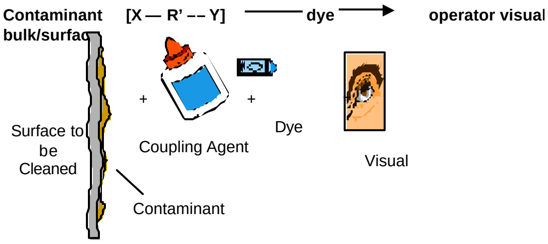
FINAL REPORT

on

Concept Evaluation of Visual Cleaning Performance Indicators (VCPI) For Real Time Cleaning Verification
(PP-1117)



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by

BF Monzyk, SP Chauhan, JT Stropki, and C Gorman; Battelle
DT Peeler and DL Ballard; Air Force Research Laboratory
SA Sirchio and MJ Bieberich; Naval Surface Warfare Center, Carderock Division

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Improving Mission Readiness Through Environmental Research

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ACRONYMS

A	Light absorbance value from a UV/visible spectrophotometer (“absorbance units”, AU, related to concentration by Beer’s Law, $A=\varepsilon*b*c$)
a*, b*	Color space coordinates for red (less green) and yellow (less blue), respectively
AFRL	Air Force Research Laboratory
ALC	Air Logistics Center
Al	Aluminum
Al2024	Aluminum 2024-T3 (a major aircraft skin structural material)
Al2024P	Aluminum 2024-T3, painted
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy
b	Cell path length (in cm or mm) for UV/visible spectrophotometric analyses
c	Concentration in molar (M) or ppm are given in texts
CA	Coupling agent, selectively bonds a dye to a particular class of contaminants
CAR	Carminic acid (same as Natural Red 4)
C.I.	Color Index
CP	Metal corrosion products
CRC	Corrosion Removal Compound
CSS	Corrosive Soluble Salt
da*	Color space red color intensity difference between reference and sample
db*	Color space yellow color intensity difference between reference and sample
dE*	Color space total color difference between reference and sample
DoD	Department of Defense
DOE	Department of Energy
dye-CA	Dye plus coupling agent (CA) molecule used to selectively label contaminants
ecotox	Environmental and toxicity issues, compatibility, properties, etc.
ε	Molar absorptivity in M^{-1} cm^{-1} (or ppm^{-1} cm^{-1})
EIS	Electrochemical Impedance Spectroscopy
EtOH	Ethanol
ES&H	Environmental Safety and Health (Industrial useage)
ES&O	Environmental Safety and Operation (Military useage)

ACRONYMS (Cont.)

esp	especially
EtOAc	ethyl acetate
FeHY80P	Steel painted HY80 alloy (major ship superstructure material of construction)
FTIR	Fourier Transform Infrared Spectroscopy
FY	Fiscal Year
GC	Gas Chromatograph
hf	hydrophobic fluid (contaminant phase), for example grease, oil or hydraulic fluid
hp DI	High Purity Deionized Water
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-MS	Inductively Coupled Argon Plasma with Mass Spectrascopic
Insol	Insoluble
L	Color space coordinate for lightness, ranges from black to white
Liq	Liquid
LO	Lube Oil MIL-L-23699
MIL-SPEC	Military Specification
MRC	Maintenance Requirement Cards (Navy)
MSDS	Material Safety Data Sheet
[M+, Cl-](aq)	Aqueous solution of a water-soluble chloride salt, e.g., NaCl
neat	The use of a compound or formulation in 100% (undiluted) form
NMR	Nuclear Magnetic Resonance
NR4	Natural Red 4 (carminic acid)
NSN	National Stock Number
NSWCCD	Naval Surface Warfare Center Carderock Division

ACRONYMS (Cont.)

NTP	National Toxicology Program database
NVR	Non-Volatile residue analysis for contaminants
PA7	Peel Away® 7 paint remover for PCMS tiles
PCMS	Passive Countermeasures System
PCT	Preliminary Cleaning Testing
(PDM)	Periodic Depot Maintenance
ppb	Parts per billion or µg/L
ppm	Parts per million or mg/L
PRF	Commercial degreaser used by the Air Force depots
Q	Quarter of a year, e.g., 1Q 00 = first 3 months of year 2000
S	Solid
SAE	Society of Automotive Engineers
SCT	Systematic Cleaning Testing
Sol	Soluble
SOW	Statement of work
SW	Sea water
TCTFE	1,1,2-trichlorotrifluoroethane (extract solvent for conventional NVR assays)
T.O.	Tech Order, used by the U.S. Air Force to specify maintenance procedures on weapons systems
TP	PCMS tiles, painted
UV/VIS	Ultra-violet/visible light (used for dye analyses)
VCPI	Visual Cleaning Performance Indicator
VO	Visual Observation method

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1.0 EXECUTIVE SUMMARY: VCPI CONCEPT VIABILITY DEMONSTRATED AND TRANSITION PLAN OFFERED

SERDP, via this project, No. PP-1117, evaluated the concept of pollution prevention via the reduction of cleaning wastes by providing process operators with real time, in-process, visually-based, cleaning status indication using visual cleaning performance indication (VCPI). Cleaning operations are a critical widespread element in the maintenance and repair of Department of Defense (DoD) and Department of Energy (DOE) weapon systems. Current cleaning performance verification procedures are slow, expensive, often limited to small areas, require highly skilled labor, and not normally suitable for real-time measurement. Under these circumstances, there usually is a tendency to overclean to reduce the frequency of depot and field processing failures associated with undercleaning. However, overcleaning increases waste volume production and waste-handling costs, consumes production time and capacity, and increases process raw material costs. Therefore, SERDP has funded this and other related efforts to identify better means to monitor DoD and DOE cleaning processes. This project successfully verified the VCPI concept, i.e. of using contaminant-selective dyes, which appear would meet ES&O requirements, to color surface contaminants, with minimal changes in the current cleaning protocols, so that cleaning operators can better use surface visual appearance to control the cleaning operation in real time. This VCPI technique is projected to reduce cleaning process waste volumes, production times, raw material consumption, and processing costs.

Only three (3) dye-CA (coupling agent) chemistries appear to be required for labeling a broad range of contaminants. Although the enclosed tests examined these three situations separately, the chemistries represented suggest that they can be combined into just one or two VCPI systems for further ease of deployment. Hence, future development should include testing combined dye-CA formulations against a broad range of contaminant types. This encouraging result promises to simplify commercialization of the VCPI technique and allow its application to a broad range of cleaning operations.

This report also provides the DoD cleaning needs, cleaning processes, background, and test system selections, cleaning procedure identification results, and prescreening cleaning testing results. Systematic cleaning test results are also provided to quantify the performance of the VCPI technique. These test results quantitatively and qualitatively validated the general VCPI concept, which justifies proceeding to advanced lab then field cleaning tests to develop VCPI procedure refinements and use formulations necessary for commercialization.

The dye-CA database review and analysis produced some 250 materials, most of which were dyes with CAs already attached. About 45 of these were selected as appearing functional as possible VCPI systems based on the mechanisms given previously (Appendix A). Seven of these dyes were selected based on the above criteria for screening (Table 7.1.5). Also listed in Table 7.1.5 are the possible means for dye introduction into the cleaning process (VCPI Technique Utilization). All seven of these dyes already contain the CA property.

Although the assessment of the safety and environmental impact of the candidate dyes would continue through any development program, the results collected during this program regarding the necessary environmental compatibility and safety requirements for inclusion into DoD cleaning operations are very encouraging and warrant proceeding with VCPI technology development.

The key results from laboratory-scale testing using panels are:

- The VCPI method has the potential to be a simple, cost-effective, real-time cleaning verification technique.
- Only a few VCPI systems appear to be needed to cover a broad range of surface contaminants on weapon systems of interest to DoD.
- Several dye-CA candidates are already commercially available for selective labeling of the target classes of contaminants.

In addition, two important DoD opportunities were discovered for using the VCPI technique to guide the selection of better cleaner/cleaning: 1) protocols removing paint stripper from PCMS tiles and 2) the identification of better cleaning protocols for cleaning hydrophobic contaminants (oil, grease, etc.) from painted surfaces.

In conclusion, it was observed that the VCPI technique was very useful for monitoring the laboratory-scale cleaning operations using test panels. It appears that the VCPI technique would be a significant benefit in helping develop better cleaners and cleaning protocols due to the real time/quick visual feedback on total surface performance that the technician receives during the cleaning operation. The next step is to determine whether these same benefits can be transferred to the field.

With the encouraging results reported herein on VCPI concept evaluation, a transition plan was prepared for commercializing this technology (Section 2.0). This plan, already underway in FY02, projects a technology development path involving refinement and field pilot tests to verify efficiency, cost, environmental compatibility, safety, and value, while developing the needed VCPI regent formulations and vendor sourcing.

2.0 TECHNOLOGY TRANSITION PLAN FOR IMPLEMENTATION AND COMMERCIALIZATION OF VCPI TECHNOLOGY FOR DOD APPLICATIONS

The successful laboratory-scale confirmation of the Visual Cleaning Performance Indication (VCPI) concept for aerospace and ship cleaning applications justifies transitioning the development of the VCPI technology to the next phase of development, and that is to transition the subject technology from the laboratory to a production environment. This transition effort is already underway (using non-SERDP funding). The laboratory testing involved a series of "proof of principal" demonstrations at the subsystems or higher level in operationally realistic environments. These environments replicated the cleaning operations that are routinely completed on large area surfaces, such as those used for the external surfaces of aircraft and ships operated by the DoD. All testing, and subject demonstrations completed by Battelle, the Air Force and the Navy, confirmed that VCPI meets current user's defined pre-paint cleaning verification needs. For the sake of discussion, the content of this document reinforces the use of VCPI for aerospace depot-level cleaning operations.

In the context of VCPI, the definition for Technology Transition (T2) includes a transitioning of the technology from the sponsoring laboratory (i.e., technology developer or Battelle) to a technology recipient (i.e., end-user or the DoD or aerospace industry). By definition, for the Air Force, the transition is complete upon a successful incorporation of VCPI into the current T.O. 1-1-691 approved cleaning specification, which defines the Air Force's requirements for cleaning military aircraft, aircraft component parts, and ground support equipment. It is recommended that the VCPI be demonstrated/validated through field testing by the technology recipient (eg., Air Force and commercial aerospace industry), and these transition tests are already underway (separate program with Hill AFB, Boeing Aircraft, Inc.). This testing would include any further refinement and/or development of the VCPI technology, as well as any actions associated with drafting the technology use methodology into a formal performance specification, process order(s), and facilitation of systems that incorporate the VCPI technology.

The subject Technology Transition Plan (TTP) serves as a draft outline of the potential follow-on efforts by Battelle, the Air Force Research Laboratory (AFRL) or Carderock (depending on whether the application is Air Force or Navy), the manufacturer of the VCPI cleaner/agent, interested logistic centers, and a host of targeted technology recipients (for the Air Force these are the ALC's, AFRL/CTIO and/or the AFCPCO). This document outlines the specific tasks that must be successfully completed prior to an acceptance of the technology. An introduction to the document includes background information, and an abbreviated summary of feedback received from numerous Air Force agencies and/or personnel that are interested in the technology for aerospace application (Table 2.2.1). This level of interest, and the "working" relationships that have been developed over the past 15 years between Battelle scientists and key personnel within each of the referenced offices is another reason why this TTP is being drafted for transitioning VCPI into aerospace cleaning application. A drafting and issuance of a complimentary TTP for Navy applications will be recommended to support a DoD wide VCPI implementation and commercialization. This TTP will support the Navy's need to monitor the removal efficiency of a commercial paint stripper from Passive Counter Measure System (PCMS) ship hull tiles prior to re-painting.

2.1 Technology Background Summary

Large area cleaning operations are a critical element in the maintenance and repair of many different weapon systems that are operated by the Department of Defense (DoD), and also processing equipment maintained by the Department of Energy (DOE). One of the major problems with both operations is verifying a complete removal of contamination from the surfaces being cleaned. Current cleaning verification procedures are either very qualitative (i.e., "water break" test) or extremely slow, expensive, and often limited to small areas. Any instrumentation that is portable and commercially available is not suitable for real-time measurements in a production environment. Under these circumstances, there is a tendency to overclean an area to reduce the frequency of depot and field processing failures that may be associated with undercleaning. Overcleaning is not desirable because of the inherent increases in raw material costs, production time, equipment "downtime", as well as the costs associated with waste volume production, handling and disposal. In response to these issues, SERDP funded a study to identify and demonstrate a better means of monitoring DoD and DOE cleaning processes.

The scope of the subject SERDP study was to examine the validity of using contaminant-selective dyes, which do not have Environmental Safety and Occupational Health (ES&O) issues, to color or tag surface contaminants. Use of these materials would have a minimal impact on current cleaning protocols, and yet provide production personnel with a better use of visual surface appearance to control the effectiveness and efficiency of approved cleaning operations. One such technique that was recommended for the SERDP investigation was a VCPI technology that was designed by engineers at Battelle. To date, a series of laboratory-based labeling and systematic cleaning tests have been completed on specific soil and dye combinations by the Air Force (AFRL/MLSA), the Navy (NSWC/NAVSEA – Carderock) and Battelle. Results from the cleaning tests confirmed the feasibility of using VCPI to measure surface cleanliness levels for various aircraft and ship cleaning applications. An implementation or transition of this technology into Air Force and Navy aircraft maintenance depot and field installations, as well as the Naval shipyards or dry dock maintenance facilities is expected to significantly reduce raw materials consumption, cleaning process waste volumes, and most importantly production processing time.

To date, the results obtained from the systematic cleaning and VCPI procedure refinement tests obtained on representative test panels validate the general VCPI concept, which justifies proceeding to a demonstration and validation testing of aircraft component parts in a production environment. Discussions with the Air Force and Navy have suggested that this process prototyping be conducted at either Robins Air Force Base (WR-ALC) on non-flight critical component parts removed from C-130 aircraft, at Tinker Air Force Base (OC-ALC) on KC-135 parts, or at Hill Air Force Base (OO-ALC) using parts from an F-16 fighter aircraft. The respective weapon system directorates at all three Air Logistics Centers have expressed a willingness to participate in the proposed investigation.

2.2 Preliminary Assessments by Key DoD Representatives

The VCPI project was reviewed at several pertinent DoD conferences as a means to solicit input from end users of DoD cleaning operations. As summarized in the following list of significant comments and recommendations (Table 2.2.1), the objectives and values of the VCPI were verified unanimously by the referenced Air Force representatives. Battelle, with the cooperation of AFRL and selected ALC personnel will initiate VCPI process implementation through a continued contact with the referenced departments and military personnel.

Table 2.2.1 2000 Air Force Corrosion Conferences Feedback 1, 2 - Participant Comments

Office	Comments of Support and Issues Raised
F-15 System Program Office (Warner Robins Air Logistics Center, GA)	• Supports need and use of VCPI concept on F-15 aircraft, Expressed concerns about dye concentration for bare and coated aircraft materials, • Primarily interested in bare metal application, • Final system should contain multiple dyes, not multiple soap solutions.
SA-ALC/SFFT Office (San Antonio, TX)	• Supports need for VCPI during aircraft cleaning and pre-paint operations, • Supports use of VCPI for routine aircraft cleaning operations, • Confirms a need to validate conformance of dye/soap system to MIL-PRF-87937 performance requirements, • Suggests possible modifications to MIL-PRF-87937 test requirements if VCPI dye is incorporated into approved products.
Air Force Materials Lab - Structural Integrity Branch Office (WPAFB, OH)	• Supports feasibility assessment of VCPI concept for AF aircraft application, • Reiterates AF concerns about dye residues on coated aircraft materials, • Wants to ensure effective transition/integration plan in place when needed.
Air Force Coating Technology Integration Office (WPAFB, OH)	• No immediate concerns with approach used to assess VCPI technology in laboratory, • Confirms a need to validate effects of VCPI on corrosion and coating adhesion prior to demonstration/validation evaluation.
Air Force Corrosion Prevention & Control Office - Consultant	• Supports VCPI concept for future use on AF aircraft, • Confirms need to remove dye residues from bare and painted aircraft structures.
AF Corrosion Prevention and Control Office (Robins AFB, GA)	• No comments or concerns raised in response to briefings, • Study is recognized as a research effort to demonstrate VCPI concept feasibility.

2.3 Recommended Applications

A summary of the “best” first process application(s) based on the lab test results, as well as those applications, which appear most promising, but are in need of more development work prior to implementation is provided in Table 2.3.1

Table 2.3.1 Recommended Applications and Degree of Readiness

	VCPI Test System ID (see text)	**Recommended for Depot- or Field-Level Pilot Testing**	**Possible Future Application Providing Improved Cleaning Processes is Provided**	**Inappropriate Application for VCPI Without Better Cleaning Protocol**
AF and Navy Applications	Al2024P-LO-ORO-500		v	X
	Al2024-NLO-ORO-60K	vv		
	Al2024-C14-CAR-500	vv		
Navy Applications	FeHY80P-SW-FG3-5000	vv		
	TP-SW-FG3-5000	vv		
	FeHY80P-G-ORO-20:0.5		v	
	TP-G-ORO-20:0.5		v	X
	TS-PA7-ORO-20:0.5		v	

vv= most favorable application, v = application possibility with more lab testing, X = not recommended for VCPI use without major improvements in cleaning protocol such to achieve substantially higher contaminant removal.

As shown in Table 2.3.1, the most preferred applications for VCPI on large area surfaces would be bare or uncoated Al2024-T3 aluminum alloy sheet, painted HY 80 steel sheet, and the painted surfaces of acoustic tiles that are used to control the radar signature of ship hulls. Suggested reasons for making these application specific recommendations include; the type and concentration level of dye/CA combination used, the VCPI delivery method, the type of cleaner(s) used, and the effectiveness/efficiency of the production-based cleaning method. An additional reason may include the level of laboratory testing that was conducted on the various VCPI Test Systems (contaminant/dye combinations) identified in Table 2.2.1. An ideal scenario would be to use a low concentration of a single dye-CA combination for multiple types of contaminants on different substrate surfaces. The selected VCPI test system would simply be added to the cleaner stock, and then be uniformly applied over the surfaces being cleaned. All removal and post-removal processing of the rinse solutions would be based on a single solution chemistry, which would eliminate the propensity for extra treatment at IWTP.

2.4 VCPI Implementation Activity

Table 2.2.1 and the respective data summaries provided in this final report support the feasibility of using the VCPI technology for cleaning verification on select materials applications. As was stated in the previous text, one such application includes the uncoated or bare surfaces of a 2024-T3 aluminum alloy. This material represents a high-strength aluminum alloy that is commonly used to fabricate the fuselage and wing skin panels of military aircraft. As referenced in Table 2.2.1, this particular alloy, and a coated steel alloy (HY 80) and PCMS foam tiles, that are used to fabricate ship superstructures were two substrate materials investigated with VCPI during the subject SERDP funded project. The investigation led to a series of laboratory-based process demonstrations supported with standardized DoD systematic (PDM) cleaning operations. Details and results for these tests are summarized in other sections of this report.

The Air Force has stated on separate occasions that the VCPI technology would have most value during the pre-paint "wash-etch-alodine" or chemical cleaning operation used on the external surfaces of aluminum aircraft structures. The quality of this Periodic Depot Maintenance (PDM) activity controls both the performance and integrity of the protective paint scheme that is applied to these structures. VCPI incorporated into the "wash" component of the pre-paint process serves to "tag" specific contaminants that may remain on the surfaces of the respective structures after an initial cleaning exercise. Once tagged, the production personnel responsible for chemically cleaning and treating the surfaces of the aircraft can then concentrate the remaining cleaning activities on only the tagged or soiled areas. This approach will not only "focus" the cleaning operation for the purpose of maximizing cleaning efficiency, but also reduce the amount of chemicals required to process the surfaces of an aircraft prior to painting. An implementation of the VCPI technology into both depot- and field-level aircraft maintenance facilities represents a considerable cost and environmental benefit to the Air Force. A successful implementation and commercialization of the process for use in a military aircraft maintenance facility will require a major cooperative effort between Battelle and several different sectors of the Air Force (AFRL, AFCPCO, ALCs, MAJCOMS, AFRL/CTIO, and SA-ALC/SFFT). Additional input and involvement from production and management personnel responsible for the representative weapon system(s) will ensure a smooth transition of the technology from "bench-scale" cleaning operations in the laboratory to full-size aircraft.

2.5 VCPI Technology Transition Plan (TTP) for Process Implementation

As was stated in the previous text, Battelle's proposed plan for transitioning VCPI to a production environment is based on the results obtained from the feasibility testing that was recently completed in the laboratory. A review of these results, and several conversations with materials specialists at WPAFB/AFRL suggest a "walk before you run" attitude regarding the technology transition process. Specifically, this SERDP project has allowed Battelle to complete the labscale Technology Demonstration phase of T2 for test panels only (not parts), or Technology Transfer. The next phase is referred to as Technology Application, and includes not only any additional testing or process refinement, but also a demonstration (DEM) and validation (VAL) of VCPI in a production environment. The following TTP addresses this need.

Battelle is recommending a three-phase TTP. An identification of the technical scope, and specific activities that will be completed in each phase is provided in the following task summaries.

2.5.1 Phase I

The scope of this phase of the program will be to develop a multi-purpose VCPI-cleaner formulation, an optimized product delivery method, and then conduct a set of laboratory tests that resolve any concerns or risks anticipated by the Air Force prior to process prototyping. A brief summary of the proposed tasking for this phase of the TTP is provided as follows:

2.5.2 Proposed Phase I. Task 1: VCPI-Cleaner Formulation Development

Battelle will work with B&B Tritech, Inc. to remove existing fluorescent dye compounds from the commercial Re-Gel® cleaner material, and then determine an optimum concentration of a specialty dye-CA combination that is selected to tag different soils or contaminants that are inherent to the external surfaces of aircraft or aircraft component parts. A goal for this task will be to re-formulate the MIL-SPEC cleaner material to achieve the desired physical and chemical properties of a *VCPI activated* alkaline cleaner. This work will serve to verify that the cleaning properties of the MIL-PRF-87937C approved cleaner are not compromised.

2.5.3 Proposed Phase I. Task 2: Delivery Optimization

Results obtained from the Navy and Air Force systematic cleaning tests serve to identify several different VCPI/cleaner delivery methods that were partially optimized on test panels in the laboratory. From these methods, a single method will be selected during this task. Process selection will be based on the requirements of the depot- and field-level production environments, and then further optimized for consistent density, distribution, and attachment of the VCPI-cleaner to the appropriate contaminants that will be applied to the appropriate aluminum alloy.

2.5.4 Proposed Phase I. Task 3: Performance Testing

A set of MIL-PRF-87937C approved performance qualification tests are recommended to better characterize any effects of VCPI on the chemical and physical properties of the Re-Gel®/VCPI cleaner formulation that will be developed early in Phase I. As directed by SA-ALC/SFTT, testing will include all material stability tests specified for the Type III cleaner materials in Sections 3.6 and 3.7 of MIL-PRF-87937C. Additional testing will include each of the material compatibility tests (i.e., corrosion, adhesion,…) referenced in Sections 3.9, 3.10, 3.12, 3.13, 3.14, 3.15, and 3.16 of MIL-PRF-87937C. Flat, riveted, and lap joint panel configurations will be included in the subject investigation. All testing protocols will be coordinated through, and approved by, the SA-ALC/SFTT, the Air Force Corrosion Prevention and Control Office (AFCPCO), and the Air Force Research Laboratory (AFRL) at WPAFB prior to conducting any laboratory-based performance testing of the Re-Gel®/VCPI cleaner.

2.5.5 Phase II

The scope of this phase of the program will be to prototype the VCPI-cleaner on unpainted aluminum aircraft component parts and full-size aircraft structures. Initial prototyping activities will be confined to the stripped surfaces of non-flight critical aircraft component parts from F-15, F-16, C-130 or KC-135 aircraft. In response to the unknown risks associated with full-scale aircraft prototyping, engineers within each of the System Program Offices (SPOs) supporting these weapon systems have endorsed a prototyping of VCPI on the component level. The results obtained from this prototyping activity will control the schedule for additional Phase II prototyping of the VCPI process on an entire aircraft that has been stripped with an Air Force approved coating removal process. Considerations will be given for the compatibility of VCPI materials with any Plastic Media Blast (PMB) residues that may remain on the surfaces of parts or aircraft stripped with a PMB depaint process. Each phase of process prototyping will be coordinated with the respective representatives at AFRL, AFCPCO, CTIO, and the appropriate ALC supporting the representative weapon system.

An additional effort that is proposed to support the process prototyping activities includes a monitoring of the physical performance of the primer-topcoat systems that are applied over airframe surfaces that are treated, and <u>not</u> treated with the Re-Gel®/VCPI cleaner material. A one year period is recommended. Maintenance of any premature coating damage or failure will be addressed on an "as-received" basis. Contingency funding will be allocated for any unanticipated field and/or depot repairs.

2.5.6 Phase III

The final phase of this TTP will be to work with the Air Force to draft a Process Order (PO) for transitioning the VCPI/cleaner material into current T.O. 1-1-691 cleaning operations that are routinely conducted on aircraft component parts and aircraft at the referenced Air Force maintenance facilities. The proposed concept is expected to reduce (1) the incidence of cleaning related failures, (2) the consumption of alkaline cleaner and acid skin brightening materials, and (3) the overall cost of cleaning all fighter and transport aircraft and related component parts for the Air Force by over $2.0 million/yr assuming a 10 percent reduction in the current cost of cleaning and inspection.

2.6 Navy Transition Plan

Although the plan described above emphasizes Air Force applications, similar Navy aircraft applications have been confirmed informally. In addition, there is a particular need to monitor removal of paint stripper (Peel-Away-7) from PCMS tiles prior to re-painting.

2.7 VCPI Chemicals Sourcing

The Re-Gel® Type IV alkaline cleaner is a MIL-PRF-87936 approved cleaner. This particular water-soluble cleaner is manufactured by B&B Tritech, Incorporated (NSN 6850-013-90-9453), and currently being used by the Air Force on off-aircraft component parts and/or full-sized aircraft at each of the three depots and numerous field sites. The thixotropic nature of the Type IV material, combined with the universal use of the product on aircraft airframe surfaces during the “wash-etch-alodine” surface preparation operations make it a good candidate medium for deploying the VCPI technology. Testing has validated chemical compatibility between the cleaner and the various dyes that are identified for aerospace application, and also the fact that a VCPI dye/cleaner material is easily removed during the T.O. 1-1-8 approved surface treatment operation. Specifically, laboratory-based systematic cleaning tests have confirmed an acceptable level of removal of any dye/contaminant residues on treated Al2024-T3 aluminum alloy structures as a result of the actual alkaline detergent cleaning step, a clean water rinse, the application and agitation of a MIL-PRF-38334 approved corrosion removal compound, a second water rinse, and then a final application of a MIL-C-5541 approved chromate conversion coating.

An incorporation of the VCPI technology into the current chemical conversion coating operation will not impact the required “flow time” of the aircraft or component part through the maintenance operation. VCPI dye-CA materials will also have only a minimal effect on the overall cost of the maintenance operation. No adverse environmental or health risks are expected as a result of process implementation.

Discussions with the President and Vice President of B&B Tritech, Inc. have resulted in a verbal agreement to support the VCPI implementation and commercialization efforts by modifying the basic formulation of the Re-Gel® product. Specifically, B&B Tritech will remove the florescent dye from the current formulation and add an agreed amount of the dye-CA candidate that has been selected for the targeted contaminants and substrates. This approach will eliminate the problems associated with any chemical mixing being performed by production personnel prior to or during the actual cleaning operation.

2.8 Commercialization Activity and Plans

Two commercial entities have expressed an interested in pursuing the VCPI technology in their operations, Boeing and B.F. Goodrich. Both organizations have offered to contribute to testing. Boeing has also offered to support testing at Battelle. These contacts are summarized below.

2.8.1 Boeing Aircraft

Contact: Paul H. Shelley, materials and process R & D, Boeing, 425-234-4171 (paul.h.shelley@boeing.com). Offered to participate in commercialization testing including preparation of test panels contaminated at standard reproducible levels in the range of 0.5-25.0 mg/ft^2. Also offered to supply funding. This funding was supplied in FY02 and testing is underway.

2.8.2 B.F. Goodrich

Contact: Ella Watson, Goodrich Corp., Chula Vista, CA 619-691-2780.

Need: Coloration of clear and colorless silicone films offered to provide a test site and contaminated parts, for example as a participant in " round robin testing".

3.0 PROJECT BACKGROUND

Cleaning operations are a critical element in the maintenance and repair of Department of Defense (DoD) and the Department of Energy (DOE) weapon systems. Current cleaning performance verification procedures are slow, expensive, and not normally suitable for real-time measurement. Under these circumstances, there usually is a tendency to overclean to reduce the frequency of failures associated with undercleaning. However, overcleaning consumes production time and capacity, thereby reducing process efficiency and increasing waste stream volume production and waste handling costs, which further increases production time and capacity, and increases process raw material costs. Therefore, SERDP has funded this and other related efforts to identify better means to monitor DoD and DOE weapon systems surface cleaning processes. This project successfully verified the VCPI concept, i.e. of using contaminant-selective dyes, which appear would meet ES&O requirements, to color surface contaminants, with minimal changes in the current cleaning protocols, so that cleaning operators can better use surface visual appearance to control the cleaning operation in real time. This VCPI technique is projected to reduce cleaning process waste volumes, production times, raw material consumption, and processing costs.

Therefore, a synergistic was assembled (Appendix B) specifically balanced to evaluate the broadly applicable VCPI concept for DoD applications, consisting of Battelle, the Air Force (AFRL), and the Navy (NSWC-Carderock).

4.0 OBJECTIVES

The objective of this 25-month investigation was to evaluate the VCPI concept as to its technical viability and potential efficacy for providing an operable real-time, whole surface cleaning performance verification method for DoD weapon systems applications, consisting of a dye-based technique.

Therefore, the project's specific objectives were the following:

- To identify significant Air Force and Navy surface contaminants and associated cleaning protocols (Task 1.1)
- To select candidate coupling agents (CA) and dyes systems (dye-CA) for evaluating the VCPI technique which provide good labeling performance, worker safety, accommodated by current waste treatment processing, and environmental compatibility (Tasks 1.2 and 1.3)
- To perform feasibility testing of the VCPI concept to determine whether the target contaminants can be selectively labeled with the dye-CA combinations. (Task 2)
- To perform systematic cleaning testing to quantify the performance of the VCPI technique (Task 3)
- To address SERDP's questions and issues regarding the technical viability, applicability, and candidate selection screening criteria of the concept (SERDP Action Items).
- To identify a commercialization path for the technology, summarized as a Transition Plan. (Task 4)

5.0 DESCRIPTION OF THE VCPI CONCEPT

The VCPI concept proposes to use a small amount of a visibly colored dye via a coupling agent (CA) with chemical and physical properties selected to attach the dye to particular classes of problem contaminants (Figure 5.1 and Table 5.1, Appendices A and B). By this means the targeted classes of contaminants are rendered visually apparent to production maintenance personnel in real-time, i.e., during cleaning operations. The dye-CA combination makes it possible to assess the presence, location, and approximate amount of contamination remaining on a surface being cleaned by simple visual observation during the cleaning operation. This capability allows the maintenance personnel to quickly and accurately control the cleaning operation in real-time and to focus the cleaning activity on areas where contamination is present.

This process control ability is expected to markedly reduce the amount of excessive cleaning, resulting in P2 benefits by reducing cleaning waste volumes. It is also expected to improve surface cleanliness by verifying complete surface cleanliness.

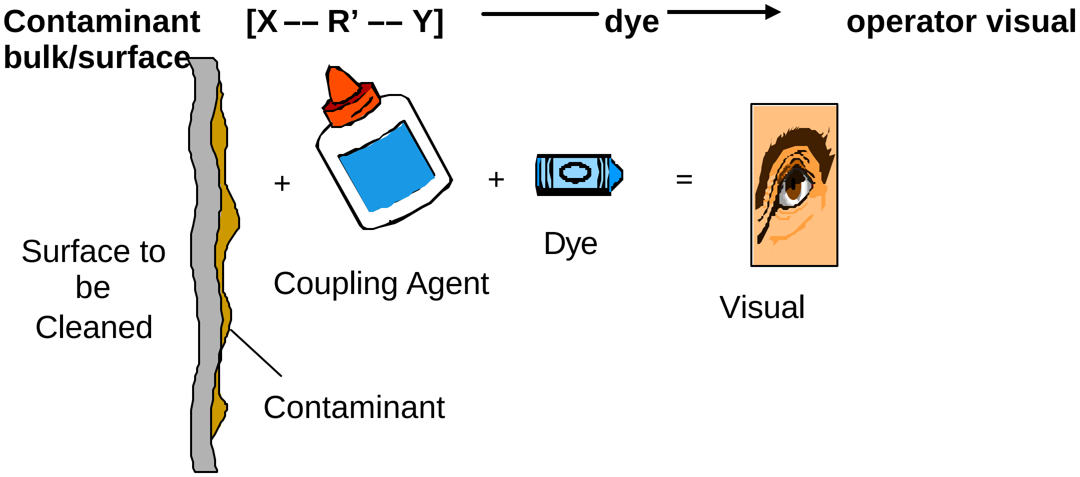


Figure 5.1 Visual Description of the VCPI Concept

Table 5.1 VCPI Technology Labeling Chemistry and Dye-CA Combinations with Contaminants

Contaminant/Dye-CA Labeling Chemistry Means	Contaminant Class/Examples
Solvation	Hydrophobic liquids, greases, oils, paint strippers, and porous polymers
Chelation	Metal Corrosion products
Ion Pairing	Corrosive Soluble "salt contamination"
Covalent Bonding	Adhesives and other solids

The VCPI method is intended to provide a qualitative output for field and depot use, but if desired, could be used to make quantitative measurements after calibration.

Detection limit and selectivity are critical features, and also, therefore, VCPI technology screening criteria. The dye must label the contaminant, but not the substrates (selectivity), and indicate the presence of contamination at problem levels, but not below (detection limit).

Benefits of the method are expected to be broadly applicable to DoD, DOE, and industrial applications, including variable/irregular-cleaning surfaces with respect to size, finish, and shape. By being incorporated into existing cleaning and/or rinse solutions, little, if any, new capital and minimal retraining of maintenance personnel will be necessary. The method should (a) reduce pollution, (b) reduce the costs associated with cleaning chemicals and labor, (c) improve the reliability of the overall cleaning operation, (d) increase the efficiency of normal cleaning operations, and thereby increasing the process throughput rate. The targeted VCPI technique is one that production personnel will be able to use with current skill levels without requiring sophisticated instrumentation or additional manpower.

6.0 TECHNICAL APPROACH

6.1 Project Tasks for VCPI Concept Evaluation as Applied to DoD Needs

As directed by SERDP in the SOW, the VCPI concept evaluation work focused specifically on DoD large area surface cleaning applications as this would result in the greatest P2 and cost savings and would have the broadest number of applications, covering both large and small surface area cleaning situations for both the DoD and DOE. Therefore, the PP-1117 project comprised the following four (4) tasks:

- Task 1 – Identification of Key DoD Cleaning Needs (Task 1.1, Appendix C), VCPI Dyes (Task 1.2), and Dye Coupling Agents (Task 1.3) with acceptable physical/chemical/environmental properties
- Task 2 – Experimental Down Selection of VCPI dye-CA candidates through Feasibility Testing of Environmentally Acceptable VCPI Candidates and Delivery Means. This task was accomplished in two (2) steps, prescreening cleaning tests (PCT) and systematic cleaning tests (SCT) (see Appendix).
- Task 3 – VCPI Concept Testing, Refinement, especially estimation of the means to use the technology within current DoD cleaning protocols (see Appendix).
- Task 4 – Transition Plan Development for deployment of the technology via field testing at the depots, etc. (Section 2.0).

6.2 VCPI Contaminant Labeling Dye-CA Selection Criteria

The fundamental approach for identifying and down selecting the containment labeling technology options was to select VCPI dye-CA chemical(s) for insertion into current DoD cleaning chemicals or operations (Appendix C) that would not significantly alter current cleaning or wastewater treatment protocols.

No additional capital equipment, analytical instrumentation, or significant operator re-training should be required to implement the technology. Environmental compatibility of waste treatment products and operator safety were paramount in the dye-CA selection criteria. It was expected that meeting such conditions would allow ready deployment of the technology. These dye-CA selections are provided in the Results (Section 7.0).

6.3 Technical Approach for Each Task

In Task 1, team members from AFRL and NSWCCD identified target surface contaminants and cleaning processes of importance to the Air Force and the Navy (Appendix C). Battelle utilized available literature and vendor information to identify and down select the candidate dye-CA materials for these cleaning processes and contaminants of concern (Section 7.0). In Task 2, AFRL and NSWCCD provided a range of test coupons and target contaminant samples to Battelle for preliminary methods development and laboratory screening of the VCPI concept, and then later for VCPI labeling of panels for systematic cleaning and material compatibility tests (Section 7.0, and Appendices A, D and E).

Results from these cleaning tests were discussed with the partners, SERDP, and cleaning chemicals vendors (Sections 2.0, 8 and 9) to arrive at final chemistry selection.

7.0 RESULTS

The data and results for the lab scale testing for the VCPI concept evaluation SERDP program No. PP-1117 are provided in this section and the associated Appendices. This information is organized according to Task Number (Section 6.0). This organization allows the substantial amount of information generated to flow in a coherent, indexable manner. For a summary of the key conclusions and recommendations the reader is referred to Sections 1.0, 2.0, and 9.0.

7.1 Selection of DoD Cleaning Needs and Associated Dye Labeling Technology Options (Task 1)

7.1.1 Identification of DoD Problem Contaminants and Associated MIL-SPEC Cleaning Operations (Subtask 1.1)

7.1.1.1 Identification of Key DoD Contaminants

This subtask was primarily addressed by the DoD partners (Appendix B). Although contaminant identification specifically targeted DoD large area weapons surfaces cleaning operations, as directed by SERDP, cleaning problems are very generic and so applicability to DOE needs and small parts cleaning at the depots are also expected. This focus was necessary to provide realistic cases with which to test the VCPI concept. The target focused on broad area cleaning problems, as per the proposal, so that the largest pollution generating operations with the most difficult cleanliness verification needs could be aided first.

Both AFRL and NSWCCD provided a listing of key DoD contaminants for the Air Force and the Navy, respectively. A summary of these contaminants and their sources is given in Table 7.1.1. Most of the contaminants are “self inflicted” problems as they are derived from valid MIL-SPEC materials which provide certain weapon systems with in-service performance, such as lubrication, but then need to be removed in cleaning operations for maintenance purposes, such as scheduled cleaning or prior to surface re-finishing activities. Examples of such contaminant materials are hydraulic fluids, lubricating oils, fuels, greases, adhesives, degreasers, paint strippers, and sealants. Metal corrosion products and certain environmentally derived contaminants, soluble corrosive salts, e.g., chloride ion from seawater, are also problem contaminants. The list for the Navy, was selected from a much larger one provided by NSWCCD. Those listed in Table 7.1.1 represent 95% of the volume of the problem contaminants. Actual contaminating product formulations are usually proprietary. However, except for solid contaminants, e.g., certain caulks and adhesives, it was desirable to search for a robust VCPI technique so that precise chemical structures would not be required for using the VCPI technique, as this would translate into field use difficulty. This simplification is possible since, as will be shown, it is believed that in the other cases, a match between general physical/chemical properties of the VCPI dye system is all that is needed, rather than selective covalent chemical bonding.

Table 7.1.1 Key DoD Weapon System Surface Contaminants

MIL Spec No.	Description	VCPI Chemical Property Type
Air Force		
MIL-R-81294	Paint Remover	Hydrophobic Liquid
MIL-DTL-83133	JP-8 Shell Turbine Fuel	Hydrophobic Liquid
MIL-PRF-83282	Hydraulic Fluid	Hydrophobic Liquid
MIL-H-5606	Hydraulic Fluid	Hydrophobic Liquid
MIL-PRF-23699	Lubricating Oil, ACFT	Hydrophobic Liquid
MIL-G-81827	Grease	Hydrophobic Paste
MIL-G-21164	Grease (MoS2)	Hydrophobic Paste
MIL-G-23549	Grease (General Purpose)	Hydrophobic Paste
MIL-S-8660	Silicone Compound	Hydrophobic Porous Polymer
MIL-A-85705	Adhesive	Polymer (polymethyl cyanoacrylate)
MIL-S-81733	Sealing and Coating Compound	Hydrophobic Polysulfide Rubbers
--	Corrosion Products	Metal Oxides/Hydroxides
--	Residual Salts	Water-soluble Salts
Navy		
MIL-L-17331	Lubricating Oil, Steam Turbine	Hydrophobic Liquid
MIL-L-9000	Lubricating Oil, Engine	Hydrophobic Liquid
MIL-L-2105	Lubricating Oil, Gear	Hydrophobic Liquid
MIL-H-17672	Hydraulic Fluid	Hydrophobic Liquid
MIL-A-907	Antiseize Compound	Hydrophobic Paste
MIL-PRF-23699	Lubricating Oil, Aircraft	Hydrophobic Liquid
MIL-H-5606	Hydraulic Fluid	Hydrophobic Liquid
DoD-G-24508	Grease, Ball and Roller	Hydrophobic Paste
MIL-G-23549	Grease, General Purpose	Hydrophobic Paste
MIL-G-24139	Grease, General Purpose	Hydrophobic Paste
MIL-G-18458	Grease, Wire Rope-Exposed Gear	Hydrophobic Paste
MIL-G-23827	Grease, Airport	Hydrophobic Paste
MIL-G-21164	Grease, Molybdenum	Hydrophobic Paste
MIL-S-8660	Silicone Compound	Hydrophobic Porous Polymer
MIL-S-45180	Sealing Compound	Hydrophobic Liquid
--	Corrosion Products	Metal Oxides/Hydroxides
--	Residual Salts	Water-soluble Salts

NOTE: Specs in bold are shared by Air Force and Navy

The contaminants listed in Table 7.1.1 fall into only three (3) broad categories with respect to the chemistry of VCPI technique (Table 7.1.2).

Table 7.1.2 Major DoD Weapons Systems Contaminant Types

Contaminant Type	Contaminants included under the Contaminant Type Classification
I	Hydrophobic fluids such as oils, hydraulic fluids, fuels, and greases (where greases are considered fluids in the present context since they represent a composition of hydrophobic mobile, low molecular weight materials in a paste physical state).
II	Water-soluble corrosive salts, e.g., seawater residue containing corrosive chloride ion.
III	Solids, such as aluminum corrosion products, passivating conversion coatings, and hydrophobic paints, rubbers, adhesives, etc.

Hence, only three (3) dye-CA chemistries appear to be required (see below) for labeling a broad range of contaminants. This encouraging result promises to simplify commercialization of the VCPI technique and allow its application to a broad range of cleaning operations.

7.1.1.2 Description of DoD Cleaning Problems, and Selection of Cleaner and Cleaning Process Test Candidates

Cleaning process specifications are important for the proper selection of VCPI systems (Subtasks 1.2 and 1.3) for two reasons. First, it is the cleaner that removes the contaminant and, in an effective VCPI system, the dye plus contaminant complex need to be removed by this cleaner simultaneously, and, as contaminant alone as not all of the contaminant molecules will be labeled with dye as this would be a needless excessive use of dye. Hence, the physical-chemical properties of the dye-contaminant complex must also match those needed for co-removal with the contaminant alone. Second, in labeling the contaminant with the dye, minimal changes from current cleaning operations were targeted. Hence, incorporating the dye into the current cleaning chemicals is the preferred approach for the VCPI technology. These VCPI "delivery vehicles" could be incorporated into the water, solvent, one of the aqueous cleaners, or strippers used in the cleaning process. As will be shown below, all of these delivery vehicle candidates were found to be efficacious with respect to cleaning process introduction.

7.1.1.2.1 Air Force – Aircraft Cleaning Needs

Good prepaint surface pretreatment at Air Force depots is essential for adequate paint coating, conversion coating formation, and sealant adhesion to provide protection against corrosion. It has proven impossible to eliminate hydrophobic fluid leaks in aircraft and so there are always areas contaminated with a combination of these fluids, oils, greases, and fuel. The most common contaminants found in aircraft depot maintenance and field operations are described in Table 7.1.3 for two weapon systems examples.

Table 7.1.3 Large Area Cleaning of Two Types of U.S. Air Force Aircraft and Associated Contaminants

Weapons System and Location:	F-16 Hill AFB	KC-135 Tinker AFB
Contaminants:	Hydraulic fluid Lubricating oil Fuel Exhaust deposits Some gun blast residues Petroleum gel Hot glue residues Tape residues PMB media residues	Hydraulic fluid Lubricating oil Fuel Chemical stripper residues Exhaust deposits Tape residues
Contaminant Locations:	Belly, lower fuselage, lower wing, gun muzzle areas, around seams prepped for PMB depaint	Belly, lower fuselage and lower wing surfaces
Cleaners:	B&B Re-Gel® MIL-PRF-87937B, Type III	ALK 660 MIL-PRF-87937B, Type II

As mentioned, these contaminants must be removed prior to application of pretreatment chemicals, sealants and coatings, or coating adhesion and corrosion problems will result. The belly and lower surfaces of the wings and horizontal stabilizers are the most likely areas to be contaminated. The water break test, designed to identify areas that are not clean of hydrophobic contaminants, is less effective in revealing contamination on these lower surfaces.

In Air Force field operations, aircraft made of either metal alloy (Al2024-T4) or often painted surfaces) must be washed at a frequency dictated by T.O. 1-1-691, Aircraft Weapons Systems Cleaning and Corrosion Control (Appendix C), to remove hydrophobic contaminants, corrosive water-soluble salts, and other contaminants that could facilitate corrosion attack.

To focus this project on large area cleaning operations, the contaminants of importance on F-16 and KC-130 aircraft, summarized in Table 7.3, were examined. The selected weapons systems (a fighter and a fuel transport) each identify specific DoD cleaning needs. Additional information in Table 7.3 includes an identification of commercial cleaners used for these aircraft at their respective depots. Since the MIL-SPEC Qualified Product List (QPL) often allows a large number of commercial products to be used, actual cleaner products in use at the ALC's, which conform to the Military Specifications vary. Barring any unexpected major chemistry differences, it is expected that one or more of the MIL-SPEC cleaners will serve as the vehicle in which the VCPI system enters the cleaning process. Therefore, the selection of a specific entry point and cleaner/contaminant combinations were identified through testing as described later in this section.

7.1.1.2.2 Navy – Cleaning Needs

For the Navy, the importance of cleanliness is realized in the area of Passive Countermeasures System (PCMS) materials, (essentially foam rubber tiles) that are applied to a substantial portion of the ship superstructure on several combatant class ships (Appendix C). Surface cleaning of the metal substrate to which the tiles are bonded (paint primed steel) is required to insure tile adhesion. Current cleaning procedures involve the use of fresh water rinse to remove water-soluble contaminants (e.g., salts from sea water) and PF Degreaser to remove oils and greases. Also used during maintenance procedures are 50/50 mixtures of isopropyl alcohol and water, and general purpose detergent. The VCPI technique under study is expected to afford volume reduction of wastes generated from these operations.

Figure 7.1.1 provides a summary of Naval cleaning needs regarding the PCMS foam tile material before and after installation. Three cleaning completion assessment points are indicated in the Figure (as VCPI test points #1, #2, and #3). Three test contaminants are involved; grease (G), soluble corrosive salts [seawater resides (SW)] and paint stripper [Peel Away® 7 (PA7)]. These areas were addressed in the VCPI concept evaluation tests.

7.1.2 Selection of Dyes and Coupling Agents (Subtasks 1.2 and 1.3)

As previously delineated, there are numerous requirements for the functionality for the dye-CA candidates. Several of these are described in the following sections, especially worker safety and health, and environmental impact/waste treatment. However, in addition to these requirements, the dye-CA candidate must be effective for the intended application. Also it was outside the scope (and unnecessary) for the team to consider the development of new dyes and CA's. Therefore, the selection of dye-CA candidates maximized the use of currently commercially available materials using known formulation science (Appendix A).

7.1.2.1 Identification of Dye-CA Candidates with Good Environmental, Safety and Occupational (ES&O) Records

Considering the physical and chemical properties of the contaminants identified in Subtask 1.1, various labeling chemical mechanisms were examined (Appendix A) and a strategy was devised for selecting suitable dye-CA test materials (Figure 7.1.2). In addition, dyes were selected that possessed the chemical reactivity and physical properties (Table 7.1.4) to provide the contaminant labeling mechanisms needed. During this down selection, efforts were made to identify the dye-CA materials that are in widespread use in consumer products, especially foods and cosmetics, including those that are naturally available with the objective of selecting dye-CA systems with acceptable health and environmental records (i.e., to meet ES&O requirements**,** Table 7.1.4). As shown in Table 7.1.4, the pertinent environmental compatibility and toxicity information was gathered from a wide range of sources designed to be a comprehensive compilation of the available ecotox data.

7.1.2.2 Down Selection of Dye-CA Candidates

As mentioned previously, the selected commercially available dyes (see above), which in all cases included attached coupling agents as supplied from the manufacturer, were selected by first compiling a computerized database on these materials using literature and vendor information on the chemical and physical properties, and on their safety and environmental compatibility. The categories of data analyzed are listed in Table 7.1.4.

The dye-CA database review and analysis produced some 250 materials, most of which were dyes with CAs already attached. About 45 of these were selected as appearing functional as possible VCPI systems based on the mechanisms given previously (Appendix A). Seven of these dyes were selected based on the above criteria for screening in Task 2. These seven candidates are listed in Table 7.1.5. Also listed in Table 7.1.5 are the possible means for dye delivery into the cleaning process (VCPI Technique Utilization). All seven of these dyes already contain the CA property.

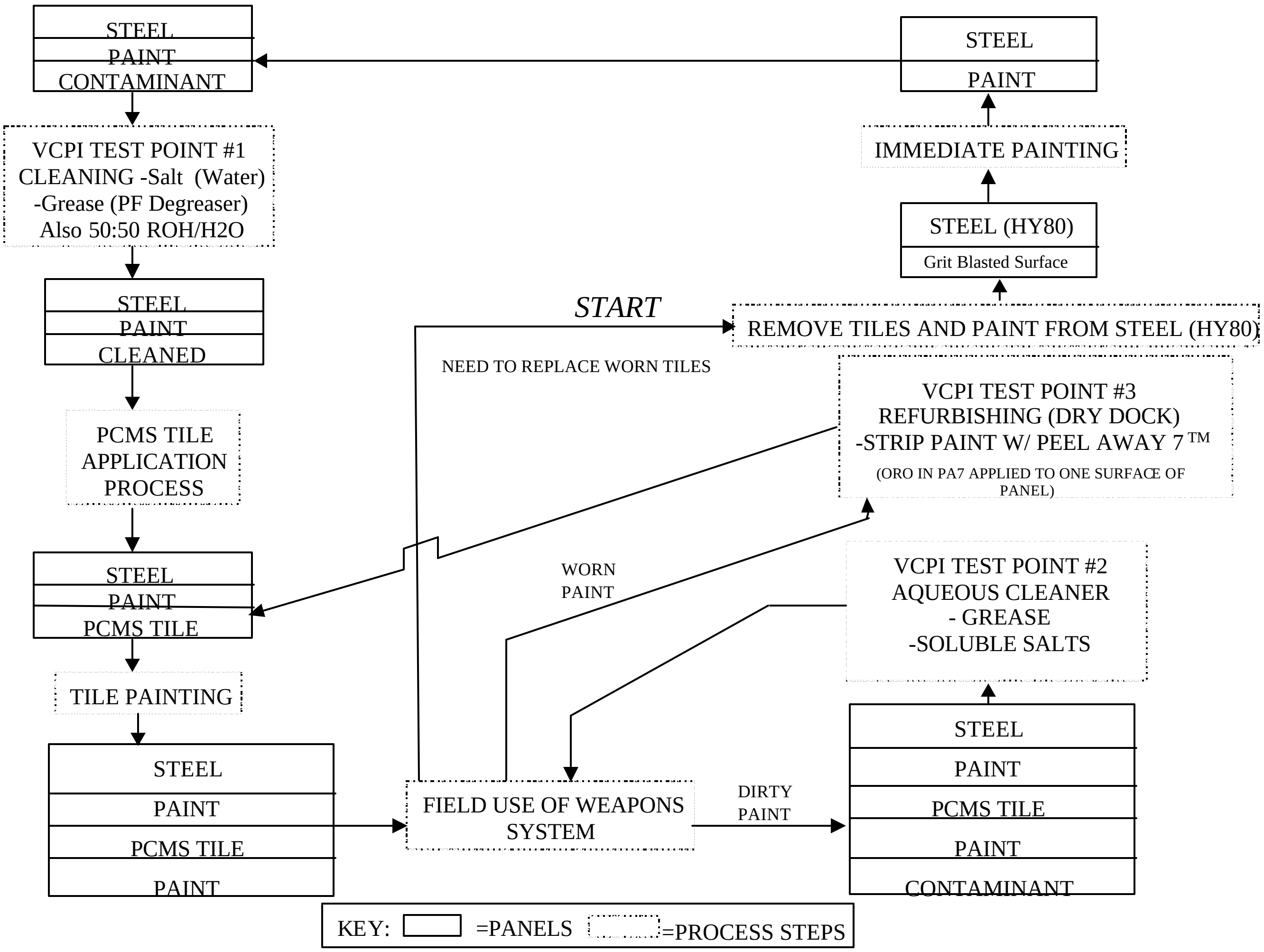


Figure 7.1.1 VCPI Test Points in Navy PCMS Tile Application (Stacked rectangles designate weapon system surface and associated coatings)

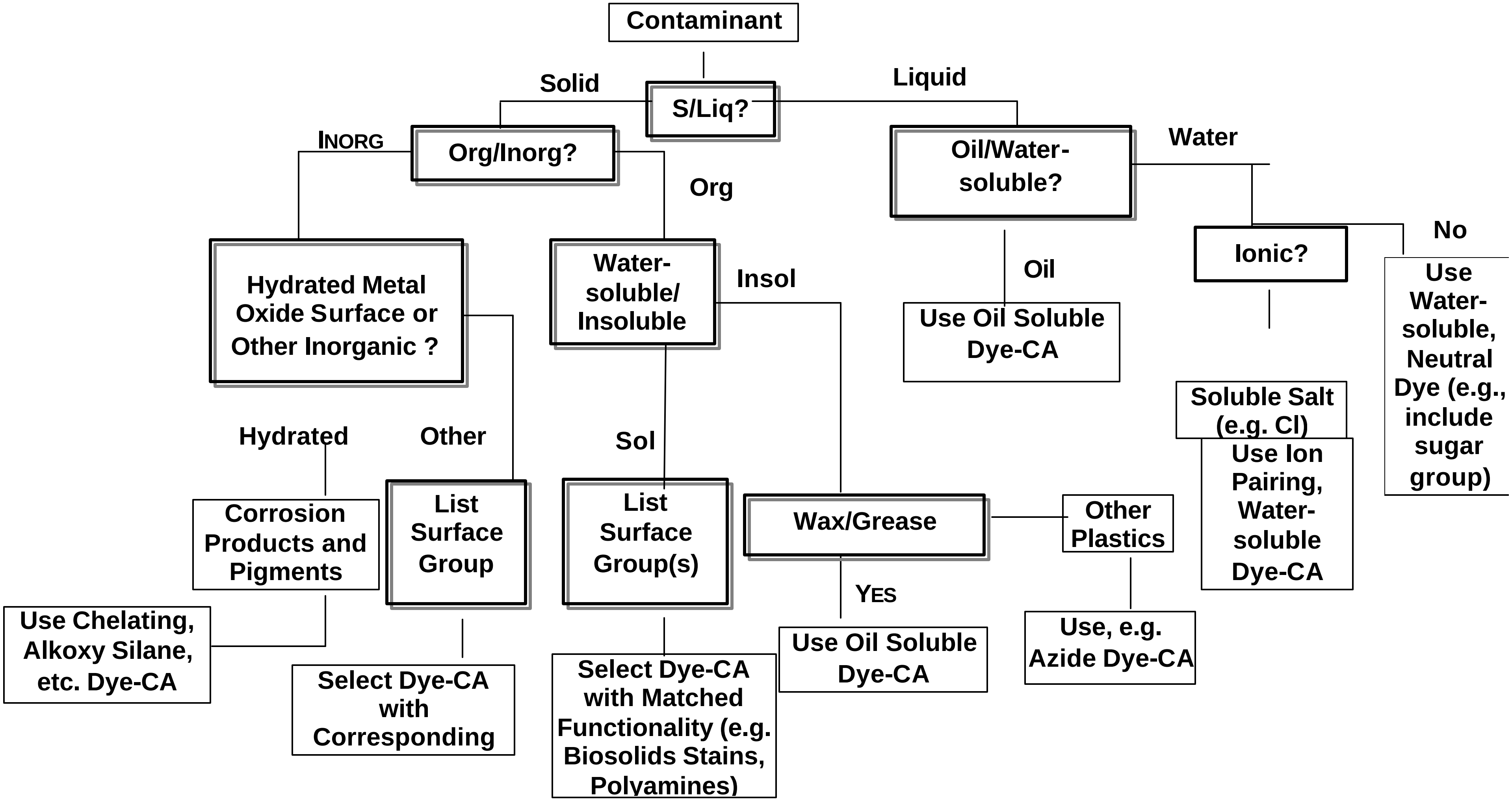


Figure 7.1.2 Dye-CA/Contaminant Selection Decision Tree for VCPI. Table 7.1.5 contains dye-CA candidates.

Table 7.1.4 Dye-CA Database Component Summary

Dye Designation	Chemical and Physical Property Description	Toxicity Information Sources/Criteria 1-15
FDA Official Name	Dye Chemical Class	MSDS Information
C.I. Constitution No.	Dye Phys/Chem Class	NTP Data Available
CAS Number	Wavelength Maxima	Appears in NTP database
Dye Application Name	Molar Absorbitivities	Appears in 40 CFR 261
C.I. Generic Name	Structural Formula	Conformation to MIL-C-87937B Sec 3
	Visual Color	Toxicity Data
	C.I. Data on Uses	Food Product Examples
	Lab Sample Source	Toxicity Assessment/ Summary/Information Needs

C.I. = Color Index

Table 7.1.5 Dye-CA Combinations Selected for Screening

Contaminant Type	Candidate Dye-CA Combination	Suggested Cleaning Process Delivery Means	CAS No.
Hydrophobic Liquids	Oil Red O D&C Violet 2 (Backup)	Solvent Wipe Aqueous Cleaner	1320-06-5 81-48-1
Corrosion Products	Natural Red 4 (Carminic Acid) Alizarin (Backup)	Aqueous Rinse Solvent Wipe Aqueous Cleaner	1260-17-9 72-48-0
Water-Soluble Salts	Food Blue 2 Food Green 3 (Backup) Basic Blue 3 (Backup)	Aqueous Rinse Aqueous Cleaner	3844-45-9 2353-45-9 33203-82-6

7.1.2.3 Potential Environmental Impact of Proposed Dyes

VCPI technology acceptance in the field relies heavily on good safety, waste treatment, and environmental attributes. Therefore, the candidate dyes (with attached CAs or dye-CA) were selected on the basis of contaminant labeling capability as well as good potential safety and environmental performance.

Until the technology is accepted by the end user via results at the depot pilot/field trial level, the final selection of dye-CA candidates cannot be made, hence back-up dye-CA systems are supplied in Table 7.1.5. The candidates listed in Table 7.1.5, selected using the process of Figure 7.1.2, appear to meet the requirements known to date for ecotox and performance. These cleaning test results have demonstrated that these compounds supply the needed level of efficacy at the lab scale in panel testing, which is the first step to gaining acceptance. The performance of these materials was examined in systematic cleaning tests (see below).

To help insure ES&O acceptability, candidate dye-CA combinations chosen for this testing were selected from dyes already in use in consumer products such as foods, cosmetics, drugs, hydraulic fluids, and clothing. Therefore, these dyes are already a component of municipal and industrial wastewater streams. The dye industry has invested decades of effort (since the 1950's) addressing the safety and environmental issues around the use of dyes. This information relating dye chemical structures to environmental and toxicological properties was gathered as part of Tasks 1.2 and 1.3 (Table 7.1.4). From these lists, a preliminary short list of dyes-CA candidates were selected (Table 7.1.5) based on DoD cleaning needs information derived in Task 1.1 (Section 7.1.1.2). In this project, the first choice dyes have gone through preliminary-validation pre-screening and systematic laboratory tests using the key contaminants (see above). Note that Natural Red 4 (NR4 or carminic acid), displaced Alizarin dye-CA as the indicator for corrosion products in order to match the low pH of process T.O.1-1-691.

The literature[1-15] in Table 7.1.4 was utilized to determine the environmental compatibility and toxicity of each dye-CA candidate from two perspectives. First, whether a specific dye is specifically called out on any of the major listings given in Table 7.1.4 as having an ecotox problem. Second, Battelle's ES&H Group performed additional and independent reviews of the available literature, including those referred to above as well as MSDS's, the Hazardous Substances Data Bank (HSDB), Registry of Toxic Effects (RETECS), Toxic Substances Control Act (TSCA) reports, etc. for the six dye-CA combinations. These results indicate that all of the current dye-CA candidates (Table 7.1.5), except one, are totally absent from these lists, and meet the DoD safety and environmental compatibility selection criteria. Only D&C Violet No. 2, which is a backup selection, appears on the National Toxicology Program (NTP) list and in the HSDB. However, candidate D& C Violet 2 by definition is cleared for use in drugs and cosmetics, and is therefore cleared by the FDA for limited human consumption (dyes are often present at low *percent* levels in pills), and skin contact (cosmetics). Oil Red O, selected for hydrophobic contaminant labeling, by far the most major DoD contaminant class is already in widespread use as a hydraulic fluid colorant.

The two food dyes in Table 7.1.5 are not reported to cause any health hazards. Similarly, Alizarin, a dye, which has been in use for many years, appears clean of health and environmental problems. Due to its criticality, the ecotox evaluation for the dye-CA systems under testing should be re-addressed at each stage of VCPI technology development and deployment. Natural Red 4, extracted from natural sources (by definition) is used to color candies and other foods bright red and appear also to not have any ecotox concerns.

The proposed usage level for dyes in VCPI systems is low, e.g., 0.02-0.05 percent since such levels are used in dyed commercial products. However, note that most of the available ecotox data pertains to ~100% pure materials. In considering organic dyes as 100% pure materials for health effects, according to the HSDB, "in general dyes and pigments do not present serious toxic hazards to workmen in conditions of industrial exposure". "Probably the greatest problem in workmen handling dyes is …superficial layers of skin become dyed". Therefore, the personal body protection used in DoD cleaning operations (MIL-PRF-87937C and T.O. 1-1-691) is expected to represent sufficient worker safety protection.

A significant step in the dye-CA selection process was the assessment of the proposed test system by the DoD staff delineated in the proposal for this purpose. A packet of information for these organizations was circulated. Comments covering safety, operability, and environmental impact were all positive and an informal list of questions to address during field trials was collected.

Although the assessment of the safety and environmental impact of the candidate dyes will continue, the results collected during this program regarding the necessary environmental compatibility and safety requirements for inclusion into DoD cleaning operations are encouraging and warrant proceeding with VCPI technology development.

7.1.3 VCPI Concept Feasibility Testing (Subtask 2.1)

The objective of this subtask was to *pre-screen* the VCPI candidates in the laboratory for contaminant labeling efficacy and to identify these labeling procedures. These tests results (Appendices D and E) provided the conditions used for the cleaning tests to follow. The materials, analytical methods, and VCPI test results used to accomplish this pre-screening are described in Appendices D and E.

Based on preliminary laboratory screening tests, the VCPI method has the potential to:

1. Be a simple and cost-effective, real-time cleaning verification technique
2. Require only a few (~3) VCPI systems to cover a broad range of surface contaminants on weapon systems of interest to DoD
3. Use already commercially available VCPI (dye-CA) candidates for selective labeling of the target classes of contaminants.

7.2 Cleaning Test Results

Pre-screening cleaning tests were run to verify labeling techniques and cleaning protocols prior to running the detailed systematic cleaning tests as described below. This approach allowed the most efficient use of resources while providing the most definitive and highest quality results.

7.2.1 VCPI Concept *Pre-screen* Cleaning Test (PCT) Results

In preparation for *Systematic* Cleaning Screening Testing (SCT) (see below), a series of *Pre-screening* Cleaning Tests (PCT) were run to set test parameters and to establish analytical methodology prior to performing the extensive detailed SCTs. This approach involved all team members and substantially improved the odds of success in the follow-on extensive SCT testing, which would consume significant resources and be fairly inflexible due to the level of planning, time consumed, number of people involved, and complicated logistics. Pre-screening bridged the lab-based knowledge base between the detailed literature-based selection of materials and chemistries (Appendix A) and detailed SCT (Appendix E). The SCT results are provided in the following section and Appendix E.

With the dye contaminant labeling chemistry already demonstrated, the objectives for the PCT were to verify that:

1. The dye and contaminant track each other through the critical step of a pertinent cleaning operation
2. The visual appearance of dyed panel surfaces is sufficient for visually following the cleaning process
3. The dye must selectively label the contaminant and not the cleaned or uncontaminated panel surface.

Representative cases from each substrate material, contaminant class and dye were selected from Table 7.2.1 for pre-screening. These tests included hydrophobic labeling and solvent cleaning of Al2024P, aqueous-based PCT results, and water-soluble corrosive salts and corrosion products. These results will now be presented.

Table 7.2.1 Test Systems Subjected to Pre-screen Cleaning Testing (PCT)

Component	Shorthand Designation
Contaminant	
▪ LO (repeated without CH2Cl2, used EtOAc for application and as NVR solvent and also applied neat)	• LO
▪ Grease (used hexane or esp. toluene for application and as NVR solvent)	• G
▪ Corrosion Products on Al2024 (5% neutral salt spray)	• C
▪ Soluble Salts (seawater residue)	• SW
▪ Peel Away® 7 Paint Stripper	• PA7
Dyes Used	
▪ ORO	▪ ORO
▪ Food Green 3	▪ FG3
▪ Alizarin	▪ ALZ
▪ Natural Red 4 (Carminic Acid)	▪ NR4 (or CAR)
Panel Materials	
▪ Al2024 Painted	▪ Al2024P
▪ Al2024 Alloy	▪ Al2024
▪ FeHY80 Painted	▪ FeHY80P
▪ Painted PCMS Foam Tiles	▪ TP

7.2.1.1 Hydrophobic Fluid Labeling Evaluation (Al2024-LO-ORO and Al2024P-G-ORO)

Figures 7.2.1.1 and 7.2.1.2 show PCT results for LO and G on Al2024P panels, respectively. The data shown are the UV/VIS spectra of the used cleaning baths and rinses (see Appendix D and E for specific experimental conditions). Previously, it was shown that the paint absorbs LO contaminant and dye when the contaminant is applied as a solution in a solvent. As both of these plots show, the dye is removed from the Al2024P surface in proportion to cleaning time. Importantly, the dye removal rate parallels the contaminant removal rate (see NVR data Figure 7.2.1.3). The slow rate of removal reflects the minimal mixing used and the tendency for hydrophobic contaminants (in this case G) to absorb into the paint.

This sorption effect was also noticed with the LO contaminant. Hence, since hydrophobic contaminants in the field appear as neat materials and not as solutions in solvents, hydrophobic contaminants hence were applied as heat materials for the SCT work. Though using neat contaminant materials does not remove the possibility that grease and oils will penetrate into paint pores, it does remove a potential artificial effect due to solvent penetration from the VCPI testing. Figures 7.2.1.1 and 7.2.1.2 also provide information on the absolute values that are involved in testing, i.e., for cleaning bath absorbencies [0.01 ~ 0.13 absorbance units (AU)], for color space readings [~0-5 (da*)] and for surface contamination levels (20 – 130 mg/ft3). These three plots also demonstrate that *quantification of contamination may be possible using the VCPI* technique, as numerical values can be placed on the surface color and contaminant levels with good precision. This quantification aspect was one request for the technology from the original SERDP SOW. Importantly, as Figure 7.2.1.2 illustrates, the desorbed

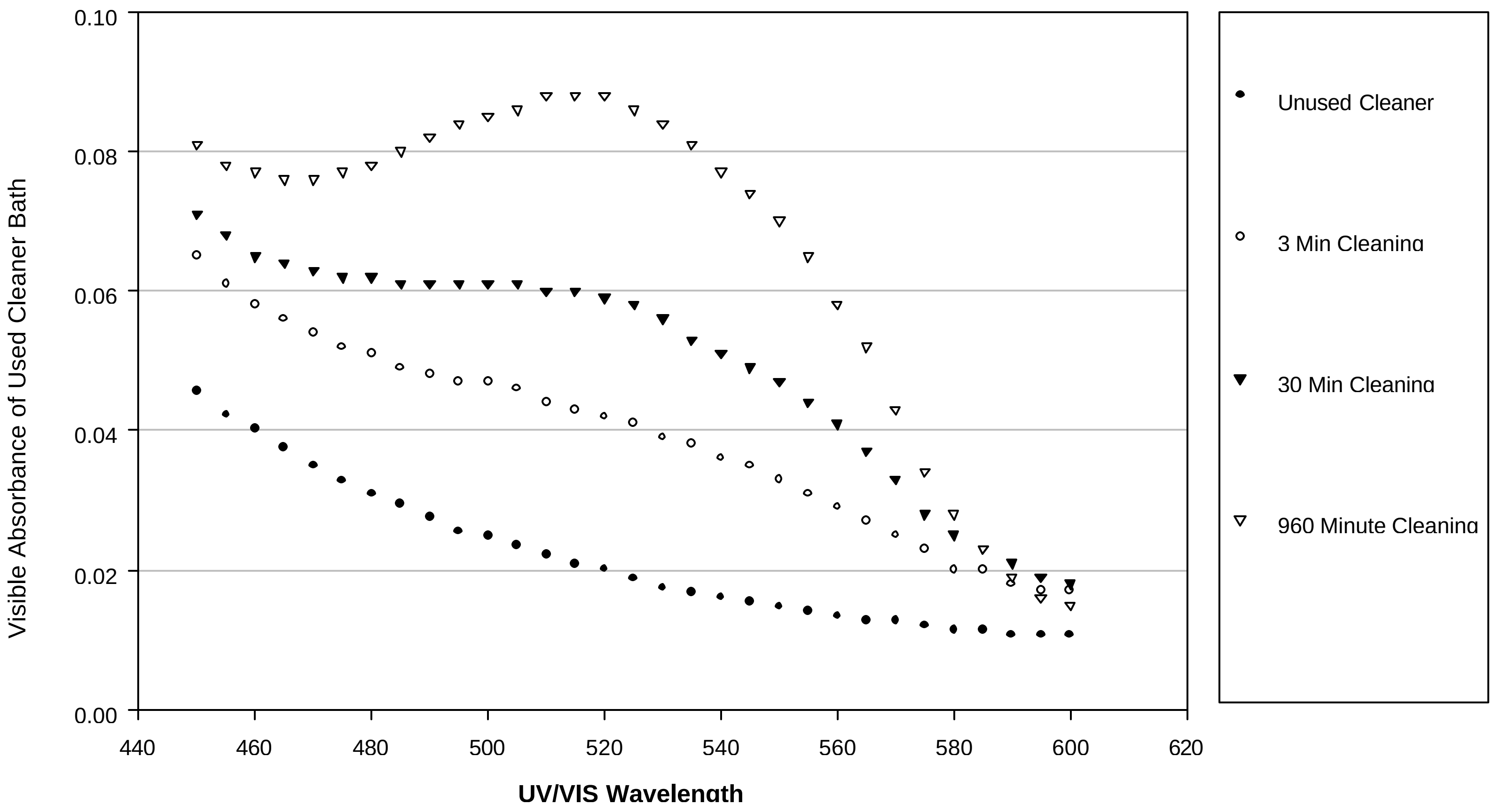


Figure 7.2.1.1 Aqueous cleaning of Al2024P-LO-ORO shows accumulation of ORO dye in aqueous cleaner (MIL-PRF-87937C, Type II) with soak time. Actual field cleaning operations involve scrubbing which dramatically shortened the time. However, in evaluating the VCPI technique at the lab scale it is necessary that cleaning is slow enough so that co-removal of dye with contaminant is continued.

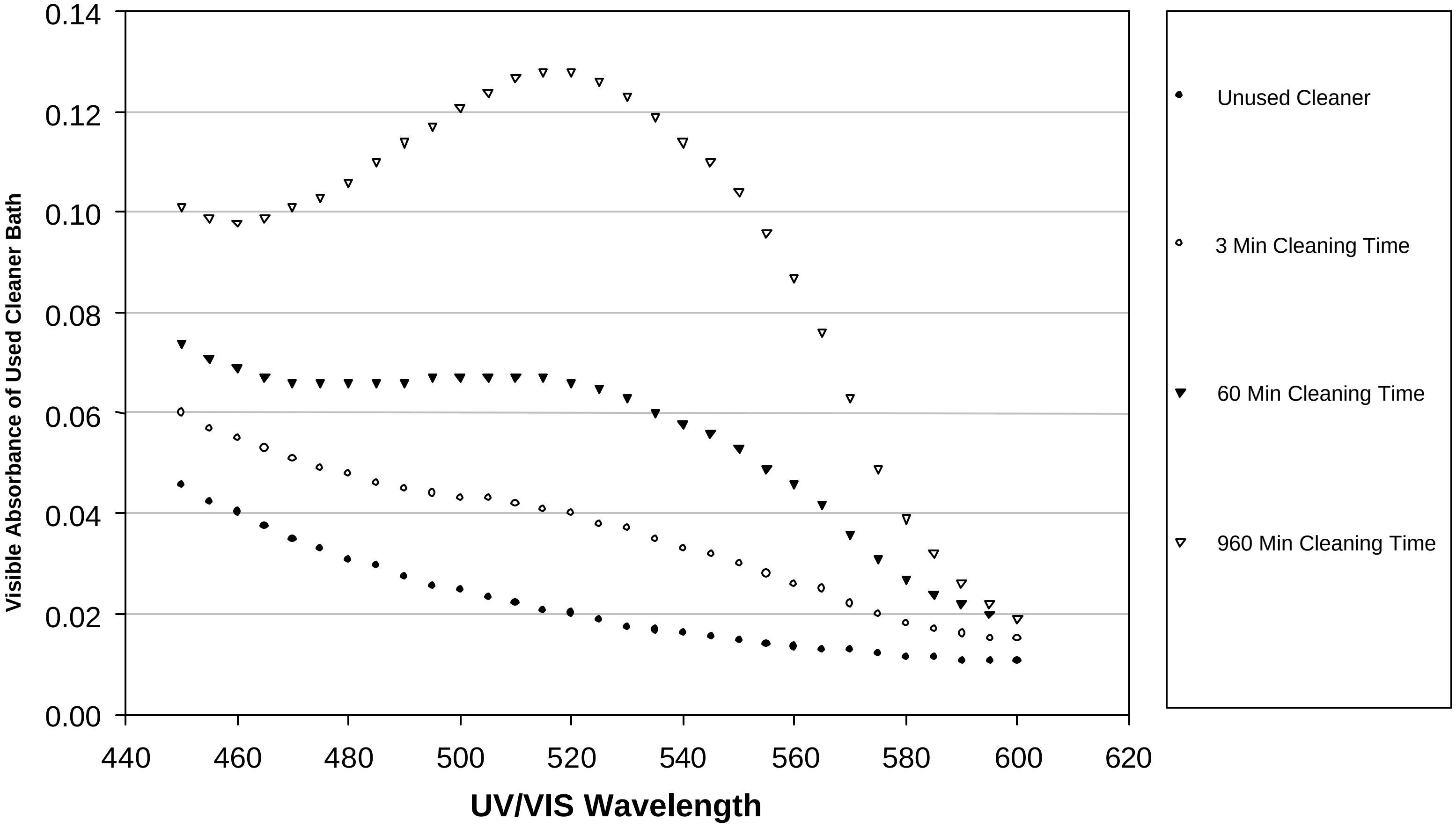


Figure 7.2.1.2 Aqueous cleaning of Al2024P-G-ORO shows accumulation of ORO dye in aqueous cleaner (MIL-PRF-87937C, Type II) with soak time. Actual field cleaning operations involve scrubbing which dramatically shortened the time. However, in evaluating the VCPI technique at the lab scale it is necessary that cleaning is slow enough so that co-removal of dye with contaminant is continued.

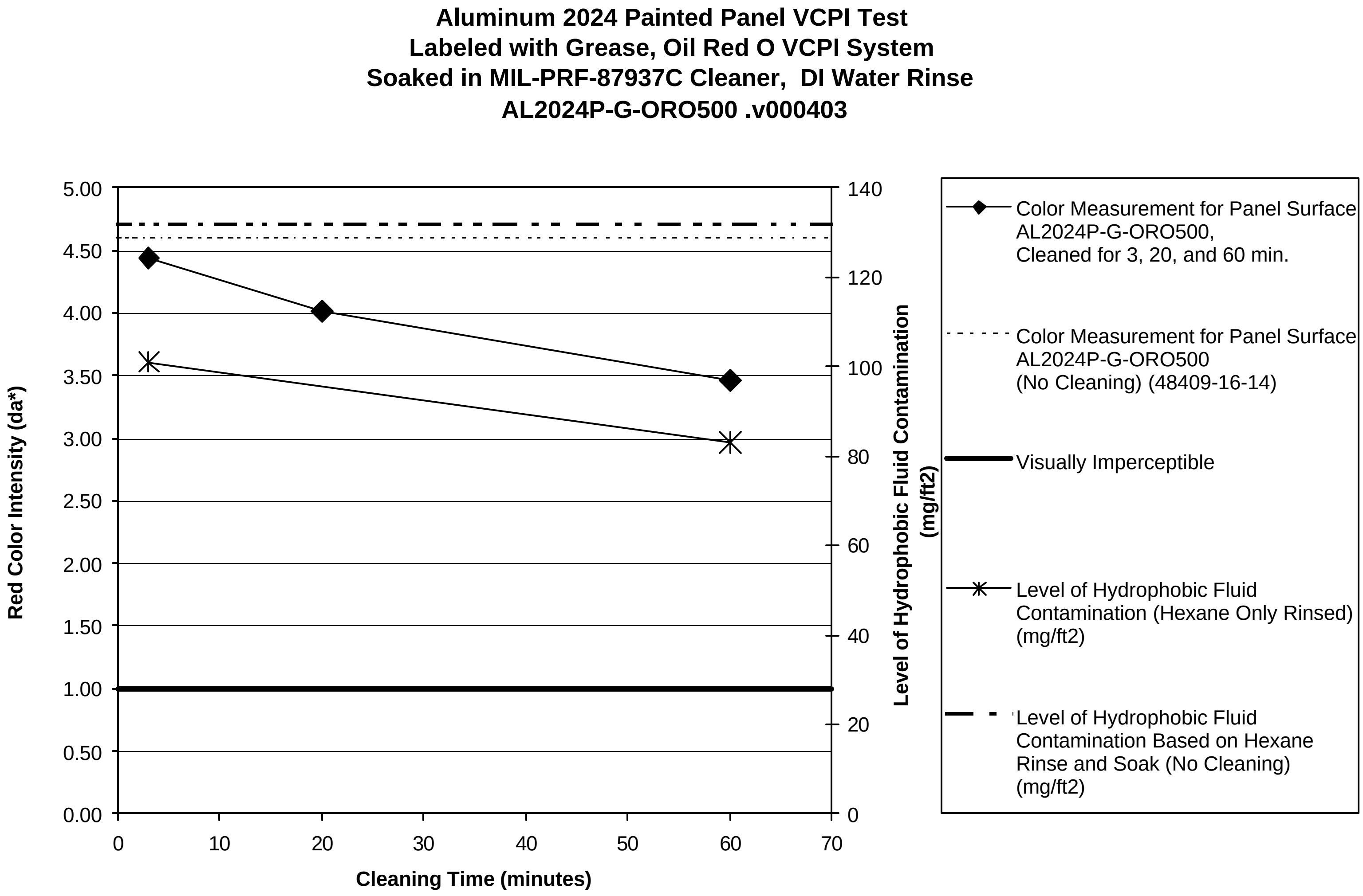

Aluminum 2024 Painted Panel VCPI Test
Labeled with Grease, Oil Red O VCPI System
Soaked in MIL-PRF-87937C Cleaner, DI Water Rinse
AL2024P-G-ORO500 .v000403

Figure 7.2.1.3 Hydrophobic Fluid Cleaning of Al2024P-G-ORO with MIL-PRF-87937C Type II Aqueous Cleaner. Illustrates qualitatively that the dye (diamond-red color intensity, da*) and grease contaminant (*) removed at the same rate, i.e., together, during the cleaning operation. Also illustrates typical levels of contaminant utilized in this testing (i.e., ~ 80-100 mg/ft^2)

spectral changes are well within the visual differentiation range to allow real time process monitoring by visual observation.

7.2.1.2 Evaluation of the Effect of Weathering on the Capability of VCPI Labeling

7.2.1.2.1 Visualization of Hydrophobic Fluid Contaminants

Figure 7.2.1.4 is color space data for Al2024P panel surfaces that received varying simulated weathering exposure to Xenon Arc UV radiation for up to 10 weeks. In agreement with visual observation, color space analysis shows that a general yellowing of the paint surface color occurs (bottom line), increasing with UV exposure time. However, this color change is small and is not large enough to interfere with the VCPI measurement parameters. All reference (non-dyed) surface changes were visually imperceptible (below the thick solid line in the figure), while the dye labeled surfaces were easily visually apparent, with da* values of 1.7-6.3. Note that the "cleaning" method used for this test was solvent stripping for labeled panels and aqueous-based for unlabeled panels. The aqueous-based cleaning method more closely represents the SCT methods. Importantly, the thoroughly cleaned labeled and reference (unlabeled) panels have the same color space with panel aging pattern despite the different cleaning methods used. The internal consistency within the two groups of data qualitatively illustrates that the applicability of the VCPI technique is not dependent upon the cleaning method used, although this conclusion needs to be re-examined with each major change in cleaning process. The solvent cleaning again showed a marked dependence on the strength of the solvent regardless of the UV panel aging time, the usual TCTFE solvent being far poorer than EtOAc solvent. Additional data on this aged-panel system is given in the next section.

7.2.1.2.2 Soluble Salt Evaluation

Figure 7.2.1.6 shows that soluble salts (as seawater residue) can be rendered visually apparent by using FG3 VCPI label in that the observed green color (-da*) lies well above the "visually apparent" cut off of ~0.5-1.0 (as -da*). These PCTs were performed by allowing seawater containing FG3 dye to dry on Al2024P panels. The data also illustrate that soluble salts are easily and quickly removed by water rinsing, as the initial green color of the surface drops from a –da* value of 4 to ~ 0 in the first quick wash. Note that chloride ion analyses of used cleaner baths from systematic testing are needed to support this conclusion. These results are supported by the fact that the FG3 dye just as rapidly reports to the cleaning bath (Figure 7.2.1.7). Equivalent results are obtained when aqueous cleaner is used, as expected for such highly water-soluble salts.

In conclusion, for soluble salts, it appears that a good use for the VCPI technique would be to provide the cleaning technician with "hit or miss" information, i.e., the surface to be cleaned could first be rinsed with a dye labeling solution until the entire surface has a green color, then the surface is washed until all the color has been removed. The simplicity of such a process is the desirable result being sought by the VCPI program.

7.2.1.3 Preliminary Estimate of Dye Use Level Required for the VCPI Technique

Figure 7.2.1.5 addresses the question of how much dye is needed on the surface being cleaned to provide sufficient visual effects. Hence, according to the y-axis of Figure 7.2.1.5, this value was as low as 1.6 mg/ft^2 of ORO for aged Al2024P panels. The results of Figure 7.2.1.5 also illustrate that contaminant removal, based on dye removal, is quantifiable and dependent upon cleaning conditions and cleaner strength. UV aging effects are measurable, but small.

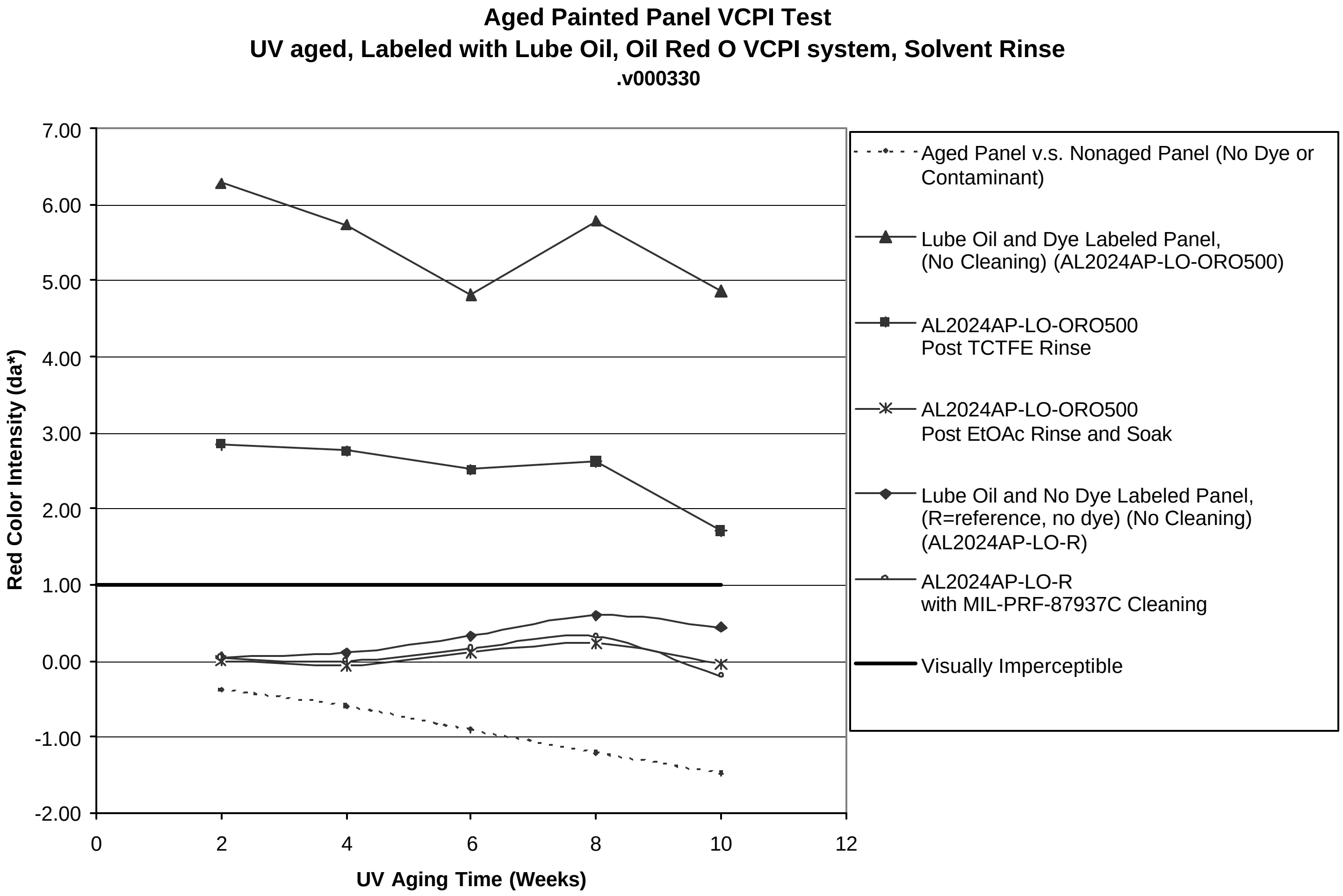


Figure 7.2.1.4 Effect of Aging on VCPI Technique surfaces above ~1.0 da* (a visibly colored red), those below either gray (if da* is near zero, or gray with a yellowish cast if da* ~ -1). Aging is visibly apparent but does not interfere significantly with the VCPI dye label color. Note also that dye completeness removal (and hence contaminant removal completeness – see text) is strongly dependent on cleaner and cleaning process need.

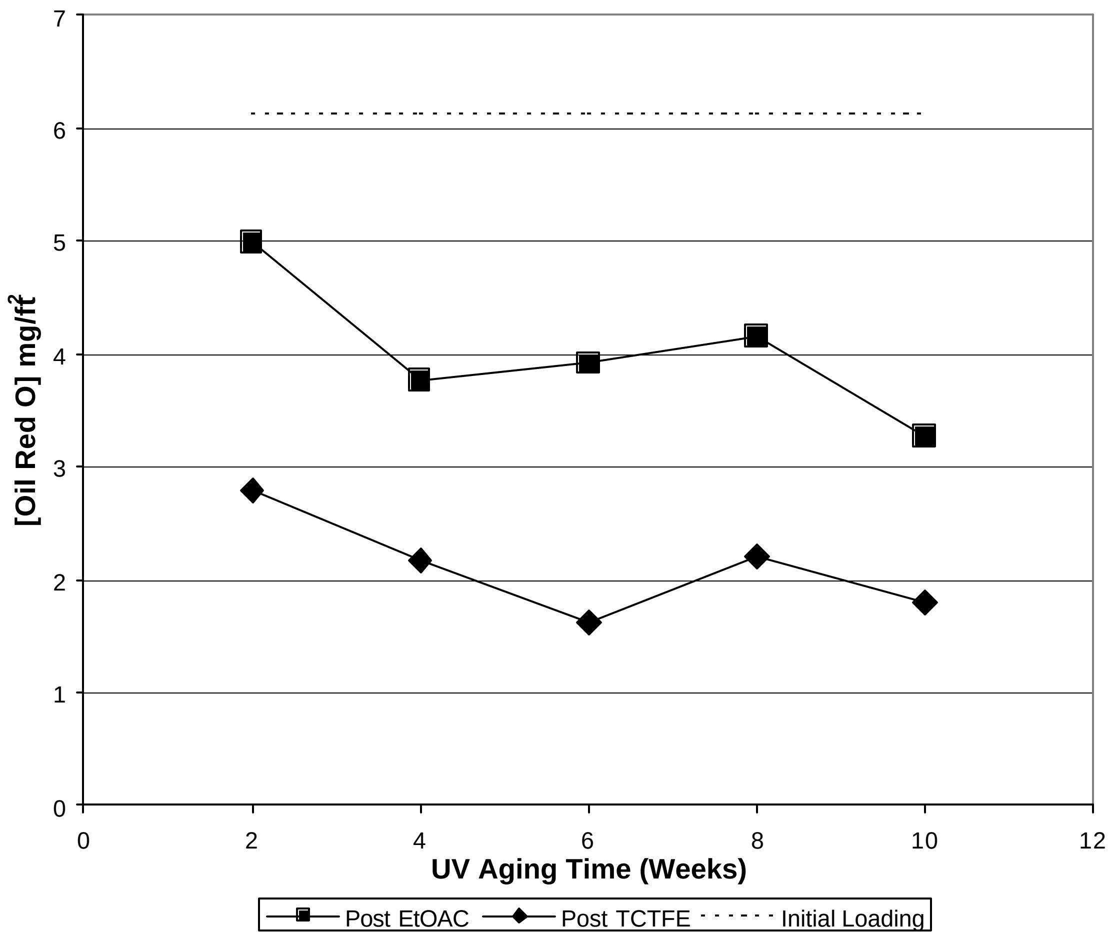


Figure 7.2.1.5 Surface dye residuals in solvent cleaners from post cleaned Al2024AP-LO-ORO panels. Illustrates that LO contaminant is still present on the surface after cleaning. This result is consistent with contaminant residual and therefore is a measurement of the amount of dye needed for adequate surface color visualization, about 2-5 mg/ORO/ft^2

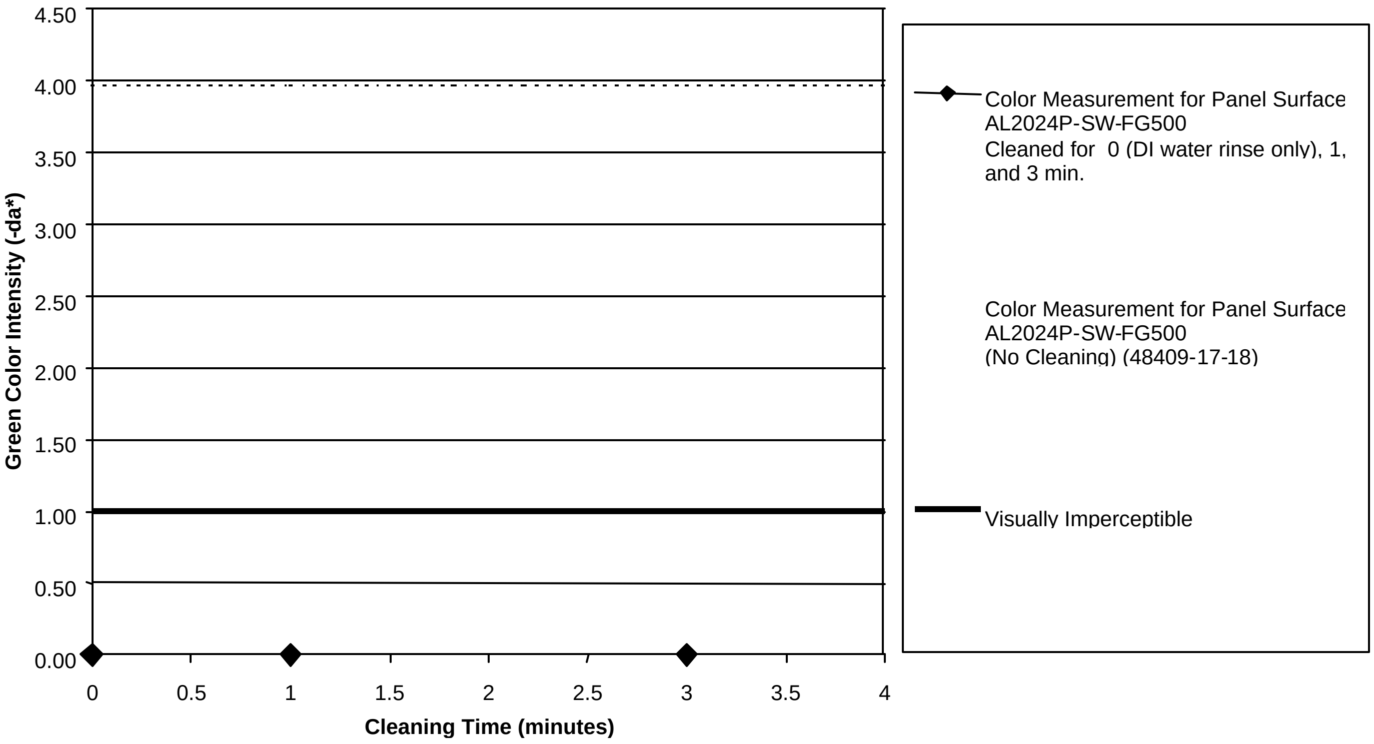


Figure 7.2.1.6 Al2024P contaminated with sea water residue (corrosive soluble salt contaminant) and labeled with FG3. Illustrates that visualization is readily achieved at 500-ppm dye level for the thin contaminant film present when panels are simply dipped in sea water and allowed to dry. This data also indicates that water-soluble salts are rapidly cleaned from the surface.

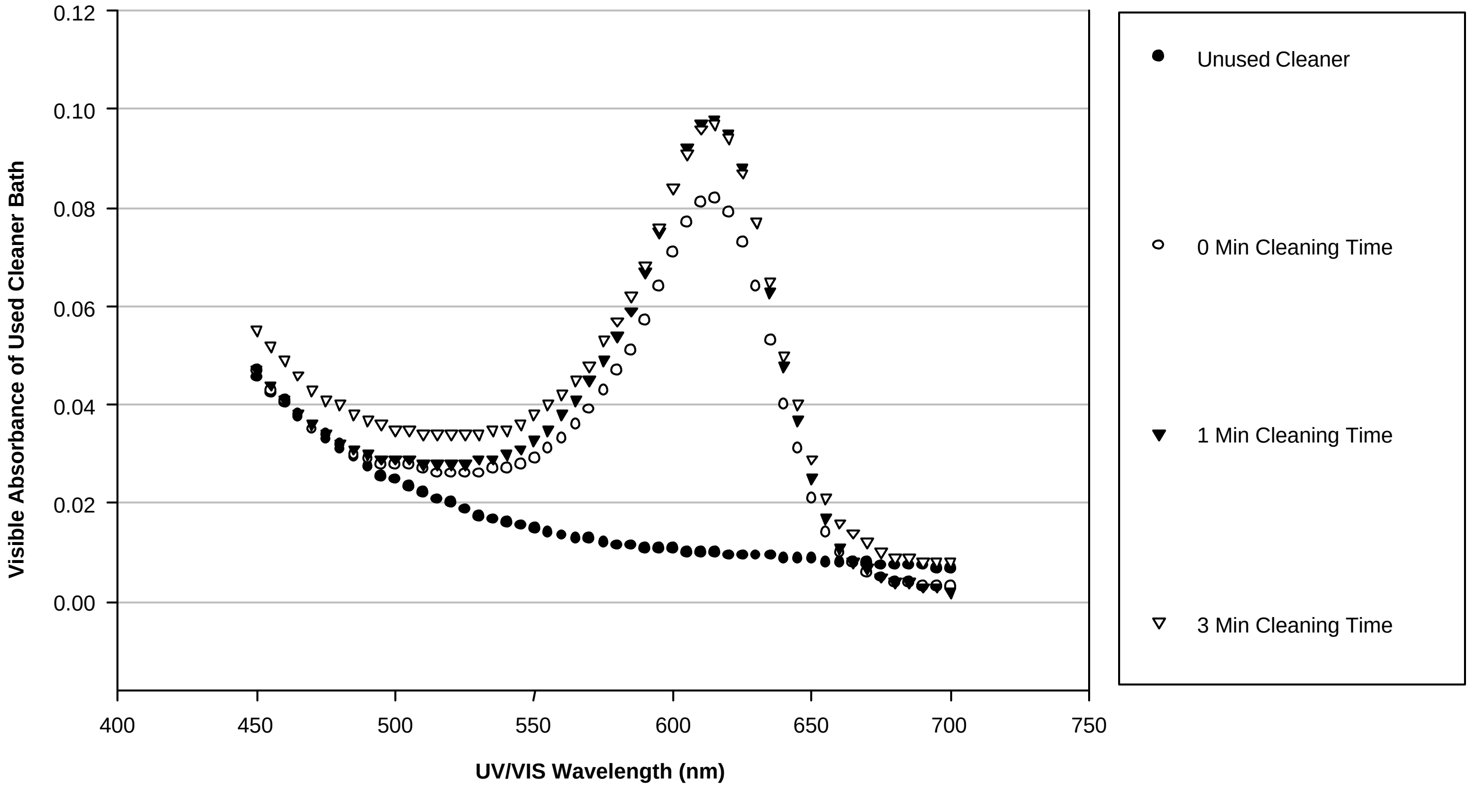


Figure 7.2.1.7 Data for the test described in Figure 7.2.1.8 illustrates that the FG3 dye reports to the cleaning solution, and quickly, during the cleaning operation. This data also suggests that quantification and monitoring of the process might be done by UV/VIS of used cleaner bath streams with field type instrumentation.

The Navy immediately paints the HY80 steel surface after depainting by grit blasting, and so a cleanliness assessment issue does not arise for the bare steel, other than the visual disappearance of the paint during grit blasting. Therefore, bare steel test panels were not tested in this program.

7.2.1.4 Metal Corrosion Product Labeling Evaluation

Metal corrosion product visualization and potential cleaning data are illustrated in Figures 7.2.1.8 and 7.2.1.9 for the Al2024 material. A neutral 5% salt fog chamber was used to corrode Al2024 panels after cleaning with Type II alkaline cleaner, and the VCPI dye was Alizarin. Corrosion removal compound (CRC, El Dorado AC-12) was used as the cleaner.

Figure 7.2.1.8 illustrates how the cleaner bath accumulates dye with soak time. The long cleaning time was designed in purposely, and is due to the use of highly corroded panels at near-stagnant soaking cleaning conditions rather than scrubbing. Hence, scrubbing is required and was used in the SCT. However, partial cleaning is needed in PCT work to allow tracking of dye (using surface UV/VIS and color space measurements) vs. contaminant removal rates, which need to be proportional.

Figure 7.2.1.9 shows that the Al corrosion product reports to the CRC cleaning bath in the needed inverse direction to the loss of dye color from the surface. This data demonstrates once again that the VCPI method allows quantification of such effects. To accomplish quantitation, surface color intensity by UV/VIS, or the magnitude of the total color difference (e.g. ΔdE^*) would need to be correlated with the remaining amount of corrosion products left on the surface. The ongoing SCT work will allow an estimate of this correlation to be calculated.

Since the CRC bath was found to be acidic, the switch was made to the backup dye for corrosion products, which binds to metal oxide films under acidic conditions, carminic acid or Natural Red 4 (NR4, Appendix A). This dye imports a purple color to aluminum alloy corrosion products and is expected to label this contaminant better than does alizarin due to lower pKa of the carboxylic acid group it contains. The downside of Natural Red 4 is cost (small laboratory quantities are $100 for 5 g). This cost/supply issue is addressed further in Section 9.0 (Subtask 4) since the NR4 dye performed very well in the SCT (Subtask 3.2).

Photos were taken of all of the VCPI test cases. As these photos normally reproduce poorly, they are being archived at Battelle.

7.2.1.5 Potential Operational Issues for VCPI

The original SERDP SOW identified environmental compatibility and waste treatability as important issues for the VCPI concept. Successfully deployed, the VCPI dyes will add significant color to the work area, i.e., aircraft cleaning on the tarmac, within the ALC, and pier side. In performing PCT and SCT work this coloration phenomena is readily apparent. Dye application work involves handling intensely colored solutions, while cleaning operations much less so, but still readily apparent.

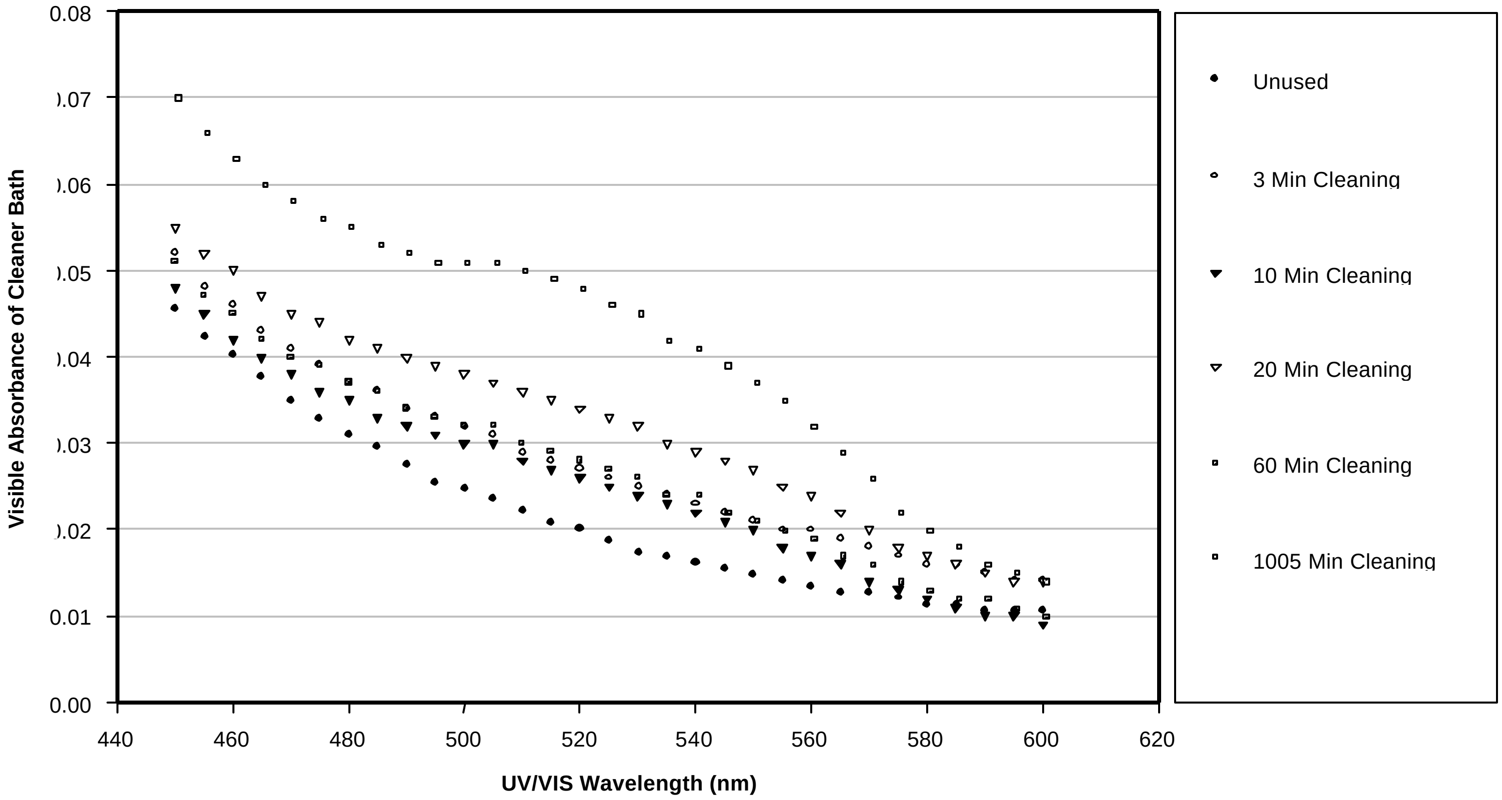


Figure 7.2.1.8 Al2024 Corrosion Products Labeling. Data represents accumulation of dye with cleaning time. Illustrates accumulation of dye in the cleaner bath with cleaning time. Note that soaking for long periods (instead of scrubbing which accomplishes cleaning) was not used in this test so that the rate of dye removal could be easily observed. These particular panels were also heavily corroded (72 hour salt fog time) to aid visualization, but which increased soak time requirements. These times were substantially reduced in systematic testing.

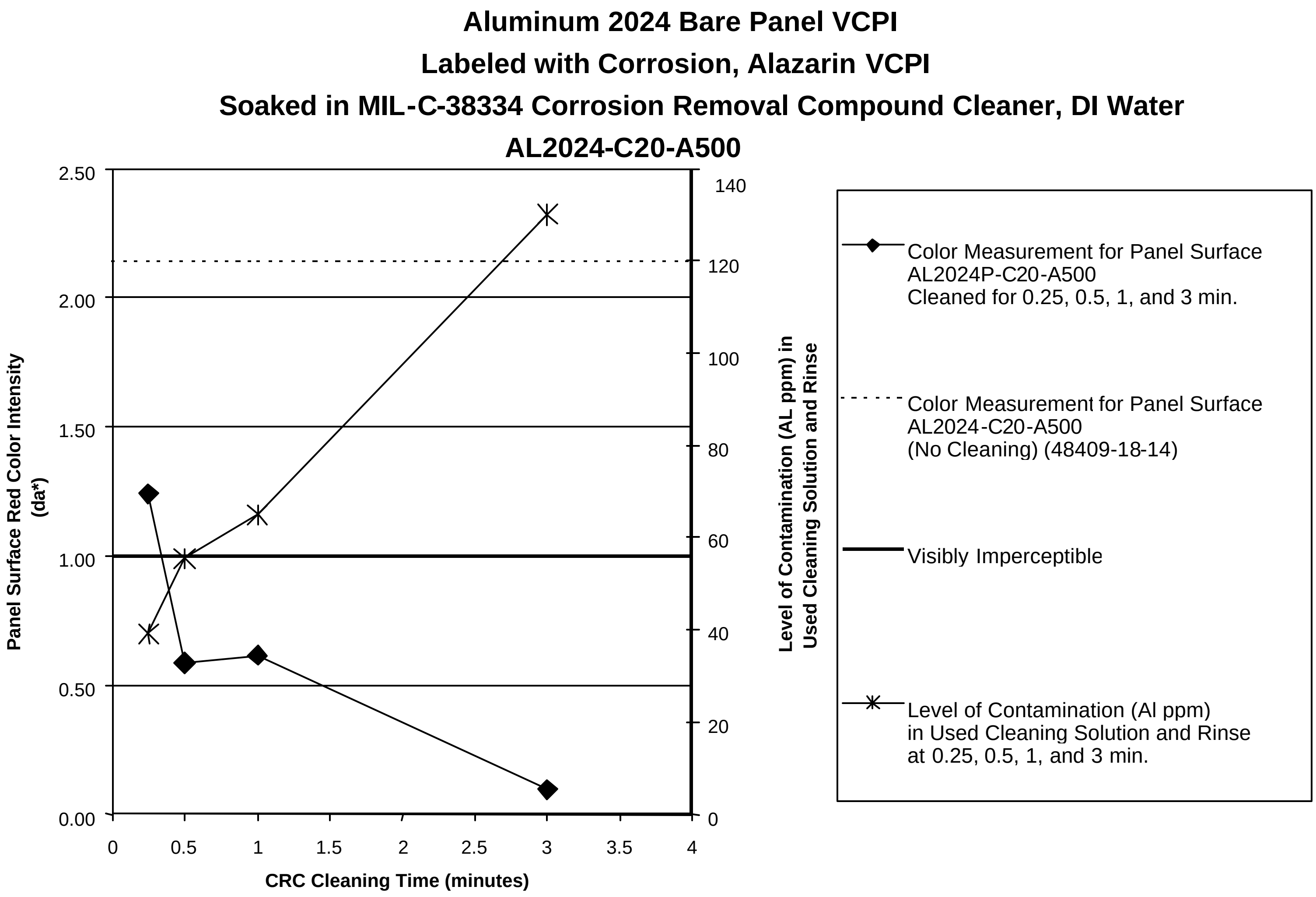


Figure 7.2.1.9 Al2024 Corrosion Product Cleaning MIL-C-38334 (CRC) Cleaner

Therefore, critical questions for the VCPI technique are whether the addition of a dye into the cleaning process has any one of the following detrimental effects relative to the un-dyed system:

- Decreased paint adhesion?
- Increased Al2024 metal corrosion rates?
- Causes unacceptable “mess” problems during use due to the addition of color to the process?
- Produce an unacceptable “stained” cleaned surface?

Addressing these questions were a part of the in-progress SCT work. During PCT work, it was possible to gather preliminary results on the first concern. Table 7.2.1 are pre-screening test results which show that corroded Al2024 panels cleaned through a lab scale version of the Re-Gel®/CRC process have the same excellent paint adhesion whether or not the VCPI dye (NR4) was present in the cleaning operation.

In addition, organic dyes do bleach with time, especially when exposed to sunlight; are biodegradable, and are removed in normal wastewater treatment operations. In addition, the VCPI dyes were selected based on their low toxicity and environmental compatibility. Hence, the work area coloration issue is expected to be at most just a nuisance.

Table 7.2.1.2. Effect of VCPI Technique on Primer Adhesion

Test System (a) (d)	Dry Adhesion Rating[b]	Wet Adhesion Rating [c]
Contaminated with Lube Oil, Labeled with Oil Red O, Passed Water Break after cleaning once	5A	5A
Contaminated with Lube Oil, Passed Water Break after cleaning once	5A	5A
Blank Panel (No Label or Contaminant) Passed Water Break after cleaning once	5A	5A
Contaminated with Corrosion, Labeled with Carminic Acid, Passed Water Break after cleaning twice	5A	5A
Contaminated with Corrosion, Passed Water Break after cleaning twice	5A	5A
Blank Panel (No Label or Contaminant), Passed Water Break after cleaning twice	5A	5A

(a) All test systems included 2024-T3 aluminum alloy substrate and cleaning protocol per Air Force approved T.O. 1-1-691 methods..

(b) 5A rating refers to no peeling or removal of coating on scribed lines. (ASTM # D3359) Panels were “X” scribed between two single scribed lines before testing.

(c) Wet adhesion is a 24 hr soak of the bottom ½ of the test panel in 72F distilled water, and then adhesion test is performed 1 minute after removal of the water soak.

(d) MIL-P-23377 epoxy primer applied in accordance with T.O. 1-1-8 approved procedures.

7.2.2 VCPI Systematic Cleaning Testing (SCT) Results (Subtask 3)

SCTs were performed to provide test data at conditions as near as possible to actual DoD depot and field practice.

7.2.2.1 Systematic Cleaning Test Systems and Logistics

Figure 7.2.2.0 illustrates the general flow of panels and information during SCT involving the projects' team members. This mode of operation maximizes the skills, capabilities, and experience of each organization. Figure 7.2.2.1 contains a detailed diagram illustrating the back-and-forth exchange of information, test materials, and test results that are involved, and which have insured end-user influence throughout the evolution of the VCPI concept testing. The fully detailed flow scheme provides the exact roles and responsibilities of each team member. Some of the detailed information available from this detailed flow scheme is:

- The panel material involved in each test
- The contaminant sources and identification
- The analytical methods utilized, both for panels and for used cleaners
- The locations for the testing, assays and preparations
- The manners in which the test results are rolled up and applied to VCPI technique refinement.

The panel labeling materials and conditions were derived as described above for the PCT and associated appendices. Appendix E provides the detailed results. The SCT data was used to verify and assess the potential of the VCPI concept (Section 2.0) and used to reveal needed refinements in the technology (Sections 1.0 and 9.0), the final deliverables for this project. As planned, with one exception, these systematic cleaning tests were performed by the Air Force (AFRL) and Navy (Carderock) with panels provided by the partners and treated by Battelle. All parties contributed analysis data and results. Carderock provided both panels and contamination for the paint stripper case as the best manner to perform those tests.

SCT test results (Appendix E) are quite extensive, requiring 100-200 panels per test system in which most measurements were made in triplicate. For manageable panel handling logistics, each test was broken up into three blocks (Tables 7.2.2.0 and 7.2.2.1), some of which were performed weeks apart. Figure 7.2.2.1 provides the detailed view of the test logistics, panel sample, and information flow between the partner laboratories involved.

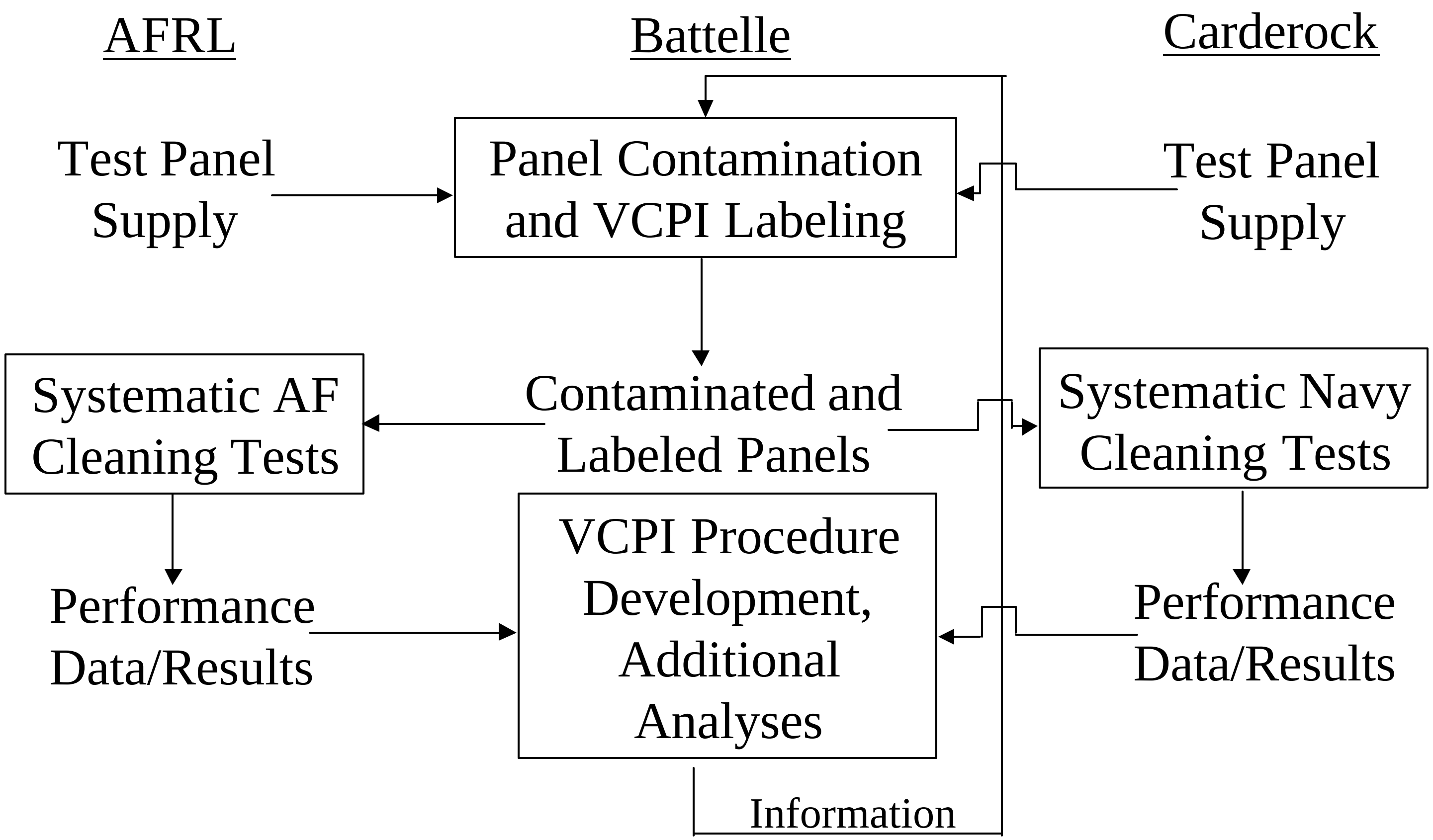
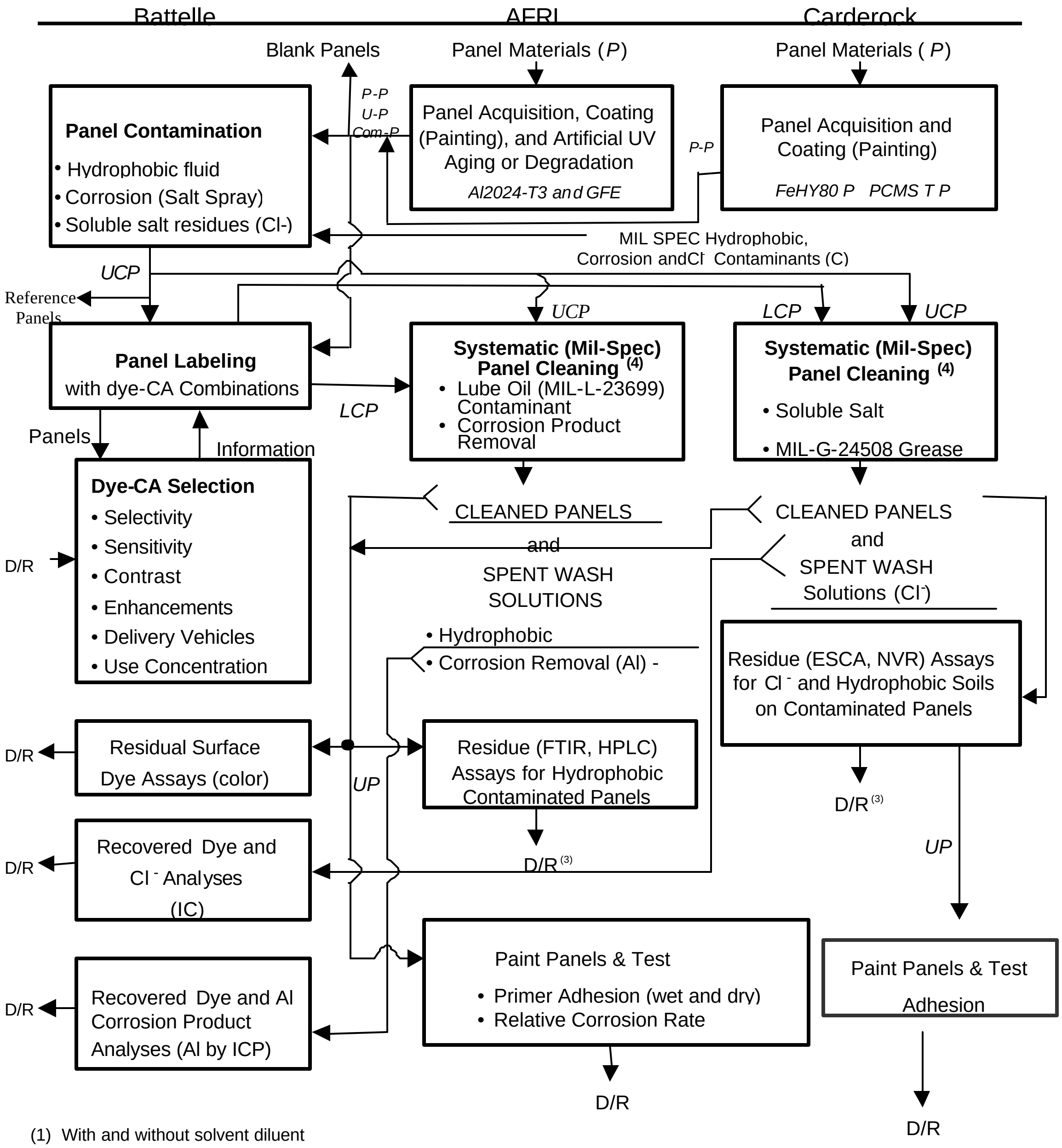


Figure 7.2.2.0 General VCPI Systematic Cleaning Test Panel and Information Flow



(1) With and without solvent diluent

(2) P-P= painted panels; U-P = unpainted metal panels; COM-P=composite panels

(3) D/R = Produced data/results (used as input into dye-CA selection and VCPI delivery method optimization

(4) Include water break test for unpainted surfaces, tests run in triplicate

(5) L=dye labeled; C=contaminated; P=panels; UCP=unlabeled contaminated panels; LCP=contaminated and labeled panels

Figure 7.2.2.1 Detailed Illustration of the *Systematic* VCPI Cleaning Test Panel and Cleaning Test Information Flow

Table 7.2.2.1 SCT – Air Force (AFRL-MLSA)

Test System Identification	Block Name or #
Al2024P-LO-ORO-500	surrogate set
Al2024P-LO-ORO-20:0.5, 0.3, 0.1, 0.05, 0.025, 0.010	dye level optimization experiment
Al2024-LO-ORO-500	48474-34-01
Al2024-NLO-ORO-60K	48474-47-01
Al2024-NLO-ORO-60K	48474-49-01
Al2024-C65-CAR-500	48474-50-01
Al2024-NLO-ORO-60K	48474-53-01
Al2024-C14-CAR-500	48474-55-01
Al2024-C14-CAR-500	48474-56-01
Al2024-C14-CAR-500	48474-57-01

Table 7.2.2.2 SCT – Navy (Carderock)

Test System Identification	Block Name or #	Cleaning Method
FeHY80P-G-ORO-20:0.5	48474-14-01	1
FeHY80P-G-ORO-20:0.5	48474-16-01	1
FeHY80P-G-ORO-20:0.3	48474-19-01	1
TP-G-ORO-20:0.5	48474-13-01	1
TP-G-ORO-20:0.3	48474-17-01	1
TP-G-ORO-20:0.1	48474-30-01	2
TP-G-ORO-20:0.05, 0.025, 0.01	dye level experiment / 48474-31-01	2
FeHY80P-SW-FG3-500	48474-15-01	1
FeHY80P-SW-FG3-500	48474-18-01	1
FeHY80P-SW-FG3-300	48474-42-01	2
TP-SW-FG3-500	48474-28-01	2
FeHY80P-G-ORO	see Appendix Table E.3.2	2
TP-G-ORO	see Appendix Table E.3.2	2
FeHY80P-SW-FG3	see Appendix Table E.3.2	2
TP-SW-FG3	see Appendix Table E.3.2	2

Cleaning Method 1= original cleaning method performed at Carderock
Cleaning Method 2= improved cleaning method performed at Carderock

7.2.2.2 Systematic Cleaning Test (SCT) Results: Interpretation of Data Plots

7.2.2.2.1 Test System Al2024P-LO-ORO

This system was pre-screened only due to the residual contaminant issue (Section 7.1.3), which led to staining after cleaning. Improved cleaning protocol and/or chemicals would be required before VCPI implementation would be possible for this test system (see Section 9.0). In fact, the VCPI technique appears ideally suited to use to identify such improved cleaners and protocols.

7.2.2.2.2 Test System Al2024-NLO-ORO

See Sections 7.2.1.1 and 7.2.2.2.1

7.2.2.2.3 Test System Al2024-C14-CAR

In this test system, aluminum 2024 (Al2024) panels were used. Reference panels were contaminated with corrosion. Labeled panels were contaminated with corrosion and labeled with Natural Red 4 (NR4) dye. Blank panels were not contaminated or labeled.

The following protocol based on T.O.1-1-691 was used to clean the panels:

1. Treat panels with 6mL of Re-Gel® cleaning solution. Dwell time = 2 minutes.
2. After 2 min. dwell, panels received 3 uni-directional swabs (1 pass per swab) across the surface with a white Scotchbrite pad.
3. Rinse with 180mL of 18 MΩ-cm deionized water. Consists of 3 rinses with a 60mL syringe. Water was heated using hot plate.
4. Apply 6mL of corrosion removal compound (CRC). The dwell time of the CRC on the surface was specified at 0, 1, and 3 minutes.
5. 2 swabs with white Scotchbrite pad (1 uni-directional pass per swab).
6. Repeat step 3.

7.2.2.2.4 Aluminum Ion Removal and Dye Removal

Figure 7.21 suggests that the visual observations appear to be more reliable and have certain advantages over instrumentation. Even though instrumentation cannot detect color past the Color Tolerance Limit, the color observation text boxes suggest that color can be observed visual below that point. This illustrates how the dye can guide the operator.

Figures 7.21 and 7.22 show visual observations of splotchy surfaces. When the panel surfaces have a splotchy appearance, the surface colors are irregular thus contamination is irregular because the removal of dye tracks the removal of contamination on the panel surface. It can be recommended that detailed testing be done to verify that the irregularity of the contamination exists on the panel surface. The larger error bar on the Figure 7.21 at 20 scrubs represents the inconsistency of contaminant distribution on the surface of the panel, as suggested above; the splotchy surface also shows the inconsistency of the contaminant. The Labeled Re-Gel® Feed Total Color Difference in Figure 7.23 shows visual observations of non-uniform purple possibly in corroded areas only. The non-uniformity of the panel accounts for the larger error bars for that sample. Figure 7.5 illustrates that it is visually apparent that all of the dye's color from the panel surface is removed with the T.O. protocol.

7.3 Systematic Material Compatibility Test Results Based on EIS Testing

Besides requirements for selective contaminant labeling and EH&O, the VCPI method must also not adversely affect the surface being cleaned. Paint adhesion and corrosion rate were selected by the DoD partners as the primary criteria for assessing material compatibility. These test results, provided in this section, indicate that no material incompatibility issues exist with respect to these two (2) criteria at the level of testing accomplished to date. All future testing would provide opportunities to continually check for material compatibility. Theoretically, no such problems are expected as such compatibility was considered in making the original dye/CA selections.

7.3.1 Experimental Procedure

7.3.1.1 Electrochemical Impedance Spectroscopy (EIS)

Panels were sheared to 1" x 3" samples. EIS test were run using an EG&G flat cell with exposed surface area of approx. 1 cm^2. The test solution was 0.1M $Na_2B_4O_7$ (sodium tetraborate). The purpose in using this passivating solution was to avoid corrosion effects during electrochemical testing. A Perkin-Elmer EG&G 273A Potentiostat with a Solartron 1250 FRA was used, along with ZPlot software. The scans were run at peak amplitude of 10 mV, with a frequency range of 50 kHz to 5 mHz. The reference voltage was 0V vs. Open Circuit Potential (OCP). The OCP is measured automatically prior to the EIS scan by the 273A; this value is used by ZPlot as the reference potential.

7.3.1.2 Adhesion

Nine additional panels (3 blanks, 3 exposed to 14 hours of ASTM B117 salt fog, and 3 exposed to 14 hours of ASTM B117 salt fog and labeled with carminic acid) were cleaned according to the above procedure, coated, and tested for adhesion properties. The coating system consisted of a MIL conversion coat, a MIL-P-23377 primer, and a MIL-C-85582 topcoat. This test was designed to ensure that no residual contaminants or dye remained on the panel surfaces and adversely affect adhesion properties.

7.3.1.3 Fourteen (14) Hour Salt Spray Panels (Block #'s 55, 56, 57)

It was determined that 65 hours of salt spray testing produced a more severe degree of corrosion than would normally be seen on aircraft. Therefore, 4 additional blocks were subjected to salt spray testing for 14 hours, which was deemed the be a realistic corrosion level based on past field experience. For each of the three blocks, there were 12 different conditions and two replicate panels per condition, for a total of 72 panels. These conditions are summarized in Table 7.2.1. The end result is that for each condition there are six replicate panels, two from each of the three blocks. For each condition, at least four replicates samples were measured electrochemically. Measurements made at times greater than two days following cleaning were not included in the data analysis.

Addressing the issue of reproducibility of replicate panels, Figure 7.3.1 shows 3 sets of Bode magnitude and phase angle plots containing replicate EIS spectra. Replicate spectra vary slightly from one another and yield a range of equivalent circuit fitting parameters; however, the fact that they are replicates is somewhat obvious from visual observation (particularly of the phase angle plot). Comparison of Figure 7.3.1 with Figures 7.3.2, 7.3.3, and 7.3.4, etc. illustrates the utility of Bode phase angle plots in tracking electrochemical changes to a system. Also of note is the fact that the spectra in Figure 7.3.1 9b are more reproducible than those in Figure 7.3.1 9a and 7.3.1 9c. This is most likely due to the fact that the salt spray creates an inhomogeneous surface that has more variation from panel to panel (Figure 7.3.5 and 7.24c) than seen in uncorroded panels.

Figures 7.3.2 to 7.3.4 show Bode magnitude and phase angle plots for panels with 14 hours of salt spray with NO dye and with 500-ppm carminic acid dye. Note the similarity between the two sets of spectra. Sixty-five hr. salt spray, without and with dye are also similar to one another, except that in 65 hr. salt spray with dye the high frequency time constant remains after 0.5 minutes of CRC treatment. For the 14 hour salt spray panels, the high frequency time constant disappears after a brief (< 10 seconds) CRC treatment.

Figure 7.3.7 shows Rcorr vs. CRC dwell time for NO corrosion with NO dye, 14 hour salt spray with NO dye, and with 500 ppm carminic acid dye. Error bars are shown on this plot represents the standard deviation of the replicate test results derived from a minimum of four measurements. As was the case for panels corroded for a 65 hour salt fog exposure, the uncorroded panels show a systematic decrease in Rcorr (or oxide thinning) as a function of CRC dwell time. Rcorr values drop sharply upon application of CRC treatment to panels that had been exposed to a 14-hour salt fog exposure and the average value continues to decrease slightly with decreasing CRC dwell time. However, all values of Rcorr after application of CRC appear to be statistically indistinguishable. The difference in Rcorr for samples exposed to salt fog and samples that were not is significant. This would suggest that corrosion of the samples caused a significant disruption of the air formed oxide on the alloys surface. The decrease in Rcorr upon application of CRC is indicative of the removal of corrosion products. Also, the error bars for the feed panels are significantly larger than for 0, 1, and 3 minutes of CRC. This is probably due to the inhomogeneous nature of the corrosion product on the surface of the uncleaned panels. Finally, it can be seen from Figure 7.3.7 that the Re-Gel® cleaning step does not significantly affect Rcorr value of the samples.

7.3.1.4 Re-Gelâ Cleaning Only

Nine additional panels were tested to observe the effect of the Re-Gel® cleaning step on panels subjected to 14 hours of salt spray with and without dye (3 panels each) and with no salt spray or dye (3 panels). Three sets of Bode magnitude and phase angle plots produced including 14-hour salt spray panels with no dye. The three replicates of 2 minute Re-Gel®, no CRC are somewhat less reproducible than in other cases. The reason for this trend is not clear. The Re-Gel® could be leaving the surface in a more inhomogeneous state leading to more scatter in the EIS data. On the phase angle plot, the high frequency sections of the 2 minute Re-Gel®, no CRC spectra appear to be in an intermediate state between the blue curve (no Re-Gel® or CRC) and the green (2 minute Re-Gel®, less than 10 second CRC). The high frequency time constant is disappearing, or at least shifting to a frequency higher than 50 kHz. The panels appear to be partially cleaned, both in visual appearance and in the EIS spectra. This is also seen in 14 hour salt spray with 500 ppm carminic acid dye. The three replicates of 2 minute Re-Gel®, no CRC show less scatter among the 3 spectra than for the 14 hr., no dye panels. Examination of the Bode phase angle plot reveals that the curves are intermediate between the others. This means that the high frequency time constant is still present (when comparing red to blue), but diminished, or perhaps shifted to higher frequency. The decrease in the high frequency phase angle for samples that have a Re-Gel® cleaning step only compared with feed panels is indicative of the removal of loose corrosion product. This can be reconciled with the fact that the Re-Gel® cleaning step does not affect Rcorr in that the loose corrosion products do not contribute significantly to the Rcorr value.

Examination of no salt spray, no dye data shows that the Re-Gel®, and no CRC are reproducible and not significantly shifted away from the blue. Taking the data as a whole would lend evidence to the fact that the Re-Gel® cleaning step removes loose corrosion product, but only minimally effects tenacious corrosion product or oxide properties.

7.3.1.5 Visual Observations

Figure 7.3.5 shows optical photographs of representative panels at various stages of the cleaning process after a 14 hour exposure in a salt fog environment. After a minimum exposure to CRC (less than

10 seconds), most of the carminic acid dye and corrosion product is gone. Further corrosion product and dye removal can be seen after 1 and 3 minute exposures to the CRC. There is very little difference between the appearance of the Al2024 surface after exposure to the CRC for 1 and 3 minutes. This is in agreement with contact angle and electrochemical impedance spectroscopy (EIS) data.

7.3.1.6 Paint Adhesion Testing

7.3.1.6.1 Al2024-T3

Table 7.3.1 are the paint adhesion test results for the Al2024-T3 system. Table 7.3.1 addresses the material compatibility of the VCPI technology via paint adhesion tests. All of the adhesion tests results are excellent. Hence, the VCPI technique did not adversely affect paint adhesion when used in normal Air Force cleaning and painting protocol (see footnotes to Table 7.3.1 for description of test conditions).

Table 7.3.1 Material Compatability Test Results for Paint Adhesion

Test System[(a)] [(d)]	Dry Adhesion Rating[(b)]	Wet Adhesion Rating[(b)]
Contaminated with Lube Oil, Labeled with Oil Red O	5A	5A
Contaminated with Lube Oil	5A	5A
Blank Panel (No Label or Contaminant)	5A	5A
Contaminated with Corrosion, Labeled with Natural Red 4	5A	5A
Contaminated with Corrosion	5A	5A
Blank Panel (No Label or Contaminant)	5A	5A

(a) All test systems included 2024-T3 aluminum alloy substrate and cleaning protocol per Air Force approved T.O. 1 -1-691 methods.

(b) 5A rating refers to no peeling or removal of coating on scribed lines. (ASTM # D3359) Panels were "X" scribed between two single scribed lines before testing.

Adhesion per ASTM D 3359 Method A, except parallel lines, 1 inch apart, also scribed over the center of the "X" across the short dimension of the panel. Scribing performed with a Hermes engraving machine.

Ratings per ASTM D 3359 Method A, where 5A indicates no peeling or removal and 0A indicates removal beyond the area of the X

Primer: MIL-P-23377G – Deft 02-Y-40, batch #43308/43309, mfd 8/00
Topcoat: MIL -PRF-85285C – Deft 03-GY-321, batch #41612/41611, mfd 2/00

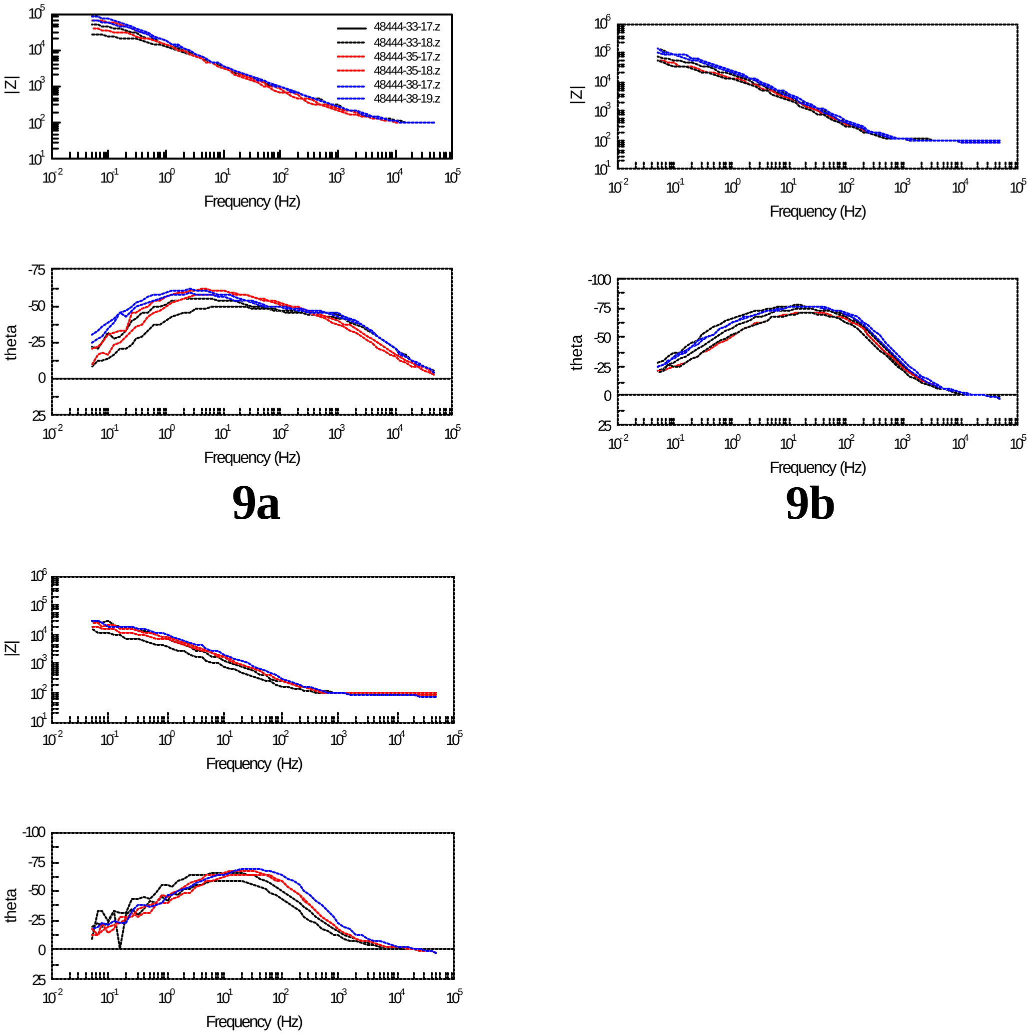
Conclusion : Systematic Cleaning Test indicates no adverse effect of VCPI technique on top coating tape adhesion

7.3.1.6.2 PCMS Tiles

Paint adhesion tests are performed using PCMS tiles that have been previously contaminated with PA7. The application of dye labeled PA7 shows significant color absorption from the dye. These tiles along with tiles treated with unlabeled PA7 and their corresponding blanks were repainted to test for adhesion properties. Such tiles were painted and allowed to dry for three days at which point a portable adhesion tester was used to analyze surface adhesion. Surface adhesion is measured by adhering four aluminum plugs to the painted surface with epoxy. Once the epoxy is dried, the aluminum plug is connected to a pneumatic pressure gauging system that measures the force needed to remove the adhered plugs. After all four aluminum plugs are removed; the pressure values are averaged revealing the numeric adhesion value for the corresponding paint, which was applied.

7.3.1.7 EIS Testing Conclusions

- EIS spectra of replicate panels subjected to various conditions (14 hour salt spray, no salt spray, Re-Gel® cleaned, CRC cleaned for various dwell times from 0 to 3 minutes) were fairly reproducible (see previous section). EIS testing at single time constant confirms reproducible results for replicate panels subjected to various conditions.
- For 14 hour salt spray panels, with and without 500 ppm carminic acid dye, Rcorr drops drastically (about half an order of magnitude) between the uncleaned and cleaned states, and continues to decrease slightly up to 3 minutes of CRC dwell. The Rcorr decrease is confirmed after CRC cleaning.
- For uncorroded panels, the EIS data shows that the Re-Gel® step does not have a significant effect on the oxide properties or the dense more strongly attached corrosion products. The Re-Gel® step does remove loose corrosion product. However, increasing CRC dwell times causes Rcorr to drop as corrosion products are removed by the CRC step. Results confirm that a partial removal of corrosion products exists with Re-Gel® cleaner and complete removal of corrosion products exists with CRC.
- Corrosion appears to significantly damage surface oxide properties.
- Surface contact angle measurements are in agreement with EIS data in that even a brief exposure to CRC significantly reduces the amount of corrosion product on the sample surface. Surface contact angles are in agreement with EIS test data (i.e., CRC removal of corrosion products).
- For panels measured 7 weeks after exposure, recovery of an air formed oxide layer is observed for panels where the corrosion products were removed. Panels that are uncleaned or only partially cleaned do not see a recovery of the contact angle to values observed prior to corrosion (uncorroded feed panel values).
- The affect of the Re-Gel® cleaning step primarily removes loose corrosion products.
- The presence of dye on the surface of the samples does not significantly affect EIS or surface contact data.
- EIS and surface contact angle are in agreement with visual observations.
- VCPI does not compromise corrosion resistance or wettability of Al2024-T3 substrate after T.O. 1-1-691 cleaning.



9a

9b

9c

Figure 7.3.1 Bode Magnitude and Phase Angle Plots of Replicate Panels for: 9a) reference, no CRC; 9b) blank, 3 minute CRC dwell; 9c) labeled, 1 minute CRC dwell.

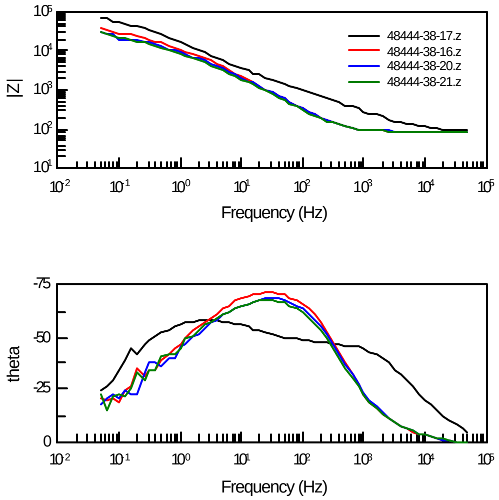


Figure 7.3.2 Bode magnitude and phase angle plots for 14 hour salt spray, reference. No CRC (48444-38-17), 0 minute CRC dwell (48444-38-15), 1 minute CRC dwell (48444-38-20), 3 minute CRC dwell (48444-38-21).

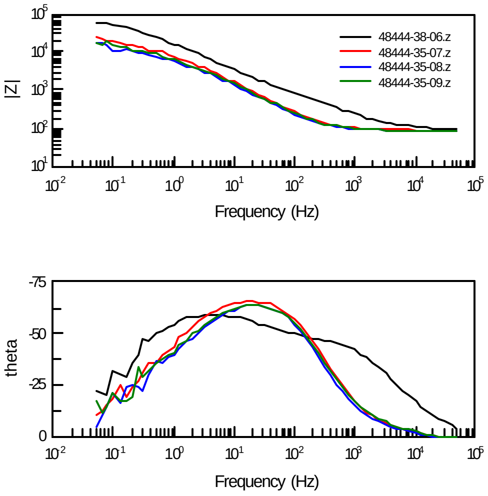
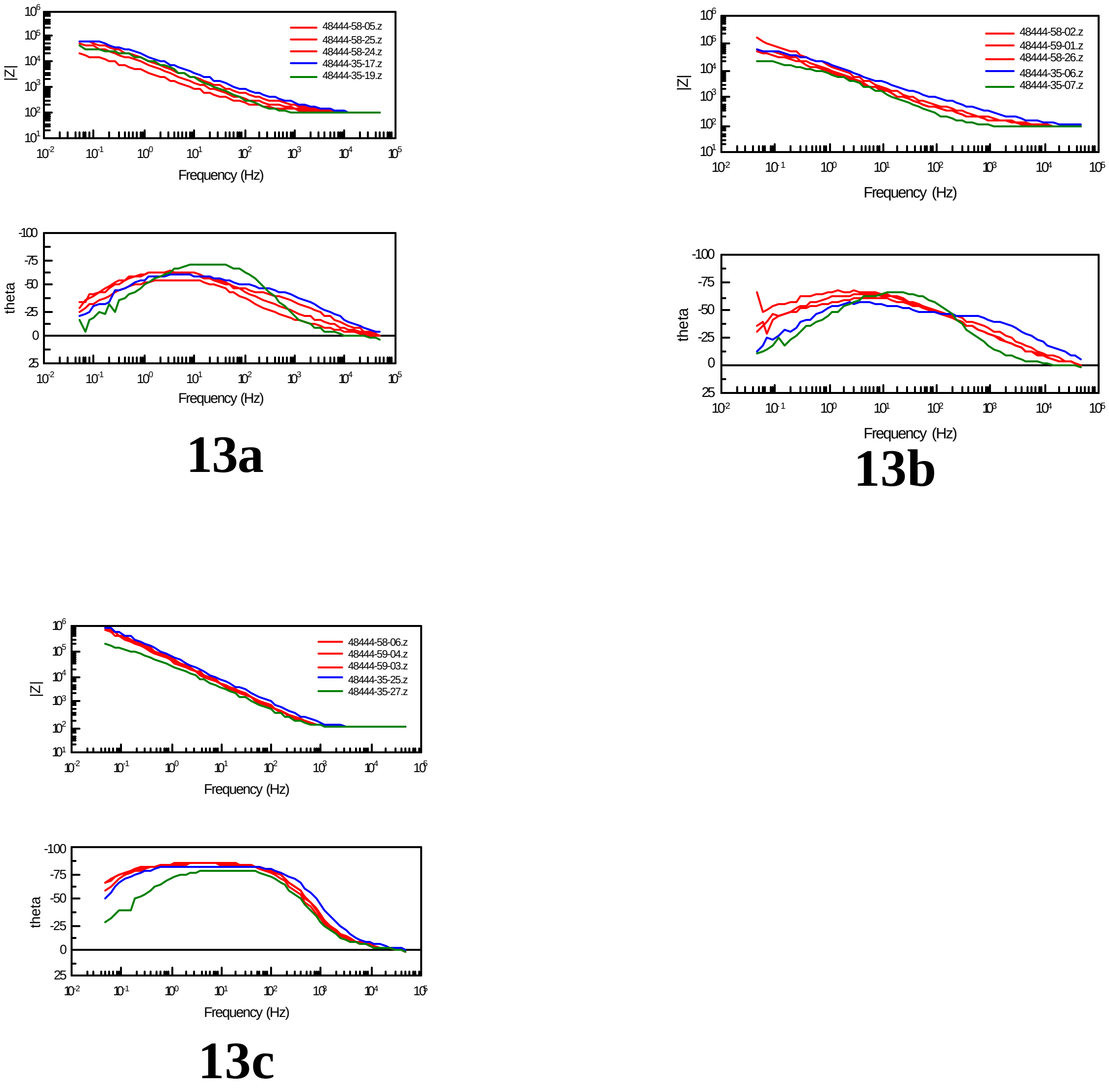


Figure 7.3.3 Bode magnitude and phase angle plots for 14 hour salt spray, labeled. No CRC (48444-38-06), 0 minute CRC dwell (48444-38-07), 1 minute CRC dwell (48444-38-08), 3 minute CRC dwell (48444-38-09).



13a

13b

13c

Figure 7.3.4 Bode magnitude and phase angle plots for 14 hour salt spray panels. 13a: reference (48444-35-17), 2 minute Re-Gelâ, no CRC (48444-58-05,48444-58-25,48444-58-24), 2 minute Re-Gelâ, 0 minute (<10 sec) CRC (48444-35-19). 13b: labeled (48444-35-06), 2 minute Re-Gelâ, no CRC (48444-58-02,48444-59-01,48444-58-26), 2 minute Re-Gelâ, 0 minute (<10 sec) CRC (48444-35-07). 13c: blank (48444-35-25), 2 minute Re-Gelâ, no CRC (48444-58-06,48444-59-04,48444-59-03), 2 minute Re-Gelâ, 0 minute (<10 sec) CRC (48444-35-27).

Figure 7.3.5 Optical Photographs of Panels Exposed to 14 Hours of Salt Fog at Various Stages of the Cleaning Process.

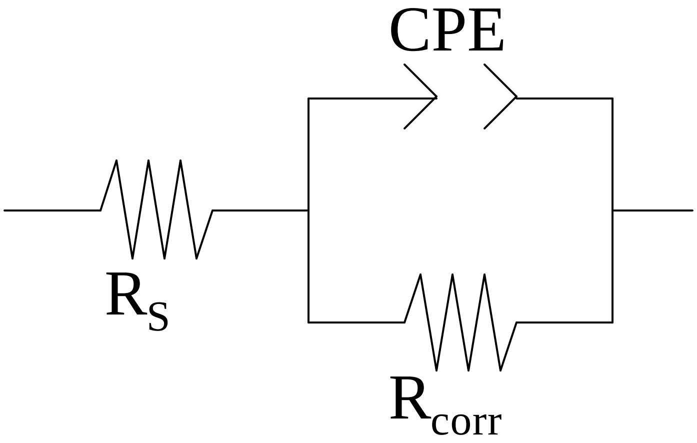
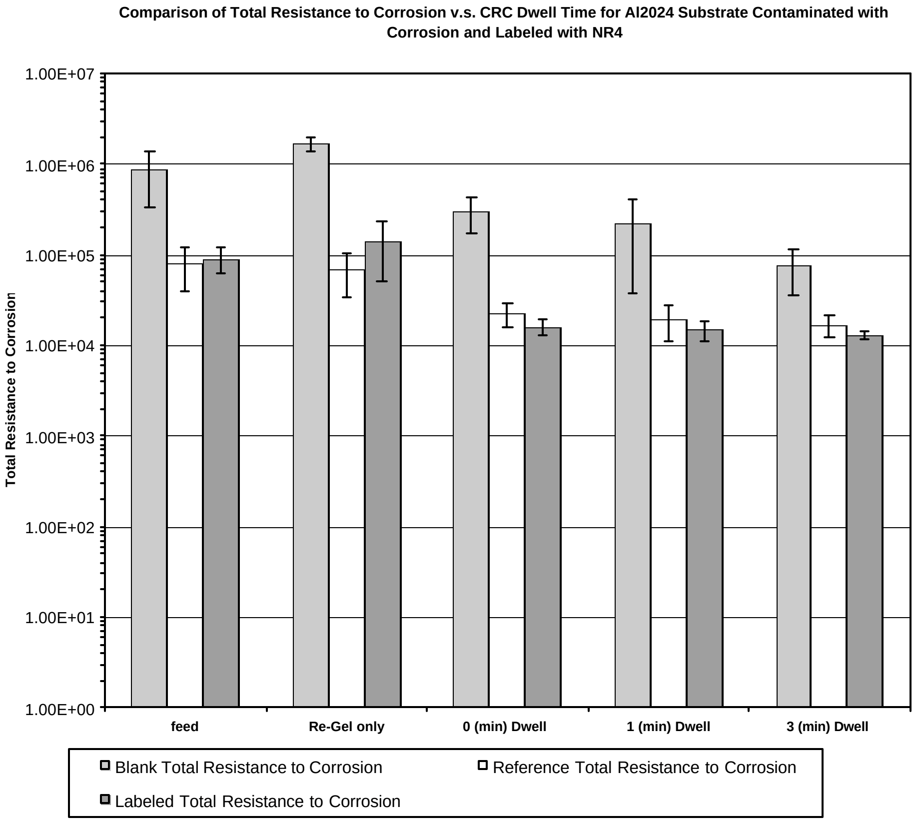


Figure 7.3.6 Equivalent Circuit Used to Fit EIS Spectra



Analyses are of panel surfaces after cleaning. Error bars are one standard deviation. (Al2024-C14-CAR-500 block 55,56,57v.20010424).

Figure 7.3.7 Total Resistance to Corrosion for Corrosion Products Labeling (Blocks 55, 56, 57)

7.4 Test Results Relating to Implementation

7.4.1 VCPI Labeling Experiment

The following steps were taken to perform the grease labeling pre-screening test:

1. A clean Al2024 panel was labeled with grease contaminant in a pattern to spell "VCPI" on the panel surface.
2. The panel was then sprayed with a film of ORO laden Re-Gel®.
3. Observations were made before the application of Re-Gel® film, immediately after the application of Re-Gel®, and while drying at 10-minute intervals. The surface was thereby rendered red in color.
4. The labeled solution used to spray the panel was analyzed via UV-Vis for ORO concentration and found to be 12,000 ppm.
5. The panel was rinsed with DI water, where upon the Re-Gel® rinsed quickly off of the surface. Simultaneously with rinsing, the letters "V-C-P-I" appeared in red, indicating that the grease was quickly labeled by the ORO held in the Re-Gel® solution, most likely as detergent vesicles.

6. Also apparent, was the observation that the clean metal was not labeled and that the labeling of the grease occurred in ≤10 minutes.
7. Photographs of the “VCPI” panel described above are available from the author.

8.0 RESPONSES TO SERDP ACTION ITEMS

8.1 Safety, Waste Treatability, and Environmental Compatibility of Dye/CA Candidates for VCPI Technology

8.1.1 Action Items

This section is the response to the 9/22/99 SERDP request for a written response to the Science Advisory Board (SAB) request for information on potential environmental impacts of the dyes that might be used in the proposed (VCPI) technology.

8.1.2 Response

Final selections of dyes and coupling agents (CAs) have not been made since in field VCPI performance cleaning tests must be completed in order to verify the selection. However, the dye selection process is in place and candidate dyes have been identified. These candidate dyes were screened for environmental compatibility as follows.

Candidate dye/CA combinations chosen for this testing were selected from dyes already in use in consumer products such as foods, cosmetics, drugs, and other widely used consumer products such as consumer hydraulic fluids and clothing. Therefore, these dyes are already a component of municipal and industrial wastewater streams and do not upset these water treatment processes.

The dye industry has invested decades of effort addressing the safety and environmental issues around the use of dyes. This information, relating dye chemical structures to environmental and toxicity properties, was gathered as part of Tasks 1.2 and 1.3 (Table 8.1). From these lists, a short list of preliminary dyes/CAs was selected based on DoD cleaning needs information derived in Task 1.1.

The references in Table 8.1 were, and will further be utilized to determine the environmental compatibility and toxicity of each dye/CA candidate from two perspectives. First, whether it is specifically called out on any of the major chemical toxicity listings as having an ecotox problem. Second, Battelle's ES&H Group performed additional reviews of the available chemical toxicity literature, including those referred to in Table 8.1 as well as MSDS's, the Hazardous Substances Data Bank (HSDB), Registry of Toxic Effects (RETECS), Toxic Substances Control Act (TSCA) reports, etc. for the six dye/CA candidate combinations. The results of these analyses indicate that all of the current dye/CA candidates (Table 8.2), save one (see below) are totally absent from these lists, and hence meet the DoD safety and environmental compatibility selection criteria. Only D and C Violet No. 2, which is a backup selection, appears on the National Toxicology Program (NTP) list and in the HSDB. However, D and C Violet 2 by definition is cleared for use in drugs and cosmetics, and is therefore cleared by the FDA for limited human consumption (dyes are often at low percent levels in pills), and skin contact (cosmetics). Oil Red O, selected for hydrophobic contaminant labeling, by far the most major DoD contaminant class, is already in widespread use as a hydraulic fluid indicator. The two food dyes in Table 8.2 are not reported to have any health problems. Similarly Alizarin, a dye, which has been in use for many years, appears clean of health and environmental problems.

Table 8.1 Databases Used to 1) Identify Dyes and Coupling Agents (Dye/CA) Candidates for Evaluating the VCPI Concept, and 2) to Down Select these Materials to Meet Toxicity, Environmental, and DoD Use Criteria

1	Cleaning Compound, Aerospace Equipment MIL-C-87937B
2	Chemfinder (http://www.chemfinder.com)
3	Vermont SIRI MSDS site (http://siri.uvm.edu/msds/)
4	National Toxicology Program (NTP) Web Site (http://ntp-server.niehs.nih.gov/)
5	40 CFR 261. Identification and Listing of Hazardous Waste CFR, Title 21 (21 CFR), Parts 70-82 (Color)
6	FED-STD-141 (Section 9)
7	"Colorants for Food, Drugs, Cosmetics, and Medical Devices", Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., Volume 6, p. 892 (1993) by John Wiley & Sons, Inc., 605 3rd Ave., New York NY 10158-0012.
8	"Dyes, Environmental Chemistry", p. 753; "Dyes, Natural", p. 784; and "Dye and Dye Intermediates", p. 542, Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed. Volume 8 (1993) by John Wiley & Sons, Inc. (New York, NY).
9	"The Sigma-Aldrich Handbook of Stains, Dyes, and Indicators", by F. J. Green, Aldrich Chem. Co., Milwaukee, WI (1990).
10	Colour Index, 3rd Ed. Volume 1-5, 1971, The Society of Dyers and Colourists, P. O. Box 224, Perkin House, 82 Grattan Road, Bradford, Yorkshire BD1 2JB, England, and American Association of Textile Chemists and Colorists, P. O. Box 12215, Research Triangle Park, NC 27709, US.
11	"Food Chemistry" Third Ed., O. R. Fennema, Ed. Mercel Dekker, Inc. (New York, NY) (1996). Chapters 10 (Colorants), 12 (Food Additives), and 13 (Toxic Subtances)
12	"Kodak Optical Products", Eastman Kodak Co., Rochester, NY (Source for Fluorescence Dyes and Data on Their Absorption and Emission Spectra).
13	Sigma-Aldrich (http://www.sigma-aldrich.com)
14	ACD/ChemSketch Version 3.50, Advanced Chemistry Development, Inc., 133 Richmond St. West, Suite 605, Toronto, ON, M5H 2L3 Canada
15	"Pigments (Organic)", Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed. Volume 19, 41 (1996) by John Wiley & Sons, Inc., 605 3rd Ave., New York, NY 10158-0012
16	"Xanthene Dyes", Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed. Supplement Volume, 811 (1998) by John Wiley & Sons, Inc., 605 3rd Ave., New York, NY 10158-0012
17	Most dye samples were found to be available in lab scale quantities from the following catalogs: Aldrich, Sigma, and ICN

Table 8.2 Candidate Dye/CA Combinations Selected (Subtasks 1.2/1.3)

Contaminant Type	Candidate Dye-CA Combination	Suggested Delivery Means
Hydrophobic Liquids	Oil Red O D&C Violet 2 (Backup)	Solvent Wipe Aqueous Cleaner
Corrosion Products	Alizarin	Solvent Wipe Aqueous Cleaner
Water Soluble Salts	Food Blue 2 Food Green 3 (Backup) Basic Blue 3 (Backup)	Aqueous Rinse Aqueous Cleaner

The proposed usage level for dyes in VCPI systems is low, e.g., 0.02 to a few percent. Most of the available ecotox data pertains to ~100% pure materials. In considering organic dyes as *100% pure materials* for health effects, according to the HSDB, "in general dyes and pigments do not present serious toxic hazards to workmen in conditions of industrial exposure". "Probably the greatest problem in workmen handling dyes is …superficial layers of skin become dyed". Therefore, the personal body protection used in DoD cleaning operations (MIL-PRF-87937C) is expected to represent sufficient worker safety protection.

A significant step in the dye/CA selection process was the assessment of the proposed VCPI test system by the DoD depot/facility staff (this report). Information was presented to these organizations for comment. Comments covering safety, operability, and environmental impact were provided (Section 2.0), which were found useful for developmental guidance and encouraging from depot acceptance perspectives.

In conclusion, although the assessment of the safety and environmental impact of the candidate dyes will continue, early results provide encouragement of their meeting the necessary environmental compatibility and safety requirements for inclusion in DoD cleaning operations.

8.2 Response to SERDP Action Item on Surface Cleanliness Measurement Methods

8.2.1 Action Item

At SERDP's request, a white paper was produced and filed with SERDP providing answers to the action item question of how cleanliness was to be measured during this project and to identify the cleanliness goals. A summary of this response is given here.

8.2.2 Response

Clear cleanliness specifications and goals were not available at the start of PP-1117 project since the list and ranking of important DoD contaminants had not yet been made. Therefore, the cleanliness goal for each large area cleaning process investigated in the PP-1117 project was established during the project for each DoD cleaning process monitoring need. The associated "measurement" technique was then identified and tested. An effort was made to ascertain how cleanliness judgments were made in the field and how best to measure them quantitatively in the lab to support VCPI technology development. The key contaminants of concern by the Air Force and Navy for monitoring fell into the three general categories: hydrophobic fluids (oils, greases, paint strippers, fuels, hydraulic fluids, etc.), metal corrosion products (especially of Al2024), and soluble corrosive salts [especially chloride ion (sea water)]. Different cleanliness assay methods are being used in the field for each of these contaminant classes, if one exists at all. These methods are described elsewhere in this report with the "cleanliness goals" and quantification potential for each.

In general, a cleanliness goal is that level of contaminant residue below which downstream treatment of the cleaned surface is not detrimentally affected by the contaminant. This is far easier said than measured. In the field, or at the depots, this condition is often related back to the cleaning operation qualitatively as a visually "clean" surface appearance (for example, loss of an "oil sheen" look to the surface), or as water break results. For laboratory use quantitative methods are available. For this project, NVR assay methods were developed for the targeted hydrophobic contaminants (LO, G, and PA7). This method development work involved the identification of solvents, other than TCTFE, which better dissolved the hydrophobic residues and which did not attack the underlying substrates. For LO contaminated Al2024P panels, this solvent is EtoAc (replaced the methylene chloride used earlier), for G this solvent is toluene for non-tiled surfaces, and pet ether for the tile application (since pet ether did not dissolve the foam rubber tiles). In addition to NVR, quantitative analytical methodologies (i.e., FTIR, EIS, ICP-MS, UV/VIS, contact angle, IC, and NVR) are in use on this project to provide level-of-contamination data to correlate with quantitative surface color space values, and to qualitative visual inspection results of the partial and fully cleaned panel surfaces. These results are also being corroborated with downstream material tests, (i.e., paint adhesion, tile adhesion, and corrosion rate comparison effects).

Hence, this project produced results, which correlate surface cleanliness with qualitative and quantitative levels of contamination (e.g., in terms of mg contaminant/ft^2 or the equivalent) (Section 7.0). In keeping within the scope of the SOW, defining "how clean is clean" was not being specifically addressed. However, the range of contamination involved in the testing is believed to encompass the full range from highly contaminated to sufficiently cleaned for the intended downstream coating purpose, or about 1-100 mg contaminant/ft^2.

8.3 Response to SERDP Action Item for PP-1117 Regarding the Proposed Cleanliness Goals of the Project

8.3.1 Action Item

"Provide the proposed cleanliness goals of the project in terms of non-volatile residue and particulate matter. If cleanliness goals have not been established, provide a plan on how and when these goals will be established".

8.3.2 Response

The cleanliness goal for each large area cleaning process investigated in this project was established during the project for each DoD cleaning monitoring need identified as significant. Acquisition and development of these goals is complete (see summaries below).

An effort was made to ascertain how cleanliness judgments were made in the field and how best to measure them quantitatively in the lab to support VCPI technology development. Particulates per se did not arise as a key contaminant for large surface area cleaning. The key contaminants of concern by the Air Force and Navy for monitoring fall into the three general categories; hydrophobic fluids (oils, greases, fuels, hydraulic fluids, etc.), metal corrosion products (especially of Al2024-T3), and soluble corrosive salts [especially salt (chloride ion), i.e. sea water]. Different cleanliness assays were used for each of these contaminant classes, these are described below along with the quantitative “cleanliness goals” for each.

In general, a cleanliness goal is that level of contaminant residual below which downstream use of the cleaned surface is not detrimentally affected by the contaminant. In the field, this condition is related back to the cleaning operation qualitatively as surface appearance or water break tests. In quantitative terms, NVR assay methods were developed for the targeted hydrophobic contaminants (a MIL spec lube oil, a grease, and a paint stripper). This development involved the identification of solvents other than trichlorotrifluoroethane, which better dissolved the hydrophobic residues and which did not attack the underlying substrate materials. For lube oil contaminated Al2024 (painted) this solvent is ethyl acetate (or methylene chloride earlier), for grease, this solvent is toluene or pet ether. In addition, we are using quantitative analytical methodologies (i.e., FTIR, EIS, ICP-MS, UV/VIS, contact angle, IC, and NVR) to provide level of contamination data to use to correlate with quantitative surface color space values and qualitative visual inspection results of the partial and fully cleaned surfaces. These results are also being corroborated with downstream material tests, (i.e., paint adhesion, tile adhesion, and corrosion rate effects). Hence, this project has been producing results, which correlate surface cleanliness with qualitative and quantitative levels of contamination (in terms of mg contaminant/ft^2 or the equivalent). In keeping within the scope of the SOW, defining “how clean is clean” results are not being specifically targeted. However, the range of contamination involved in the testing is believed to encompass the full range from highly contaminated to sufficiently cleaned for the intended downstream coating purpose, or about 1-100 mg contaminant/ft^2.

More specifically, the answer to this action item question differs depending on panel material tested and contaminant type as follows:

8.3.2.1 Hydrophobic Impurities On Painted Surfaces (i.e., grease, lube oil or paint stripper contaminants on Al2024, graphite filled epoxy, PCMS foam tile, or HY80 steel)

8.3.2.1.1 Cleanliness Test Used in the Field or Laboratory Simulation of Field Testing

In this case, cleanliness is difficult to quantify, as the water break test is not effective on the hydrophobic paint surface. Hence, cleanliness is determined by the Air Force by the visible disappearance of the lube oil sheen from the surface. The VCPI technique, when coupled with NVR assays, has indicated that this method does not “see” that portion of the oil absorbed into the paint, which may be a substantial amount, e.g. >40%.

8.3.2.1.2 VCPI Project Laboratory Quantification of Contaminant Levels

8.3.2.1.2.1 NVR Method

Cleanliness on the above surfaces are being determined quantitatively by the NVR method in the case of lube oil using ethyl acetate leaching for painted Al2024 (this method was developed to replace the methylene chloride-based method used early in the project). In the case of grease on painted tile, pet ether was used as the extracting solvent as it was found not to quickly attack the foam tile, as did the other solvents mentioned here. Toluene, and to a lesser extent hexane, was found to be fairly effective for NVR assaying grease on painted metal, e.g., painted HY80 steel or painted Al2024. However, the toluene needs to be carefully removed from the sample with mild heating and vacuum.

Interestingly, based on the VCPI technique, solvents were found to carry hydrophobic contaminants into the pores of these paints, perhaps through thinning and wetting mechanisms. Therefore attention is required to thoroughly rinse and to cleaner selection to avoid spreading contamination in this manner, which might result in topcoat adhesion failure if not removed. Importantly, this phenomenon was visually apparent only when dye was present to show the location of the hydrophobic contaminant within the paint pores. When such staining was found, then it was removable with a suitable solvent, along with the oil or grease, as verified by NVR. However, this stain may not be removable from painted Al2024-T3 using the current Air Force cleaning protocol and cleaners. Hence, if removal of hydrophobic contaminants from within paint pores is desirable, and it is not certain at this time whether or not it is, then the VCPI method would be an efficient technique to use to guide the selection of better cleaning methods and/or cleaners.

Therefore, for painted surfaces without dye, NVR analysis was found to be the most straightforward analytical method to use to assay for cleanliness with respect to hydrophobic contaminants. In addition, the VCPI technique was found to be very useful in facilitating this or any other cleaning or solvent stripping technique. The NVR method does require careful weighing techniques and does not identify the chemical form of the hydrophobic contaminant.

8.3.2.1.2.2 HPLC Method

HPLC of extracts is expected to also provide a good contaminant assay method using solvents similar or the same as those listed above for NVR, or others such as acetonitrile. The HPLC instrument is calibrated with the known contaminant in this case (lube oil). However, for unknown hydrophobic contaminants, or an unknown mixture of hydrophobic fluid contaminants, then the technique becomes very qualitative unless very extensive testing (slow and costly) is performed. While qualitative, HPLC can give an indication of the general chemical nature of the contaminant as well as an indication of its removal during cleaning.

8.3.2.1.2.2 FTIR Method

FTIR spectra of contaminated painted surfaces are complicated by the large background absorption of the organic polymer of the paint coating. Hence, IR spectra are complex and difficult to resolve with low levels of contaminants in the presence of large amounts of paint polymer with many overlapping absorption bands. Therefore, IR methods are not being used in this case.

8.3.2.2 Metal Surfaces with Hydrophobic Contamination

8.3.2.2.1 Cleanliness Test Used in the Field or Laboratory Simulation of Field Testing

Water wets metals if they do not contain adsorbed hydrophobic materials. Therefore, the Air Force uses the water break test if the test surface is not flat or nearly flat. In this *case*, the water break test is easily applied and allows the cleanliness of a large area to be assessed with respect to hydrophobic contamination. This method for hydrophobic contaminants on metal surfaces is satisfactory on vertically oriented surfaces, but not for the critical under-wing or under-belly surfaces, which are often most contaminated by hydrophobic fluids. Hence, there is a need to assay for cleanliness in these cases. It is hoped that the VCPI technique can fill this need.

Air Force also uses water break following cleaning off of corrosion products and using a “corrosion removal compound” (CRC), which is phosphoric acid/fluoride/surfactant based. Note that this test is not a measure of completeness of removal of corrosion products, but rather a verification that the entire surface has been treated through the aqueous cleaner (Re-Gel®) plus CRC processes. Any re-work is done using CRC only, not Re-Gel®, as the CRC contains suitable surfactants for detergent action removal of hydrophobic fluid contaminants.

The Navy immediately paints the bare HY80 steel surface after de-painting by grit blasting, and so a cleanliness assessment issue does not arise and is not made, other than the visual disappearance of the paint during grit blasting. The main issue in cleaning with the Navy is on painted surfaces and foam tiles (see below).

8.3.2.2.2 VCPI Project Laboratory Quantification of Contaminant Levels

With the metallic surface of Al2024-T3, background spectral interference is minimal for the FTIR technique. Hence, this technique is being applied for hydrophobic fluid contaminant (lube oil) analysis in the case of Al2024. Since very little porosity exists in metals relative to paint, staining (penetration of dye labeled hydrophobic fluid into the metal surface) is not an issue (see above). Two IR wavelengths are being used in this analysis chosen to be representative of the lube oil contaminant. The dye use level is normally too low to be assayed by this method in the presence of the other organics, and is instead being analyzed by colorimetric means previously described.

During this VCPI concept assessment program, it has been determined using the above analytical techniques that with Al2024-T3 (Air Force) metal surfaces and lube oil contaminant, the thin level of hydrophobic contaminant is readily cleaned off in seconds with ReGel cleaner and mild scrubbing. Therefore, in this case, the cleanliness assessment has more to do with whether an area was “hit” or completely missed in during the cleaning operation (i.e., the missed area in car waxing phenomenon). Therefore, the value in the VCPI technique in this case is to readily visualize these missed areas, both during initial labeling and during cleaning.

HPLC of CH_3CN extracts of metal surfaces is being used to determine residual lube oil contaminant levels on Al2024-T3.

Polarization testing is being used as a measure of bare Al2024 metal surface cleanliness by comparing relative corrosion rates of sample panels [labeled and unlabeled (reference) lube oil contaminated then “completely” cleaned panels] with cleaned blank panels.

8.3.2.3 Metal Corrosion Products on Metal Surfaces

8.3.2.3.1 Cleanliness Test Used in the Field or Laboratory Simulation of Field Testing

The Air Force uses water break following cleaning using a corrosion removal compound (CRC). This method for hydrophobic contaminants on metal surfaces is satisfactory on vertically oriented surfaces, but not for near horizontal surfaces, especially the critical under-wing or under-belly surfaces, which are often most contaminated by hydrophobic fluids.

The Navy immediately paints the HY80 steel surface after de-painting by grit blasting, and so a cleanliness assessment issue does not arise and is not made, other than the visual disappearance of the paint during grit blasting. Foamed tiles do not contain corrodible metal components.

8.3.2.3.2 VCPI Project Laboratory Quantification of Contaminant Levels

Corrosion levels for Al2024 T3 are being determined indirectly by capturing the Al ion as it is removed from the surface by the Re-Gel®/CRC process operated for time periods up to that specified in the T.O. This used cleaner is then analyzed for Al by ICP-MS. As the detection limit for Al by this method is in the low (<10) ppb range, and the removed Al levels are in the tens or hundreds of ppm, Al removal rates and amounts can be determined to high precision and accuracy.

Surface contact angle also gives some indication of cleanliness (with respect to hydrophobic organic contaminants) and/or roughness of Al2024-T3 after cleaning with CRC. Both the removal of corrosion by-products and surface roughening effects were observed as a function of CRC exposure time.

8.3.2.4 Soluble Corrosive Salts (Se a Water Residues)

Cleanliness test used in the field or laboratory simulation of field testing: This contaminant class is of interest to both the Navy and the Air Force. Currently the only field assay is the disappearance of visual salt deposits accumulated from dried seawater.

8.3.2.4.1 VCPI Project Laboratory Quantification of Contaminant Levels

In the lab, anion ion chromatography (IC) is being used for precise and accurate determinations of chloride ion as it appears in the cleaning bath. Although very definitive for lab use, IC is too complex, and with a significant instrumental down time, to be used routinely in the field.

Attempts were made to use ESCA to analyze for surface chloride ion on cleaned and feed panels, but the detection limit was not low enough to obtain data at the needed levels.

9.0 CONCLUSIONS AND TECHNOLOGY PROJECTIONS BASED ON LAB AND BENCH-SCALE CLEANING TEST RESULTS

9.1 Conclusions from Cleaning Test Results

The cleaning test results appear to validate the basic VCPI concept, i.e., that it promises to provide a real time cleaning process-monitoring capability. This result meets the success criteria for the PP-1117 project. This finding resulted from both pre-screening and systematic cleaning tests. Hence these results validate proceeding to the next commercialization steps, which focus on the identification of which cleaning operations would be the most suitable for field testing. This conclusion that the VCPI concept for cleaning process monitoring works in principle is based on the following specific laboratory-scale findings:

- Surface contaminants can be rendered visually apparent using dyes, even at the thin film and spotty conditions of contaminants on materials important to the DoD.
- The VCPI technique does in fact make it much easier to monitor the cleaning operation visually in real time. In fact the VCPI technique has allowed quick cursory evaluation of cleaning times, labeling times, solvents, aqueous cleaners, corrosion deposit thickness, contaminant uniformity, etc. to be readily assessed during the course of this work.
- The dye and contaminant was demonstrated to track each other through the cleaning process, as required for all systems tested.
- The selected dyes do not tend to label unwanted surfaces, i.e., “clean” surfaces. Hence, the original hypothesis appears to be accurate, i.e., that there are commercial dyes already available with suitable physical-chemical properties and industrial/environmental compatibility to use for the VCPI technique.
- Numerous contaminants can be labeled with one of just three dyes. As the identification of contaminants range widely, this feature is particularly valuable. Otherwise, numerous dyes would be necessary, thereby limiting and/or complicating the use of the technology.
- Deployment of the VCPI technique to the cleaning operation with little change to the overall process appears possible, at least to some contaminant classes, especially PA7, soluble corrosive salts, and to aluminum corrosion products (see below).
- Based on preliminary laboratory screening tests, the VCPI method has the potential to be a simple and cost-effective, real-time cleaning verification technique.

9.2 Preliminary Projection of VCPI Deployment Alternatives

A key element of deploying VCPI technology is the identification of a method(s) by which the dye can be applied to the contaminant in the cleaning process. The originally projected methods for accomplishing labeling in the field are still valid given the cleaning test results from this program. However, now more specifics can be added with respect to contaminant types, cleaners, cleaning processes, and vessel or aircraft surface materials. A summary of these deployment opportunities follows:

9.2.1 Corrosion Products Labeling

Corrosion products and corrosive soluble salt removal may be the easiest to deploy as only a water solution of dye is needed to apply the dye to the contaminant on the surface to be cleaned.

9.2.2 PA7 Paint Stripper Labeling

PA7 paint stripper appears to only need to have dye added to it by the PA7 vendor, which is only an add and mix operation. On-surface hydrophobic contaminant labeling is the most difficult case and this was demonstrated at the lab scale with panels. In accomplishing these labeling tests, a number of approaches were identified for labeling these key classes of contaminants. The approaches should be screened in field tests to access efficiency and operability (i.e., application via an aqueous alkaline cleaner, a water rinse, or via an accepted solvent wipe such as ethanol or isopropyl alcohol).

9.2.3 Cost of Natural Red 4

Several low cost VCPI (dye/CA) candidates are commercially available for selective labeling of the target classes of contaminants. However, NR4 dye is somewhat expensive depending upon use rate (see below). Therefore, it is recommended that vendors pursue economies of scale for bulk pricing or that substitution equivalents be pursued.

The potential technology delivery system options are given in Table 9.1.

Table 9.1 VCPI Dye Delivery System - Preliminary Concepts (1)

Contaminant Class	**Contaminant Examples (* = specifically tested in this work)**	**Water Rinse Delivery Systems** { i.e. Aqueous Solutions (e.g., mild alkaline cleaners), non-VOC solvent-based solutions (i.e. IPA/EtOH)}, or "rinse water" with a wetting agent, etc. }	**Aqueous Colloid – Based Delivery Systems** {e.g., degreasers, emulsions, aqueous rust inhibitors, or detergents}
Solids	• Corrosion Products (*) • Conversion Coats	All	All
Hydrophobic Fluids	• Oils (*) • Greases (*) • Paint Strippers (*) • Fuels • Hydraulic Fluids	Non-VOC solvent-based solutions (i.e., of IPA/EtOH)	All
Corrosive Water-soluble Salts	• Chloride Ion • Soluble Salts • Seawater (*)	All	Applicable, but probably not necessary unless coupled with at least one of the other contaminant classes?

(1) VCPI dye delivery systems may benefit from gel forming formulations since these would allow longer contact times with the surface to be cleaned, and would enable more complete utilization (less waste) of the dye.

9.3 Projected VCPI Technique Application Issues and Findings

Based on these prescreening test results and ongoing systematic cleaning testing (to be summarized in the final report), we preliminarily conclude that the VCPI technique generally does provide the desired facilitation of cleaning operation and contaminant location identification features sought for by the SERDP PP-1117 program. Results to date suggest that the best first VCPI applications may be: PA7 paint stripper for foam PCMS tiles, Al2024 corrosion product removal, and soluble salt removal. Hydrophobic contaminant applications also appear to be valuable, but identification and verification of the means for deploying the VCPI technique development is to surface hydrophobic contaminants farther behind.

The VCPI technique illustrates that contaminants LO or PA7 do penetrate porous underlying surfaces (paint and tile, respectively), and that current cleaners may not or may (respectively) provide sufficient removal of those absorbed contaminants depending on the specific cleaner, use technique, and/or cleaning protocol used. If the contaminant is not completely removed, then some dye will be left with it, resulting in a stained surface appearance.

Without the VCPI technique, cleaning verification varies with basis material and includes 1) post corrosion removal water break testing (for Al2024 metal surfaces), 2) surface oil sheen appearance and general surface appearance, or 3) over cleaning for painted surfaces, or paint or tile adhesion. VCPI promises to provide one method to monitor surfaces in all of these cases, although the specific dye in use will differ, this should be transparent to the user since different cleaning chemicals are used in each case.

During this VCPI concept assessment program, it has been determined using the above analytical techniques that, with Al2024 metal surface and LO contaminant, the thin level of hydrophobic contaminant is readily cleaned off in seconds with Re-Gel® cleaner and mild scrubbing. The situation and results are similar for the corrosive soluble salts case. Therefore, in these cases, the cleanliness assessment has more to do with whether an area was "hit" at least once or completely missed during the cleaning. The value in the VCPI technique in this case is to readily identify (visualize) these missed areas, both during initial labeling and during cleaning.

9.4 Preliminary Estimate of Dye Use Level Required for the VCPI Technique

Figure 7.13 addresses the question of how much dye is needed on the surface being cleaned to provide sufficient visual effects. Hence, according to the y-axis of Figure 7.13, this value was as low as 1.6 mg/ft^2 of ORO for aged Al2024P panels. The results of Figure 7.13 also illustrate that contaminant removal, based on dye removal, is quantifiable and dependent upon cleaning conditions and cleaner strength. UV aging effects are measurable, but small.

9.5 Preliminary Dye-CA Cost Estimate

9.5.1 Oil Red O Example

For the Oil Red O Dye-CA candidate, the preferred ratio for the 30-125 mg oil/ft^2 of contaminant per panel area is estimated to be in the 40-200 mg/L range. Using the mid-value of 80 mg oil/ft^2 and an oil/dye v/w ratio of 120, the weight of dye/ft^2 is 0.67 mg dye/ft^2, or substantially below the 3 mg/ft^2 of even highly cleaned surfaces. At laboratory scale, Oil Red O is $21/100 g or $95/lb. Bulk prices are anticipated to lower this cost to about $10/lb. Based on these values, the cost of dye per 1000 ft^2 (670 mg) is estimated to be about $0.015. If dye losses in the operation are 90%, then the cost per 1000 ft^2 of aircraft surface would be $0.15. This preliminary cost seems reasonable.

In terms of the amount of ORO dye that would be needed to apply the VCPI technique to all USAF F-16 aircraft, the following parameters were gathered:

- The area of an F-16 aircraft is 1900 ft^2.
- There are 88 F-16 aircrafts that are cleaned on 30-day intervals, 992 F-16 aircrafts are cleaned on 90-day intervals, and 330 F-16 aircrafts are cleaned on 120-day intervals.
- The amount of dye needed to label the aircraft is 2 mg ORO/ft^2 (see Results Section 7.0).
- The amount of Re-Gel® needed for dye deployment is 1,200 mg ORO per liter of Re-Gel® (see Results Section 7.0).
- From the above values, the following ORO demand was calculated.
- 11,426,600 ft^2 of F-16 aircraft are cleaned annually.
- In order to clean these F-16 aircraft using the VCPI method, 5.0 lb ORO and 1904 L of Re-Gel® are needed per year.

Note that detailed field tests are needed before reliable cost figures can be developed.

Some additional comments can be added to this subject as follows. One cost parameter for VCPI utilization will be the dye consumption rate per aircraft or vessel cleaned, which will in part be related to the area cleaned. The amount of the dye *bonded* to the contaminant on the surface is probably not a key parameter. Rather, the amount of dye *wasted* while administering dye to the contaminated surface could be far more costly depending on the application technique and labeling chemistry. If label yields are high or if VCPI formulation dye concentrations are low, then low costs of administering the technique is expected. Hence, gelling cleaning formulations, such as Re-Gel®, are expected to provide ideal labeling vehicles. Also, the lower the cost for the dye component, the greater can be the inefficiencies of labeling since larger amounts of dye may be used to compensate for inefficiency. These VCPI dye application approaches should be examined quantitatively using cleaning test results during pilot and field trials.

9.5.2 Natural Red 4 Example

NR4 is the only VCPI dye candidate with a significant per-lb cost. Commercial sourcing for NR4 supplies may be important to control raw material cost. NR4 has been shown to be an excellent VCPI label performer in the cleaning tests as it provides highly selective metal corrosion product labeling chemistry (Figure 9.1) and yet only requires a water rinse/soak to use. NR4 is expensive for small, high purity, lab-scale quantities ($1000/lb). This cost may drop to ~$100/lb at the industrial scale and technical grade. A bulk estimate was obtained from a chemical supply vendor for carminic acid of $402.50 per lb for 1000 lb. NR4 would probably be cheaper if a synthetic surrogate can be found, or if the market for VCPI is sufficiently large to enable some cost reduction from an economy of scale factor for the raw material. Fortunately, for NR4, the labeling reaction (Figure 9.1) yield appears to be very high yield (estimated at > 80% from appearance), resulting in little unused dye waste. This price for NR4 translates into 22 cents per 1000 ft^2 treated at 1mg dye/ft^2 of surface cleaned. Although this cost may be palatable in many cases, for example in parts cleaning or crevice corrosion, a search for ways to decrease this cost through contract sourcing by the detergent supplier, minimization of NR4 consumption rates, or surrogate identification is warranted. Note that any NR4 substitution dye must also have the equivalent good ES&H/ES&O fit. These points should be considered again in executing the transition plan.

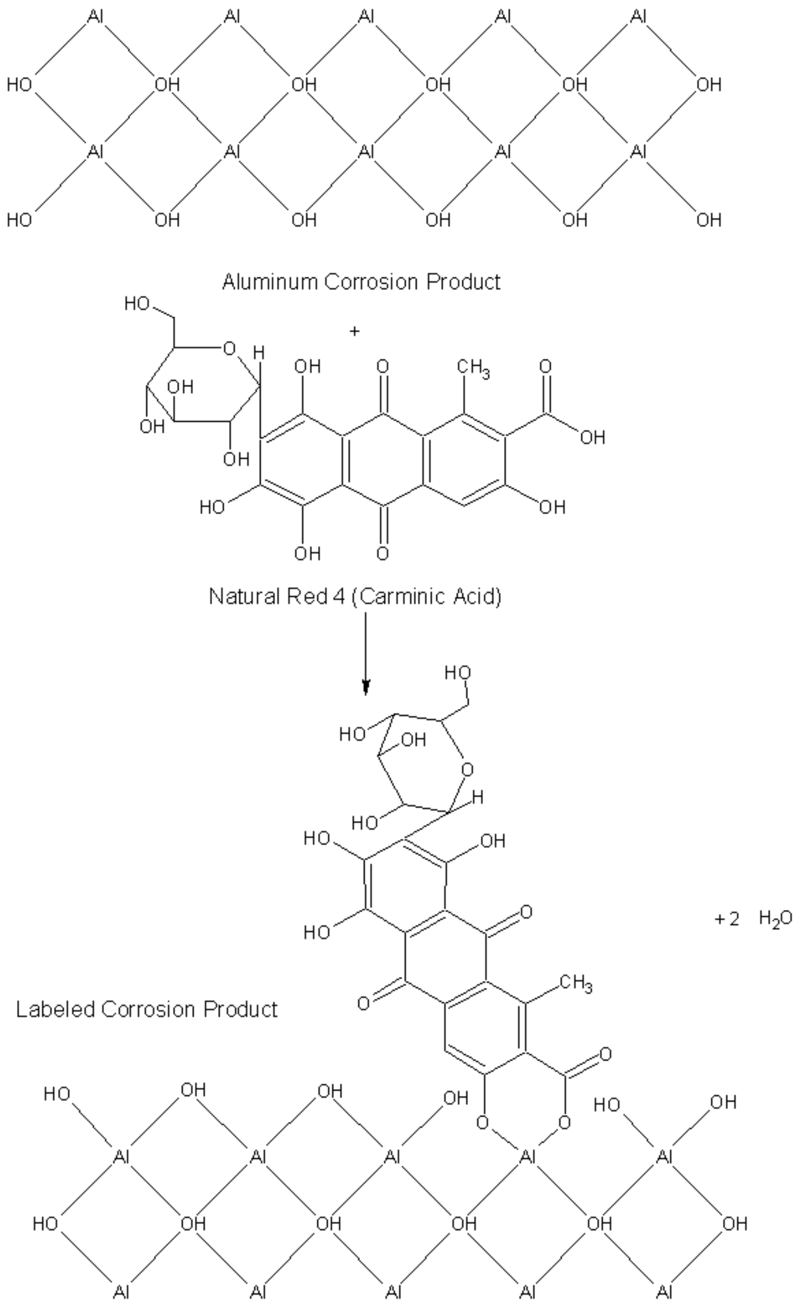


Figure 9.1 Metal Corrosion Product Labeling Chemistry

Alternatively, since the key fundamental chemical structure of NR4 is not inherently expensive, i.e., many low cost dyes have the basic polycyclic structure of NR4 (Figure 9.1), a dye manufacturer might be approached to consider manufacturing NR4, or a surrogate of it, as part of a relationship with a cleaner formulation supplier. NR4 appears to represent a new commercial product opportunity for a specialty chemical manufacturer. This approach may be attractive for the specialty cleaning company given the potential large volume of the cleaning VCPI market and the familiar difficulty that cleaning products companies have in product differentiation. These, and other such options, were considered in formulating the transition plan (Section 2.0).

9.6 Overall Conclusions

In conclusion, it was observed that, at the lab and bench-scale cleaning tests, that the VCPI technique is a practical and economical method for monitoring certain large area DoD cleaning operations. It appears that the VCPI technique would also be a significant benefit in helping develop better cleaners and cleaning protocols due to the real time/quick visual feedback on performance that the technician receives during the cleaning operation. It will be important to determine whether these same benefits can be transferred to the field. The method also appears very suitable for cleaning small parts. These last two recommended applications appear to provide good avenues for first steps in commercialization of the technology. Therefore, the key conclusions from the cleaning and associated test results are as follows:

- The VCPI chemical formulation used to label corrosion product contaminant does not compromise system material of construction corrosion resistance or wettability, i.e. of Al2024-T3 substrate after T.O. 1-1-691 cleaning
- The VCPI technique usefulness concept was verified for six important DoD (AF & Navy) cleaning needs
- The VCPI technique provides the desired facilitation of real-time, total surface cleaning operation and contaminant location identification features sought for by the SERDP PP-117 SOW
- The VCPI selectively labels contaminates and not the surface being cleaned
- The VCPI technique indicates that a substantial portion of “all” hydrophobic contaminants penetrate certain porous surfaces (paint and tile) during the paint cleaning or stripping operation
- The VCPI technique clearly indicates that current cleaners and/or cleaning protocols leave a substantial portion of hydrophobic contaminants within paint or PCMS tile coatings, and that in such cases, the VCPI method will leave a residual color in the porosity of the surface as there is residual contaminate there (see Recommendations), indicating that the VCPI technique appears would be an excellent method to screen for better cleaning agents and protocols
- The VCPI technique clearly illustrated that corrosive soluble salt and corrosion product contaminants are removed efficiently using current MIL spec cleaners and DoD cleaning protocols from all tested system materials, hence in these cases, the VCPI technique is valuable in providing “hit or missed” information to the on-going cleaning operation
- VCPI technique guides the cleaning operation and appears may provide a fairly quantitative assessment of cleanliness if the effort is made to calibrate the response for a particular protocol, contaminant class, and surface composition type.

Regarding the approach to the testing, we can say that running the numerous test systems in blocks, as sets of three, was an effective and practicable approach. This justification is conveyed through the consistency amongst the different blocks reported in the plots. Hence the conclusions presented in this report are supported by systematic cleaning tests and supportive analyses performed in triplicate. In addition, those from prescreening testing obtained from a second laboratory support the detailed test results.

10.0 VCPI PRESENTATIONS AND PUBLICATIONS

1. “FY99 Annual Report on Visual Cleaning Performance Indicators (VCPI) for Cleaning Verification”, SERDP PP-117, December 22, 1999
2. 2000 Air Force Corrosion Conference Proceedings, Macon, Georgia, March 13-16, 2000
3. 2000 DoD/Industry Aerospace Coatings Conference Proceedings, Norfolk, Virginia, May 23-25, 2000
4. Joint Services Pollution Prevention Conference and Exhibition Proceedings, San Antonio, Texas, December 6-9, 1999
5. DoD NDIA/Picattiny Chapter P2 Conference, November 18, 1999
6. Partners in Environmental Technology Technical Symposium and Workshop, Arlington, Virginia, November 30 – December 2, 1999
7. Partners in Environmental Technology Technical Symposium and Workshop, Arlington, Virginia, November 28-30, 2000
8. VCPI SERDP P-1117 project final report (this document).
9. “FY00 Annual Report on The Evaluation of the Concept of Using Visual Cleaning Performance Indicators (VCPI) For Cleaning Verification”, SERDP PP-117, January 18, 2001

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APPENDIX A

Selection of Dyes and Coupling Agents
(Subtasks 1.2 and 1.3)

A.1 Utilization of Commercially Available Dye Information

The VCPI technology identification and development strategy for identifying CA-dye combinations in use is depicted in Figure A.1. This strategy maximizes the use of the extensive knowledge base already in place for the dye, CA, and cleaning industries. Well established dye and CA science technologies exist in product areas such as manufactured foods, clothing, coatings, inks, plastics, cosmetics, drugs, plastics, etc. In each of these instances, the dye provides a cosmetic (color) or functional (tracer) role and is suitably coupled to the product. Likewise, formulation and cleaning science exists in product areas such as detergent-based cleaners, rust inhibitors, paints, processing aids, etc.

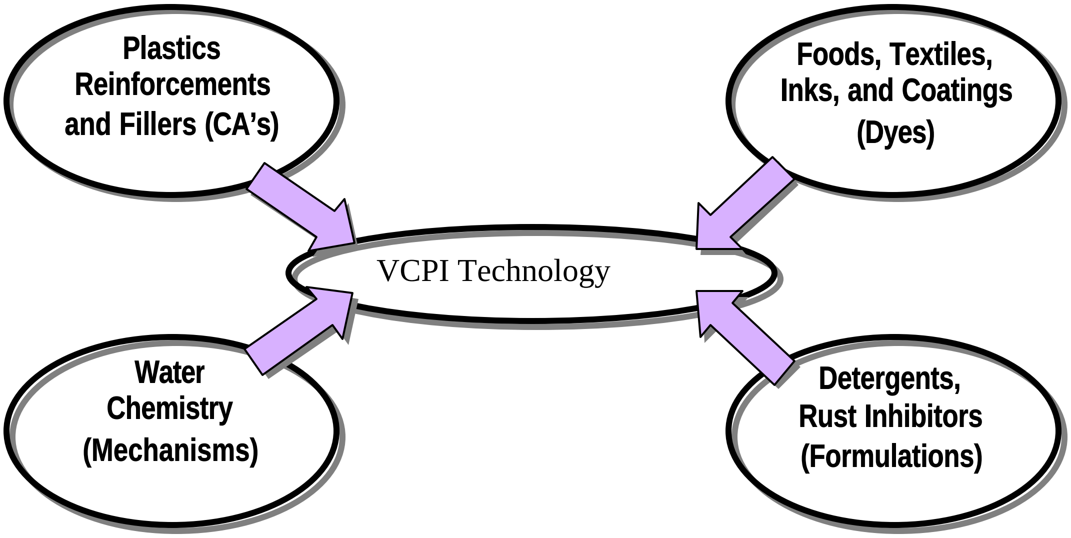


Figure A.1 Developing the VCPI Method by Capitalizing on Proven Technologies from Other Fields

Three examples serve as a presidence that the VCPI concept technology may be efficacious in cleaning applications.

White clothing takes on a yellow "dingy" coloration as UV chromophores develop in the material due to oxidation and staining. This yellowing appears because the UV electronic absorption bands, "UV chromophores", of these new species "tail" into the visible spectrum, thereby absorbing a portion of the purple-blue region, leaving the yellow-red to produce the dingy color. To counteract this effect, fluorescent dyes are added to laundry detergents which are substantive (absorbed preferentially) to textile fibers. The UV light from room and daylight then excite these dyes causing them to fluoresce in the blue portion of the spectrum, thus replacing the light absorbed by the UV absorbing chromophores. Hence, the clothing appears brighter and whiter to the eye. Therefore, the phenomenom of adding a dye during a cleaning process to enhance the appearance of a surface to the human eye is not only possible, but is in widespread use. Note, however, that in this case the fabric and not the contaminant is the target for the dye. Normally dyes in detergents serve a role of making the product more visually appealing to the consumer, i.e., provide a cosmetic effect, and to help distinguish one product from another.

A second example, showing that dye labeling is effective for thin films, is the case where a dye, a biochemical protein “stain”, is used by dentists to render bacteria on the surface of the teeth visible. In this case, the process is to aid in cleaning (brushing) teeth. The labeled teeth can then be brushed at locations where the red color (bacterial protein stain dye) can be visually seen to exist, and then only for as long as the dye color is apparent. The selectivity is such that, once the dye color is gone, the bacteria population has been reduced to acceptable levels.

As a third example, dyes also serve functional effects in hydrocarbon products such as oils, fuels, hydraulic fluids, leak detecting fluids, and antifreezes. Here the critical role of the dye is to visually distinguish the various products apart from one another, since without the dye, they would appear and physically handle similarly. In these applications the dye provides a safety feature in that it clearly differentiates these combustible and/or toxic nearly water-white products from water.

To meet the demand of these many industries, dye manufacturers and distributors provide a significant range of dye-CA chemistries. Some general examples of chemical groups involved are given in Table A.1. This industry with associated literature provides a large amount of test information on formulating or coupling dyes into products, and on their waste treatment, biodegradability and toxicity issues. Much of this information is available from the open literature, vendor catalogs, reference materials, and other sources (1-19).

Table A.1 General Chemical Categories of Commercially Available Coupling Agents and Dye Information

Commercially Available Coupling agents (X – R´ – Y):

- X (contaminant binding functionality):
- alkoxy silanes, titanates, alkyl, aryl, amines, phosphonates, quaternary ammonium, riazines, alkyl sulfates, vinyl sulfones, pyrimidines, azides, zirco-aluminates, etc.
- R´ (bridging group linkage): alkyl, triazine, sulfone, etc. (can possess hydrophobic and hydrophilic character)
- Y (compatibilizing group): mines, esters, epoxides, vinyl, sulfonates, etc.

Commercially available dye types:

- Application Dye Types: reactive, food, drug, cosmetic, solvent, fast, etc.
- Chemical Groups: Azo, triphenyl methane, natural (e.g., β-carotene), anthraquinone, xazine, xanthene, etc.

The preferred approach in selecting dyes and CA for VCPI testing was to select dyes in which a suitable coupling agent functionality was already incorporated into the dye product from the manufacturer. This approach has proven effective in this project and promises to speed deployment of the VCPI method by minimizing the need for possibly new chemical compounds formation issues, which could lead to additional requirements for registration and ecotox testing.

A.1.1 Potential Contaminant Labeling Mechanisms

Several chemical mechanisms are envisioned as being useful for labeling contaminants in surface cleaning. These mechanisms are based on well known chemical reactions and were used to help select dye-CA combinations for the target DoD contaminants. Importantly, the specific mechanisms appear sufficiently selective to target classes of contaminants and not just single contaminant species, yet they are believed to be selective enough not to have specific affinities for the material surface being cleaned.

A brief description of the three labeling mechanisms (one of each of the contaminant categories, i.e., hydrophobic fluids, corrosion products, and water-soluble salts) is provided in the following text.

A.1.1.1 Labeling Hydrophobic Fluid Contaminants

To produce color, dyes need at least eight conjugated double bonds with some non-bonding electrons available for the $n \rightarrow \pi^*$ electronic transitions which give rise to the observed color. This requires dyes of molecular size >16 atoms of C, N, and O. Often dyes have twice this number of atoms due to pendent groups, which tune solubility and color. Greases and oils contain molecules in the C_{10-40} range, which are free to move (by fluid flow or diffusion) within the hydrophobic fluid phase. Therefore, due to this similarity in size, it would not be viable to covalently bond a dye to such molecules because then the labeled molecule will no longer behave, as does the bulk. Therefore, the VCPI approach in this case is to administer a dye, which is highly soluble in the hydrophobic fluid (hf) and not in water (aq), i.e.,

$$\text{Dye (aqueous)} \Leftrightarrow \text{Dye(hydrophobic fluid phase)} \qquad (A.1)$$

$$\text{Distribution coefficient (Kd)} = [\text{dye}]\text{h.f.} / [\text{dye}]\text{aq} \quad >> 1 \qquad (A.2)$$

Hence, such dyes will be oil soluble (e.g., solvent dyes or disperse dyes). For example, the red dye in hydraulic fluid is usually a “Solvent” Red dye. Table A.2 lists a number of disperse and solvent dyes, which might be used for hf contaminant VCPI systems. As can be seen, wide ranges of chemical groups are represented, raising hopes that suitable safe and environmentally acceptable dyes exist for the VCPI technology applied to hf contaminants. Two approaches were identified for devising the VCPI system for hydrophobic fluid contaminants, solvent applied, and colloid applied. These approaches are described below.

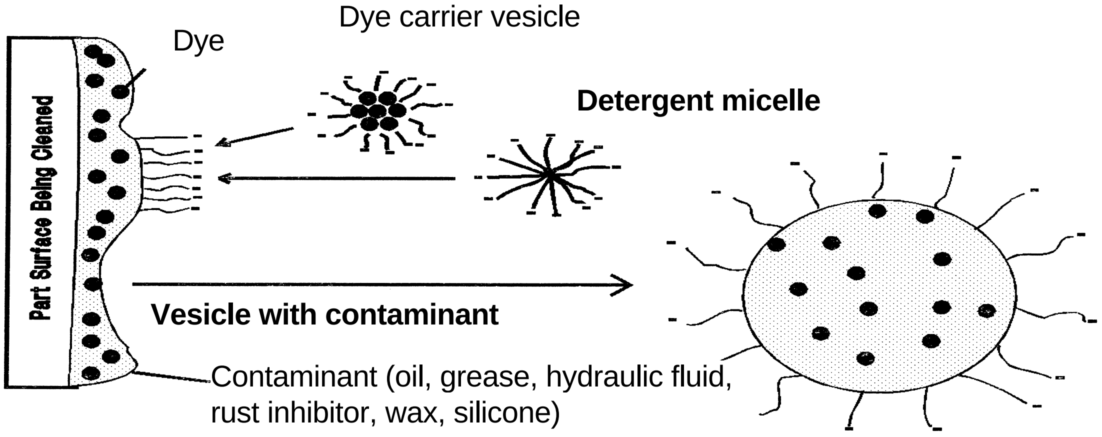
In solvent applied approach, the selected dye would first be dissolved in the normal MEK, toluene, or other wipe solvent. Long term this dyed solvent could be provided by vendors. When this solvent is applied to the equipment surface in the usual manner as a precleaning step wipe or wash solution, the dye absorbs into the hydrophobic fluid thereby imparting a color to it. Some “soak” time would facilitate labeling. Most of the thicker areas of the fluid contaminant may also be removed in this precleaning step. However, any residual contamination would appear visually as colored areas. These areas then could be cleaned further using non-dyed solvents or aqueous cleaners as required by the tech orders or process orders.

Table A.2 Examples of Dyes Soluble in Hydrophobic Fluids.
Preliminary Candidates for Labeling Hydraulic Fluids, Fuels, Oils, and Greases.

Hydrophobic Fluid Soluble Dye Name	C.I. No.	Chemical Class
D&C Violet No. 2	60725	Anthraquinone
D&C Green, No. 6	61565	Anthraquinone
D&C Red No. 17	26100	Azo
Oil Red O	26125	Azo
b-Carotene	75130	Carotenoid (olefinic)
Turmeric	75300	*b*-Diketone
D&C Yellow No. 11	47000	Quinoline

Figure A.2 depicts an alternative aqueous, colloid-based, VCPI labeling technique. This method uses aqueous detergents, not a solvent, to transport the dye to the hydrophobic liquid contaminant for spontaneous labeling. This transport would be accomplished via the action of the colloids, which are a well-characterized critical component of a detergents performance. In fresh cleaner diluted to use concentration, these colloids are small (e.g., < 0.3 micron) “micelles”. As the cleaner accumulates hydrophobic contaminants, these micelles enlarge to vesicles, i.e., > 0.3 micron colloids, filled with contaminants dispersed in water due to their outer layer of surfactant. The surfactant, or “detergent”, accomplishes this dual phase role by having a hydrophilic polar end group, which interacts strongly with water and a hydrophobic moiety which mixes easily with molecules of the hydrophobic liquid.

The visualized mechanism of action of the detergent solubilizing/dispersing the hf contaminant (Figure A.2) is for a micelle to layer out on the surface of the fluid, followed by inter mixing of hydrophilic groups, and then gradually break away in vesicle form, with this detergent assembly now containing a portion of the hydrophobic liquid encapsulated within. Repeating this cycle again and again with fresh micelles eventually solubilizes all of the contaminant fluid, which provides a sufficient detergent capacity by the cleaner. The mechanism of dispersion for charged vesicles is electrostatic repulsion of the similarly charged colloids, or hydrophilic solubilization if the surfactant is non-ionic.



Note: Dye may also be introduced via solvent cleaner or as water solution

Figure A.2 Aqueous Colloid-Based VCPI Labeling Concept

For applying VCPI technology using the above described detergent action mechanism, already a part of cleaner formulated action, it is proposed to first incorporate the dye into the micelles of the cleaner (or an aqueous pre-rinse with detergent). Due to the intense color of the commercial dyes, very little, if any, of the detergent capacity will be required to do this. On adding the cleaner or pre-wash solution to the surface to be cleaned, the micelle/hydrophobic liquid interaction spontaneously occurs (Figure A.2) causing the fluid to become dyed by diffusion and fluid flow. The greater the viscosity and thickness of the hydrophobic liquid, the more benefit will be gained from longer contacting (soak) times and increased temperature.

A.1.1.2 Labeling Water-Soluble Ionic Contaminants

Water-soluble inorganic salts, if present on metal surfaces, work with available moisture, to catalyze their corrosion. Chloride ion-based corrosion often occurs through a deeply penetrating "pit" mechanism making this form of corrosion particularly damaging. Crevice corrosion is also serious, as it is hard to detect and occurs at joints. The role of the dissolved salt in enhancing corrosion rates is twofold. Soluble salts provide an electrical conductivity connection between cathodic and anodic areas on the metals surface. A galvanic electrochemical cell is formed involving an oxidant (normally atmospheric oxygen, O_2, or a dissimilar metal such as silver), and a reducing agent (the metal, normally aluminum or iron). Chloride ion is particularly efficacious in catalyzing metal corrosion as it also provides inner sphere electron transfer between metal ions and surfaces, and it is ubiquitous in the environment, especially seawater. All of the salts of chloride ion are of concern as DoD/DOE contaminants are very water-soluble; especially at the low ppm levels needed for chloride ion catalyzed corrosion mechanisms.

The VCPI approach to labeling the salts takes advantage of their high water solubility and the fact that ions dissolve in water, and spontaneously scramble with respect to the counter ion with which they are paired, i.e.,

$$[\mathrm{Dye}+, \mathrm{X}-](aq) \quad + \quad [\mathrm{M}+, \mathrm{Cl}-](aq) \quad = \quad [\mathrm{Dye}+, \mathrm{Cl}-](aq) \qquad (A.3)$$

This phenomenon is spontaneous and is driven by the thermodynamic entropy of mixing. Actually, in solution, a cation "cloud" surrounds each anion in solution and visa versa. (Chloride concentrations in the mission/home-based environment drive aircraft wash and rinse schedules. Presence of chloride in the bulk environment has been found to be a driver of corrosion damage.) Therefore, in implementing the VCPI concept to soluble salts, the surface containing the chloride ion contaminant will be contacted, via, e.g., an aqueous rinse or detergent solution in the normal course of the cleaning process, which also contains a highly water-soluble cationic dye. Cationic dyes are usually based on protonated amines, quaternary amines, or amine oxazines. Therefore, in the case of chloride ion and water-soluble contaminant salts in general, the CA is the labile ionic bond between Cl- and the positively charged dye, and the constituents on the dye which renders it highly water-soluble, normally sulfonate anionic groups or sugar groups or other salt. Hence, when the color is washed clean from the surface, then so is the corrosive chloride ion. It is important that the dye be very water-soluble and has a low affinity for the metal surface. A sulfonated dye with some steric hindrance around the planer chromophore is expected to offer these properties. The net charge on the dye is ideally only +1 so that other potential charge-charge or charge-surface interactions are avoided or at least minimized.

A.1.1.3 Labeling Solid Contaminants

In this mechanism, the dye of the VCPI system is covalently bonded to the solid phase contaminant. Figure A.3 depicts a general approach for accomplishing this bonding to metal corrosion contaminants, identified in Subtask 1.1 as a key DoD need. For corrosion contaminants, complexation is used to couple the dye to metal ions present in the corroded area (normally aluminum ion, Al^{3+} for the DoD needs). The coupling agent is chosen to be already a part of the dye as a chelating group, e.g., as α-dihydroxy aromatic, α-hydroxy carboxylate aromatic, or perhaps sulfonate groups. The chelate group binds surface metal ions. The dye concentration would be low enough such that there is only sufficient dye to bind only the metal ions located near the surface of the corrosion solids pores. Sulfonic acid-based dyes are used if the VCPI application needed is in the acid strip step, carboxylates for water wash step, and α-dihydroxy aromatics for alkaline cleaners of the surface cleaning operation. Therefore, the pH of the cleaning operation is used to select the functional dye bonding groups from complexing ligands based on sulfonic acid, carboxylic acids, hydroxylated aromatics, and amines. All would be of low concentration. Only bidentate chelating groups will be selected to prevent waste disposal issues, which occur with chelating agents containing much higher denticities, e.g., 4-7.

A.1.1.4 Examples of Dye-CA Selection Strategy

Based on the candidate labeling mechansims discussed above, a decision tree, shown in Figure 7.1.2, was constructed to help identify dye-CA candidates. Applying the contaminant lubricating oil to the scheme in Figure 7.1.2 guides one to the proper dye-CA chemistry choice in the following manner:

Step 1: Lubricating oil is a liquid – go right

Step 2: Lubricating oil is oil soluble – go down

Step 3: Conclude that the dye-CA compound needs to be an oil soluble dye-CA VCPI candidate. Such chemicals are available commercially as “solvent” or “disperse” dyes (7,9,10,17). These dyes are neutral compounds with about four short (1 or 2 carbons) alkyl groups making up the “CA” functionality to provides the affinity for the lubricating oil.

A second example is for water-soluble salts, which lead to coating disbondment and structural corrosion if not removed from the metal surface prior to primer and topcoat application. In this case, the water-soluble salt is considered dried solid residue that will be removed in an aqueous cleaning operation. Therefore, in the case of soluble salts, Figure 7.1.2 guides one to liquid (right), then to water-soluble (right), then to ionic form, which results in the selection of highly water-soluble ionic dyes. Food coloring dyes are usually of this form (although many of them do not have cationic groups as a part of their structure).

A third example of using the selection scheme in Figure A.1.2 is for metal corrosion products (Figure A.3). In this case, the contaminant is a solid inorganic (therefore, exit left in the first two decision steps). Metal corrosion products in the presence of air and moisture usually corrode to hydrated oxides, e.g., AlOOH in the case of aluminum metal. Therefore, the selection should be a metal ion complexing dye, for example Natural Red 4 (or NR4, or carminic acid). NR4's adjacent hydroxyl-carboxylate and hydroxyl-hydroxyl groups bind to the metal causing ionization of the binding groups, which causes the number of molecular bonds participating in molecular orbital delocalization, thereby resulting in lower energy level spacing between these the bonding/nonbonding/excited state orbitals, causing the absorption band maxima to shift towards the visible from the UV, which causes the normally light yellow compound to form a deep reddish purple color (see below). Therefore, only the labeled corrosion product is reddish purple colored.

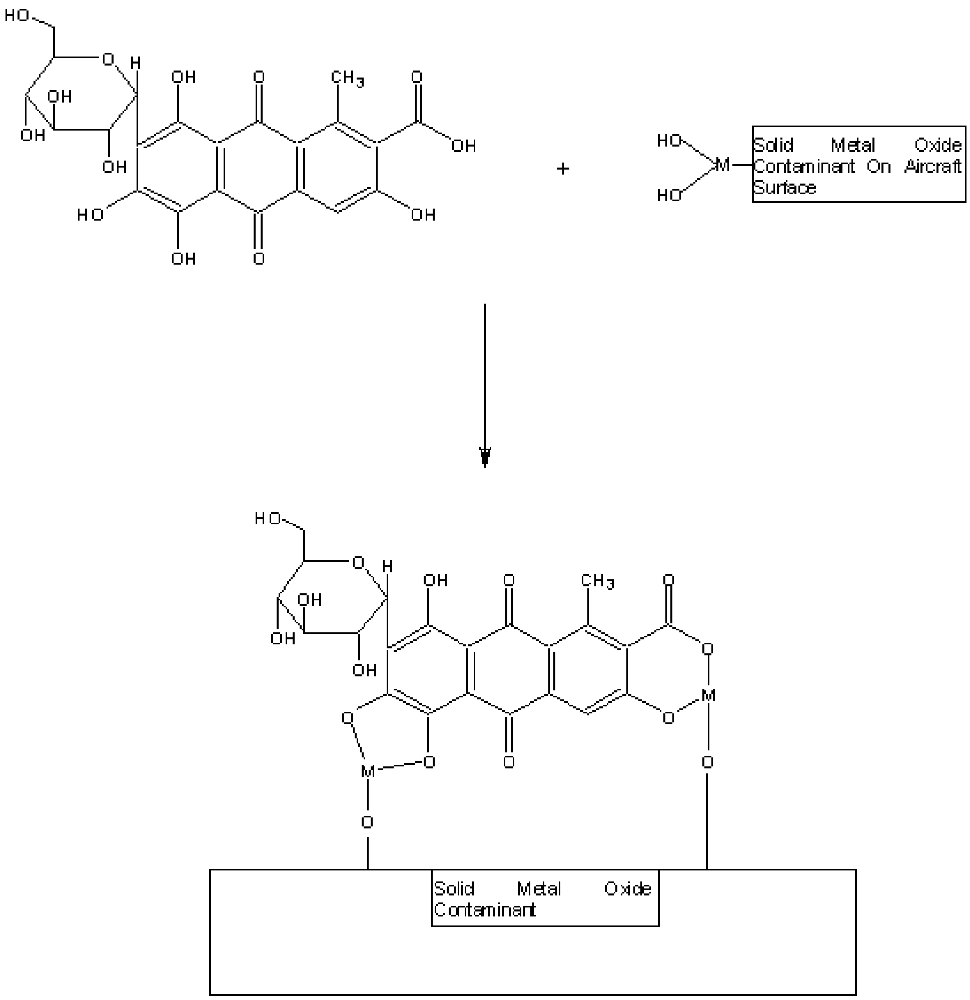


Figure A.3 VCPI Concept for Labeling Solid Corrosion Contamination (Metal-OH). Coupling is by surface metal ion complexation. Dye shown is Carminic Acid (A.I. 75470). HO-M represents metal surface corrosion products. Both metal binding sites are shown, but most likely only one binding site will be utilized at a time.

APPENDIX B

VCPI PROJECT TEAM PERFORMERS

Name	Organization	Expertise	Role
Dr. Deborah Peeler Donna Ballard	USAF AFRL-MLSA	Materials, Corrosion Control and Coatings	Test Samples, VCPI Performance, USAF Inte
Dr. Scott Sirchio Mary Jo Bieberich	U.S. Navy NSWC-Carderock	Materials, Coatings	Test Samples, VCPI Performance, USN Interf
Bill Yeager		Technician	Cleaning, NVR, Material
James Dante	UDRI (Support to USAF)	Corrosion Testing	UDRI Group Leader
Shannon Craycraft		Analytical	Chromatography, Cleanin
John Buhrmaster		Technician	Cleaning
Dr. Bruce Monzyk	Battelle	Process Chemistry	Principal Investigator, ne process and product development
Colleen Gorman		Chemical Engineer	VCPI Candidate screenin panel preparation
John Stropki		Cleaning, Corrosion Control	Panel Testing Logistics DoD user interface
Kevin Spahr		Analytical	Color Measurement
Chad Cucksey		Chemist	UV VIS, panel labeling
Dr. Satya Chauhan		Cleaning Verification, P2 in Cleaning	Liaison with Process Use

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APPENDIX C

DoD Surface Cleaning Processes Targeted for VCPI Application Testing
(Subtask 1.1)

C.1 Air Force Field Cleaning Protocol

The cleaning procedure preceding Al2024 repainting is described in Air Force Technical Order 1-1-691 (T.O.1-1-691). This procedure is summarized below, and in Figure C.1.

C.2 Air Force (T.O. 1-1-691)

Alkaline cleaning of Al2024 with rinses, followed by acidic corrosion removal compound (CRC) treatment and rinsing (bare substrates only).

Technique Sequence: Manual Scrub with ScotchBrite pads
Apply Alkaline Cleaner (MIL-PRF-87937C)
Soak Time = 2 minutes
Scrub Time = 3 scrubs - no pass/fail criteria (possible future VCPI test point?)
Rinse Time = 2 minutes
Apply CRC (MIL-C-38334 or SAE 1640) (panel surfaces must remain wet)
CRC Soak Time = 3-5 minutes
CRC Scrub Time = 2 scrubs (VCPI test point)
Rinse Time = 2 minutes
Water Break Test (fail? → return to CRC application step; pass? → proceed to chromate conversion coating, then to drying and painting)

Figure C.1. Air Force Systematic Cleaning Process for Surfaces Al2024 (Aircraft)

C.3 Navy PCMS Tile Cleaning Requirements Summary

Figure C.2 provides a summary of Naval cleaning needs regarding the PCMS foam tile material before and after installation. Three cleaning completion assessment points are indicated (as VCPI test points #1, #2, and #3). Three test contaminants are involved; grease (G), soluble corrosive salts [seawater resides (SW)] and paint stripper [Peel Away® 7 (PA7)].

C.4 Navy Field Cleaning Protocol for PCMS Foam Tile

Figure C.3 provides the detailed re-tiling cleaning protocol. Note that the stripped steel is immediately primed and so does not need cleanliness inspection/verification. As shown, two different cleaners are used for grease and soluble salt removal; water followed by PF degreaser when at the dock just prior to re-tiling the painted steel, and an aqueous detergent, general purpose-nonionic, MIL-D-16791 (So Sure®, by LHB Industries, Part #1064006) when cleaning the installed tiles painted surface for these same contaminants.

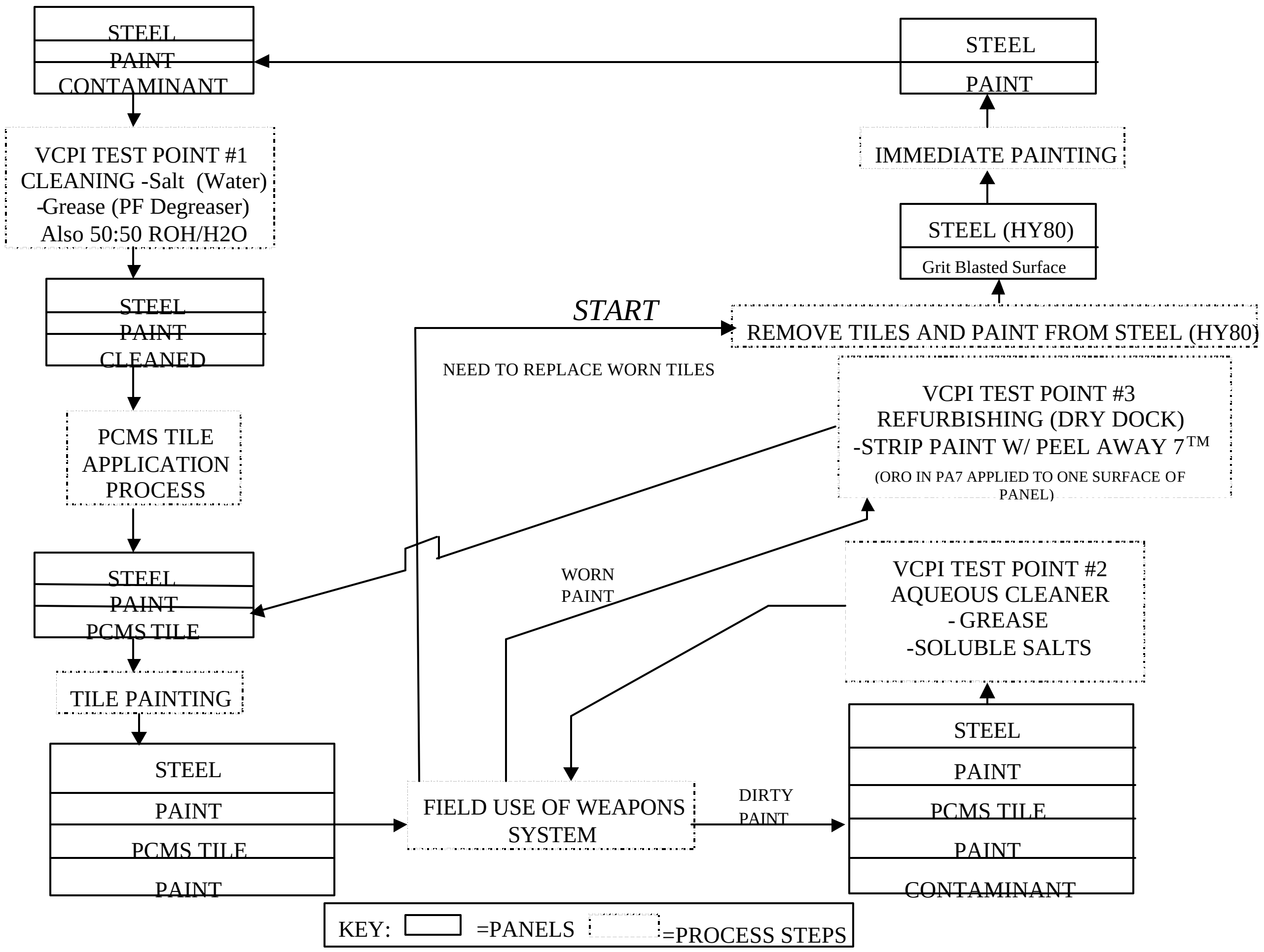

Figure C.2 VCPI Test Points in Navy PCMS Tile Application

<u>Navy (SHIPALT CG 4700300K)</u>

Standard PCMS Tile application process

Step 1. Preparation of Primed Steel Surfaces (no VCPI testing needed)

Technique: *Fresh water rinse*
Air dry time = 1 hour
Solvent degreaser wipedown
Air dry time = 5 minutes
Abrasive media blast and air cleaning
Primer application

- *no surface preparation if primed within 8 hours of blasting*
  after 8 hours, surfaces need to be washed with 50/50 mixture of fresh water and alcohol. Flash rust must be removed with 200-grit sandpaper prior to primer application.

Step 2. PCMS Tile Application (VCPI Test Point)

Technique: *Light abrasion (ScotchBrite 7447 pads)*
Wipedown of abraded surfaces with PF32 Degreaser (VCPI test point)
Air dry time = 5 minutes
Wipedown with 50/50 mixture of water and alcohol
Air dry time = 2 minutes
Apply tile

Additional VCPI test points enter during repainting of tiles and general field cleaning of painted tile surfaces.

Figure C.3. Navy Systematic Cleaning Process for PCMS Tile and Painted Surfaces (ships)

APPENDIX D

Materials And Methods

D.1. Laboratory VCPI feasability testing results: Analytical methods development and cleaning test procedures (Subtasks 2.1 and 2.3)

This Appendix provides the materials and methods for the VCPI feasibility prescreen testing. The actual VCPI feasibility tests results are given in Section 7.2.1.

D.1.1 Materials

Low concentrations of contaminants in recovered samples were expected since contamination thicknesses are thin and the panels are fairly small. Therefore all syringes, cleaning glassware, and polypropylene and glass storage bottles used in this study were thoroughly cleaned and rinsed using 18 MΩ deionized water. After cleaning, care was taken to prevent contamination of the cleaned samples and rinse solutions that were used for further analysis. Gloves were worn to handle only the edges of all samples. Contaminant specific procedures are given in the following sections.

AFRL provided test samples of MIL-SPEC contaminants. These samples are listed in Table D.1.1.

Table D.1.1 MIL-SPEC Contaminant Materials Provided by AFRL Representing Key DoD Hydrophobic Contaminants.

Battelle Sample Identification	MIL-SPEC	Description
47616-78-9	MIL-DTL-83133	JP-8 Fuel
47616-78-10	MIL-PRF-83282	Hydraulic Fluid
47616-78-11	MIL-H-5606	Hydraulic Fluid
47616-78-12	MIL-PRF-23699	Lubricating Oil

Most of the dyes, coupling agents, and solvents were purchased from Sigma-Aldrich, Inc. (Milwaukee, WI). Some coupling agents were purchased from United Chemical Technologies, Inc. (Bristol, PA). Additional dyes were purchased from ICN Biomedicals, Inc. (Costa Mesa, CA). General laboratory supplies were purchased from VWR Scientific Products Corp. (Pittsburgh, PA). Low cost quality controlled Aluminum 3105 test coupons, used in early method development work, were purchased from Q-Panel Lab Products (Cleveland, OH).

Aluminum 2024 Test Panels (bare and painted) were prepared by AFRL. These samples are described in Table D.2.2.

Type II Cleaning Compound and Corrosion Removal Compound (MIL-C-87937B and MIL-C-38334) were purchased from Chemsol, Inc. (Farmington Hills, MI). Type IV Cleaning Compound (MIL-C-87937B) was purchased from Safety Kleen (Groveport, OH).

Table D.1.2 Test Panels Prepared by AFRL Representing Unpainted and Painted DoD Materials.

Battelle Sample ID	Description
47616-82-3	Alloy: 2024 T3 Bare Al 2.75x6x0.032" 75 Panels
47616-82-6	Alloy: 2024 T- Bare Al 2.75x6x0.032" Conversion Coat: MIL-C-5541 (Alodine 1200S) Primer: MIL-P-85582B Type I Class C2 (Deft 44-GN-24) Topcoat: MIL-PRF-85285C Type I (Deft 03-G4-321, Color # 36173 (Gray)) 75 Panels
47616-82-11	Alloy: 2024 T3 Bare Al 2.75x6x0.032" 75 Panels
47616-82-14	Alloy: 2024 T3 Bare Al 2.75x6x0.032" Conversion Coat: MIL-C-5541 (Alodine 1200S) Primer: MIL-P-85582B Type I Class C2 (Deft 44-GN-24) Topcoat: MIL-PRF-85285C Type I (Deft 03-G4-321, Color # 36173 (Gray)) 75 Panels

D.1.2 Analytical Methods

Five analytical techniques were adapted for dye-CA screening using test panels (Table D.1.3). Each of these techniques will now be described as they are applied to dye-CA screening testing, along with an example of their use.

Table D.1.3 Analytical Techniques Developed for Selecting Dye-CA Candidates for Screening

Technique	Application
UV/Visible Spectrophotometry	Bulk solution quantitative analysis of dyes, and surface qualitative and semi-quantitative analysis for dyes applied to panels
Color Space Analysis	Quantitation of surface color (to compare with visual inspection), and of surface concentration of dye
Nonvolatile Residue (NVR) Analysis	Quantitation of surface contamination to correlate with dye concentration
Visual Inspection	Qualitative analysis of surface color under several controlled lighting conditions. Used to relate the color produced to what an operator would see in actual use
Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)	Supporting surface analysis to the NVR method for quantitation of surface contamination

D.1.2.1 Solution UV/Visible Spectrophotometry Assay for Bulk Dye Solution Characterization

Solution phase UV/Visible spectrophotometric analyses were preformed using a Hach DR/4000U UV/Vis Spectrophotometer. Visible spectra were of most interest (~350nm-1100 nm). The spectrum and molar absorbtivity of each dye was determined, as needed, using the following procedure. A 1000 ppm dye stock solution was prepared by weighing 250.0 mg of the dye into a 250-mL volumetric flask and adding ~150 mL of 1-octanol. The flask was agitated overnight on a shaker table to insure complete dissolution. The time to attain complete dissolution varied amongst solid dyes from minutes to hours.

Hence, pre-made liquid concentrates may be the best forms to use in preparing dye-CA delivery systems. The volume was brought to the 250-mL mark by adding additional 1-octanol. The flask was then inverted ~20-30 times for complete mixing. Neat 1-octanol was added to a 1 mm quartz UV/Vis cell. This cell was placed into the Hach UV/Vis and served as the zero reference. Next, the matched 1-mm cell was filled with the 1000-ppm dye solution, and the spectrum was collected from 190 –1100 nm. The resulting spectra was plotted and the molar absorptivity calculated from the data ($A = \varepsilon * b * c$).

To prepare a Beer's Law linearity check, a series of concentrations of the dye were prepared by diluting appropriate amounts of the stock solution in 1-octanol. Spectra were recorded for each concentration (the useful range was determined to be 0.75 - 600 ppm depending upon the dye and the test). The absorbance value at a wavelength of maximum absorbance was plotted for each solution. Only absorbance values of 2 or less were used. A plot of these values against concentration was generated (Beers Law plot, Figure D.1.1). This plot represented the calibration curve for the dye at the wavelength of maximum absorbance. The response is linear over more than two orders of magnitude (Beer's Law is obeyed). Samples of the dye at unknown concentrations were placed in the 1-mm quartz cell and spectra obtained on the UV/Vis spectrophotometer. By noting the absorbance value at the wavelength associated with the calibration curve, a value for concentration (c) could be readily read or calculated from $A=\varepsilon*b*c$. This process was repeated for the dyes as needed to identify surface absorbance spectral readings (see below) and to verify solution preparations.

D.1.2.2 Color Space Analysis for Quantification of Dye on Panel Surfaces & Measurement of Color Contrasts

A Data Color, Inc. surface reflectance instrument was found to be particularly valuable in assaying quantitatively for both surface dye and color contrast in a manner that can be related to what is visually observed. This technique was developed by the dye/pigment industry involved with consumer products. It was found to fit well with the VCPI method development requirements. Importantly, color space analysis quantifies what the human eye sees with respect to color in contrast to background color.

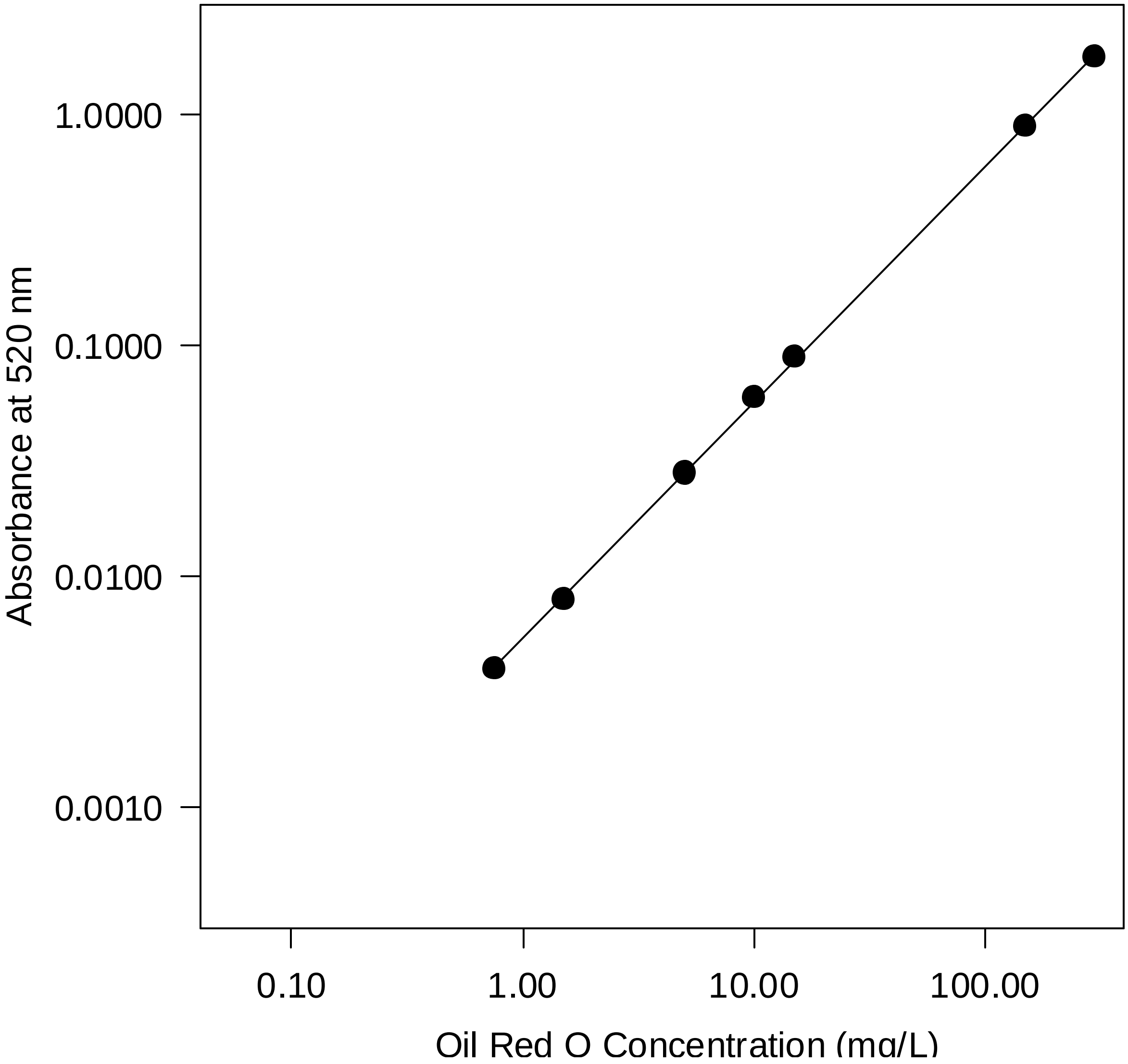

Figure D.1.1 Beers Law Plot for Oil Red O in 1-octanol. A plot of solution absorbance values versus concentration. Parameters: b=1.00 mm, l max = 520 nm, Slope = 10.5 ppm-1cm-1 (= 24,500 M-1cm-1) (R2=0.999).

Color space consists of a green, yellow, red, and blue color scale coordinates that are located in a plane at 90 degrees to each other. These colors are normally reduced to just two variables in the normal "x" and "y" sense by replacing red with "less green" and blue with "less yellow" (Figure D.1.2). These two variables are given the variable symbols of "a*" for red and "b*" for yellow, where increasing "a*" indicates increasing red color (less green), and increasing "b*" indicates increasing yellow color (less blue). The solid circle at the center of the diagram provides a measure of the magnitude of change that is perceptible to the human eye and is based on market testing experience from the dye/pigment industry. Since the sample readings in Figure D.1.2 (solid square and circle) lie along the "a" axis with positive values indicates that the color will appear reddish to the observer, as it did. Note that the gray test panels being used in these tests as reference represent coordinates at the center of the dark circle. Hence, the reddish color is easily distinguished from the background/reference color for this example. The arrow through the center circle indicates the direction the circle is from the center of color space (pure gray). The third dimension of color space lies perpendicular to the "a*" and "b*" coordinate plane. This "lightness" parameter or "dL*", ranges from black (negative values), through gray at dL*=0, to white (positive values). The relative value of dL* to the reference is given by the bar on the right side of the plot.

Note that the small +b* component (yellow color) for the samples read in Figure D.1.2 is significant in that the +b* value is greater than the radius of the black circle. This yellow color is due to the slight yellow color of the lube oil contaminant (which was measured independently by UV/Visible spectrophotometric analysis) into which the Oil Red O was dissolved. Therefore, color can be quantitatively measured and is reported as values which resolve each color component, in this case Oil Red O dye and MIL-PRF-23699 lubricating oil, and the degree of lightness (also see "VCPI Feasibility Test Results" below).

The Data Color instrument also was used to record the surface absorption spectrum of coatings. These spectra are comparable to the bulk UV/Visible spectra and are useful for qualitative dye identification, and semi-quantitative surface analysis for the dye. Representative spectra are given in Figure D.1.3 for both a cleaned aluminum surface and that same surface with lubricating oil/dye contamination (see below for panel contamination procedure).

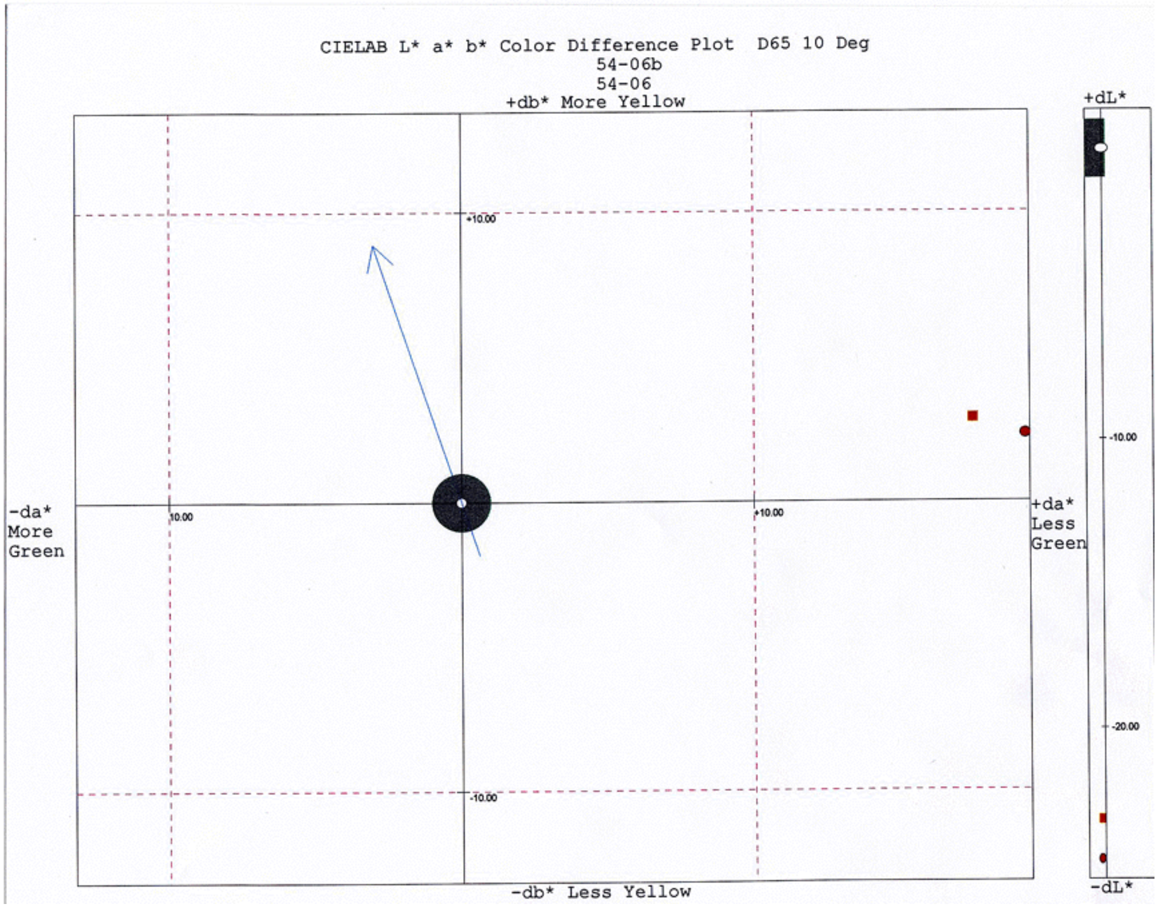

Figure D.1.2 Color Space Plot Produced by the Data Color Instrument. The solid square and circle symbols represent actual sample readings from two areas of the same test panel. The panel was labeled with 500 ppm Oil Red O dissolved in 2% lubricating oil a solution of methylene chloride (the solvent rapidly evaporates leaving the lubricating oil/dye residue on the surface). The test panel surface is Al2024. Note that 'less green' is red, and 'less yellow' is blue. See text for further description and data analysis techniques.

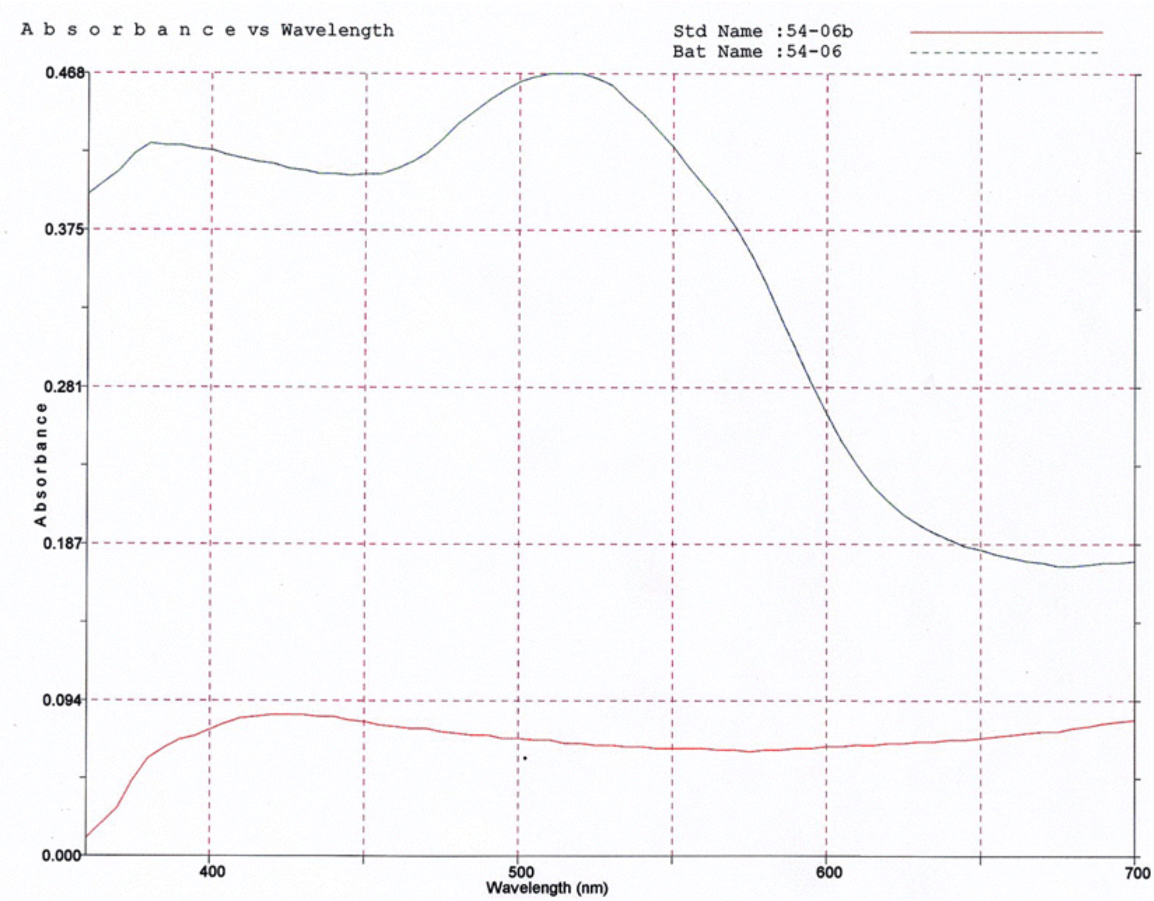

Figure D.1.3 Surface Absorption Spectra for a Cleaned Aluminum Surface (bottom) and the same Surface with Lubricating Oil (MIL-L-23699) Contaminant Labeled with Oil Red O as described in the footnote to Figure D.1.2. The lubricating oil to dye ratio is 2:1 (v:w). The very large absorbance values relative to the blank indicate much lower dye use levels would be functional (see Figure D.1.5). This method illustrates how quantitative and semi-quantitative measurements of contaminants could be made using the VCPI technique with calibration (for more on quantitation see caption to Figure D.1.5).

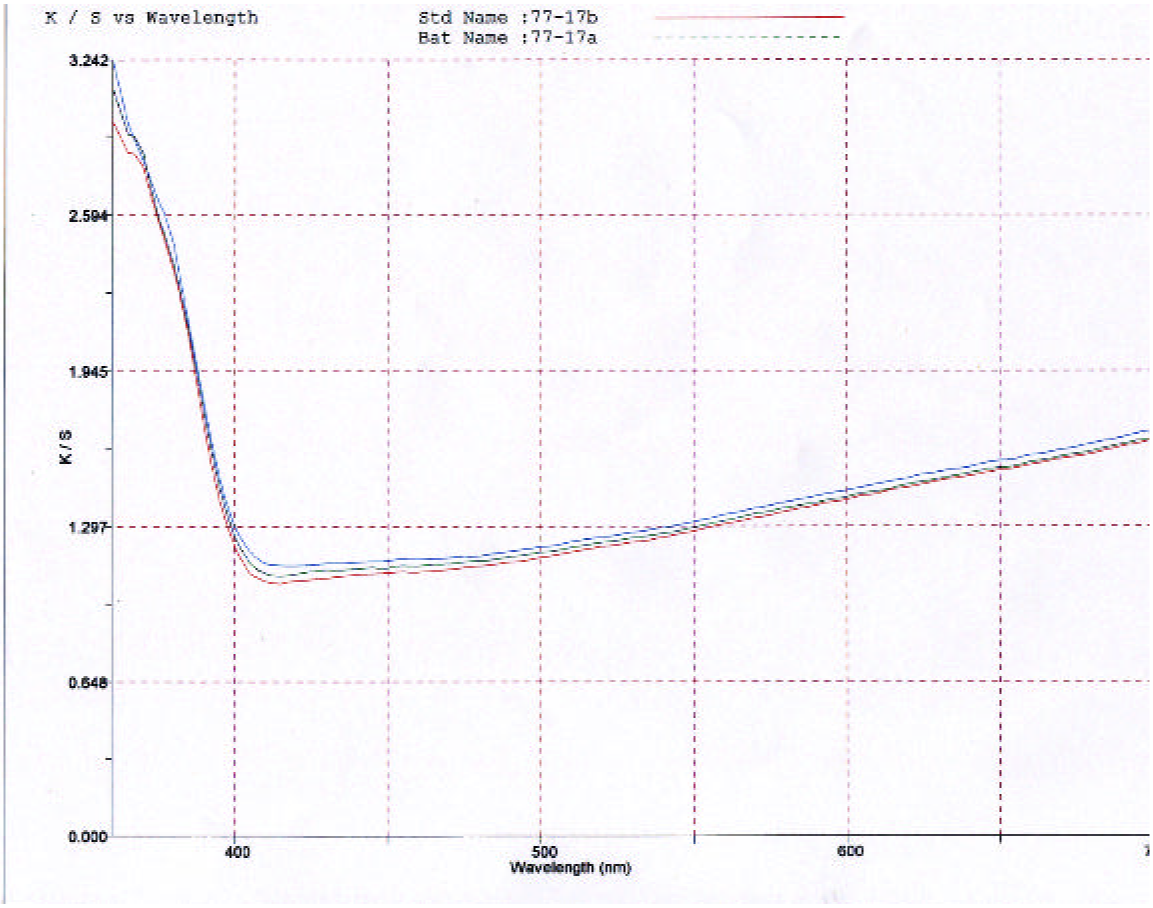

Figure D.1.4 Surface Visible Absorption Spectra of Three Painted Panels Illustrating the Good Panel-to-Panel Precision

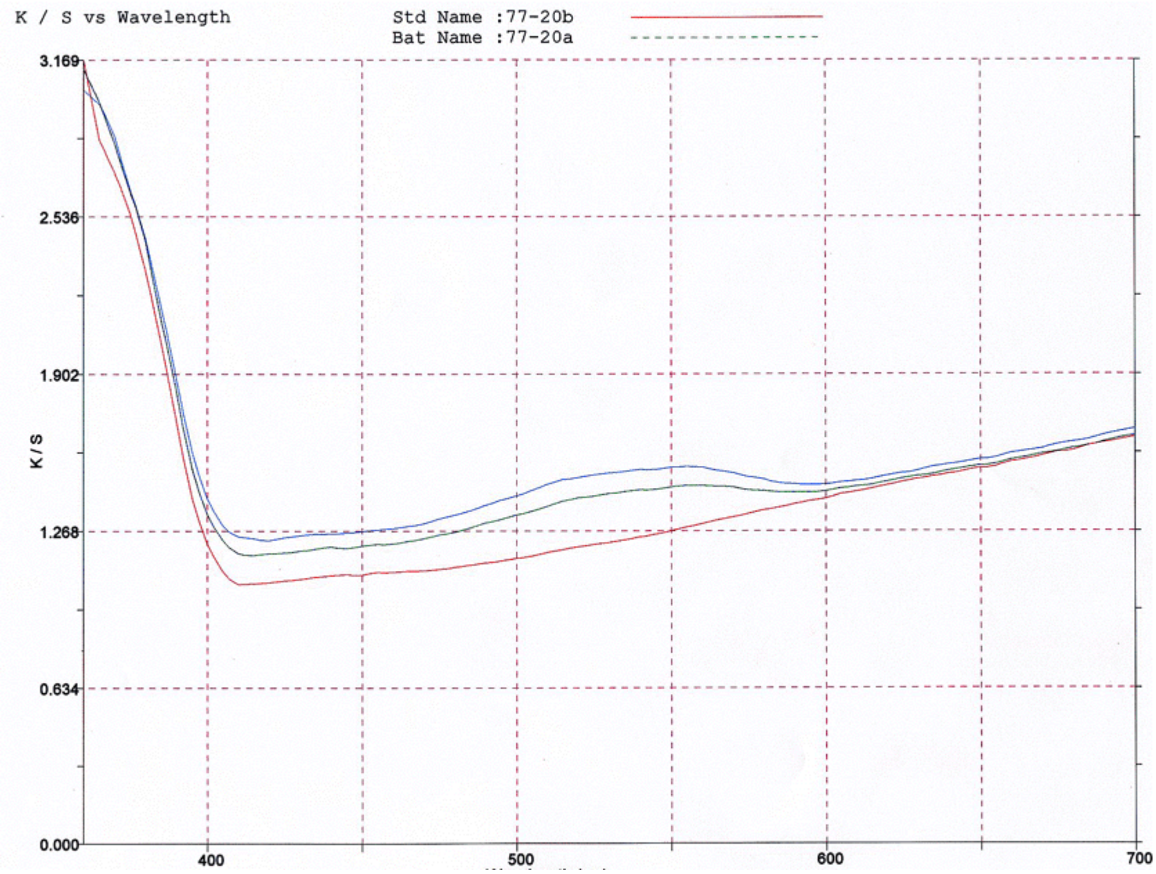

Figure D.1.5 Surface Reflectance (absorbance) UV/Visible Spectrophotometric Analysis of Contaminated Painted Al2024 Test Panels. Illustrates the presence of Oil Red O dye (absorbance peak at ca. 505-550 nm) for the top two curves (repeat scans), against the reference (top of half of panel, bottom curve). Concentration of dip bath was 500 mg/L Oil Red O and 2.0 percent lubricating oil in CH_2Cl_2 (lubricating oil: dye ratio of 20,000:500 or 40 V/W).

There was some acceptable level of variability in the surface reflectance absorption spectra of unpainted panels that reflected the previous handling of the aluminum. These variations are expected in future field use as well. These variations were within a relatively small range and did not interfere with dye analysis. To accommodate this variability, panels were analyzed by dipping only the bottom half into the labeling solution so that the top half remained uncoated and was then used as a reference. On the other hand, the painted panels showed a large degree of reproducibility (Figure D.1.4). A coating containing a low level of dye was then easily distinguishable when added to this coating (Figure D.1.5).

D.1.2.3 Non-Volatile Residue (NVR) Analysis for Assaying Contamination and Dye on Panel Surface

NVR analysis provides a quantitative assay for the amount of surface contamination present on the panels. This measurement was critical for the tracking of contaminant and dye. The visible absorption measurement described above was used to assay for the dye and these results were then correlated with the level of contamination so that a measurement of dye labeling selectivity and extent of co-removal of dye and contaminant could be made. Some ATR-IR measurements were made as a check on the NVR assays (see below). Due to the small net weight values, it is critical that care is taken to avoid any losses or contamination from all sources during the procedure. In addition, prevention of static buildup on the analytical balance avoids slow settling times. Reproducibility and precision was determined from triplicate measurements.

An example of the NVR assay as it was developed from MIL-STD-1359B for dye-CA screening will now be described. The apparatus shown in Figure D.1.6 was set up and operated in a fume hood.

A solvent blank was prepared for the NVR test using the following procedure:

1. Washed a small round-bottomed (RB) flask with Alconox® lab glassware alkaline detergent cleaner followed by a thorough water rinse with 18 MΩ-cm deionized water. The flask was allowed to dry briefly, then rinsed with a small portion of methylene chloride. The flask was then dried in an oven at ~110 C for ~1 hour. The flask was transferred to a desiccator containing DriRite® desiccant and allowed to cool.
2. The clean, dry and cool flask was then tared to the nearest tenth of a milligram.
3. Added 75.0 mL of methylene chloride (or other solvent as called for in the test) to the flask, then attached the flask to the apparatus as in Figure D.1.6.
4. Distilled the solvent from the flask through the air cooled reflux column, and then condense in the water cooled condenser, and collect in the Erlenmeyer receiver flask.

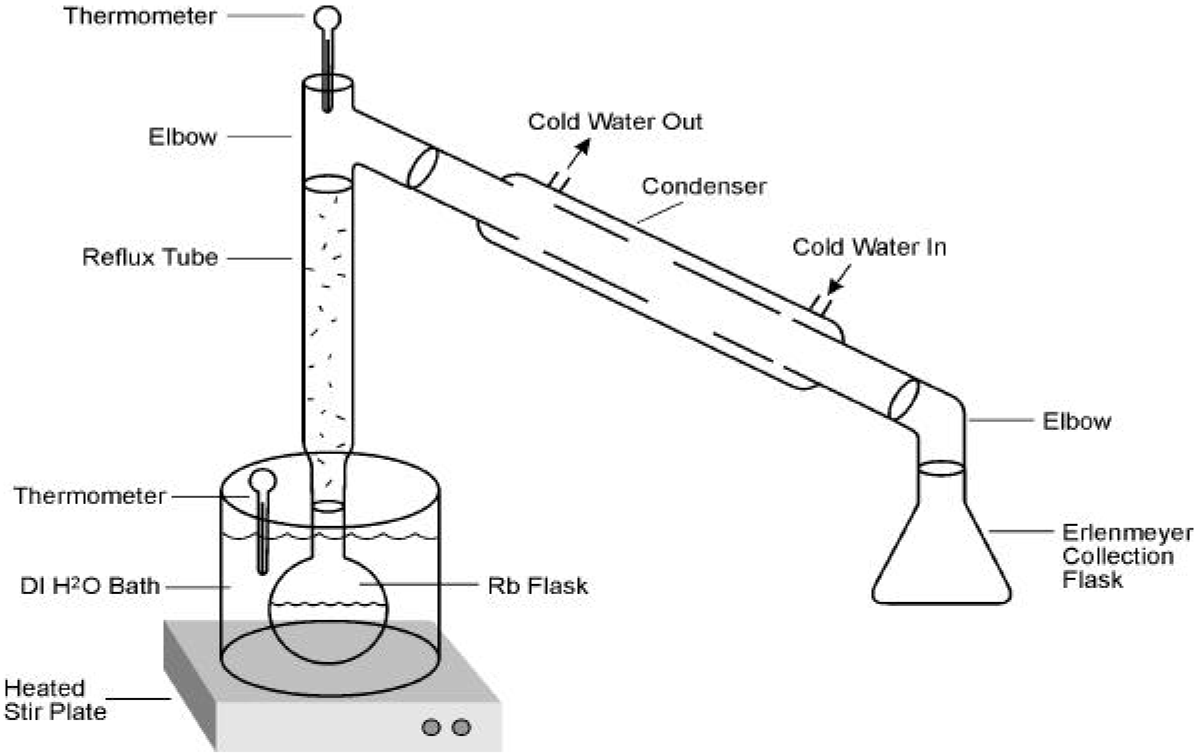

Figure D.1.6 Non-Volatile Residue Analys is Apparatus (Rb = round bottom flask)

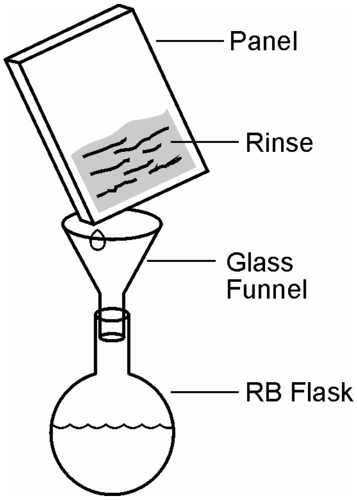

Figure D.1.7 Method of Quantitatively Rinsing Panels to Recover Surface Contaminants for NVR Analysis

5. When about 10-mL of the methylene chloride remained in the bottom of the RB-flask, the heating bath was removed and the flask was allowed to cool to room temperature.
6. Air was driven across the top of the RB-flask to evaporate the last portion and traces of solvent.
7. The outside of the flask was wiped clean with a lint-free cloth and placed in a desiccator for ~1 hour.
8. The flask was reweighed to the nearest tenth of a milligram.
9. Subtracted the mass of the clean flask from the mass of the RB flask after the NVR test to determine the amount of residue in 75.0 mL of the solvent. This weight represents a correction factor to the contaminant weight derived from the analysis below.

The following procedure was used to perform the NVR test on a contaminated panel.

1. Correct the weight using the weight normalized to the same volume of solvent used that was determined in the blank test. Report the net, corrected contaminant weight.
2. Washed a small round-bottomed (RB) flask with Alconox®, rinsed thoroughly with deionized water, allowed to dry briefly, then rinsed with a small aliquot of methylene chloride. Next, the flask was dried in an oven at ~110 C for ~1 hour. Allowed the flask to cool in a desiccator.
3. Tarred the clean, dry flask to the nearest tenth of a milligram.
4. Rinsed the contaminated panel into the preweighed RB flask using a funnel, see Figure D.1.7. The panel was rinsed using a jet from a wash bottle with methylene chloride solvent (or other solvent to be tested) until the surface of the panel no longer appeared contaminated by visual examination. This usually required ~50-75 mL of solvent.
5. The flask was attached to the apparatus depicted in Figure D.1.6.
6. Distilled the solvent from the flask through the air cooled reflux column, and then condensed in the water cooled condenser, and collected in the Erlenmeyer receiver flask.
7. When about 10-mL of the methylene chloride remained in the bottom of the RB-flask, the heating bath was removed and the flask was allowed to come to room temperature.
8. Air was driven across the top of the RB-flask to evaporate the last portion and traces of solvent.
9. The outside of the flask was wiped clean with a lint-free cloth and placed in a desiccator for ~1 hour.
10. The RB flask was reweighed to the nearest tenth of a milligram.

11. Subtracted the mass of the clean flask from the mass of the flask after the NVR test to determine the amount of residue on the contaminated test panel.

D.1.2.4 Visual Observation (VO) Inspection Station with Controlled and Selectable Lighting

Visual Observation (VO) is a critical component of characterizing and selecting VCPI methodology as, ultimately in field use of the VCPI method, visual observation will be heavily relied upon to routinely monitor and guide the cleaning process in real time, along with the water break test where it can be applied. The instrument used for VO was a MacBeth SpectraLight Model # SPL75B Series 890629 unit. This unit is a hood type device with several lighting choices (see below). Visual observations of contaminated and reference panels were made as follows:

1. The panels were placed approximately in the center of the viewing area.
2. Room lights and all ambient lights were turned off.
3. The “Daylight” viewing option on the SpectraLight was selected.
4. Notes on the appearance of the panel under these lighting conditions were recorded as observations, diagrams, and photographs. The same person made all of the observations.
5. The “Cool White Fluorescent” option on the SpectraLight was then selected.
6. Step 4 was repeated.
7. The “UV Light Only” option on the SpectraLight was then selected.
8. Step 4 was repeated.
9. The panels were removed, and the entire process was repeated for verification. The procedure was performed with panels individually or as sets as per the specific test.

The variations in appearance with lighting condition were very significant, suggesting that lighting might be used to enhance sensitivity and contrast.

D.1.2.5 ATR-IR for Surface Contaminant Analysis

Attenuated total reflectance infrared (ATR-IR) spectroscopy was used to analyze bulk and thin films on panel surfaces for both qualitative and quantitative contaminant identification. This method provides high sensitivity to low levels of contamination and the capability to rapidly measure a number of different contaminants separately. However, it was found to require significant recalibration when switching from aluminum to painted aluminum panels. The method was also found not suitable for dye analysis unless the dye was present at high levels, levels found to be larger than the VCPI application requires. The instrument used for ATR-IR was a Digilab FTS-60A Fourier transforms infrared spectrometer equipped with MCT liquid nitrogen cooled detector for rapid data acquisition and Spectra-Tech grazing angle reflectance optics. The analysis conditions were 80° angle of incidence, 400 accumulated scans, 40 kHz scan speed, and wide-band MCT detector. The blank reference spectrum was obtained by scanning a clean and non-coated area of each aluminum test panel. Then a contaminated panel area (bottom half) was scanned and the absorption band intensity was measured. Results were reported as IR absorption vs. residual contaminant level as measured by gravimetric measurements.

D.1.2.6 Panel Contamination Procedure – Application of Lubricating Oil Contaminant

A summary of the procedures used to contaminate the surfaces of the various test panels is provided below. Note that these procedures are for dye-CA screening tests only and do not represent examples of VCPI contaminant labeling techniques to be used in the field.

Panels were coated with lubricating oil contaminant and dye for VCPI concept screening using the following procedure. Exactly 10.0 g of MIL-L 23699 lubricating oil was delivered to a 500-mL volumetric flask and filled it to the mark with spectrophotometric grade methylene chloride to make a 2% (w/v) solution. Transferred this solution to a labeled glass bottle until ready for use. This solution represents the "contaminant only" solution.

Delivered 10.0 g MIL-L-23699 lubricating oil into a 500-mL volumetric flask, add 250.0 ± 0.1 mg Oil Red O (CI # 26125, CAS # 1320-06-5), mixed (solution only took a few seconds), then filled the flask to the mark with spectrophotometric grade methylene chloride to make a 2% (w/v) lubricating oil, 500 ppm (mg/L) Oil Red O solution. This solution was transferred to a labeled glass bottle until ready for use. This solution represents the "contaminant plus dye" solution.

Individual panels were coated with the above VCPI test systems as follows:

1. Diamond scribe-numbered panels were pre-cleaned in accordance with the procedures specified below (Section D.1.2.7).
2. Each panel was then either dipped in the "contaminant only" solution or the "contaminant plus dye" solution. The panels were either dipped to the halfway point (for spectroscopy analysis), or completely immersed (for NVR testing).
3. A clean Kimwipe® was wetted with methylene chloride and used to wipe the backside of the panel after removal from the test solution to remove any contaminant or contaminant plus dye on the backside of the panel.
4. The coated panels were allowed to dry in the horizontal position (to minimize pooling of the contaminant at the bottom of the panel and the formation of a thickness gradient over the length of the panel) until ready for analysis. Panels were supported by small (~1 in. diameter) plastic spacers to insure that the contaminant from the front side of the panel did not wick onto the surrounding table area.

These panels "flash" dry in <1 min. due to the high volatility of the CH_2Cl_2. Since the CH_2Cl_2 evaporates, the residue is just lube oil or lube oil with dye. The V/W ratio of contaminant to dye in the film produced in the above test example is 20,000/500 or 40. During the screening tests, this ratio was varied as high as 200 and as low as 0.2.

D.1.2.7 Panel Precleaning Method

The following procedure was used for cleaning both painted and unpainted 3105 and 2024 Aluminum alloy test panels.

An alkaline cleaning solution was prepared as follows. Added 25.0 g trisodium phosphate, 25.0 g sodium carbonate and 1.00 ± 0.01 g sodium lauryl sulfate to a 1-L volumetric flask. Then add ~600 mL deionized water and mix thoroughly until all of the solid dissolves, followed by deionized water to the 1-L mark on the flask. This solution was mixed well and then the solution was transferred to a labeled Nalgene bottle.

Each test panel was then pre-cleaned using the following procedure:

1. Engraved a unique laboratory record number on each panel using an electric engraving pen.

2. Heat the alkaline cleaning solution (prepared above) to 75° ± 2° C on a magnetic stirring hotplate.
3. In a fume hood, degreased the panel by immersing in toluene with manual agitation for ~10 seconds. Drain the panel over the toluene bath, then allow it to air dry by hanging for ~ 2 minutes in the draft of the hood.
4. Dip each panel into the heated alkaline cleaning solution for 1 minute, then removed the panel and allow it to drain for ~ 10 seconds.
5. Immerse the panel in high purity deionized water (18.2 MΩ-cm) for 2 minutes and allow to drain for ~10 seconds.
6. Repeat step 5 with a second rinse bath.
7. Perform the water break test as per MIL-STD-1359B, part 5.2.1.3. If the panel fails, return to step 3. If panel passes, continue to step 8. In all cases, the panels passed with water break test the first time through.
8. Allow panel to hang dry until ready for use.

D.2 VCPI CONCEPT EVALUATION AND CLEANING METHODS DEVELOPMENT (Task 2)

D.2.1 VCPI Concept Feasibility Testing Methods (Subtask 2.1)

D.2.1.1 Hydrophobic Fluids – Estimate of Detection Limit and Sensitivity

With the results from Task 1, the materials and information were in place to perform preliminary VCPI concept screening testing. Lubricating oil was selected from the contaminants provided by AFRL to use for the concept screening test work since it was a fairly clear, free flowing, hydrophobic liquid of low volatility. The following section describes the lab scale analytical methods developed to perform the experimental work for labeling lube oil (LO) and monitoring the dye-CA system for it (Oil Red O, or ORO, Figure D.2.1), especially the relation between analytical sensitivity and detection limit with visual color appearance and color space measurements. The materials involved are also described.

Figure D.2.2 is a plot of the absorbance of an aluminum panel surface coated with lubricating oil containing high concentrations of Oil Red O [up to 1000 ppm in the CH_2Cl_2 dip bath with Oil Red O/lubricating oil ratio of 1:1 (w:v)]. Figure D.2.3 is a plot using the same solutions, but the red color space parameter, a*, is plotted instead of absorbance. Measurements were made up to 5000 ppm dye concentration and were found still to be efficacious, but not as sensitive (lower slope). However, since concentrations of dye >1000 ppm are believed to be well above that needed for the VCPI application (see below), this portion of the calibration curve is not needed and so is not included in Figures D.2.1 or D.2.3.

The value of the a* parameter is immediately apparent in comparing the intercepts of these two plots. The absorbance values approach a y intercept while the a* approaches zero. Hence, the a* value is read relative to “zero” (the reference background) while the absorbance is read against a larger background absorbance. Critically, in all cases, the red dye was found to be visually apparent at all dilutions of Oil Red O tested with no special lighting required. Since the oil was applied at “typical” low contaminant levels, e.g. 30-125 mg/ft^2, and since the dye is visually apparent for both metal and painted backgrounds, we conclude that the fundamental technical requirement -- that being that a dye has sufficient color intensity at the thin layer condition of low levels of contamination is verified. This result apparently is possible due to the additive effect across at least a sizable portion of the visible spectrum, since single wavelength calculations would indicate color very borderline for being visually apparent. For example, a 500 mg/L solution of 432 g/mole Oil Red O dye, with $\varepsilon = 24{,}500$ M-1cm-1 would have an absorbance at 520 nm (λmax) of 0.3 for a contaminant oil layer thickness of 0.1 mm, i.e., a visible, but fairly light color intensity. Figure D.1.3 is the visible absorption spectrum of a 300 ppm Oil Red O solution in 1-octanol. The minimal absorption at a λ value > 600 nm gives the dye its red color, i.e., light of wavelengths 600-1100 nm is transmitted by the dye. The large εmax value (24,500 M-1cm-1) is also important in that the wavelength of light that is absorbed is absorbed very efficiently, which increases that portion of the incident white light that is reflected as red.

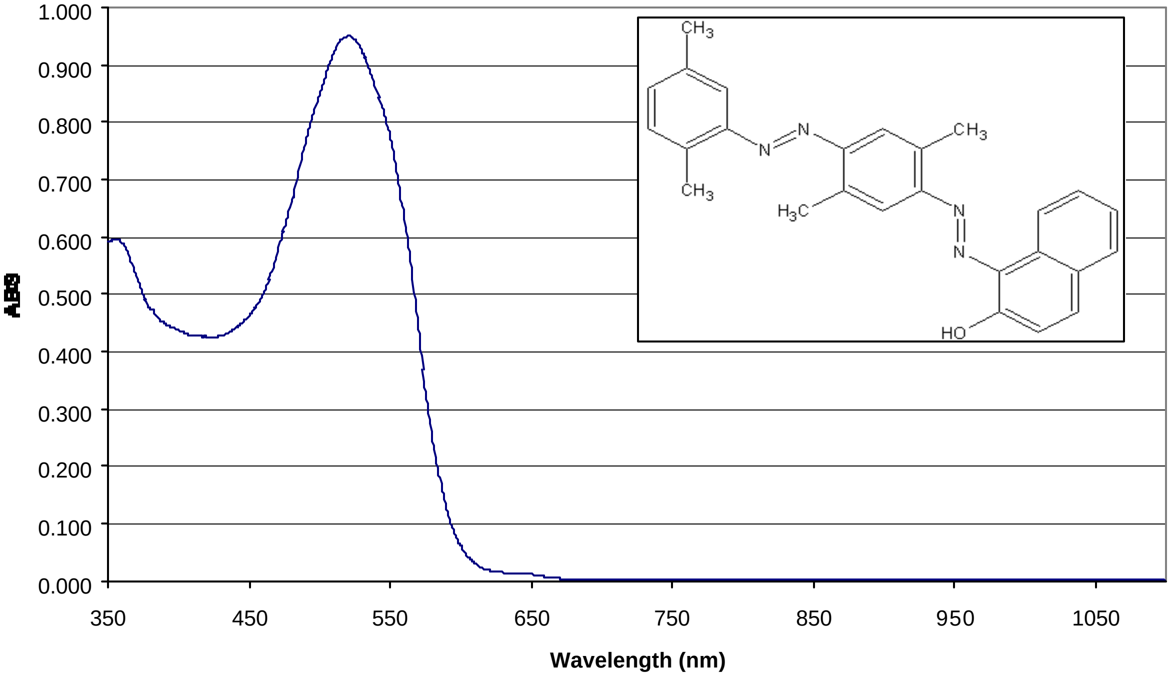

Figure D.2.1 Oil Red O (ORO)Visible Absorption Spectrum and Molecular Formula

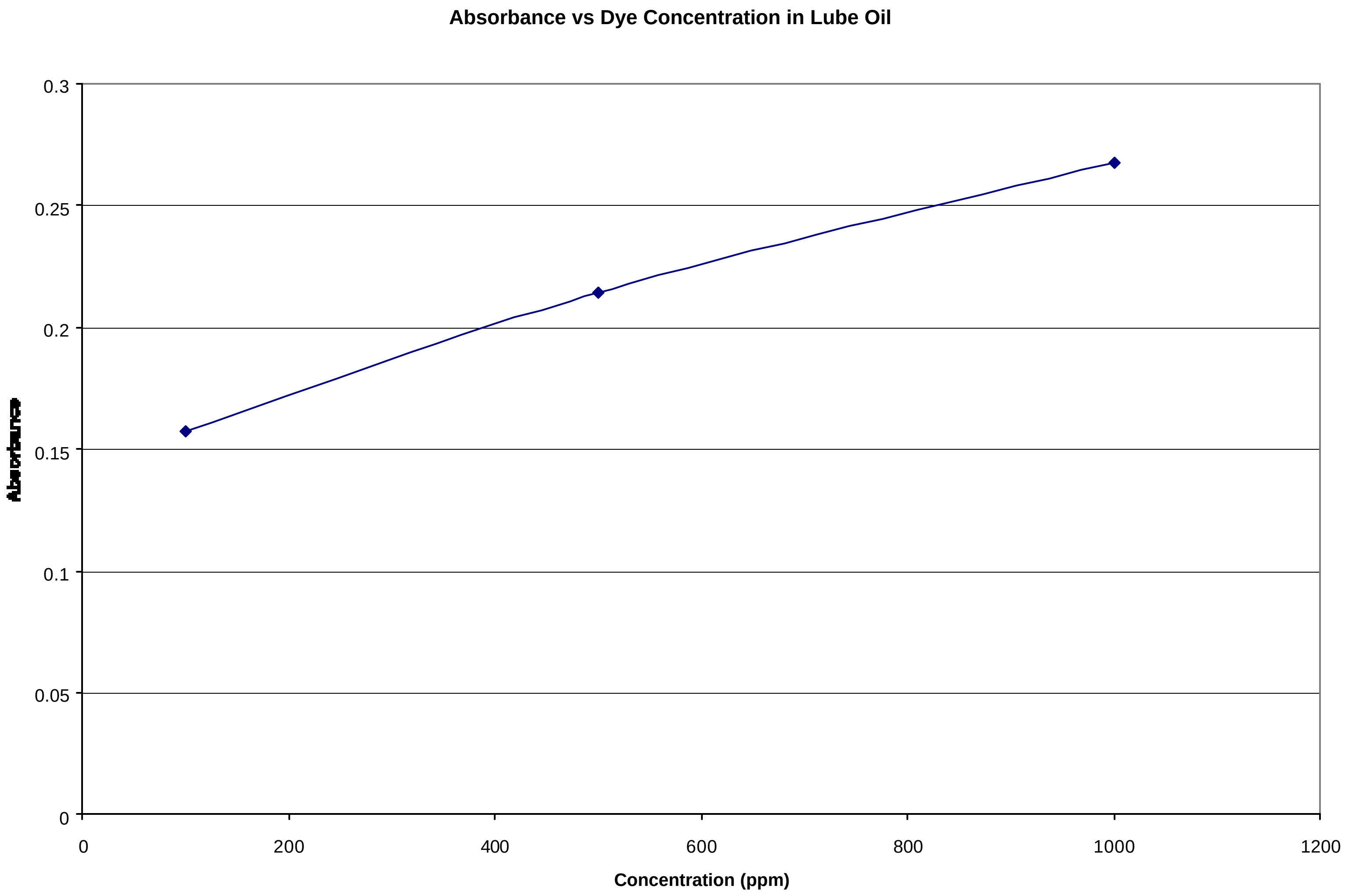

Figure D.2.2 Absorbance at 520 nm vs. Oil Red O Concentration after Application to an Aluminum Surface. The dye was applied using a CH_2C_{l2} dip solution also containing 2 vol.% lubricating oil. The Oil Red O is as a film on Al 3105 surface. The ratio of lube oil to dye in the dried film at the “1000 ppm” mark is 2:1 (vol.: wt.).

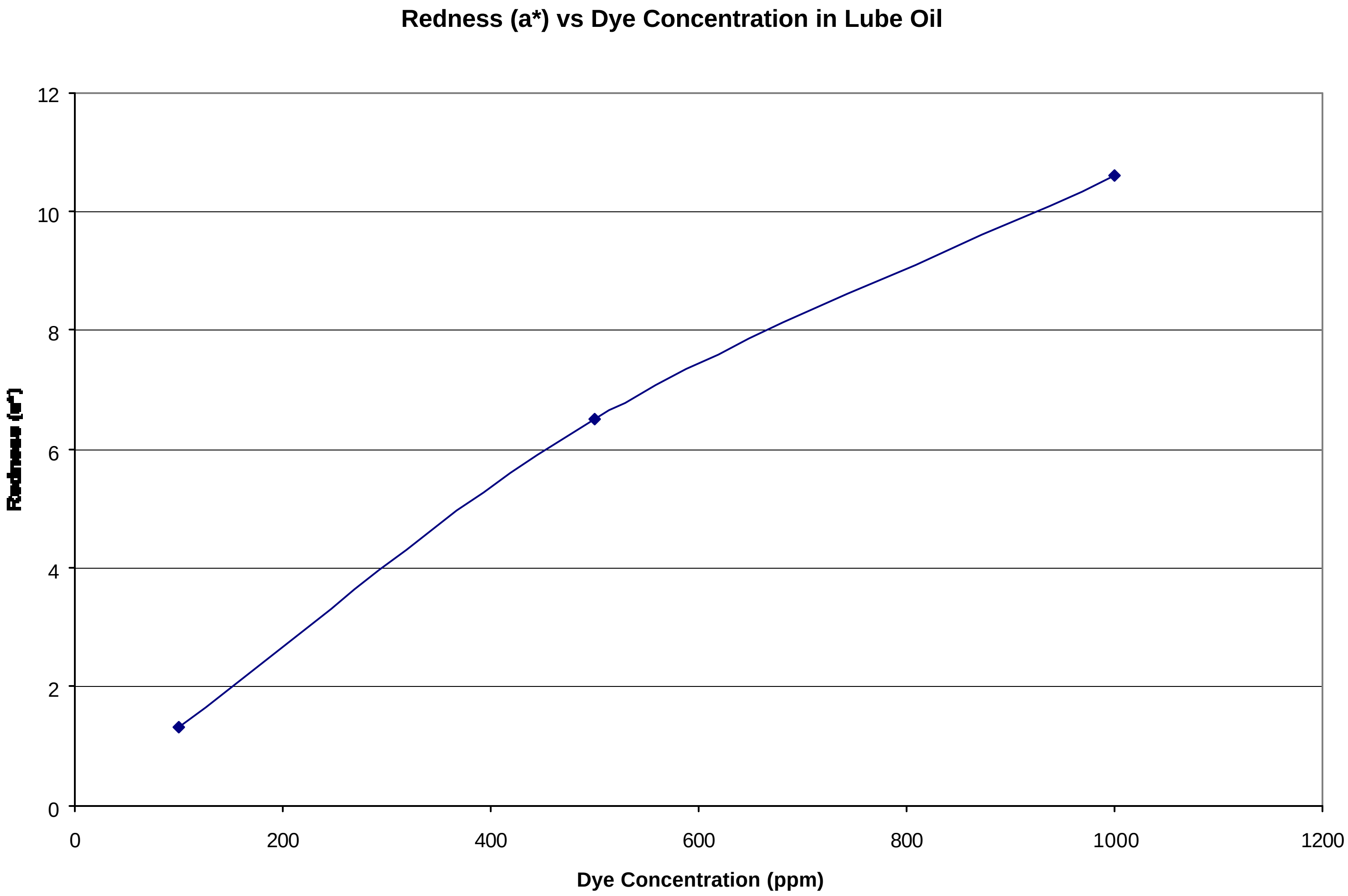

Figure D.2.3 Red Color Space a* Parameter Plot for Oil Red O on Al 3105 Surface. Same sample and application conditions as for Figure D.1.1. The zero intercept indicates that the a* parameter responds to just the dye content on this material surface.

Essentially no portion of the red light is absorbed (zero absorbance at > 670 nm) for Oil Red O (Figure D.2.1). This observation suggests that, although found not to be needed in the current work, a possible further increase to the sensitivity of the method is still further possible by increasing the *intensity* of the white light impinging on the surface (i.e., a bright work light), the intensity of the reflected red light should also increase, at least to a point. Alternatively, filters (for example, as might be supplied as worker safety glasses) might be used to absorb the shorter (< 650 nm) wavelengths, thereby increasing the selectivity of the eye for the red color. Lastly, since the eye is most sensitive to 500 nm light (~ green), another means to enhance sensitivity and selectivity might be to use a green dye of high ε value, at e.g. > 20,000 M-1cm-1. To this end, D&C Violet 2, a Solvent dye, was selected for possible evaluation. However, this dye is on the NTP list, but has a favorable D&C (drug and cosmetic use) rating (Appendix C). Therefore, if this improvement in sensitivity and contrast is needed, then either a replacement oil soluble green dye would be sought, or a more thorough ecotox assessment of D&C Violet 2 will be justified.

D.2.1.2 Hydrophobic Fluids – Selectivity

An important requirement for the VCPI technology is that the label only tags the contaminant and is removable along with the contaminant during the cleaning operation. Therefore, a large number (~175) of panels were prepared with lubricating oil coating with and without dye (Oil Red O), at a wide range of lubricating oil and dye concentrations. Multiple number panels were prepared per test condition to provide a sufficient number of replicate samples for each analytical method. Initially, the tests utilized low cost Al 3105 panels for methods development, and then DoD materials, Al2024 panels, painted and unpainted. The following text describes an example of detailed results, which indicate that the dye-CA VCPI label accompanies the lubricating oil contaminant during at least solvent cleaning, does not leave a noticeable residual, and provides the visualization of the contaminant during the operation.

Figure D.2.4 is one overall *laboratory* pre-screening procedure that was developed to test the VCPI concept. In this test, panels are initially degreased (see below for additional specific procedures), alkaline cleaned, then subjected to a water break test to verify surface cleanliness. The panels are then allowed to air dry for a short time, then they are dipped into a test solution of volatile solvent containing the lubricating oil contaminant and dye at a particular test condition, most often a vol:wt. ratio of 40:1 oil:dye. The panel is dipped fully for NVR tests, but only half way for the spectroscopic analysis methods so that the top half of the panel can be used as a reference or blank. Dyed and undyed panels are also prepared. For the lubricating oil hydrophobic fluid, the cleaner chosen was initially 1,1,2-trichloro-1,2,2-trifluoro ethane (TCTFE) as per the published NVR procedure (see Methods and Materials). Although a solvent is used in these prescreening tests, future testing will use MIL SPEC aqueous cleaners. TCTFE cleaner was found to rapidly and efficiently remove both the oil and the dye from the Al2024 *unpainted* panels. When TCTFE was used to rinse *painted* Al2024 panels, the lubricating oil visually appeared to rinse away just as easily as did the unpainted panels, i.e., the shinny “wet” look of the oil film was removed and replaced by the dull gray matte look of a clean painted panel. However, when the *dyed*, oil coated panel was rinsed with TCTFE, a substantial amount (based on visual color intensity) *of the red dye color remained on the panel.* However, switching to a more aggressive cleaner solvent, methylene chloride, instantly removed all of the dye color from the painted panel by visual inspection.

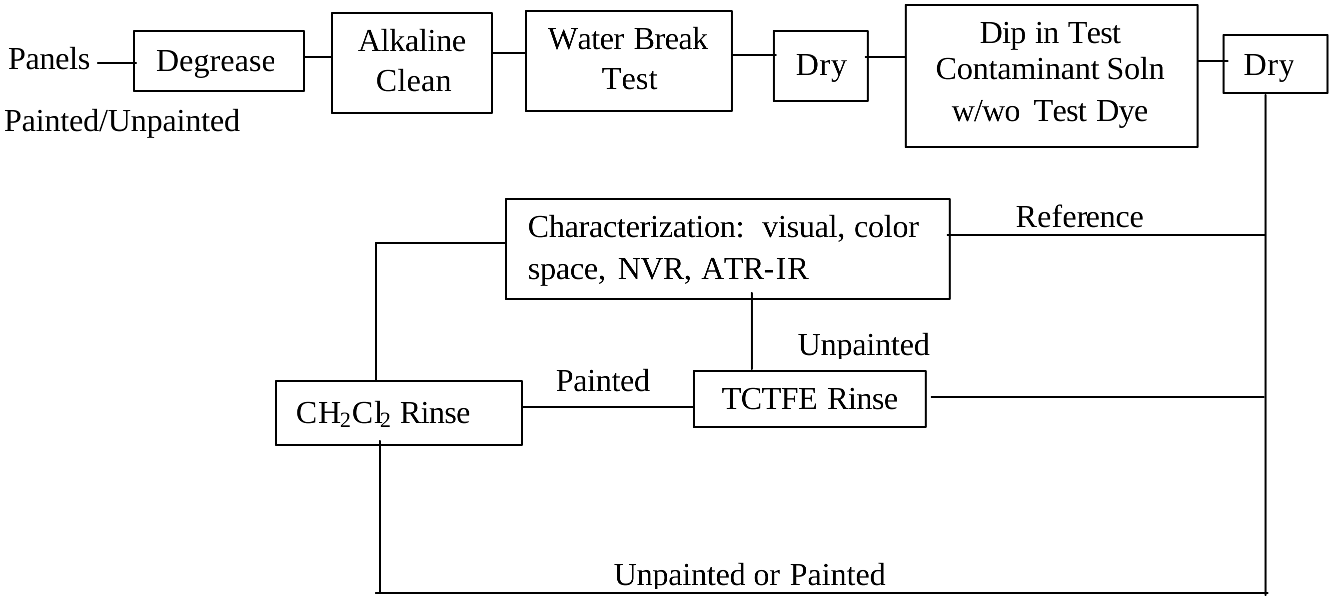

Figure D.2.4 VCPI Panel Treatment Procedure for Unpainted and Painted Panels. Dye/CA Prescreening Method

To determine whether just the dye remained on the painted surface after TCTFE rinsing, or whether the dye was indicating that the lubricating oil also was not being removed by the TCTFE, gravimetric NVR tests were performed. Figure D.2.5 is an example of one of the high precision tests run to answer this critical selectivity question. As Figure D.2.5 shows, clean Al2024 panels were dipped either in 2% lubricating oil methylene chloride solution, or this mixture containing 0.05% Oil Red O (contaminant:dye v/w ratio of 40). The coating was allowed to flash dry (methylene chloride evaporation) with the panels lying flat after dipping. Both the wet effect of the lubricating oil and the red color of the dye are readily visible. The next step was to rinse the right half of the dipped bottom half of the panel with TCTFE. The panel without dye appeared to be thoroughly rinsed. However, the panel with VCPI label showed a clear residual red color even after repeated rinsing. NVR analysis (Figure D.2.5) indicated that in fact a substantial amount of lubricating oil still remains on the panel. Only 43% of the lubricating oil was removed by the TCTFE rinse. Hence, *without the dye, an incorrect conclusion was drawn* – the apparently clean panel side for the dyeless case only appeared clean despite the fact that *57% of the lubricating oil remained!* By visual inspection, the amount of red color fading appeared to be in proportion to the amount of lubricating oil removed. Hence, with the dye, the proper conclusion was drawn regarding degree of cleanliness.

Finally, the panels were rinsed with the more aggressive solvent (Figure D.2.5). In this case, the red color is quickly and completely removed by visual observation. Likewise, NVR analysis indicated that 55% of the original lubricating oil is removed with the second rinse. Hence, 98% of the lubricating oil is removed with the two rinses, with no residual red color remaining on the panel. This experiment indicates that the VCPI concept is valid for the lubricating oil contaminant system. Presumably similar results would be obtained with other liquid hydrophobic contaminants. These results justify future tests that target determination of detection limits, optimization of dye use concentration, and applications testing using other hydrophobic contaminants of importance to DoD, which are much different than lubricating oil, such as grease and silicone caulks.

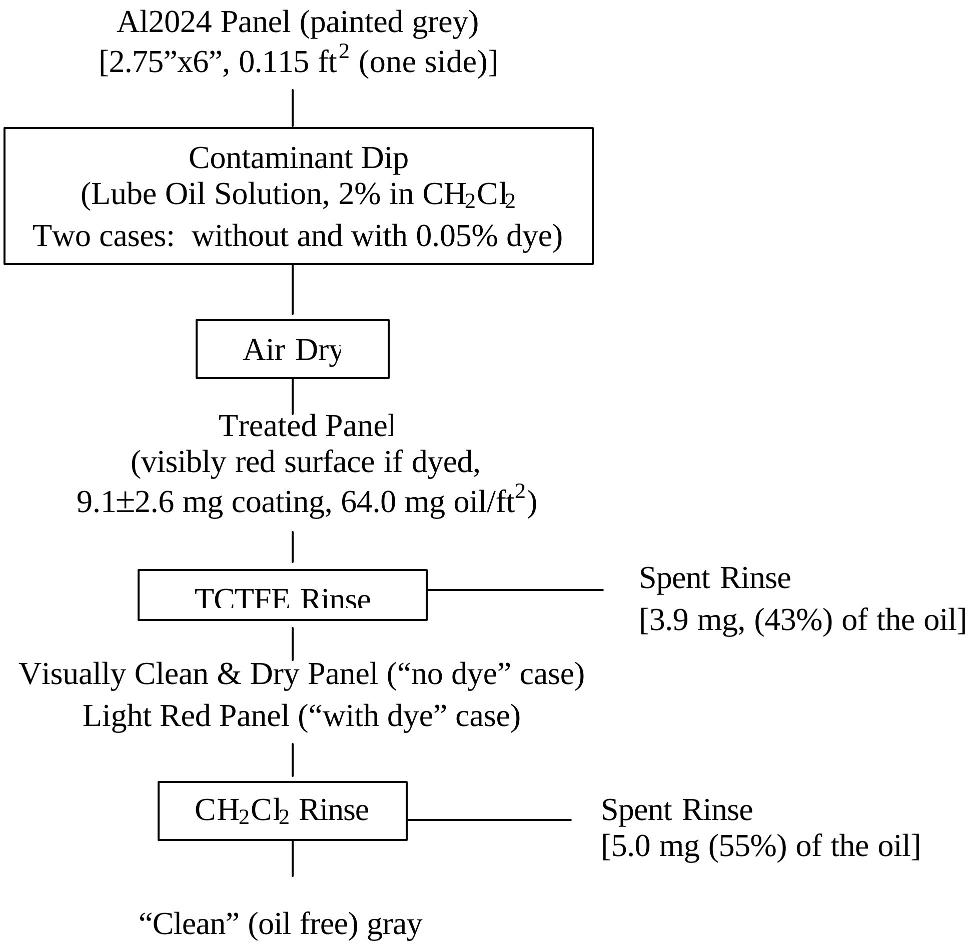

Figure D.2.5 VCPI Concept Fundamental Feasibility Quantitative Test Results Based on the NVR Method

D.2.1.3 Preliminary Dye-CA Cost Estimate

The quantitative analytical results from Section D.2 were used to perform preliminary cost estimate for dye usage in applying the VCPI technology at the commercial scale.

For the Oil Red O Dye-CA candidate, the preferred ratio for the 30-125 mg oil/ft^2 of contaminant per panel area is estimated to be in the 40-200 mg/L range. Using the mid-value of 80 mg oil/ft^2 and an oil/dye v/w ratio of 120, the weight of dye/ft^2 is 0.67 mg dye/ft^2, or substantially below the 3 mg/ft^2 of even highly clean surfaces. At laboratory scale, Oil Red O is $21/100 g or $95/lb. Bulk prices are anticipated to lower this cost to about $10/lb. Therefore, the cost of dye per 1000 ft^2 (670 mg) is estimated to be about $0.015. If dye losses in the operation are 90%, then the cost per 1000 ft^2 of aircraft surface would be $0.15. This preliminary cost seems reasonable. Data from Tasks 2 and 3 were used to refine this VCPI raw material cost projection.

D.3 Cleanliness Testing – Laboratory and Field

This section describes the techniques used to assay for these contaminants on the various test panel surfaces.

D.3.1 Hydrophobic Impurities on Painted Surfaces

As described, hydrophobic contaminants selected consist of G, LO, or PA7 residuals on Al2024P, TP, or FeHY80P steel.

D.3.1.1 Cleanliness Test Used in the Field

For painted surfaces, cleanliness is difficult to quantify in the field, as the water break test is not effective on the hydrophobic surface. Hence, cleanliness is determined visually by the Air Force by the visible disappearance of the LO sheen from the surface. The VCPI technique, when coupled with non-volatile residue (NVR) assays, has indicated that this visual method does not "see" that portion of the oil absorbed into the paint, which may be a substantial amount, e.g. >40% of the original oil sheen present. Therefore, a good field technique for monitoring painted surfaces does not appear to exist. Occasional spot checks can be made using one or more of the techniques given in the next section but these are not amenable to high % area coverage and routine use. Hence, overcleaning is about the only technique useable in this case. Therefore, assessment of painted surface cleanliness is where the VCPI technique appears to be needed.

D.3.1.2 VCPI Project Laboratory Quantification of Surface Hydrophobic Contaminant Levels

A number of analytical methods are effective for laboratory scale organic oils and greases. These methods range from quick, simple, and low cost methods such as NVR analysis, to high cost methods such as high performance liquid chromatography (HPLC), electron scattering for chemical analysis (ESCA), Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR), gas chromatograph (GC), ultra-violet/visible (UV/VIS), etc. All of these analytical methods require substantial training to implement. The sophisticated chromatographic methods can have significant down time. Methods such as ESCA and EIS require substantial skill in data reduction and reference systems chosen. The methods selected for the VCPI concept assessment work use many of these techniques and are described below.

D.3.2 Hydrophobic Contamination on Metal Surfaces

This section deals with those analytical methods suitable for assaying for hydrophobic fluids on metal surfaces, which do not tend to absorb such contaminants. Nor do the metals interfere seriously by adding to spectral backgrounds. Hence, a number of good techniques are available for this case.

D.3.2.1 Cleanliness Test Used in the Field or Laboratory Simulation of Field Testing

Two cleanliness test methods are being used as described in Table D.3.1.

D.3.2.2 VCPI Project Laboratory Quantification of Contaminant Levels

The laboratory techniques were used to quantify contaminants on panel surfaces and used cleaning baths are summarized in Table D.3.1.

D.3.3 Metal Corrosion Products on Metal Surfaces

Al2024 aircraft alloy is the metal surface used for corrosion product VCPI labeling technique assessment. The following subsections describe the cleanliness testing used for this surface, for both field and laboratory use.

D.3.3.1 Cleanliness Tests Used in the *Field*

The test methods routinely used in the field to assess cleaning completeness with respect to corrosion product removal is visual inspection, water break test, and paint adhesion.

D.3.3.2 VCPI Project Laboratory Quantification of Metal Corrosion Product Contaminant Levels

The amount of corrosion product was determined indirectly as given below. Contact angle was also measured on CRC cleaned panels by ICP as given in Table D.3.1.

D.3.4 Soluble Corrosive Salts (Sea Water Residues)

Although seawater is a complex blend of inorganic, organic, and biological components, it is well known that the halides are the primary cause of metal corrosion from this source. By far the dominant halide in seawater is chloride ion.

D.3.4.1 Cleanliness Test Used in the *Field* or Laboratory Simulation of Field Testing

This contaminant class is of interest to both the Navy and the Air Force. Currently the only field assay is the gross disappearance of visual salt deposits (encrustations) accumulated from dried seawater.

D.3.4.2 VCPI Project Laboratory-Scale Quantification of Soluble Salt (Cl-) Contaminant Levels

Chloride ion is known to be the key corrosive component of seawater. Ion chromatography (IC) was found to be an excellent lab-scale method for quantitatively analyzing for this ion. The method was a typical general purpose IC method and so need not be described in detail here.

Table D.3.1 Summary Panel Assay Methodologies (Subtask 2.2)

Technique	Application
Visual Inspection	Panel Surfaces Before and After Testing Under Controlled Lighting Conditions
NVR Using EtOAc	Total Coating Assay – Lube Oil
NVR Using Pet Ether or Toluene	Total Coating Assay – Grease (pet ether for tiles)
Color Space and Surface UV/VIS	Dye Analysis: Relate Results to Visual Inspection
ATR-IR	Surface Hydrophobic Contaminant Analysis on Metal Surfaces
UV/VIS of Used Cleaning Solutions	Determine Dye Content
Ion Chromatography for Chloride Ion	Soluble Salt (seawater) Analysis
EIS	Relative Corrodability of Al2024 Cleaned with/without Dye Present
Contact Angle	Surface Cleanliness of Metals
ICP-MS for Al	Al Levels in Used Cleaning Solutions
Paint Adhesion	Surface Cleanliness Measurement (coating debonding under dry and wet conditions)

D.4 DETAILED LABORATORY PROCEDURES FOR SYSTEMATIC CLEANING TESTS (SCT) (Subtask 3)

This Appendix collects the detailed laboratory procedures developed using PCT work. This information includes experimental techniques, experimental procedures, materials and chemicals used, panel labeling procedures, and analyses methods for used cleaning baths and cleaned panel surfaces. Only that information not already included in the bulk of the report is included here.

D.4.1 Preparation of Hydrophobic Contaminant Labeling Solutions

D.4.1.1 Preparation of 2% (w/v) LO Solution with ethyl acetate (500mL solution)

1. Weigh 10.0g MIL-L-23699 LO.
2. Place the 10.0g MIL-L-23699 LO into a clean 500mL volumetric flask.
3. Add ~300mL ethyl acetate and swirl until mixed completely.
4. Fill to the 500mL mark with ethyl acetate, stopper and mix to make a 2% (w/v) solution.
5. Place in a glass jar and label the jar. This solution is contaminant only. Mark clearly that solution contains LO and ethyl acetate.

D.4.1.2 Preparation of 2% (w/v) LO with 500ppm ORO solution (500mL solution)

1. Weigh 10.0g MIL-L-23699 LO.
2. Place the 10.0g MIL-L-23699 LO into a 500mL volumetric flask.
3. Weigh 250.0 mg ORO.
4. Add 250.0 mg ORO to the 500mL volumetric flask.
5. Add ~300mL ethyl acetate and swirl until mixed completely.
6. Fill to the 500mL mark with ethyl acetate to make a 2% (w/v) LO, 500ppm ORO solution.
7. Place in a glass jar and label the jar. This solution is contaminant plus dye. Mark clearly that solution contains LO, ORO, and ethyl acetate.

D.4.1.3 Preparation of 2% (w/v) Grease Solution with Toluene (500mL)

1. Weigh 10.0g grease.
2. Place the 10.0g grease into a 500mL volumetric flask.
3. Add ~300mL ethyl acetate and swirl until mixed completely.
4. Fill to the 500mL mark with toluene to make a 2% (w/v) solution.
5. Place in a glass jar and label the jar. This solution is contaminant only. Mark clearly that solution contains grease.

D.4.1.4 Preparation of 2% (w/v) Grease, 500 ppm ORO solution (500mL solution)

1. Weigh 10.0 g grease.
2. Place the 10.0 g grease into a 500mL volumetric flask.
3. Weigh 250.0 mg ORO.
4. Add 250.0 mg ORO to the 500mL volumetric flask.
5. Add ~300mL ethyl acetate and swirl until mixed completely.
6. Fill to the 500mL mark with toluene to make a 2% (w/v) grease, 500ppm ORO solution.
7. Place in a glass jar and label the jar. This solution is contaminant plus dye. Mark clearly that solution contains grease.

D.4.1.5 Preparation of Grease/Dye Mixture

1. Tare a porcelain crucible on the travel balance (precision to one-hundredth of a gram). Add 20-40 grams of Mobil grease to the crucible. (20 g could be stretched to label all the tiles in a Test System. 30 or 40 grams will provide a little “breathing room” in case mistakes are made or technique is less than optimal.)
2. Measure the appropriate amount of ORO dye in an aluminum pan on the analytical balance and then add the dye to the grease in the crucible.
3. Using a wooden tongue depressor, mix the dye and grease well for several minutes.
4. Transfer the grease/dye mixture to a 50-mL centrifuge tube, and label the tube appropriately.
5. Cover the tube in foil to prevent photo-degeneration of the dye.

D.4.1.6 Preparation Of Dye/Seawater Solution

1. Into an aluminum pan, measure out the appropriate amount of FG3 dye.
2. Rinse the dye into a volumetric flask with some seawater to obtain a complete transfer.
3. Fill the flask with seawater to the line and mix well.
4. Store the dye solution in a labeled, amber bottle.

D.4.2 Precleaning Panels

1. Etch panels to be cleaned with individual number (notebook # -pg. # - line #) on back of panel in top section only.
2. Use ethyl acetate to remove all stamped lettering from back of panels.
3. Under fume hood, degrease panel in toluene for 10 seconds with manual agitation.
4. Air dry panel by hanging.
5. Immerse panel in 1:3 MIL-PRF-87937C cleaner ± 75°C being stirred on a magnetic stirring plate, for 1 minute.
6. Drain panel over 1:3 MIL-PRF-87937C solution for 10 seconds.
7. Rinse panel in HPDI water for 2 minutes.
8. Drain panel over HPDI water rinse solution for 10 seconds.
9. Rinse panel in second HPDI solution for 2 minutes, drain 30 seconds.
10. Perform water break test on panel. If panel passes water break test, then continue to Step 11. If panel fails, then return to Step 5.
11. Hang panel to dry overnight, then use promptly.
12. Record initial weight of panel when needed for particular experiment (to ± 0.1 or ± 0.01 mg).
13. Measure and record physical dimensions of panel when needed for particular experiment.
14. Wrap panel in Kim-Wipe®.

D.4.3 Al2024 and Al2024P Panel Labeling

D.4.3.1 Panel Labeling (Using Hydrophobic Solutions) for Painted Surfaces (Al2024P)

1. Pour contaminant and contaminant plus dye solutions (from C.1) into beakers.
2. Dip each panel (cleaned as in C.2) half way (or completely as called for by the test protocol) in “contaminant only” solution or the “contaminant plus dye” solution for 1 minute.
3. Place the coated panel horizontally onto rods to insure that the contaminant from the front side of the panel does not spread onto the surrounding table area or to the back of the panel. Panel needs to be completely flat.
4. Let panel dry in horizontal position for a minimum of 15 minutes.
5. Squirt specified solvent onto a Kim-Wipe® (ethyl acetate for LO and toluene for grease).
6. Wipe the backside of the panel while holding the panel parallel with the table to remove any “contaminant only” or “contaminant plus dye” solution on the backside of the panel.
7. Place the coated panel horizontally onto rods or small plastic spacers to insure that the contaminant from the front side of the panel did not spread onto the surrounding table area.
8. When panel is dry on both sides, bring panel to data color room for analysis. Record color space results in appropriate notebook.
9. After panel has been tested with the data color unit, take panel to light box inspection station. Record observations in appropriate notebooks that panel was viewed under controlled lighting inspection station.

D.4.3.2 Panel Labeling (Using Hydrophobic Solutions) for Al2024

1. Weigh the precleaned panel to ± 0.01 mg.
2. Using a disposable pipette, drip the appropriate contaminant (either labeled or unlabeled) onto the panel.
3. Using a clean Kim-Wipe®, spread the contaminant uniformly over the appropriate area (either 100% or 50% coverage as called for in the specific test being run).
4. Using another clean Kim-Wipe®, wipe off any excess contaminant.
5. Reweigh the panel to ± 0.01 mg.
6. Store and transport horizontally.

D.4.3.3 Panel Labeling (Using Corrosion) for Al2024

1 After pre-cleaning the panel (see C.2 above) to protect LRB # and hole at top of panel (see C.2 above), wrap the top of the panel with electrical tape.

2 Place panel in 5% neutral salt spray for 14 hours at ASTM B-117 test conditions to obtain sufficient corrosion on front surface.

3 After removing panel from chamber, rinse panel thoroughly with DI water while rubbing surface with index finger, which is covered by latex glove.

4 Allow panel to dry, and then wrap panel in Kim-Wipe®.

5 After removing electrical tape off panel, hang panel on hook, and lower hook into 500ppm NR4 (carminic acid).

6 Allow panel to dwell in 500ppm carminic acid overnight (for initial testing, later this time was substantially shortened).

7 Remove panel from carminic acid in morning, rinse panel, and allow panel to dry vertically.

8 After removing electrical tape, skip steps 5 through 7 for reference panels.

9 The backup corrosion product dye, Alazarin, can substitute directly in the above procedure.

D.4.4 Labeling PCMS Foam Tiles (T and TP)

D.4.4.1 Grease on TP

1. Apply a piece of platters' tape, approximately 1" x 3", to the back, top center of each tile.
2. Using the electric scribe, engrave the 9-digit LRB number into the tape just applied. (This allows the LRB number to be identified more easily than if it were engraved directly into the foil.)
3. Use the grease/dye mixture prepared in C.1.5.
4. Obtain a squeegee. Before selecting one that has never been used, check the labels on the used squeegees to determine if one of them has been used for the current grease/dye ratio. (The same squeegee may be used on both painted steel panels and foam tiles – the dye/grease ratio must, however, be specific to each squeegee. Before using the squeegee, use 50% isopropanol and a Kim-Wipe® to remove any dust or residual grease).
5. Obtain a Teflon® knife and a 500-mL glass beaker. If necessary, clean the Teflon® knife with 50% isopropanol or ethyl acetate.
6. Obtain ~ 20 g dye-free Mobil grease to be used on the reference tiles. (This doesn't have to be neat grease. It could have been applied and removed from previous reference tiles.)
7. For both the reference and labeled tiles, randomly weigh at least two of each subset before and after applying the grease or grease/dye mixture. (A minimum of eight tiles should be weighed in this manner from each block: 2 labeled 50%, 2-labeled 100%, 2 reference 50%, and 2 reference 100%). Use the analytical balance for all weight measurements.
8. Begin by applying the grease to the reference tiles. Once all have been completed, proceed to the labeled tiles. This order is not crucial, but it will help to prevent contamination of the reference tiles with the dye. In between the reference and labeled tiles, clean the Teflon® knife with ethyl acetate, wipe any grease out of the beaker with a Kim-Wipe® and

disassemble and clean the squeegee. A different squeegee should be use for the grease/dye mixture and the dye-free grease. See Step 9-17 for details on the labeling procedure.

9. For the 50% tiles apply a thin coating of the grease with the Teflon® knife on the bottom half of the tile. (The Teflon® knife may be placed in or on top of the glass beaker when the knife isn't in use.)
10. Holding the tile in one hand and the squeegee in the other, push the squeegee down the tile, beginning just above the grease.
11. Set the tile down on Kim-Wipe® and remove the grease from the squeegee with the Teflon® knife. Return as much grease as possible to the centrifuge tube. Remove the remainder of the grease from the squeegee with a Kim-Wipe®. If the coating on the tile is even and uniform, skip to Step 10. Otherwise continue with Step 9.
12. To even out the grease on the tile (if necessary) push the squeegee down the tile a second time. (The blade of the squeegee must be clean for this to be effective.)
13. Once the tile has a satisfactory coating of grease, remove the grease from the edges with a Kim-Wipe®.
14. Weigh the tile if applicable and place it on a panel rack.
15. For the 100 % tiles, follow Steps 6-11, except spread the grease over the entire tile, save the top ¼". Begin to push the squeegee down the tile from this clean area at the top.
16. At the conclusion of the entire block, thoroughly clean the Teflon® knife and the squeegee, and label the squeegee if it was used for a new test system.
17. Store the feed tiles separately from those to be cleaned.

D.4.5 Painted Steel Panels FeHY80P

D.4.5.1 Grease on FeHY80P

1. Using the electric scribe, engrave the 9-digit LRB number into the top, back center of each panel.
2. Apply 50% isopropanol to a Kim-Wipe® and wipe down the front of each panel. After having cleaned the panels, re-stack them only if a Kim-Wipe® is placed between each panel. (This will prevent any rust from rubbing off onto the clean painted surface.)
3. Use the grease/dye mixture that has already been prepared (see C.1.5).
4. Obtain a squeegee. Before selecting one that has never been used, check the labels on the used squeegees to determine if one of them has been used for the current grease/dye ratio. (The same squeegee may be used on both painted steel panels and foam tiles – the dye/grease ratio must, however, be specific to each squeegee.) Before using the squeegee, use 50% isopropanol and a Kim-Wipe® to remove any dust or residual grease.
5. Obtain a Teflon® knife and a 500mL glass beaker. If necessary, clean the Teflon® knife with 50% isopropanol or ethyl acetate.
6. Obtain ~ 20g dye-free Mobil grease to be used on the reference tiles. (This doesn't have to be neat grease. It could have been applied and removed from previous reference panels.)
7. For both the reference and labeled panels, randomly weigh at least two of each subset before and after applying the grease or grease/dye mixture. (A minimum of eight panels should be weighed in this manner from each block: 2 labeled 50%, 2 labeled 100%, 2 reference 50%, and 2 reference 100%.) Use the travel balance for all weight measurements. (The panels are too heavy for the analytical balance.)
8. Begin by applying the grease to the reference panels. Once all have been completed, proceed to the labeled panels. This order is not crucial, but it will help to prevent contamination of the reference panels with the dye. In between the reference and labeled panels, clean the Teflon® knife with ethyl acetate, wipe any grease out of the beaker with a Kim-Wipe® and disassemble and clean the squeegee. A different squeegee should be use for the grease/dye mixture and the dye-free grease. See Steps 9-17 for more details on the labeling procedure.
9. For the 50% panels apply a thin coating of the grease with the Teflon® knife on the bottom half of the panel. (The Teflon® knife may be placed in or on top of the glass beaker when the knife isn't in use.)
10. Holding the panel in one hand and the squeegee in the other, push the squeegee down the panel, beginning just above the grease.
11. Set the panel down on Kim-Wipe® and remove the grease from the squeegee with the Teflon® knife. Return as much grease as possible to the centrifuge tube. Remove the remainder of the grease from the squeegee with a Kim-Wipe®. If the coating on the panel is even and uniform, skip to Step 10. Otherwise continue with Step 9.
12. To even out the grease on the panel (if necessary) push the squeegee down the panel a second time. (The blade of the squeegee must be clean for this to be effective.)
13. Once the panel has a satisfactory coating of grease, remove the grease from the edges with a Kim-Wipe®.
14. Weigh the panel if applicable and place it on a panel rack.

15. For the 100% panels, follow Steps 6-11, except spread the grease over the entire panel, save the top above the hole. Begin to push the squeegee down the tile from this clean area at the top, level with the bottom of the hole.
16. At the conclusion of the entire block, thoroughly clean the Teflon® knife and the squeegee, and label the squeegee if it was used for a new test system.
17. Store the feed panels separately from those to be cleaned.

D.4.6 Water-Soluble Corrosive Salts

D.4.6.1 Seawater on FeHY80P

1. Place a piece of platters' tape on the back of each panel sufficiently long enough to completely cover the back. This can be done most efficiently by rolling out a long piece of tape, placing the panels painted side up on the tape, and then cutting the tape and trimming it to the edges of each panel. A small amount of the tape may be folded over onto the front of each panel.
2. Using the electric scribe, engrave the 9-digit LRB number into the tape just applied, at the top center of the back of each panel.
3. Apply 50% isopropanol to a Kim-Wipe® and wipe down the front of each panel.
4. Use the seawater/dye mixture prepared in C.1.7.
5. Obtain approximately six tall 1-L beakers and three rubber stoppers, approximately 1" thick.
6. Begin by dipping the reference panels. Once all have been completed, proceed to the labeled panels. This order is not crucial, but it will help to prevent contamination of the reference panels with the dye. See Steps 7-14 for more details on the labeling procedure.
7. Fill 3 beakers (or 4 if 8 beakers are available) with ~ 500mL seawater, for 50% reference panels. (The seawater doesn't have to be neat; seawater used on previous reference panels may be reused.) Place each beaker on top of a rubber stopper and position them directly below the clips of the dipper.
8. Secure a cleaned, taped panel in each clip with a beaker below it.
9. Ensure that the timer next to the control dial is set for 60 seconds. Lower the panel into the beakers at setting "10" on the dipper. Once the dipper stops lowering the panel, adjust the setting to "3." The dipper will automatically remove the panels from the beakers.
10. Once the dipper has stopped in the upper position, remove the panels from the clips and allow them to dry flat (on micro-beakers or steel rods) at least fifteen minutes.
11. Once the panels have dried, wipe the backs with a HPDI water saturated Kim-Wipe® and then place the panel on a panel rack.
12. For 100% reference panels, add seawater to each beaker to increase the volume in each to ~925mL. Then follow Steps 8 – 11. A small pool of liquid will cling to the panel on both sides where the clip had been touching it. Dab away this liquid with a Kim-Wipe®.
13. Before beginning the labeled panels, rinse each clip with HPDI water.
14. For the labeled panels, begin with clean beakers, substitute dye/seawater solution for the seawater, and follow the steps above outlined for the reference panels (including wiping off the back of the panels after allowing them to dry).
15. After dipping all the reference and labeled panels, again rinse the clips with HPDI water and rinse out all the beakers used with HPDI water. Soak the beakers in the micro-bath before using again.
16. Store the feed panels separately from those to be cleaned.

D.4.6.2 Seawater on Foam Tiles

1 Place a piece of platters' tape on the back of each tile sufficiently long enough to completely cover the back and wide enough to cover the edges and to overlap about ¼'' on the front. This can be done most efficiently by rolling out a long piece of tape, placing the tiles painted side up on the tape, and then cutting the tape and trimming it as necessary. Fold the tape under at the corners (like wrapping a gift) so as to keep water from seeping beneath the tape.

2 Using the electric scribe, engrave the 9-digit LRB number into the tape just applied, at the top center of the back of each panel.

3 Use the seawater/dye mixture prepared in C.1.6.

4 Obtain approximately six tall 1-L beakers and three rubber stoppers, approximately 1" thick.

5 Begin by dipping the reference tiles. Once all have been completed, proceed to the labeled tiles. This order is not crucial, but it will help to prevent contamination of the reference tiles with the dye. See Steps 6-14 for more details on the labeling procedure.

6 Fill 3 beakers (or 4 if 8 beakers are available) with ~ 500mL seawater, for 50% reference tiles. (The seawater doesn't have to be neat; seawater used on previous reference panels may be reused.) Place each beaker on top of a rubber stopper and position them directly below the clips of the dipper.

7 Secure a cleaned, taped tile in each clip with a beaker below it.

8 Ensure that the timer next to the control dial is set for 60 seconds. Lower the tile into the beakers at setting "10" on the dipper. Once the dipper stops lowering the tile, adjust the setting to "3." The dipper will automatically remove the tiles from the beakers.

9 Once the dipper has stopped in the upper position, remove the tiles from the clips and allow them to dry flat (on micro-beakers or steel rods) at least fifteen minutes.

10 Once the tiles have dried, wipe the backs with a HPDI water saturated Kim-Wipe® and then place them panel on a panel rack. (Check for water dripping out of the tape at the bottom corners of the tiles.)

11 For 100% reference tiles, add seawater to each beaker to increase the volume in each to ~ 900mL. Then follow Steps 7 – 10. A small pool of liquid will cling to the tile on both sides where the clip had been touching it. Dab away this liquid with a Kim-Wipe®.

12 Before beginning the labeled tiles, rinse each clip with HPDI water.

13 For the labeled tiles, begin with clean beakers, substitute dye/seawater solution for the seawater, and follow the steps above outlined for the reference tiles (including wiping off the back of the tiles after allowing them to dry).

14 After dipping all the reference and labeled tiles, again rinse the clips with HPDI water and rinse out all the beakers used with HPDI water. Soak the beakers in the micro-bath before using again.

15 Store the feed tiles separately from those to be cleaned.

D.4.7 Analysis of Used Cleaners

D.4.7.1 UV/Vis

Same method used as in Appendix D.

D.4.7.2 ICP-MS

Conventional ICP-MS was used to measure the Al concentration in used cleaners and rinses.

D.4.7.3 IC

Conventional Ion Chromatography (IC) was used to measure chloride ion (Cl^-) concentration in used cleaners and rinses.

D.4.8 Analysis of Panel Surfaces

D.4.8.1 Data Color

Same method used as in Appendix D.

D.4.8.2 FTIR

FTIR was used as a method to determine the cleanliness of the Al2024 panels contaminated with LO before and after cleaning. To date, FTIR scans have been performed on 2 blocks of samples contaminated with LO. The Perkin-Elmer FTIR system employed a ZnSe ATR crystal with a sampling area of approximately 1 by 2 inches. The sample stage was purged with nitrogen to reduce background peaks associated with water and carbon dioxide. 25 scans were performed on each sample and averaged to reduce scatter in the data. A reference scan was performed to establish a baseline using an Al2024 blank. This reference scan was subtracted from each subsequent sample scan to further reduce the noise in the data. The crystal was cleaned after each sample measurement with a 50/50 mixture of ethanol and chloroform and blown dry with dry nitrogen to remove as much oil and dye contaminant as possible from the crystal surface. A scan was performed on an Al2024 blank after each cleaning step to ensure no contaminant oil peaks remained on the crystal.

D.4.8.3 Surface Contact Angle

For panels contaminated with LO or exposed to 14 hours of ASTM-B117 salt fog, surface contact angle measurements were performed to determine the wettability of the samples before and after cleaning. The presence of surface contaminants as well as surface roughening can be detected using this technique. A Melles Griot TANTEC model CAM-Micro instrument was used to measure the surface contact angle of 24 panels with 6 different surface conditions. Twelve panels from one block of LO contaminated samples and 12 panels from one block of samples exposed to 14 hours of ASTM-B117 salt fog have been tested. The LO block consisted of three separate conditions: labeled, reference, and blank Al2024. One feed panel and three other panels with 6, 12, or 18 scrubs from each condition were measured. The corrosion block also contained three separate conditions: labeled, reference, and blank Al2024. One feed panel and three panels with 0, 1, or 3 minute CRC dwell time from each condition were measured.

A five-microliter droplet of DI water was placed onto the panel surface. Using the contact angle meter at the back of the instrument, an assessment of surface contact angle was made in degree. Contact angle values ranging from 0 to 120 could be measured. This procedure was duplicated 4 times on each panel.

The average of these four angle measurements was used for data analysis. This was done to account for heterogeneities in the panel surface resulting from residual contaminants.

D.4.8.4 Electrochemical Impedance Spectroscopy (EIS)

EIS testing was used to quantify the change in the Al2024 surface as a function of exposure time to the CRC cleaning procedure. The parameter of interest for this study was the low frequency impedance at 50 MHz. This overall impedance a 50 MHz is a measure of the combination of the resistance of the surface oxide film of the aluminum alloy as well as the charge transfer resistance across the metal/solution interface. Sodium borate was used as the test electrolyte to stabilize the Al2024 surface and prevent further corrosion of the samples in the test environment. Thus all changes observed in the low frequency impedance are a result of the difference in cleaning procedure (i.e. CRC dwell time).

A 1" x 3" section of each sample was sheared off and used for the EIS testing. Impedance tests were run using an EG&G flat cell with an exposed surface area of approximately 1 cm2. A Perkin-Elmer EG&G 273A Potentiostat with a Solartron 1250 FRA was used, along with ZPlot® software. The scans were run at an amplitude of 10 mV rms, with a frequency range of 50 kHz to 5 MHz.

D.4.8.5 Non-Volatile Residue (NVR) Analysis

Previously cleaned test coupons using the aforementioned method were analyzed for non-volatile residues (NVR) using the following procedure. Each test coupon having dimensions 3 x 6 inches was analyzed using only a 3 x 3 inch square, making up only half of the total surface of the coupon. Flat cotton square shaped swabs (2 x 2 inch) were used to perform the tests. The method consisted of tarring the balance and weighing all of the cotton swabs first, using rubber gloves and tweezers to handle the swabs. Once a single swab was weighed for each test coupon, the value was recorded. The application of petroleum ether to each test coupon was now implemented. This step involved applying 1 ml of petroleum ether, which was delivered from a glass syringe onto the test coupon over the 3 x 3 inch area. Once the solvent was applied, the cotton swab was used to wipe the area clean. Long strokes with minimal pressure were used to clean the surface.

Once the area was wiped clean, the cotton swabs were allowed to dry completely. After all of the cotton swabs were dry, each one was weighed again without tarring the balance from the original weighings. This was done to ensure any variations in recalibration that are spawned from tarring would not be a factor.

The data was then compiled by subtracting the mass of the cotton swab before cleaning from the mass of the cotton swab after cleaning. The difference of the two values yields the mass of the NVR.

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APPENDIX E

VCPI CONTAMINANT LABELING AND CLEANING TEST RESULTS

Methods were developed to prepare dye labeled (or just "labeled") and unlabeled contaminated test panels, and for cleaning these panels at the lab scale using DoD cleaning protocols. During "pre-screening" cleaning testing, these labeled panels, with references and blanks, were subjected to abbreviated cleaning protocols and compared to "feed" (non-cleaned) panels, to provide quick preliminary checks on the dye labeling performance to help select dyes and application conditions for the systematic cleaning tests. These pre-screening test results are given in Section E.1 below, followed by the systematic cleaning test results as Section E.2. These sections support Section 7 of the report.

E.1. Pre-Screening Cleaning Testing And Approach For Systematic Cleaning Tests (Subtask 3.1)

The pre-screening VCPI dye-CA chemistry selection criteria were as follows:

- Whether the dye was visibly apparent at the thin layer conditions represented by the contaminant layer on the test panel surface,
- Whether the dye bonded selectively to the contaminant,
- That the dye did not bond to the panel surface material,
- Whether the dye and the contaminant are removed together using cleaning process chemistry.

In addition, this pre-screening work provided test specimens for development of supportive analytical and cleaning test procedures.

Once these criteria were satisfied for a test case, the particular VCPI system was deemed ready for systematic cleaning tests performed by the Air Force or Navy team members, now well underway. The panel contamination and dying procedures will now be described in general. Specific procedures were given in Appendix D.

E.1.1 Contaminant Application to Panels and Labeling Techniques for VCPI Cleaning Testing

Table E.1.1 summarizes the listing of targeted DoD large area cleaning surface needs and specific contaminants tested. Table E.1.2 provides the correlation between contaminant chemical property type and recommended VCPI dye labels. The definition of two of the contaminants has been further clarified since last year's annual report. The first of these, residual water-soluble salts, are exemplified best by seawater residues and so this source was used to represent this contaminant. The second contaminant, important to the Navy, is Peel Away® 7 (PA7) paint stripper residue. This mildly hydrophobic, gel-based material is used to strip paint from PCMS (Passive Countermeasures System) foam tiles prior to repainting. PA7 residuals interfere with paint adhesion and hence must be thoroughly removed. PA7 falls into the hydrophobic contaminant VCPI classification, and so was labeled using the dye being investigated for this class of contaminants, ORO. The remaining contaminants, grease, lube oil, and aluminum alloy metal corrosion products are as before. Natural Red 4 (NR4) is being used for corrosion product labeling, instead of Alizarin, because of the acid nature of corrosion removal compound (CRC). Appendix C describes the labeling chemistries involved with each contaminant class selected. Each of the contaminant labeling procedures developed in this program is described in general terms in the subsections below.

E.1.2 Painted Al2024

Aluminum 2024-T3 (Al2024P) panels, coated with paint (primer and topcoat, see Appendix B for description and MIL specs of paint systems used) were contaminated with either dilute and neat lube oil (LO) with or without label (i.e., dye, ORO). B & B Re-Gel® (MIL-PRF-87937C, Type III) was used to clean the panels using lab-scale versions of AF T.O.-1.1.8.691 as described below.

Table E.1.1 Panel Substrate Materials and Contaminants Used for Cleaning Tests

Surface Material	Contaminant Target[c]	DoD Need[b]
Al 2024-T3 (painted)	Lubrication Oil (hf, MIL-L-23699)	AF (and Navy) AF (and Navy)
Al 2024-T3	▪ Aluminum hydroxides/oxides from 14 hour neutral 5% salt spray (CP) ▪ Lubrication Oil (hf, MIL-L-23699)	AF (and Navy)
HY80 Steel [painted MIL-P-24441 approved primer (Formula 150, Type I) and topcoat (Formula 151, Type I) system before tiling]	▪ Soluble Salt (CSS, Seawater) ▪ Grease (hf, MIL-G-23549)	Navy (and AF) Navy (and AF) Navy (and AF)
PCMS Foam Tiles (painted) MIL-PRF-24763	▪ Soluble Salt (CSS, Seawater) ▪ Grease (hf, MIL-G-23549)	Navy Navy
PCMS Foam Tiles (repainting)	Peel Away® 7 paint stripper (hf)	Navy
Graphite-Filled Epoxy (painted)	Lubrication Oil (hf, MIL-L-23699)	AF

[a] See Appendix H for detailed labeling procedures.

[b] Refers mainly to contaminant. Organization listed outside of parentheses performed the detailed cleaning tests.

[c] Contaminant Types are given in parentheses, hf = hydrophobic fluid.

[d] Tentatively assumed equivalent to painted Al 2024-T3.

Table E.1.2 VCPI Systems (Selected Dye -CA Combinations)

Contaminant Type	Candidate Dye -CA Combination [Backups] (color in label form)	Suggested Use Method	Specific Contaminant Used in VCPI Screening
Hydrophobic liquids	▪ Oil Red O ▪ [D&C Violet 2]	▪ Solvent wipe ▪ Aqueous cleaners ▪ Formulated with PA7	▪ Lubrication oil (MIL-L-23699) ▪ Grease (MIL-G-23549) ▪ Peel Away® 7 Paint Stripper
Metal corrosion products	▪ Natural Red 4 (same as Carminic Acid (reddish purple)] ▪ [Alizarin (purple)]	▪ Water rinses ▪ Solvent wipe ▪ Aqueous cleaners	Corroded Al2024-T3 (hydrated Al_2O_3)
Corrosive water-soluble salts (e.g., seawater)	▪ Food Green 3 (Fast Green FCF) ▪ [Food Blue 2] ▪ [Basic Blue 3]	▪ Water rinse ▪ Aqueous cleaner	Seawater residue (essentially Cl–)

A gelling agent may be included for best performance, as is already in use with certain MIL-SPEC cleaners, for example B&B Re-Gel® (Type III cleaner)

E.1.3 Al2024

Aluminum 2024-T3 (Al2024) metal alloy panels were contaminated, labeled, and cleaned using the same reagents that were used above for Al2024P. Also, Al2024 panels were "contaminated" in 5% neutral salt spray to produce adherent surface corrosion products. These corrosion products were labeled with Natural Red 4 (NR4, carminic acid) by soaking in a water solution of this dye. B & B Re-Gel®, and an El Dorado AC-12 corrosion removal compound (CRC) were used to clean the panels using lab scale versions of AF T.O.-1.1.8 as described below.

E.1.4 HY80 Steel Coated with Paint System MIL-P-2441

HY80 steel panels coated with paint system MIL-P-2441 (FeHY80P) panels were contaminated with soluble salts [seawater (SW)] and labeled with Food Green 3 (FG3), or contaminated with grease (G) MIL-G-23549 and labeled with ORO. The FeHY80P panels were cleaned with water and PF degreaser. The cleaning process was recommended by NSWC-Carderock in accordance with the requirements specified for the Navy's countermeasures 470 Ship System. The referenced system and subsystem are *Passive Countermeasures System (PCMS) 4722* and *Passive ECM 4720*, respectively. The procedure is described below.

E.1.5 Painted PCMS Tiles

PCMS tiles were coated with paint system MIL-PRF-24763 (TP). TP panels were contaminated and labeled with the same materials, as was FeHY80P. As described below, several cleaning operations for these tiles were used depending upon the cleaning process being simulated (see below). The cleaning process was recommended by NSWC-Carderock in accordance with the same requirements specified in

Appendix C. TP panels were cleaned with MIL-D-16791 general-purpose detergent to remove soluble corrosive salt residues and grease, or stripped of the paint with Peel Away® 7 (PA7), labeled with ORO.

E.2 Cleaning Procedures and Protocols

This section describes the cleaning procedures and reference protocols used in the VCPI concept evaluation work. Three procedures were of interest. The field and depot cleaning protocols represent the ultimate industrial-scale deployment process and so served as the starting point for selection of laboratory scale procedures. From these, lab-scale *prescreen* cleaning procedures and lab-scale *systematic* cleaning protocols were devised. These protocols are organized below according to whether they are performed by the Air Force or the Navy.

E.2.1 Air Force Application Lab-Scale Prescreen Cleaning Procedure

Soak panel in 1:3 diluted MIL-PRF-87937C Re-Gel® cleaner solution [later tests used neat (undiluted) Re-Gel®] for specified times of the test in Pyrex® glass tray while mixing with a stir bar. Label the cleaning boundary after cleaning the panel. Obtain tare weights, net weights, and post rinse weights. Weigh tray empty, then with cleaner, then after soak, and finally after rinse. Rinse in DI water for 30 seconds. Label each analysis sample from each group with the cleaning time. Maintain a written record of all readings and observations. Place each panel with treated side up flat on two plastic cups of size much smaller than the panel width/length. Allow panel to air dry. Perform surface data color analysis. Perform visual inspection analysis by MacBeth Light Box under daylight, CWF (cool white fluorescent), and UV (ultraviolet) settings. For daylight and CWF condition, compare the different panels. For UV setting, report appearance of any fluorescence effect.

E.2.2 Air Force Lab-Scale Systematic Cleaning Protocol

This section describes the procedure for cleaning both LO and corrosion product contaminated samples by methods designed to closely simulate procedures used at the depots.

E.2.2.1 LO Contaminated Samples

Three different panel conditions; bare Al2024, Al2024 contaminated with LO (LO) only, Al2024 contaminated with LO and labeled with ORO dye, were exposed to a cleaning process using neat B&B Re-Gel®. In order to achieve incremental levels of cleanliness, either 6, 12, or 18 scrubs were used to clean the samples. Both 50% and 100% panel coverage samples were prepared depending upon analytical method to be used for the subsequent surface assay(s). For panels that were 100% contaminated, 6 mL of Re-Gel® were applied to the sample surface. This treatment was followed by scrubbing the panels with the specified number of scrubs using a Scotch-Brite™ pad, and then a final rinse using 180 mL of deionized water. For panels that were 50% covered with LO, 3 mL of Re-Gel® were applied to the contaminated half of the sample surface. As before, this was followed by scrubbing the samples with the specified number of scrubs, and then a final rinse using 120 mL of deionized water.

The cleaning process began by suspending each panel across the mouth of a beaker with the contaminant side up. Using a syringe, the specified amount of Re-Gel® was spread uniformly across the panel test area. In preliminary tests, it was found that Re-Gel® rapidly removed LO, reaching water break quickly. Therefore, the cleaner was not allowed to dwell on the surface of the panel, but was immediately scrubbed using a white nylon Scotch-Brite™ pad, and then rinsed using deionized water. This shortened reaction time was used in an effort to collect samples representing partially cleaned surfaces to determine if the dye and contaminant were being removed together versus stepwise, a critical dye-CA selection criterion. All soap and rinse water was collected within the beaker. The solution and Scotch-Brite™ pad were agitated with a Teflon® stirring rod in order to blend any residual oil and dye trapped within the nylon fibers with the bulk solution. Finally, the rinsate was transferred to clean, amber-colored, glass sample bottles for further analysis. The cleaned panel was sent to surface analysis.

E.2.2.2 Corrosion Contaminated Samples

Three different panel conditions were prepared; bare non-corroded Al2024, corroded Al2024 prepared using a 14-hour salt fog exposure, and corroded Al2024 using a 14-hour salt fog exposure prior to being dyed with NR4. These panels were subjected to a cleaning process using B&B Re-Gel® cleaner and El Dorado AC-12 corrosion removal compound (CRC). Initially, each of the panels was cleaned with a two-minute Re-Gel® soak and 4 light scrubs, followed by a 180 mL deionized water rinse. CRC was then applied to the wet panels immediately after the Re-Gel® was rinsed off. Various levels of corrosion removal were achieved by varying the CRC dwell time. Dwell times were 0, 1, and 3 minutes followed by two scrubs with a white Scotch-Brite™ pad and a final deionized water 180 mL rinse. The CRC rinsate was collected in a beaker and transferred to amber-colored polypropylene sample bottles for further analysis.

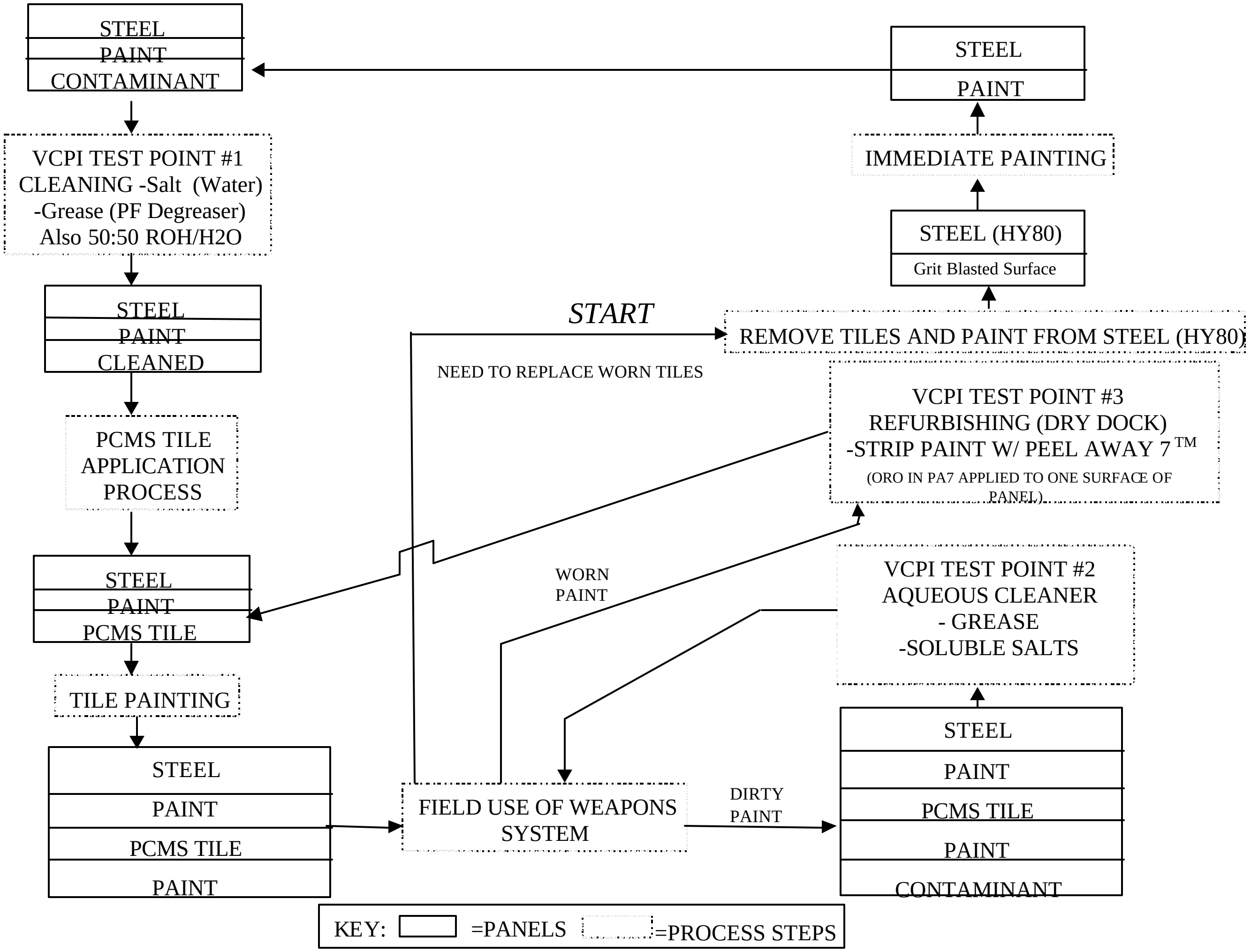


Figure E.1 VCPI Test Points in Navy PCMS Tile Application

E.2.3 Navy Application Lab-Scale Prescreen Cleaning Procedure

Same as for Systematic Cleaning.

E.2.4 Navy Lab-Scale Systematic Cleaning Protocol

E.2.4.1 PCMS Tile Application

The two procedures being used are provided in Figure E.2. These procedures represent laboratory versions of the field procedures (Appendix B).

Navy (SHIPALT CG 4700300K)

Standard PCMS Tile application process

Step 1. Preparation of Primed Steel Surfaces (no VCPI testing needed)

Technique: *Fresh water rinse*
Air dry time = 1 hour
Solvent degreaser wipedown
Air dry time = 5 minutes
Abrasive media blast and air cleaning
Primer application

- *no surface preparation if primed within 8 hours of blasting*
- *after 8 hours, surfaces need to be washed with 50/50 mixture of*
- *fresh water and alcohol. Flash rust must be removed with 200-grit sandpaper prior to primer application.*

Step 2. PCMS Tile Application (VCPI Test Point)

Technique: *Light abrasion (ScotchBrite 7447 pads)*
Wipedown of abraded surfaces with PF32 Degreaser (VCPI test point)
Air dry time = 5 minutes
Wipedown with 50/50 mixture of water and alcohol
Air dry time = 2 minutes
Apply tile

Additional VCPI test points enter during repainting of tiles and general field cleaning of painted tile surfaces.

Figure E.2 Navy Cleaning Protocol and Cleanliness Test Points for Re-Tiling of HY80 Steel (Submarines) with PCMS Foam Tiles

E.2.4.2 PCMS Tiles

Foam PCMS test tiles were coated with contaminants of either saltwater or grease, covering 50% of the painted surface. Two 60 ml glass syringes were used to apply the detergent and rinse. One syringe was filled with 15 ml of general purpose non-ionic cleaner, while the other syringe was filled with 15 ml of deionized water. The test coupons were held in hand on a steep angle over a large high-walled aluminum weighing boat. Using the glass syringe, 5 ml of the general-purpose detergent was applied to the test panel, at which point a nylon bristled brush was implemented to clean the surface of the panel. Gentle single-pass stokes with minimal pressure were used in each cleaning step. This process was repeated a maximum of two more times for a total delivered volume of 15 ml of detergent. In cases that required fewer cleaning steps, the remaining detergent was simply added to the residual rinse in an effort to keep all solutions totaling a final volume of 30 ml. After application of the detergent and subsequent cleanings, the syringe containing the deionized water was used to rinse the tile and brush one final time, and to give a complete rinse of the aluminum weighing boat after the residual rinse was poured into a 40 ml amber glass bottle.

E.2.4.3 FeHY80P-SW-FG3-5000

For this test system, FeHY80 steel painted panels were used. Reference panels were contaminated with seawater. Labeled panels were contaminated with seawater as well as labeled with Food Green 3 dye. See Appendix D for explanation of labeling method known as dipping method. When the seawater contaminant is dry on the panel, the chloride levels fall within the following range: 10-22 mg/ft^2. The remaining panels were left uncontaminated and without dye labeling.

The FeHY80P steel test panels were coated with contaminants seawater, covering 50% of the painted surface. A glass syringe filled with 30 ml deionized water was used to deliver the cleaning agent. The test coupons were held in hand on a steep angle over a large high-walled aluminum weighing boat. Using the glass syringe, 10 ml of cleaning agent was applied to the test panel, at which point a nylon bristled brush was implemented to clean the surface of the panel. Gentle single-pass stokes with minimal pressure were used in each cleaning step. This process was incremented in sets of one pass, 10 passes, and 20 passes, with a total delivered volume of 30 ml of cleaning agent. After the application of the cleaning agent and subsequent brush passes, the remaining cleaning agent in the syringe was used to rinse the tile and brush one final time, and to give a complete rinse of the aluminum weighing boat after the residual rinse was poured into a 40 ml amber glass bottle.

E.2.4.4 Chloride Ion Contamination and Dye Removal

Figures E.3.7 to E.3.9 show that the removal of the FG3 dye tracks the removal of the chloride ion contamination from the panel surface. The reference panels, which are contaminated with the chloride ion, but are not labeled with dye, show more variability in the data. This suggests that an operator cleaning the panels can infer the amount of contaminant removed based on the amount of dye that is removed from the panel surface. When the panels are not labeled with dye, no conclusion can be observed visually as to the amount of contamination removed from the panel surface.

E.2.4.5 Removal of Chloride Ion and Total Color Difference, dE*

Conveyed in Figures E.3.10 to E.3.12, when the panel surfaces have a splotchy appearance, the surface colors are irregular. It can be inferred in this case that the contamination is irregular because the removal of dye tracks the removal of contamination on the panel surface. It can be recommended that detailed testing be done to verify that the irregularity of the contamination exists on the panel surface. The larger error bar on Figure E.3.12 at 20 scrubs represents the inconsistency of contaminant distribution on the surface of the panel, as suggested above; the splotchy surface also shows the inconsistency of the contaminant.

E.2.4.6 TP-SW-FG3-5000

This test system includes labeled, reference, and blank painted PCMS tiles. The labeled tiles were contaminated with seawater and labeled with FG3 dye. The reference tiles were contaminated with seawater. The blank tiles were neither contaminated nor labeled with dye. After contaminating the reference and labeled tiles, through using the dipping method referred to in Section H.1, the range of chloride levels on the panel surfaces were as follows: 15-65 mg/ft^2.

Foam PCMS test tiles were coated with contaminants of grease, covering 50% of the painted surface. A single syringe filled with 30 ml of deionized water was used with no application of detergent to the surface. The test coupons were held in hand on a steep angle over a large high-walled aluminum weighing boat. Using the glass syringe, 10 ml of the deionized water was applied to the test panel, at which point a nylon bristled brush was implemented to clean the surface of the panel. Gentle single-pass stokes with minimal pressure were used in each cleaning step. This process was incremented in sets of one pass, 10 passes, and 20 passes, with a total delivered volume of 30 ml of cleaning agent. After application of the remaining detergent and subsequent brush passes, the syringe containing the deionized water was used to rinse the tile and brush one final time, and to give a complete rinse of the aluminum weighing boat after the residual rinse was poured into a 40 ml amber glass bottle.

E.2.4.7 Chloride Ion Contamination and Dye Removal

Figures E.3.13 to E.3.15 show that the removal of the FG3 dye tracks the removal of the chloride ion contamination from the panel surface. As mentioned and explained previously, this suggests that an operator cleaning the panels can infer the amount of contaminant removed based on the amount of dye that is removed from the panel surface. When the panels are not labeled with dye, no conclusion can be observed visually as to the amount of contamination removed from the panel surface.

E.2.4.8 Chloride Ion Contamination and Total Color Difference, dE*

Figures E.3.16 to E.3.18 show that the dye is removed quickly from the panel surface.

The squares and the triangles show that the dye guides the operator as to how much contamination is removed from the panel. The squares represent panels labeled with the FG3 dye while the triangles represent reference panels that were not labeled with dye.

It is visually apparent from the color observations to fully clean the dye’s color from the panel surface.

Figures E.3.16 to E.3.18 show that the visual observations appear to be more reliable and have certain advantages over instrumentation.

As briefly explained, a splotchy appearance on a panel surface means that the surface colors are irregular thus the contamination is also irregular because the chloride ion contamination vs. dye removal plots show that the dye removed from a panel will track the contamination removed from the panel.

E.3 Systematic Cleaning Test (SCT) Data Plots

E.3.1 Pre-labeled Contaminant Test Systems

Table E.3.1 serves as a key to the SCT test system codes. Table E.3.2 provides a key to the SCT test result plots, which follow.

Table E.3.1 Key For Test System Identification For Systematic Cleaning Testing

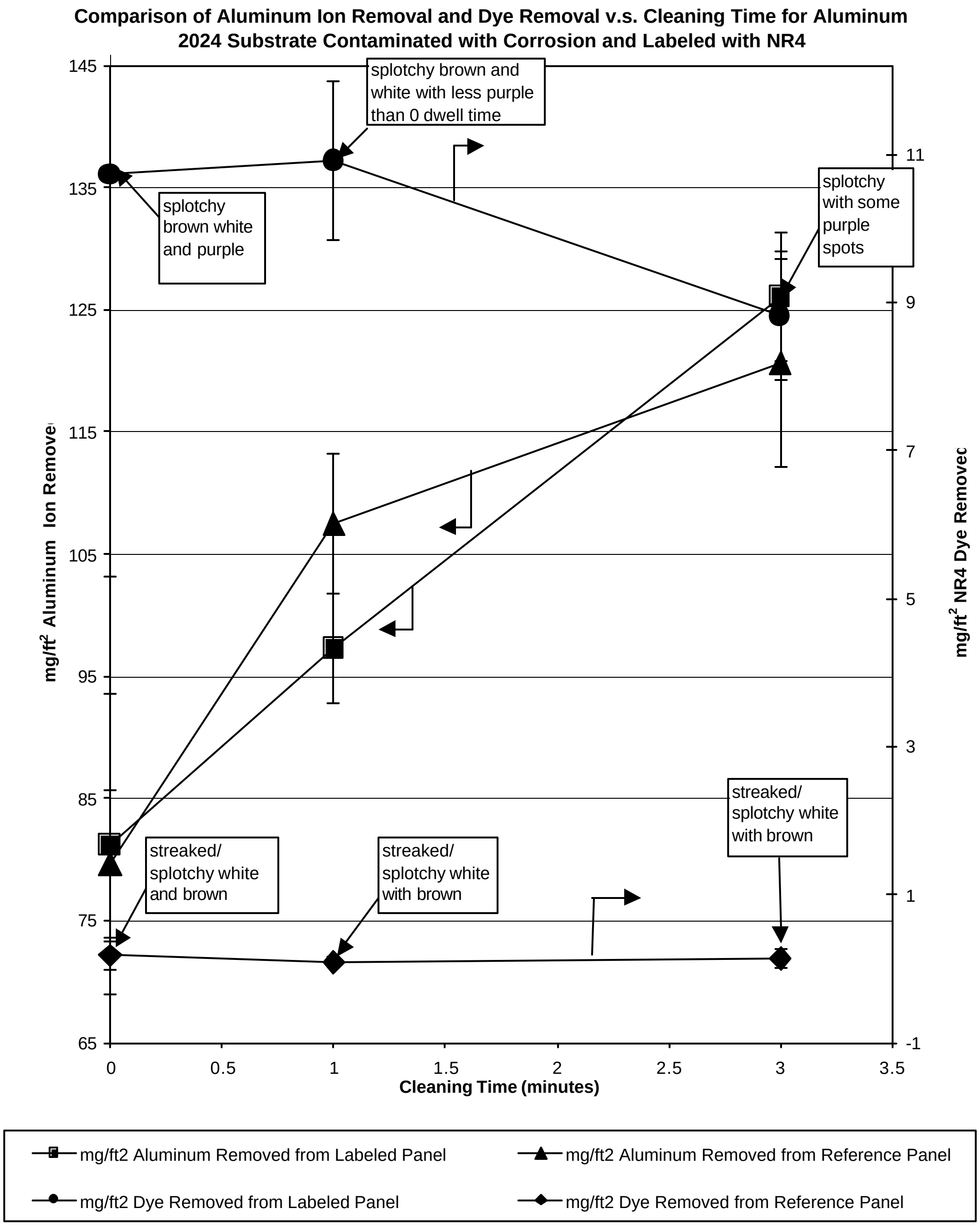
Base Material	Contaminant	Dye	Cleaning Time
Al2024 = Aluminum 2024 A = Aged P = Painted	LO = Lube Oil G = Grease SW = Sea Water C20 = Corrosion 20 Hrs in Salt Chamber B = Blank (no treatment)	ORO = Oil Red O 500 = Dye Concentration, 500 ppm R = Reference, No Dye CAR = Carminic Acid FG = Food Green 3	3 = 3 Min. 0.25 = 15 Sec.

Example: Al2024AP-LO-ORO500-3

This identification represents an aluminum 2024 aged, painted panel labeled with the contaminant lube oil and 500 ppm Oil Red O dye solution and then cleaned for 3 minutes.

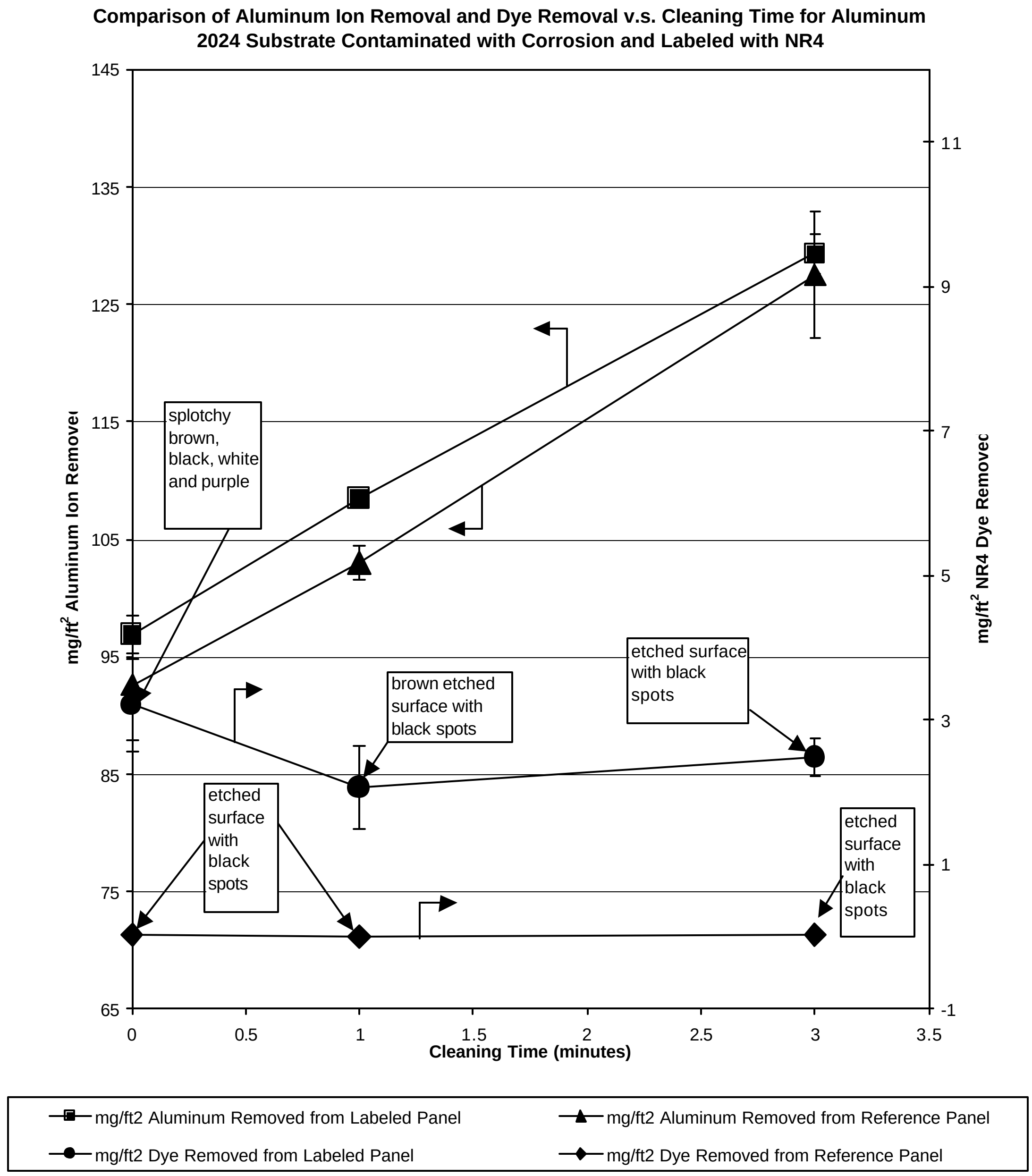
Table E.3.2 Key to SCT Test Result Plots

Figure No.	Description
E.3.1	Dye and Contaminant Removal for Corrosion Products Labeling (Block 55)
E.3.2	Dye and Contaminant Removal for Corrosion Products Labeling (Block 56)
E.3.3	Dye and Contaminant Removal for Corrosion Products Labeling (Block 57)
E.3.4	Total Color Difference and Contaminant Removal for Corrosion Products Labeling (Block 55)
E.3.5	Total Color Difference and Contaminant Removal for Corrosion Products Labeling (Block 56)
E.3.6	Total Color Difference and Contaminant Removal for Corrosion Products Labeling (Block 57)
E.3.7	Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 76)
E.3.8	Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 82)
E.3.9	Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 83)
E.3.10	Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 76)
E.3.11	Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 82)
E.3.12	Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 83)
E.3.13	Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on PCMS Painted Tiles (Block 69)
E.3.14	Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on PCMS Painted Tiles (Block 78)
E.3.15	Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on PCMS Painted Tiles (Block 79)
E.3.16	Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on PCMS Painted Tiles (Block 69)
E.3.17	Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on PCMS Painted Tiles (Block 78)
E.3.18	Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on PCMS Painted Tiles (Block 79)
E.3.19	Level of Contamination and Dye Removal for Hydrophobic Contaminant Labeling on FeHY80 Painted Steel Panels (Block 75)
E.3.20	Level of Contamination and Dye Removal for Hydrophobic Contaminant Labeling on FeHY80 Painted Steel Panels (Block 80)



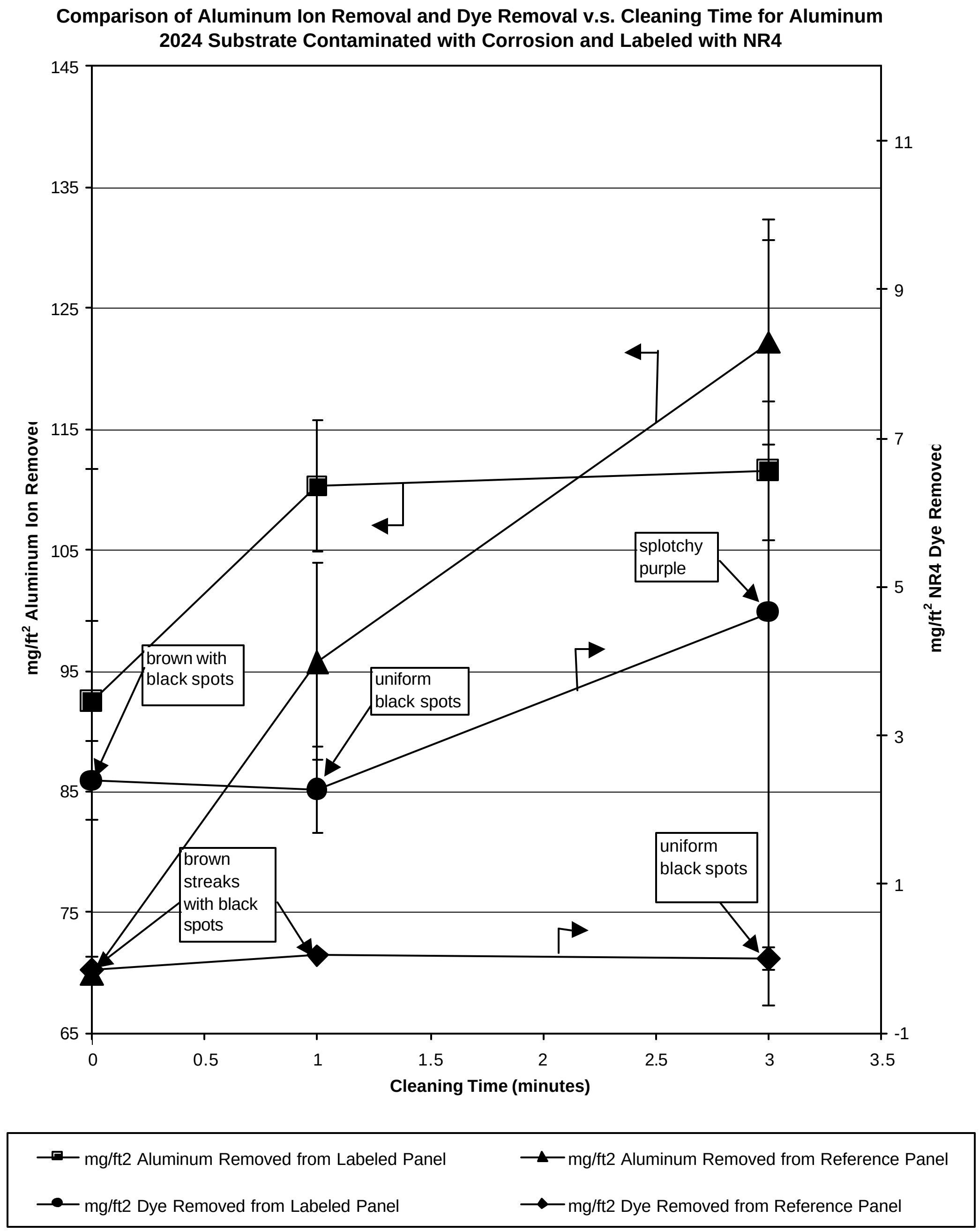
Analyses are of used cleaner baths from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and some circles are smaller than the symbols. (Al2024-C14-CAR-500 v.20010424 block 55)

Figure E.3.1 Dye and Contaminant Removal for Corrosion Products Labeling (Block 55)



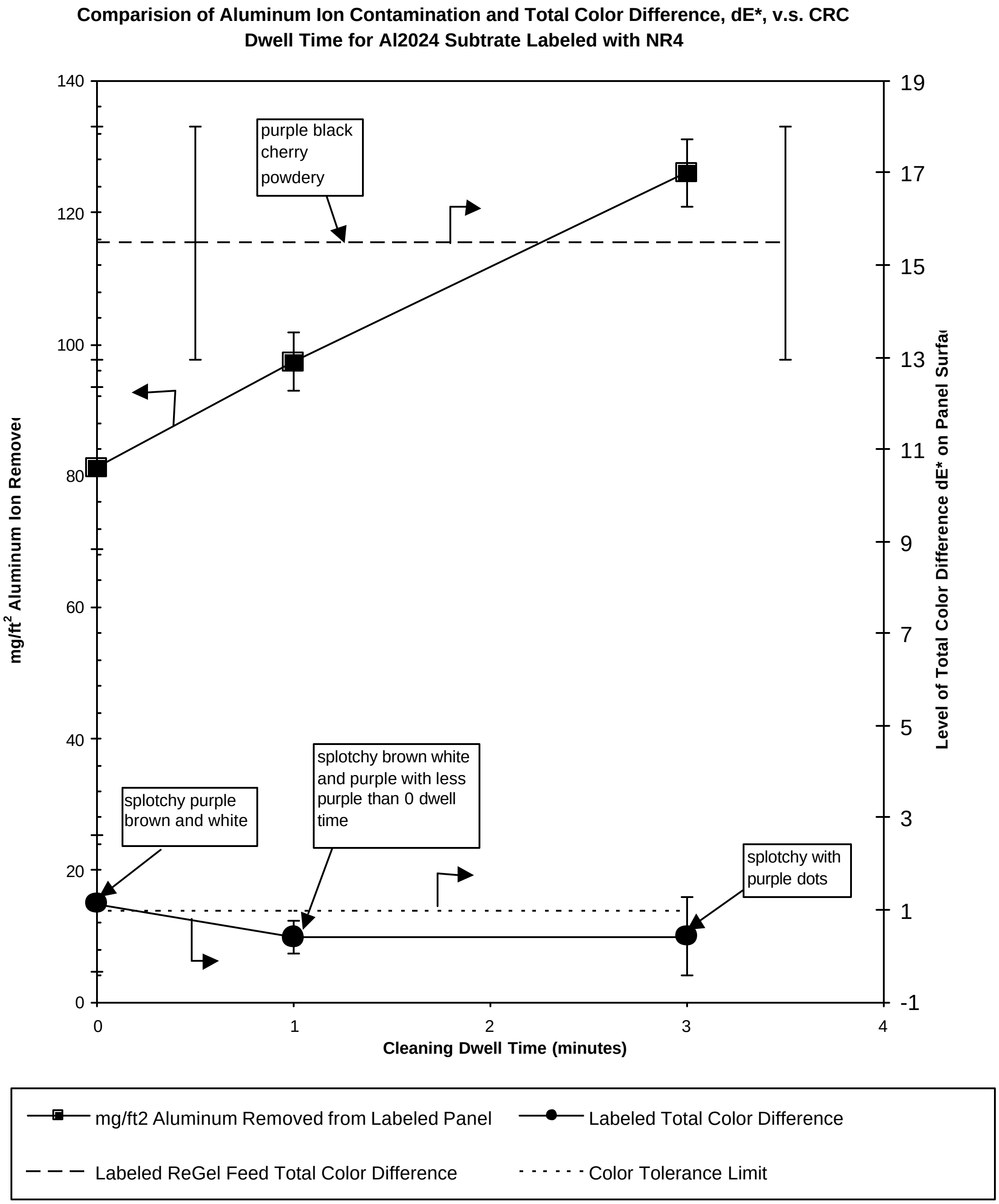
Analyses are of used cleaner baths from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and some squares are smaller than the symbol. (Al2024-C14-CAR-500 v.20010424 block 56)

Figure E.3.2 Dye and Contaminant Removal for Corrosion Products Labeling (Block 56)



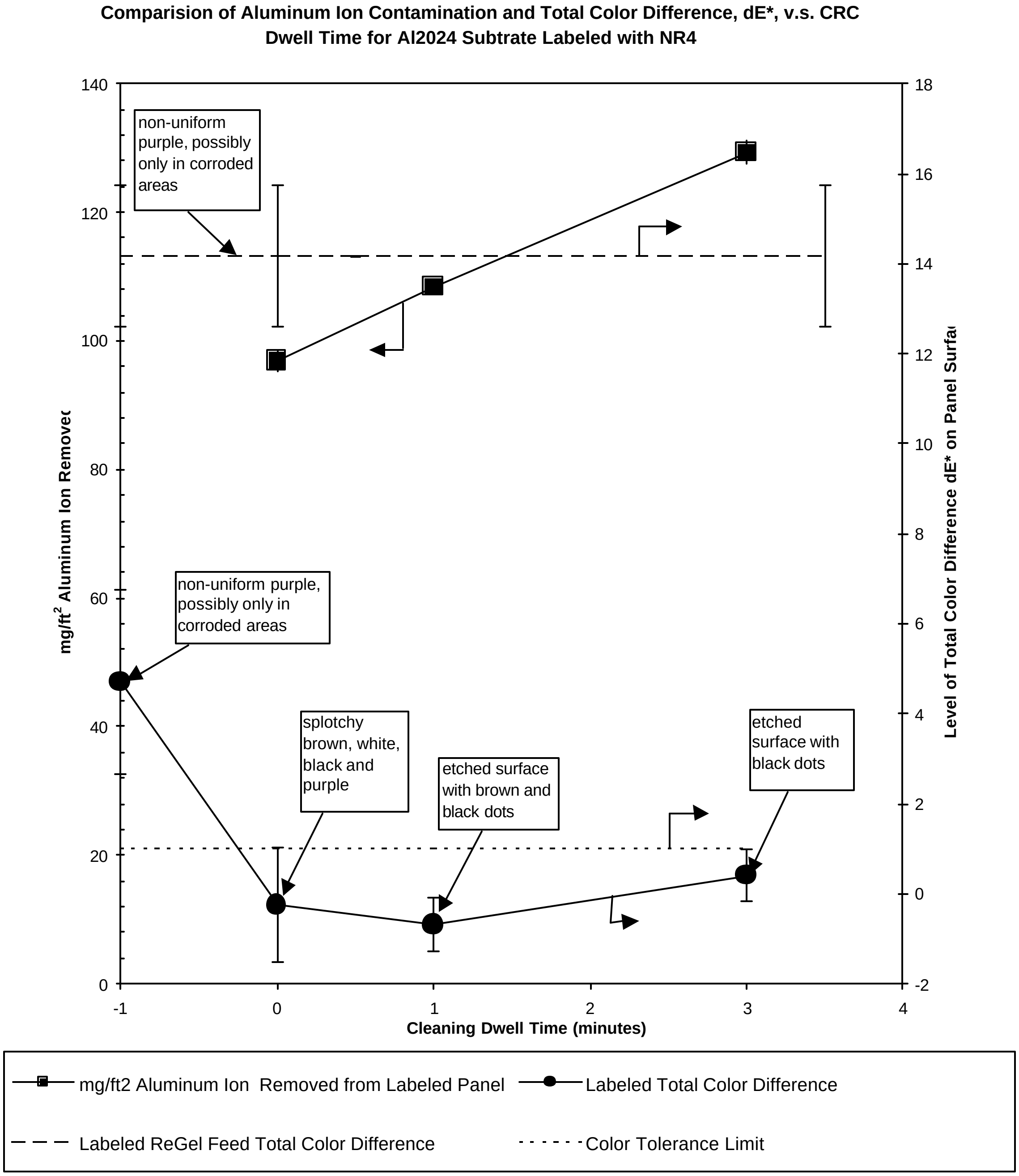
Analyses are of used cleaner baths from panel cleaning. Error bars are one standard deviation. Error bars for some diamonds are smaller than the symbol. (Al2024-C14-CAR-500 v.20010424 block 57)

Figure E.3.3 Dye and Contaminant Removal for Corrosion Products Labeling (Block 57)



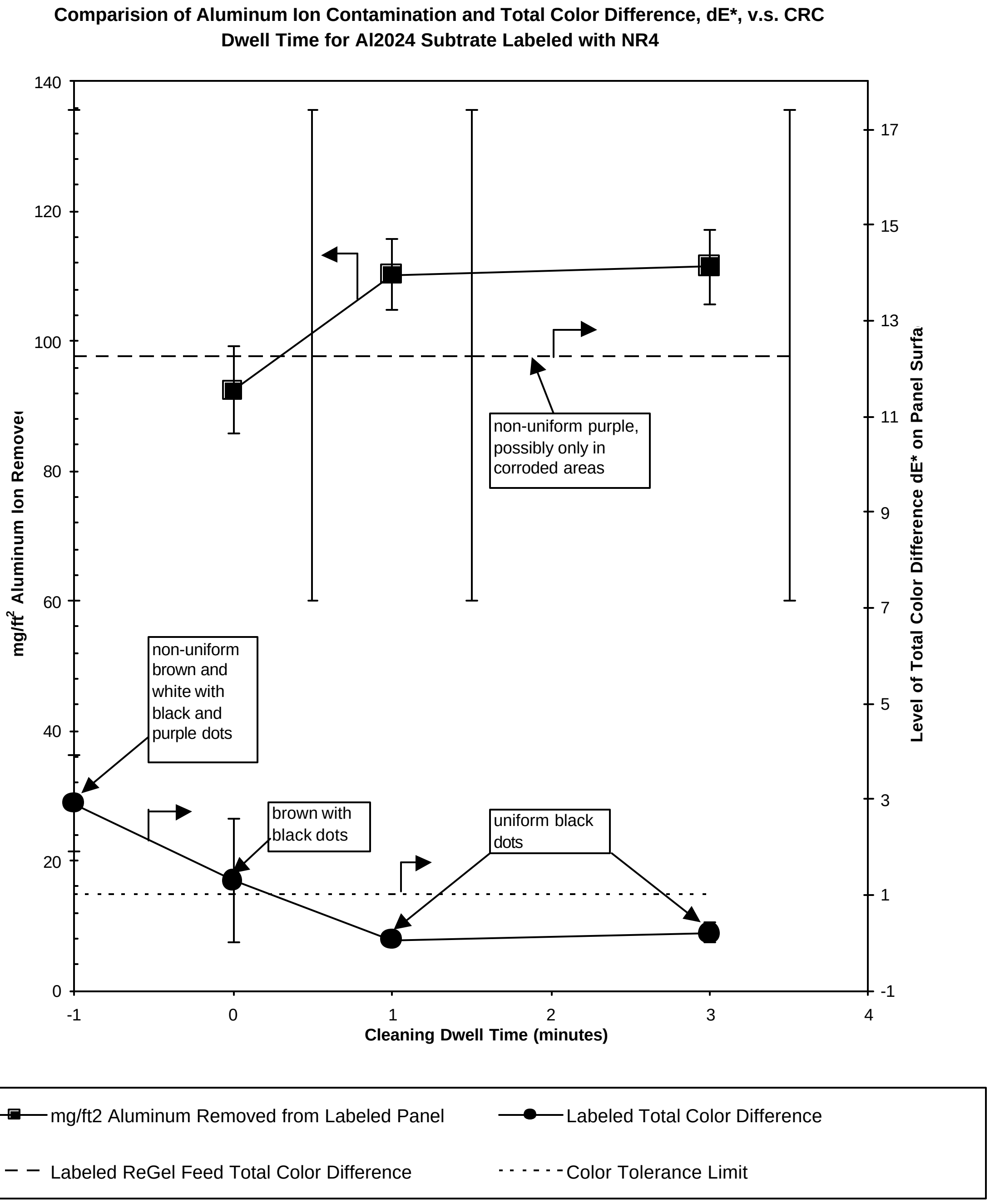
Analyses are of panel surfaces after the application of MIL-C-38334 (AC-12) Corrosion Removal Compound for a specified amount of time. Feed panels have not been cleaned with B & B ReGel or Corrosion Removal Compound. 0 min represents removal of the CRC immediately after application. Error bars are one standard deviation for two readings on the same panel. (Al2024-C14-CAR-500 block 55 v.20010424)

Figure E.3.4 Total Color Difference and Contaminant Removal for Corrosion Products Labeling (Block 55)



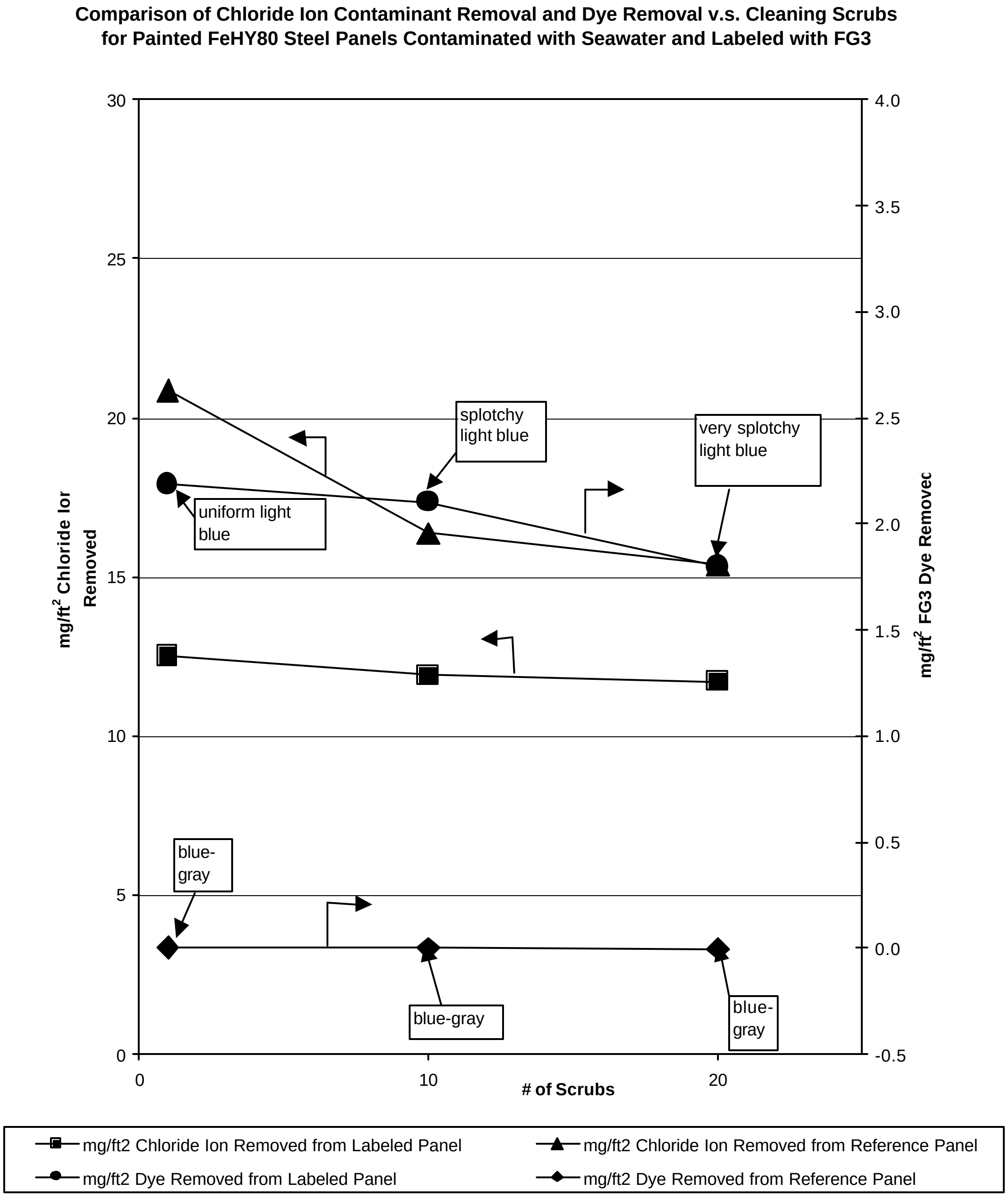
Analyses are of panel surfaces after the application of MIL-C-38334 (AC-12) Corrosion Removal Compound for a specified amount of time. Feed panels have not been cleaned with B & B ReGel or Corrosion Removal Compound. 0 min represents removal of the CRC immediately after application. Error bars are one standard deviation for two readings on the same panel. Error bars for squares are smaller than the symbols. (Al2024-C14-CAR-500 block 56 v.20010424)

Figure E.3.5 Total Color Difference and Contaminant Removal for Corrosion Products Labeling (Block 56)



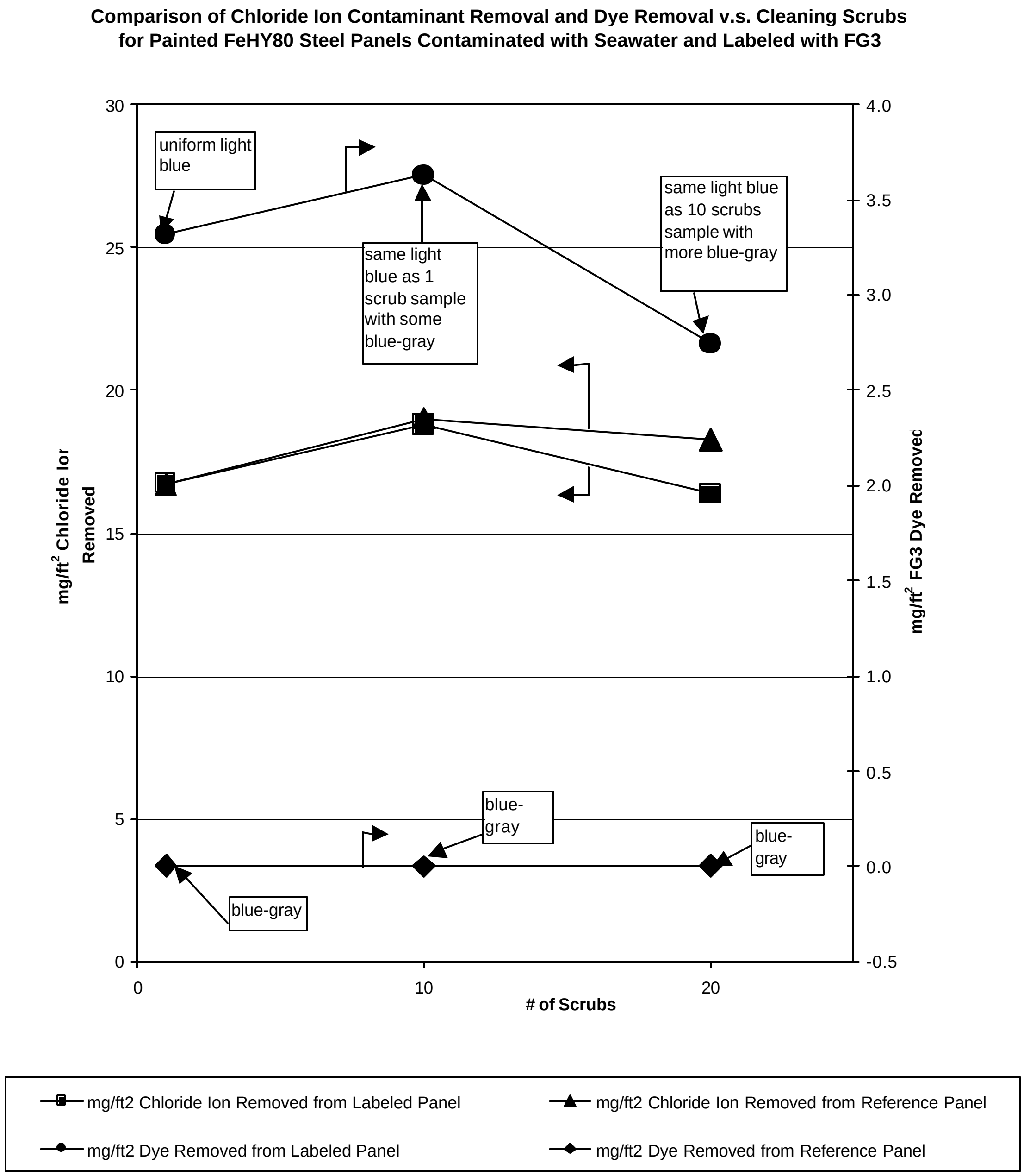
Analyses are of panel surfaces after the application of MIL-C-38334 (AC-12) Corrosion Removal Compound for a specified amount of time. Feed panels have not been cleaned with B & B ReGel or Corrosion Removal Compound. 0 min represents removal of the CRC immediately after application. Error bars are one standard deviation for two readings on the same panel. Erroe bars for some circles are smaller than the symbols. (Al2024-C14-CAR-500 block 57 v.20010424)

Figure E.3.6 Total Color Difference and Contaminant Removal for Corrosion Products Labeling (Block 57)



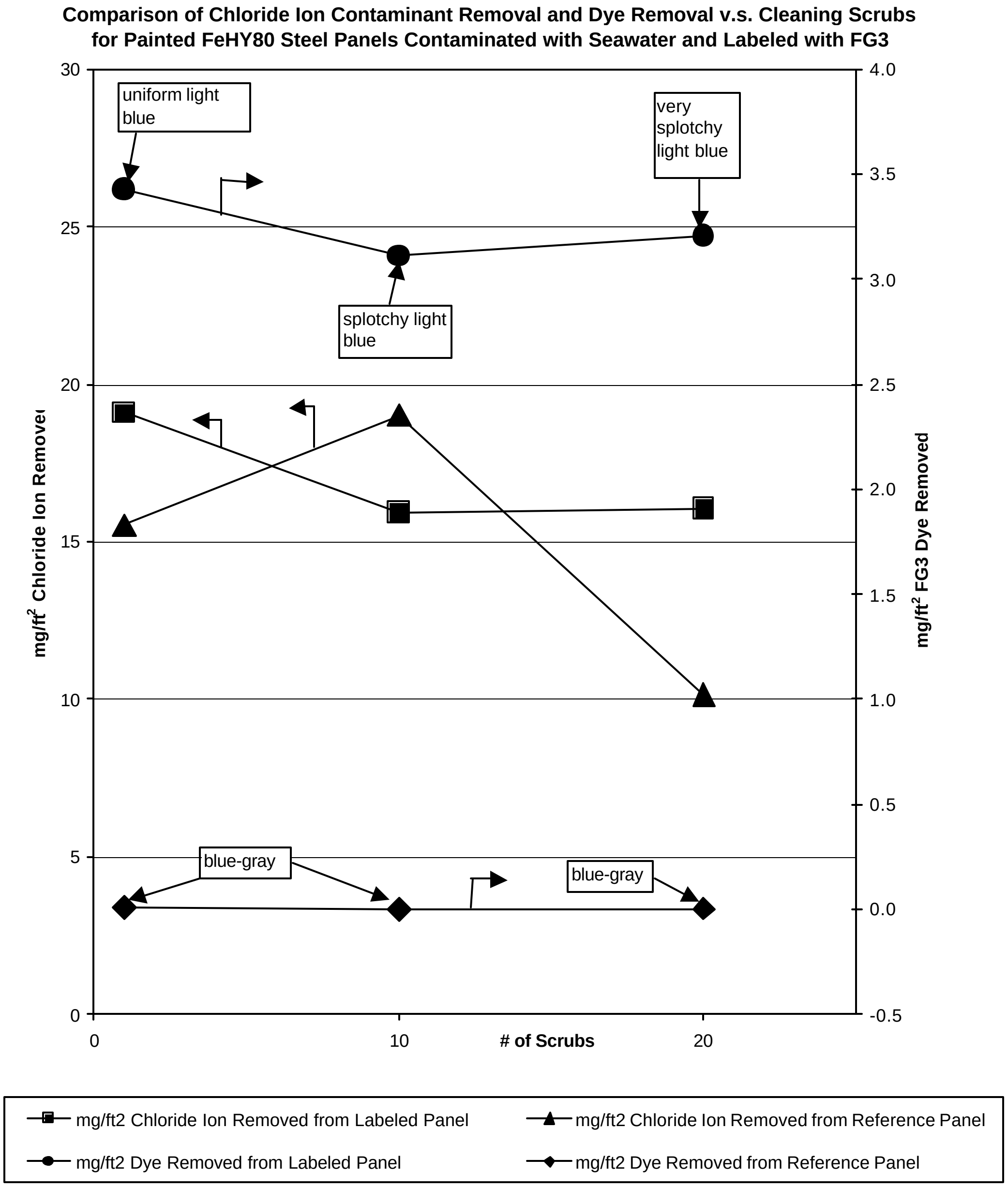
Analyses are of used cleaner baths from panel cleaning. Original panels surfaces appear blue-gray without label. (FeHY80P SW-FG3-5000 v. 20010423 block 76)

Figure E.3.7 Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 76)


Comparison of Chloride Ion Contaminant Removal and Dye Removal v.s. Cleaning Scrubs for Painted FeHY80 Steel Panels Contaminated with Seawater and Labeled with FG3

Analyses are of used cleaner baths from panel cleaning. Original panels surfaces appear blue-gray without label.
(FeHY80P-SW-FG3-5000 v. 20010423 block 82)

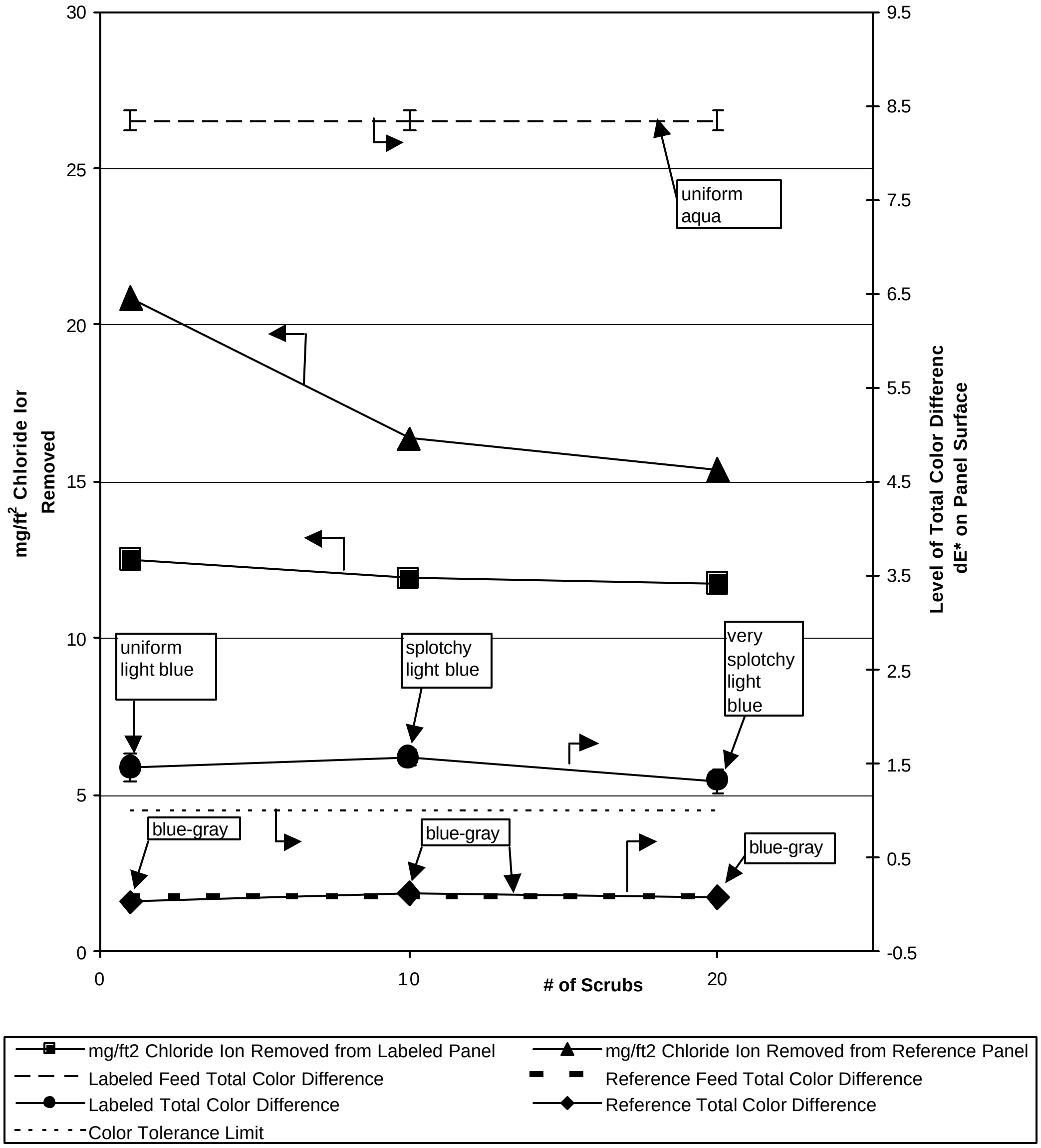
Figure E.3.8 Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 82)



Analyses are of used cleaner baths from panel cleaning. Original panels surfaces appear blue-gray without label. (FeHY80P-SW-FG3-5000 v. 20010423 block 83)

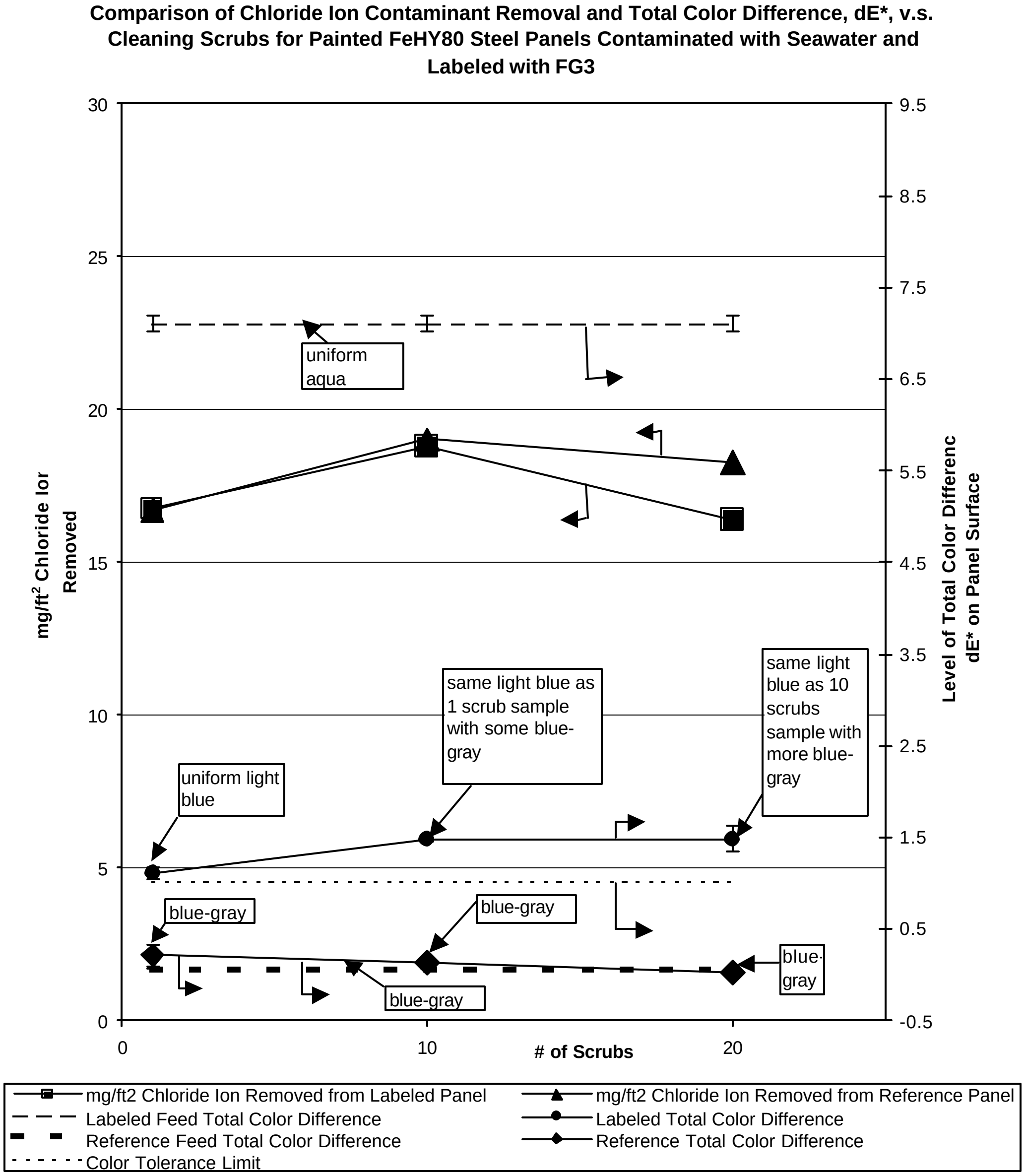
Figure E.3.9 Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 83)

Comparison of Chloride Ion Contaminant Removal and Total Color Difference, dE*, v.s. Cleaning Scrubs for Painted FeHY80 Steel Panels Contaminated with Seawater and Labeled with FG3



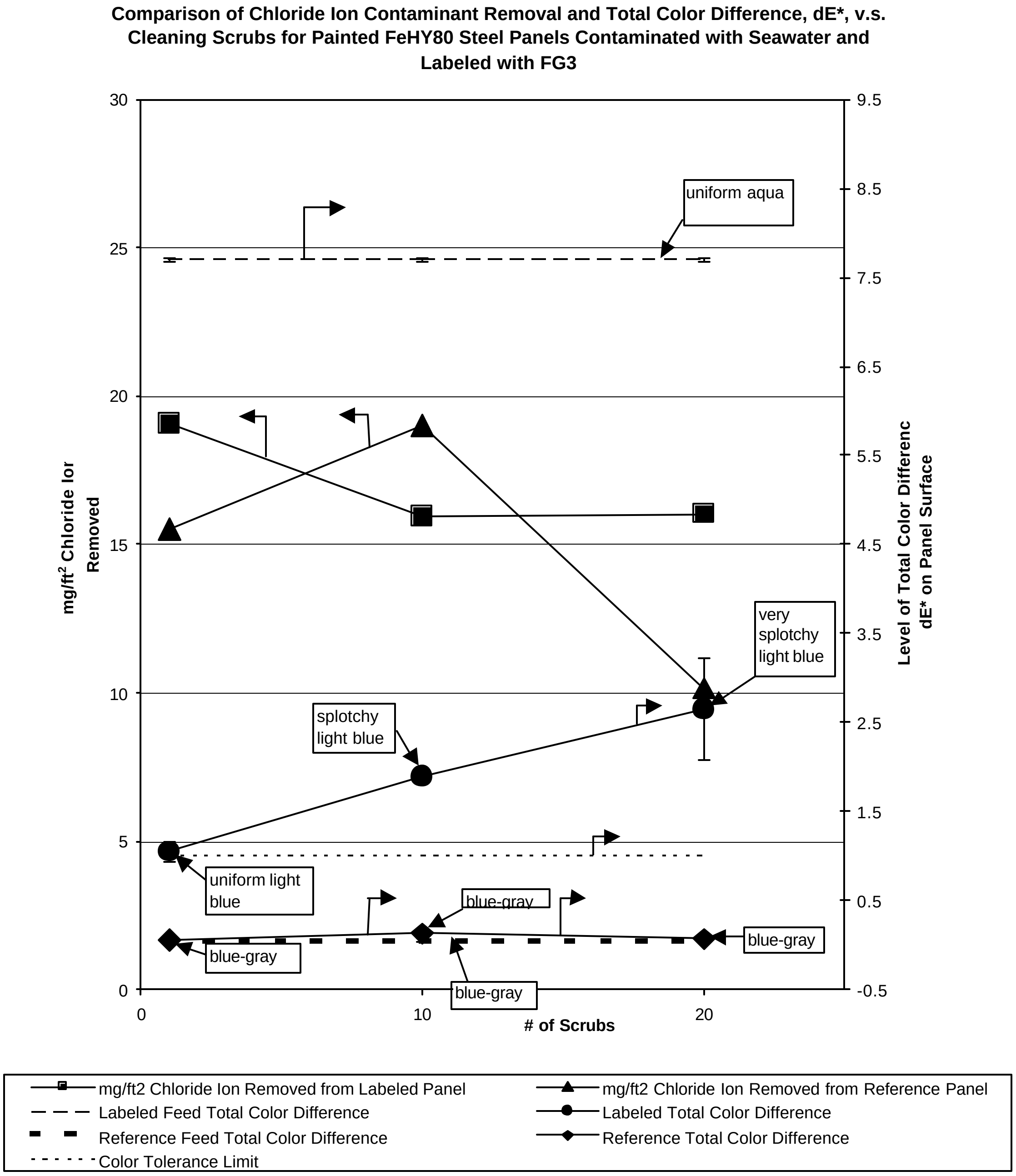
Analyses are of used cleaner baths and panel surfaces after panel cleaning. Error bars are one standard deviation. Error bars for circles and diamonds are smaller than they appear. Original panels surfaces appear blue-gray without label. (FeHY80P-SW-FG3-5000 v. 200104123 block 76)

Figure E.3.10 Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 76)



Analyses are of used cleaner baths and panel surfaces after panel cleaning. Error bars are one standard deviation. Error bars for circles and diamonds are smaller than the symbols. Original panels surfaces appear blue-gray without label. (FeHY80P-SW-FG3-5000 v. 20010423 block 82)

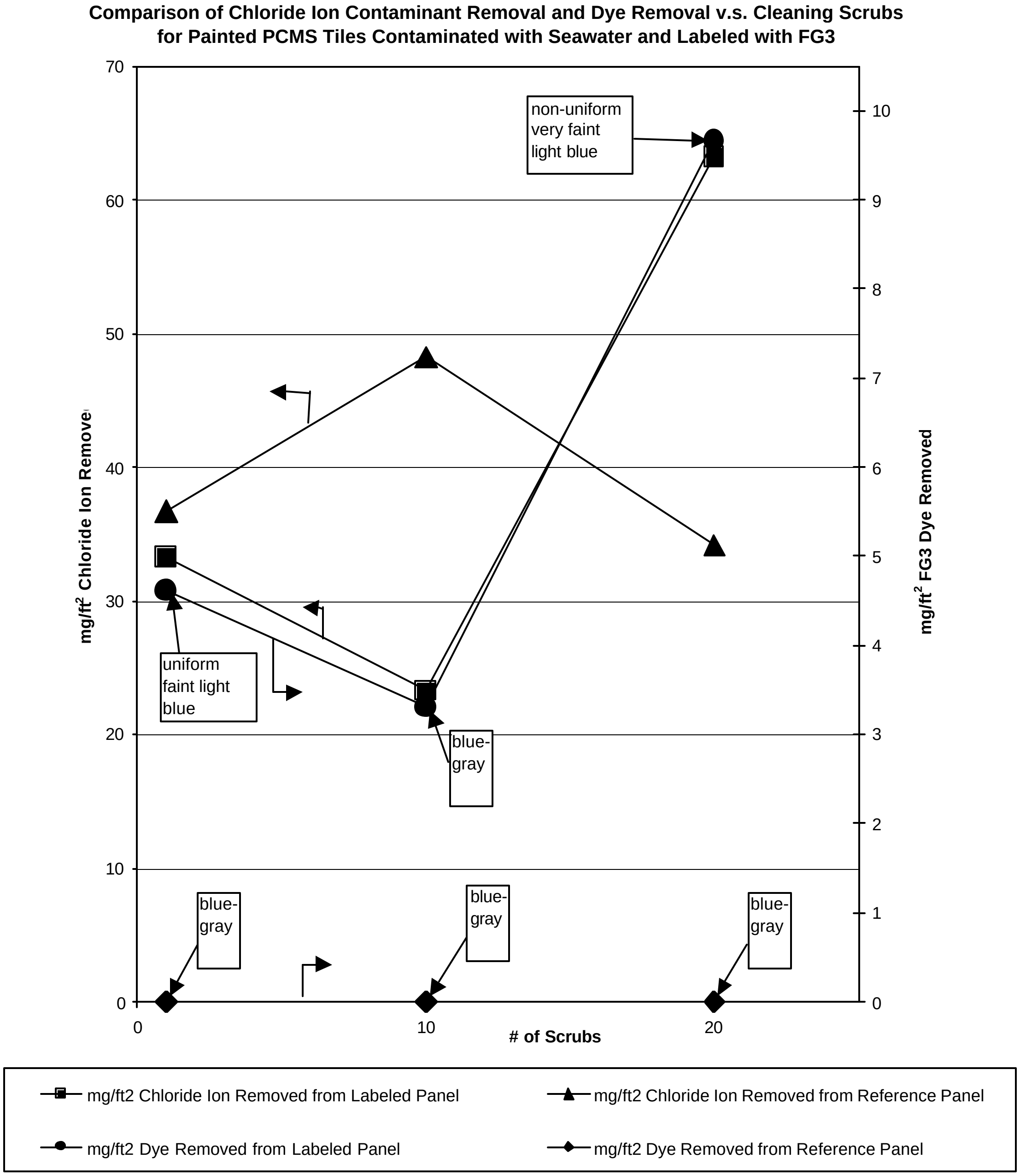
Figure E.3.11 Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 82)



Comparison of Chloride Ion Contaminant Removal and Total Color Difference, dE*, v.s. Cleaning Scrubs for Painted FeHY80 Steel Panels Contaminated with Seawater and Labeled with FG3

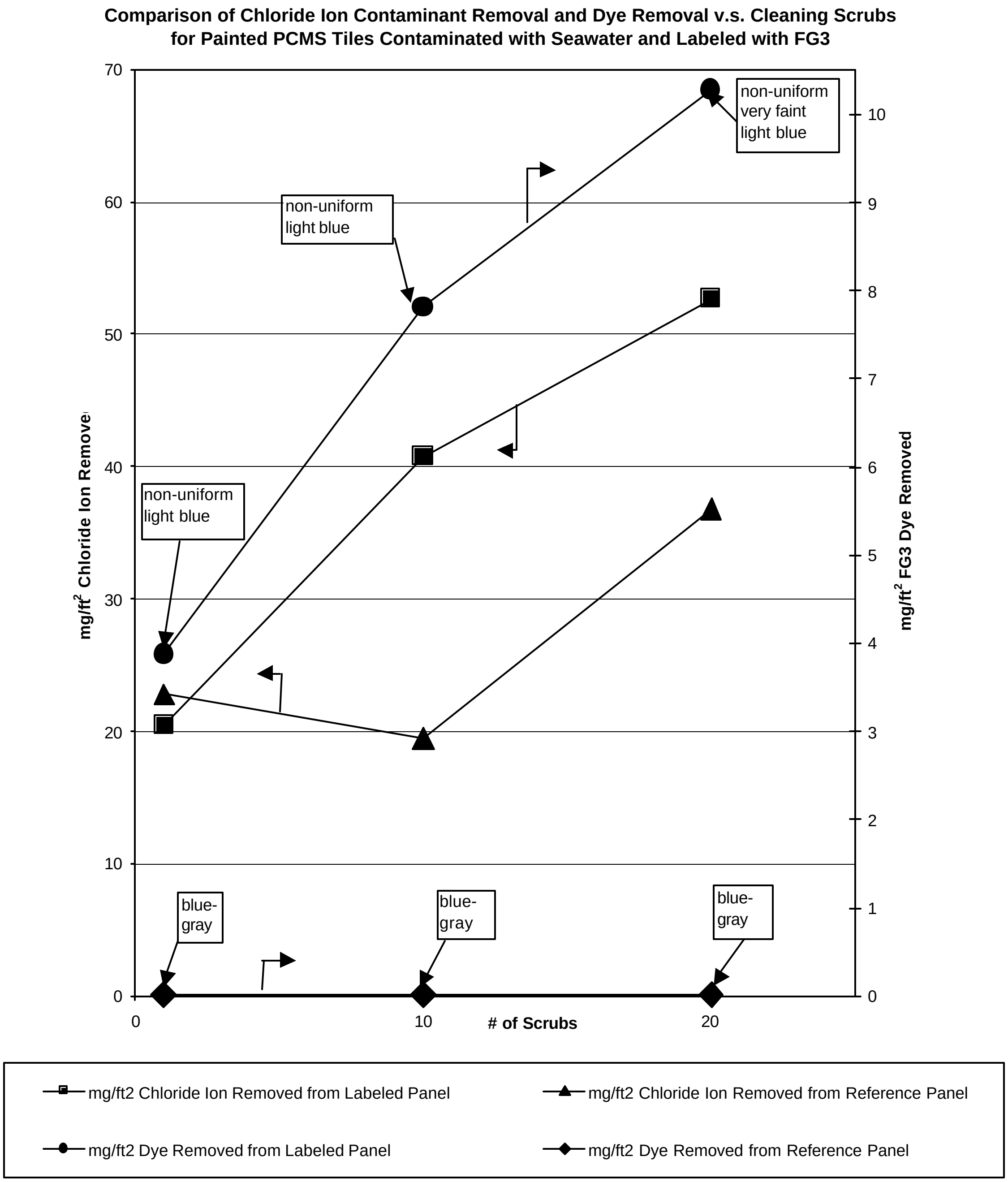
Analyses are of used cleaner baths and panel surfaces after panel cleaning. Error bars are one standard deviation. Error bars for circles and diamonds are smaller than the symbols. Original panels surfaces appear blue-gray without label. (FeHY80P-SW-FG3-5000 v. 20010423 block 83)

Figure E.3.12 Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on FeHY80 Painted Steel Panels (Block 83)



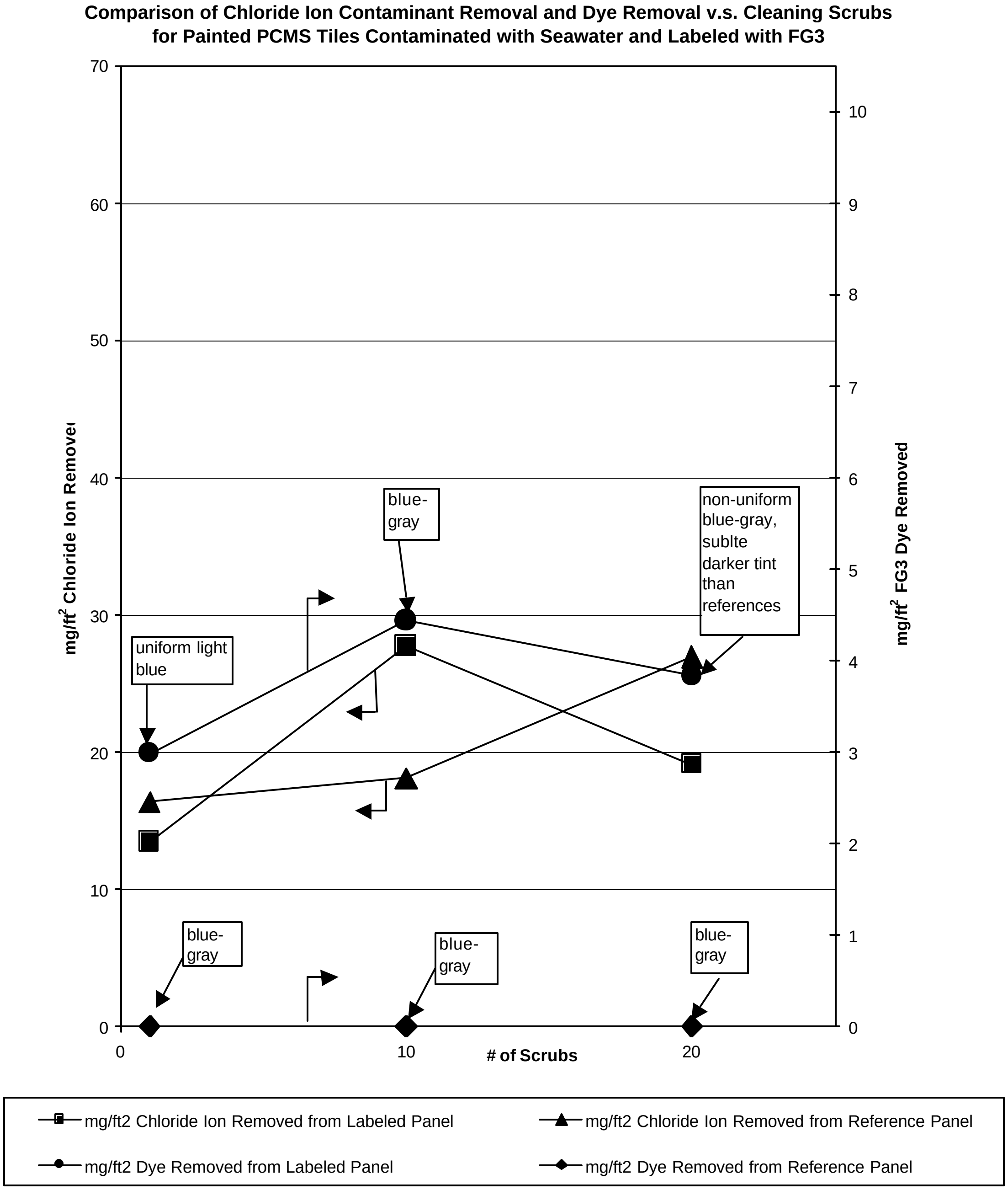
Analyses are of used cleaner baths from panel cleaning. Plot illustrates that VCPI dye removed from panels track chloride ion removed from panels during the cleaning operation. Plot also suggests possible better control achieved with the VCPI system, i.e. squares and circles track each other. (TP-SW-FG3-5000 v.20010417 block 69)

Figure E.3.13 Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on PCMS Painted Tiles (Block 69)



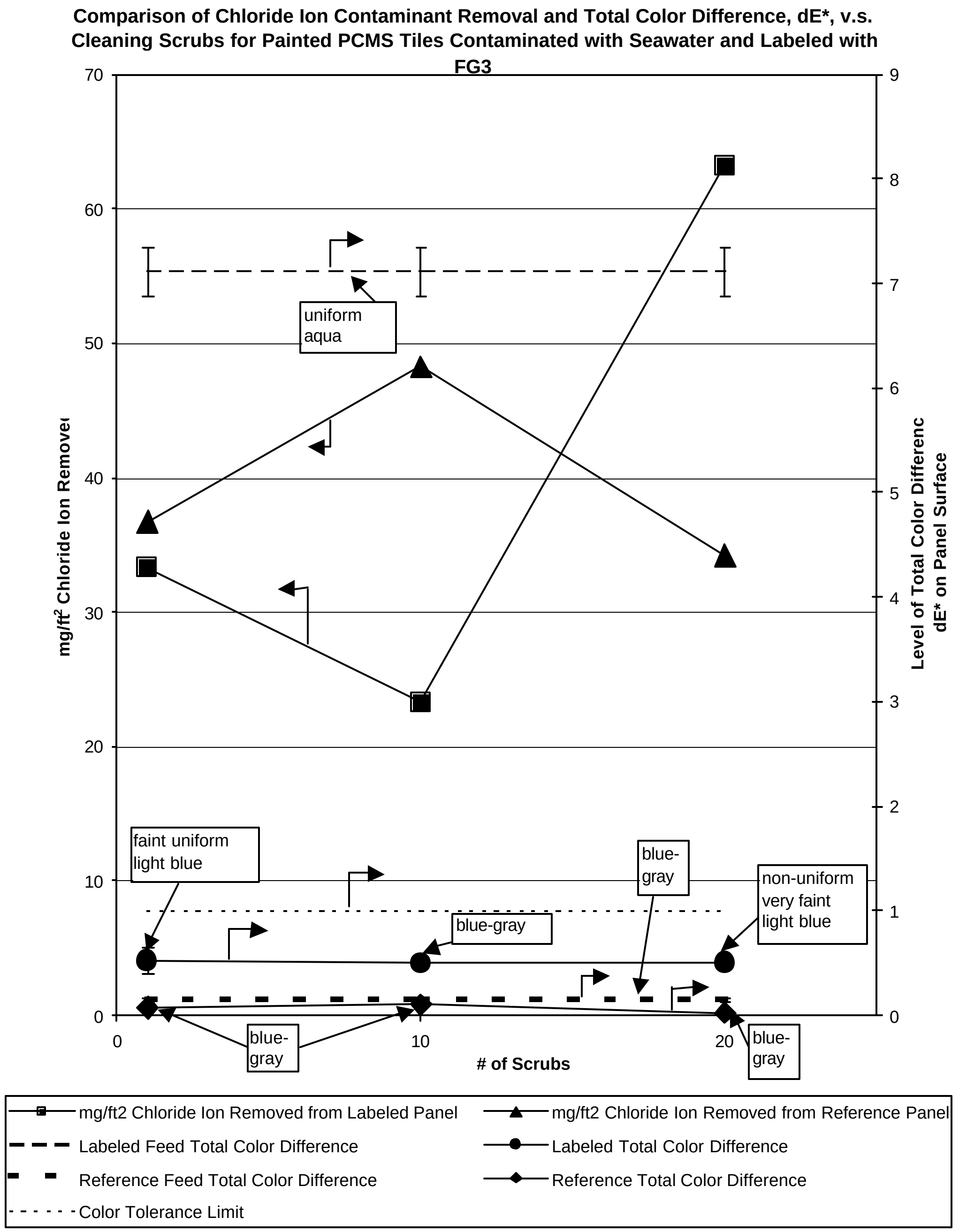
Analyses are of used cleaner baths from panel cleaning. Plot illustrates that VCPI dye removed from panels track chloride ion removed from panels during the cleaning operation. Plot also suggests possible better control achieved with the VCPI system, i.e. squares and circles track each other. (TP-SW-FG3-5000 v.20010417 block 78)

Figure E.3.14 Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on PCMS Painted Tiles (Block 78)



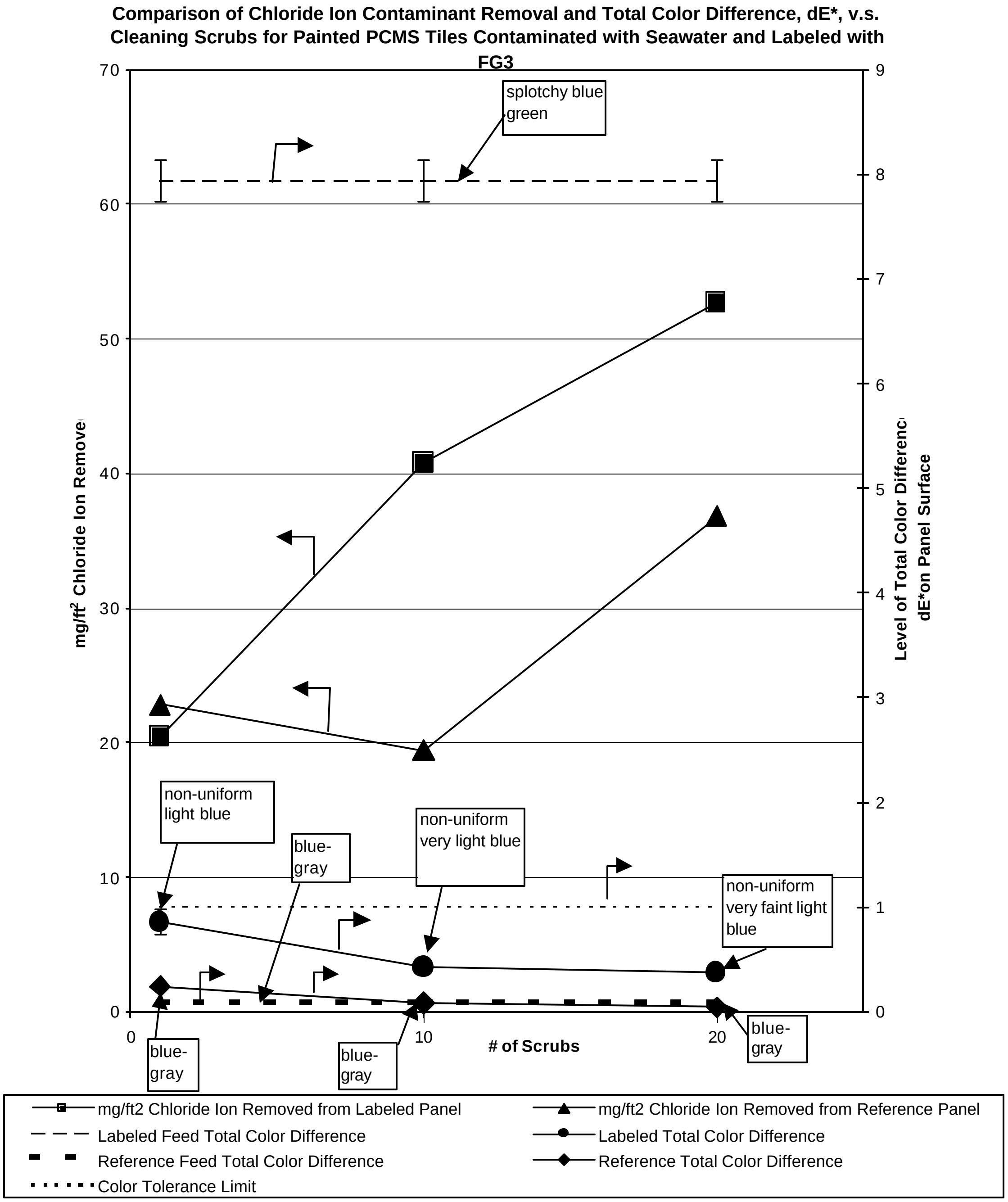
Analyses are of used cleaner baths from panel cleaning. Plot illustrates that VCPI dye removed from panels track chloride ion removed from panels during the cleaning operation. Plot also suggests possible better control achieved with the VCPI system, i.e. squares and circles track each other. (TP-SW-FG3-5000 v.010417 block 79)

Figure E.3.15 Chloride Ion Removal and Dye Removal for Soluble Salts Labeling on PCMS Painted Tiles (Block 79)



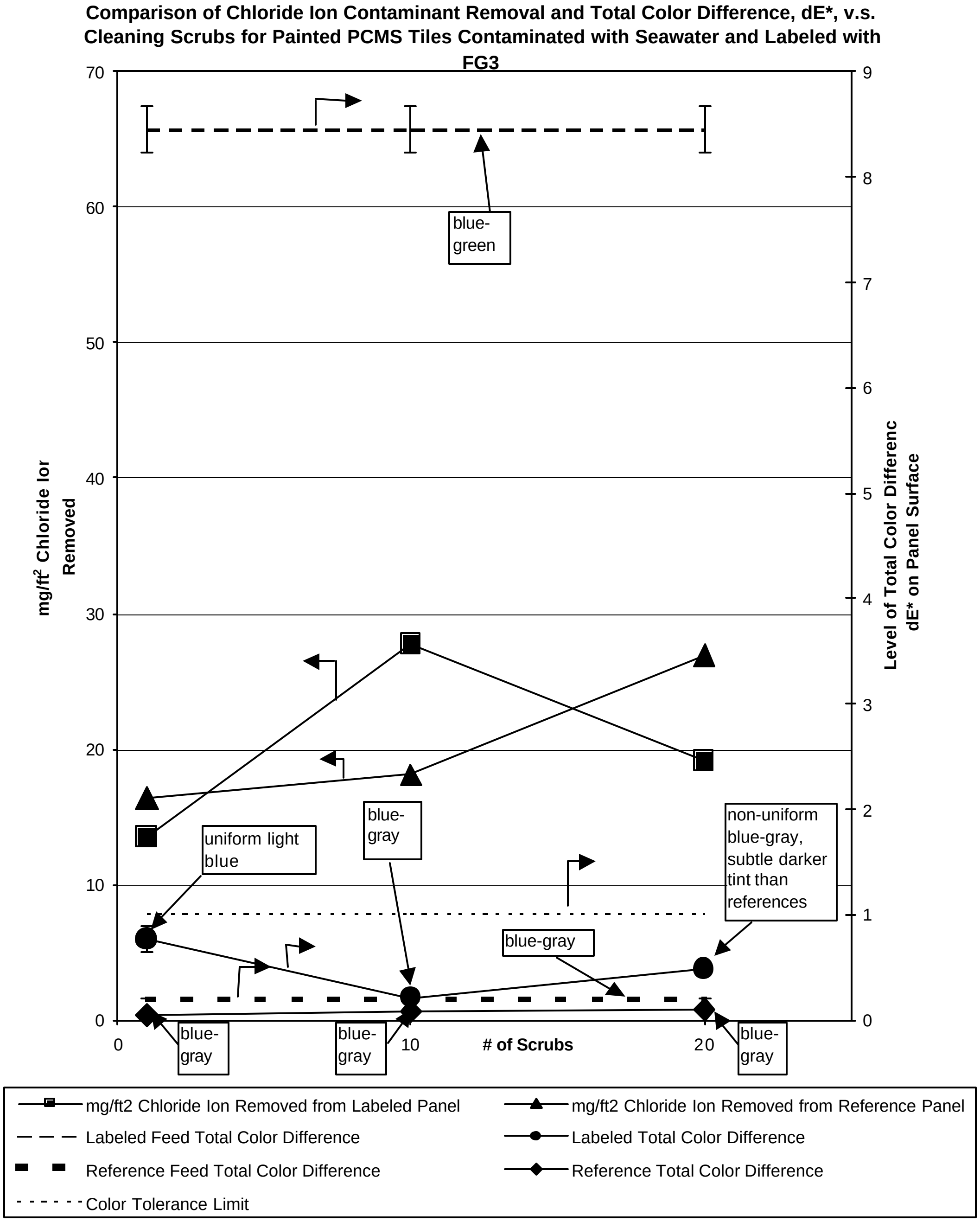
Analyses are of used cleaner baths from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and circles are smaller than the symbols. Original panel surfaces appear blue/gray without label. (TP-SW-FG3 v.010423 block 69)

Figure E.3.16 Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on PCMS Painted Tiles (Block 69)



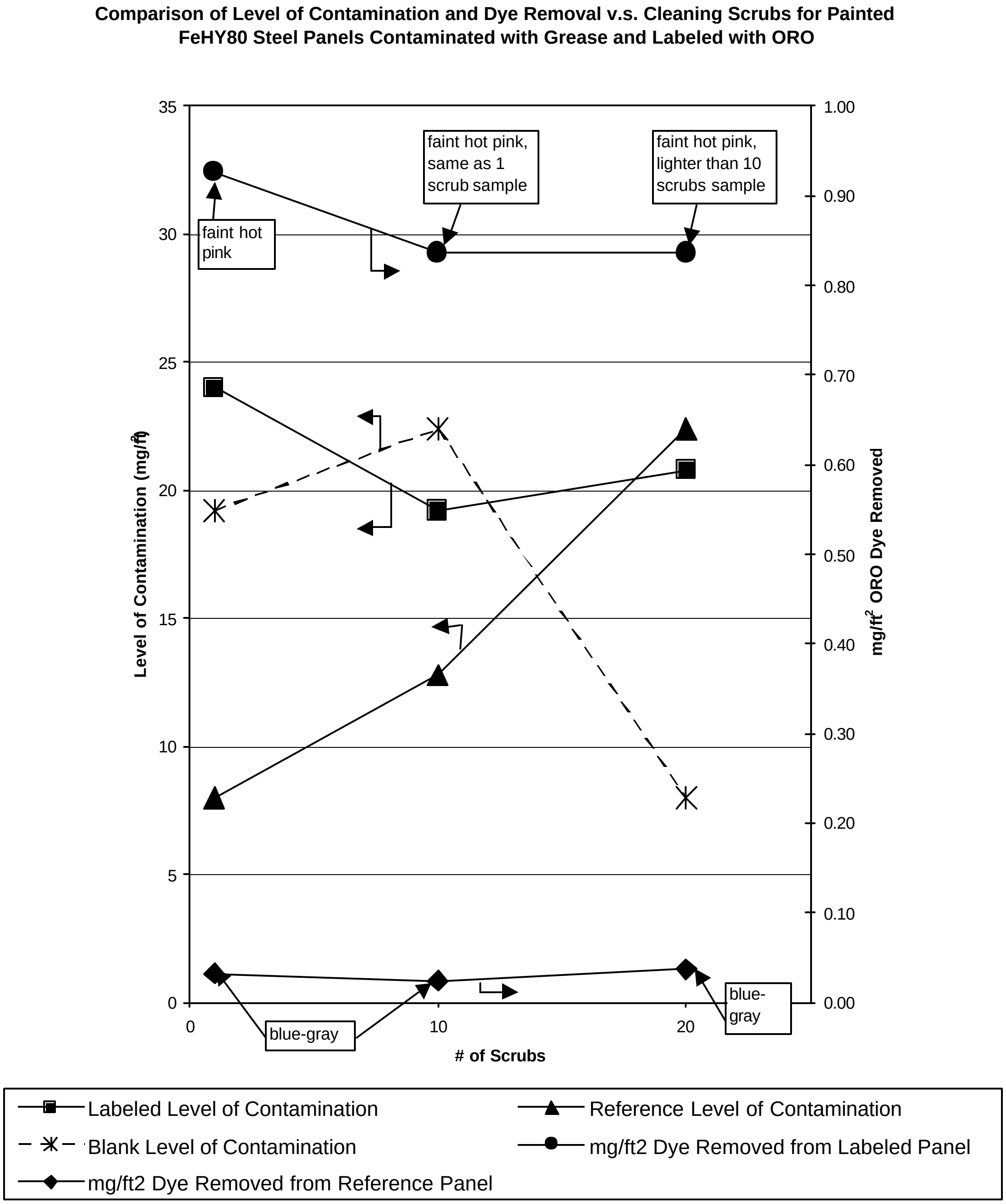
Analyses are of used cleaner baths from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and circles are smaller than the symbol. Original panel surfaces appear blue/gray without labels. Splotchy blue-green color on labeled feed panel possibly from fingerprints on panel surface. (TP-SW-FG3 v.010423 block 78)

Figure E.3.17 Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on PCMS Painted Tiles (Block 78)



Analyses are of used cleaner baths from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and circles are smaller than the symbols. Original panel surfaces appear blue/gray without label. (TP-SW-FG3 v.010423 block 79)

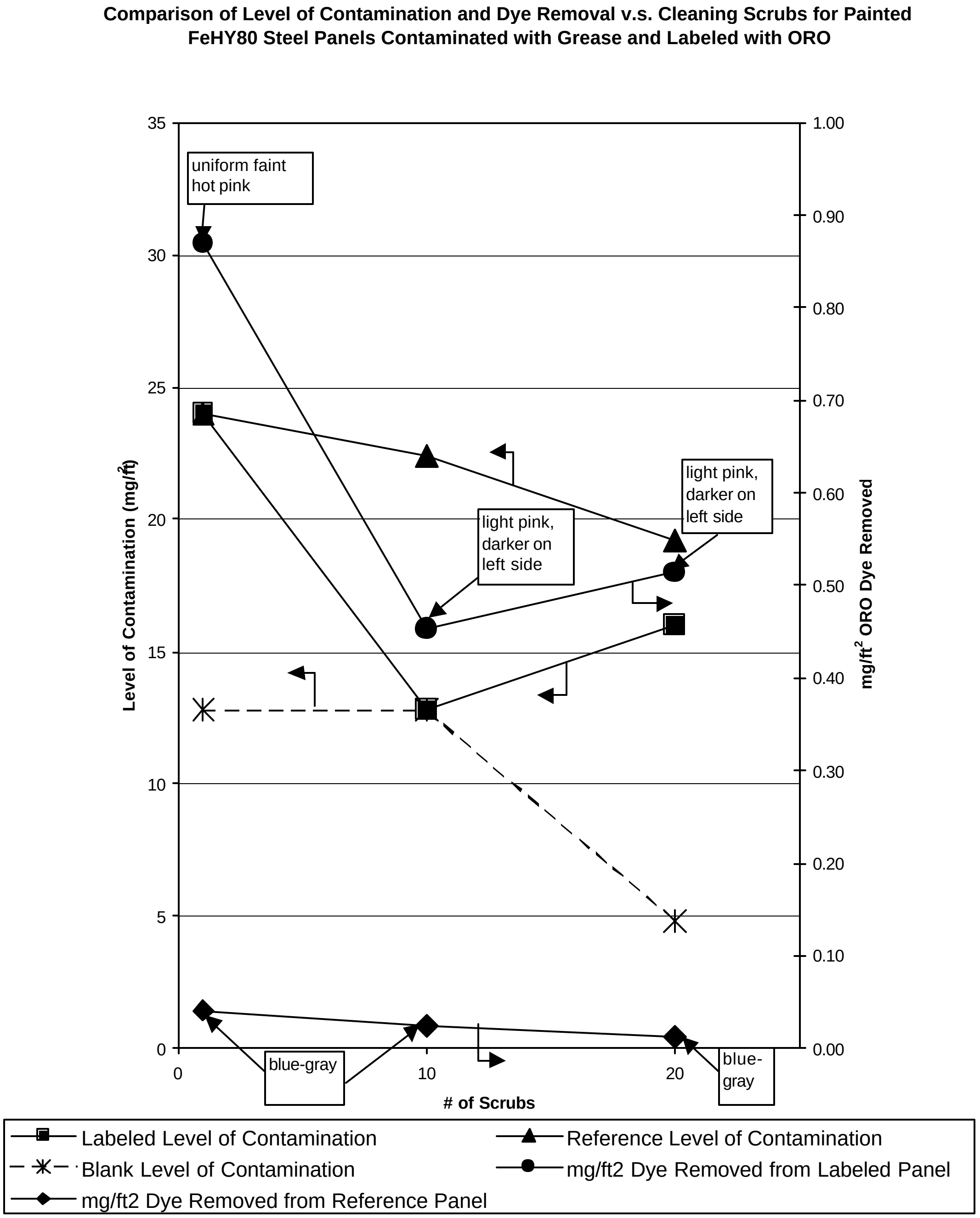
Figure E.3.18 Chloride Ion Removal and Total Color Difference for Soluble Salts Labeling on PCMS Painted Tiles (Block 79)



Comparison of Level of Contamination and Dye Removal v.s. Cleaning Scrubs for Painted FeHY80 Steel Panels Contaminated with Grease and Labeled with ORO

Analyses are of cleaner baths and panel surfaces from panel cleaning. Original panel surfaces appear blue/gray without label. (FeHY80P-G-ORO-20:0.5 v. 20010420 block 75)

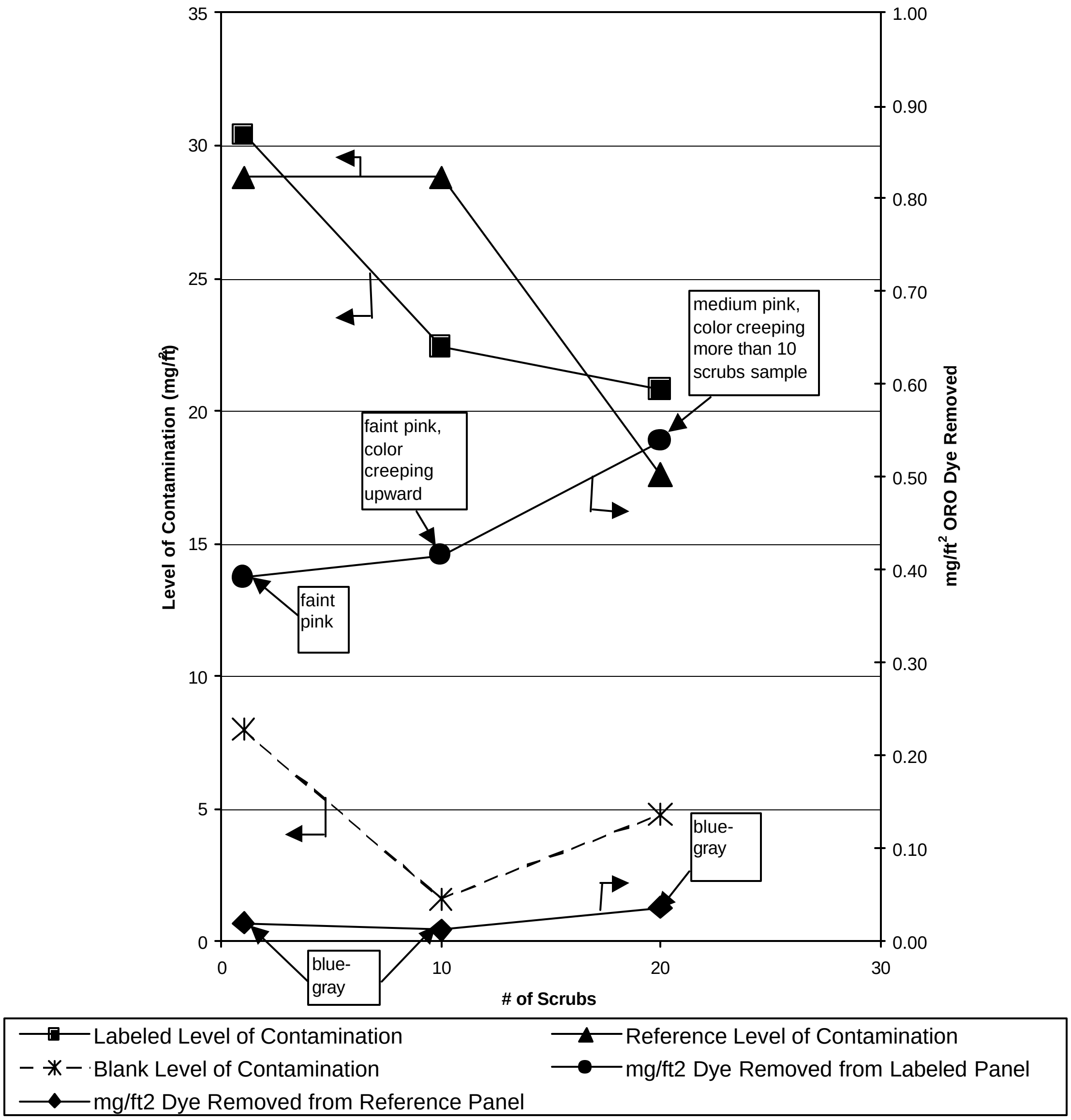
Figure E.3.19 Level of Contamination and Dye Removal for Hydrophobic Contaminant Labeling on FeHY80 Painted Steel Panels (Block 75)



Comparison of Level of Contamination and Dye Removal v.s. Cleaning Scrubs for Painted FeHY80 Steel Panels Contaminated with Grease and Labeled with ORO

Analyses are of cleaner baths and panel surfaces from panel cleaning. Original panel surfaces appear blue/gray without label. (FeHY80P-G-ORO-20:0.5 v. 20010420 block 80)

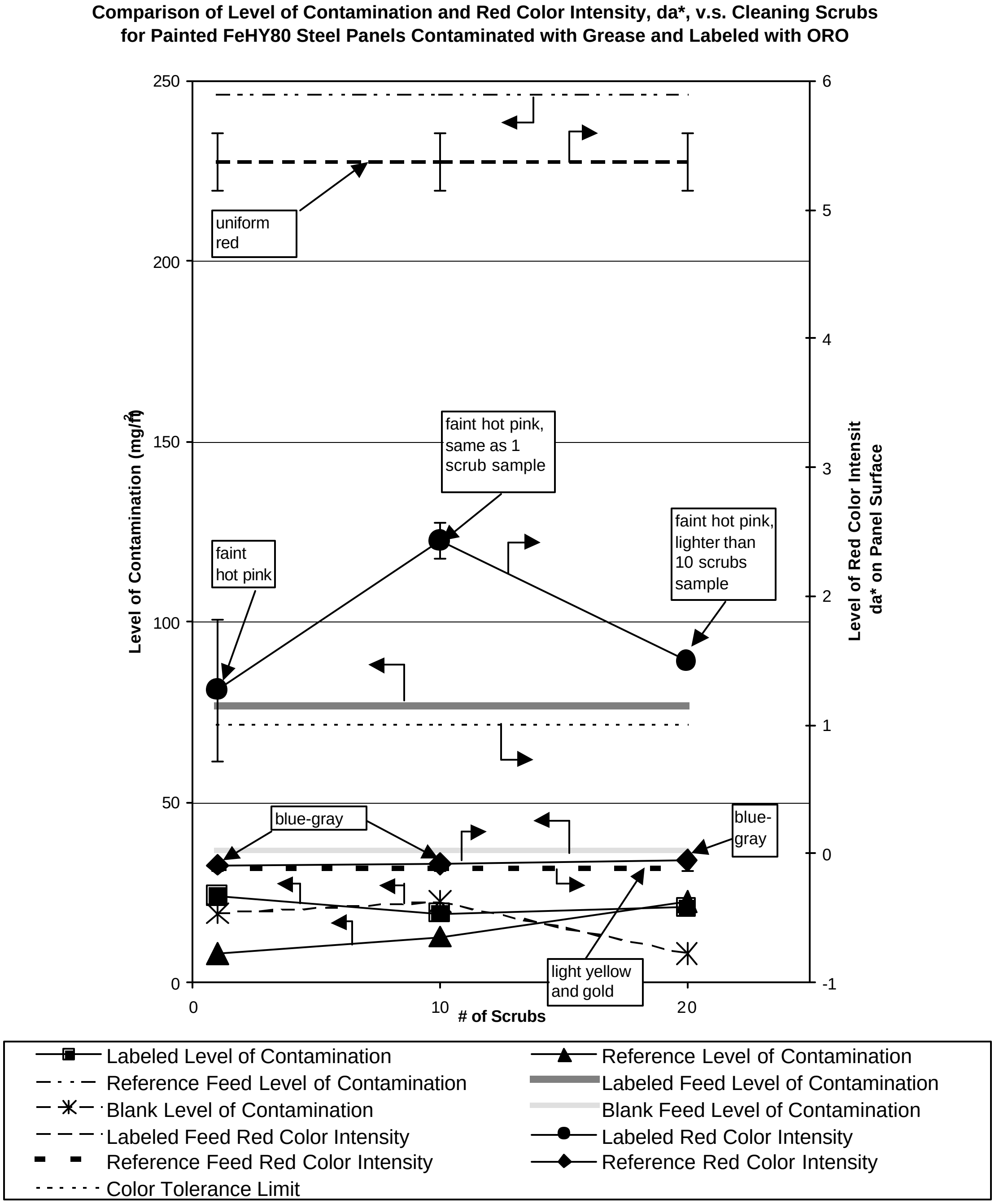
Figure E.3.20 Level of Contamination and Dye Removal for Hydrophobic Contaminant Labeling on FeHY80 Painted Steel Panels (Block 80)



Comparison of Level of Contamination and Dye Removal v.s. Cleaning Scrubs for Painted FeHY80 Steel Panels Contaminated with Grease and Labeled with ORO

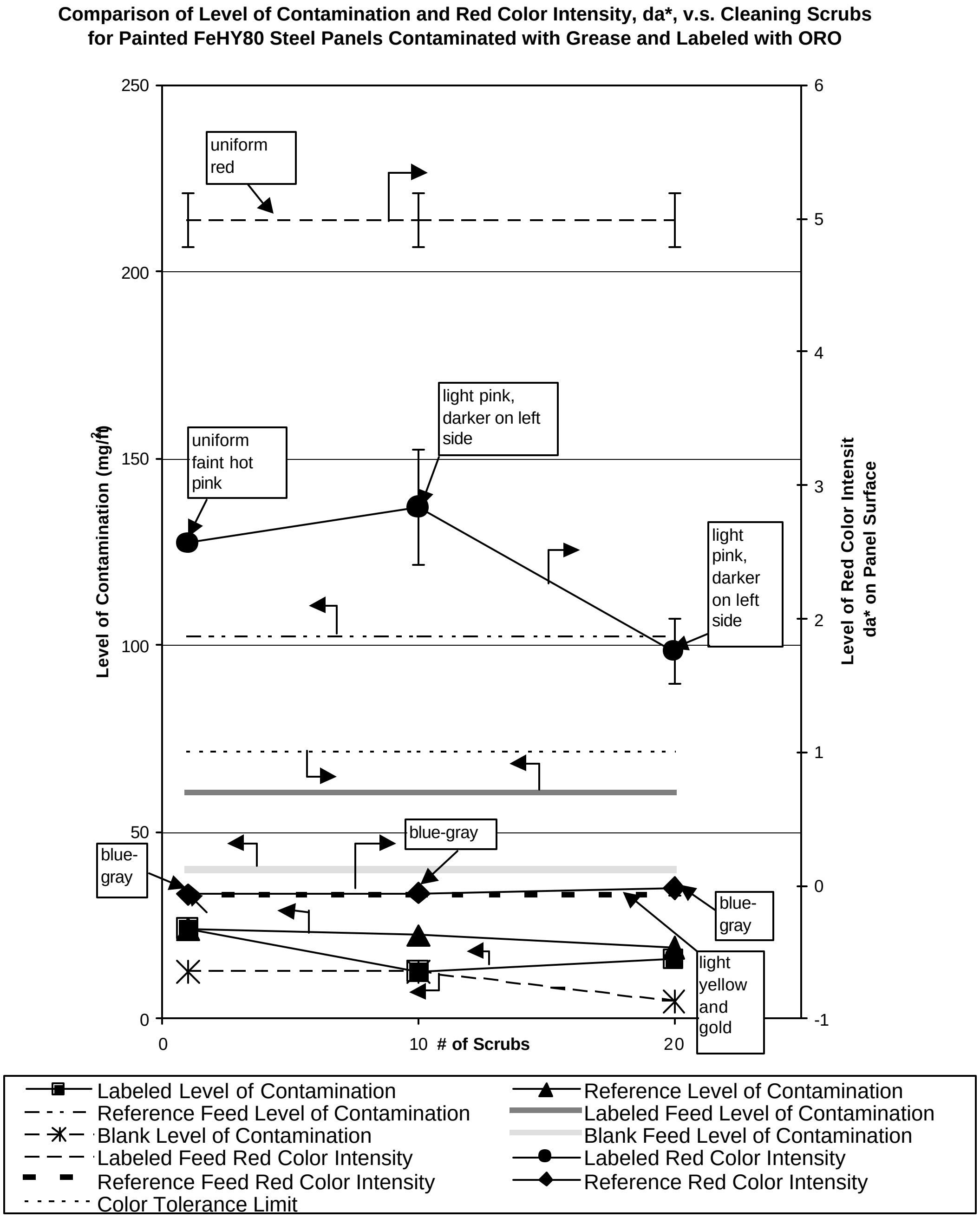
Analyses are of cleaner baths and panel surfaces from panel cleaning. Original panel surfaces appear blue/gray without label. (FeHY80P-G-ORO-20:0.5 v. 20010420 block 81)

Figure E.3.21 Level of Contamination and Dye Removal for Hydrophobic Contaminant Labeling on FeHY80 Painted Steel Panels (Block 81)



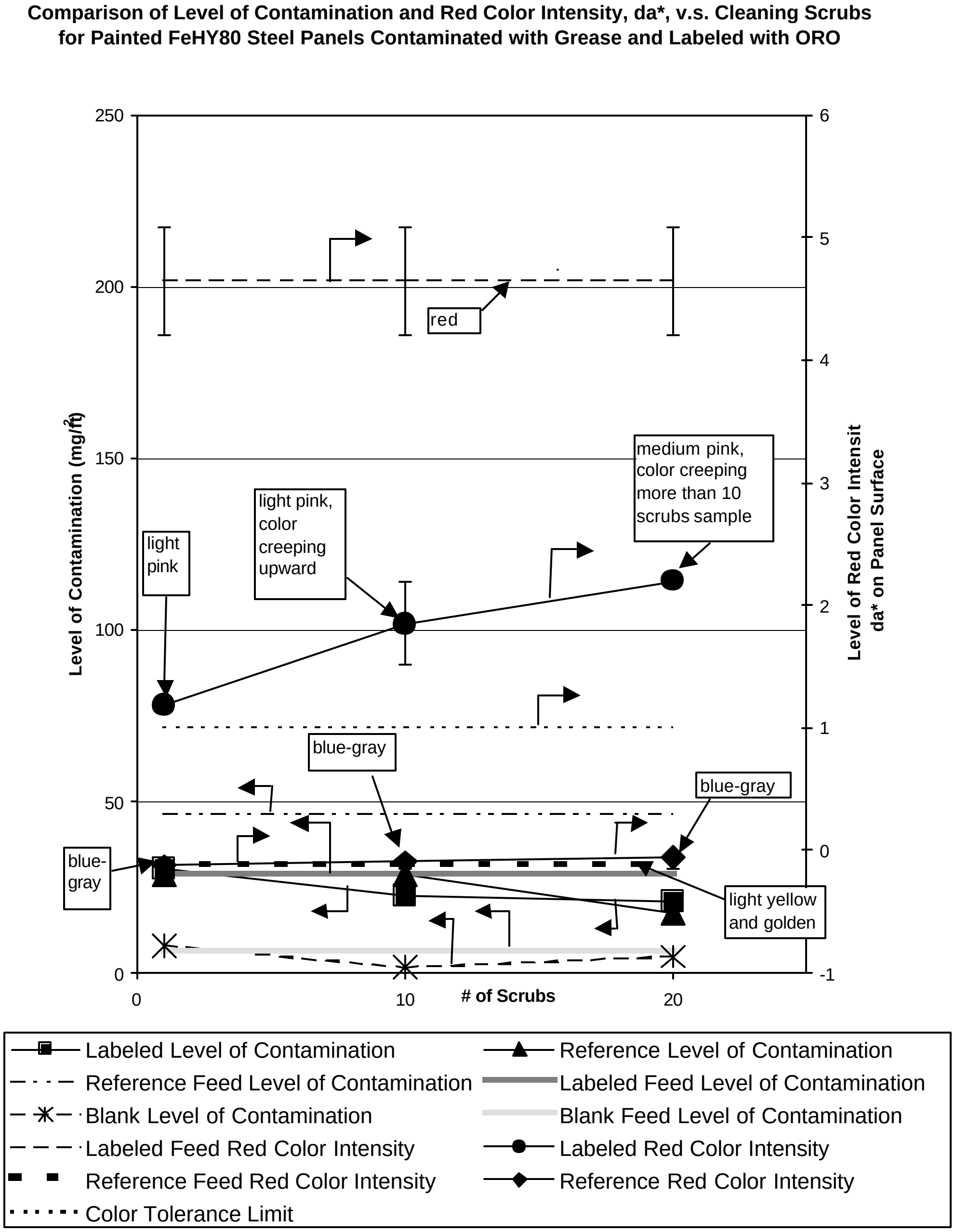
Analyses are of used cleaner baths and panel surfaces from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and circles are smaller than the symbols. Original panel surfaces appear blue/gray without label. Overlap exists between reference and feed red color intensity. (FeHY80P-G-ORO-20:0.5 v. 20010420 block 75)

Figure E.3.22 Level of Contamination and Level of Red Color Intensity for Hydrophobic Labeling on FeHY80 Painted Steel Panels (Block 75)



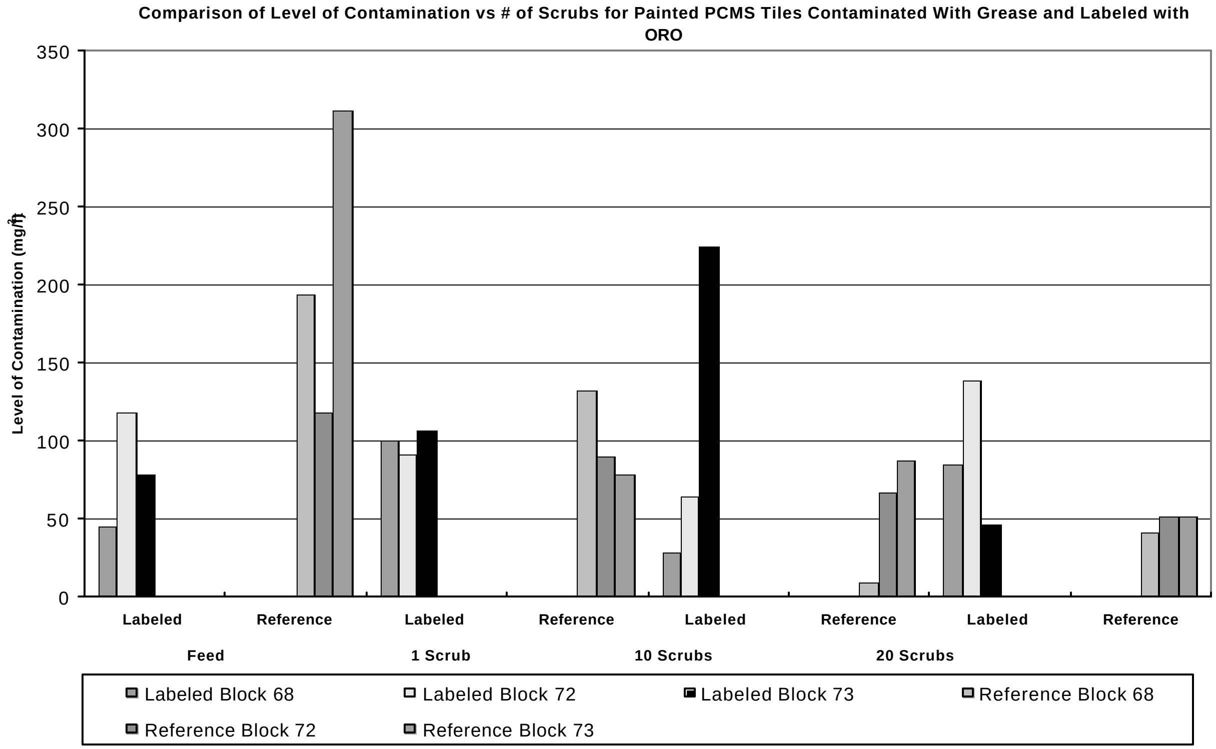
Analyses are of used cleaner baths and panel surfaces from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and circles are smaller than the symbols. Original panel surfaces appear blue/gray without label. Overlap exists between reference and feed red color intensity. (FeHY80P-G-ORO-20:0.5 v. 20010420 block 80)

Figure E.3.23 Level of Contamination and Level of Red Color Intensity for Hydrophobic Labeling on FeHY80 Painted Steel Panels (Block 80)



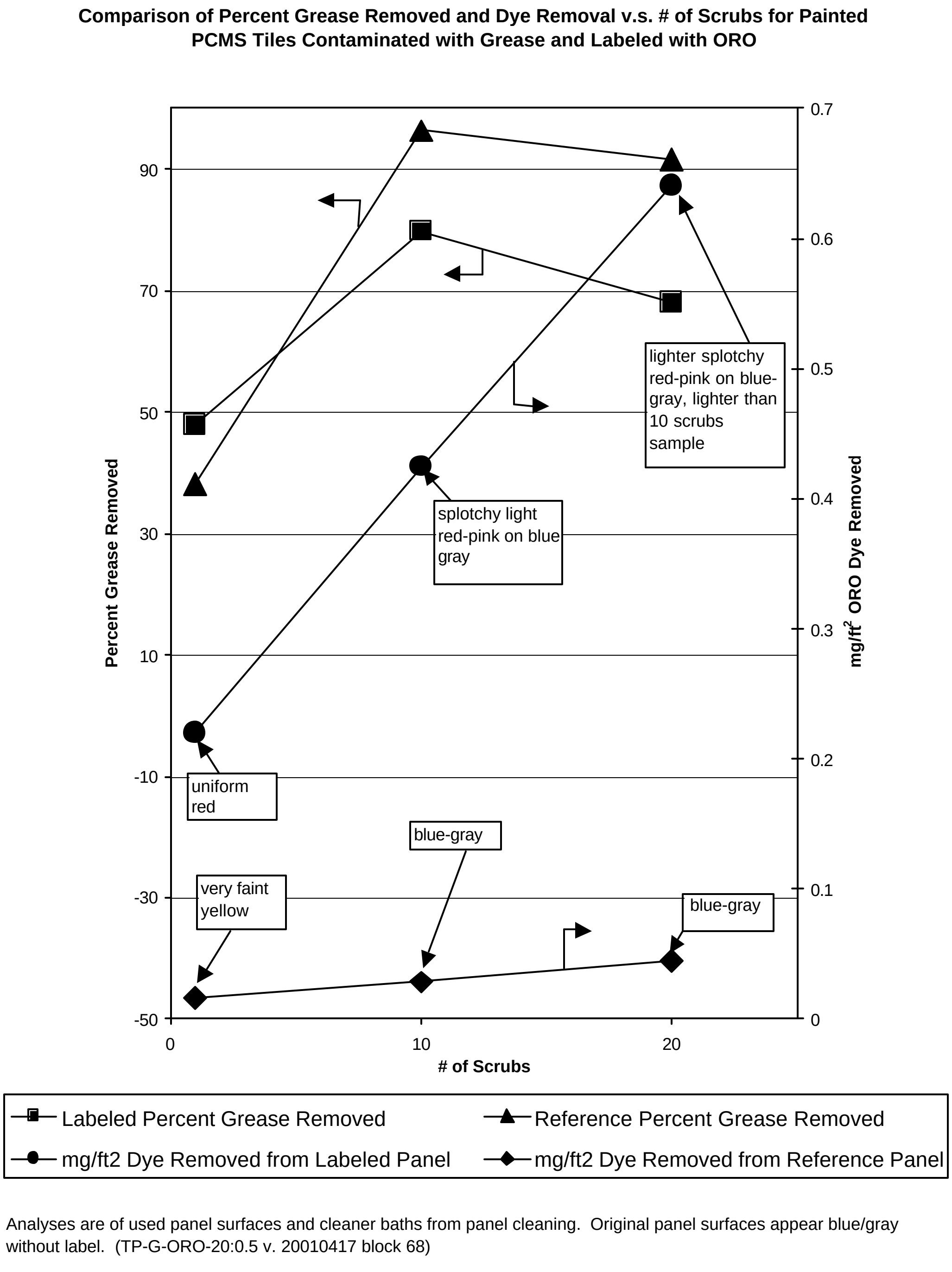
Analyses are of used cleaner baths and panel surfaces from panel cleaning. Error bars are one standard deviation. Error bars for diamonds and circles are smaller than the symbols. Original panel surfaces appear blue/gray without label. Overlap exists between reference and feed red color intensity. (FeHY80P-G-ORO-20:0.5 v. 20010420 block 81)

Figure E.3.24 Level of Contamination and Level of Red Color Intensity for Hydrophobic Labeling on FeHY80 Painted Steel Panels (Block 81)



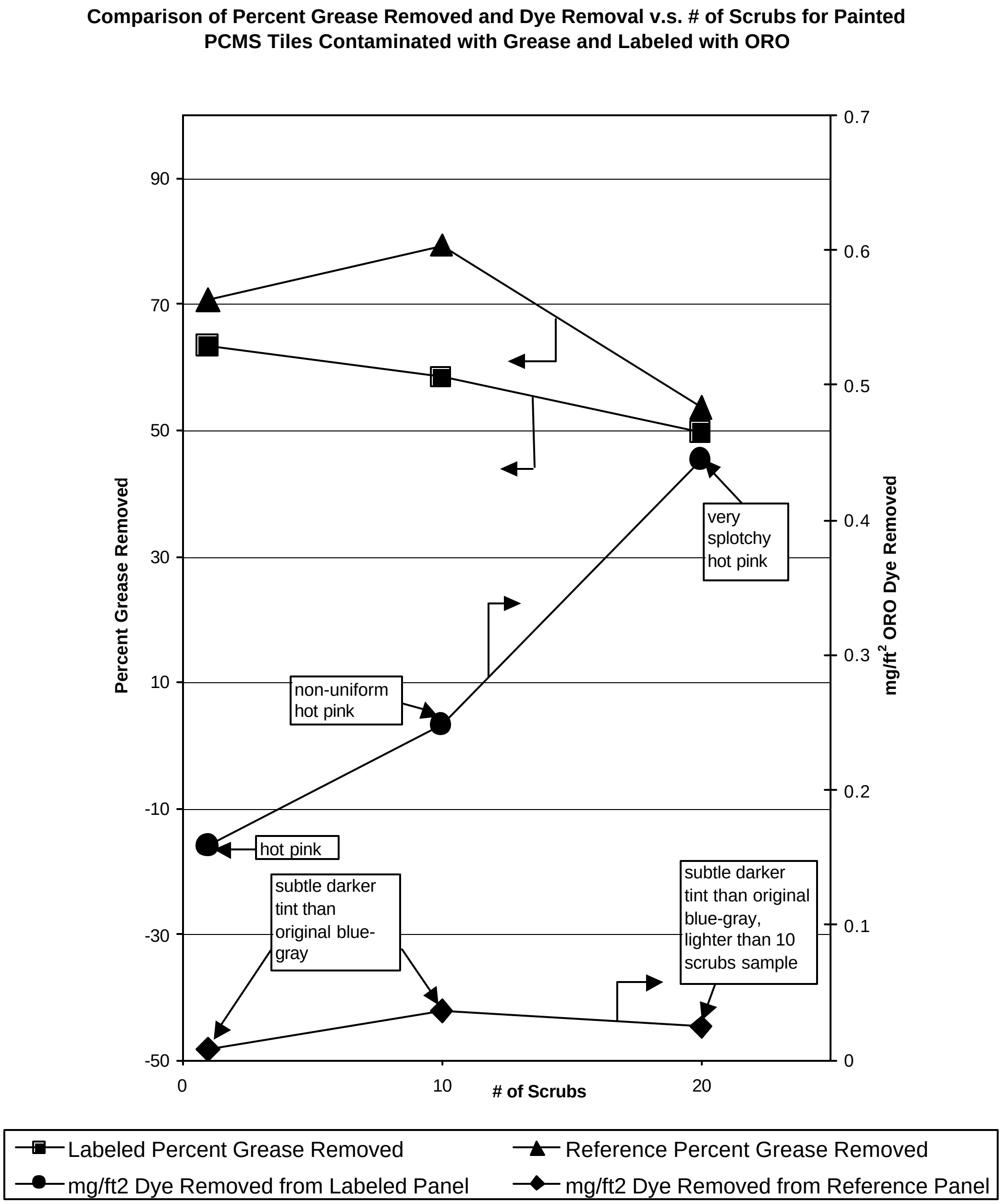
Analyses are of panel surfaces. Plot shows the varied amount of grease contamination through comparing each block.
(TP-G-ORO-20:0.5 v.20010420 block 68,72,73)

Figure E.3.25 Level of Contamination for Hydrophobic Labeling on Painted PCMS Tiles (Blocks 68,72,73)



Analyses are of used panel surfaces and cleaner baths from panel cleaning. Original panel surfaces appear blue/gray without label. (TP-G-ORO-20:0.5 v. 20010417 block 68)

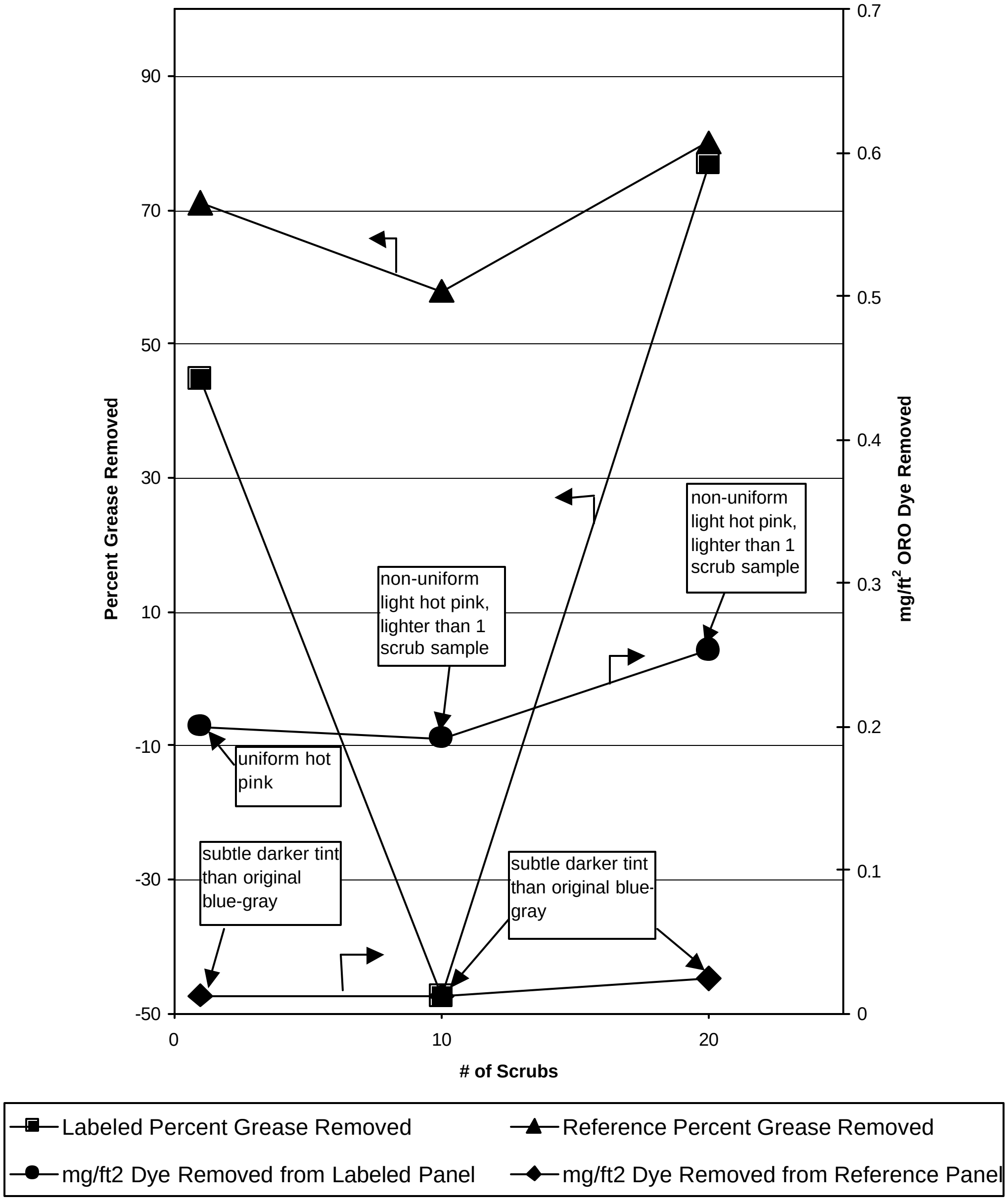
Figure E.3.26 Percent Grease Removal and Dye Removal for Hydrophobic Labeling on Painted PCMS Tiles (Block 68)



Analyses are of used panel surfaces and cleaner baths from panel cleaning. Original panel surfaces appear blue/gray without label. (TP-G-ORO-20:0.2 v. 20010423 block 72)

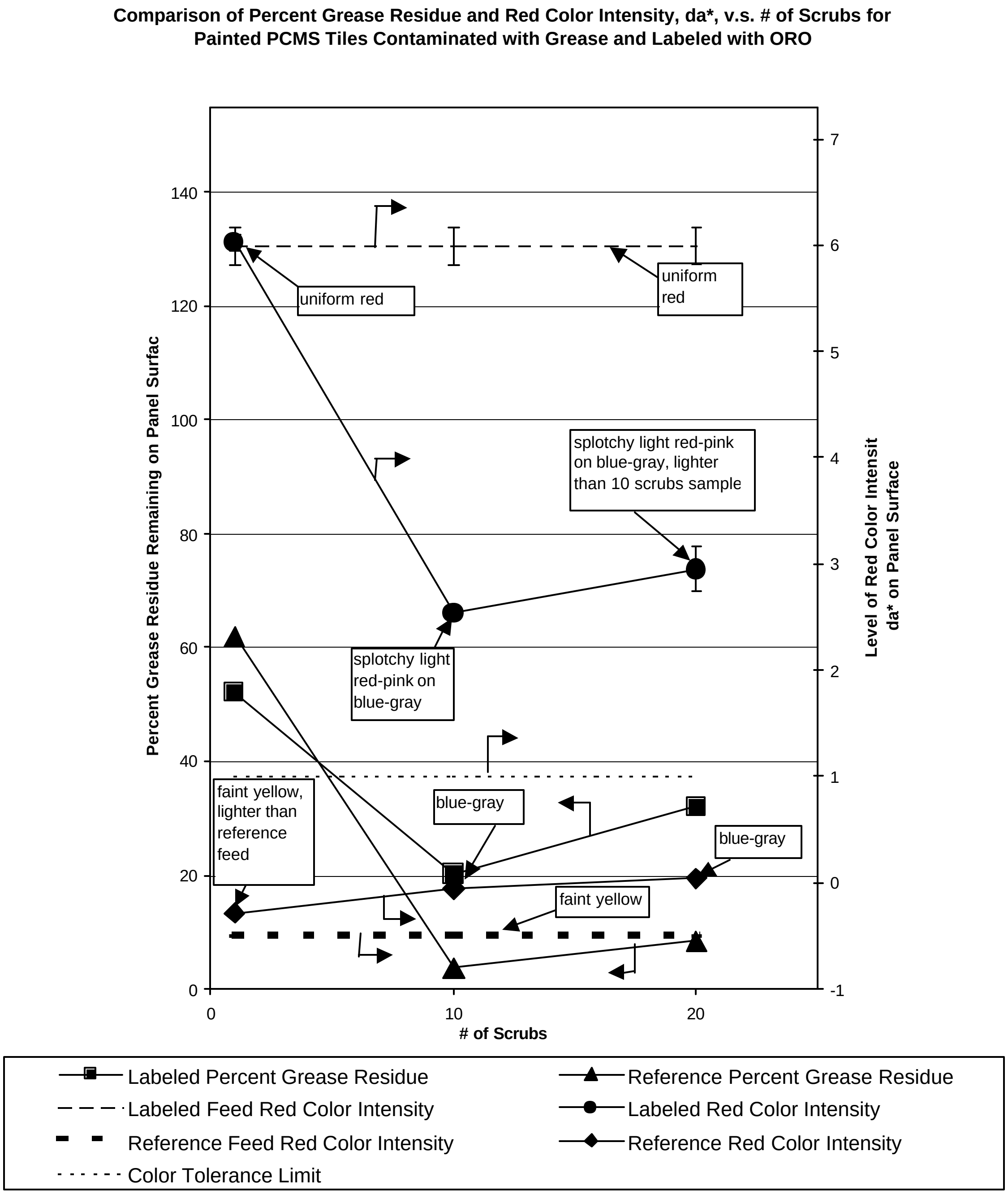
Figure E.3.27 Percent Grease Removal and Dye Removal for Hydrophobic Labeling on Painted PCMS Tiles (Block 72)

Comparison of Percent Grease Removed and Dye Removal v.s. # of Scrubs for Painted PCMS Tiles Contaminated with Grease and Labeled with ORO



Analyses are of used panel surfaces and cleaner baths from panel cleaning. Original panel surfaces appear blue/gray without label. (TP-G-ORO-20:0.5 v. 20010423 block 73)

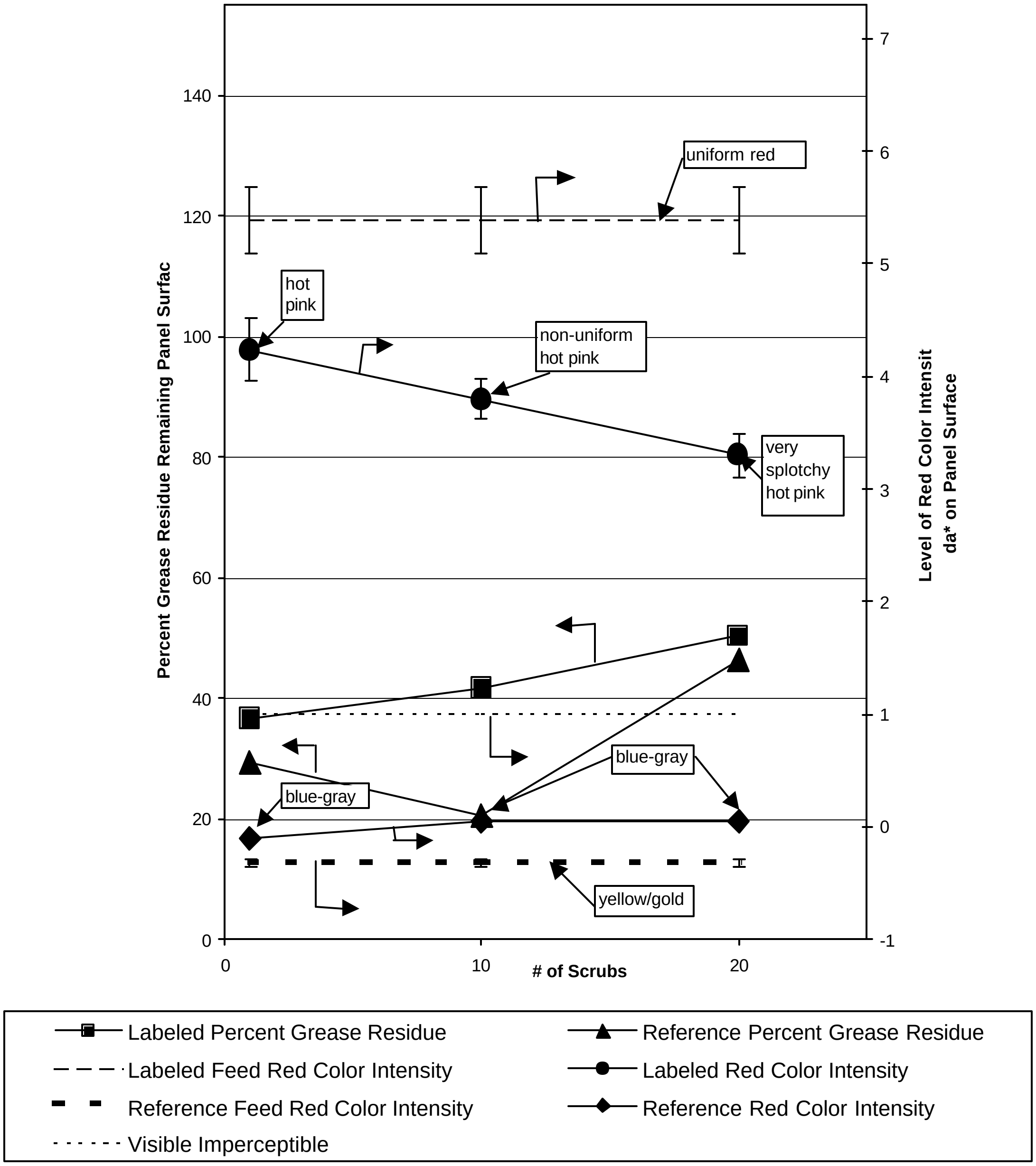
Figure E.3.28 Percent Grease Removal and Dye Removal for Hydrophobic Labeling on Painted PCMS Tiles (Block 73)



Comparison of Percent Grease Residue and Red Color Intensity, da*, v.s. # of Scrubs for Painted PCMS Tiles Contaminated with Grease and Labeled with ORO

Analyses are of panel surfaces. Error bars are one standard deviation. Error bars for circles and diamonds are smaller than symbols.
Original panel surfaces appear blue/gray without label.
(TP-G-ORO-20:0.5 v. 20010417 block 68)

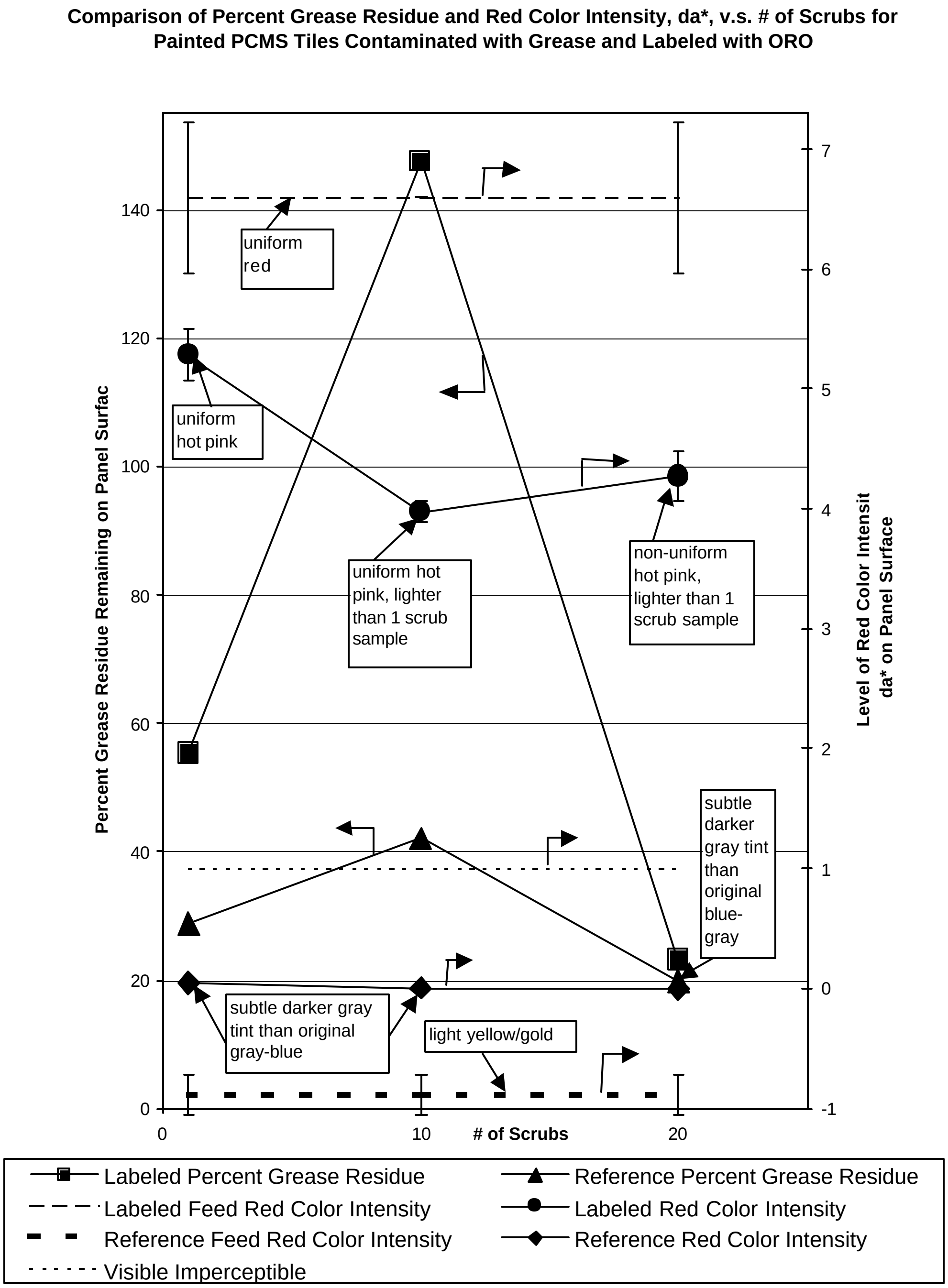
Figure E.3.29 Percent Grease Residue and Level of Red Color Intensity for Hydrophobic Labeling on Painted PCMS Tiles (Block 68)



Comparison of Percent Grease Residue and Red Color Intensity, da*, v.s. # of Scrubs for Painted PCMS Tiles Contaminated with Grease and Labeled with ORO

Analyses are of panel surfaces. Error bars are one standard deviation. Error bars for diamonds are smaller than they appear. Original panel surfaces appear blue/gray without label. (TP-G-ORO-20:0.2 v. 20010417 block 72)

Figure E.3.30 Percent Grease Residue and Level of Red Color Intensity for Hydrophobic Labeling on Painted PCMS Tiles (Block 72)



Analyses are of panel surfaces. Error bars are one standard deviation. Error bars for diamonds are smaller than the symbols. Original panel surfaces appear blue/gray without label. (TP-G-ORO-20:0.5 v. 20010412 block 73)

Figure E.3.31 Percent Grease Residue and Level of Red Color Intensity for Hydrophobic Labeling on Painted PCMS Tiles (Block 73)

E. 3.2.4 Co-Addition of Contaminant and Label: System TS-PA7-ORO-20:0.5

For this test system, tiles stripped with Peel Away 7® (PA7) paint stripper were used. Levels of contamination were determined using NVR.

Systematic cleaning was not implemented in the analysis of dye/resin residuals from PA7 because It was observed that PA7 penetration properties tend to draw the ORO dye deep into the porous rubber surface of the PCMS tile. Once absorbed into the rubber, it remains quite difficult to remove any of the residual PA7 and the dye it contains. Continued cleaning offers no surface reduction of dye intensity. After application of PA7, dye absorbed panel surfaces were analyzed using UV/Vis and NVR. UV/Vis was performed by collecting the removable surface dye/resin residue left behind by the PA7 application. A 2x2 inch cotton square soaked with isopropanol was used to wipe the tile. Once all removable dye is deposited on the cotton square and removed from the tile, the cotton square is soaked in 30 ml of isopropanol, thus allowing the dye to be lifted from the cotton fibers and be drawn into the 30 ml portion of isopropanol. Once the dye/resin is removed from the cotton square and dissolved in the 30 ml isopropanol, the solution is transferred to a 40 ml amber glass bottle.

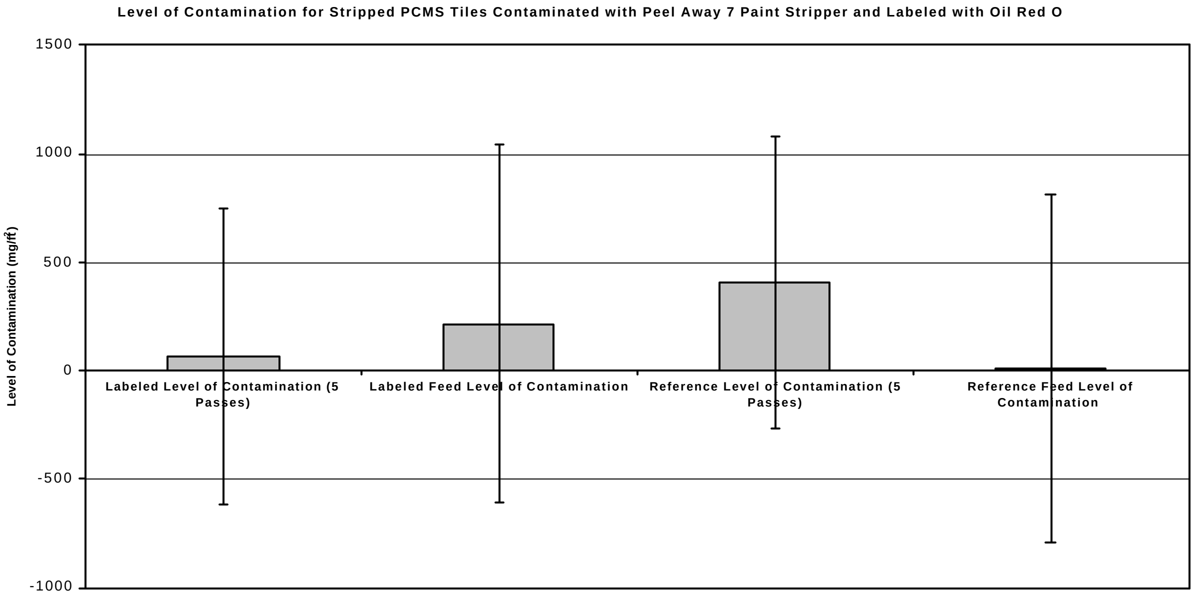
NVR analysis of the residual dye/resin left behind from the application of PA7 was conducted using a glass beaker and petroleum ether. The glass beaker is weighed and it's mass recorded. The beaker is then filled with petroleum ether and the PCMS tile placed vertically in the solvent. With the solvent covering exactly half of the tile,(3x3 inch area), the dye/resin which is absorbed into the rubber is draw out by the petroleum ether and dissolved into the bulk of the solvent. After five minutes of soaking, the residuals appear to be removed from the rubber. The tile is then removed from the petroleum ether and allowed to dry. The beaker containing the petroleum ether and dye/resin is given time for the evaporation of the petroleum ether. Once all of the petroleum ether is gone, the beaker is weighed again and its mass recorded. The mass difference in regard to the prior beaker measurement reveals the mass of residuals extracted from the rubber.

Figure E.3.32 represents that the NVR technique removed zero level of contamination within experimental error with an average of 175 (+/- 745) mg/ft^2.

Figure E.3.33 illustrates the difference of dye removal between labeled and reference panels are 0.05 mg/ft^2 with a red black cherry panel after cleaning. This result shows that the majority of the dye still remains within the rubber surface.

Figure E.3.34 compares the da* and dE* values for various samples. The da* and dE* values are similar which shows that the da* parameter contributes the most for this test system.

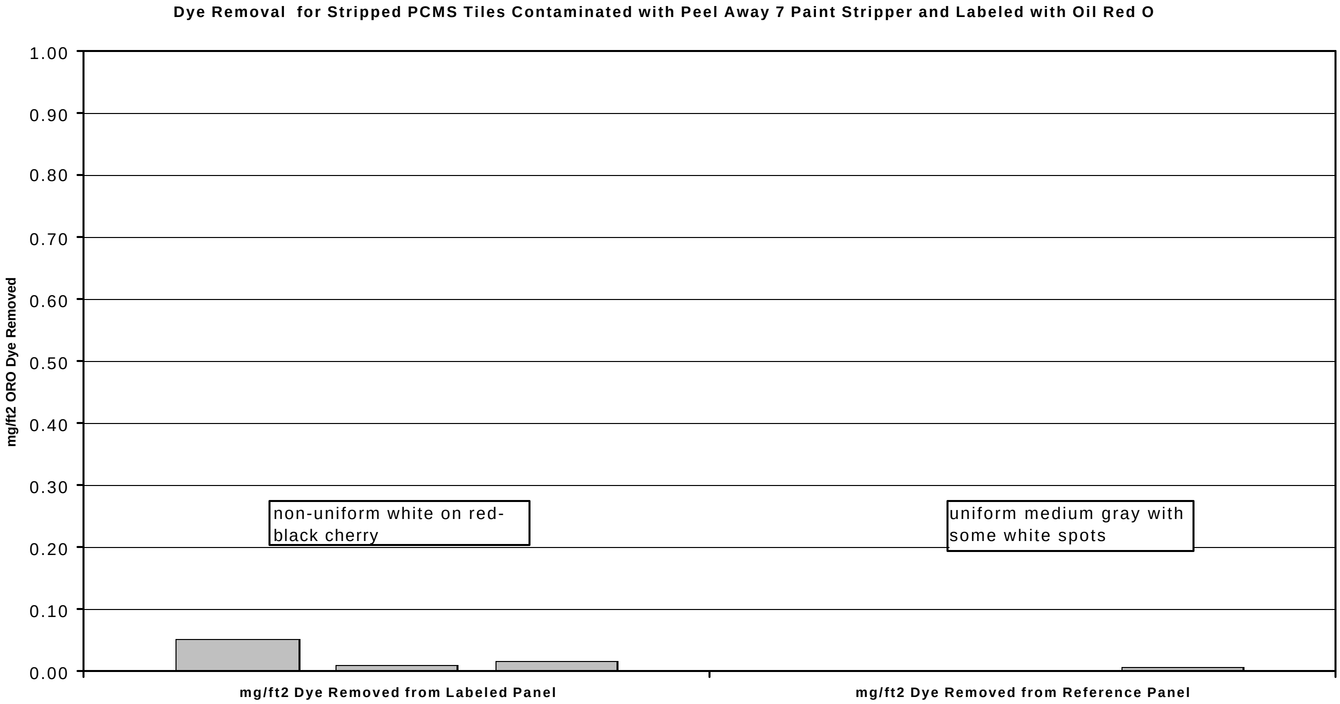
All 3 plots confirm that the dye is tracking **WITH** contaminant leaving a visually red/black cherry color and Peel Away® 7 after cleaning.



Level of Contamination for Stripped PCMS Tiles Contaminated with Peel Away 7 Paint Stripper and Labeled with Oil Red O

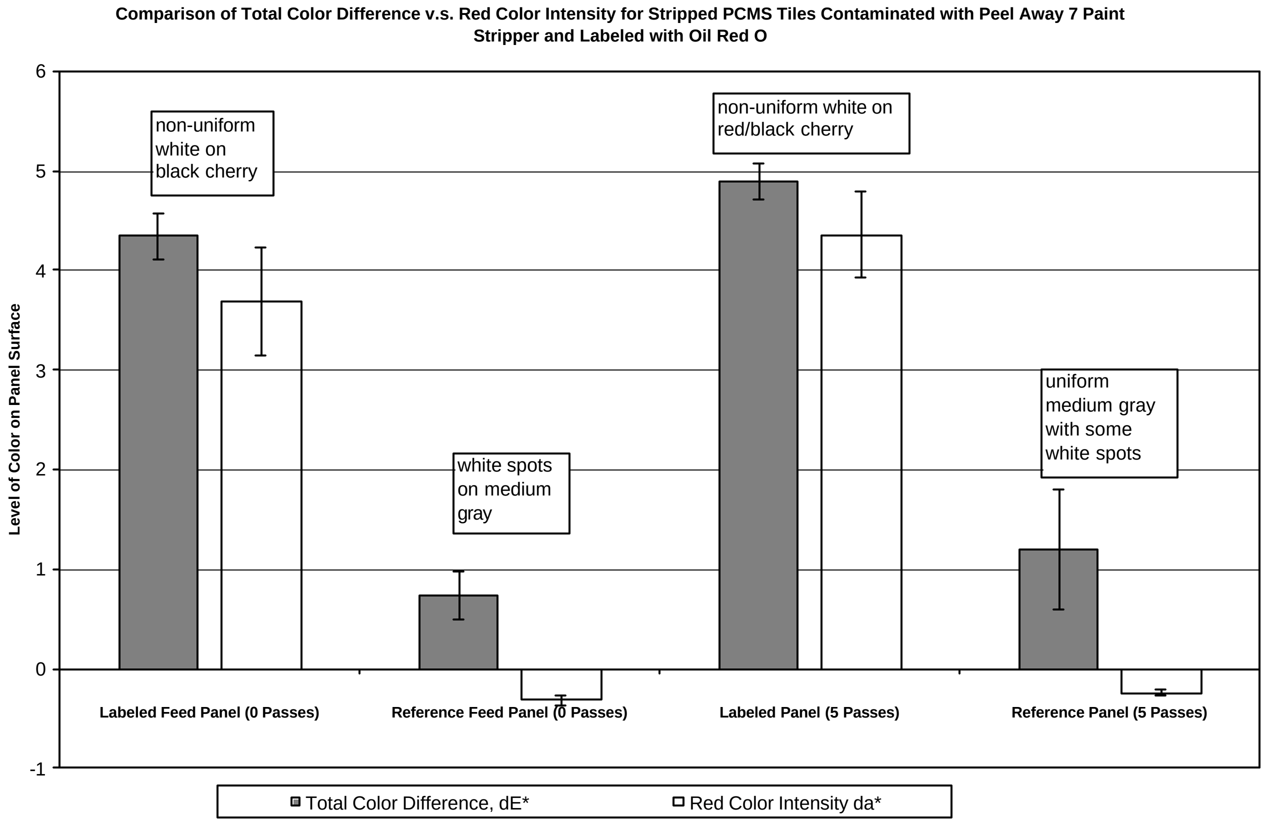
Analyses are of panel surfaces. Petroleum ether did not contrubite to the level of contamination. A reference feed sample (48444-97-23) has been excluded because the data point was deviant by a factor of 10. (TS-PA7-ORO-20:0.05 v. 20010424 block 86)

Figure E.3.32 Level of Contamination for Peel Away^{Ò} 7 Labeling (Block 86)



Analyses are of used cleaner baths from panel cleaning. Some samples for mg/ft2 Dye Removed from Reference Panel have values of zero and therefore do not appear on the graph. Original stripped tile surface is medium gray. (TS-PA7-ORO-20:0.05 v. 20010420 block 86)

Figure E.3.33 Dye Removal for Peel Away® 7 Labeling (Block 86)



Analyses are of panel surfaces. Original stripped tile surface is medium gray. (TS-PA7-ORO-20:0.05 v. 20010420 block 86)

Figure E.3.34 Level of Color on PCMS Tiles for Peel Away® 7 Labeling (Block 86)

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