ARL-TR-9931 • JULY 2024

Non-Chrome Posttreatment for Zinc ASTM B633

by Lindsey Blohm, Thomas Braswell, and John Kelley

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ARL-TR-9931 ● JULY 2024

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DEVCOM Army Research Laboratory

REPORT DOCUMENTATION PAGE

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED START DATE	3. DATES COVERED END DATE
July 2024	Technical Report	10/02/2022	1/01/2024

4. TITLE AND SUBTITLE
Non-Chrome Posttreatment for Zinc ASTM B633

5a. CONTRACT NUMBER	5b. GRANT NUMBER	5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER	5e. TASK NUMBER	5f. WORK UNIT NUMBER
TMR 22-02		

6. AUTHOR(S)
Lindsey Blohm, Thomas Braswell, and John Kelley

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
DEVCOM Army Research Laboratory ATTN: FCDD-RLA-MC Aberdeen Proving Ground, MD 21005	ARL-TR-9931

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
DEVCOM Safer Alternatives for Readiness (SAFR) Program Office		

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
ORCID: Lindsey Blohm, 0000-0003-1041-2511

14. ABSTRACT
There are currently no qualified non-chrome posttreatments for zinc (Zn) plating for US Army applications, necessitating the investigation of novel non-chrome systems for passivation of Zn plating and commercially available alternatives to validate and demonstrate on Zn plating for ground vehicle and aviation platforms. Following a memo from the Assistant Secretary of the Army, it is a high priority to find a qualified chrome alternative. Chromic acid, a known human carcinogen, is targeted for replacement as it is undergoing increased regulatory restrictions. Building on previous work performed by the US Army Combat Capabilities Development Command (DEVCOM) Army Research Laboratory (ARL) and US Army Aviation and Missile Command G-4, ARL will perform a battery of testing on industrial sealers and two novel technologies, comparing them with hexavalent chromium and trivalent chromium control systems. Performance objectives with acceptance criteria have been developed. Testing includes adhesion, corrosion resistance, and electrochemical behavior.

15. SUBJECT TERMS
Sciences of Extreme Materials, chromate, posttreatment, ASTM B633, molybdate, cerium, neutral salt spray

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	C. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UU	20

19a. NAME OF RESPONSIBLE PERSON	19b. PHONE NUMBER *(Include area code)*
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STANDARD FORM 298 (REV. 5/2020)
Prescribed by ANSI Std. Z39.18

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1. Introduction

There is increasing pressure for Department of Defense maintenance facilities to reduce or eliminate the use of hexavalent chromium (Cr[VI]). Cr(VI) is listed as a known human carcinogen by the International Agency for Research on Cancer and the American Conference of Governmental Industrial Hygienists. Chromium (Cr) and its inorganic compounds are also coming under increasingly restrictive regulation. The urgency of Cr elimination is emphasized by a memorandum from the Under Secretary of Defense for Acquisition, Technology and Logistics titled *Minimizing the Use of Hexavalent Chromium (Cr^{6+})*, which states that the need to eliminate Cr(VI) is an "extraordinary situation."[1] Additionally, the Assistant Secretary of the Army of Acquisition Logistics and Technology issued a memorandum to establish policy to eliminate the use of Cr(VI) in Army weapon systems.[2]

Per requirements of the memorandum, all surface pretreatments (conversion coatings and wash primers) need to eliminate Cr(VI) from all new weapon systems by 20 September 2024 and existing system modifications must be hexavalent chromate free.[2] Additionally, the Army Environmental Requirements and Technology Assessments requirement PP-2-02-06 titled *Toxic Metal Reduction in Surface Finishing of Army Weapon Systems* has been established.[3] This report addresses that requirement by aiming to eliminate Cr(VI) in posttreatment sealers for electroplated zinc (Zn).

There are currently no Cr(VI)-free posttreatment sealers for Zn plating approved by the American Society for Testing and Materials (ASTM) B633[4] for use on ground vehicles and aviation platforms. The purpose of this report is to develop and formulate a non-chrome posttreatment process to meet the requirements of ASTM B633. Many of the non-chrome sealers tested are commercial off-the-shelf products formulated for ferrous and nonferrous metals but have not been tested specifically on electroplated Zn. Additionally, two process modifications were designed using molybdenum (Mo) and cerium (Ce) that have shown promise in literature.

1.1 Molybdate Rinse

There is a breadth of research demonstrating high performance of phosphate-based systems with the added incorporation of molybdate to protect Zn substrates.[5–14] Some studies have shown materials that yield a strong corrosion performance with only with pH adjustments and small amounts of H_3PO_4 or $NaH_2PO_3 \cdot 2H_2O$.[15,16] There was some work with inhibition efficiency (60%–92%) benefits demonstrated for molybdate-only systems, with the exclusion of phosphate.[6,8,14,17,18] With these benefits, the literature demonstrates molybdate is a promising alternative, especially with the combination of a silane seal. With a silane seal, it has been shown that molybdate rinses can perform closely to that of a Cr pretreatment.[15,16] If the pH is adjusted to 5 for corrosion resistance, the Mo-rich coatings will form at a threshold below which detrimental cracking occurs.[9–11,19] When it comes to salt selection, the oxidation states of Mo providing the best inhibition efficiencies are Mo(V) and Mo(VI), while Mo(IV) has lower inhibition efficiency.[6,10]

1.2 Cerium Rinse

A stable coating of Ce^{4+} and Ce^{3+} complexes (e.g., cerium phosphate powder [$CePO_4 \cdot H_2O$] and cerium(III) nitrate [$Ce(NO_3)_3$]) make Ce-based passivating layers.[20] These passivating layers, from 2 pH upwards, are found to be insoluble. $Ce(NO_3)_3$ treatments form an effective barrier layer, resulting in retardation of the cathodic half-cell reaction and hence inhibiting oxygen transport to the metal substrate. It has been shown that a corrosion inhibition efficiency of 89% with a Ce-only treatment (with a synergistic bilayer structure identified) improves to 98.7% with an additional silane seal process.[21]

2. Experimental Procedure

2.1 Materials

Panels of American Iron and Steel Institute 4130 alloy steel (4 × 6 × 0.032 inches) for electroplating were prepared in accordance with ASTM B633[4] service condition 4. Baseline panels were sealed with trivalent chromium [Cr(III)] and Cr(VI) sealers, as per the matrix.

2.2 Sealer Application

Sealers were immersion applied in ambient laboratory conditions. A list of sealers applied provided in Table 1. Panel cleanliness was ensured by checking for a water-break “free” surface prior to sealer application. Processes and dwell times for each sealer varied by manufacturer, and each process was followed per technical data sheet and manufacturer guidance. All panels were forced-air dried using laboratory air to avoid puddling and/or flash rust. Dry panels were wrapped and sealed in paper impregnated with volatile corrosion inhibitor until testing was performed. MIL-PRF-23377K epoxy primer was applied in accordance with MIL-DTL-53072G.[22,23] Figure 1 shows a representative panel following sealer application prior to testing.

Table 1 Sealer matrix

Sealers	Supplier	Formulation
Bonderite M-NT 5700	Henkel	Fluorides
Zircobond (4200)	PPG	H_2ZrF_6
S-Bond S20	PPG	Silane
Molybdate rinse + S-Bond S20	Sigma Aldrich + PPG	Literature suggested process
Cerium rinse + S-Bond S20	Sigma Aldrich + PPG	
580 NC	SurTec Intl	Fluorides
555	SurTec Intl	Synthetic polymers, nonionic surfactants
Tri-Chrome	Lanthane Yellow 334/335	Control systems
Hex-Chrome	Enthox EZY	

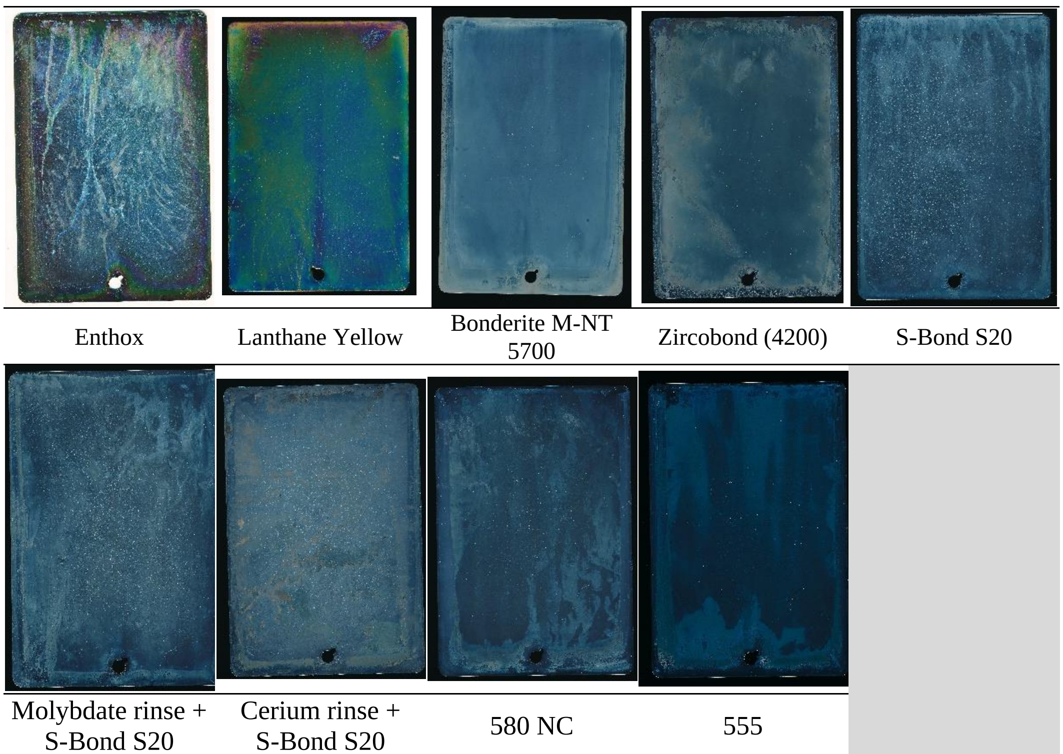

Fig. 1 Panels following sealer application prior to testing

2.2.1 Molybdate Rinse Application

A bath of 10 g/L sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) (adjusted to pH 5 using drop-wise additions of $Na_2MoO_4 \cdot 2H_2O$) was used at 60 °C. Panels were immersed in the bath for 40 s followed by air-drying. Subsequently, panels were sealed with S-Bond S20 per supplier instructions.

2.2.2 Cerium Rinse Application

A bath of 20 g/L $Ce(NO_3)$ was made and used. Panels were immersed in the bath for 30 min followed by air-drying. Subsequently, panels were sealed with S-Bond S20 per supplier instructions.

3. Test Methodologies

3.1 Accelerated Corrosion: Neutral Salt Fog (ASTM B117)

The test coupons of Zn-electroplated aluminum were placed in neutral salt fog using an Auto Technology Standard Salt Fog Chamber (Model 22; Fig. 2) in accordance with ASTM B117.[24] Panels were fixed in polypropylene trays with the primary surface facing outwards at an angle no more than 15º from the vertical. Test panels were evaluated using criteria based upon the sealed substrate. Electroplated Zn coupons were made in sets of five, measured 3 × 6 inches in size, and exposed for 12 h. Cr(VI) and Cr(III) sealed baseline panels were tested for 96 h. The appearance of any corrosion products emerging from the base metal or plating was considered failure. Upon completion of testing, the panels were rinsed in deionized water, air-dried, and scanned on a flatbed scanner (Cannon CanoScan 9000F Mark II). A representative panel from each set was then cleaned in 0.25% HNO_3 to remove all corrosion product and scanned on the flatbed scanner.

Fig. 2 Neutral salt fog corrosion chambers used for testing

3.2 Paint Adhesion: Wet Tape Adhesion Test (FED-STD-141D/ ASTM D3359)

Test coupons of Zn-electroplated aluminum and chrome baselines, in sets of three, were primed with MIL-PRF-23377K[23] in accordance with MIL-DTL-53072G[22] and allowed to fully cure before undergoing adhesion testing. Wet tape adhesion testing was performed in accordance with FED-STD-141D Method 6301[25] and rated according to ASTM D3359 Method A.[26] The coupons were then visually assessed for damage in accordance with ASTM D3359.[26]

3.3 Paint Adhesion: Dry Tape Adhesion Test (ASTM D3359)

Test coupons of Zn-electroplated aluminum and chrome baselines, in sets of three, were primed with MIL-PRF-23377K[23] in accordance with MIL-DTL-53072G[22] and allowed to fully cure before undergoing adhesion testing. Dry tape adhesion testing was performed and rated according to ASTM D3359 Method B.[26]

3.4 Performance Objectives

Working with the US Army Aviation and Missile Command G-4 and relevant specifications, performance objectives were established for the sealed legacy coatings. A full overview of the performance objectives is given in Table 2.

Table 2 Performance objectives

Material	Test methods	Data requirements	Performance objectives
ASTM B633 Zn plating	Accelerated corrosion	ASTM B117 ASTM B633	No corrosion products acceptable
	Paint adhesion	ASTM D3359 Method A, FED-STD-141D Method 6301	No intercoat separation, adhesion rating ≥ 4A
		ASTM D3359 Method B	No intercoat separation, adhesion rating ≥ 4B

4. Results

4.1 Accelerated Corrosion: Neutral Salt Fog (ASTM B117)

Representative test panels following neutral salt fog (ASTM B117[24]) are shown in Fig. 3. It is evident that only the baselines, Enthox and Lanthane Yellow (Hex-Chrome and Tri-Chrome, respectively), met the performance objective of showing no corrosion products. The remainder of the panels had significant corrosion products although very different morphologies. The rest of the panel images are shown in the Appendix. A representative panel was cleaned with 5% HNO_3 and is shown in Fig. 4. As evident from Fig. 3, there are significantly different corrosion morphologies per posttreatment test; however, this was not investigated further due to all products not meeting performance objectives.

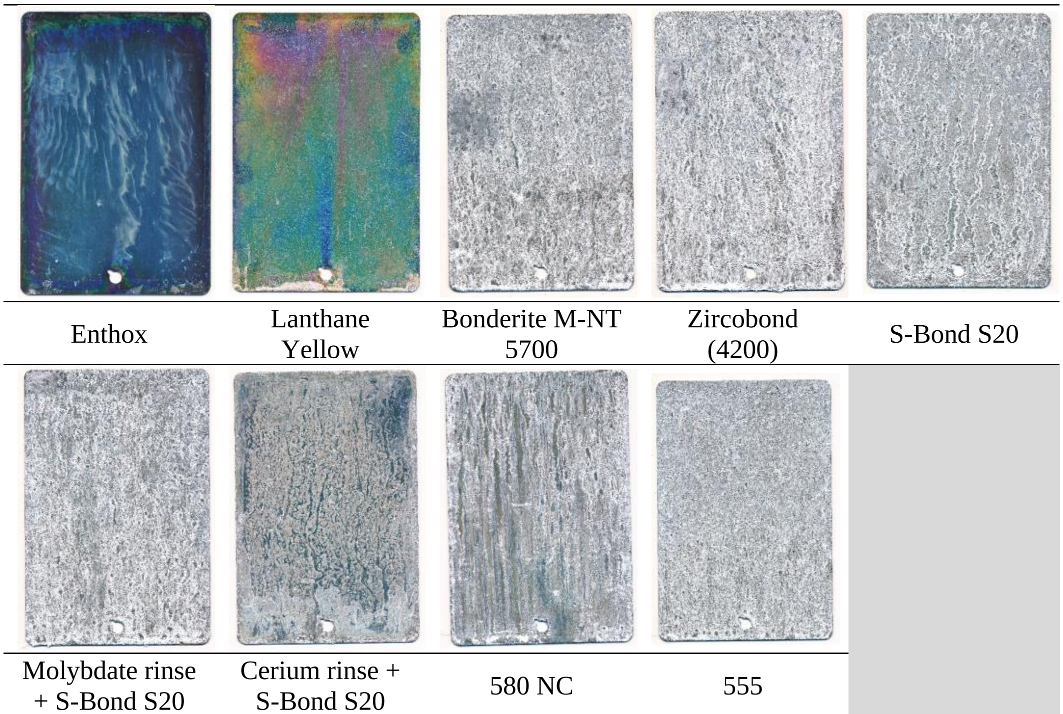

Fig. 3 Panels following ASTM B117

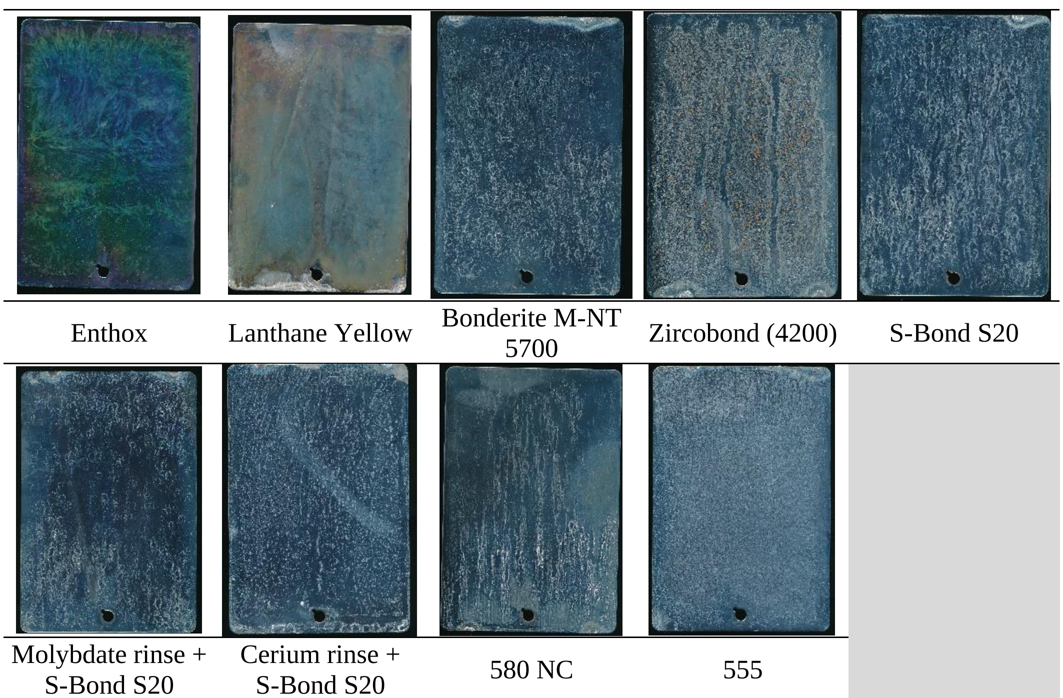

Fig. 4 Panels following B117, cleaned with 5% HNO_3

4.2 Paint Adhesion (ASTM D3359)

Wet and dry tape adhesion results, per Sections 3.2 and 3.3, are displayed in Fig. 5. Dry adhesion results are in black and wet adhesion results are in yellow. The requirement is denoted by a horizontal bar at an adhesion rating of four. As shown, all panels met the performance criteria for wet and dry adhesion except for the baselines, Enthox and Lanthane Yellow (Hex-Chrome and Tri-Chrome, respectively).

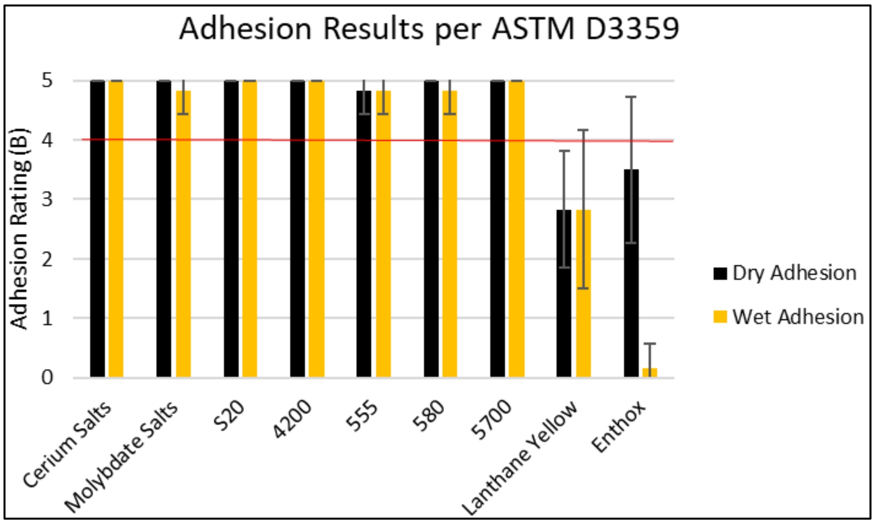

Fig. 5 Adhesion results per ASTM D3359 (wet and dry)

5. Summary and Conclusions

A non-chrome posttreatment sealer is sought for Zn plating conforming to ASTM B633[4] for use on ground vehicle and aviation systems. Seven non-chrome posttreatments (two novel and five commercially available) were tested against two chrome-containing baselines. Of the seven non-chrome posttreatments tested, none were able to meet accelerated corrosion, however all met the paint adhesion requirement for MIL-DTL-53072G.[22] Interestingly, the non-chrome posttreatments performed better than the chrome-containing baselines for paint adhesion. Nevertheless, the poor corrosion results prevent any of the non-chrome products from being approved and recommended for use on military systems. Although the Lanthane Yellow and the Enthox met neutral salt fog requirements (ASTM B117), they are not recommended for use under military coatings because of the poor paint adhesion. The non-chrome posttreatment systems that perform well in paint adhesion, although not performing well uncoated in salt spray, may perform well as part of a complete coating system. However, in this test, none of the non-chrome candidates tested were able to meet the performance objectives for unpainted corrosion per ASTM B633 and thus are not selected for demonstration.

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Appendix. Panels Following Neutral Salt Spray (ASTM B117)

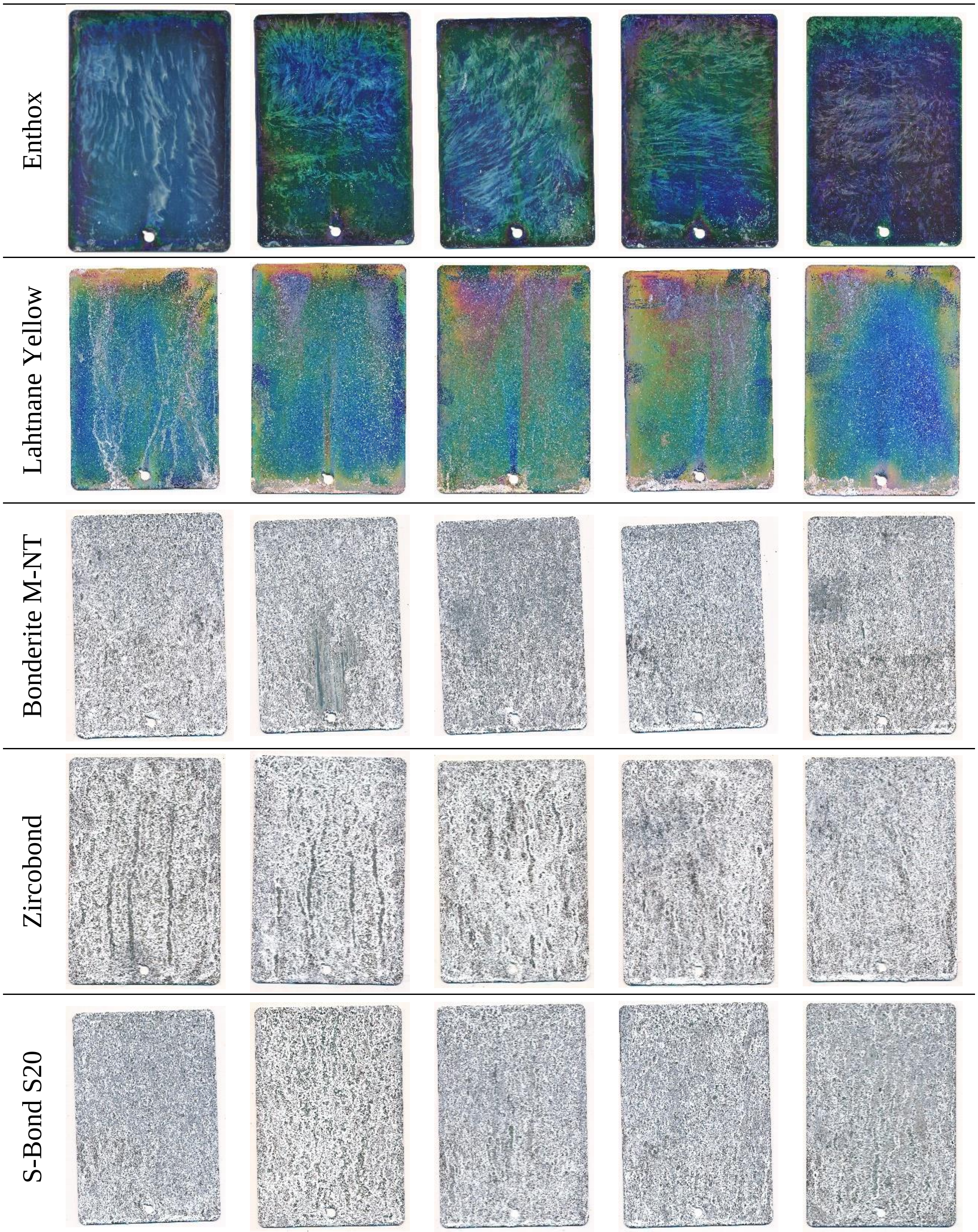

Fig. A-1 Panels following neutral salt spray (ASTM B117)

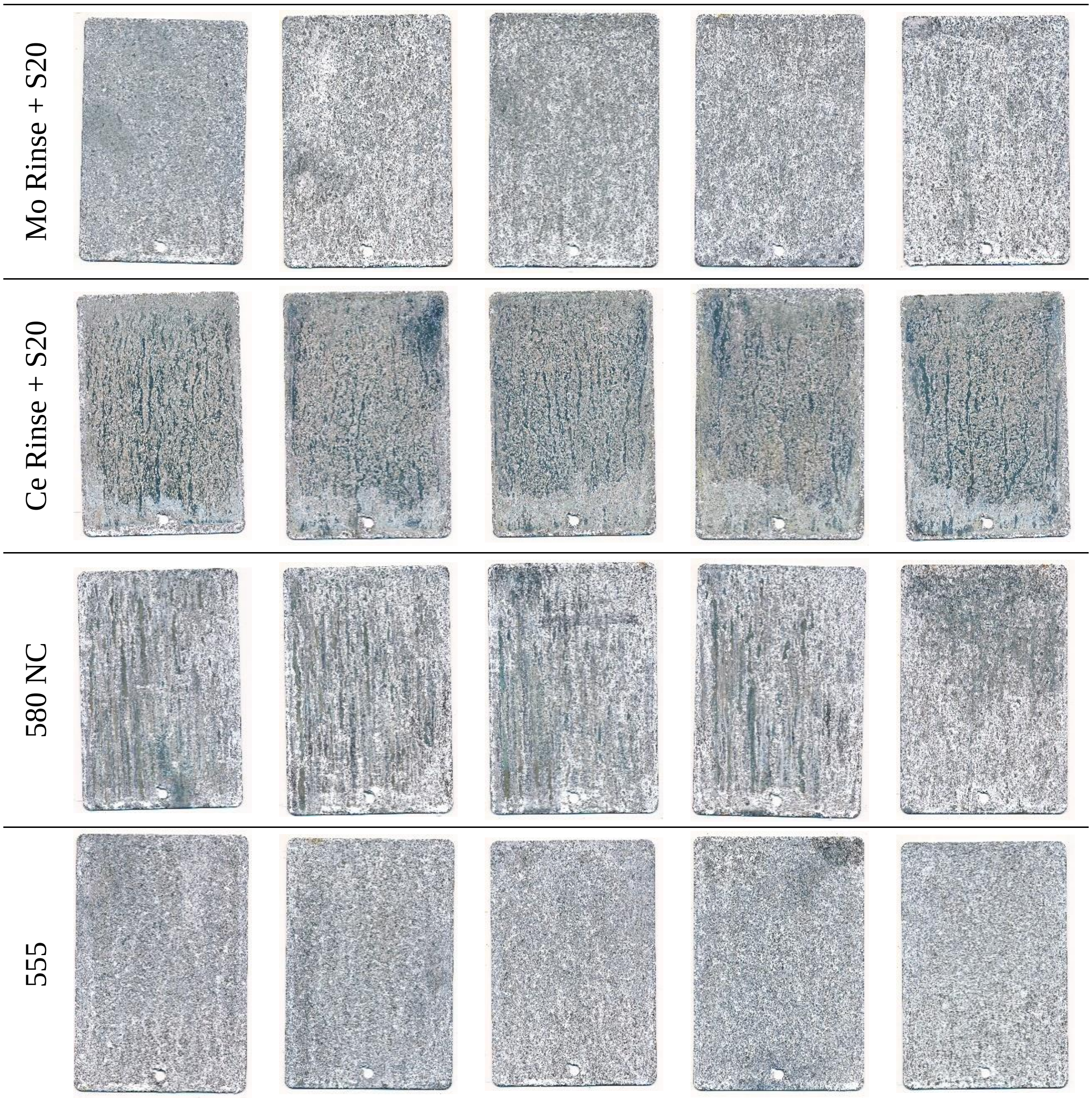

Fig. A-1 Panels following neutral salt spray (ASTM B117) (continued)

List of Symbols, Abbreviations, and Acronyms

ASTM	American Society for Testing and Materials
Ce	cerium
$Ce(NO_3)_3$	cerium(III) nitrate
Cr	chromium
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
HNO_3	nitric acid
Mo	molybdenum
$Na_2MoO_4 \cdot 2H_2O$	sodium molybdate dihydrate
Zn	zinc