Three analytical cleanliness measurement techniques confirm effectiveness of a new custom cleaning system.

Aqueous Degreasing of Aluminum and Steel Tubing Satisfies Stringent Specifications

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For the cleaning of aluminum and steel tubing, Lockheed Fort Worth Company (LFWC) has replaced its 1,1,1-trichloroethane cold cleaners and trichloroethylene vapor degreasers with an aqueous alkaline degreaser system.

The project began in 1987 as a laboratory investigation of alternate cleaning methods[1] for minimal hazardous material use and emissions, as part of the LFWC long-term goal of "zero discharge" hazardous waste and emissions.[2] Startup and shakedown of the new system began in December of 1992. As of November 1993, 100 percent of the tubing manufactured at LFWC (including oxygen tubing) has been cleaned in the aqueous system.

The setup consists of two alkaline cleaner tanks, three rinse tanks, and one forced-air drying oven. Each tank is constructed of stainless steel, holds 800 gallons of liquid, and is serviced by a centrifugal pump. The fluid in each tank is circulated through eductors which increase effective flow. The cleaner tanks are charged with a solution of alkaline cleaner in deionized water while the rinse tanks contain deionized water only.

Tubing to be cleaned is placed into aluminum mesh baskets that are then lowered into the tanks by an overhead conveyor. Pieces range in size from 0.19 to 3 inches, inside diameter, and can measure as much as 4 feet in length. Spray wands located on the sides of each tank allow operators to spray the tubing with alkaline cleaner, deionized water, or filtered air as required. After cleaning, tubes are dried in a recirculating forced-air oven.

Cleaner Systems and Steps

The LFWC alkaline cleaning system is divided into two basic subsystems:

- The *rough wash* subsystem, replacing a 1,1,1-trichloroethane cold cleaning tank, consists of a cleaner tank and a rinse tank. Its purpose is to remove gross contamination from tubing. The tubes are then either dried in the oven and returned to the shop floor for additional work or they are cleaned a second time in the final wash.
- The *final wash* subsystem, replacing a trichloroethylene vapor degreaser, consists of a cleaner tank and two rinse tanks. Its purpose is to remove the last traces of contaminants before tubing is placed into stock. The final rinse tank is monitored with a conductivity meter, and a deionized water flush keeps the concentration of alkaline cleaner from dragout below a set level.

The general procedure adopted for tubing cleaning is as follows:

1. Using cotton string, tie the tubing in vertically-oriented bundles in the wire mesh baskets.
2. Spray the fittings on the tubing with cleaner to ensure that forming fluids are not trapped underneath. Flush the interior of "coiled" tubing (i.e., that having a bend that can entrap liquid) with cleaner.
3. Immerse the basket in the rough wash tank and process per specifications.
4. With compressed air, spray any adhering foam off of the tubing and basket. Blow out coiled tubing.
5. Immerse the basket in the rough rinse tank and process per specifications.
6. Blow out each tube with filtered compressed air.
7. Repeat the above cleaning process using the final wash tank followed by consecutive rinses in the two final rinse tanks. Blow out each tube with filtered compressed air.
8. Dry tubing in an oven.

Table 1
Water-Emulsifiable Forming Fluids

FLUID	USE	VISCOSITY (SUS @ 100°F)	CHLORINATED?
A	Swaging Operations	8000	Yes
B	Tube Bending (External lubricant)	250	Yes
C	Tube Bending (Internal lubricant for small-diameter tubes)	8000	Yes
D	Tube Bending (Internal lubricant for small-diameter tubes)	4500	No
E	Anti-spatter (for laser cutting)	Water-like	No

Table 2
CFC-113 Extraction/Gravimetric Analysis of Residue In Bare Aluminum Tubing

TUBING EXTRACT	WT. OF BEAKER AND RESIDUE (gm ± 0.0001 gm)	WT. OF BEAKER (gm ± 0.0001 gm)	WT. OF RESIDUE (gm ± 0.0002 gm)	SURFACE AREA OF TUBING (sq. in.)	NON-VOLATILE RESIDUE FROM TUBING (mg/sq. ft.)
Solvent Control (50 ml)	28.6281	28.6273	0.0008	n/a	n/a
Tubing Extract A (50 ml)*	64.3708	64.3691	0.0017	73.1	1.8 ± 0.8
Tubing Extract V (50 ml)**	63.1433	63.1305	0.0128	73.1	23.6 ± 0.8

** Tubing cleaned in alkaline system* *** Tubing cleaned in vapor degreaser*

Initial testing of the alkaline system revealed that the non-water-emulsifiable fluids then being used for bending, swaging, and cutting operations in the tube shop were difficult to remove in the aqueous system. This required that all forming fluids be replaced with suitable water-emulsifiable substitutes. Water-emulsifiable fluids are more easily removed by alkaline cleaning systems and are less likely to leave a separate phase atop the cleaning solution, thereby avoiding redeposition of oils onto the tubing.

Table 1 (page 15) lists the water-emulsifiable replacements selected based upon testing, as well as the viscosities of the fluids and whether they contain chlorinated additives.

Reference 3 offers a complete discussion of the implementation process for the aqueous alkaline cleaning system.

Cleanliness Assessment

During the implementation process, ultraviolet (UV) light was used extensively to confirm that the aqueous cleaning process had successfully removed the forming fluids. The water-emulsifiable forming fluids used on the interior surfaces of the tubing fluoresce strongly under UV light.

One major concern in switching from a vapor degreaser to an aqueous system is whether oxygen tubing is adequately cleaned. LFWC is not presently required to conduct a quantitative analysis of the non-volatile residue remaining in its oxygen tubing after cleaning. The contract covering manufacture of the F-16 fighter[4] states that "the oxygen system shall be designed and installed in accordance with MIL-D-19326."

The version of MIL-D-19326 in effect at the time of the F-16 contract approval was MIL-D-19326F, which states in paragraph 3.9 that "the completed installation shall be free of oil, grease, fuel, water, dust, dirt, objectionable odors, or any other foreign matters, both internally and externally prior to introducing oxygen in the system."[5] Oxygen tubing cleaned in the aqueous system at LFWC meets these criteria based upon visual inspection under normal and UV lighting.

Note, however, that the latest version of MIL-D-19326, version H, states in paragraph 3.9 that "the internal surface of the system shall not exceed a maximum of non-volatile residue of 3.0 milligrams per square foot of surface area" as determined by extraction with CFC-113 per MIL-STND-1359B.[6] At present, LFWC is not contractually required to meet the requirement of MIL-D-19326H.

Nevertheless, the cleanliness level of oxygen tubing cleaned at LFWC was determined in an effort to evaluate the ability of the aqueous system to meet the cleanliness requirements of future aircraft programs. Three analytical methods were employed: CFC-113 extraction per MIL-STND-1359, thermogravimetric analysis, and inorganic carbon determination.

CFC-113 Extraction

The CFC-113 extraction/gravimetric analysis ensured that oxygen tubing cleaned in the aqueous alkaline system was clean enough to meet the requirement called out in MIL-STND-1359B. As previously noted, this states that the maximum non-volatile residue on the interior surfaces of gaseous oxygen and LOX system components should not exceed 3.0 milligrams per square foot.

For this test, five 2-foot-long sections of bare 6061-T6 aluminum tubing were cut from 0.250-inch OD stock tubing with a wall thickness of 0.028 inch. The interiors of all tubes were evenly coated with a water-emulsifiable forming fluid, which would normally be used in the interior of oxygen tubing during bending operations.

The tubing sections were then cleaned in the LFWC aqueous alkaline system as previously described. After cleaning, the tubes were flushed with 50 ml of 1,1,2-trichloro-1,2,2-trifluoroethane per Reference 6. The solvent was evaporated and residue weight determined. As shown in Table 2, the amount of non-volatile residue was found to be an acceptable 1.8 ± 0.8 milligrams per square foot of tubing internal surface area.

An identical set of five 2-foot-long tubing sections contaminated with the forming fluid were placed vertically in a basket and vapor degreased in 1,1,1-trichloroethane for 10 minutes. According to its manufacturer, this forming fluid can be removed in a degreaser when used as a neat oil.

Figure 1
Apparatus for Thermogravimetric Analysis

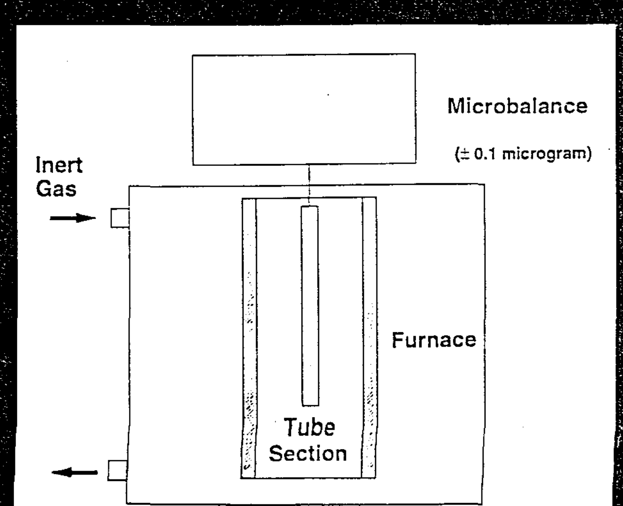


Figure 2
Thermogravimetric Analysis of Bare Aluminum Tubing (5°C Per Minute in Argon)

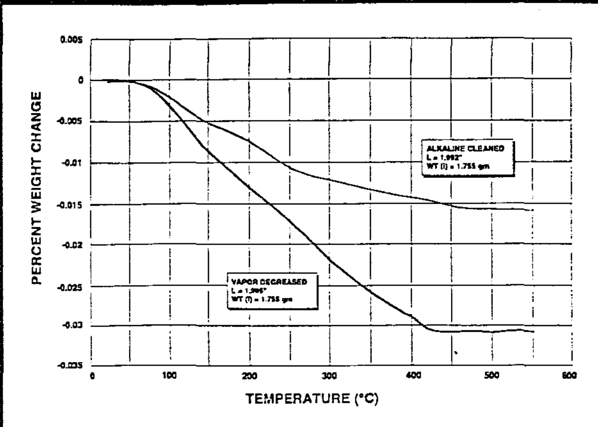
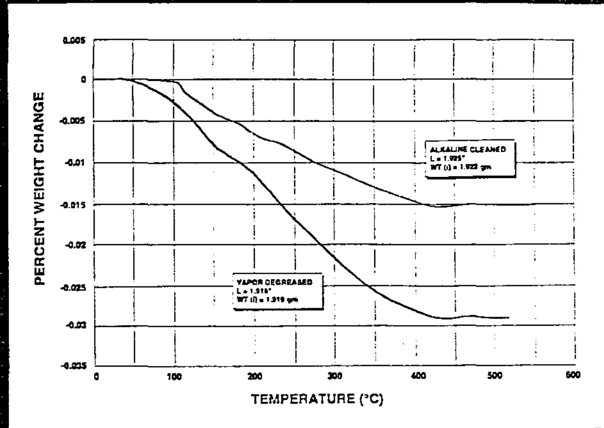


Figure 3
Thermogravimetric Analysis of Anodized Aluminum Tubing (5°C Per Minute in Nitrogen)



The degreased tubing sections were similarly extracted with 1,1,2-trichloro-1,2,2-trifluoroethane and the weight of extracted residue determined. The amount of non-volatile residue in the vapor-degreased tubing was found to be 23.6 ± 0.8 milligrams per square foot of internal surface area (see Table 2).

Thermogravimetric Analysis

In thermogravimetric analysis, the test sample is heated in an inert gas stream, contaminants are volatilized, and the weight loss is measured (see Figure 1, page 16). The minimum weight loss detectable by this technique is typically 0.1 microgram with a precision of 10 ppm.

For this test, two identical 2-inch-long sections of bare 6061-T6 aluminum tubing were cut from 0.250-inch OD stock tubing having a wall thickness of 0.028 inch. The exterior of each tube was buffed with 400-grit silicon carbide paper to remove lettering. The interiors of both tubes were then evenly coated with the forming fluid. One of the sections was then cleaned in the LFWC aqueous alkaline system along with the tubing sections used for the CFC-113 extraction/gravimetric analysis. The other section was placed vertically in a basket and vapor degreased with 1,1,1-trichloroethylene for 10 minutes.

The tubing sections were then sent off-site for thermogravimetric testing, whereby they were heated to 550°C under a flowing argon atmosphere, and weight loss was monitored. Figure 2 shows the percent weight change vs. temperature for both specimens. The weight of both stabilized at approximately 425°C.

The tube section cleaned in the alkaline system had a weight loss of 0.0160 percent while the tube cleaned in the vapor degreaser had a loss of 0.0310 percent. These percentages correspond to a contaminant level of 14.6 and 28.2 milligrams per square foot of surface area respectively (see Table 3, page 20). The inner and outer surface area of each tube was used for the calculation since contaminants from both surfaces were involved.

The thermogravimetric analysis was repeated using two identical sections of anodized 6061-T6 aluminum tubing, each 21.5 inches long by 0.25 inch in diameter with a wall thickness of 0.035 inch. These sections were not cut to size before cleaning, but were cut from longer cleaned tubing sections. The interiors of both tubes were evenly coated with the forming fluid.

One of the tubing sections was then cleaned in the LFWC aqueous alkaline system as previously described. The other was placed vertically in a basket and vapor degreased with 1,1,1-trichloroethylene for 35 minutes. Sections (approximately 2 inches in length) were cut from the central portion of each tube using a tubing cutter that had been vapor degreased with 1,1,1- trichloroethylene for 35 minutes. Great care was taken not to contaminate the tubing sections with fingerprints, etc.

Sent off-site for thermogravimetric testing, the tubing sections were heated to over 500°C under a flowing nitrogen atmosphere and the weight loss was monitored.

Figure 4
Apparatus for Inorganic Carbon Determination

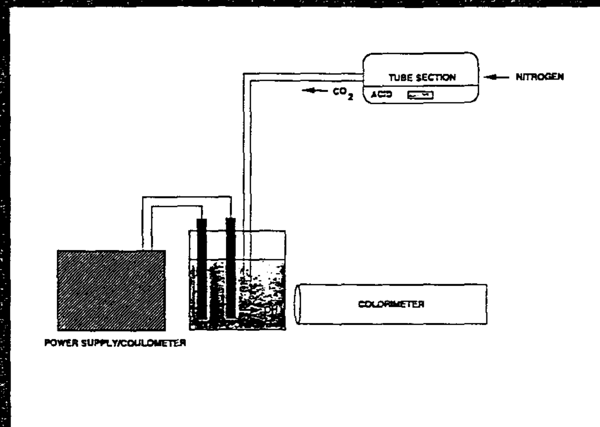


Table 3
Thermogravimetric Analysis of Residue in Bare Aluminum Tubing

CLEANING METHOD	WT. OF TUBING SECTION (gm)	SURFACE AREA OF TUBING SECTION (sq. in.)	VOLATILIZED CONTAMINANTS (% by wt.)	VOLATILIZED CONTAMINANTS (mg/sq. ft.)
Aqueous System	1.755	2.78	0.0160 ± 0.001	14.6 ± 0.9
TCE Vapor Degreaser	1.755	2.78	0.0310 ± 0.001	28.2 ± 0.9

Table 4
Thermogravimetric Analysis of Residue on Anodized Aluminum Tubing

CLEANING METHOD	WT. OF TUBING SECTION (gm)	SURFACE AREA OF TUBING SECTION (sq. in.)	VOLATILIZED CONTAMINANTS (% by wt.)	VOLATILIZED CONTAMINANTS (mg/sq. ft.)
Aqueous System	1.922	2.60	0.0155 ± 0.001	16.5 ± 1.1
TCE Vapor Degreaser	1.919	2.60	0.0290 ± 0.001	30.8 ± 1.1

Figure 3 (page 18) shows the percent weight change vs. temperature for both specimens. The weight of both stabilized at approximately 425°C. The tube section cleaned in the alkaline system had a weight loss of 0.0155 percent while the tube cleaned in the vapor degreaser had a loss of 0.0290 percent. These percentages correspond to a contaminant level of 16.5 and 30.8 milligrams per square foot of surface area respectively (see Table 4).

Table 5
Inorganic Carbon on Anodized Tubing

CLEANING METHOD	WT. OF TUBING SECTION (gm)	SURFACE AREA OF TUBING SECTION (sq. in.)	INORGANIC CARBON (% by wt.)	INORGANIC CARBON (mg/sq. ft.)
Aqueous System	1.236	1.67	<0.0021	<2.2
TCE Vapor Degreaser	1.028	1.38	0.0038 ± 0.0002	4.1 ± 0.2

Inorganic Carbon Determination

In this method, inorganic carbon (carbonate, bicarbonate) on the test sample cleaned with the aqueous system or with a vapor degreaser is converted to carbon dioxide with an acid digestion. The carbon dioxide is dissolved in an aqueous solution and the carbonic acid formed is titrated with electrochemically-generated base. The endpoint is detected with a colorimeter[7,8] (see Figure 4, page 19).

Tubing sections for this test were cut from the same anodized aluminum used to provide specimens for the thermogravimetric analyses. As previously stated, these tubes were evenly coated with the forming fluid inside and then cleaned in the aqueous system or in a vapor degreaser.

Sections (approximately 0.5 inch in length) were cut from the central portion of each tube using a tubing cutter that had been vapor degreased with 1,1,1-trichloroethylene for 35 minutes. Great care was taken not to contaminate the tubing sections with fingerprints, etc. before sending them off-site for analysis.

The tubes cleaned in the vapor degreaser had an inorganic carbon level of 4.1 milligrams per square foot of tubing surface area (see Table 5). Those cleaned in the aqueous system had an inorganic carbon level of less than 2.2 milligrams per square foot of tubing surface area. This value represents the lower limit of detection for this technique; the amount of inorganic carbon present was below this limit.

Discussion of Results

CFC-113 extraction of bare aluminum tubing cleaned in the LFWC aqueous cleaning system followed by gravimetric analysis of the extracted residue showed that the amount of non-volatile residue in the tubing was 1.8 milligrams per square foot. This degree of cleanliness satisfies MIL-STND-1359B, requiring a non-volatile residue level of less than 3.0 milligrams per square foot. The extracted residue appeared to consist mainly of a white particulate matter.

In contrast, tubing cleaned in a vapor degreaser did not meet the requirements of MIL-STND-1359B. CFC-113 extraction of vapor-degreased tubing yielded 23.6 milligrams per square foot of a non-volatile residue consisting mainly of an oily substance containing some white particulate matter.

Interestingly, thermogravimetric analysis of bare aluminum tubing cleaned in the aqueous system indicated that the contamination level was 14.6 milligrams per square foot — significantly higher than the contamination level determined by CFC-113 extraction. This would suggest that significant quantities of polar substances not removed by CFC-113 extraction may be present in aqueous-cleaned tubing.

On the other hand, thermogravimetric analysis of bare aluminum tubing cleaned in a vapor degreaser indicated a contamination level of 28.2 milligrams per square foot — very similar to the level determined by CFC-113 extraction (23.6 milligrams per square foot). This would suggest that the contaminants in the vapor-degreased tubing were non-polar or a mixture of polar and non-polar materials (such as unremoved forming fluid) and were readily removed by CFC-113 extraction.

Thermogravimetric analysis of anodized aluminum tubing cleaned in the aqueous system or in a vapor degreaser indicated contamination levels almost identical to those seen with bare aluminum tubing.

Inorganic carbon determination of carbonates/bicarbonates on anodized aluminum tubing indicated that the amount of inorganic carbon on tubing cleaned in the aqueous system was less than that on tubing that had been vapor degreased.

Answers and Questions

Conclusions can be drawn from the experimental data:

- The LFWC aqueous cleaning system can clean oxygen tubing sufficiently to pass the requirements of MIL-D-19326H, which uses CFC-113 extraction as an analytical tool.
- Thermogravimetric analysis revealed that there are probably more contaminants in aqueous-cleaned tubing than are detected by CFC-113 extraction. This analysis indicated, however, that aqueous-cleaned tubing is cleaner than vapor-degreased tubing.
- Inorganic carbon determination revealed less inorganic carbon on aqueous-cleaned tubing than on vapor-degreased.

Further testing must be performed to confirm these observations. Thermogravimetric analysis appears to be a promising analytical technique to replace or complement the use of CFC-113 extraction/gravimetric analysis for the quantification of contaminants in tubing.

Additional work must be done to identify the contaminants that remain in tubing after aqueous cleaning. These contaminants appear to be only partially removed by CFC-113 extraction, which suggests that they are polar in nature. PC

References

1. *Weltman, H.J. and Evanoff, S.P., "Replacement of Halogenated Solvent Degreasing with Aqueous Immersion Cleaners," Proceedings of the 46th Annual Purdue Industrial Waste Conference, Lewis Publishing Co., Chelsea, MI, 1991.*
2. *Evanoff, S.P., "Hazardous Waste Reduction in the Aerospace Industry,"* Chemical Engineering Progress, *April 1990.*
3. *Woodrow, T.A.; Koepsel, K.M.; and Karnes, J.O., "Aqueous Alkaline Degreasing of Aircraft Tubing," Proceedings of the 1994 International CFC and Halon Alternatives Conference, Washington, DC, Oct. 24-26, 1994.*
4. *16PS002B, "F-16 Air Vehicle," 1 Feb. 1982, p. I-107, paragraph 3.7.1.9.10.1 (revised on 26 Dec. 1984 under ACSN 3125).*
5. *MIL-D-19326F, "Design and Installation of Liquid Oxygen Systems in Aircraft, General Specification for," 18 Oct. 1978.*
6. *MIL-STND-1359B, "Military Standard Cleaning Methods and Procedures for Breathing Oxygen Equipment," 24 June 1987.*
7. *Huffman, E.W.D., Jr.,* Microchemical Journal, *22, 567-573 (1977).*
8. *Boniface, H.J. and Jenkins, R.H.,* Analyst, *96, 37-46 (1971).*

About the Author

Dr. Thomas A. Woodrow, an engineering specialist with LFWC (Fort Worth, TX), has 15 years of experience in the chemical and aerospace industries. His current interests include alternative cleaning methods and the use of ultrafiltration for the regeneration of aqueous cleaners. He holds a Ph.D. in organic chemistry and an M.S. in inorganic chemistry from Texas Christian University.