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The Effects of Chemical Wash Additives on the Corrosion of Aerospace Alloys in Marine Environments

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ABSTRACT: This paper presents the methodology for comparing the relative effectiveness of four chemical products used for rinsing airplanes and helicopters. The products were applied on a weekly basis to a series of flat alloy panels exposed to an oceanfront, marine environment for one year. The results are presented along with comparisons of exposures of the same alloys that were not washed, were washed with seawater, or washed with de-ionized water.

Keywords: Corrosion, rinsing airplanes, rinsing helicopters, aluminum, titanium, steel, magnesium, aerospace, atmospheric corrosion, marine atmosphere

INTRODUCTION

Aircraft corrosion. Corrosion is a very difficult problem that costs commercial air fleet operators millions of dollars annually. The costs of corrosion in terms of military readiness cannot be measured, but they are believed to be even higher than for commercial operators. Military hardware must often be shipped in haste to remote locations where it is operated in harsh environments with less time for maintenance and with limited maintenance facilities.

Fig. 1 shows a typical Army refueling station during the deployment to the Persian Gulf in 1991. The facilities at forward installations like this are very limited and maintenance of equipment takes a back seat to operational demands. As a result of this combination of limited facilities and high operational demands, military aircraft often experience substantial corrosion damage during field deployment. Fortunately, much equipment spends a fair amount of its time in rear locations where facilities are not this limited and attempts at corrosion control and remediation are possible.

Figure 1. Helicopter refueling operation during Operation Desert Storm [1]

A number of proprietary products are marketed for rinsing airplanes and helicopters for both the civilian and military markets. Unfortunately, these products have not been impartially evaluated, and government decision-makers do not have reliable data for making decisions on whether or not these products work and are worth their expense.

The purpose of this project was to determine if a number of proprietary cleaning compounds could be used to prolong the life of Army aircraft deployed under circumstances such as are shown in Fig. 1. The project was undertaken to compare the efficiencies of a number of commercial rinsing products and to determine if they offered measurable advantages over rinsing with water having no detergents or other chemical additives. A secondary purpose was to determine if these same products would reduce corrosion during training and other operations at rear areas where maintenance facilities are less limited.

Atmospheric corrosion test site: The NASA Kennedy Space Center Beach Corrosion Test Site (BCTS) has the highest corrosivity of any long-term exposure site in North America. This is documented in Table 1, which compares the corrosivity of the Kennedy beach side location with other test sites. For this reason, the Army initiated a program to test alloys and corrosion control methods at the NASA-Kennedy Space Center. Any deployment of Army aircraft at locations away from the beach would be less corrosive, as shown in Fig. 2, which documents the rapid decrease in corrosion rates as distances from the beach increase.

Table 1. Comparison of corrosion rates of carbon steel at various test locations:[2]

Location	Type Of Environment	µm/yr	Corrosion rate (a) mils/yr
Esquimalt, Vancouver Island, BC, Canada	Rural marine	13	0.5
Pittsburgh, PA	Industrial	30	1.2
Cleveland, OH	Industrial	38	1.5
Limon Bay, Panama, CZ	Tropical marine	61	2.4
East Chicago, IL	Industrial	84	3.3
Brazos River, TX	Industrial marine	94	3.7
Daytona Beach, FL	Marine	295	11.6
Pont Reyes, CA	Marine	500	19.7
Kure Beach, NC (80 ft. from ocean)	Marine	533	21
Galeta Point Beach, Panama CZ	Marine	686	27
Kennedy Space Center, FL (beach)	Marine	1070	42

(a) Two-year average

Figure 2. Changes of corrosion rate with distance from the ocean [3]

EXPERIMENTAL PROCEDURES

Alloys tested. The alloys shown in Table 2 were chosen by the Army as being representative of the kinds of alloys most commonly used on military aircraft.

Table 2. Alloys tested in this program

UNS Alloy Designation	Military Handbook 5 Designation[6]	Military Handbook 5 Common Name	Composition	Designation This Study	Comments
G43400	1206	4340	Fe-0.4C, 1.8 Ni, 0.8 Cr, 0.25 Mo	4340	
S45850	1220	18Ni(250) Maraging	Fe, 18 Ni, 7.5 Co, 5 Mo, Ti, Al	C-250	
S35500	1505	AM-355	Fe, 15.5 Cr, 4.5 Ni, 3 Mo	AM-350	
S13800	1510	PH 13-8 Mo	Fe, 13 Cr, 8 Ni, 2 Mo	PH 13-8 Mo	
A92024	3203	2024	Al, 4.5 Cu, 1.5 Mg, 0.6 Mn	2024/8625	Anodized IAW Mil 8625 Type 1
J9100	3204	2024	Al, 4.5 Cu, 1.5 Mg, 0.6 Mn	2024/5541	Anodized IAW Mil 5541 Type 1
A97075			Al, Zn 5.6, 2.5 Mg, 1.6 Cu, 0.3 Cr	7075	
M11311	3601	AZ31B	Mg, 3 Al, 1 Zn	4377/3171 or Mg	Surface treated IAW SAE-AMS-M-3171
R65400	3607	Ti-6Al-4V	Ti, 6 Al, 4 V	Ti-6Al-4V or Ti	

The relative corrosion resistance of these alloys was evaluated in comparison tests where the alloys were exposed to the marine atmosphere with no rinsing and to rinsing with either ocean water or de-ionized water.

Chemicals Tested. Table 3 shows the chemical analyses of the proprietary cleaning products tested. Several of them are marketed with trade names implying that they will eliminate salt or chlorides.

Table 3. Chemical analyses of cleaning agents tested

	Sample Identification			
	#1	#2	#3	#4
ANIONS (ppm)				
Fluoride	nd	nd	3,477	nd
Chloride	110	60	nd	232
Nitrite	91	131	nd	314
Nitrate	94	nd	166	9,511
Phosphate	25,191	65	80	nd
Sulfate	1,152	92	227	529
CATIONS (ppm)				
Sodium	7,930	2,367	1,453	nd
Ammonium	nd	1,919	134	36,053
Potassium	5,537	116	280	1,023
Magnesium	nd	nd	nd	nd
Calcium	48	56	60	nd

Nd: not detected, below lower detection limit

Exposure Testing. Flat panel specimens were exposed to the marine atmosphere environment in racks manufactured in accordance with standard industrial procedures (Fig. 3).[4] The alloys discussed above are undergoing a two-year exposure test at the Test Station.

Figure 3. View of Beach Corrosion Site and coupon configuration

Rinsing Procedures. The flat specimens were washed once each week with a pressure sprayer and the proprietary chemicals listed in Table 3 diluted according to the manufacturer's instructions.

Cleaning Procedures. The coupons placed outdoors at the Kennedy Space Center Beach Corrosion Test Site September 29, 2000 were retrieved on October 5, 2001 for photographs before the cleaning process. A cleaning process was determined for each metal type using ASTM G-1, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, as a guideline. All coupons were mechanically cleaned by using a pressure washer to remove the gross corrosion products, followed by a five-minute ultrasonic bath, dried, and weighed. After the water-based mechanical cleaning process, the coupons were set up to be chemically cleaned in a specific solution according to metal type, designed to remove the corrosion product with minimal dissolution of the base metal. The chemical cleaning process was repeated on each specimen several times with the mass loss determined after each cleaning. The removal of the corrosion products was confirmed by examination with a low power microscope. After the coupons were cleaned they were re-tagged, photographed, and bagged for storage and further analysis.

RESULTS

Weight Loss. Only the 4340 alloy coupons lost a significant amount of mass, in the range of 4 to 18 grams, or 0.5 to 3 % weight. The relatively large weight loss is due substantially to deploying the metal in an un-coated state. All other coupon weights were changed by only a noise level, in the range of 0.01 grams weight gain for aluminum, to 1.0 grams average weight loss for alloy 4377 (magnesium) with 3171 coating. The weight loss of all metals related to rinse agents and controls is shown in Table 4, along with pitting ratings where applicable. Coupon weight loss is shown by worst-case loss, average loss of replicate samples, and ranking of rinse performance (1=best, 7=worst). Also, the pitting density ratings of 2500/m2 (A1) to 500,000/m2 (A5) are included in Table DD for those coupons with visible pitting.

Table 4. Coupon weight loss and pitting analysis, showing coupon with worst-case loss, average loss of replicate samples, and pit density

Metal:	Rinses	Worst Case	Avg. Weight	ASTM G-46 Rating*
4340 Steel	4	9.996	7.631	N/A
	3	11.315	10.696	
	1	13.888	10.653	
	Exposure	14.312	11.278	
	2	14.625	10.923	
	Seawater	16.107	15.714	
	DM Water	17.177	13.509	
2024/ 8625 Alum-inum	1	0.149	0.067	A-0,B-0,C-0
	DM Water	0.403	0.170	A-0,B-0,C-0
	Exposure	1.173	0.437	A-0,B-0,C-0
	Seawater	1.299	0.459	A-1,B-1,C-1
	4	0.302	0.128	A-1,B-1,C-1
	2	0.091	0.056	A-2,B-1,C-1
	3	0.089	0.068	A-2,B-1,C-1
2024/ 5541 Alum-inum	Exposure	0.067	0.051	A-0,B-0,C-0
	DM Water	0.232	0.091	A-0,B-0,C-0
	Seawater	0.041	0.028	A-1,B-1,C-1
	2	0.395	0.139	A-2,B-1,C-1
	1	0.035	0.029	A-2,B-1,C-1
	3	0.227	0.200	A-2,B-1,C-1
	4	0.116	0.086	A-3,B-1,C-1
7075 Alum-inum	1	0.687	0.279	A-3,B-1,C-1
	DM Water	0.548	0.231	A-3,B-1,C-1
	Exposure	1.607	0.606	A-3,B-1,C-1
	2	0.121	0.294	A-3,B-1,C-1
	3	0.865	0.521	A-4,B-1,C-1
	Seawater	0.243	0.140	A-4,B-1,C-1
	4	0.938	0.623	A-5,B-1,C-1

Metal:	Rinses	Worst Case	Avg. Weight	ASTM G-46 Rating*
Mg AZ31B	1	0.775	0.770	A-3,B-1,C-1
	Seawater	1.038	1.020	A-3,B-2,C-1
	4	0.95	0.932	A-4,B-1,C-1
	2	1.016	0.994	A-4,B-1,C-1
	DM Water	0.898	0.887	A-4,B-1,C-1
	3	1.186	1.118	A-4,B-1,C-1
	Exposure	0.947	0.916	A-4,B-1,C-1
PH 13-8 Stainless Steel	2	0.036	0.034	No visual difference
	3	0.064	0.058	
	1	0.047	0.041	
	4	0.017	0.009	
	Seawater	0.052	0.047	
	DM Water	0.045	0.041	
	Exposure	0.059	0.059	
AM-350 Stainless Steel	2	0.029	0.027	No visual difference
	3	0.029	0.028	
	1	0.03	0.026	
	4	0.026	0.026	
	Seawater	0.035	0.035	
	DM Water	0.035	0.031	
	Exposure	0.041	0.036	
Titanium Ti-6Al-4V	2	-0.022	-0.010	No visual difference
	3	-0.011	-0.007	
	1	-0.014	-0.009	
	4	-0.013	-0.008	
	Seawater	-0.017	-0.010	
	DM Water	-0.022	-0.014	
	Exposure	-0.005	-0.001	

* Micro-photgraghs were taken of 1 cm x 1 cm @ 10x and compared with each other for visual and ASTM G46 rating.

Appearance of Coupons. As expected, the 4340 steel showed the most severe corrosion due to its low alloying and lack of coating. The titanium (Ti-6Al-4V), AM-350, and the PH 13-8 Mo showed no significant changes in appearance due to the exposure, regardless of rinse agent. Both the 2024/8625 and the 2024/5541 aluminums showed minor surface pitting while the magnesium (AZ31B) and the 7075 aluminum showed moderate to high pit density for the non-ferrous alloys. The 7075 also showed exfoliation indicative of intergranular corrosion along the edges of most of the samples especially in the areas in contact with the ceramic retainers. Figure 5 shows typical coupons after one-year exposure.

Figure 4. Intergranular corrosion evidence in alloy 7075 with CRA # 4

Figure 5. Typical coupons exposed for one year

Pitting Analysis. Table 5 shows the results of rating the coupons according to ASTM G46 standard chart. Pit ratings B and C are shown, each with five levels, 1 through 5:

- Pit size average from 0.5 mm2 (B1) to 24.5 mm2 (B5)
- Pit depth average from 0.4 mm (C1) to 6.4 mm2 (C5).

Table 5. Analysis of coupons with significant pitting

7075 Rinse	Pit Area mm^2	ASTM rating	Pit Depth mm	ASTM rating	Mg(AZ31B) Rinse	Pit Area mm^2	ASTM rating	Pit Depth mm	ASTM rating
#1	0.0038	B-1	0.018	C-1	#1	0.0707	B-1	0.092	C-1
#2	0.0079	B-1	0.036	C-1	#2	0.2552	B-1	0.184	C-1
#3	0.0038	B-1	0.024	C-1	#3	0.3318	B-1	0.125	C-1
#4	0.0064	B-1	0.052	C-1	#4	0.1963	B-1	0.042	C-1
Seawater	0.0133	B-1	0.034	C-1	Seawater	0.5281	B-2	0.098	C-1
DM H2O	0.0020	B-1	0.032	C-1	DM H2O	0.1590	B-1	0.124	C-1
Exposure	0.0113	B-1	0.044	C-1	Exposure	0.2827	B-1	0.128	C-1
2024/8625 Rinse	Pit Area mm^2	ASTM rating	Pit Depth mm	ASTM rating	**2024/5541** Rinse	Pit Area mm^2	ASTM rating	Pit Depth mm	ASTM rating
#1	0.0000	B-1	0.000	0	#1	0.0133	B-1	0.046	C-1
#2	0.0020	B-1	0.004	C-1	#2	0.0095	B-1	0.030	C-1
#3	0.0079	B-1	0.040	C-1	#3	0.0314	B-1	0.032	C-1
#4	0.0095	B-1	0.022	C-1	#4	0.0380	B-1	0.050	C-1
Seawater	0.0028	B-1	0.020	C-1	Seawater	0.0452	B-1	0.046	C-1
DM H2O	0.0000	B-1	0.000	0	DM H2O	0.0000	B-1	0.000	0
Exposure	0.0000	B-1	0.000	0	Exposure	0.0000	B-1	0.000	0

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3. J.D. Morrison, Report on the Relative Corrosivity of Atmospheres at Various Distances from the Seacoast, NASA-Kennedy Space Center Report MTB 099-74.

4. Standard Practice for Conduction of Atmospheric Corrosion Tests on Metals, ASTM G-50-76(97).

Fig 1

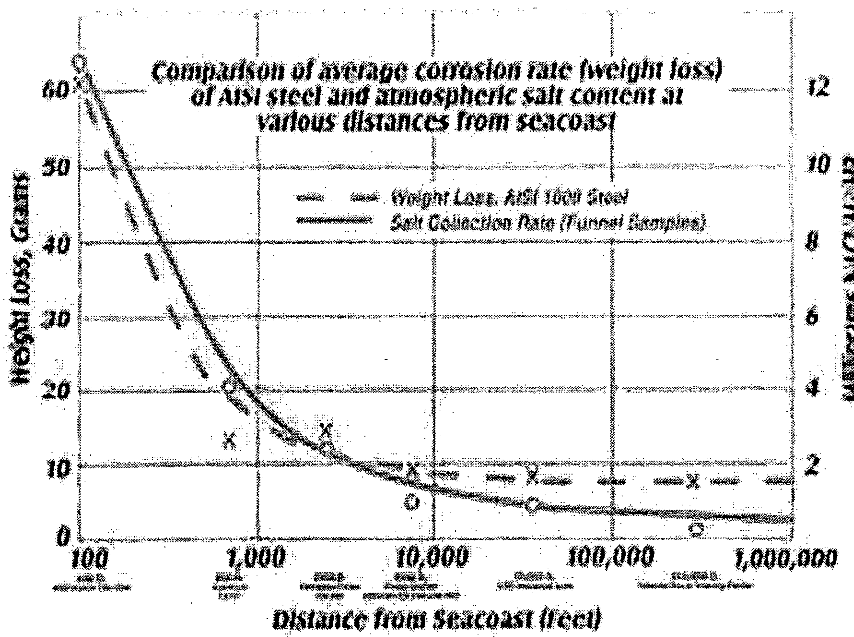
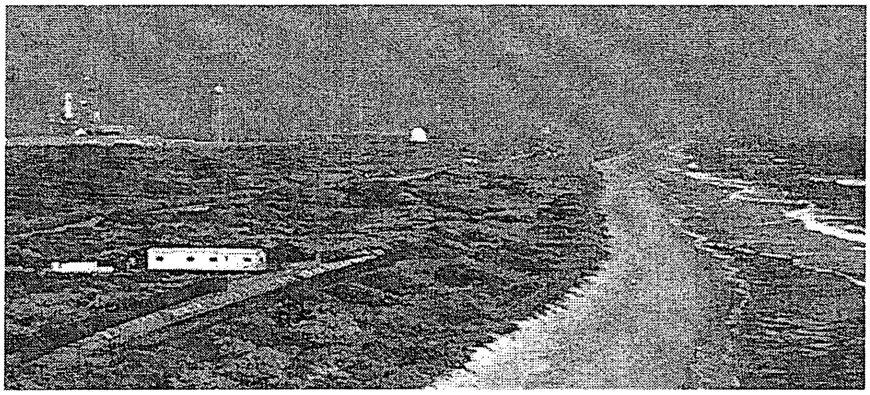
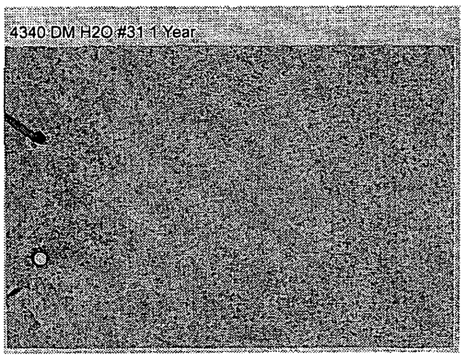


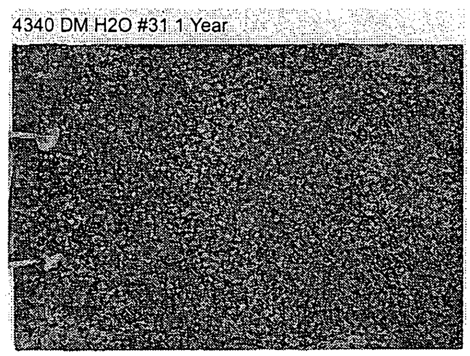
Figure 2: Changes of corrosion rate with distance from the ocean [3]



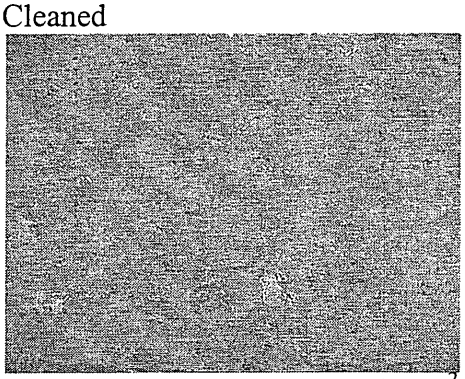
Beach Corrosion Test Site



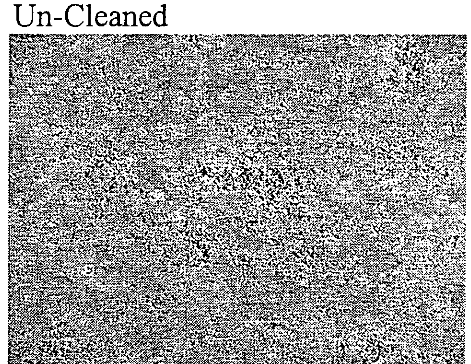
Cleaned



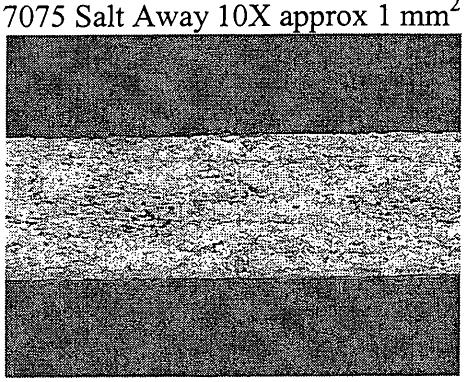
Un-Cleaned



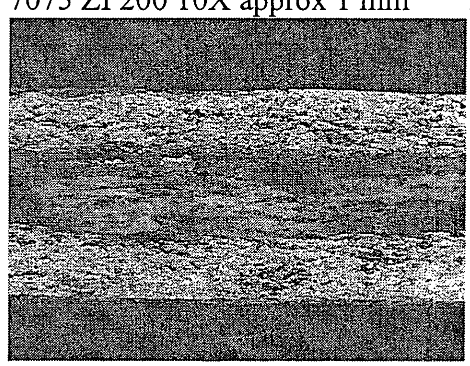
7075 Salt Away 10X approx 1 mm^2



7075 ZI 200 10X approx 1 mm^2



7075 Edge View Salt Away 25X



7075 Edge View ZI 200 25X