

Molybdates: An Alternative to Hexavalent Chromates in Corrosion Prevention and Control

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Introduction

Hexavalent chromates have been the preferred corrosion inhibitor in military systems for years. Chromate conversion coatings are specified in MIL-STD-808, "*Finishes, Materials and Processes for Corrosion Prevention and Control in Support Equipment*", for aluminum, magnesium, and plated steel. A number of primers are formulated with zinc or strontium chromate. Passivation treatments for stainless steels frequently specify chromic acid. Some anodic coatings specify baths containing chromic and sulfuric acid and a post treatment or rinse with aqueous sodium dichromate. Even water-based primers formulated for volatile organic compound (VOC) compliance in such areas as southern California contain chromate-based corrosion inhibitors. Chromates are decreasing in industrial use, however, as concerns about their environmental risks and toxicity increase. One pollution prevention approach is to substitute analogs of chromates in similar applications. Molybdate is one such analog of lower toxicity.

Federal Environmental Regulations

A number of environmental regulations now control hexavalent chromate.

- Toxic Substances Control Act (TSCA). Under TSCA, the Environmental Protection Agency (EPA) must be notified 90 days prior to manufacture. EPA may restrict or prohibit manufacture where there is unreasonable risk to the environment. EPA also has the authority to require testing for health or environmental effects. No current regulation specifies molybdate.
- Resource Conservation and Recovery Act (RCRA). RCRA regulates the treatment, storage, transportation, and disposal of hazardous waste (HW). The EPA HW number for hexavalent chromium is D007. Under RCRA molybdenum compounds are not listed.
- Clean Air Act Amendments of 1990 (CAAA90). Currently, there are 189 hazardous air pollutants (HAP) listed in section 112 of CAAA90, including hexavalent chromium. National environmental standards will be promulgated in 1996 for industries using these HAPs. Molybdenum compounds are not listed in section 112.
- Superfund Amendments and Reauthorization Act (SARA) Title III. Under SARA Title III, the Emergency Planning and Community Right-to-know Act (EPCRA), chromium compounds are reportable under section 313. Of the molybdenum compounds, currently only molybdenum trioxide is reportable. No current regulation specifies molybdates.

Occupational Safety and Health

The Occupational Safety and Health Administration (OSHA) sets a ceiling or time weighted average permissible exposure limit (PEL) for many compounds found in the workplace. The PEL

for all chromates (as CrO_3) is currently set at 100 mg/m^3 . The molybdate PEL is set at 5 mg/m^3 for water soluble compounds and 10 mg/m^3 for water insoluble. By comparison, the PEL for respirable nuisance dust is 5 mg/m^3 . Further, the American Conference of Government Industrial Hygienists (ACGIH) has recommended a threshold limit value (TLV) of $0.5 \text{ micrograms/m}^3$ for all chromates. In determining PELs, OSHA considers the TLVs established by ACGIH. OSHA has indicated that a new rule for chromates could be promulgated as early as first quarter 1996. The PEL will probably be in the range of $0.5 - 5.0 \text{ micrograms/m}^3$. If this new rule is adopted, companies using chromates could incur significant costs protecting their workers from chromate dust and fumes.

Discussion

The molybdate anion was described as a corrosion inhibitor as early as 1939 in two patents for alcohol-based antifreezes.¹ Since then, the application of molybdates has been studied and greatly expanded. However, molybdates have not been used as extensively as chromate-based corrosion inhibitors partly because molybdate is a weaker oxidizing agent than chromate. In general, higher concentrations of molybdate are required to achieve the same results. The higher cost of molybdate has also tended to limit its use to closed systems such cooling waters. Also, molybdate is not as effective as chromate when used alone which, in the past, limited its use in ferrous applications.

Steel

Molybdate is an anodic inhibitor. Scanning electron microscope (SEM) microprobe studies of mild steel coupons pitted in chloride solution showed molybdate migration to the center of the pit. Very little molybdenum was found outside the pit. This precipitation of molybdate in the most active area of the pit can lead to inhibition of the pitting process under the right conditions. One possible mechanism for this precipitation is that the molybdate ions adsorb on the surface of the iron and form a complex with the ferrous (Fe^{+2}) ions. This complex is not stable, but in the presence of dissolved oxygen the ferrous ions oxidize to ferric (Fe^{+3}) ions which form an insoluble protective barrier of ferric molybdate.² This insolubility extends over a fairly wide range of pH ($5.5 - 8.5$) and seems to be relatively insensitive to temperature. This mechanism also helps explain why molybdate (even at high concentrations) requires the presence of an oxidizing agent to be effective in corrosion protection of steels.

Further evidence for the anodic pitting protection behavior of molybdates is the synergistic corrosion protection afforded by combining molybdates with the cathodic inhibitor, zinc. See table 1.

Solution Ratio	Corrosion Rate mpy	Average Pit Depth mm
10mg/L Mo	22	0.083 - 0.085
2 mg/L Zn	17	0.078 - 0.080
10 mg/L Mo 2 mg/ L Zn	9	0.039 - 0.041

Table 1. Corrosion rates for zinc and molybdate treatments on mild steel. Source: Reference 3

hexavalent chromate has been attributed to its tendency to form trivalent species which are incorporated into a passive film. A similar effect (reduction of Mo(VI) to Mo(IV)) explains the enhanced passivity of molybdate films. The formation of molybdic acid at anodic sites would also tend to precipitate insoluble polymolybdates thus forming a barrier to further anodic dissolution. Other research on molybdate films formed on 304 has indicated a greater stability if the film is formed in the lower transpassive region. The films were observed to be resistant to chloride and acid media. Researchers credited the corrosion resistance to an increase in film thickness, increase in Fe^{+3}/Fe^{+2} , and the presence of molybdenum in the film.

Aluminum

Aluminum, particularly those alloys from the 2000 and 7000 series, are subject to attack from a variety of species including chloride (pitting corrosion) and many aqueous solutions (general corrosion) since its protective oxide layer is soluble in many acids and bases. Chromate conversion coatings have been used for years in the protection of aluminum because of their excellent corrosion resistance and stability of a three dimensional film. In conversion coating of aluminum, molybdates have been observed to form thicker films than chromates. However, this film is not as robust since it forms primarily by adsorption rather than incorporation into the surface film lattice as chromates do. Electrochemical incorporation of molybdates into an aluminum passive film seems to provide a more adherent film. Evidence for the incorporation of molybdates is provided by X-ray Photon Spectroscopy (XPS) analysis which showed reduction of Mo(VI) to Mo(IV), a mechanism analogous to reduction of hexavalent chromate. This passivity remained even after vigorous rinsing and drying of samples.

Titanium

Titanium has been alloyed with molybdenum to improve its corrosion resistance in nonoxidizing acids. This beneficial effect is attributed to an enrichment of molybdenum in the passive layer. The role of molybdate ions in passivation of titanium in deaerated, boiling 1 N sulfuric acid was investigated through a combination of measurements. Titanium shows a rapid activation and high corrosion rate when immersed in deaerated, boiling 1 N sulfuric acid. Upon addition of small amounts of molybdate (0.003M, 0.015M, and 0.03M), the corrosion rate was seen to decrease. Similarly, the addition of increasing amounts of molybdate (0.004M, 0.02M, and 0.04M) over time to a solution of 1N sulfuric acid caused rapid passivation of the Ti electrode. Titanium and its alloys exhibit a natural oxide, TiO_2 , which gives it excellent corrosion resistance in most media. The beneficial surface oxide film forms spontaneously and instantly when fresh metal is exposed to air and/or moisture.¹⁵ The rapid corrosion of Ti prior to addition of molybdate observed in this experiment indicates that this surface oxide was dissolved in the deaerated sulfuric acid solution. The subsequent passivation film formed upon the addition of molybdate was characterized. This adherent, acid resistant film was examined by Auger and ion scattering spectroscopy. Mo and Ti were found as well as Na^+ . The presence of Na^+ indicates that the molybdate species was present as an anion rather than as MoO_2 or MoO_3 . Researchers proposed a dual film of sodium molybdates and sodium titanium molybdates.

Molybdates in Paint Pigments

A number of primers and self-priming topcoats have been developed using insoluble molybdates as anticorrosive pigments. Federal specification TT-P-645B was revised to cover a zinc molybdate based alkyd primer. It replaces TT-P-645A which specified zinc chromate as the corrosion inhibitor. Sherwin-Williams Chemicals conducted an accelerated corrosion test of the two primers. Traditionally salt spray testing has been the standard for laboratory testing of coatings. But a number of other factors contribute to the degradation of a protective coating and the resultant corrosion. Frequently, these variables are cyclic in nature such as time of wetness/dryness and weathering. Two test methods more effectively duplicate the cyclic nature of these environmental variables.

- Prohesion Test. A cyclic wet/dry salt spray procedure using dilute ammonium sulfate (1 hour salt spray at ambient temperature and 1 hour dry-off at 35° C)
- Corrosion/Weathering. Prohesion test with UV/condensation cycles. Panels are cycled at one week intervals between a 4 hour UV exposure at 340nm/60° C and a 4 hour condensation at 50° C.

All tests were performed on scribed panels of mild steel. The results are summarized in table 2.

Test	Zinc Chromate Primer	Zinc Molybdate Primer
100 Hour Prohesion	Extensive Corrosion in and around Scribe	Mild Corrosion confined to Scribe
336 Hour Corrosion/Weathering	Extensive Corrosion in and around Scribe	Mild Corrosion in and around Scribe
672 Hour Prohesion	Extensive Scribe-line Corrosion with Creepback	Extensive Scribe-line Corrosion with less Creepback
1008 Hour Corrosion/Weathering	Extensive Scribe-line Corrosion with Creepback	Extensive Scribe-line Corrosion with less Creepback

Table 2. Corrosion Tests on Mild Steel Panels with Zinc Chromate and Zinc Molybdate Primers.

Source: Reference 13

The zinc molybdate based primer was the more effective corrosion inhibitor in this series of tests. At the time of these tests, these were not accepted test methods by the American Society for Testing and Materials (ASTM) or the Steel Structures Painting Council (SSPC). Further, the standard for comparison of different corrosion inhibiting materials is still ASTM B117, *Standard Test Method of Salt Spray (Fog) Testing*, on many programs. However, prohesion and corrosion/weathering have since been incorporated into the following test methods.

- Prohesion. ASTM G85, *“Standard Practice for Modified Salt Spray (Fog) Testing”*
- Corrosion/Weathering. ASTM D4587, *“Standard Practice for Conducting Tests on Paint and Related Coatings and Materials Using a Fluorescent UV- Condensation Light- and Water- Exposure Apparatus”*

In 1985 the U. S. Navy launched a program to remove lead and chromate from its corrosion inhibiting paints.¹⁴ A corollary goal was to develop one-coat (self-priming) systems which would

have the coverage, adhesion, and corrosion protection of a primer and the aesthetics and weather resistance of a topcoat. These direct-to-metal (DTM) coatings would also save time and materials and reduce volatile organic compound (VOC) emissions.

The corrosion inhibiting compounds in each of these DTM coatings consists of zinc molybdate and other pigments including organic zinc and phosphate. This is similar to the approach used for closed loop cooling systems where combinations of water-soluble molybdate and zinc or phosphates were used.^{3,4} These DTM coatings take advantage of this synergy. The pigment combination used in each of these coatings consists of the following ratio.

- 2 parts zinc molybdate
- 1 part zinc phosphate compound
- 0.1 part organic zinc

Under Navy patents, a number of DTM coatings have been formulated based on this pigment combination and a variety of resins including lustreless polyurethane, epoxy-polyamide, alkyd, and acrylic.

A number of molybdate-based primers are qualified to military or federal specifications or are pending qualification. All are chromate-free.

- MIL-P-28577A, "*Primer, Water-Borne, Acrylic or Modified Acrylic for Metal Surfaces*"
- MIL-P-85658, "*Paint, Water Displacing*"
- TT-P-645B, "*Primer, Paint, Zinc Molybdate, Alkyd Type*"
- TT-P-2756, "*Polyurethane Coating; Self-Priming Topcoat, Low Volatile Organic Compound (VOC)*"

In addition, two primer specifications covering epoxy resins now permit non-chromate corrosion inhibitors. These are MIL-P-85582, "*Primer, Water-Borne, Epoxy*" and MIL-P-23377, "*Primer Coatings: Epoxy, High Solids*".

Conclusions

Environmental and health and safety regulations regarding chromates are creating the need for less toxic alternatives which still meet system requirements for corrosion prevention and control. Molybdates are an alternative which offer low toxicity. Other compounds such as phosphates, zinc or dissolved oxygen used in conjunction with molybdate enhance its passivating effect on mild steel cooling structures. Researchers have produced passive films from solutions of sodium molybdate on stainless steel, aluminum, and titanium.

The enhanced corrosion resistance of molybdates when used with other corrosion inhibiting compounds has been incorporated into paint pigments. A number of water insoluble molybdates have been formulated with zinc phosphates and organic zinc in a variety of resins. At this time there are at least four military or federal specifications covering molybdate based primers. All are chromate free.

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