Army Research Laboratory

Accelerated Corrosion Results for Zinc/Nickel-Plated Automotive Parts Posttreated With Trivalent Chromate Rinse

by Chris E. Miller, Brian E. Placzankis, and I. Carl Handsy

ARL-TR-5361 September 2010

NOTICES

Disclaimers

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

ARL-TR-5361 **September 2010**

Accelerated Corrosion Results for Zinc/Nickel-Plated Automotive Parts Posttreated With Trivalent Chromate Rinse

Chris E. Miller and Brian E. Placzankis
Weapons and Materials Research Directorate, ARL

I. Carl Handsy
U.S. Army TACOM-TARDEC

REPORT DOCUMENTATION PAGE						*Form Approved OMB No. 0704-0188*
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**						
1. REPORT DATE *(DD-MM-YYYY)* September 2010		**2. REPORT TYPE** Final				**3. DATES COVERED (From - To)** January 2006–May 2007
4. TITLE AND SUBTITLE Accelerated Corrosion Results for Zinc/Nickel-Plated Automotive Parts Posttreated With Trivalent Chromate Rinse						**5a. CONTRACT NUMBER**
						5b. GRANT NUMBER
						5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Chris E. Miller, Brian E. Placzankis, and I. Carl Handsy*						**5d. PROJECT NUMBER**
						5e. TASK NUMBER
						5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-WMM-C Aberdeen Proving Ground, MD 21005-5069						**8. PERFORMING ORGANIZATION REPORT NUMBER** ARL-TR-5361
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)						**10. SPONSOR/MONITOR'S ACRONYM(S)**
						11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.						
13. SUPPLEMENTARY NOTES *U.S. Army TACOM-TARDEC, AMSTA-TR-E1 MEPS1267, Warren, MI 48397						
14. ABSTRACT Electroplated zinc/nickel components posttreated with trivalent chromate rinse were randomly selected from production lines of a German automotive manufacturer. Both rack- and barrel-plating processes were represented among the samples. These components were then exposed to one of two accelerated corrosion environments, ASTM B 117 (Standard Method of Salt Spray [Fog] Testing, *Annu. Book ASTM Stand.*, **1997**) or GM 9540 (*Accelerated Corrosion Test*; General Motors Engineering Standards, 1997). Performance under accelerated corrosion conditions far exceeded expectations suggesting viable military use with little or no additional capital expenditure.						
15. SUBJECT TERMS zinc-nickel, corrosion, hexavalent chromate alternatives, chromium, electroplating, posttreatments, ASTM B 117, GM 9540, TCP						
16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**		**19a. NAME OF RESPONSIBLE PERSON** Chris E. Miller
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	UU	24		**19b. TELEPHONE NUMBER** (*Include area code*) 410-306-0849

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures

Acknowledgments

The authors would like to thank Joerg Hohnloser of Gaertner-Klinger for supplying the parts used in these exposures.

INTENTIONALLY LEFT BLANK.

1. Procedure

Parts that were rack or barrel plated with 0.2–0.5 mil zinc/nickel, zinc, or zinc/iron and posttreated with a version of tri-chromate process (TCP—MIL-DTL-5541,[1] Type III) were randomly taken from the assembly line floor of an automotive plant in Germany. These 17 different parts, ranging from brackets to fluid lines and threaded couplers, generally remain unpainted on an automobile. One sample of each part was retained as a virgin control sample, with the remaining parts being divided into two groups, where each group was exposed to a specific accelerated chamber corrosion testing protocol.

The first group was exposed as-received to standard 5% NaCl salt fog in a Harshaw Model 22 chamber following procedures described in ASTM B 117.[2] Samples were examined periodically for appearance of red rust on any surface. Once rust appeared, samples were removed and the exposure time noted.

A CCT-NC-20 cyclic corrosion test chamber from Autotechnology was used to perform the GM 9540[3] test on the second group of parts. GM 9540 consists of the repetition of 18 separate stages, including salt (1.25% solutes by mass: 0.9% NaCl, 0.1% $CaCl_2$, 0.25% $NaHCO_3$) water mist, humidity, drying, ambient, and heated drying. The environmental conditions and duration of each stage for one complete GM 9540 cycle are given in table 1. Sample components were not scribed prior to exposure. Periodic inspections of the components were made. The criterion for termination was the appearance of red rust. Terminated components were removed, with the length of exposure noted. In addition, standard plain carbon steel calibration coupons described in GM 9540 and supplied by GM were initially weighed, exposed to the same accelerated corrosion conditions as the test components, and subsequently monitored for mass loss at intervals set by the specification. Mass losses measured for steel coupons used for this test were within parameters stated in the GM specification.

2. Results

The length of exposure for each specimen type in that lot and the average for all specimen types are presented in table 2. Barrel-plated parts were part nos. 2, 3, 6, 10, 11, and 12.

[1]MIL-DTL-5541. *Chemical Conversion Coatings on Aluminum and Aluminum Alloys* **2007**.
[2]ASTM B 117. Standard Method of Salt Spray (Fog) Testing. *Annu. Book ASTM Stand*. **1997**.
[3]GM 9540. Accelerated Corrosion Test; *General Motors Engineering Standards* **1997**.

Table 1. GM 9540 cyclic corrosion test details.

Interval	Description	Interval time (min)	Temperature (±3 °C)
1	Ramp to salt mist	15	25
2	Salt mist cycle	1	25
3	Dry cycle	15	30
4	Ramp to salt mist	70	25
5	Salt mist cycle	1	25
6	Dry cycle	15	30
7	Ramp to salt mist	70	25
8	Salt mist cycle	1	25
9	Dry cycle	15	30
10	Ramp to salt mist	70	25
11	Salt mist cycle	1	25
12	Dry cycle	15	30
13	Ramp to humidity	15	49
14	Humidity cycle	480	49
15	Ramp to dry	15	60
16	Dry cycle	480	60
17	Ramp to ambient	15	25
18	Ambient cycle	480	25

Table 2. Length of exposure until first rust appeared (number of samples based on availability).

Part No.	ASTM B 117							GM 9540					
	Hours						Average	Cycles					Average
1	10,468	6048	11,856	—	—	—	9457	324	118	—	—	—	221
2	7104	5076	—	—	—	—	6090	475	475	—	—	—	475
3	2752	2752	2928	4536	2352	2752	3012	420	582	582	590	590	553
4	1500	720	720	—	—	—	980	27	94	—	—	—	61
5	5076	5076	—	—	—	—	5076	649	260	—	—	—	455
6	5544	—	—	—	—	—	5544	170	—	—	—	—	170
7	12,624	10,536	12,792	—	—	—	11,984	680	680	—	—	—	680
8	1392	—	—	—	—	—	1392	30	—	—	—	—	30
9	168	304	—	—	—	—	236	8	8	—	—	—	8
10	5026	4536	—	—	—	—	4781	641	632	—	—	—	637
11	9960	9960	9960	—	—	—	9960	171	649	—	—	—	410
12	5076	4536	3392	—	—	—	4335	366	553	—	—	—	460
13	8496	2592	5076	—	—	—	5388	47	44	—	—	—	46
14	5544	—	—	—	—	—	5544	44	—	—	—	—	44
15	720	—	—	—	—	—	720	27	—	—	—	—	27
16	552	552	—	—	—	—	552	27	27	—	—	—	27
17	720	—	—	—	—	—	720	21	—	—	—	—	21

3. Discussion of Results

Steel parts zinc/nickel-plated and posttreated with TCP were tested using the same specification as cadmium-plated parts with a hexavalent chromium seal. For the specification SAE-AMS-QQ-P-416,[4] the minimum acceptable corrosion resistance criterion is that after 96 h of ASTM B 117 exposure, there should be no appearance of white cadmium corrosion products, pitting, or base metal corrosion products. The Metal Finishing Handbook cites examples of zinc-plated parts rack and barrel plated with a hexavalent chromium rinse lasting 400 and 300 h in neutral salt spray.[5] Similarly plated samples post treated with trivalent chromium rinse lasted 450 and 200 h in neutral salt spray, respectively. Since zinc/nickel is generally superior over steel, it is believed that plated parts surviving in excess of 336 h of ASTM B 117 exposure will exhibit "good" performance in the engine compartment of a vehicle. Similarly, parts surviving between 40 and 80 cycles of GM 9540 exposure before first evidence of red corrosion are also considered to have "good" corrosion performance. By both of these criteria, only one of these parts (part 9—a brake line connector with a sliding threaded coupling that had the lowest rating for both protocols) did not have "good" corrosion metrics. As seen in figures 1–3, this part has a complex shape, with some surfaces of the line that could have been shielded during the plating and sealing operations.

Figure 1. Brake line connector prior to exposure.

[4]SAE-AMS-QQ-P-416. *Plating, Cadmium (Electrodeposited)*; Society of Automotive Engineers: Warrendale, PA, October 2004.

[5]Metal Finishing Handbook 6A, *103,* pp 384–384.

Figure 2. Brake line connector following ASTM B 117 exposure.

Figure 3. Brake line connector following eight cycles GM 9540 exposure.

Conversely, there were seven parts that exhibited exceptional corrosion resistance during both accelerated exposure protocols. The best combined rating was for the bushings (part 7) shown in figures 4–6. This part lasted 36× the “good” criterion for ASTM B 117 and 15× the “good” criterion for GM 9540. Other parts that had exceptional performance in both exposures were the bracket (part 11, barrel plated; figure 7), the rocker arms (part 2, barrel plated; figure 8), the

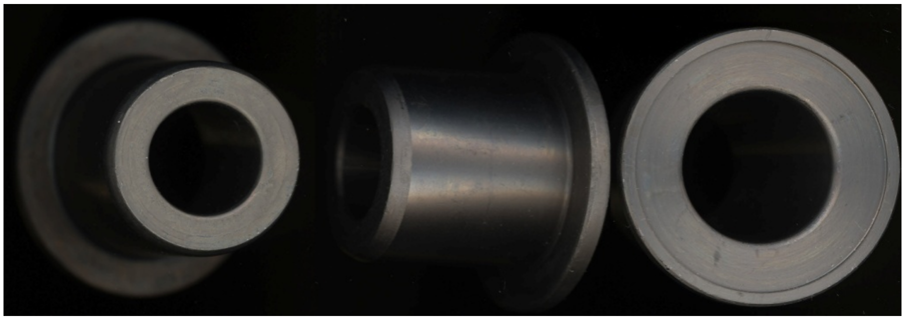


Figure 4. Bushing before exposure.

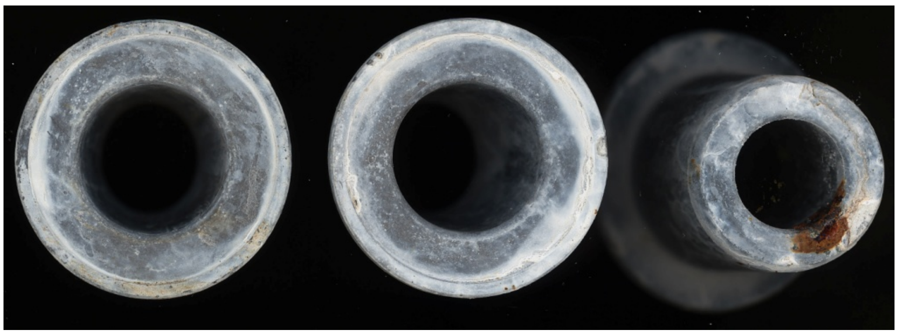


Figure 5. Bushings following 12,792, 12,624, and 10,536 h of ASTM B 117 exposure.

Figure 6. Bushings following 680 cycles of GM 9540 exposure.

Figure 7. Bracket before exposure.

Figure 8. Rocker arms before exposure.

hydraulic fluid diverter (part 5; figure 9), the hex head fluid line caps (part 10, barrel plated; figure 10), the outside threaded hex head fluid cap (part 12, barrel plated; figure 11), and the fluid line part (part 3, barrel plated; in figure 12). All of these parts have relatively simple shapes that provided ample access for the plating solution and the sealer to all surfaces. For interior surfaces, the diameter-to-length ratio was large and the three threaded parts all had coarse threads; so, again, the plating solution and the sealer had ample "throwing power."

Figure 9. Hydraulic fluid diverter before exposure.

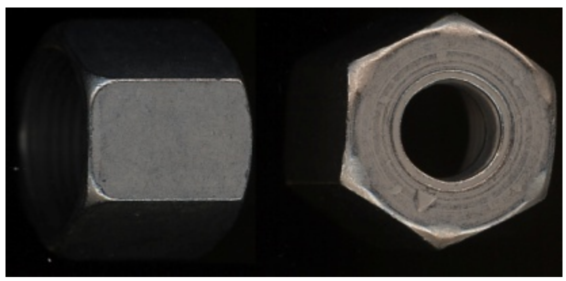


Figure 10. Hex head fluid line cap before exposure.

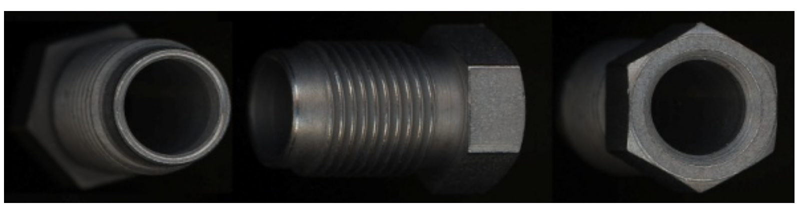


Figure 11. Hex head with outside threaded fluid cap before exposure.

Figure 12. Fluid line part before exposure.

There are three additional categories, based on performance in the two accelerated tests, that the remainder of the parts fell into. The first of these included parts that had superlative performance during ASTM B 117 exposure, whereas the GM 9540 performance was only three or four times the 40 cycle criterion for "good" performance. Both the threaded U-bracket (part 1; figures 13–14) and the Allen-keyed threaded plug (part 6, barrel plated; figures 15a and b) fall into this category. Finer threads on the bracket and a geometry that may retain chamber test fluids may have contributed to their relatively poorer performance in GM 9540.

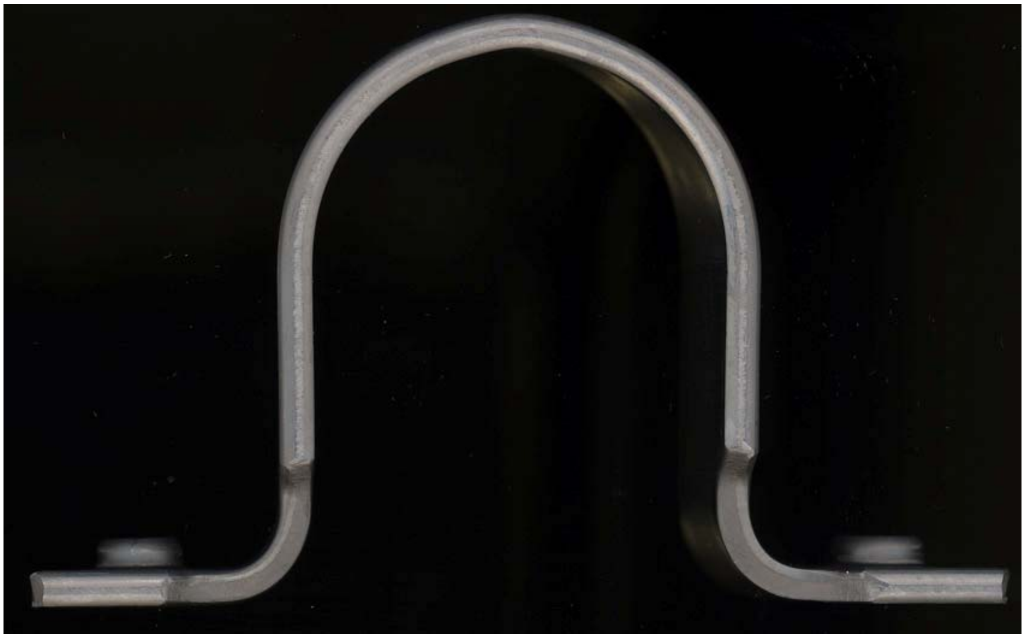


Figure 13. Threaded U-bracket before exposure.

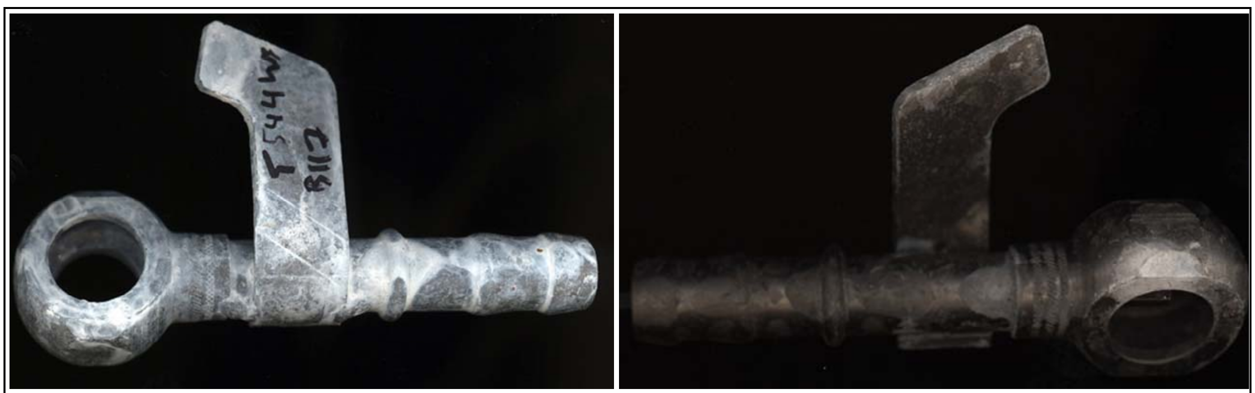
Figure 14. Threaded U-bracket following GM 9540 exposures.

(a) (b)

Figure 15. Threaded plug before and after 170 cycles of GM 9540 exposure.

The next performance category contained those parts that sustained exposures more than three times the required 336 hours of ASTM B 117 exposure, but they had only the requisite 40 cycles of GM 9540 exposure. This group included unidentified component A (part 14; figures 16 and 17), a sleeve (part 13; figures 18 and 19), fluid line (part 8; figures 20 and 21), and an unidentified component B (part 4; figures 22 and 23). In general, these parts had shapes that were more complex, with smaller diameter-to-length ratios, and two that had welds that created crevices. The three parts with a tubular component often had corrosion develop well down the inner diameter of the tube.

Figure 16. Unidentified component A before exposure.



(a) (b)

Figure 17. Unidentified component A following 5544 h of ASTM B 117 and 44 cycles of GM 9540 exposure.

Figure 18. Sleeve before exposure.

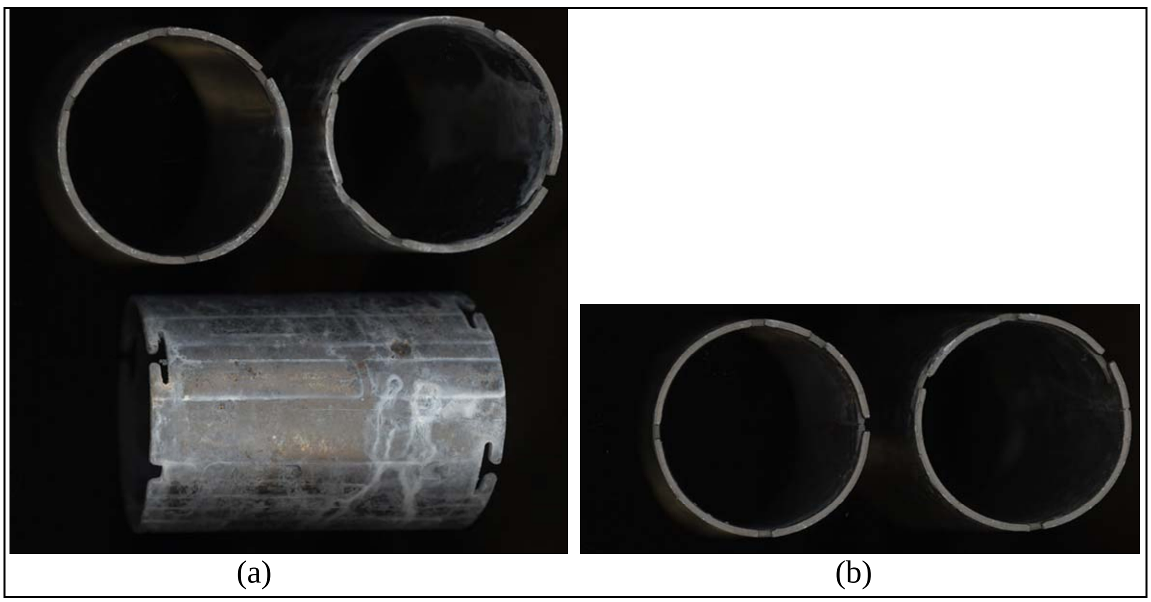


Figure 19. Sleeves following an average of 5388 h of ASTM B 117 exposure and an average of 47 cycles of GM 9540 exposure.

Figure 20. Fluid line before exposure.

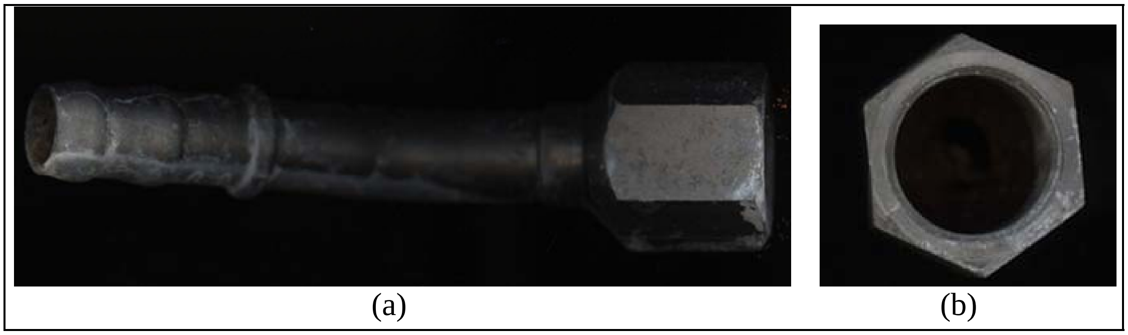


Figure 21. Fluid line following 1392 h of ASTM B 117 and following 30 cycles of GM 9540 exposure.

Figure 22. Unidentified component B before exposure.

Figure 23. Unidentified component B following an average of 980 h of ASTM B 117 exposure and an average of 61 cycles of GM 9540 exposure.

The final category of performance included those parts that merited up to twice the “good” exposure time for ASTM B 117 exposures and were slightly substandard for a “good” GM 9540 performance rating. The three parts in this category were a bracket plated with zinc-iron (part 15; figures 24 and 25), a similarly configured bracket plated with zinc (part 16; figures 26 and 27), and a fluid line (part 17; figures 28 and 29). There does not appear to be a significant difference between the performances of the two brackets in this group despite the different plating compositions. The fluid line in this group was geometrically similar to the one in the previous group, with the main difference being that the inner diameter of this fluid line was half that of part 8. This contributed to the inferior performance during the ASTM B 117 exposure.

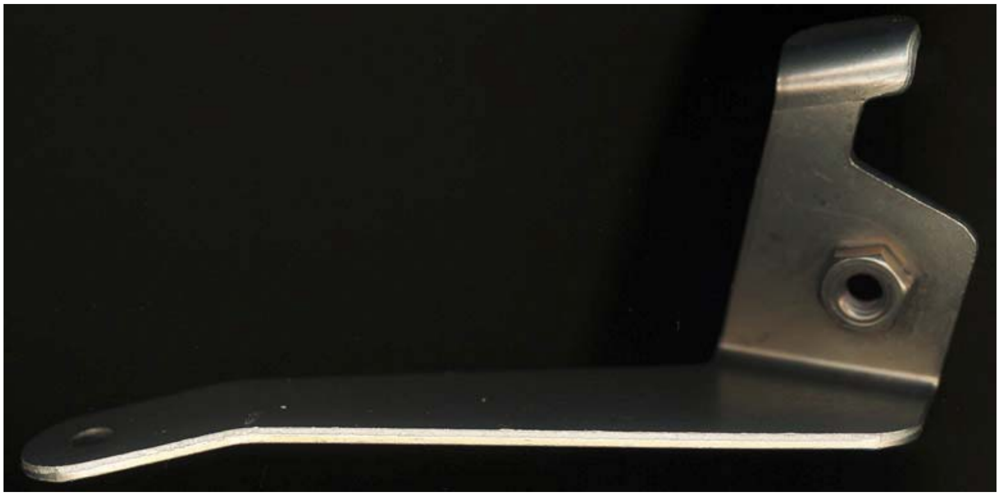


Figure 24. Bracket coated with zinc/iron before exposure.

Figure 25. Bracket coated with zinc/iron following 720 h of ASTM B 117 and 27 cycles of GM 9540 exposure.

Figure 26. Bracket coated with zinc before exposure.

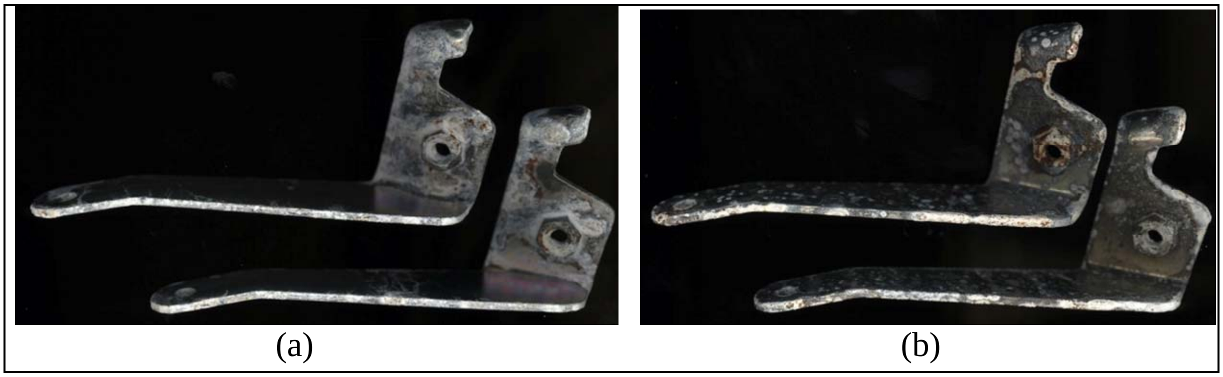


Figure 27. Bracket coated with zinc following exposure of 552 h in ASTM B 117 and 27 cycles in GM 9540.

Figure 28. Fluid line before exposure.

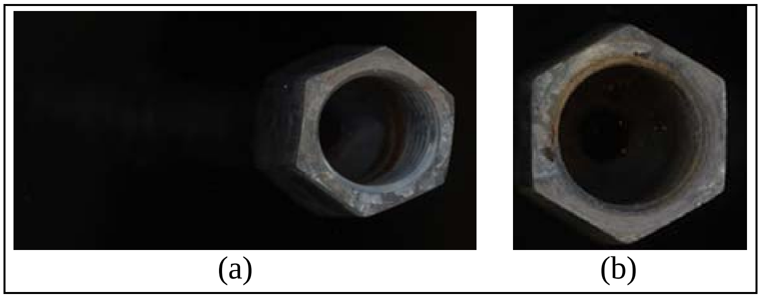


Figure 29. Fluid line following exposure of 720 h in ASTM B 117 and 21 cycles in GM 9540.

All of the parts that were exposed to either of the accelerated corrosion tests were given postplating treatments with TCP. In all but one case (part 9), the ASTM B 117 performance exceeded that which would be considered “good;” in many cases, it was significantly so. The same performance criterion using the GM 9540 procedure was achieved by only two-thirds of the parts. Of those that met the criterion, 9 of 10 greatly surpassed it.

Of the top nine most corrosion-resistant parts, six were barrel plated. The remaining eight parts all were rack plated. It is not clear whether the geometry that allowed for plating solution access and drainage also made the parts good candidates for barrel plating or if barrel plating is inherently superior to rack plating. The single best overall performer in both exposures was rack plated.

4. Conclusions

Postplating treatment with TCP improves the performance of most zinc/nickel-plated components. Better than half of the parts exposed to ASTM B 117 survived beyond 5000 h. Nearly half of the parts survived beyond 400 cycles of GM 9540.

GM 9540 seems to be a more rigorous test for screening performance. There generally was moderate correlation between the two accelerated corrosion tests. There were two glaring exceptions (parts 13 and 14) where the ASTM B 117 exposure resulted in an “exceptional” rating, but where the GM 9540 exposure resulted in a lower but “good” performance rating. Barrel-plated parts appear to perform better than rack-plated parts, although this performance may be due to the geometries of the parts rather than the application process.

NO. OF COPIES	ORGANIZATION
1 (PDF only)	DEFENSE TECHNICAL INFORMATION CTR DTIC OCA 8725 JOHN J KINGMAN RD STE 0944 FORT BELVOIR VA 22060-6218
1	DIRECTOR US ARMY RESEARCH LAB IMNE ALC HRR 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RESEARCH LAB RDRL CIM L 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RESEARCH LAB RDRL CIM P 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RESEARCH LAB RDRL D 2800 POWDER MILL RD ADELPHI MD 20783-1197
	ABERDEEN PROVING GROUND
1	DIR USARL RDRL CIM G (BLDG 4600)

INTENTIONALLY LEFT BLANK.