Iron-Stain Reduction from Alkyd Paint Films

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INTRODUCTION

This poster presents a case study in the removal of disfiguring iron and organic staining from an alkyd paint on an aluminum-alloy, Korean-war-era missile, the "Bullpup".

The original storage container was severely rusted, causing orange-brown staining to the painted surface.

Bullpup *segments in original crate, before treatment (BT).*

Limited research is available on chelation of iron stains from within alkyd paint films. As such, existing procedures used for other substrates were adapted.

Two experiments were designed to evaluate chelators:

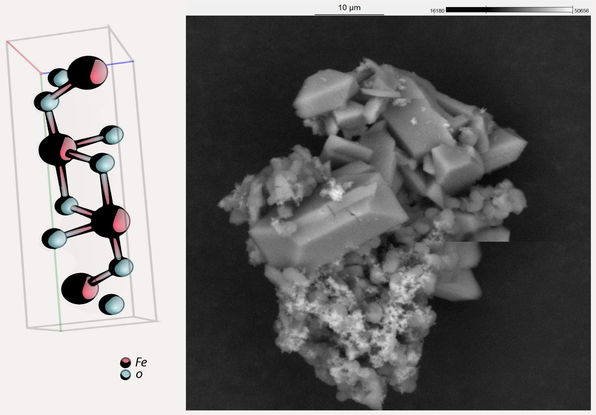
1) Replication of iron staining on an alkyd paint film
2) Stain-removal testing

MOCK-UP PREPARATION & ANALYSIS

Test coupons were prepared with an historic alkyd formulation sprayed onto 2024 aluminum alloy. Various methods were evaluated to achieve consistent staining.

A four-month bath in a corrosive, ion-rich slurry of acetic acid, hydrogen peroxide, and fine steel wool achieved the most faithful result (see center panel).

Analyses before and after staining—including pXRF, Raman, XRD, and SEM–EDS—reflected introduction of iron salts containing Fe^{2+} and Fe^{3+} into the paint film.



Unit cell of goethite (left). Iron oxide mixture with SEM (right).

TESTING

These coupons were then used to test three different stain-removal modalities:

- iron-specific chelators: EDTA
- reduction agents: sodium dithionite
- protonation using acids: oxalic acid

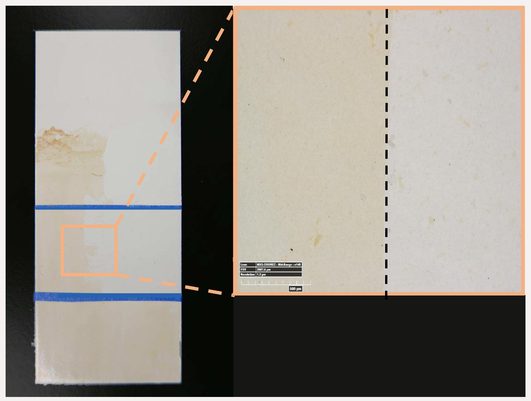
To identify a limited "palette" of appropriate pHs to test, graphs of equilibrium constants showed cross-sections of activity that most reagents had in common. A single molarity (0.15M) was tested at these pHs.

pH	picolinic acid	maltol	L-cysteine	aceto-hydroxamic acid	oxalic acid, sodium	citric acid, sodium	EDTA	sodium dithionite (SDT)	phosphoric acid, sodium	1:1 SDT: EDTA
9.2	9.2	9.2	9.2	9.2			9.2		9.2	
8.3				8.3		8.3	8.3		8.3	8.3
7.3					7.3	7.3		7.3	7.3	7.3
6					6	6		6		
4					4				4	
3					3				3	
BT										
AT										

...ed coupons before and after chelation testing. Each column of coupons relates to the reagent listed in the chart above.

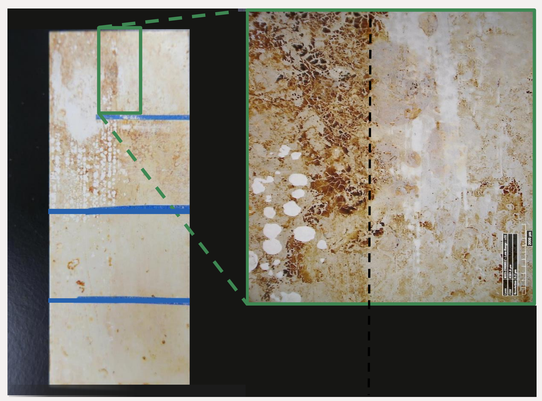
RESULTS

VERY EFFECTIVE: Oxalic acid (0.15M at pH 4)



Oxalic acid in DI water (0.15M at pH 4.0) in a cellulose-powder poultice was effective when applied for 30 minutes. The surface was then rinsed with pH-adjusted water (pH 4.0).

EFFECTIVE: Acetohydroxamic Acid (0.15M at pH 9.2)



Acetohydroxamic acid in DI water (0.15M at pH 4.0) in a cellulose-powder poultice was effective when applied for 60 minutes. The surface was then rinsed with pH-adjusted water (pH 9.2).

LESS EFFECTIVE:

Picolinic acid	Minimal reduction
Maltol	Minimal reduction + reddening
L-cysteine	Minimal reduction for expense
Sodium dithionite (SDT)	Color change; no reduction

INEFFECTIVE:

EDTA	No reduction, alone or with SDT
Citric acid	No change
Phosphoric acid	No change
Ascorbic acid	Darkening + reddening

TREATMENT RESULTS

The Bullpup missile was successfully treated with 7% oxalic acid (w/v) in DI water on a TEK-wipe poultice.

BT, nose cone (left). AT, following oxalic acid (right).

BT, segment (top). AT, following oxalic acid (bottom).

Description	BT	AT	Δ E
Warhead, aft			32.7
Warhead, aft			30.9
Warhead, aft			20.3
Motor, forward			16.8
Nose			31.1
Nose			21.0
Nose, aft			18.3

Colorimetry was performed to describe stain reduction following poulticing. Above, L*a*b* values are visualized as HEX codes to show color change and a visually significant ΔE value. Additionally, analysis of the poultices detected iron species removed during treatment.

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