Evaluation of Performance Test Methods For an Aqueous Cleaner

855 7

~~P-05724~~

24,145
PDF

by Thomas M. Tam, Ralph Wyngarden and Anthony F. Naylor

Three test methods—weight gain, optically stimulated electron emission (OSEE), and nonvolatile residue (NVR)—were evaluated as a means of measuring the performance of an aqueous cleaning bath. It was found that the weight gain method is easy to reproduce and has the broadest range of sensitivity. This method is accurate enough for general metal surface cleaning. OSEE is the most sensitive method, but is limited to low levels of contamination. Of the three methods, NVR is the least desirable.

Historically, metal surfaces have been prepared for chemical processing by vapor degreasing, using chlorinated solvents, such as 1,1,1-trichloroethane (TCA). Because of environmental concerns and government regulations, industry is phasing out the use of Ozone Depleting Chemicals (ODCs), such as TCA. An intensive industry-wide effort is underway to find suitable replacements for TCA. Lockheed Missiles & Space Company Inc. (LMSC) has a pollution prevention goal of eliminating all use of TCA.

The most common replacement for TCA vapor degreasing is aqueous cleaning. LMSC has identified an aqueous immersion cleaner suitable for its applications. This cleaner is now being implemented at LMSC as a replacement for TCA vapor degreasing.

To control this aqueous cleaning solution, a vendor-suggested titration method is being used. This method only measures the alkalinity of the bath. To better control the bath, a method of measuring the actual performance of the bath is desired. Techniques such as the water-break test, visible inspection, and black light inspection can be used. The problem with these methods is that they do not give objective numerical results. In most cases the evaluation depends on an operator's judgment, and it is difficult to apply pass/fail criteria consistently. It is desirable to have a test method that would be able to indicate the bath performance on a numerical scale, and be quick, simple and inexpensive.

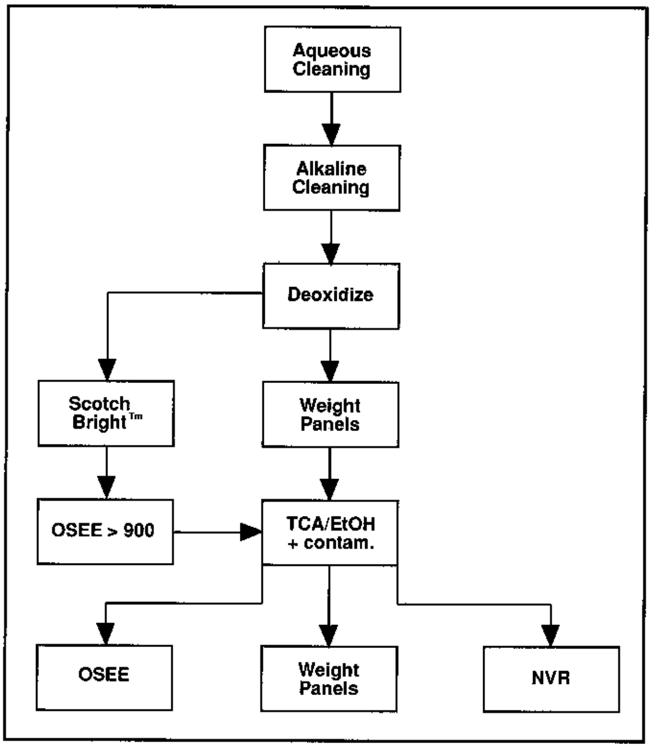


Fig. 1—Preparation of panels for weight gain, OSEE and NVR analysis.

This study consists of two parts. The first part evaluates three tests, weight gain,[1] optically stimulated electron emission (OSEE),[2,3] and nonvolatile residue (NVR).[4] None of these methods is new. They have been applied to determine the surface contaminant concentration. The intent was to compare the dynamic ranges of the methods under comparable conditions. The second part of this study used the three tests to evaluate the aqueous cleaner at different operating conditions (e.g., solution contaminant concentrations, and agitation). In addition, based on the results, we were able to compare the pros and cons of the test methods objectively.

Experimental Procedure

Preparation of test panels

Aluminum test panels (4 x 7 x 0.0625 in., 7075-T6) were used throughout this study. Figure 1 shows the steps used to clean the panels. Ten panels for each of the three test methods were processed and evaluated.

Deposition of contaminants

A mixture of contaminants consisting of machine coolants and lubricants (Table 1) was dissolved in two liters of TCA/EtOH (ethanol) solvent (75/25 V/V). These four contaminants were chosen as they are the most commonly used lubricants/machine coolants from LMSC's machine shops.

Cleaned panels were immersed in the solvent for 30 ± 5 sec, withdrawn from the solvent, and the excess solvent allowed to drain off. The panels were air dried overnight. As the solvent evaporated, an even layer of contaminant was deposited on the

Table 1
Composition of the Contaminant Mixture

Contaminant	Make Up (% wt/wt)
Rust Lick[a]	40
Acculube[b]	40
Tap Magic[c]	10
Aluma Cut[d]	10

[a] ITW Devon Co., Danvers, MA
[b] ITW Fluid Products Group, Norcross, GA
[c] Steco Co., Little Rock, AR
[d] Mistic Metal Mover, Inc., Princeton, IL

Fabulous Flexi-Liner®

The original loose hanging tank liner

Revive 'Leaking' Tanks Protect New Tanks

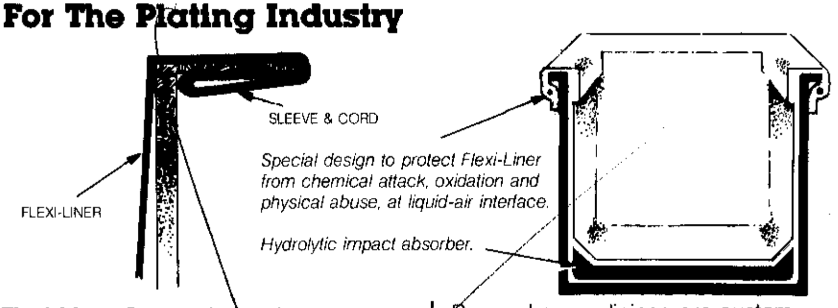
Flexi-Liners are patented* and trademarked; they are fabricated in one piece for any shape and size tank. We normally make shipment of your **Flexi-Liner** within a few days after receipt of your order; however, in an emergency, very often we can ship the same day. We keep a file of our customers' tanks, by number, with all pertinent data so that if shipment is urgent, all we need is your tank number and we have the specifications for fabrication.

Flexi-Liners offer the plating industry the following advantages: various thicknesses; free-hanging; corrosion resistance; requiring no bonding, no tank modification or sandblasting; easy, inexpensive installation; long lasting and maintenance free.

Best of all, down time is at a minimum because **Flexi-Liner** delivery is fast, saving you costly delays while your tank sits idle.

We don't just make tank liners, we make them fast and have been for nearly thirty years.

Flexi-Liner Is The Loose Hanging Tank Liner For The Plating Industry



Flexi-Liner Corporation makes great easv drop-in plating tank liners fast and guaranteed!

Flexi-Liners are pre-fabricated with built in outlets. They are custom made to fit your tanks.

Black liner for moderate to room temperatures and mild chemical solutions, excellent for rinse bath. White liners for solution temperatures exceeding 150° with high concentrates of corrosive and oxidizing chemicals, i.e., hard chrome.

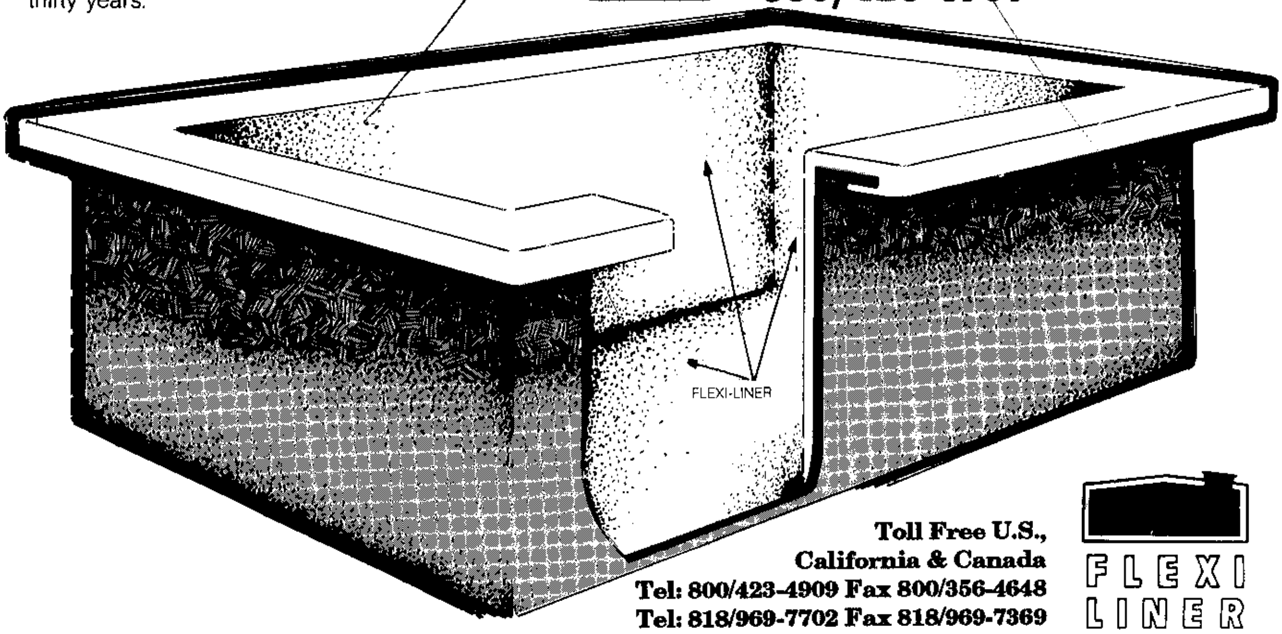
Remember our linings are custom-manufactured to fit your specific tank. We provide 24 hr. emergency fabrication at no extra cost. You can easily install them yourself, often in 3 to 5 minutes. All outlets, overflow-weir, etc. are built in by **Flexi-Liner.**

Flexi-Liner resists plating solutions, requires no bonding and offers liner thickness up to 0.125".

*PATENT NOS. 3 068 561 • 3 167 207

Suitable for **Pickling** and **Anodizing** Aluminum

For immediate information call Toll Free 800/423-4909



Toll Free U.S.,
California & Canada
Tel: 800/423-4909 Fax 800/356-4648
Tel: 818/969-7702 Fax 818/969-7369

Flexi-Liner Corporation
165 N. ASPAN ■AZUSA, CALIFORNIA 91702

FLEXI LINER CORPORATION

Free Details: Circle 126 on postpaid reader service card.

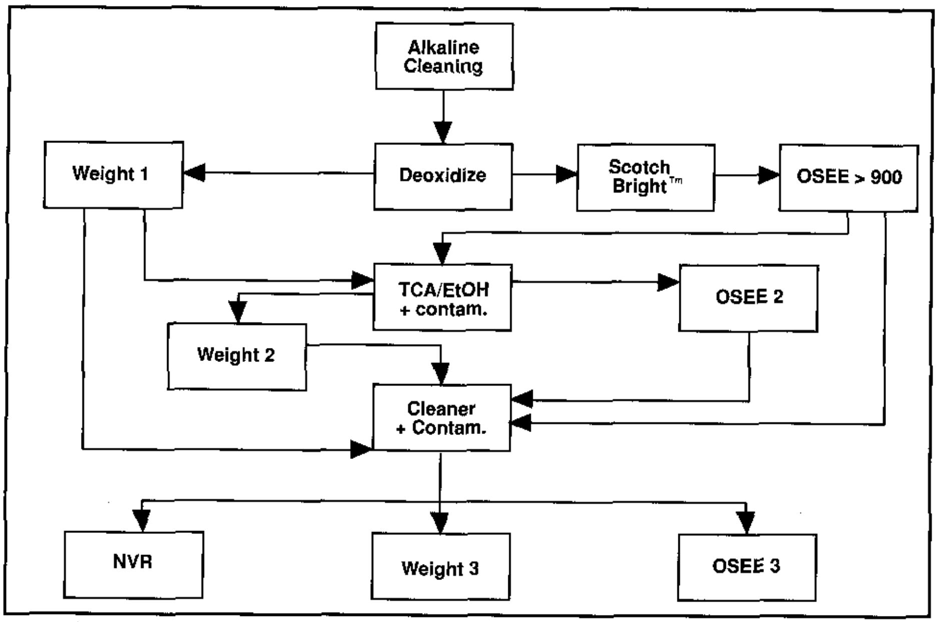


Fig. 2—Steps in preparation of panels for aqueous cleaning.

surface. By varying the concentration of contaminant in the TCA/EtOH solvent, the amount of contaminant deposited per unit area could be varied in a reproducible manner. The reproducibility of the amount of contaminant deposited on the panels was found to be ± 0.5 mg/ft^2.

A TCA/EtOH (75/25 V/V) solvent was used as the carrier to deposit the contaminant on the panels. The reasons for choosing this solvent mixture were:

1. The contaminants will easily dissolve in the solvent.
2. The contaminated solvent will wet the panel, evaporate easily, and leave behind an even film of contaminant.
3. The NVR test uses the same solvent. It was assumed that if the same solvent was used as the carrier, whatever was deposited onto the surface would be removed by the NVR test.

Figure 1 shows the steps that were used to prepare panels for analysis by weight gain, OSEE and NVR.

Weight Gain

An analytical balance[a] that produces readings of 5 significant figures was used to determine weight gain. A single panel was weighed 10 times. The reproducibility of the panel weight was found to be ±0.09 mg.

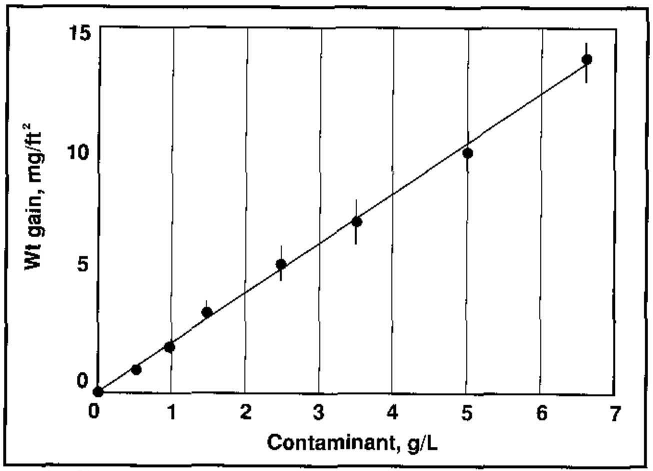


Fig. 3—Change in panel weight vs. contaminant concentration in TCA/EtOH.

Optically Stimulated Electron Emission (OSEE)

The OSEE used in this study was a single-channel system (OP 1020).[b] It used a sensor[c] to generate UV light and collect electrons emitted from the surface. The system is also equipped with a stepping motor for X-Y scanning. The distance from the sensor to the panel surface was set manually with a micrometer adjustment and was accurate to 0.001 in. A PC/AT™, was used to control the system and the X-Y scanning. A total of 300 readings was obtained for each panel. The data were recorded as mean, maximum, minimum, and standard deviation.

Nonvolatile Residue (NVR)

The ASTM F 331-72 NVR method was used to determine the amount of contaminant deposited on the panels. The solvent used was a mixture of TCA/EtOH (75/25 V/V). The solvent was evaporated in an evaporator, and the residue was weighed to 0.01 mg on an analytical balance.[a]

Aqueous Cleaning

(Laboratory-Scale Aqueous Cleaning System)

A small tank containing 43 L of an alkaline aqueous cleaner was used in the experiment. The concentration of the solution was maintained between 14 and 15 percent, at a temperature of 130 ±5 °F. A small, variable-speed magnetically coupled pump agitated the solution. The flow rate was monitored by a variable-area flow meter.

Panel Cleaning

In the first series of tests, the impact of solution contamination was determined by processing both contaminated and clean panels in the aqueous cleaner at different levels of solution contamination. Table 1 shows the composition of the contaminant mixture used. Figure 2 shows the steps used to prepare the panels for weight gain, OSEE and NVR testing. The panels evaluated by OSEE were dried with compressed nitrogen, and the OSEE response was measured immediately. The panels evaluated by weight gain and NVR were left to stand at ambient conditions for at least eight hr before measuring.

Two different methods were used to rinse the panels after aqueous cleaning. The first method was merely to immerse the panels in the rinsewater (stagnant rinse), the second method involved moving the panels up and down in the rinsewater to provide agitation (agitated rinse).

Results and Discussion

Evaluation of the 3 test methods

The first part of this study determined the range of sensitivity of the three tests to the amount of contaminant adhering to the aluminum surface. Table 2 shows the weight gain, OSEE and NVR data.

Figure 3 shows the dependence of weight of deposited contaminant (weight gain) on the concentration of contaminant

---

[a] Model AT-201, Mettler Instrument Co., Hightstown, NJ
[b] OP 1020, Photo Acoustic Tech. Inc., West Lake, CA 91361
[c] OPX 110, Photo Acoustic Tech. Inc., West Lake, CA 91361

Table 2
Amount of Contaminant Deposited on Test Panels At Different Concentrations of Contaminant in TCA/EtOH

Contaminant*	Wt.1 (std. dev.)**	OSEE (std. dev.)	NVR (std. dev.)†	Wt.2 (std. dev.)‡
0	0.06(0.03)	917(71)	0	-0.2(0.3)
0.50	1(0.2)	405(35)	0.18(0.24)	0.4(0.2)
1.0	1.8(0.5)	320(63)	0.12(0.18)	0.5(0.4)
1.5	3.3(0.3)	245(147)	1.38(0.33)	0.97(0.07)
2.5	5.8(0.8)	253(38)	2.06(0.63)	1.0(0.3)
3.5	7(1)	125(29)	4.3(1.2)	0.8(0.2)
5.0	9.6(0.8)	62(29)	5.22(0.8)	1.1(0.4)
7.5	13.2(0.7)	33(16)	—	—

*Concentration of contaminant dissolved in TCA/EtOH (g/L)
**Weight of contaminant deposited on panels (mg/ft²)
†Nonvolatile residue (mg/ft²)
‡Weight of contaminant left on panels after NVR test (mg/ft²)

in the TCA/EtOH solvent. The plot shows that the weight of contaminants deposited on the panels is proportional to the increase in solution contaminant concentration. The equation for the least squares best fit line is y = 2.041X - 0.0242, with a correlation coefficient (r^2) of 0.99. The weight gain method of contaminant application and measurement has been shown to give similar results by other researchers.[1] Because the weight change is a direct measure of what is being deposited, it was used to evaluate the other tests.

Figure 4 shows the dependence of the OSEE response on the weight gain. The OSEE response is inversely proportional to the weight gain. It is very sensitive to low levels of contaminant (less than 1 mg/ft²). The OSEE response levels off at a minimum value when the weight gain exceeds 10 mg/ft². The sensitivity range of the OSEE response with the system used is from 1 to 10 mg/ft². Figure 4 also shows the dependence of the NVR measurement on the weight change. It was found that the NVR test is not sensitive to small amounts of contaminant adhering to the panel (more than 2 mg/ft²). Although the NVR test shows a trend similar to that of weight gain at high solution contamination concentrations, the values are lower than those from the weight gain. If it is assumed that whatever contaminants are deposited on the surface can be removed, the NVR values should be equal to those from the weight gain. It was determined by weight gain that a considerable amount of the contaminants still adhered to the test panels after NVR testing (col. 5 of Table 2). In addition, totaling the NVR weight and the weight of residue remaining on the panel after NVR still does not result in an overall mass balance for the contaminant. A possible explanation is that the contaminant contains volatile materials that evaporate during the NVR test. A comparison of the dynamic ranges of the three test methods is shown in Fig. 5.

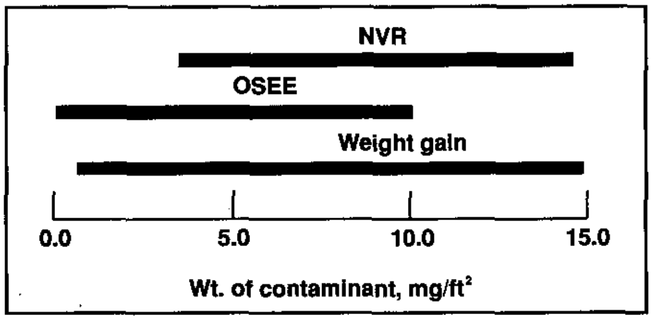


Fig. 5—Comparison of the dynamic ranges of weight gain, OSEE and NVR.

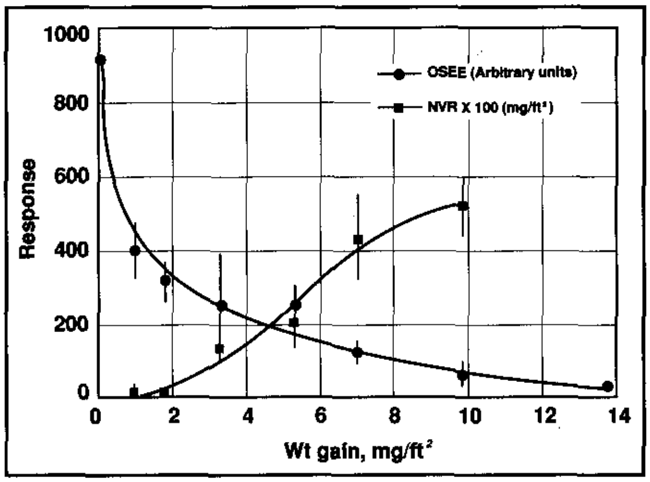


Fig. 4—OSEE response and NVR vs. change in panel weight.

Aqueous Cleaning[5]

The second part of this study determined the way in which different concentrations of solution contamination can affect the performance of the cleaner. The cleaner evaluated is an aqueous type consisting of surfactants, builders and corrosion inhibitors. It is designed as an emulsifier that removes contaminants from the surface and keeps them in suspension. The purpose of this part of the study was to determine:

- Which of the three test methods can best be used to measure the efficiency of the cleaner;
- The solution contaminant concentration that will cause the cleaner to fail to remove and emulsify the contaminants from a surface;
- The level of solution contaminant concentration at which the solution contaminants deposit onto a clean surface.

Two sets of panels were used. They were all pre-cleaned as described in the experimental procedure section. The first set of pre-cleaned panels was contaminated by depositing 14 mg/ft² of the contaminant on the surface. This set of 'dirty' panels was used to measure the effectiveness of the aqueous cleaner. A second set of 'clean' panels was used to measure redeposition of the contaminant from the cleaner. Both sets of panels were processed in the cleaner with different known concentrations of contaminant. After cleaning, the panels were evaluated by weight gain, OSEE and NVR. The data are given in Table 3.

The weight gain and OSEE data show that at a given solution contaminant concentration, the amount of contaminant

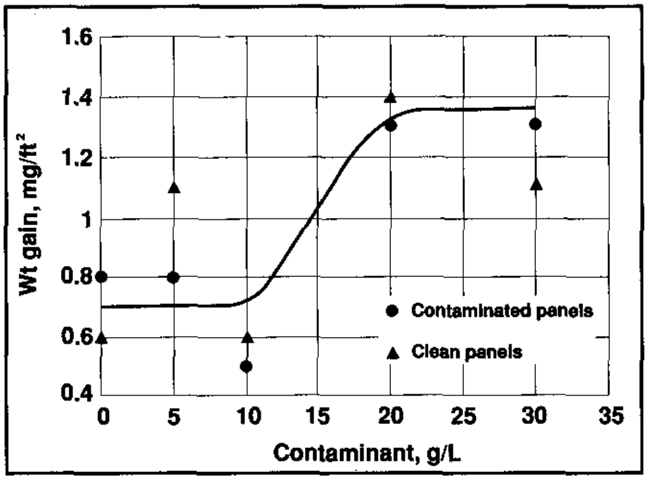


Fig. 6—Panel weight change vs. contaminant concentration in the aqueous cleaner.

Table 3
Amount of Contaminant Adhering to Test Panels After Processing by Contaminated Cleaner

Contaminant[a]	Wt 1 (std. dev.)[b]	Wt 2 (std. dev.)[c]	OSEE (std. dev.)	NVR (std. dev.)[d]
0	0	0.6(0.4)	675(112)	0
	14.4(0.4)	0.8(0.3)	475(130)	1.2(1)
5	0	1.1(0.2)	636(114)	0.4(0.2)
	14.0(0.2)	0.8(0.1)	496(84)	0.35(0.07)
10	0	0.6(0.2)	661(140)	0.7(0.4)
	14.4(0.6)	0.5(0.3)	558(52)	0.4(0)
20	0	1.4(0.3)	282(69)	0.15(0.07)
	14.2(0.2)	1.3(0.2)	233(130)	0.2(0.3)
30	0	1.1(0.3)	397(118)	0.15(0.07)
	14.0(0.6)	1.3(0.2)	145(53)	0.2(0)

[a] Concentration of contaminant added to the cleaner (g/L)

[b] Weight of contaminant deposited on the panels from TCA/EtOH solvent. Zero (0) mg/ft² indicates the clean panels (mg/ft²)

[c] Weight of contaminant left on the panels after cleaning by cleaner with added contaminant (mg/ft²)

[d] mg/ft²

Table 4
Effect of Agitation on Ability of the Cleaner to Clean And Prevent Re-deposition of Contaminant

	"Clean" Panel		"Dirty" Panel	
Flow rate[a]	Wt 1 (std. dev.)	OSEE (std. dev.)	Wt 2 (std. dev.)[b]	OSEE (std. dev.)
1. Variable process flow and agitated rinse water				
0	1.4(0.3)	837(96)	1.2(0.2)	806(119)
1	0.6(0.2)	593(71)	0.60(0.2)	552(74)
3.8	1.0(0.4)	665(210)	0.8(0.3)	804(121)
Average	**1**	**700**	**0.9**	**720**
2. Variable process flow and non-agitated rinse water				
0	3(1)	231(44)	4.4(0.9)	233(67)
1	1.3(0.2)	397(118)	1.1(0.3)	145(53)
3.8	2.0(0.3)	205(46)	2.3(0.4)	212(61)
Average	**2**	**278**	**2.6**	**197**

[a] Flow rate of cleaner L/min

[b] Weight of contaminant left on panels after being processed by cleaner (mg/ft²)

remaining on the panels and the amount re-deposited on the panels were the same. The results suggest that the contaminant adhering to the surface is in equilibrium with the solution contaminant concentration.

Figures 6 (weight gain) and 7 (OSEE) show the dependence of contaminant adhering to the surface on the solution contaminant concentration. Both sets of data show a similar trend. It should be noted that the curves shown in both figures are not the 'best-fit' curves, but instead are curves that the authors felt best represent the meaning of the data. The curves were plotted between the extremes of the points. The sigmoid shapes are thought to represent the best fit. Also, it should be noted that when the contaminant concentration reaches about 10 g/L, a distinct oil/cleaner separation was observed.

The NVR data shows no trends at all (column 5 in Table 3). This is probably because the amount of contaminant adhering to the panels, determined by weight change, is less than 2 mg/ft², which is below the sensitivity range of the NVR method.

Agitation

The effects of agitation of both the cleaner and rinse water were studied. Table 4 shows the results.

Both the weight gain and OSEE data show that agitation of the cleaner has no affect on the ability of the solution to clean or re-deposit contaminants. Agitating the subsequent rinse, however, produced cleaner panels. For example, based on weight gain data, the stagnant rinse removed about 85 percent of the contaminant, and the agitated rinse removed about 93 percent.

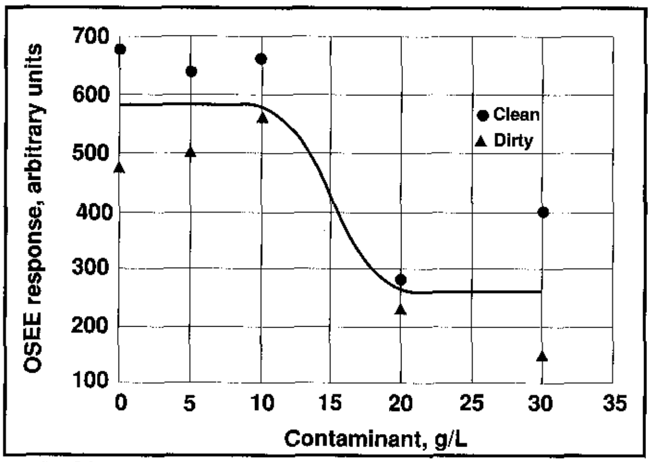


Fig. 7—OSEE response vs. contaminant concentration in the aqueous cleaner.

Conclusions

The first part of this study evaluated three test methods that can be used to monitor the performance of an aqueous cleaner. The test methods were weight gain, OSEE and NVR. The weight gain method has the widest dynamic range. It yields numerical data that are easy to reproduce, and are probably accurate enough to measure the performance of a cleaner for general metal surface cleaning. This method can be used as a routine process control procedure. The shortcoming of this method is that it is impractical for use on production hardware—test panels would be necessary.

For surface contamination between 1 and 10 mg/ft², OSEE is the most sensitive test method. It can be adapted as an online monitoring and non-destructive test method on actual hardware. Another advantage of OSEE, compared to other methods, is that it may be used to map large areas of contamination on a part (in our experiment an area of 3 x 4 in. was mapped). There are other surface analytical techniques, such as electron spectroscopy for chemical analysis (ESCA). Secondary ion mass spectroscopy (SIMS), etc., that will give more detailed surface information[6] These techniques, however, are limited to small surface areas (e.g., about 2 mm² maximum analysis area).

For low levels of surface contaminants, the NVR method is the least sensitive. First, even if the cleaner were loaded with contaminants up to 30 g/L, it is still able to clean surfaces to better than 2 mg/ft² of contaminant, which is below the sensitivity range of NVR. However, it is unlikely that a bath with this level of contaminant would still be used for production. Second, NVR only measures what is being removed by the TCA/EtOH solvent; it cannot measure what is being left on the surface. Third, the NVR method uses TCA/EtOH as the solvent to clean the surface, therefore continuing to use an ODC that aqueous cleaners were designed to replace.

In the second part of the study, it was demonstrated that the weight gain and OSEE tests can be used objectively to evaluate the efficiency of a cleaner under different conditions. The conclusions from this part of the study of the cleaner are:

- The cleaner will clean the surface to equilibrium with respect to solution contaminant concentrations;
- Agitation of the process solution is not important, but agitation of the rinse can improve the effectiveness of the cleaner significantly.

Although this study was concerned only with a limited number of contaminants and a single cleaner, the methodology should be applicable to different matrices of contaminants and cleaners.

References

1. M.D. Pedley et al., Ignition of Contaminants by Impact of High-Pressure Oxygen, in *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres,* 3rd vol. ASTM STP 986, D.W. Schroll, Ed., American Society for Testing & Materials, 1987; pp. 305-317.
2. A. Arora, *J. Environmental Sci.,* **28**(6), 30, 1985.
3. M.K. Chawla, *Plat. and Surf. Fin.,* **77**, 30, (June, 1990).
4. Standard Test Method for Nonvolatile Residue Halogenated Solvent Extract for Aerospace Components, American Society for Testing & Materials, vol. 10.05, 269 (1989).
5. C.D. D'Riuz, *Aqueous Cleaning as an Alternative to CFC & Chlorinated Solvent Based Cleaning,* Noyes Publications, Park Ridge, NJ, 1991; p. 40.
6. A.C. Greene, R.D. Cormia and Q.T. Phillips, *Microcontamination,* **10**, 37 (March, 1992).

Tam

About the Authors

Dr. Thomas M. Tam is employed as a process control engineer by Lockheed Missiles & Space Company, Inc., 1111 Lockheed Way, Sunnyvale, CA 94086. He has 13 years' industrial experience in electrochemical plating, chemical sensors, metal surface finishing, and statistical process control. Dr. Tam earned his PhD from the University of California at Davis. Before joining Lockheed, he was a post-doctoral fellow for two years at the Lawrence Berkeley Laboratory.

Ralph Wyngarden is employed by Lockheed Missiles & Space Co. as a process control engineer in process evaluation and optimization of surface finishing processes. He holds BS and MS degrees in chemical engineering from San Jose State University and the University of Idaho, respectively.

Anthony Naylor is a staff engineer at Lockheed Missiles & Space Co. In this capacity he has worked on a number of environmental programs aimed at reduction of environmental impact of metal finishing activities at Lockheed. He has made extensive use of statistical experimental design to optimize and validate less hazardous processes in the manufacturing area. He is a Registered Environmental Assessor in the state of California.