### Technical Article

## Desirable Features of a Non-Chromate Conversion Coating Process

by K. Sampath\*

An innovative constraints-based modeling approach was used to identify desirable features of a low-cost replacement to chromate conversion coating process for aluminum alloys. Identified features included use of a coating bath containing appropriate cations relative to the position of the aluminum substrate in the EMF series and with ionic radii and coordination numbers comparable to those of Al(III), Cr(III) and Cr(VI) ions, availability of cations in multiple valence states, decreasing solubility of reaction products with increasing pH and their ability to form waters of hydration. Limited experiments showed that a coating bath containing Mn(VI) ions provided conversion coatings with adequate promise, thereby validating the utility of this novel modeling approach.

Both chromate conversion coatings and paints based on chromates are widely used in preventing or mitigating corrosion-related problems in structures and components made of aluminum alloys.<sup>1</sup> These surface coatings resist corrosion and wear, and also promote paint adhesion.

Commonly, these protective coatings are produced by immersion, electrostatic spraying, swabbing or brushing techniques that use either chromates (as potassium or strontium chromate), dichromates (as potassium dichromate), phosphates (as orthophosphoric acid) or fluorides (as either sodium or potassium fluoride or hydrofluoric acid).

Occasionally, electrolytic methods are also used to obtain protective surface coatings, using chromic, sulfuric or oxalic acid as the electrolyte. These methods are also known as anodizing treatments.

When a chromate conversion coating is applied to an aluminum alloy component, the substrate surface reacts with the chemical solution. The metal surface is converted into a tight adherent coating, all or part of which consists of an oxidized form of the substrate metal. The chromium ions in the solution are partially reduced from a higher to a lower valency state (*e.g.*, from hexavalent Cr(VI) to trivalent Cr(III)), with a concurrent rise in the pH of the coating bath. When dried, the coating that is initially gelatinous

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

Recent events have made the search for hexavalent chromate substitutes all the more important. But what exactly are the features of a low-cost replacement conversion coating process for aluminum alloys? The author takes a novel modeling method to sift through all the possibilities. This interesting approach gives is information that may point in the right direction.

# Table 1Typical chemical compositionOf a chromate conversion coating bath2

Type of Compound	Chemical Formula	Amount
Orthophosphoric acid	H <sub>3</sub> PO <sub>4</sub>	63.7 g/L (8.5 oz/gal)
Sodium fluoride	NaF	4.5 g/L (0.6 oz/gal)
Chromic oxide	CrO <sub>3</sub>	9.7 g/L (1.3 oz/gal)

(*i.e.*, gel-like) undergoes hardening, becomes hydrophobic, less soluble in water and more abrasion resistant. The resulting conversion coating on the aluminum surface offers corrosion resistance and an anchoring surface for organic finishes, such as a paint topcoat.

The chemical composition of the chromate conversion coating is indefinite as it contains varying amounts of reactants, reaction products, waters of hydration and other anions, such as fluorides and phosphates. In the presence of corrosive conditions, the hexavalent Cr(VI) ions that are incorporated into the coating leach out, and possibly tie-up the free electrons and thereby provide exceptional corrosion resistance.

However, solutions containing Cr(VI) ions have been determined to be carcinogens. The U.S. Environmental Protection Agency (EPA) has included hexavalent chromium on its list of toxic chemicals for voluntary replacement, and has promulgated strict air emission and waste disposal standards to curtail the use of hexavalent chromium. These developments have created a need for alternative chemical conversion coating compounds that do not contain Cr(VI) ion, but either meet or exceed the protective properties displayed by the hexavalent chromium-based compounds.

Furthermore, from legacy and cost standpoints, any alternative must involve only minor modifications to the present process stream so that it becomes readily acceptable. However, while a cost-effective and environmentally benign alternative that provides protection comparable to that of chromium is needed, how does one find such an alternative? Currently, no known rational methods are available for identifying alternatives to Cr(VI).

Clearly, the identification of potential alternatives to chromates must be based on a fundamental understanding of the corrosion-inhibiting mechanism. Although the use of chromates as corrosion inhibitors has evolved over

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#### Table 2 Compounds Commonly Found In Chromate Conversion Coatings<sup>3</sup>

Type of Compounds	Chemical Formula*
Oxides, hydroxides	$M_{x}O_{y}, M_{x}(OH)_{y}$
Chromates	$M_x CrO_4, M_x CrO_7$
Cr oxides, hydroxides	$Cr_{2}O_{3}, Cr_{2}O_{3}, CrOOH, Cr(OH)_{3}, Cr_{2}O_{3}, nH_{2}O$
Cr chromates	$Cr(OH)CrO_4$ , $Cr_v(CrO_4)_v$
Substrate (M*) Derived	$PO_4$ , F <sup>-</sup> compounds, etc.
Cr with other anions	$\operatorname{Cr}_{v}(\operatorname{PO}_{4})_{v}$ , etc.
*M = substrate metal.	× + y

several decades, much of this use is based on empirical knowledge. To date, a fundamental or molecular level understanding of the chemical/physical mechanism(s) by which they operate has not emerged. For example, Cr(VI) in the coating is believed to provide both corrosion protection and a self-healing ability. Not only is it unclear exactly what functional role chromates play, it is not known what chromate replacement complexes need to do to ensure long-life coating systems. There is very little current work that addresses the electrochemical behavior of chromate replacement compounds. Under its Multiple University Research Initiative, the Air Force Office of Scientific Research (AFOSR) has been supporting research projects that address this basic need to understand mechanisms of chromate inhibition. Most other efforts to identify chromate alternatives lack a basic mechanistic approach and is typically focused on industry practices involving trial-and-error methods followed by comparative or benchmark testing.

Furthermore, as with chromate conversion coatings, the corrosion inhibitor paint chemistry for aluminum substrates relies on the extensive use of Cr(VI) in the form of strontium chromate, which is incorporated into both the surface pretreatment and the primers as a highly effective corrosion inhibitor. Besides mandating the removal of chromates in conversion coatings and paint chemistries, the new environmental regulations are also forcing paint materials and processing technology to move away from the use of formulation chemistries involving volatile organic contaminants (VOCs) and hazardous air pollutants (HAPs). These ingredients must soon be substantially reduced or eliminated from the paint technology base. Although formulation technology has begun to move toward compliance, the available environmentally compliant paint systems have so far provided less than satisfactory performance. Current comparative evaluations show that adhesion, coating durability, weathering and corrosion protection have suffered.

### **Objectives**

In order to develop effective non-chromate conversion coatings and paint formulations, we need a fundamental understanding of the chemical and/or physical processes and mechanisms of corrosion protection that occur when chromate-based coatings are applied on metal surfaces, especially aluminum and its alloys. In the absence of such an understanding, an innovative constraints-based modeling approach can be used to identify the desirable features of a potential alternative to the chromate conversion coating process. This approach is based on the following two key principles: (1) consolidating existing and perceived knowledge into a coherent set of mutually inclusive constraints (or requirements) and (2) using the set of constraints to identify cost-effective and time-sensitive potential alternatives that limit the experimental space and reduce inherent risks.

The use of both constraints-based modeling and controlled experiments offers the potential to identify a cost-effective alternative to the chromate conversion coating process. The actual

### Table 3 Typical Analysis of a Chromate Conversion Coating on a Zinc Substrate⁴

Component	Content (wt%)
Cr(VI)	8.7
Cr(III)	28.2
Zn(II)	2.1
$S(SO_4)$	3.3
Na	0.3
H,O	19.3
0	Balance

modeling is based on a critical assessment of various known and perceived events that occur during the chromate conversion coating process. These events are perceived primarily to overcome gaps in known knowledge. The above assessment is used to impose a set of mutually inclusive or coherent constraints on the experimental conditions and develop an understanding of the effects of these constraints on coating quality and performance, with no adverse effects on either the environment or the health and safety of workers.

The specific objectives of this article, then, are to:

- provide a basic understanding of chromate conversion coating processes and coatings based on known and perceived events,
- 2. describe recent efforts in the development and evaluation of non-chromate conversion coating processes,
- 3. describe a constraints-based model that allows the development of a non-chromate conversion coating process and
- 4. prescribe a set of experimental constraints that leads to the identification of alternatives to chromates used in the chromate conversion coating process.

It must be recognized that the alternative chemical compounds identified by this effort also offer themselves for evaluation as alternatives to chromates used in paint chemistries.

### Critical Assessment Of Chromate Conversion Coating Processes

As mentioned previously, chromate conversion coatings provide corrosion resistance and improve paint adhesion. The development of successful non-chromate conversion coatings requires, as a prerequisite, a critical assessment of the chromate conversion coating process. This understanding must be based on the following issues:

- 1. the type of compounds or ions present in chromate conversion coating baths,
- 2. the effects of these compounds or ions on different types of substrate materials and
- 3. the effects of the compounds or ions present in the coating on corrosion resistance and paint adhesion.

Additionally, one must assess the functional roles of the various processing steps involved in a typical chromate conversion coating process, and in particular, the effects of each of the processing steps on substrate surface condition. This assessment is necessary to distinguish critical steps from non-critical ones for identifying alternatives to chromates, identify processing steps that will allow compliance with current and emerging regulations and develop/ establish appropriate quality control methods.

An initial literature review of chromate conversion coatings indicated that theoretical or empirical models based on a rationalized

Table 4			
	Electromoti	ve force series <sup>11</sup>	
No.	Electrode Reaction	Standard Electrode Potential E (Volts) at 25°C (77°F)	
1	$K = K^{+} + e^{-}$	-2.922	
2	$Ca = Ca^{++} + 2e^{-}$	-2.87	
3	$Na = Na^+ + e^-$	-2.712	
4	$Mg = Mg^{++} + 2e^{-}$	-2.34	
5	$Be = Be^{++} + 2e^{-}$	-1.70	
6	$Al = Al^{+++} + 3e^{-1}$	-1.67	
7	$Mn = Mn^{++} + 2e^{-}$	-1.05	
8	$Zn = Zn^{++} + 2e^{-}$	-0.762	
9	$Cr = Cr^{+++} + 3e^{-}$	-0.71	
10	$Ga = Ga^{+++} + 3e^{-}$	-0.52	
11	$Fe = Fe^{++} + 2e^{-}$	-0.440	
12	$Cd = Cd^{++} + 2e^{-}$	-0.402	
13	$In = In^{+++} + 3e^{-}$	-0.340	
14	$Ti = Ti^+ + e^-$	-0.336	
15	$Co = Co^{++} + 2e^{-}$	-0.277	
16	$Ni = Ni^{++} + 2e^{-}$	-0.250	
17	$Sn = Sn^{++} + 2e^{-}$	-0.136	
18	$Pb = Pb^{++} + 2e^{-}$	-0.126	
19	$H_2 = 2H^+ + 2e^-$	0.000	
20	$Cu = Cu^{++} + 2e^{-}$	0.345	
21	$Cu = Cu^+ + e^-$	0.522	
22	$2Hg = Hg_{2}^{++} + 2e^{-}$	0.799	
23	$Ag = Ag^{+} + e^{-}$	0.800	
24	$Pd = Pd^+ + e^-$	0.83	
25	$Hg = Hg^{++} + 2e^{-}$	0.854	
26	$Pt = Pt^{++} + 2e^{-t}$	~ 1.2	
27	$Au = Au^{+++} + 3e^{-}$	1.42	
28	$Au = Au^+ + e^-$	1.68	

understanding of the chromate conversion coating processes were currently unavailable. In general, producing a chromate conversion coating on a substrate material involves several processing steps, including initial cleaning and desmutting of the substrate, surface conditioning or activation, application of the chromate conversion coating, sealing and final drying of the coating. However, the review did not reveal the use of significant industrial quality control measures (except for coating weight measurements) to assess the quality after each processing step.

In general, when present in processing solutions, chloride ions were found to deter the quality and performance of chromate conversion coatings. Therefore, processing solutions free from chloride ions and deionized (DI) water are used for processing and rinsing the parts between each of the above main processing steps. Each of the main processing steps involves several variables such as type of chemicals, their individual strength level (concentration), temperature, agitation and process time.

During the initial cleaning step, organic contaminants on the surface are removed using aqueous, high pH alkaline solutions. The cleaners usually also contain inhibitors to control the rate of chemical attack as aluminum is easily corroded by alkaline solutions. After cleaning, the aluminum substrate is dipped or sprayed with a deoxidizer. Previously, a mixture of three parts of nitric acid and one part hydrofluoric acid was used for deoxidation. However, as this mixed acid solution caused misting problems, nowadays compounds such as ferric salts, persulfates and peroxides are used for deoxidation. The deoxidizer removes any remaining surface oxides on the aluminum.

Previous investigations have clearly shown that a thorough cleaning of the substrate material is essential to obtain uniform and high performance chromate conversion coatings. In fact, evaluating the ability to achieve a uniform conversion coating is an inexpensive and simple test to determine the effectiveness of surface cleaning methods. The addition of a wetting agent such as sodium alkyl aryl sulfonate to the coating bath helps to produce a uniform and continuous coating. The addition of fluoride, nitrate and phosphate ions may activate the surface of aluminum and aid the uniform formation of the surface gel.

During the initial stages of the conversion coating reaction, a superficial layer of the substrate surface is converted into a thin layer of gel. The name "conversion coating" is derived from this processing step. This gel is often characterized as an amorphous hydrated oxyhydroxide (*i.e.*, AlOOH  $nH_2O$ ). During subsequent chromate coating reaction, the substrate surface reacts with the coating bath. Table 1 shows the typical chemical composition of a coating bath.<sup>2</sup>

This coating bath is operated at a pH of 1.2 to 2.2. During chromating, the chromic oxide reacts with the orthophosphoric acid. In this reaction, Cr(VI) is partially reduced to Cr(III), and the pH correspondingly increases. The increase in pH at the substrate interface is commonly attributed to the liberation of hydrogen gas (*i.e.*, the reduction in hydrogen ion concentration of the bath), a combination of dissolved oxygen with hydrogen ions to form waters of hydration, or both, as the following two electrochemical reduction reactions are known to occur at the cathode in acidic baths.

$$\begin{array}{c} 2\mathrm{H}^{\scriptscriptstyle +}+2\mathrm{e}^{\scriptscriptstyle -} \twoheadrightarrow \mathrm{H_2} \\ \mathrm{O_2}+4\mathrm{H}^{\scriptscriptstyle +}+4\mathrm{e}^{\scriptscriptstyle -} \twoheadrightarrow 2\mathrm{H_2}\mathrm{O} \end{array}$$

In neutral or alkaline solutions, oxygen reduction occurs at the cathode, leading to the formation of a hydroxide.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH$$

The above cathodic reduction reaction indicates that a hydroxide coating of the substrate can be obtained on the substrate surface when the hydroxide is insoluble in near neutral or alkaline solutions. This reaction forms a uniform coating consisting of a hydrated precipitate, possibly  $CrPO_4$ · $6H_2O$  and  $Cr(H_2PO_4)_3$ · $xH_2O$  or  $Cr(NO_3)_3$ · $9H_2O$ , depending on the type of the chemical constituents present in the coating bath. These hydrated precipitates may be hydrophobic.

The chemical composition of the coating is indefinite as it contains varying amounts of the substrate, reactants, reaction products, waters of crystallization (hydration) and other anions such as fluorides and phosphates. Table 2 summarizes compounds commonly found in chromate conversion coatings.<sup>3</sup>

The Cr(III) and Cr(VI) ions in the bath may substitute for the Al(III) (substrate) cations in the surface gel. As Cr(III) and Cr(VI) ions have an ionic radius similar to that of the Al(III) ion, the above ionic substitutions may be expected to provide residual compressive stress on the coating surface. Furthermore, when in contact with moisture, the high surface tension forces associated with polar bonds present in hydrated precipitates may allow self-healing (closing) when corrosion spots occur or a sharp incision is made through the coating surface.

Substitution with Cr(III) ions is believed to allow hardening of the gel and contributes to the increased wear resistance of the coating. The Cr(VI) ions leach out when the coating contacts moisture, and combine with free electrons to form Cr(III) ions. This reduction reaction has enormous significance, as the removal of the free electrons is a necessary and vital condition for improving corrosion resistance. It must be emphasized that this reduction reaction and its beneficial effect on corrosion resistance are intimately tied with the multivalent state of chromium. Other compounds in the coating are believed to impart specific colors to the coating to either enhance appeal or provide camouflage, while also contributing to an increase in coating thickness. Table 3 shows a typical analysis of a chromate coating on a zinc substrate.<sup>4</sup> The ratio of Cr(III) to Cr(VI) ions in the coating is quite important in achieving the desired protective properties. Once the conversion process is complete, the aluminum substrate is removed from the conversion coating bath. The substrate is subjected to a final rinse, dried, sealed in a sealant bath or prepared for final painting with an organic topcoat. To prevent staining and aid air drying, the final rinse may consist of hot DI water.

### Recent Developments In Non-chromate Coating Processes

In recent years, several U.S. companies and universities have engaged in independent or cooperative research and developmental efforts on non-chromate coating processes.<sup>5,6</sup> These efforts include developing both conversion coatings and other non-conversion coatings. The basic objective of these efforts has been to provide an alternative, cost-effective, non-chromate (conversion or nonconversion) coating process that would allow the metal finishing industry to comply with current and emerging regulations and thereby gain a significant global market share of this vital surface treatment technology. Many of these efforts have focused mainly on aluminum and its alloys. Most of these non-chromate coating processes are still under continuous development and evaluation. Some companies have either already developed or use proprietary non-chromate coating processes that allow environmental compliance. It must be recognized that these processes are not necessarily cost effective.

The application of a proprietary conversion coating process\*\* on several different wrought and cast aluminum alloys was evaluated by the National Defense Center for Environmental Excellence (NDCEE). Monitored by the Naval Air Warfare Center, Warminster, PA,7 this effort evaluated the final coating quality. This approach is limited in that it can provide insights into coating quality only when a significant number of test coupons with protective coatings show acceptable quality. When this process was previously evaluated at the Naval Air Warfare Center, it showed acceptable coating quality on several wrought aluminum alloys such as 2024-T3, 7075-T6 and 6061-T6. However, when the recommended coating procedures were duplicated at the NDCEE, coatings with acceptable quality were not obtained. Specifically, the coatings did not meet the requirements of the ASTM B117 salt fog test.8

A cooperative project on "Alternatives to Chromium for Metal Finishing" performed by the National Center for Manufacturing Sciences (NCMS) evaluated the corrosion resistance, electrical contact resistance and paint adhesion of 29 chromium-free candidate commercial coatings, provided by 12 suppliers on five different aluminum alloys (A356, 2024-T3, 3003, 6061-T6 and 7075-T6).<sup>9</sup> This project included the aforementioned proprietary conversion coating process and evaluated the quality of different types of conversion coatings on the above aluminum

alloys. This study determined that the proprietary process provided coatings with acceptable quality only on A356 cast aluminum alloy. The A356 cast aluminum alloy is considered to be at the bottom of a list that rates the order of difficulty in producing successful coatings in aluminum alloys. Therefore, successful coatings were commonly expected in this cast alloy. Despite demonstrating promising results in A356 aluminum alloy, the NCMS study was not entirely acceptable to the U.S. Department of Defense (DOD), as NCMS did not perform the comprehensive testing required by the military specification MIL-C-5541E.

Another NCCC process, called the "stainless aluminum" coating process, has been developed at the University of Southern California.<sup>10</sup> In this process, the test coupon is initially immersed in boiling cerium nitrate and cerium chloride solutions. Subsequently, the test coupon is subjected to anodic polarization in a molybdate (Mo) solution, producing a non-chromate conversion coating. Uniform coatings have been produced on commercial pure, 6061-T6, 2024-T3 aluminum alloys and aluminum/silicon carbon (Al/ SiC) composite test coupons. The stainless aluminum coating process allows substitution of Ce(III) ions and Mo(VI) ions (instead of Cr(III) and Cr(VI) ions) into the protective coating. Immersion testing of coated test panels in a salt bath has shown that the coatings were free of localized corrosion. Long-term exposure of a test coupon that contained a scratch on the treated surface also showed no corrosion. However, when either Ce(III) ions or Mo(VI) ions were used independently in a conversion coating, the coating did not provide acceptable test results. Furthermore, considering that anodic coatings generally cause a fatigue debit (perhaps arising from surface imperfections), the stainless aluminum coatings may need additional evaluation of their fatigue properties.

At this time, it is not certain whether the above two coating processes would produce protective coatings with acceptable quality on other wrought aluminum alloys, such as 7075-T6 and 5083-H131, that show higher levels of difficulty in producing corrosion-resistant coatings. The application of these non-chromate coating processes on other aluminum alloys has not been evaluated or reported in the open literature.

# Table 5Coordination numbers and radiiOf selected metallic cations12,13

Element	Metallic Cation	Coordination Number(s)	Ionic Radius (Å)
Aluminum	Al(III)	4,6	0.39, 0.54
Chromium	Cr(III)	6	0.62
Chromium	Cr(VI)	4	0.26
Cerium	Ce(III)	6, 8, 12	1.01, 1.14, 1.29
Gallium	Ga(III)	4,6	0.47, 0.62
Manganese	Mn(III)	6	0.58
Manganese	Mn(VI)	4	0.26
Molybdenum	Mo(VI)	6,7	0.59, 0.73
Scandium	Sc(III)	6, 8, 12	0.745, 0.87, 1.116
Selenium	Se(VI)	4,6	0.50, 0.42
Titanium	Ti(III)	6	0.67
Tellurium	Te(III)	6	0.56
Vanadium	V(III)	6	0.64
Tungsten	W(VI)	4,6	0.42, 0.60

Note: When an ion exhibits two or more coordination numbers, the ionic radius increases with increasing coordination number, except for selenium.

## Table 6 A Select List of Manganese-based Chemical Compounds

Chemical Name	Chemical Formula	Solubility
Manganese acetate	$Mn(C_2H_3O_2)\cdot 2H_2O$	
Manganese orthophosphate	MnPO <sub>4</sub> •xH <sub>2</sub> O	Slightly soluble in water
Manganous phosphate	Mn(PO <sub>4</sub> ), 7H,O	Insoluble in water
Manganous phosphate	MnHPO <sub>4</sub> ·3H <sub>2</sub> O	Slightly soluble in water
Manganous pyrophosphate	MnP <sub>2</sub> O <sub>2</sub> ·3H <sub>2</sub> Õ	Insoluble in water

<sup>\*\*</sup> Sanchem Safegard CC™, Sanchem, Inc., Chicago, IL.

### Development of a Constraints-based Model

A critical assessment of the chromate conversion coating process showed the following essential features:

- 1. The chromate bath is a clear acidic solution (pH 1.2 to 2.2).
- 2. During chromating, precipitation of hydrated compounds occurs on the substrate and the pH of the bath increases at the substrate interface.
- 3. Several hydrated compounds containing chromate, nitrate, phosphate or a combination of these anions are formed.
- 4. The reduction reaction occurs with the liberation of hydrogen gas, formation of waters of hydration or both.
- 5. Fluoride, nitrate or phosphate anions are present in the coating bath perhaps as activators; they also enter the surface coating.

Further, it appears that the chief aspects of the chromate coating process are:

- 1. the Cr(VI) to Cr(III) reduction reaction,
- 2. the increase in bath pH at the interface
- the resulting precipitation reaction involving hydrated compounds and
- 4. the ratio of Cr(III) to Cr(VI) in the coating.

The precipitation reaction can be expected to occur when the products of the reaction (chromates, nitrates and phosphates of chromium or the substrate) show decreased solubility with increasing bath pH. Any proposed modeling effort must address the above chief features of the chromate conversion coating process. Similarly, a consideration of any potential alternative to the chromate conversion coating process must incorporate these chief features. In particular, the initial effort must focus on identifying chemicals that show a decrease in solubility with increasing pH in the range of from 2.0 to 7.0, while also forming waters of hydration.

Further, to provide corrosion resistance, the cation of the chemicals that form the precipitate must be positive (*i.e.*, less negative) in the electromotive force (EMF) series relative to the substrate, and their EMF values should be close to each other. Table 4 shows the EMF series for various electrode reactions involving selected basis metals and their corresponding standard electrode potentials.<sup>11</sup>

Modeling efforts should consider methods or solutions that provide one or more chemicals satisfying the above sets of constraints. Additionally, such chemicals or their solutions must be environmentally benign and cost effective.

Based on the above analysis, the following constraints, all of which are mutually inclusive, can be used in proposing a model for identifying an alternative to the chromate conversion coating process:

- 1. The processing solution must be clear with no precipitates.
- The processing solution must contain a wetting agent such as sodium alkyl aryl sulfonate to provide a uniform and continuous coating.
- 3. The processing solution must contain fluoride, perchlorate, nitrate, phosphate, sulfate or as many of these anions as necessary to activate the surface of the substrate and enter the coating as well.
- 4. The pH of the processing solution must be capable of being varied in the acidic range of pH 1.2 to 5.0.
- 5. The solution of these salts must react with the substrate, raise the pH of the coating bath locally at the bath/substrate interface and form hydrated precipitates that are insoluble in near neutral and alkaline solutions.
- 6. The precipitate that forms a hydrated compound must also contain cations in multiple (*e.g.*, III and VI) valence states.

- 7. The cation forming the hydrated precipitate must be positive in the EMF series with respect to the substrate.
- 8. The precipitates that form on the substrate during processing should exhibit waters of hydration.
- To preserve the waters of hydration in the coating, the processing temperature must be kept under 100°C (212°F).

The above constraints-based model is proposed based on common industry observations and the underlying (known and perceived) scientific understanding. While the ratio of Cr(III) to Cr(VI) ions in a chromate conversion coating is perhaps quite important in achieving the desired protective properties, such a constraint for potential alternatives to chromate coating processes is not explicitly considered in this modeling approach. Rather it is intended to be achieved by controlling the pH of the coating bath. The relevance of the above constraints to the controlled experiment requires validation by experiments and analysis of the data.

In addition to the above set of constraints, two additional constraints can be offered based on an analysis of the ionic radii and coordination numbers for Al(III), Cr(III) and Cr(VI) ions. Table 5 shows the ionic radii and coordination numbers of candidate metallic cations in either the (III) or (VI) valence state.<sup>12,13</sup> Among these candidate cations, it is interesting to note that Mn(III) and Mn(VI) have radii similar to those of Al(III), Cr(III) and Cr(VI) ions. Coincidentally, Table 5 also includes data for the Ce(III) and Mo(VI) ions used in the stainless aluminum procedure developed at the University of Southern California. As these two ions exhibit a size either larger than the Al(III), Cr(III) and Cr(VI) ions, or a non-matching coordination number with either the Cr(III) or Cr(VI) ions, one may expect that the reactions involving these chemicals would require long processing times and high temperatures.

Interestingly, both the proprietary conversion coating process and the stainless aluminum coating process appear to support the added set of constraints based on ionic radius. For example, the proprietary conversion coating process uses potassium permanganate that contains manganese as Mn(VII). Depending on the nature of the chemical reactions between the chemicals in the bath and the substrate, one may expect the potassium permanganate solution to provide both Mn(III) and Mn(VI) ions into the coating. However, at this time, it is not clear whether the chemical reactions involving potassium permanganate allow Mn(III) and Mn(VI) ions to enter the coating and, if so, whether they exhibit the same set of coordination numbers as those of the Cr(III) and Cr(VI) ions, respectively. Chemical analyses of the protective coatings produced with the proprietary conversion process are currently unavailable. The success of the process in producing protective coatings on a range of aluminum alloys should largely depend on the effectiveness of the above substitutions.

The "stainless aluminum" coating process uses cerium (Ce(III)) ions to harden or strengthen the coating and Mo(VI) ions to provide corrosion resistance and the ability to self-heal. Understandably, when either of these two ions is used independently in a coating, the coating does not provide acceptable test results.

As mentioned previously, Table 5 also identifies other candidate metallic cations in (III) and (VI) valence states that exhibit a coordination number similar to those of the Cr(III) and Cr(VI) ions. Chemicals that contain many of these metallic cations are inherently expensive. Despite this cost aspect, it is interesting to note that several previous investigations have used many of these metallic cations to evaluate their ability to provide protective coatings, and such coatings have shown varying degrees of corrosion resistance.

### **Model Validation**

In order to validate the model, one must first identify chemicals that can satisfy the variety of constraints imposed by the model. This identification would require an examination of the specific characteristics of various chemicals, relative to specific substrate materials.

With regard to aluminum-based alloys, manganese-based chemicals could serve as potential alternatives to chromate-based solutions, based on the sizes of the Mn(III) and Mn(VI) ions versus those of Al(III), Cr(III) and Cr(VI) ions, and the electropositive nature of manganese (1.05V at 25°C; 77°F) relative to aluminum (-1.67V at 25°C; 77°F) substrate. Mn(III) and Mn(VI) ions also offer the greatest promise in terms of availability, cost and ease of handling.

Understandably, the success of any non-chromate conversion coating process that involves manganese ions in multiple valence states (*e.g.*, III and VI) will depend largely on the effectiveness of their substitution. Processing conditions that enhance the thermodynamic and kinetic factors that allow the substitution of Mn(III) and Mn(VI) ions into the gel should contribute to improving the corrosion resistance of the non-chromate conversion coating, while those processing conditions that limit the substitution of Mn(III) and Mn(VI) ions into the gel will contribute to the limited success or failure of the coating. The ratio of Mn(III) to Mn(VI) ions in the coating could also be a significant factor affecting the protective properties of the coating.

Based on the set of constraints proposed in the model, manganese-based chemicals could be identified that (1) dissolve in acid to provide a clear solution with a pH ranging from about 2.0 to 5.0 and (2) react with the aluminum substrate to form a precipitate that is insoluble in near neutral solutions or shows decreasing solubility with increasing pH and also form waters of hydration. Limited experiments could be performed to evaluate the coating characteristics of such chemicals.

Table 6 shows a number of manganese-based chemicals that show solubility in acid (*i.e.*, pH < 7.0), and the ability to add water of hydration, besides having limited solubility in water. The actual experiments must contain reactants that will provide one of the chemicals listed in Table 6 as a reaction product.

The reactants could include chemical compounds with fluoride, perchlorate, nitrate, phosphate or sulfate anions that would activate the substrate surface, a wetting agent, such as sodium alkyl aryl sulfonate, that would facilitate the formation of a uniform and continuous coating, and either a reducing or oxidizing agent to provide manganese ions in multiple valence states. Prior to reaction with aluminum, all of these chemicals must provide a clear solution, with a pH ranging from 2.0 to 5.0.

Sampath<sup>14,15</sup> describes a non-chromate conversion coating process for aluminum alloys that uses a solution based on potassium manganate ( $K_2MnO_4$ ). While this solution provided acceptable results, further refinements to both the coating bath and processing steps may produce non-chromate conversion coatings with exceptional performance.

In a manner similar to Table 6, additional lists of selected chemicals could be generated based on the other cations (Ce, Ga, Mo, Sc, Se, Te, Ti, V and W) listed in Table 5. The electronegativity of these elements relative to the substrate (Table 4) must first be established. If the element is electropositive with respect to the selected substrate, then a chemicals database can be used to identify chemical compounds based on these cations that exhibit solubility in an acid, reduced solubility with increasing pH (or insolubility in water), an ability to form waters of hydration and also provide cations in multiple valence states. After ascertaining those characteristics, a clear coating bath can be prepared which contains the appropriate reactants, activators and wetting agents. Testing and evaluation would then follow.

#### **Future Work**

In order to further reduce the risks associated with the experimental work, one could use the above constraints-based modeling approach together with a chemical and molecular database. This database will enable one to identify chemical compounds that have the following characteristics:

- 1. The cation exhibits multiple valence states.
- 2. The cation is less electronegative compared to the substrate.
- 3. The ionic size of the cation is comparable to Al(III), Cr(III) or Cr(VI).
- 4. The chemical compound reacts with the substrate and forms a hydrated precipitate.
- 5. The precipitate is soluble in acid, insoluble in water and exhibits decreasing solubility with increasing pH.

These characteristics would qualify the chemical compound as a potential candidate for forming a protective surface coating on the selected substrate, provide corrosion resistance. The polar bonds associated with the hydrated form of the precipitate would allow self-healing.

Next, molecular dynamics simulation techniques can be used to identify the surface phenomena that inhibit corrosion or prevent corrosion from occurring. This methodology is currently used in surface science, pharmaceutical and biotechnology research. These molecular simulations can be used to evaluate various molecular configurations during the equilibrium stage. The evaluations can be based on adhesion energy, degree of bonding between the substrate and the coating and conformation and position of the coating molecule with respect to the substrate atom or molecule.

The use of both the database and molecular dynamics simulation could provide a fundamental understanding of the roles of Cr(VI) and Cr(III) in forming a corrosion-resistant protective coating when chromate-based coatings are applied on metal surfaces, and also enable one to identify alternative chemical compounds that would provide similar characteristics. Subsequent use of controlled experiments can be expected to allow appropriate validation of the chemical and/or physical processes and mechanisms of corrosion protection in both chromate and non-chromate conversion coatings.

When the modeling, simulation and experimental work lead to a coating that is hydrophobic and exhibits a residual compressive stress condition at the surface, the corrosion resistance and selfhealing ability of this coating should be comparable to those of the chromate conversion coatings. Following the successful demonstration of a non-chromate conversion coating, it may be necessary to perform appropriate risks assessments and cost assessments of the new technology.

### **Summary & Conclusions**

A new constraints-based model has been proposed to identify the desirable features of an alternative to the chromate conversion coating process, and appropriate chemical compounds that are more likely to provide effective alternatives to chromates and dichromates for producing non-chromate conversion coatings. This model identifies and recommends specific chemical compounds containing Mn(III) and Mn(VI) ions to replace Cr(III) and Cr(VI) ions, based on a variety of constraints that include ionic radii and coordination numbers comparable to those of Al(III), Cr(III) and Cr(VI) ions, the availability of the cation in multiple valence states, decreasing solubility of the reaction products with increasing pH and their ability to form water of hydration. Prior work<sup>14</sup> describes a non-chromate conversion coating process for aluminum alloys that uses a bath containing potassium manganate that validates this new constraints-based model. The results of this constraintsbased modeling approach are applicable in identifying appropriate chemicals suitable for paint chemistries as well.

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### Metallization/Planarization

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