Materials Compatibility Testing in RSRM ODC-Free Cleaner Selection

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ABSTRACT

Government regulations have mandated production phase-outs of a number of solvents, including 1,1,1-trichloroethane, an ozone-depleting chemical (ODC). This solvent was used extensively in the production of the Reusable Solid Rocket Motors (RSRMs) for the Space Shuttle. Many tests have been performed to identify replacement cleaners. One major area of concern in the selection of a new cleaner has been compatibility. Some specific areas considered included cleaner compatibility with non-metallic surfaces, painted surfaces, support materials such as gloves and wipers as well as corrosive properties of the cleaners on the alloys used on these motors. The intent of this paper is to summarize the test logic, methodology and results acquired from testing the many cleaner and material combinations.

Introduction

Historically, Thiokol Propulsion used 1.4 million pounds of 1,1,1-trichloroethane (commonly known as TCA, methylchloroform, or "trich") annually to produce the Space Shuttle Reusable Solid Rocket Motors (RSRMs). In 1990 the United Nations Montreal Protocol and the Clean Air Act Amendments required the phase out of production of this chemical due to its ozone depleting potential. Thiokol set up a program to reduce usage as quickly as possible and acquired an Essential Use Exemption to allow continued use in critical areas. Once the major uses of TCA, such as vapor degreasing, were eliminated, all other uses were investigated. A matrix was created which identified all substrates cleaned as well as potential contaminants in each case and subsequent bondlines. Vapor degreasing involved only cleaning aluminum and steel hardware. The remaining uses involved over a hundred various substrates and bondlines. One of the major concerns during this phase was compatibility between the cleaner replacement candidates, the substrates being cleaned and the processing materials used to perform the cleaning. Table 1 shows the complete list of cleaners evaluated. Only results from some of the down-selected cleaners are reported here.

NON-METALLIC COMPATIBILITY

A usage matrix was created which identified the uses of TCA. This matrix included the substrates being cleaned, the contaminants being removed and the subsequent process or bond. The substrates were categorized into one of six major families; metals, elastomers, phenolics, hybrids, paints or miscellaneous. During the screening phase, a few representative and/or critical substrates from each family were selected for testing with a large number of cleaners. As the number of cleaners was reduced, the number of substrates being tested was increased. Prior to implementation, all substrates were tested for compatibility with the selected cleaner.

Many things were considered while the test protocol was developed. Many of the substrate families created unique compatibility concerns and testing needs. As a result, compatibility tests were designed to address the needs of each substrate family. Another objective was to utilize industry standard tests such as ASTMs or test procedures applied by other Shuttle contractors so that data could be shared within the Shuttle community.

The substrates themselves varied in form and availability, so many ASTMs were used as guides and were not strictly adhered to. Compatibility testing for non-metallic, non-coated surfaces was based on ASTM D471, "Standard Test Method for Rubber Property-Effect of Liquids".

Deviations from the standard were necessary to accommodate testing the different substrates in a timely fashion. The ASTM specifies a standard coupon size for testing; however the coupon size in this test was tailored depending on the substrate tested. All coupons of a single substrate remained consistent to allow comparison between cleaners and the current TCA baseline. The ASTM also specifies a standard hole size be drilled in each coupon to allow suspending them in test solution; however, the coupons were hung by wrapping a thin stainless steel wire around them and hanging them from the sides of the test vessel submersed in solution.

Specimens were weighed to the nearest 0.1 mg, measured in three locations per side to the nearest 0.001 inches to determine volume, and measured for hardness at five different positions to determine the average starting hardness. Hardness readings were made on each coupon that had sufficient thickness to make that reading meaningful. Three coupons per cleaner were placed in beakers and labeled with the cleaner type and specimen number. Enough solvent was added to completely immerse the specimens. The beakers were covered with aluminum foil and the edges sealed with tape. Tests were conducted at ambient conditions in the absence of direct light.

Table 1 – Candidate Cleaners

Abbreviation	Cleaner	Description
ACE	Acetone and water	90% acetone and 10% water by volume
AC3	AmberClean Q3	Aqueous, non-terpene citrus base
AXT	Ax-It	Water, sodium metasilicate, surfactants
BA1	Bio-Act 113	1-Methyl-4-(1-methylethenyl)-cyclohexane
BA4	Bio-Act 145	Aliphatic hydrocarbons, propanol, (2-methoxy-methylethoxy)
PCG	Bio-Act PCG	High purity limonene
BTE	Borothene E (a.k.a. Leksol)	N-propylbromide
BSD	Brulin SD 1291	3-ethoxypropionate Dipropylene glycol methyl ether
DG5	Degreeze 500 LO	Ether alcohols, 1-butoxy-2-propanol, 1-(2-methoxypropoxy)-2-propanol
DS1	DS-108	Ethyl S(-)hydroxyprionate, ether alcohol 1-propoxy-2-propanol
EC5	Eco-solv 5	propylene glycol t-butylether PGME acetate, Isopar H, others
EXT	Ensolv XT	1-methyl-4-(1-methylethyl)-cyclohexane, menthene 8% N-propylbromide
HFE	HFE-7100	Methylnonafluorobutylether, methylnonafluoroisobutylether
HTF	HTF-60	Terpene alcohol, n-methyl pyrolidone, dibasic ester
HS9	Hurrisafe 9575	Aqueous with Propylene glycol, limonene, propyl ether
IC4	InproClean 4000T	Aqueous with terpenes
VER	Vertrel MCA Plus	Decafluoropentane, dichloroethylene, cyclopentane, dimethylbutane
KZ2	Kyzen 9200	Fluorinated and brominated hydrocarbons
OX1	Oxsol 100	1-chloro-4-(trifluoromethyl) benzene
PFH	PF 145 HP	3,3-diemthylhexane, alkylbenzenes
PFK	PF d'Ink	Alkylbenzenes, 1-methyl-2-pyrrolidinone
PFI	PF Ionsol	aliphatic hydrocarbons, heptanol
PFC	PFC-265-81	Octamethyltrisiloxane, perfluorobutyl ether
PL4	Plus-4	d-limonene, 2-(1,1-dimethylethoxy)ethanol, methylpyrrolidinone
PML	Purasolv ML	methyl lactate ester methyl-S(-)-2-hydroxypropionate
TEP	Teksol EP	Branched alkanes, d-limonene

Substrate coupons soaked in candidate cleaners for time periods of 1 hour, 22 hours and 70 hours were evaluated. A post-test evaluation was added later in the program to inspect substrates after they had been removed from the cleaners for 24 hours. After each time period and at the end of the test, the above described mass, volume and hardness was measured. Precision of the mass measurements in evaluations after soaking was reduced to the nearest 1 mg since samples constantly change weight as absorbed solvent evaporates. The time interval between removal of the specimens from the liquid and hardness testing was not less than 2 minutes nor more than 3 minutes.

A statistical Analysis of Variance or ANOVA was used to determine if the percent changes in weight, volume, or hardness are significantly different, at the 95% confidence level, for any of the candidate cleaners as compared to TCA. In this test, any change (measured in absolute magnitude) in substrate mass, volume or hardness is undesirable. The goal was to identify cleaners that caused no more change in our substrate measurements than TCA caused.

The quantity of change was identified as significantly greater (worse), significantly less (better) or statistically equivalent (same) to the TCA baseline.

This test does not replicate the effects of hand cleaning with the candidate cleaners, but rather gives a comparative analysis of how the cleaners affected the substrates after various soak periods. It also gives an extremely conservative view of how the substrates would react if they were accidentally in contact with the cleaners for longer periods than just the handwipe. Materials such as cured and uncured elastomeric insulations, cured adhesives, phenolics, wire coatings and a wide variety of miscellaneous substrates were tested using this immersion test. Table 2 summarizes those cleaners that registered responses "worse" than TCA. Blocks that are checked had no cleaners register a response worse than TCA.

Table 2. Elastomer Compatibility Analysis of Variance Summary.

Substrate	Weight Change Worse than TCA	Volume Change Worse than TCA	Hardness Change Worse than TCA
SFEPDM	✓	PCG	BA4, PCG, PFK, PL4
ASNBR	✓	✓	PFK
Dow Corning 90-006	✓	✓	BA1, BA4, PL4
Glass Cloth Phenolic	BA1, BA4, PL4	✓	✓
PR-1422 Polysulfide	✓	✓	✓
EA-946	✓	✓	✓
Cork	✓	PFK	PL4
Carbon Cloth Phenolic	BA1, BA4, PL4	PL4	✓
EA-913NA	✓	✓	✓
Dow Corning RTV 732	✓	✓	✓
Viton	PL4	PL4	✓
Conductive Floor, Stone Hard	✓	✓	✓
Herculite, green, conductive	BA1, BA4, PCG, PFD	PCG	NA
Herculite, white	BA1, BA4, PCG, PFD, PL4	BA1, BA4, PCG, PL4	NA
Mix Bowl Lid	✓	✓	PCG, BA4, PL4
01-401009 Neoprene	✓	BA1, PCG, PL4	BA1, BA4, PCG, PL4
Phenolic, silica-cloth, cured	PFH, PL4	PFH, PL4	✓
5716 PVC	✓	✓	PFD, PL4
STW5-2738 Rubber, Silicone	BA1, BA4, PCG, PFD, PL4	BA1, BA4, PCG, PFD, PL4	BA1, BA4, PCG, PFD, PL4
Silastic J	BA4, PFD	BA4, PFD	BA1, PL4
Glass-filled Teflon	BA4, PFD	✓	PFD, PL4
Adhesive, 3M EC2615XLW	✓	✓	BA4
TIGA RTG (DP-070198)	✓	✓	BA4
6850 CFEPDM, cured	BA4, PCG, PFD, PL4	BA4, PCG, PFD, PL4	BA4, PCG, PFD, PL4
LSC Retainer material	BA1, BA4, PCG, PFD, PL4	BA1, BA4, PCG, PFD, PL4	BA1, BA4, PCG, PFD, PL4
Natural Rubber, cured	BA4, PCG, PFD, PL4	BA4, PCG, PFD, PL4	BA4, PCG, PFD, PL4
Lexan	✓	✓	✓
3192 EPDM Current, Cured	BA4, PFD, PL4	BA4, PFD, PL4	BA4, PFD, PL4
3403 EPDM Cured, (3192 with aged Nordel)	BA4, PFD, PL4	BA4, PFD, PL4	BA4, PFD, PL4
7862 EPDM Current, Cured	BA4, PFD, PL4	BA4, PFD, PL4	BA4, PFD, PL4
3410 EPDM Cured, 7862 aged Nordel	BA4, PFD, PL4	BA4, PFD, PL4	BA4, PFD, PL4
3411 SFEPDM Reformulated, Cured	BA4, PFD, PL4	BA4, PFD, PL4	BA4, PFD, PL4

Painted Surfaces

Painted and coated substrates were tested using ASTM F502, "Standard Test Method for Effects of Cleaning and Chemical Maintenance Materials on Painted Aircraft Surfaces" as a guide. After the base substrate was prepared and painted using standard methods, the coating was allowed to fully cure. Half of the painted surface was then exposed to the cleaner candidates or TCA for thirty minutes in a 100°F oven. Each half of the painted surface, exposed and unexposed, was then visually inspected for streaking, discoloration and blistering. Softening of the coating was tested using a series of pencils of varying hardness to determine the softest pencil that could rupture the coating.

The hardness measurement was repeated three times on both the unexposed and exposed half of the panel. The amount of change a cleaner caused within a panel was compared to the amount of change TCA caused within a panel using ANOVA. None of the cleaners affected the painted surfaces worse than TCA. A summary of coatings tested is listed in Table 3.

Table 3. Paint Compatibility Analysis of Variance Summary.

Substrate	Cleaners tested	Tested hours after exposure
Dexter Crown primer/paint	PCG, PFH, BA4, BA1, PFD, PL4	24 hours
Rust-Oleum primer/paint	PCG, PFH, BA4, BA1, PFD, PL4, PRP	24 hours
Deft Primer	PCG, PFH, BA4, BA1, PFD, PL4	24 hours
Teflon Coated Metal	PCG, PRP	24 hours
Gel Coat, Yellow	PCG, BA1, BA4, PFD, PL4	24 hours
Gel Coat, Yellow	PFD, BA4	0, 1, 24 hours
Gel Coat, White	PFD, BA4	0, 1, 24 hours
Chemlok 205/220 Dried	PCG, BA4, PL4	0, 24, 72 and 168 hours
Chemlok 205/220 Cured	BA4, PL4	0, 24, 72 and 168 hours
Chemlok 205/233 Dried	PCG, BA4, PL4	0, 24, 72 and 168 hours
Chemlok 205/233 Cured	PCG, BA4, PL4	0, 24, 72 and 168 hours
Chemlok 205/236A Dried	PCG, BA4, PL4	0, 24, 72 and 168 hours
Chemlok 205/236A Cured	PCG, BA4, PL4	0, 24, 72 and 168 hours
Eccobond 56C	PCG, BA1, BA4, PFD, PL4	24 hours

Process Materials

Process materials were analyzed in triplicate via solvent extraction to determine the potential for substances to be leached from the materials. The process materials were soaked in the selected cleaners for an hour at ambient temperature. Following the soak time, the cleaner solution was tested by infrared (IR) analysis for substances that had been dissolved from the process materials.

A gravimetric test for an increase in non-volatile residue (NVR) was conducted by evaporation of cleaners and weighing the residue. Control tests were performed on the neat solvents to determine IR response and NVR. These are shown in Table 4.

None of the process support materials showed any silicone but did give a wide range of slip agent and polymer processing materials. The results were such that a meaningful comparison between solvents is not possible.

First, there was a huge difference in the amount of the residue left by the different solvents. For solvents with a large NVR there was a larger difference between each blank sample NVR than the total contaminants that could be extracted from many of the process support materials. For example, the residue mass for the three blanks of BioAct 113 was 0.0278g, 0.0256g and 0.0264g. Even though each blank gave a fairly consistent quantity of residue, the difference between the highest and lowest blank was 0.0022g. If we use TCA as the solvent (the lowest solvent NVR) to determine the possible mass of each support material NVR extract we, find that only four process support materials gave a residue above 0.005g and many were 0.003g or lower. This means the amounts of residue expected from most of the support materials is below 50% of the difference expected in NVR from sample to sample using the same solvent. In other words, the mass expected for the NVR for most support materials is not within the experimental error for the solvent NVR.

Second, the amount of solvent residue from several cleaners was so large their IR signature completely covered any possibility of seeing the process support material extracts. One might mistakenly assume that several solvents did not extract out as many contaminants from the support materials. However, this does not mean that the solvent did not extract out the same amount of contaminants as other solvents with little or no NVR. It is more likely that the amount of the solvent residue is so much larger than the extracted support material NVR that the IR signature could not be seen. Support material responses that could be identified are shown in Table 5.

Another caution when interpreting the data is apparent when the data are used to quantify the amount of extract residue from each support material. When the average blank residue was subtracted from the support material residue it usually gave a negative number for solvents with a large NVR.

Table 4. Extraction Cleaners and NVR.

Solvent	Residue in Grams / Milliliter	Normalized NVR
TCA	0.0001/10 ml	1
BIOACT 145	0.0012/6 ml	20
PLUS 4	0.0028/10 ml	28
PF-145HP	0.0032/6 ml	53
PF DEGREASER	0.0038/6 ml	63
BIOACT 113	0.0263/6 ml	438

Table 5. Process Material Support Material Data.

Process Support Material	Extracted Residue	Relative Amount Extracted NVR
Velostat	Aliphatic Hydrocarbon	Moderate
Pink Poly	Aliphatic Diamine	Moderate
Follower Plate Plastic	None Identified	
Cotton Glove	Aliphatic Oil	Weak
Nylon Brush	None Identified	
Sand Paper	Polyethylene Glycol	Moderate
Tex Wipe	Aliphatic Carboxylic Acid	Weak
Rymplecloth (Deroyal Hermitex	Aliphatic Carboxylic Acid	Weak
Rymplecloth (American Fiber #301)	Aliphatic Oil and Acid	Weak
NBR Gloves	Polymethylstyrene, NBR, and additives	Strong
Vinyl Gloves	Dioctyl Phthalate Plasticizer (DOP)	VERY Strong
Nylon Squeegees	Nylon	Moderate to Weak
Brushes (Hollis Ind. #AL2562)	None Identified	
Scotch Bright Pad (Tan)	Polyurethane	Moderate
Scotch Bright Pad (Maroon)	None Identified	
Scotch Bright Pad (Green)	Styrene Butadiene Rubber (SBR)	Moderate
Nitrile Rubber	Aliphatic Oil and NBR	Very Strong
Polywipes	Terephthalic Rubber	Moderate
Polyethylene Squeeze Bottle	None Identified	
Neoprene	Aliphatic Oil and additives	Strong
Polyethylene Squeeze	None Identified	

Corrosion

The effects the candidate cleaners had on bare metal surfaces in terms of corrosion were evaluated using ASTM F483, "Standard Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals" as a guide. ANOVA was used to determine if the rate of change in weight ($mg/cm^2/24$ hrs) is significantly different, at the 95% confidence level, for any of the candidate cleaners as compared to TCA. Differences in absolute magnitude significantly greater than TCA are categorized as "worse", while differences in absolute magnitude significantly less than TCA are categorized as "better". Two substrates were tested, 7075 aluminum and D6AC steel. These results are shown in Table 6 and Table 7.

Most cleaners tested showed no compatibility concerns with aluminum although some of the aqueous cleaners did cause pitting and discoloration. Many of the cleaners tested did cause some spotting or discoloration on the steel after 168 hours. Some of the least compatible cleaners caused rusting or pitting on steel after only 24 hours. The aqueous cleaners did not show worse compatibility than the organic-based cleaners on steel, as was the case for aluminum.

Table 6. Aluminum Compatibility Analysis of Variance Summary

WEIGHT CHANGE			
CLEANER	RATING	COMMENTS	LOSS RATE ($mg/cm^2/24$ hr)
TCA	Same		-0.0000021
BA1	Same		-0.0000021
BA4	Same		-0.0000020
PCG	Same		-0.0000016
PL4	Same		-0.0000035

Table 7. D6AC Compatibility Analysis Of Variance Summary

Weight Change			
Cleaner	Rating	Comments	Loss Rate ($mg/cm^2/24$ hr)
TCA	Same	24 hours: None. 168 hours: Light discoloration.	+0.0000007
BA1	Same	Light discoloration	+0.0000046
BA4	Same	Spotted discoloration.	-0.0000010
PCG	Same	Light discoloration	+0.0000037
PL4	Same		+0.0000008

Conclusions

The most important function of a cleaner is the ability to remove soils from a given substrate, followed closely by compatibility with the substrate to be cleaned.

On polymer substrates, a wide range of responses was noted, based on the particular solvent-material combination. Responses ranged from almost no change for phenolic materials to complete dissolution for uncured rubber materials. The test methods used for softening, swelling, and weight gain provided valuable data for cleaners selection.

Paint softening tests showed that most paints were resistant to solvent effects. The materials affected by the solvents tested were intended as adhesives rather than paint such as the Chemlok family of adhesives. Data that showed solvent incompatibility with cleaners were useful to show where the cleaners cannot be allowed or should be used cautiously.

Process material tests showed that a wide range of slip agent and polymer processing materials could be extracted with the solvents, but it was difficult to make meaningful comparisons between solvents. The difficulties in making such a comparison were the small amount of material extracted versus the larger amount of non-volatile residue in the cleaners and the IR signal from the cleaner masked the material extracted.

Metal corrosion tests showed most cleaners were compatible with aluminum. Several cleaners showed compatibility similar to TCA on steel although TCA produced light discoloration. Several cleaners showed about the same weight loss as TCA, but produced discoloration, rust and slight pitting the test coupons.