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N95-31795**Environmentally Compatible Hand Wipe Cleaning Solvents**

By

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Several solvents of environmental concern have previously been used for hand wipe cleaning of SRB surfaces, including 1,1,1-trichloroethane, perchloroethylene, toluene, xylene, and MEK. USBI determined the major types of surfaces involved, and qualification requirements of replacement cleaning agents.

Nineteen environmentally compatible candidates were tested on 33 material substrates with 26 types of potential surface contaminants, involving over 7,000 individual evaluations. In addition to the cleaning performance evaluation, bonding, compatibility and corrosion tests were conducted.

Results showed that one cleaner was not optimum for all surfaces. In most instances, some of the candidates cleaned better than the 1,1,1-trichloroethane baseline control.

Aqueous cleaners generally cleaned better, and were more compatible with nonmetallic materials - such as paints, plastics, and elastomers. Organic base cleaners were better on metal surfaces.

Five cleaners have been qualified and are now being implemented in SRB hand wipe cleaning operations.

Introduction

The Montreal Protocol, 1990 Clean Air Act Amendments, President Bush's edict on ozone depleters, and the forthcoming Aerospace Manufacturing and Rework National Emission Standards for Hazardous Air Pollutants (NESHAPs) have shifted aerospace industry's environmental compliance methodology from an "end of the pipe" strategy to one of prevention and elimination. This is not an easy change. The aerospace community faces a special challenge since many of their materials must withstand rigorous use conditions.

USBI Co. is responsible for design, acquisition, assembly, test, and refurbishment of the nonmotor segments of the Space Shuttle Solid Rocket Boosters (SRBs). USBI was given a Technical Directive (TD) by the National Aeronautics and Space Administration (NASA) in 1991 to assess the impact of forthcoming environmental regulations on the materials and processes utilized on the Space Shuttle SRBs. The assessment indicated one of the materials/processes which would be significantly impacted by the new regulations was hand wipe cleaning. Hand wipe cleaning is a manual contamination removal procedure utilized in the processing of components with sufficient size, delicacy, or limited usage to preclude development of immersion or automated cleaning techniques. Common solvents used for hand wipe cleaning of SRB components are 1,1,1-trichloroethane, xylene, perchloroethylene, methyl ethyl ketone (MEK), and toluene. Hand wipe cleaning was found to account for approximately 27% of the total Volatile Organic Compound (VOC) emissions at the USBI production site in Florida. As a result, NASA directed USBI to define and qualify environmentally compatible replacements for the solvents currently in use.

Test Matrix / Variables

The hand wipe solvent replacement task was a major undertaking due to the large number of processes that used 1,1,1-trichloroethane and the other solvents. Cleanliness levels and possible effects on subsequent processes also had to be considered. The variables evaluated in the test program included: substrates, contaminants, and candidate cleaners. The substrates were determined by review of company drawings, and procedures. From this review forty substrates were chosen for testing (table 1).

Table 1. SRB Surfaces Selected For Testing

304 Stainless Steel	Hypalon - sealcoat
4130 Low Alloy Steel	Inconel 718 (Ni-base superalloy)
Aft Skirt Kick Ring Cover - (phenolic)	K5NA
Akzo primer (epoxy)	Low Volatile Akzo primer (epoxy)
Akzo topcoat (epoxy)	Low Volatile topcoat (epoxy)
Aluminum - anodized	MCC/USI (epoxy sprayable composite)
Aluminum - bare (2219)	MSA-2 (epoxy sprayable composite)
Aluminum - Alodined (chromate conversion coated)	MSA-3 (epoxy sprayable composite)
Aluminized tape No. 425	Nitrile rubber
Booster Trowelable Ablative (BTA)	Plastic sealant caps
Cork P50 sheet	PR 855 Foam
Deft primer (water-based epoxy)	PR 1422 (polysulfide sealant)
Deft topcoat (urethane)	PR 1770 (polysulfide sealant)
EA 934 - shim (epoxy)	Rust-Oleum primer (organic zinc rich)
Electrical cable sheath - (Teflon)	Rust-Oleum topcoat (epoxy)
Ethylene propylene rubber (EPR)	Silicone rubber
Flex hose (Resisto-Flex)	SLA-220 - TPS (silicate)
Forward Skirt Aft Seal - D Seal	Urethabond - sealcoat (urethane)
Forward Skirt Aft Seal - Neoprene	Viton rubber
Glass/Gold - electrical connector	XXX 409 - shim (phenolic)

The contaminants used in the study were identified by shop floor interviews, review of processes, and non-volatile residue witness plates. The possible sources of contamination generation are facility, process, and opportunity. Facility contaminants are generated by machinery or fixtures at the processing site. Examples are diesel exhaust, hydraulic fluid, methyl isobutyl ketone (MIBK), etc. Residues which pass from one processing step to the next are considered process contaminants. Tapes, greases, ultrasonic coupling agents, etc. are possible process contaminants. Contaminants of opportunity are those contaminants which do not have a documented presence during the normal operation of the facility or process. Fingerprints, insecticides, and hand lotion are examples of contaminants of opportunity.

The contaminant list is especially critical in any cleaner study and therefore all pertinent contaminants needed to be identified. Much of the work on SRB contaminant identification was accomplished by a previous study, "Surface Preparation and Verification For Bonding" (1). In order to simplify the test program, several contaminants were omitted due to chemical similarity to other contaminants. In addition, some of the contaminants tested, specifically the particulates, were combined to form a "cocktail" or mixture. This mixture consisted of facility dust, dirt, MSA-2 dust, cork dust, paint dust, Insta-Foam dust, and Hypalon dust. The final number of contaminants utilized in the test program was 23 (table 2). Determination of the substrate/contaminant combinations for the test matrix followed the flow diagram in Figure 1.

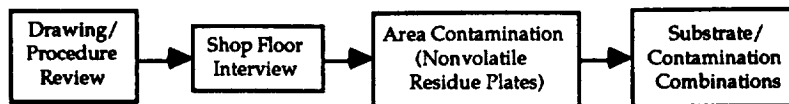


Figure 1. Flow Chart of Methodology for test matrix

Table 2. Contaminants Selected For Testing

880 C&C Grease	Molybdenum grease
Ardrox dye penetrant	Particulates:
Chalk	Cork residue/dust
Echo Ultragel II	Facility dust
Fingerprints	Hypalon dust
Flight grime	Insta-Foam dust
Glo Bright	MSA-2 residue/dust
Grease pencil	Paint dust
HD Conoco Grease	PR 1422
High temperature tape	Teflon spray
Hydraulic fluid	Vacuum pump oil
Magnaflux dye penetrant	Vinyl tape
Marking ink	Walnut hulls
Masking tape	

Several criteria were used to select the candidate cleaners. Material Safety Data Sheets (MSDSs) from possible candidate cleaners were reviewed for toxicity; worker safety hazards, physical properties (including flash point and vapor pressure); and storage, disposal, and shipping requirements/restrictions. The cleaning ability of potential cleaners was initially evaluated by vendor interviews and review of their data sheets. The chemical components of the cleaners were also reviewed by MSDS, data sheets, and vendor interview. Nineteen cleaners were chosen for testing (table 3).

Table 3. Cleaners Selected for Testing

CLEANER	VENDOR
409 Cleaner	Clorox
815 GD	Bulin & Company, Inc.
815 MX	Bulin & Company, Inc.
Allied Signal Volatile	Allied Signal
Axarel 6100	Du Pont
Blue Gold	Modern Chemicals Inc.
D. K. Solvent	DuBois
D99 Cleaner	Tiodize Co. Inc.
Fantastik	Dow Chemical
Jettacin	DuBois
Key Chem 01000	Stuart - Ironsides, Inc.
Key Chem 06000	Stuart - Ironsides, Inc.
PF Degreaser	PT Technologies, Inc.
Prime	DuBois
Propanol/Ethanol	-----
Reveille	DuBois
Siloo Glass Cleaner	Siloo
Simple Green	Sunshine Makers, Inc.
Solvo Cleaner 68-FD	Quaker Chemical Corporation

A full factorial of the three variables, substrates, contaminants, and candidate cleaners, would have consisted of over 17,000 combinations. Therefore, the experiment was designed to examine only those contaminants which were pertinent for a given substrate. The total number of combinations was thereby reduced to approximately 3,000.

Methods

The hand wipe solvent replacement program consisted of three phases: down selection, qualification, and implementation. Phase I, the down selection process, included performance evaluation of the cleaners, and initial compatibility testing. The test methodology for the program is shown schematically in Figure 2.

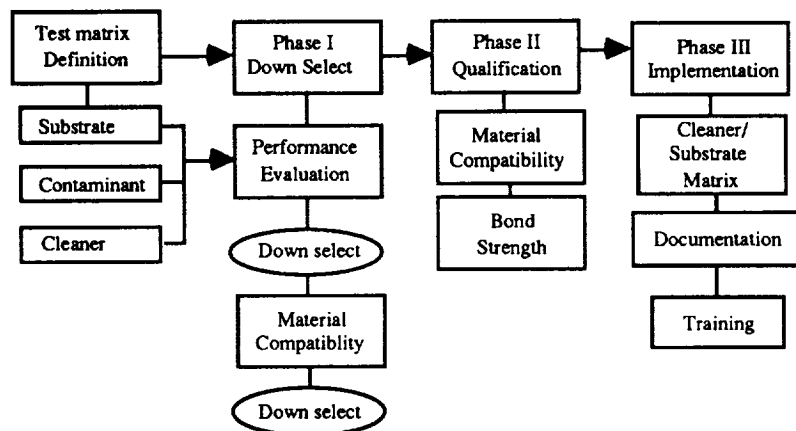


Figure 2. Project Flow Chart

The performance evaluation testing examined the cleaning ability of the candidate cleaners with respect to the substrates and contaminants. This quick and simple test was designed to identify, early in the program, cleaning weaknesses of the candidates. Performance evaluation measured the amount residue left on a substrate coupon after contaminating with a specific contaminant and then cleaning with a candidate cleaner. The residue was measured gravimetrically and, where applicable, water break free. In all tests, 1,1,1-trichloroethane was used as a control solvent. Where appropriate, other solvents were also used as controls. In addition, the performance evaluation testing also identified some compatibility concerns. By identification of the cleaning weaknesses it was possible to reduce the number of candidates examined in the next phase of testing.

After performance evaluation seven viable cleaners remained. These cleaners were then tested for compatibility using ASTM F 483: "Total Immersion Corrosion Test" (9) and ASTM D 471: "Standard Test Method for Rubber Property - Effect of Liquids" (5). Total Immersion tested the compatibility of the cleaners to the metal substrates, and "Standard Test Method for Rubber Property - Effect of Liquids" tested the compatibility of the cleaners to the non metallic materials. Because of the duration of exposure to the candidate cleaners these tests were considered very conservative compared to actual use conditions. 1,1,1-trichloroethane was used as the control solvent in all testing.

At the end of the Phase I testing, five candidate cleaners were selected for qualification (Phase II). Factors other than the test data were also considered in the final down selection process. These factors included: cost analysis, worker safety, and environmental impact.

Phase II of the solvent replacement project consisted of qualifying the candidate cleaners through compatibility and bond strength testing. Compatibility testing in Phase II was accomplished by exposures, under special conditions, of the candidate cleaners to metals and paint systems utilized on the SRB. Compatibility of the cleaners on metal substrates was qualified using ASTM F 1110: "Sandwich Corrosion Test" (6) and ASTM F 485: "Effects of Cleaners on Unpainted Aircraft Surfaces" (2). The sandwich

corrosion test was used to determine if the cleaners had an effect on faying surfaces. The "Effects of Cleaners on Unpainted Aircraft Surfaces" test was used to evaluate the cleaners potential for staining metal surfaces. ASTM F 502: "Effect of Cleaners and Chemical Maintenance Materials on Painted Aircraft Surfaces" (2) was used to determine the compatibility of the cleaners to SRB paint systems. 1,1,1-trichloroethane was used as the control solvent in all tests. Since, there are no ASTM procedures available for evaluating compatibility of cleaners to spacecraft surfaces, the ASTM aircraft procedures were used.

Bond strength testing in qualification examined the effect of the candidate cleaners on paint system adhesion and bond properties of adhesives, sealants, and Thermal Protection Systems (TPSs). ASTM D 4541: "Pull-Off Strength of Coatings Using Portable Adhesion Testers" (4) was used to assess potential effects the cleaners might have on SRB paint systems. ASTM D 1002: "Strength Properties of Adhesives in Shear by Tension Loading (Metal to Metal)" (7) was used to determine effect of the cleaners on the bond strength of adhesives and sealants. ASTM D 1623: "Tensile and Tensile Adhesion Properties of Rigid Cellular Plastics" (8) was used to determine the effect the candidate cleaners had on the bond strength of TPSs. Flatwise tensile testing was also used to assess the effect of the candidate cleaners following a long term exposure to conditions seen by the SRB hardware during processing. Specimens were bonded with 2216 epoxy were tested after six months of exposure and will be tested again after twelve months of exposure. Lastly, the specimens cleaned with the candidate cleaners were tested in flatwise tension at 150°F to evaluate to determine if the elevated temperature bond strength of 2216 epoxy was significantly affected. The elevated temperature testing was also repeated after six months of production facility exposure and will be repeated again after twelve months of exposure. 1,1,1-Trichloroethane was used as the control solvent for all tests.

Results

The tests showed that 1,1,1-trichloroethane was not the best cleaner for most of the surfaces. Prior to the down select, on most substrates 1,1,1-trichloroethane was ranked in the top 50% of the cleaners tested. Following down select, 1,1,1-trichloroethane was determined to be the worst cleaner for some of the substrates. None of the cleaners tested was found to consistently perform the best for all substrates examined. It was discovered that the organic cleaners performed better on some substrates while the aqueous cleaners performed better on other substrates. The major distinction appeared to be whether the substrate was metallic or non-metallic. Organic cleaners performed better on the metallic surfaces while the aqueous cleaners performed better on the coated and rubber based materials. An example of data from a performance evaluation test is shown in table 4.

Table 4. Data for Example Cleaner on 304 Stainless Steel

Contaminant	Sample No.	Applied (mg)	Residue (mg)	Water Break Free
Control	1	---	0	pass
	2	---	0	pass
	3	---	0	pass
Particulates	1	5.1	0	pass
	2	5.9	0	pass
	3	5.9	0	pass
Echo Ultrigel II	1	416.3	1.7	pass
	2	501.5	0.7	pass
	3	321.8	1.1	pass
Glo Bright	1	37.0	0	pass
	2	42.3	0	pass
	3	28.6	0	pass
Fingerprints	1	0.3	0.2	pass
	2	0	0	pass
	3	0.2	0.1	pass
Conoco Grease	1	433.6	0	pass
	2	339.9	0.1	pass
	3	540.6	0	pass

Based on the results of the performance evaluation Jettacin, Prime, Blue Gold, Key Chem 01000, PF Degreaser, Reveille, Fantastik, and ethanol were chosen for continued testing. PF Degreaser, Key Chem 01000, Reveille, and ethanol are organic cleaners. Jettacin, Prime, Blue Gold, and Fantastik are aqueous or semi aqueous cleaners.

The results of the metallic compatibility tests show that none of the metal surfaces were affected by the organic cleaners evaluated. There were slight effects, statistically, displayed in conjunction with some of the aqueous cleaners used in the evaluation. However, all of the candidate cleaners were deemed to be compatible from an engineering viewpoint.

The results of the Standard Test Method for Rubber Property (Effects of Liquids) showed that, for each substrate tested, there was at least one candidate cleaner which was compatible. In fact, for the majority of the substrates, 1,1,1-trichloroethane did not display the highest degree of compatibility observed. The majority of the cleaners did not perform well on the cork substrate. This was apparently due to the porosity of the material. The cleaners soaked into the cork thus requiring a significantly longer dry time than was associated with the other substrates. Ethanol was the only candidate which displayed a reasonable dry time on cork.

Every cleaner was compatible with all of the paint systems used except Hypalon. Only the aqueous cleaners were found to be compatible with Hypalon. Acceptable bond strengths were exhibited by all paint systems except for Rust-Oleum and Urethabond when cleaned with ethanol.

Jettacin, Prime, PF Degreaser, Reveille, and ethanol were chosen for qualification. However, the preliminary aerospace NESHAPs incorporated vapor pressure limits of 45 mm Hg for hand wipe cleaners. This ruling meant ethanol was no longer an acceptable candidate. Isopropanol was suggested as a substitute and therefore added to the test program.

All the bonding tests showed at least one cleaner was as good as or better than 1,1,1-trichloroethane.

Conclusions

The USBI effort was successful in defining and qualifying environmentally compatible cleaners for Solid Rocket Booster hand wipe operations. The cleaners qualified were Prime, Jettacin, and Reveille by DuBois, PF Degreaser by PT Technologies, Inc., and isopropanol. Based on the test program results and direction from the end customer a matrix of cleaners versus substrates was generated. The matrix was as follows:

Metals	Reveille
Painted Surfaces	Reveille
- Hypalon	Prime
Thermal Protection Systems	Reveille
- Cork	Isopropanol
Rubber Materials	Prime
Foams	Prime
Composite Materials	Reveille
Electrical	Isopropanol
Sealants	Reveille

Hand wipe cleaning processes are used extensively throughout USBI's SRB operations. Because of this, over 600 documents were affected by the hand wipe solvent replacement task. Updating of these documents should start in the fall of 1994. As the documents are updated, the new cleaners will be incorporated into the USBI production cleaning operations. If delays are avoided, by the summer of 1995 all production hand wipe cleaning will be done with the new environmentally compliant cleaners. Training of the technicians in the use of the cleaners will be conducted as the cleaners are implemented.

The replacement of hazardous materials is an important challenge faced by today's industry. There are significant costs associated with testing, qualification, and implementation of such replacements. However, the long term costs of not replacing such materials may be even more expensive. The implementation of these cleaners has numerous benefits. Through the use of the new cleaners, an ozone depleting substance will be eliminated, hazardous waste generation will be decreased, the potential for exposure to toxic materials will be reduced, and the processing of SRB hardware will, in some cases, be improved through the use of more effective cleaners.

Acknowledgment

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