abbreviations used in this paper are given in italics.

1. Virgin AA 2024 sample without any coating and non-corroded (NC) (*Blank/NC*)
2. TCP-coated and non-corroded (NC) sample (*TCP/NC*)
3. TCP-coated samples exposed to 744 hr (31 days) of NSS are abbreviated as:
   - o TCP/NSS/744hr.
4. TCP-coated samples exposed to SO_2 salt spray having different exposure periods (24 hrs, 72 hrs, 148 hrs) are abbreviated as:
   - o TCP/SO_2/24hr
   - o TCP/SO_2/72hr
   - o TCP/SO_2/148hr

We have followed the same nomenclature as above for the hexavalent chromium process. Here, "TCP" is replaced with "1200S."

Determination of Cr(VI) on coated and corroded panels using UV-visible spectroscopy

A method for determining Cr(VI) on coated and corroded aluminum alloys based on diphenylcarbazide chemistry was used[17,18] It is known that 1,5-diphenylcarbazide (DPC) reacts with Cr(VI) under acidic conditions to form a dark pink-colored Cr-diphenylcarbazone complex that shows an absorption peak at 540 nm which can be detected using UV-visible spectroscopy.[19] For the Cr(VI) analysis, deionized water was heated to almost boiling and 25 mL was added to AA 2024 coated coupons (16 coupons of size 1.9 × 2.5 cm). After 5 min, the coupons were rinsed with fresh deionized water with the rinse being conserved in the beaker. The solution was acidified with 1.0 mL of 4.5M H_2SO_4. After cooling to room temperature, the solution was transferred to a 50-mL volumetric flask. A 600-μL aliquot of 0.02 M diphenylcarbazide solution was added. This solution was prepared by dissolving 0.50 g of diphenylcarbazide in 50 mL acetone and 50 mL of water. After a 2.0-min incubation time, 10 mL of 0.4M sodium dihydrogen phosphate buffer solution was added to raise the pH and stop the reaction. The solution was diluted to 50 mL and the absorbance of the solution at 540 nm was obtained using an HP 8452A diode array UV-vis spectrophotometer. A calibration curve ($R^2 = 0.9994$) was obtained by preparing a series of standard $K_2Cr_2O_7$ solutions in order to interpolate the concentration of Cr(VI) in a sample. The same reaction described above was carried out for the standards. Absorbance of the prepared solutions was obtained less than 30 minutes after final dilution to 50 mL. Results are expressed as μg Cr(VI)/cm^2 of aluminum panel. Each experiment was performed in duplicate.

Determination of Cr(VI) content on aluminum panels deposited with a chromium conversion coating from treatment solutions

The Cr(VI) contents of unused and used TCP and 1200S coating solutions were determined before and after immersion coating two 7.6 × 25.4 cm aluminum panels for 5.0 min respectively. The difference in Cr(VI) content of the unused and used solutions would give the amount of Cr(VI) deposited on the substrate. The purpose of this test was to determine if any Cr(VI) formed in the solution after the coating process, in the case of TCP. This method is based on the EPA 7196A method of determining dissolved Cr(VI) in ground water or industrial wastes.[17] The immersion bath consisted of 97 mL of TCP coating solution, 2.0 mL 1,5-diphenylcarbazide (DPC) (prepared by dissolving 250 mg in 50 mL acetone) and 1.0 mL 10 vol% H_2SO_4 . In order to make up the TCP-containing dip bath, 97 mL of TCP was mixed with 2.0 mL of 1,5-diphenylcar-

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** *(1) SurTec 650 chromit AL TCP™, SurTec International, Zwingenberg, Germany; Middleburg Heights, OH.*
(2) Alodine™ T5900, Henkel Surface Technologies, Madison Heights, MI.

*** *Alodine™ 1200S, Henkel Surface Technologies, Madison Heights, MI.*

bazide (250 mg diphenylcarbazide in 50 mL acetone) and 1.0 mL of 10 vol H_2SO_4. The total volume was kept at 100 mL. The 1200S-containing dip bath was made by diluting 500 μL of 1200S with 80 mL of water. Then 2.0 mL of 1,5-diphenylcarbazide (250 mg diphenylcarbazide in 50 mL acetone) and 1.0 mL of 10 vol% H_2SO_4 were added. The volume was then made up to 100 mL with deionized water. A low concentration of 1200S solution was used in comparison to TCP because the 1200S solutions have a very high Cr(VI) content. Before measuring the absorbance, all solutions were diluted by a factor of two. The used and unused solutions were shaken and incubated at room temperature for 5 to 10 min before the absorbance at 540 nm was recorded using an HP 8452A diode array UV-vis spectrophotometer.

Validation of Cr(VI) detection method

In order to validate the above described Cr(VI) detection test, 500 μL each of the TCP and 1200S solutions were placed onto the surfaces of 1.9 × 2.5 cm AA 2024 blank coupons. The coupons were then air-dried. The same diphenylcarbazide-based Cr(VI) analysis described earlier was used.

Detection of Cr(VI) in the corrosive leachate and analysis of residues on the surface after corrosion

TCP/NC and *1200S/NC* coupons were corroded using acid and salt solutions and the Cr(VI) content of leachates and the surface residues were determined. *TCP/NC* and *1200S/NC* coupons (eight 2.5 × 2.5 cm coupons) were immersed in 30 mL of 1M H_2SO_4 and 1M NaCl solutions for specific times, *i.e.*, 24 and 48 hr. The beakers were covered with vinyl film. After the given aging time, unaided visual observations about the condition of the coupon were recorded. Aliquots of each solution were tested for the presence of Cr(VI) with DPC solution using the same method as described earlier, for the analysis of the chromium conversion coated aluminum panels. However, two different calibration standards containing $K_2Cr_2O_7$ solutions with 1M H_2SO_4 and 1M NaCl, respectively, were prepared. The color of the solution after adding DPC was also recorded. A pink color formation indicates the presence of Cr(VI).

TCP/NC and *1200S/NC* coupons were also subjected to harsh acidic conditions by placing drops (200 μL) of 4M H_2SO_4 and 4M HNO_3 on the surface of a 2.5 × 2.5 cm coupon without letting the acid flow out from the surface. After the given aging time, the surface of the coupon was tested for the presence of Cr(VI) by applying a drop (200 μL) of DPC solution. The residue on the surface was visually observed to check for the formation of any dark pink colored spots at this point, which would be indicative of the presence of Cr(VI). Residues were then extracted from the surface and their Cr(VI) content was detected using a similar procedure using UV-visible spectroscopy as described above. The total volume was kept to 25 mL. In the case of the salt solutions, the solutions had to be acidified prior to analysis. If more than 0.1 μg/cm^2 of Cr(VI) was detected then the presence of Cr(VI) was considered to be positive. In another test, 125 μL of fresh TCP and 1200S coating solutions were acidified with strong acids (pH of solution = 0) and subjected to DPC analysis using the same procedure. The solution volume was made up to 25 mL before recording the absorbance. Since very dilute solutions were being used, the inherent green color of the TCP solution did not interfere with the test conditions. This test was performed in order to check if any Cr(VI) formed in the TCP solution when treated under harsh acidic conditions.

Surface analysis with scanning Auger electron spectroscopy (AES)

Auger electron spectroscopy was employed to determine relative amounts of surface elements in the blank and treated AA 2024 samples. The Auger data were acquired using a Physical Electronics model PHI 610 scanning Auger microprobe. The Auger transitions were excited using an electron beam of 3 keV and a diameter of approximately 1 μm. To minimize sample charging by the electron beam and backscattering of specular electrons into the energy analyzer, samples were tilted by 30Å. On each sample three random spots were analyzed. The data presented for each element represent the average of the values measured of these three spots.

Results

Detection of Cr(VI) on coated and corroded panels

UV-visible spectroscopy was employed to quantify the amount of Cr(VI) on the TCP and 1200S-coated and corroded panels. No Cr(VI) was detected on the *TCP/NC*, *TCP/NSS/744hr* and *TCP/SO_2* samples. The *1200S/NC* sample contained 0.81 μg Cr(VI)/cm^2. The *1200S/NSS/744hr* sample had 0.09 μg Cr(VI)/cm^2. However, no Cr(VI) was detected on any other *1200S/SO_2* samples.

Detection of Cr(VI) in used and unused treatment solutions

The Cr(VI) analysis on treatment solutions done before and after coating two AA 2024 panels are presented here. The used and unused treatment solutions were subjected to diphenylcarbazide tests. The objective of this test was to assess whether Cr(VI) was formed in the solution during the coating process. No Cr(VI) was detected in the unused TCP solutions and used TCP solutions after coating the panels. For the unused 1200S, a level of 1678 ppm Cr(VI) was obtained while a level of 960 ppm was obtained on the used treatment solution. This difference corresponds to 718 ppm of Cr(VI) or 232 μg of Cr(VI)/cm^2 was deposited on the on the two panels. This is shown in Table 1, Value #2. The decrease in Cr(VI) content here is due to coating onto the aluminum panel.

Validation of the Cr(VI) detection method

Known amounts (500 μL) of TCP and 1200S solutions were placed on respective TCP and 1200S coupons which were subjected to diphenylcarbazide analysis. Since the exact amount of Cr(VI) contained in the deposited coating is known, this test should provide information as to whether our detection method itself was producing any Cr(VI) in TCP. Detection of a higher value than the expected value would indicate that our testing method itself was producing Cr(VI).

Results are presented in Table 1. No Cr(VI) was detected on the aluminum panels coated with TCP solution (Table 1, Values #3 and #4). A level of 50 μg/cm^2 of Cr(VI) was detected in the 1200S-coated aluminum panels (Table 1, Value #3). The quantity of Cr(VI), corresponding to 500 μL of 1200S solution, expected to be on the 1200S coated coupon was 177 μg/cm^2 (Table 1, Value #4). This value is based on the Cr(VI) content of the 1200S solution. The difference in Values #3 and #4 could be due to some of the Cr(VI) being converted to the more stable Cr(III) species.

Detection of Cr(VI) in the corrosive leachate and analysis of residues on the surface after corrosion

Detection of Cr(VI) in blank 2024 panels by acidification of the substrate: Table 2 shows results for acid and salt corrosion tests done on blank 2024 alloy. Qualitative tests of the solutions with

Table 1

Cr(VI) content determined by UV-vis for TCP/NC and 1200S/NC samples

Value #	Sample description	Hexavalent chromium content	
		TCP (μg/cm^2)	1200S (μg/cm^2)
1	Cr(VI) content on the coated Al panel before corrosion	0	0.81
2	Cr(VI) content deposited on the Al panel obtained by measuring the difference between unused and used immersion coating solutions	0 μg/cm^2 (0 ppm)	232 μg/cm^2 (718 ppm)
3	Cr(VI) value deposited on the Al panel using 500 μL of coating solution	0	50
4	Cr(VI) value expected to be deposited on the Al panel using 500 μL of coating solution	0	177

Table 2

Qualitative estimation of Cr(VI) on blank aluminum alloy coupons after treatment with acid or salt solutions for 16 hr

Aluminum alloy	1 M H_2SO_4	4 M H_2SO_4	Conc. H_2SO_4	4 M HNO_3	Conc. HNO_3	1 M NaCl
Initial observations of 1” × 1” aluminum alloy test coupons and solutions after 16 hr of immersion.	Slight darkening of coupon; solution clear	Complete blackening both sides of coupon; solution clear	Brown flakes on coupon and surface of solution; thin dense milky layer at bottom of solution; solution yellow	No apparent effect on coupon; solution clear	No apparent effect on coupon; solution yellow	Some black spotting on bottom of coupon; solution clear
Cr(VI) detection after 16 hr of immersion in acid solution. Detection was done after decanting the solution off the coupon.	Possibly positive	Positive	Positive	Negative*	Negative*	Negative
Cr(VI) on the surface of Al alloy after 16 hr of immersion in solution	Positive	Negative$^+$	Negative	Negative	Positive	Positive

*Blank tests show that HNO_3 can mask the results of a positive test for Cr(VI).
$^+$The black layer on the test coupons may have masked a positive result for the test.

DPC revealed that Cr(VI) was liberated from blank 2024 aluminum alloys when the alloys were immersed in H_2SO_4. Due to the masking effect of HNO_3 on the DPC solution test, the results of those solution tests were inconclusive. Cr(VI) was not liberated into solution from the alloy in 1M NaCl. Surface tests of the coupons revealed that Cr(VI) was present at the surface of blank 2024 aluminum alloy coupons that had been immersed in 1M H_2SO_4. Coupons immersed in concentrated HNO_3 also tested positive for Cr(VI) at the surface of the coupon. Surprisingly, even coupons immersed in 1M NaCl for 16 hr tested positive for the presence of Cr(VI).

Detection of Cr(VI) in leachates obtained after corrosion: Table 3 shows the Cr(VI) content of TCP or 1200S coated aluminum coupons that were immersed in 30 mL acidic or salt solutions for 24 and 48 hr. Detection was done on leachates using UV-visible spectroscopy. It was visually observed that treatment with a solution of 1M H_2SO_4 formed a uniform grey layer on the surface in the case of *TCP/1M H_2SO_4/24hr*. Treatment with NaCl did not cause any apparent change on the surface. No Cr(VI) was detected in any of the samples. A level of 0.37 μg/cm^2 Cr(VI) was detected in *1200S/1M H_2SO_4/48hr* and 0.2 μg/cm^2 was detected in *1200S/1M NaCl/48hr*. The solutions tested for UV-visible spectroscopy were slightly pink in color. A pink color clearly indicates the presence of Cr(VI). In the case of the TCP samples, no Cr(VI) was detected on treatment with 1M H_2SO_4 and 1M NaCl for 48 hr. The solution obtained after addition of DPC was brownish in color but not pink.

Table 3

TCP and 1200S coated 2024 coupons were immersed in acid and salt solutions for 24 or 48 hr. Visual observations of the surface before adding DPC solution and detected Cr(VI) content are given

#	Sample	Visual observations without the addition of DPC on the surface	Cr(VI) (µg/cm^2)
1	*TCP/1M H_2SO_4/24hr*	Uniform pinkish grey layer forms on the coupons. Solution is yellowish brown in color after combining with DPC.	Not detected
2	*1200S/1M H_2SO_4/24hr*	No apparent effect on the surface.	Not detected
3	*TCP/1M NaCl/24hr*	No apparent effect on the surface.	Not detected
4	*1200S/1M NaCl/24hr*	No apparent effect on the surface.	Not detected
5	*TCP/1M H_2SO_4/48hr*	Uniform pinkish grey layer forms on the coupons with black residues.	Not detected
6	*1200S/1M H_2SO_4/48hr*	Coating comes off easily. Pinkish grey residues seen on the surface.	0.37
7	*TCP/1M NaCl/48hr*	No apparent effect on the surface.	Not detected
8	*1200S/1M NaCl/48hr*	No apparent effect on the surface.	0.2

Detection of Cr(VI) in surface residues obtained after corrosion: Table 4 shows data for samples that had undergone corrosion under various acidic conditions. For this test, two types of acids were used, 4M H_2SO_4 and 4M HNO_3. The purpose of this test was to determine if any Cr(VI) formed on the surface under very severe corrosive conditions. Visual observations were made before and after the addition of a drop of DPC on the surface. Formation of a pink color on the surface after the addition of DPC indicates the presence of Cr(VI). The residues were then extracted from the surface and analyzed for Cr(VI) using UV-visible spectroscopy by the procedure mentioned in the experimental section.

In case of the *TCP/4M H_2SO_4* sample, a pinkish grey layer formed on the surface. Addition of DPC on the surface showed a very slight pink color, indicating that some Cr(VI) might be forming on the surface. In contrast, the *1200S/4M H_2SO_4* sample showed a thin film formation that was distinctly pink in color after the addition of DPC. Quantitative UV-vis analysis of the three samples did not detect any Cr(VI). In the case of the HNO_3 treated samples, the *TCP/4M HNO_3* sample showed a dark pink color formation on the surface after the addition of a drop of DPC, clearly indicating that some Cr(VI) formed at this point. However, when the residue was extracted from the surface and analyzed, no Cr(VI) was detected and the pink color also disappeared. In the case of the *1200S/4M HNO_3* sample a thin pink film formation was observed after adding DPC. Film formation was not seen in any TCP samples.

Detection of Cr(VI) in acidified solutions of TCP and 1200S: In order to confirm that the TCP solution did not contain any Cr(VI) under acidified conditions, both 1200S and TCP solutions were treated with concentrated H_2SO_4 and concentrated HNO_3. The results are given in Table 5 and pictures are provided as a visual aid in Fig. 1. Clearly, on combining with DPC, the acidified TCP solution did not form any Cr(VI) (Fig. 1). The 1200S solution on the other hand gave 55 and 76 ppm of Cr(VI) in concentrated H_2SO_4 and concentrated HNO_3 respectively (Table 5). The difference in these values is due to different acids being added to the 1200S solutions.

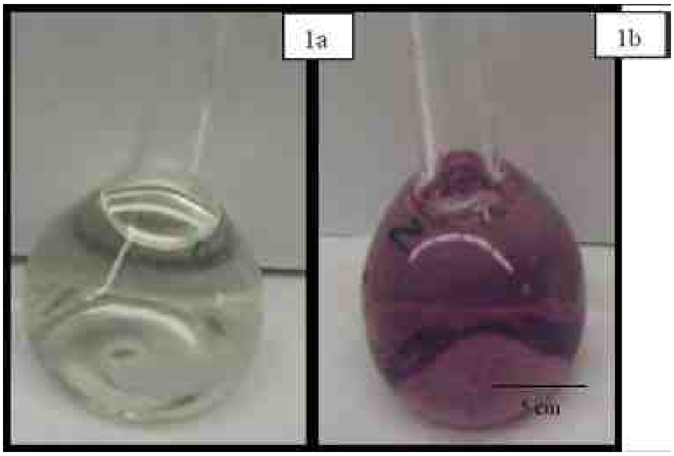

Figure 1—*HNO_3-acidified (a) TCP and (b) 1200S solutions after the addition of DPC.*

Elemental analysis of the surface using Auger electron spectroscopy

TCP/NC versus 1200S/NC: Figure 2 shows Auger data of *TCP/NC*, *1200S/NC* and *Blank/NC* samples. *TCP/NC* had a higher concentration of sulfur than the *1200S/NC* and *Blank/NC* due to chromium sulfate in the TCP coating solution.[20] The surfaces revealed trace presence of elements like zinc, magnesium and copper, which is the typical composition of the AA 2024 alloy.[4] Overall, Auger analysis confirmed the presence of chromium and zirconium as a part of the TCP coating along with sulfur and trace amounts of fluorine.

TCP/NSS/744hr versus 1200S/NSS/744hr: AES data for TCP and 1200S-coated samples that had undergone NSS corrosion treatment for 744 hr is presented in Fig. 3. Comparison of Figs. 2 and 3 shows much less chromium (1 - 2%) on the surfaces of both *TCP/NSS/744hr* and *1200S/NSS/744hr*. In *TCP/NSS/744hr*, the zirconium concentration measured was highly scattered on all three Auger

Table 4

Effect of concentrated acid on TCP and 1200S coated 2024 coupons after 6-hr treatment. Visual observations of the surface before and after adding DPC solution are given. Detected Cr(VI) content has been described as positive (> 0.1 μg/cm²) or negative (< 0.1 μg/cm²)

#	Sample	Visual observations before addition of DPC drop on the surface	Visual observations after addition of DPC drop on the surface	Cr(VI) by visual observation of the panels	Cr(VI) after extraction and UV-vis analysis
1	TCP/ 4M H_2SO_4	Black residue formed on the surface.	Very light pink color formation observed after a few minutes. No film formation observed.	May be positive	Not detected
2	1200S/ 4M H_2SO_4	Black residue formed on the surface.	No pink color formation initially. After few minutes, a dark pink color film observed on the surface.	Positive	Not detected
3	TCP/ 4M HNO_3	White rust formed on the surface with some residues.	Pink color formation on the surface seen. No film formation observed.	Positive	Not detected
4	1200S/ 4M HNO_3	White rust formed on the surface.	Pink color formation seen on the surface. The color intensifies with time and forms a film on the surface.	Positive	Not detected

Table 5

Cr(VI) content of acidified TCP and 1200S coating solutions

#	Acidified coating solution	Observation after adding DPC	Cr(VI) (ppm)
1	TCP + conc. H_2SO_4	No pink color formation	0
2	1200S + conc. H_2SO_4	Dark pink color forms	55
3	TCP + conc. HNO_3	No pink color formation	0
4	1200S + conc. HNO_3	Dark pink color forms	76

spots with a standard deviation value of 13.2 (data not shown here) after corrosion. Other than the elements reported above, metals like copper, zinc and magnesium are present in trace amounts, which is the typical composition in AA 2024 alloy.[4] However, there was no significant increase in metal concentration on the surface before and after corrosion. The presence of chloride and fluoride was not very high on the *TCP/NSS/744hr* and *1200S/NSS/744hr* samples. Sulfur was detected on NSS corroded samples.

TCP/SO_2 versus 1200S/SO_2: Figure 4 shows TCP and 1200S samples that had undergone treatment according to ASTM G85-02 Annex A4 (SO_2). In this section, samples have been referred to as *TCP/SO_2* without the exposure time being specifically mentioned. The discussion is applicable to all three exposure times, viz. *TCP/SO_2/24hr*, *TCP/SO_2/72hr* and *TCP/SO_2/148hr*. The same nomenclature is followed for *1200S/SO_2* samples. The chromium content of *1200S/SO_2* and *TCP/SO_2* was ~1 - 2%. There was an increase in aluminum content from 3.7% in *TCP/NC* in Fig. 2 to almost 50% in *TCP/SO_2* in Fig. 4. Zirconium was not detected on *TCP/SO_2* samples. The copper content on the *TCP/SO_2* samples in Fig. 4 was much more than on the *TCP/NC* in Fig. 2, as an increase from 0.3% to almost 12% is seen (compare Figs. 2 and 4). This increase in copper is not seen in comparing the *1200S/NC* and *1200S/SO_2* samples (compare Figs. 2 and 4).

Discussion

The objective of a trivalent chromium based coating is to ensure the absence of residual Cr(VI). TCP coatings have a major advantage in that they do not contain any residual Cr(VI) as evidenced from results presented in Table 1. Used and unused TCP coating solutions analyzed before and after coating showed that no Cr(VI)

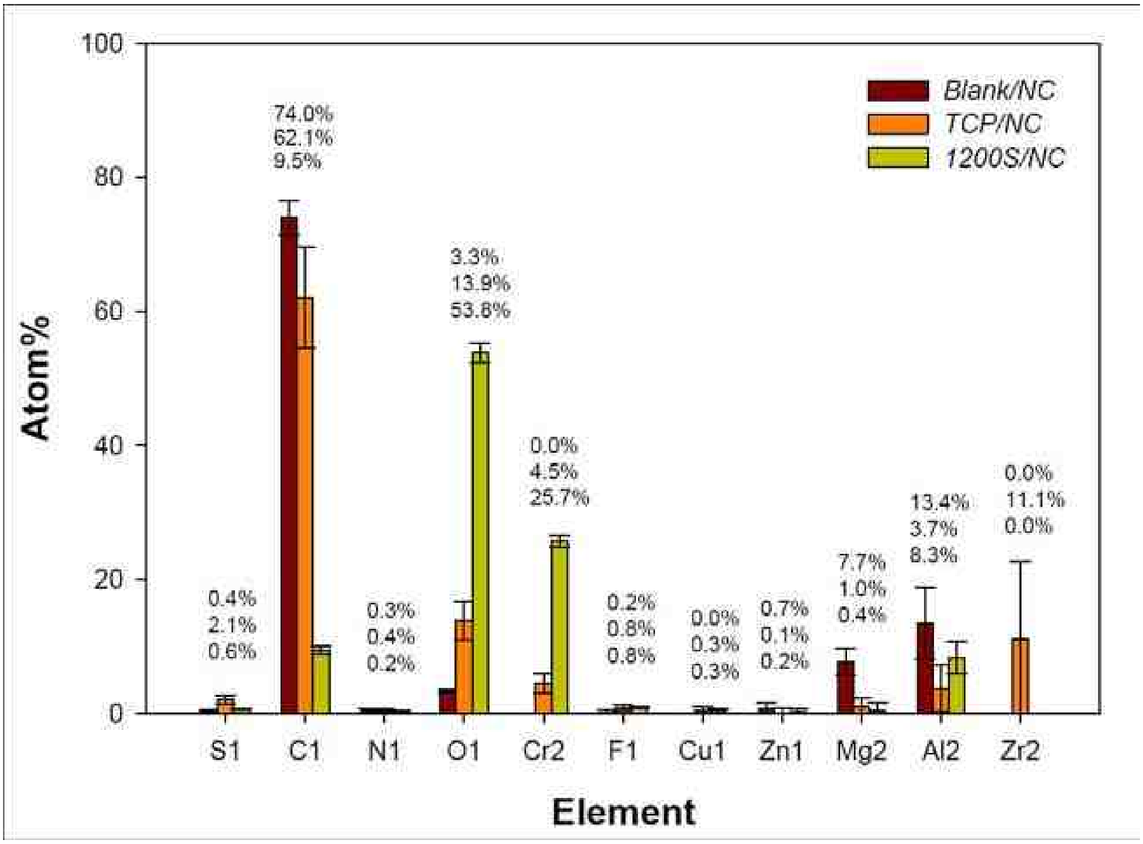

Figure 2—*Auger electronic spectroscopy data for TCP/NC, 1200S/NC and Blank/NC. The vertical bars display the average concentration of the elements taken from three spots on each sample.*

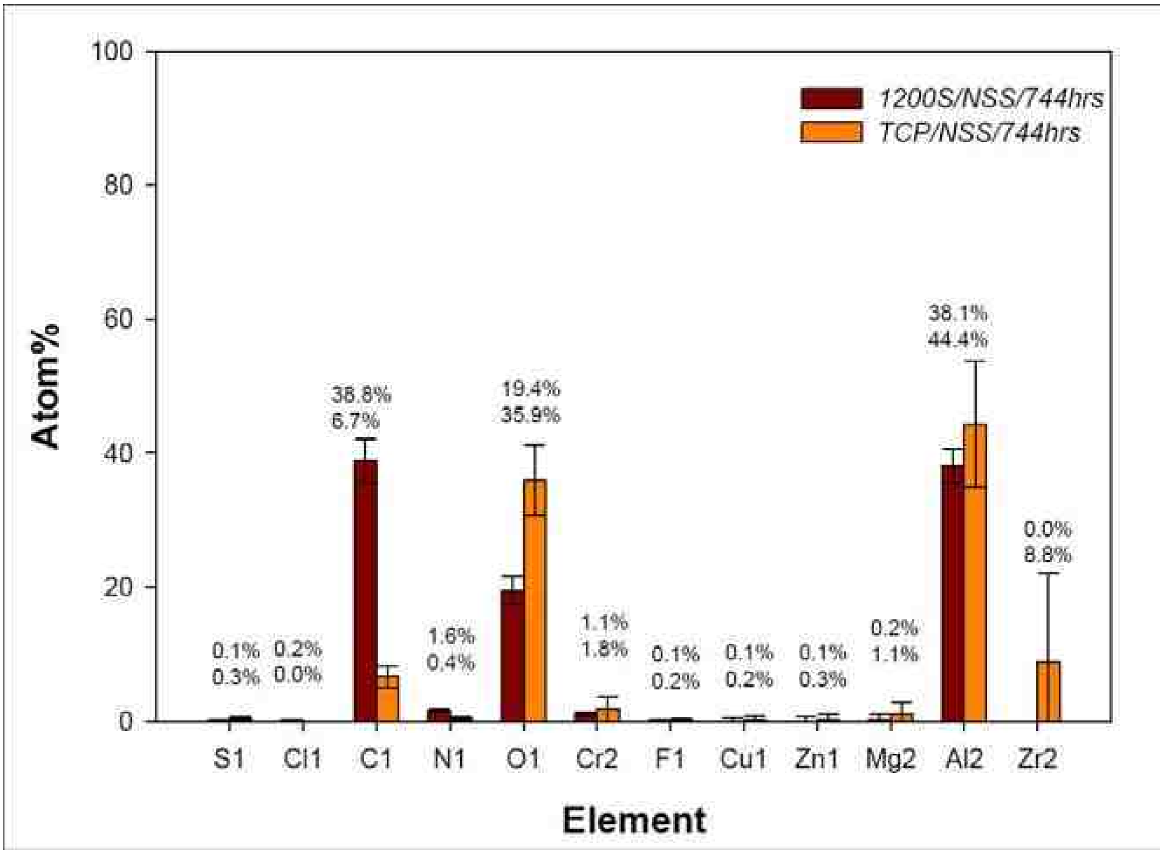

Figure 3—*Auger electronic spectroscopy data for TCP/NSS/744hr and 1200S/NSS/744hr. The vertical bars display the average concentration of the elements taken from three spots on each sample.*

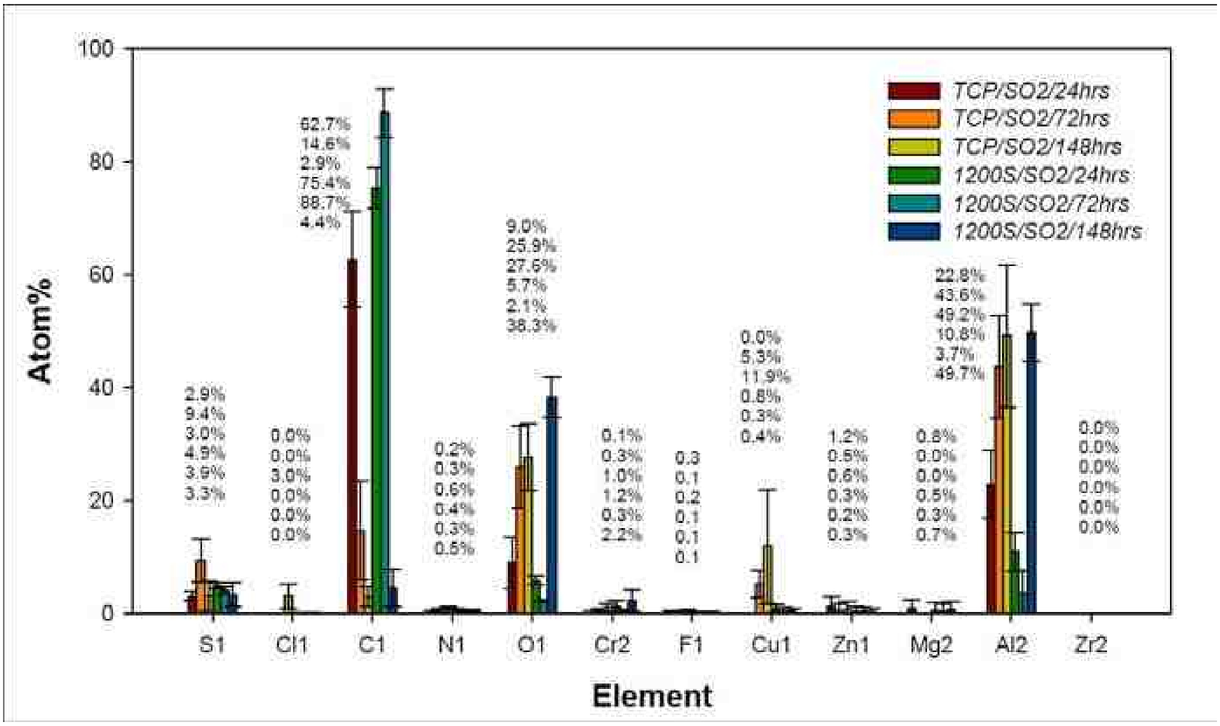

Figure 4—*Auger electronic spectroscopy data for TCP/SO$_2$ and 1200S/SO$_2$ samples after different SO$_2$ exposure times are shown. The vertical bars display the average concentration of the elements taken from three spots on each sample.*

formed during the coating process. This indicates that no oxidation of Cr(III) to Cr(VI) occurred during any time of the coating process or there was no Cr(VI) in the used TCP solution. Cr(VI) analysis of the coupon (Table 1) containing a known amount of TCP solution did not show any Cr(VI) because no Cr(VI) species was used in the preparation of the TCP solutions unlike 1200S. Significant levels of Cr(VI) were detected in 1200S solution (Table 1). The 1200S coatings do contain residual Cr(VI).[21,22] This also proves that the test method for determining Cr(VI) did not cause oxidation of any Cr(III). Diphenylcarbazide testing combined with UV-vis analysis of coated and corroded TCP samples exposed to NSS and SO$_2$ proved that no Cr(VI) was present in the TCP coated and corroded samples unlike *1200S/NC* and *1200S/NSS/744hr* samples.

TCP and 1200S coated 2024 substrates did show the likelihood of some Cr(VI) species forming on the surface when exposed to very severe acids (4M H$_2$SO$_4$ and 4M HNO$_3$) directly in contact with the coated substrate. However, this was not the case in less corrosive solutions of 1M NaCl or 1M sulfuric acid (Table 3). In both *TCP/NC* and *1200S/NC*, a pink color spot was observed on the surface when the residue obtained on the coated surface, after being directly exposed to 4M acid, was reacted with DPC, which is indicative of Cr(VI).[19] This Cr(VI) was still below the detection limit of our test and could not be quantified. Also, no Cr(VI) was detected when TCP coated and corroded samples were analyzed by the DPC test after they had undergone NSS and SO$_2$ fog treatment. Hence, the only evidence that some kind of Cr(VI) might be forming during the corrosion process comes from unaided visual observation of the pink color formed immediately after the addition of DPC to a strongly acidified TCP coated substrate aged for few hours (Table 4). This could indicate that the Cr(VI) is a transient species and is seen (by way of pink coloration) only when the coating is in contact with very highly acidic medium and not after normal salt fog exposure. However, the corroded surface of the bare 2024 alloy itself produced a brown colored compound as a corrosion product with concentrated H$_2$SO$_4$ (Table 2). This definitely posed difficulty in making accurate visual observations.

Hence, several possibilities arise at this point:

1. A transient Cr(VI) species forms on the TCP coating under severe oxidative conditions,
2. The corrosion product is masking the detection of the Cr(VI) species or
3. The pink color seen is due to the Cr(VI) coming from the bare substrate (Table 2).

Further experimentation on acidified TCP solution clearly proved that no Cr(VI) formed by acidification of TCP coating solution, unlike the 1200S coating solution (Table 5). Thus the acidification of TCP solution itself was not converting Cr(III) to Cr(VI). It must also be acknowledged that a 4M acid condition directly in contact with the coating is not truly representative of the realistic environment in which these chromium coated substrates are generally put to use, unlike the ASTM B117 tests.[15]

In conventional chromate conversion coatings, the coating solution contains Cr(VI), which is converted to an insoluble Cr(III) oxide layer after coating on the substrate,[21] but the coating still does contain residual Cr(VI). This is also proven by our tests (Table 1). The coating formed on the surface is a mixture of Cr(III) and Cr(VI) oxides.[23] Corrosion is inhibited by the migration of Cr(VI) to the corroded spots.[24]

Unlike the above case of 1200S, a trivalent chromium-based coating like TCP does not have Cr(VI) in the treatment solution. Even though the exact nature and mechanism of the action of Cr(III) on the surface of the alloy is unclear at this juncture, we hypothesize that a polymeric film forms on the surface with the zirconate species as the backbone of the film. The nature of this film could be the basic chromium species with flourozirconate branching. The probable structure of the film which has chromium chloride is shown in Fig. 5 and analogous compounds are formed with sulfates.[25]

Because the reaction is associated with the release of acid, it is likely that under acidic conditions the reaction is reversed and the branched film formed on the surface of the alloy is not stable. This is supported by the corrosion tests conducted in acid. The etching out of the zirconate and reaction of the ZrF_6 species on the aluminum could cause precipitation of the branched Cr(III) polymeric species. Under drastic acidic/oxidative conditions, it may even be possible to form Cr(VI) as a transient species.

One of the mechanisms by which a conversion coating provides protection is through the formation of an insoluble barrier on the surface that can inhibit oxygen adsorption on re-deposited copper and chlorine adsorption on aluminum.[23] The detection of chlorine and copper on the corroded surface can provide clues as to whether the coating is able to act as an efficient barrier against corrosion. We used Auger electron spectroscopy (AES) as a detection tool for this purpose.

AES data showed that the chromium content of *TCP/NC* was less than that in *1200S/NC*. *1200S/NC* had higher concentrations of oxygen and chromium (25%) than *TCP/NC*, which had only 4%. However, aluminum seems to be more exposed on *1200S/NC* compared to *TCP/NC*. No zirconium was detected in *1200S/NC*. In *TCP/NSS/744hr*, the percentages of copper and other alloying elements did not increase even after 744 hr of corrosion exposure (Fig. 3). Thus, there seems to be less alteration in the surface composition of the alloy. Significant amounts of zirconium seen on *TCP/NSS/744hr* indicates that the coating was still present on the surface after 744 hr of treatment. However, in the SO_2 treated samples, there was an increase in copper content on the *TCP/*SO_2 samples (Fig. 4) as the corrosion time increased. The chromium content (~1 - 2%) on *1200S/*SO_2 and *TCP/*SO_2 samples suggests that the coating was almost degraded.

The increase in aluminum content from 3.7% in *TCP/NC* in Fig. 2 to almost 50% in *TCP/*SO_2 in Fig. 4 suggests that the coating was being depleted/degraded during the corrosion protection activity. Copper rich surfaces come from the de-alloying of intermetallic phases, especially the S-phase (Al_2CuMg) and re-deposition of copper on the alloy surface. These reactions are enhanced under acidic conditions.[26] Even a thin layer of TCP coating appears to provide sufficient protection against chloride ion adsorption as seen from the negligible levels of chlorine detected on the *TCP/NSS/744 hr* and *TCP/*SO_2 samples. Sulfur compounds are a part of the TCP coating[20] and they too might play a key role in the inhibition process. TCP appears to form a barrier on the alloy that is able to resist corrosion.

Conclusions

This study suggests that TCP chromium content is Cr(III)-based unlike conventional chromate coatings. Conclusions from various experiments conducted on AA 2024 alloys confirm this and are listed below:

1. The TCP solution does not contain Cr(VI), fresh or used, even when exposed to oxidizing chemicals.
2. The TCP coating does not contain Cr(VI), as-deposited or corroded, unless such species form in a transient, non-detectable state.
3. Under very aggressive oxidative conditions, it is likely that Cr(VI) forms, either as a transient species, or potentially from the metallic chromium content in the substrate itself. The results do not conclusively show this one way or the other. It is important to note, however, these severe conditions are not representative of any exposure during operational environments.

Future work

It is possible that a transient Cr(VI) species forms during the acid treatment, but is converted back to the more stable Cr(III) form very quickly and hence is not detected by our test method. Hence, mechanistic studies about how TCP protects the AA 2024 substrate, XPS studies for species identification and studies about the composition of the TCP conversion coating as deposited on the surface (For example, if chromium is mixed throughout or clustered together at specific areas, and if TCP contains a corrosion inhibitor, where does the inhibitor deposit and how does it function?) would provide more thorough understanding of such systems.

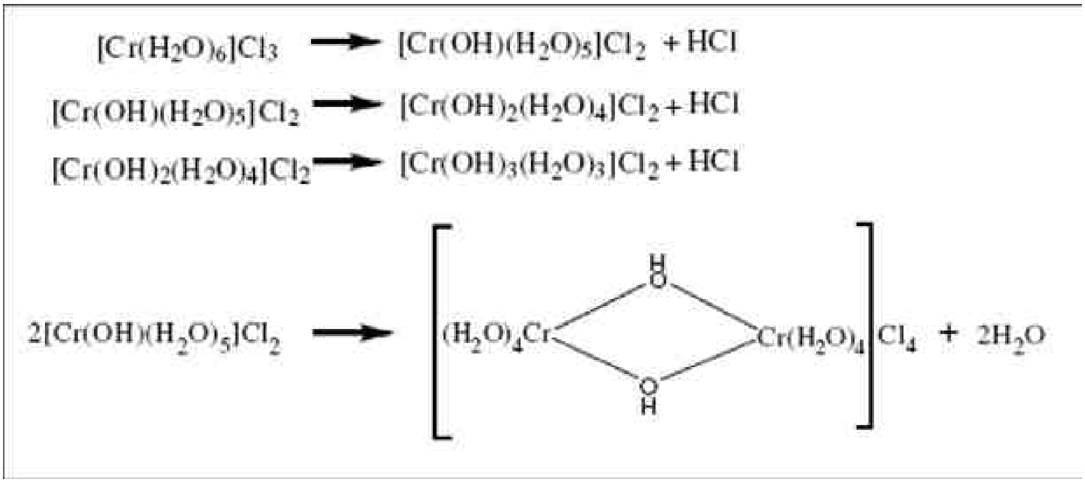

Figure 5—*Possible mechanism for film formation of TCP on the aluminum alloy surface.*

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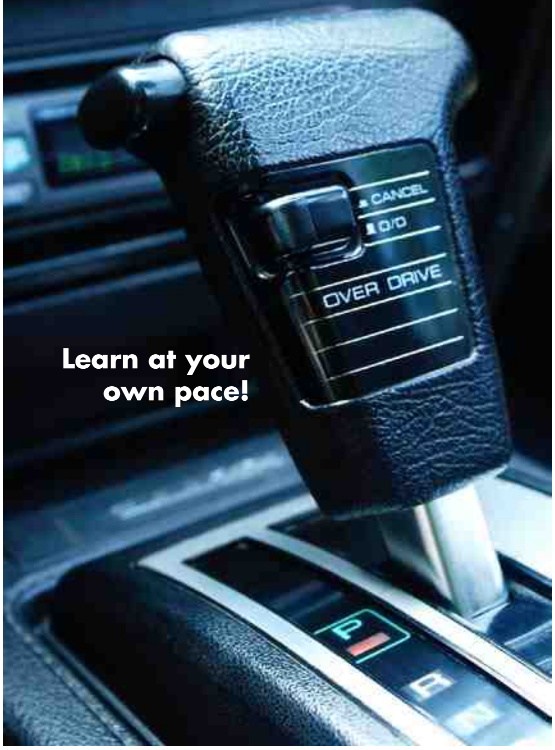


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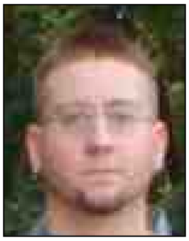
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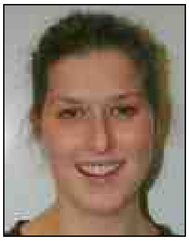
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