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Blake F. Bradford
Laura A. Wurth
Pramod D. Nayate
Thiokol Propulsion
Brigham City, UT

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ISSUES RELATED TO CLEANING COMPLEX GEOMETRY SURFACES WITH ODC-FREE SOLVENTS

Blake F. Bradford, Laura A. Wurth, Pramod D. Nayate
Thiokol Propulsion
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ABSTRACT

Implementing ODC-free solvents into full-scale reusable solid rocket motor cleaning operations has presented problems due to the low vapor pressures of the solvents. Because of slow evaporation, solvent retention is a problem on porous substrates or on surfaces with irregular geometry, such as threaded boltholes, leak check ports, and nozzle backfill joints. The new solvents are being evaluated to replace 1,1,1-trichloroethane, which readily evaporates from these surfaces. Selection of the solvents to be evaluated on full-scale hardware was made based on results of subscale tests performed with flat surface coupons, which did not manifest the problem. Test efforts have been undertaken to address concerns with the slow-evaporating solvents.

These concerns include effects on materials due to long-term exposure to solvent, potential migration from bolthole threads to seal surfaces, and effects on bolt loading due to solvent retention in threads. Tests performed to date have verified that retained solvent does not affect materials or hardware performance. Process modifications have also been developed to assist drying, and these can be implemented if additional drying becomes necessary.

INTRODUCTION

Solvent candidates that have been selected to replace 1,1,1-trichloroethane (TCA) in the Space Shuttle reusable solid rocket motor (RSRM) hand cleaning operations typically have lower vapor pressures and evaporate more slowly than TCA. This has presented challenges in some operations, which require cleaning of surfaces with irregular geometry. Slow drying of the solvents on these surfaces can result in solvent being retained for long periods of time on a surface, and have the potential to affect hardware performance.

The solvents initially selected as replacement candidates were evaluated extensively to obtain data for properties such as solubility, compatibility, and dry time. Testing began initially with a large number of solvents, and these were down selected to a smaller number for more extensive testing. Testing of the initial group of solvents was limited to flat coupon testing, and solvent retention problems were not manifested during these tests. Problems with slow evaporation were discovered after solvent selections had been made and full-scale test articles were being processed.

Areas of difficulty have included bolthole cleaning in RSRM Nozzle and Final Assembly manufacturing processes, cleaning of nozzle backfill joints, and cleaning of non-flat or porous surfaces where solvent is likely to be retained. Concerns were whether long-term exposure to solvents affected materials, and whether hardware performance will be affected by entrapped solvent.

PROBLEM

Concerns relating to slow evaporation in recessed or porous areas have been addressed by extensive compatibility evaluations under extreme solvent exposure conditions. For the most part, materials have not been adversely affected. Where compatibility concerns were identified, process controls have been implemented to minimize exposure, and in some cases solvent candidates have been eliminated from specific areas.

The scope of work documented in this paper is limited to the problems with cleaning boltholes and nozzle backfill joints.

There have been two major challenges to bolt-hole cleaning.

1. The down-selected solvents have been less effective than TCA in dissolving grease in boltholes.
2. Since these solvents evaporate very slowly, in some cases the holes could not be completely dried without some mechanical assistance.

There were concerns that solvent and/or grease would remain in bolthole threads at the time of bolt installation. Solvent could adversely affect lubricity of the threaded joint, and, thereby, alter bolt pre-loads after torque-down. Due to the proximity of greased O-rings to threaded holes on most joints, solvent migration upon or after bolt installation was another concern.

The concern with the nozzle joints is that long-term exposure might affect the phenolic nozzle material or adhesion of RTV backfill sealant to the phenolics. When the flame surfaces adjacent to backfill joints are wiped with solvent prior to application of tape for RTV retention in the backfill joint, it is possible for solvent to run into the backfill gap and contaminate surfaces that have had RTV primer applied. The low vapor pressures of ODC-free solvents would prevent their evaporation from the narrow, deep backfill joint.

TEST METHODS

The testing documented in this paper addresses the concerns with solvent retention in boltholes and nozzle backfill joints. Bolthole cleaning tests evaluated effects on bolt loading and solvent migration. Backfill joint tests attempted to simulate the extent of solvent intrusion and evaluated the effects on backfill sealant adhesion.

BOLTHOLE CLEANING

EFFECTS ON TORQUE AND PRE-LOAD

Testing was performed to determine what effect residual ODC-solvents have on bolt pre-loads and torquing on bolts installed using normal procedures. Tests have been completed on Final Assembly nozzle-to-case joint bolts, and these are representative of tests that are still to be performed on igniter joints and nozzle bolted joints.

Tests were performed on full-scale nozzle-to-case joint simulation articles. PF™ Degreaser, manufactured by PT Technologies, was selected as the final solvent replacement candidate for Final Assembly. Testing compared resultant bolt torques and preloads using a PF Degreaser cleaning process, with the baseline TCA process.

The RSRM nozzle-to-case joint is illustrated in Figure 1. The nozzle is installed with the case in an upright position, so that the axial boltholes are in a vertical position and the radial holes horizontal during cleaning. The test used an aft dome and fixed housing

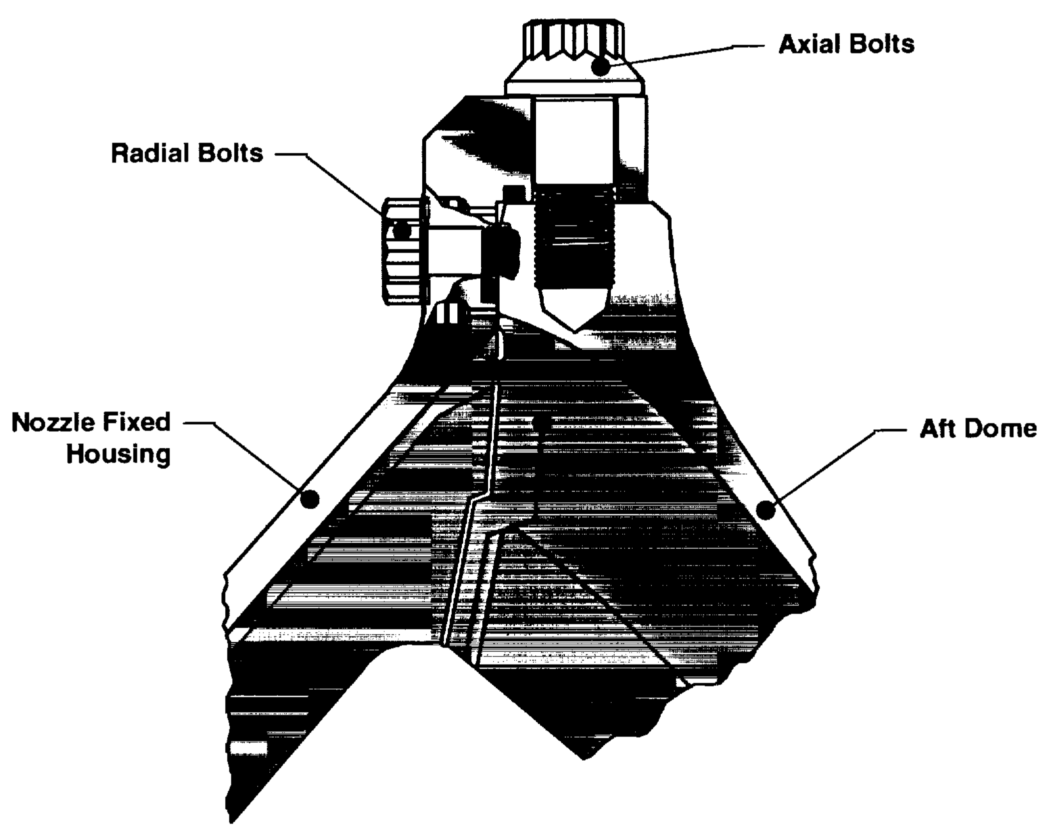


Figure 1. RSRM Nozzle-to-Case Joint Bolt Configuration

to simulate a nozzle assembly. Ultrastrain radial and axial bolts and boltholes were cleaned. The hole cleaning process involves flooding the holes with solvent, vacuuming the bulk solvent, and drying with a cloth to remove any remaining solvent. Holes were prepared according to the following cleaning procedures/conditions of surface dryness:

- Cleaned per baseline process with TCA.
- Cleaned with PF Degreaser, vacuumed, and wiped completely dry to meet current inspection criteria for dryness. This typically required using compressed air to assist drying.
- Cleaned with PF Degreaser, vacuumed, and wiped dry per current procedure (no additional drying).
- Cleaned with PF Degreaser, vacuumed, and left wet (no wiping, to represent a possible worst case condition).

The bolts were prepared by cleaning with the solvent that correlated to the cleaned boltholes. In the first part of the test, bolts were dried completely before applying a lubricating coating to the bolts. In the second part, the process was repeated with bolts that were intentionally left partially wet (semi-dry) before applying the lubricating coat. Bolts were loaded per standard manufacturing procedures and measured for preload, torque, and angle. The test was run twice for each part, varying the hole locations cleaned with each method each time.

SOLVENT MIGRATION TEST

The solvent migration testing had two goals: first, assessment of solvent effectiveness for grease removal from helicoil-equipped threaded holes, and second, determination of the extent of residual solvent migration from hole threads into assembled joints. Since one of the possible consequences of migrating solvent is breakdown of grease needed for corrosion protection, the solvent migration testing also included a saltwater immersion corrosion test to examine the effects of residual solvent on joint corrosion integrity. Since this study was performed as part of a solvent selection process, testing was performed on several candidate solvents. These solvents included Re-Entry® Prepsolv and Re-Entry® Plus 4, manufactured by Petroferm, and PF Degreaser. TCA was used as a control for all tests.

Test articles consisted of small pieces of the aft exit cone shell Joint 1 (the joint of RSRM nozzle forward and aft exit cones) surface excised from a scrap aft exit cone shell. The mating side of the test joints consisted of machined steel plates that simulated the Joint 1 portion of the forward exit cone. Each article contained two 0.5-in. threaded holes and appropriately sized through-holes on the matching top-plate. Prior to use, each aft exit cone piece was refurbished such that joint sealing surfaces and threaded holes complied with flight specifications. Non-mating surfaces of both aft exit cone pieces and top-plates were painted with the appropriate RSRM paint/primer system. Immediately prior to testing, manufacturing personnel installed helicoils in the test piece threaded holes using standard practices.

Three test articles were provided for each candidate solvent and TCA control. The cleaning performance testing was conducted using all three test articles. Cleaning performance was confirmed by visual inspection and by Fourier Transform Infrared spectroscopy (FTIR). Two of the three test articles were used to evaluate the relative extents of solvent migration under two different storage conditions.

Gas chromatography/mass spectrometry (GC/MS) headspace analysis was used to evaluate solvent migration. In the first solvent migration test, solvent-cleaned joints were assembled, held for one hour at ambient conditions, then disassembled and sampled for solvent analysis at various locations in the joint. The second solvent migration test was similar to the first, except the assembled joints were held for 24 hours at 120° ± 10°F to simulate longer duration storage. In cases where the results of this second solvent migration test showed solvent migration to positions on the seal surface of 0.5 cm or more, the third test article was used to conduct a corrosion test to determine if the solvent migration had any effect on saltwater penetration into the joint.

NOZZLE BACKFILL JOINT CLEANING

The nozzle backfill joint cleaning had two goals: first, to determine to what extent solvents penetrate nozzle backfill gaps during flame surface cleaning, and, second, to assess the effect of residual solvents on adhesion of silicone elastomer thermal barriers injected into the backfill gaps. Figure 2 shows a typical RSRM nozzle backfill gap, along with solvent wiping areas, and silicone elastomer bonding surfaces.

Tests were conducted on simulated backfill gaps, which consisted of phenolic panels clamped together with a shim to simulate a nozzle backfill gap. Three edges of the panel were taped, leaving one edge to simulate the flame surface of the nozzle. The clamped panels were fixed at an angle that would simulate joint orientation. Figure 3 shows the test fixture. One set of panels was prepared for each ODC-free solvent and for the TCA control.

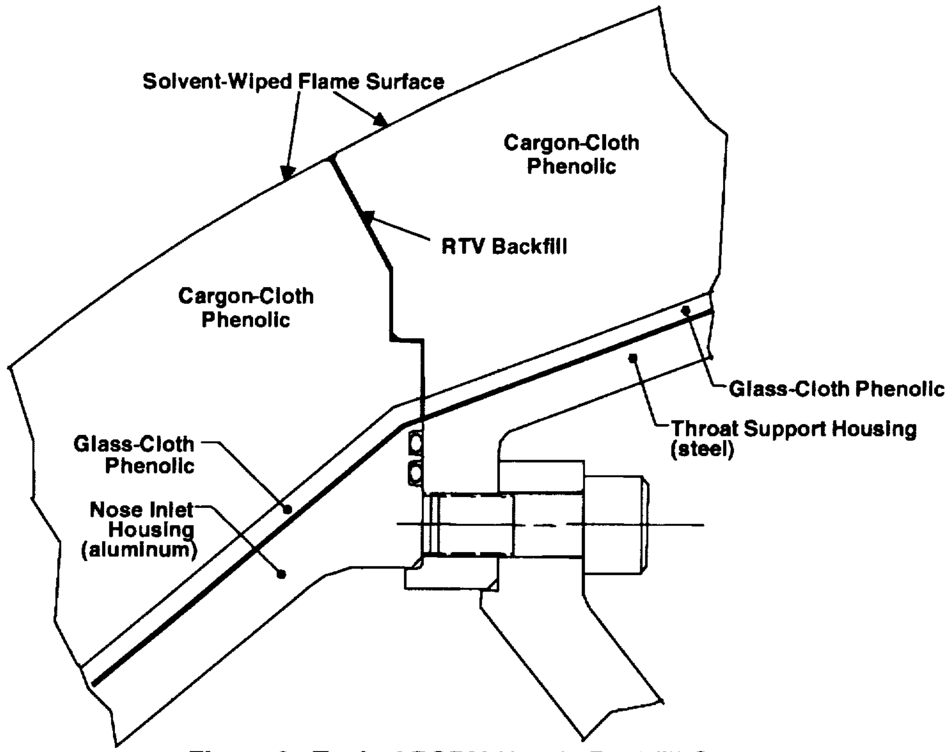


Figure 2. Typical RSRM Nozzle Backfill Gap

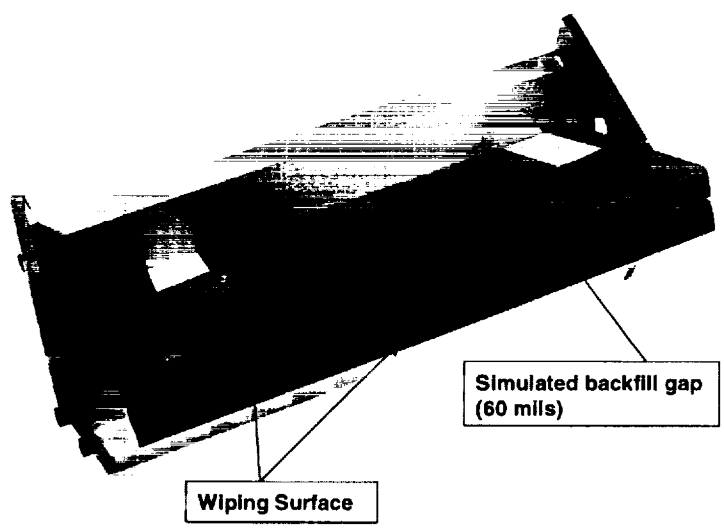


Figure 3. Simulated Backfill Gap Test Fixture

Wipe cloths saturated with solvent were used to wipe vigorously over the edge of the simulated joint. After wiping, the test fixture was allowed to sit one hour to simulate the shortest delay time between flame-surface solvent wiping and silicone elastomer injection. At the end of the one-hour hold, the test fixture was disassembled to determine the extent of solvent intrusion due to the wiping operation.

RTV primer was applied to a carbon cloth phenolic panel dried using standard manufacturing procedures. A thin film of ODC-free solvent was applied over the primed surface to simulate the worst-case condition observed from the solvent intrusion test. Tensile adhesion buttons were bonded to the ODC-free solvent-covered surface using the backfill RTV (Dow Corning® 90-006) one hour after solvent application. The RTV was mixed and cured according to manufacturing procedures. The process was repeated for each solvent. Tensile buttons were tested at 0.5 in. per minute and 72 +/- 3°F.

RESULTS

BOLTHOLE CLEANING

TORQUE/PRELOAD TESTS

Results of the bolt load evaluation are summarized in Tables 1-4. Each table contains results for either axial or radial bolts, in either a dry or semi-dry condition. In each table, A-basis limits were calculated based on the TCA-cleaned boltholes. The averages and ranges for load and torque values are listed for each cleaning method. The cleaning methods for the holes are as follows:

A = TCA cleaned per current process
B = PF Degreaser cleaned, completely dried
C = PF Degreaser cleaned, semi-dry
D = PF Degreaser cleaned, wet

Table 1. Axial Bolts (dry)

Clean Method	Load (lb)		Torque (ft-lb)	
	A-basis: 121,596 - 188,738		A-basis: 1727 - 3181	
	Average	Range	Average	Range
A	155,167	121,230 - 167,215	2454	1858 - 3039
B	157,200	147,607 - 162,395	2468	2220 - 2630
C	154,072	123,404 - 175,561	2501	1937 - 2945
D	152,318	134,560 - 157,931	2575	2236 - 2929

Table 2. Radial Bolts (dry)

Clean Method	Load (lbs)		Torque (ft-lb)	
	A-basis: 33,886 - 64,620		A-basis: 392 - 551	
	Average	Range	Average	Range
A	49,253	36,592 - 56,199	471	422 - 526
B	52,450	47,794 - 55,143	492	456 - 539
C	48,499	41,322 - 54,459	453	396 - 496
D	54,493	49,214 - 58,506	483	436 - 549

Table 3. Axial Bolts (semi-dry)

Clean Method	Load (lb)		Torque (ft-lb)	
	A-basis: 140,652 - 175,562		A-basis: 1892 - 3072	
	Average	Range	Average	Range
A	158,106	148,417 - 168,675	2482	2157 - 3071
B	158,818	137,226 - 169,821	2497	2157 - 2882
C	154,595	134,053 - 170,671	2416	1968 - 2677
D	156,385	149,614 - 163,996	2542	2189 - 2740

Table 4. Radial Bolts (semi-dry)

Clean Method	Load (lb)		Torque (ft-lb)	
	A-basis: 31,203 - 67,455		A-basis: 374 - 530	
	Average	Range	Average	Range
A	49,329	35,223 - 57,062	452	416 - 532
B	53,504	48,552 - 58,875	455	399 - 496
C	50,153	43,471 - 57,675	443	386 - 516
D	54,513	50,573 - 59,600	467	416 - 506

No significant differences were observed in the torque and pre-load values in any of the tests. All values were well above engineering requirements. The level of the dryness of the holes did not appear to affect bolt loading. It was concluded from this testing that using PF Degreaser to clean bolts and boltholes per current inspection criteria yields acceptable bolt loading. Similar tests are in progress for other bolted joints, using the applicable ODC-free solvents.

SOLVENT MIGRATION TESTS

Threaded Hole Cleaning Performance

The FTIR analysis of baseline wipes taken from threaded boltholes and top plates showed trace amounts of aliphatic hydrocarbons and esters, typical of clean metal surfaces.

Visual inspection noted no grease residues in any of the cleaned holes; however, evidence of residual solvent could be seen in the hole threads cleaned with ODC-free solvents. Greased and cleaned holes were sampled with Teflon filters along the length of both boltholes and the top-plate through-bore. Since precise sampling of each test article was not possible, the amount of grease and solvent residues could not be quantified. Table 5 summarizes the results of FTIR analysis of cleaned holes. Prepsolv (PRP) and Plus 4 (PL4) appear to have been somewhat better than TCA and PF Degreaser (PFD) for grease removal.

Solvent Migration

Although the GC/MS headspace analysis is very sensitive to low levels of solvent in the presence of HD-2 grease, the variability inherent in the Teflon wipe sampling only allowed for a semi-quantitative analysis. Table 6 shows approximate wiped areas for each sampling location.

In order to account for the presence of grease and the Teflon wiper in headspace analysis, standards were run which consisted of 100 μg of solvent applied to an HD-2 grease contaminated Teflon wipe in a 10 ml headspace vial. Since two of the tested solvents, Plus 4 and PF Degreaser, contained multiple components, solvent concentration in wiped samples was determined individually for each solvent component. Analysis of the 100 μg standards showed that not all of the components of each solvent were detectable with the GC/MS headspace analysis. Table 7 lists the individual components of both Plus 4 and PF Degreaser and notes those that were detectable.

Table 5. FTIR analysis of greased and cleaned boltholes

Subscale Specimen Number	Cleaning Solvent	Results from Analysis of Wipe Samples
1	PRP	Small amount of HD-2 grease and residual solvent
2	PRP	Small amount of HD-2 grease and residual solvent
3	PRP	Small amount of HD-2 grease and residual solvent
4	PFD	HD-2 grease and residual solvent
5	PFD	HD-2 grease and residual solvent
6	PFD	HD-2 grease and residual solvent
7	PL4	Small amount of HD-2 grease and residual solvent
8	PL4	Small amount of HD-2 grease and residual solvent
9	PF4	Small amount of HD-2 grease and residual solvent
10	TCA	HD-2 grease, no solvent detected
11	TCA	HD-2 grease, no solvent detected

Table 6. Wiped Areas at Sampling Locations

Sampling Location	Approximate Area Wiped
1 Through-hole	5 cm^2
2 Behind hole	0.25 cm^2
3 0.5 cm beside hole	0.5 cm^2
4 2.0 cm beside hole	0.5 cm^2
5 O-ring	0.5-in. section of O-ring removed
6 O-ring groove	1 cm^2
7 Threaded bolthole	8 cm^2

Table 7. Detected Components of Plus 4 and PF Degreaser

PF Degreaser			Plus 4		
Component	Abundance	Detectable	Component	Abundance	Detectable
Undecane	40%	Yes	d-Limonene	75%	Yes
Dodecane	36.5%	Yes	1-tert-butoxy-2-propanol	10%	Yes
Decane	8%	No	dipropylene glycol ethyl ether	10%	Yes
Tridecane	7.5%	Yes	methyl pyrrolidone	5%	No
d-Limonene	7.5%	Yes	BHT	200-250 ppm	No
Tetradecane	0.5%	No			
BHT	25 ppm	No			
BHT	25 ppm	No			

Figures 4 and 5 show sampling locations (as defined in Table 6) superimposed over a photo of the disassembled test article joint surface. A value of "0" indicates that the compound in question was not detected in the sample. Tables with GC/MS headspace results for wipe samples taken from "short-duration" and "long-duration" migration studies are also shown in these figures.

Several important points can be noted from Figure 4 (short-duration samples):

- There is a large variability in the amount of solvent removed from threaded holes using vacuum. This can be see by comparing values for holes "A" and "B" for the same solvent in the short duration samples.
- At locations inside or immediately adjacent to threaded holes, ODC-free solvents are present in higher concentrations than TCA.
- At locations farther from threaded holes, ODC-free solvents and TCA have similar surface concentrations.
- In the case of PF Degreaser, the long chain hydrocarbon components (undecane and dodecane) are preferentially retained over the limonene component, as shown by an increase in the ratio of hydrocarbon-to-limonene concentrations. This apparent depletion in the limonene component could be due to the preferential evaporation during removal of solvent by vacuum.

From Figure 5 (long duration samples), additional points can be noted:

- TCA appears to move out of the assembled joint under the simulated long duration storage conditions. This is shown by the lower TCA concentrations on and adjacent to both "A" and "B" holes compared to those of the short duration TCA samples.
- ODC-free solvents do not appear to be affected by long duration storage conditions. Solvent concentrations in and adjacent to threaded holes do not appear to change significantly from short duration to long duration conditions. The variability in solvent surface concentration resulting from the vacuum solvent removal technique appears to outweigh those from the short vs. long duration storage conditions.

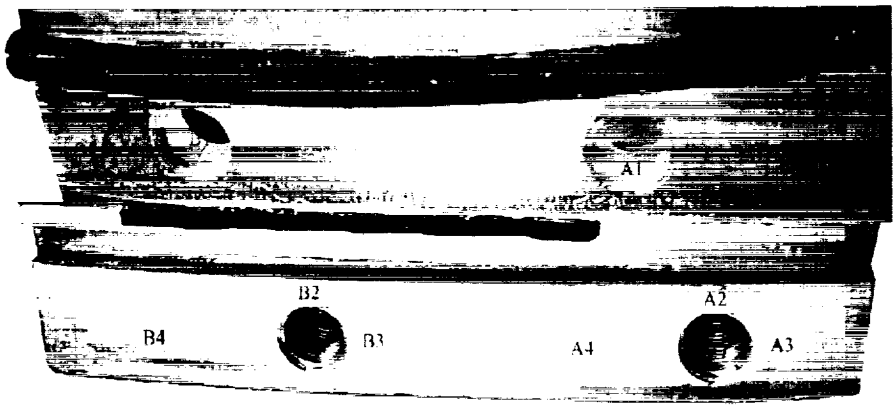
Results from the corrosion evaluation showed no signs of grease breakdown or saltwater intrusion of any of the evaluated solvents.

NOZZLE BACKFILL JOINT CLEANING

Results of the solvent intrusion testing are shown in Figure 6. In each case, the photos were taken of disassembled test fixtures at the end of the one-hour hold. In general, the amount of solvent intrusion at the end of the one-hour hold correlated with solvent vapor pressure, with the higher vapor pressure solvents showing the lowest levels of solvent intrusion. The amount of the solvent left on the bond surfaces of the adhesion test panels simulated the condition of the panels shown in Figure 6.

Results of the backfill RTV sealant adhesion are shown in Table 8.

Tensile strength results varied among the solvents tested, but the failure modes were all thin film failures against the tensile button. This indicates that the adhesion against the phenolic panel was not affected by solvent exposure to the panel. Any effects of the solvent on RTV properties have been addressed in solvent/material compatibility tests.



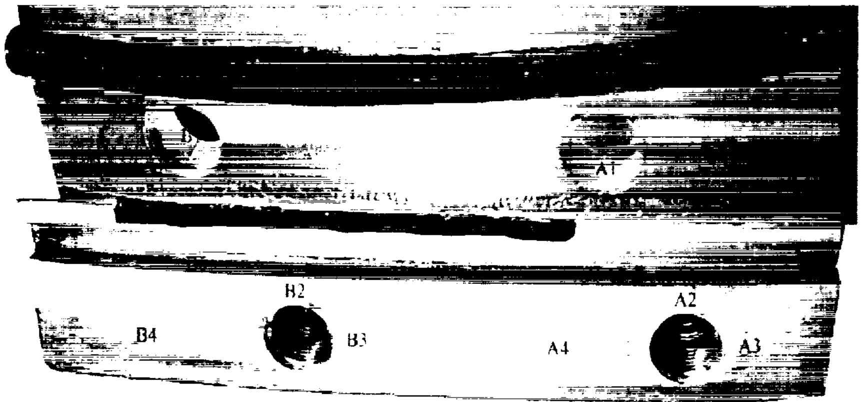
PF Degreaser – Short Duration ($\mu g/cm^2$)			
Location	Undecane	Dodecane	Limonene
A1	753	916	40
A2	474	811	36
A3	331	601	29
A4	27	0	3
A5*	52	107	2
A6	40	48	3
A7	487	614	38
B1	280	562	12
B2	134	152	5
B3	1703	2346	76
B4	0	0	0
B5*	24	0	2
B6	47	84	5
B7	674	968	40
*Units should be µg per sampled o-ring section			

Plus 4 – Short Duration		
Location	1-tert-butoxy-2-propanol ($\mu g/cm^2$)	Limonene ($\mu g/cm^2$)
A1	5	59
A2	5	172
A3	5	112
A4	0	2
A5*	9	68
A6	0	5
A7	75	375
B1	4	56
B2	19	248
B3	3	60
B4	0	4
B5*	0	11
B6	0	3
B7	18	170
*Units should be µg per sampled o-ring section		

PRP – Short Durations	
Location	Limonene ($\mu g/cm^2$)
A1	98
A2	338
A3	466
A4	5
A5*	2
A6	2
A7	68
B1	25
B2	18
B3	122
B4	2
B5*	2
B6	2
B7	11
*Units should be µg per sampled o-ring section	

TCA– Short Durations	
Location	TCA ($\mu g/cm^2$)
A1	32
A2	44
A3	28
A4	4
A5*	5
A6	5
A7	23
B1	54
B2	15
B3	723
B4	8
B5*	5
B6	4
B7	21
*Units should be µg per sampled o-ring section	

Figure 4. Short Duration Solvent Migration



PF Degreaser –Long Duration (μg/cm^2)			
Location	Undecane	Dodecane	Limonene
A1	213	340	5
A2	924	1145	81
A3	254	359	17
A4	0	0	10
A5*	35	24	1
A6	37	47	4
A7	1011	1091	91
B1	224	425	4
B2	344	470	18
B3	237	282	9
B4	0	67	3
B5*	0	20	1
B6	40	0	4
B7	1066	1327	32
*Units should be μg per sampled o-ring section			

Plus 4 – Long Duration		
Location	1-tert-butoxy-2-propanol (μg/cm2)	Limonene (μg/cm2)
A1	0	15
A2	0	106
A3	0	29
A4	0	5
A5*	0	4
A6	1	10
A7	26	570
B1	0	4
B2	0	7
B3	0	22
B4	0	5
B5*	0	5
B6	0	5
B7	24	246
*Units should be μg per sampled o-ring section		

PRP – Long Durations	
Location	Limonene (μg/cm2)
A1	3
A2	106
A3	60
A4	4
A5*	4
A6	8
A7	299
B1	129
B2	23
B3	29
B4	10
B5*	4
B6	2
B7	187
*Units should be μg per sampled o-ring section	

TCA- Long Durations	
Location	TCA (μg/cm^2)
A1	0
A2	1.1
A3	1.9
A4	0.9
A5*	1.0
A6	0.2
A7	0.5
B1	0.2
B2	0.5
B3	0.9
B4	0.0
B5*	0.0
B6	0.4
B7	1.6
*Units should be μg per sampled o-ring section	

Figure 5. Long Duration Solvent Migration

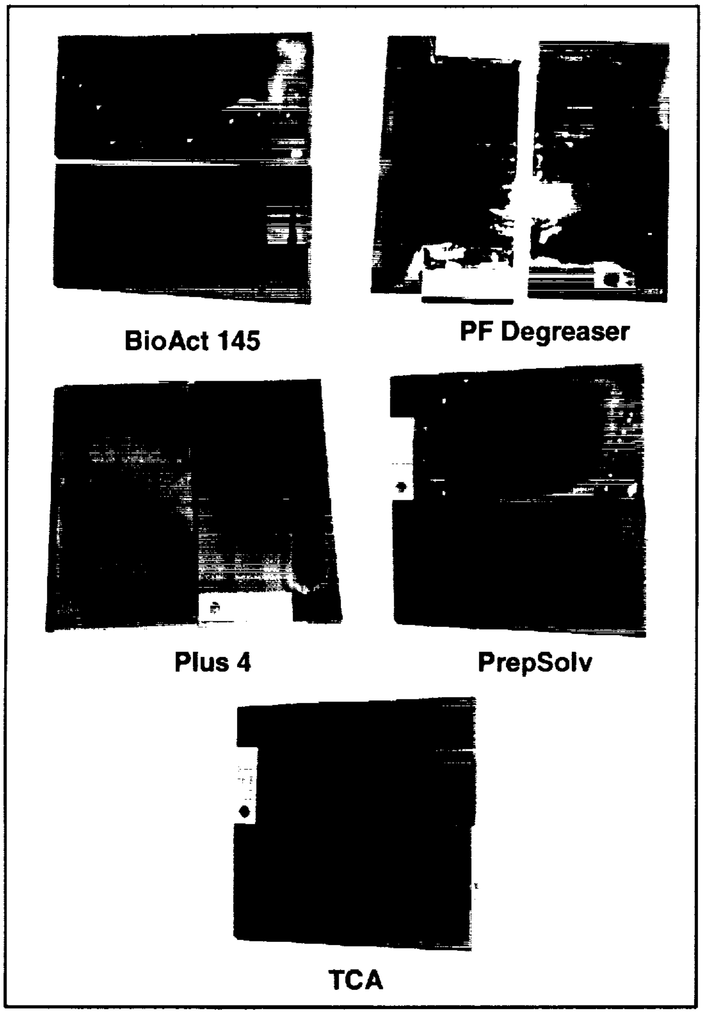


Figure 6. Simulated Backfill Gap Solvent Intrusion

Table 8. RTV Backfill Joint Simulation Adhesion Results

Solvent	Tensile Strength Average (psi)	Standard Deviation	Failure Mode
TCA	282.7	19.02	Thin film RTV against tensile button
BA4	287.3	32.2	Thin film RTV against tensile button
PFD	230.0	45.93	Thin film RTV against tensile button
PRP	271.6	21.97	Thin film RTV against tensile button
PL4	196.0	38.4	Thin film RTV against tensile button

CONCLUSION

It appears that ODC-free solvents can be implemented in processes that involve cleaning surfaces of irregular geometry, with few changes to current procedures. In future tests in which drying may prove to be critical for some applications, mechanical drying methods have been developed that could be implemented. The testing performed thus far has shown no permanent effects of these solvents on RSRM hardware performance.