CLEANING LABORATORY EVALUATION SUMMARY

SCL #:	1996
DateRun:	07/31/1996
Experimenters:	Jay Jankauskas
ClientType:	E-Beam Equipment Manufacturer
ProjectNumber:	Project #1
Substrates:	Copper
PartType:	Coupon
Contaminants:	Cutting/Tapping Fluids, Lubricating/Lapping Oils, Oxides, Oil
Cleaning Methods:	Ultrasonics
Analytical Methods:	Gravimetric, Microphotography, Visual
Purpose:	FINAL TUR ASSESSMENT

Experimental Procedure:

E-Beam Equipment Manufacturer produces electron bean systems used for curing of coatings and inks. When producing this machinery, various parts will come in from machine shops that need to be cleaned of oils, dirt and other particulates. Of particular importance to their cleaning needs is the copper grids used in the window section of E-Beam Equipment Manufacturer's electron beam system. These copper grids are welded into a window frame and covered with titanium foil. This window area is a critical component of E-Beam Equipment Manufacturer's electron beam systems since it allows electrons to flow through the window while sealing the vacuum chamber which operates at 10-6 Torr. Therefore, the copper grids must be free of oils and oxides prior to welding to ensure proper operation of the vacuum and sufficient weld strength to withstand the vacuum pressure.
Before the copper grids are welded into the window frame, the grids must be removed of cutting fluids and copper oxide in order to achieve a satisfactory weld strength. The current chemistries that E-Beam Equipment Manufacturer uses for their various cleaning jobs are:

Product Name pH Comments
Kester Products #5520 cleaner .7 Used to remove copper oxide from grids.
Blue Coral Inc. Mag Wheel Cleaner 1.2 Used in conjunction with the Kester #5520 for grid cleaning.
Sun Products Degreaser 12.1 Used mainly to clean oils off of stainless-steel parts.

E-Beam Equipment Manufacturer performs their cleaning in a large sink on their production floor. The appropriate chemistry is applied on the part to be cleaned via a spray bottle. The parts are then scrubbed with Scotch-Brite pads until cleanliness is acceptable. Rinsing is done with water and/or alcohol depending on the part. All effluent cleaning solutions and rinse water are discharged down the drain to an MWRA sample point.
Due to the cleaning chemistries used and the nature of the cleaning, E-Beam Equipment Manufacturer has had MWRA violations due to pH and copper content. Due to this, E-Beam Equipment Manufacturer is currently looking for an alternative cleaning process and/or treatment method for their effluent stream to comply with all applicable regulations. E-Beam Equipment Manufacturer contacted the Surface Cleaning Laboratory for assistance with this project.

TESTING PERFORMED AT SCL
Two different solutions were looked into at the SCL. The first method involved treatment of E-Beam Equipment Manufacturer's current waste stream to meet MWRA standards. Since E-Beam Equipment Manufacturer generates a small waste stream (10 gal/day) the treatment method that stands out to be the most viable solution is evaporation. Using an evaporator to treats E-Beam Equipment Manufacturer's current waste stream has a number of problems:
1) The presence of phosphoric acid in the waste stream will be corrosive to ventilation equipment.
2) Copper and oils will be effectively removed but the phosphoric acid will be released into the atmosphere (some of the pollution source will not be Eliminated but will merely be shifted from water to air)

If E-Beam Equipment Manufacturer is to go with evaporation, they need to make their waste stream less corrosive. To try to accomplish this, the SCL looked into alternative aqueous chemistries that act as a copper brightener. Most copper brighteners contain a large amount of acid that attack the oxide immediately, however the acid also attacks the copper base metal which means that more copper is dissolved than necessary (thus the high ppm of copper in the wastestream). There are a few newer neutral aqueous cleaners out there that contain brightening agents that will attack the copper oxide while keeping the base metal attack to a minimum. The SCL found the following three different chemistries that were pH neutral and were supposed copper brighteners:

Product Name Comments

Inland Tech Citra-Safe Research performed by Lawrence National Laboratories stated that Citra-Safe was effective in removing copper oxide at room temperature.
Oakite Products Inproclean 4000T A semi aqueous pine terpene blend that was previously tested at the SCL. Proved to remove copper oxide when diluted with water.
Petroferm Inc. Bioact 50 A neutral pH aqueous solution that brightens copper and brass.

The above chemistries were tested against E-Beam Equipment Manufacturer's current chemistries and a variety of other acidic aqueous solutions for three important performance criteria:

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1) Removal efficiency of various cutting fluids.
2) Ability to brighten copper at room temperature.
3) Corrosion effects on base metal copper.

Detailed procedures and test results are shown on the attached SCL test report.

Results:

TURI SURFACE CLEANING LABORATORY

DATES: August 1st-August 23rd

EXPERIMENTER: Jay Jankauskas

CLIENT: E-Beam Equipment Manufacturer

SUBSTRATE MATERIAL(S): Copper

CONTAMINANTS: Various copper cutting fluids

ANALYTIC METHODS: Gravimetric and Microscopic.

The purpose of this trial is to find a cleaning chemistry for E-Beam Equipment Manufacturer that will conform to these three requirements.

1) Must be able to effectively remove cutting fluids and oxide from copper parts.

2) Cleaning chemistry must be as close to neutral as possible. This will help E- Beam Equipment Manufacturer comply with pH effluent limits and will reduce their copper discharge by reducing base metal attack.

3) An easy, cost-effective method must be devised to remove copper from effluent stream in order to comply with the MWRA 1.5 ppm discharge limit. Although requirement 2 should reduce this copper content, it will not totally eliminate it.

The first phase of the test involved evaluating the cleaning efficiency of several cleaning agents in removing cutting oils used to process copper parts. Cleaning efficiency was tested on 2"x2" 110 copper coupons contaminated with four different cutting oils which are shown below in Table 1.

Table 1: Cutting Oils used for E-Beam Equipment Manufacturer

Company Name-Trade Name	Chemical Composition
Citgo Petroleum Inc.-Cutting Oil 140	Refined Petroleum Oils, Highly Sulfurized Hydrocarbon Polymer, Chlorinated Alpha Olefin, Sulfurized Fatty Compound, Anti-mist agent.
Cooks Industrial Lubricants-Cook-Cut 20	Petroleum-Based Lubricating Oil, Sulfurized Fatty Oil Esters, Sulfurized 1 Decene, Chlorinated Paraffin.
Cooks Industrial Lubricants-Cook-Cut G165	Petroleum-based Lubricating Oil, Triglyceride, Ditertiary Dodecyl Polysulfide.
Cooks Industrial Lubricants-Cook-Cut 4984 Dark	Petroleum-Based Lubricating Oil, Sulfurized Fatty Oil Esters, Sulfurized 1-Decene.

All cleaning solutions tested were diluted to five percent. Cleaning was performed for five minutes at room temperature in a beaker with stirbar agitation. After cleaning the coupons were rinsed in 16.4 Ohm DI water for 10 seconds and then dried in a convection oven for one hour. Cleaning efficiency was determined by a gravimetric method. The coupons were weighed before and after contamination and after cleaning. The results from the gravimetric tests are shown in Table 2 and Figure 1.

Table 2: Percent Cleaning Efficiencies of Various Cleaning Agents on Cutting Oils.

	CUT 20		4984 Dark		Citgo 140		Cut G165	
Product	Ave.	StDev.	Ave.	StDev.	Ave.	StDev.	Ave.	StDev.

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Mag Wheel Cleaner	42.47	12.3	66.64	1.70	25.50	10.31	37.38	15.59
Valtron Sp2700KB	48.20	4.20	57.29	7.96	38.85	2.86	39.77	14.87
Mirachem 250	40.96	16.66	40.73	15.65	10.33	11.51	37.83	22.60
Kester 5520	15.03	3.78	42.83	5.40	11.08	8.05	55.10	9.70
Calgon Geo-Guard 3015	14.30	4.07	35.51	12.53	12.35	6.31	43.93	10.65
Calgon AC-8015	37.74	15.41	38.21	11.95	28.96	2.80	36.62	16.26
Sun Products Degreaser	54.34	21.91	33.38	19.11	44.86	17.56	70.31	12.49
Oakite Inproclean 4000T	64.00	13.13	66.93	23.29	73.26	1.57	35.00	1.13

The cleaning chemistries were also tested for their ability to remove copper oxide. One drop of each concentrated cleaning chemistry was placed E-Beam Equipment Manufacturer's copper part for one minute and then wiped off with an alcohol wipe. The copper part was viewed under a microscope at 100 times magnification. The microscope was then directed to a spot that showed half of the reaction spot and half of an unreacted spot. This area was then photographed with the lab's microcam. Scanned images of these photos are shown in Figure 2. The effectiveness of removing the copper oxide is determined by the brightness of the reacted side. Images that appear darker (Mirachem 250 and Calgon Geo-Guard 3015) were ineffective whereas brighter images (Oakite 4000T and Kester 5520) were effective.

All cleaning chemistries were tested for their tendency to attack copper base metal. For this test, three 2"x2" copper coupons from the lab were immersed in a 5% solution of each chemistry for 24 hours at room temperature. Before immersion all copper oxide was stripped off the coupons with an iron brush, the coupons were cleaned in a Crest 40kHz ultrasonic unit for 5

minutes and then rinsed with isopropyl alcohol. The coupons were weighed before and after immersion and a weight percent corrosion was calculated for one year period (the one year period is a standard used by most manufactures of cleaning chemicals). The results are shown below in Table 3 and Figure 3.

Table 3: Calculated weight percent base metal corrosion for a one year period.

Cleaning Chemical	pH of Conc	Ave	StDev.
Valtech Valtron 2700 KB	3	7.62	1.03
Kester 5520	0.7	8.45	0.82
Mag Wheel Cleaner	1.2	6.05	0.35
Calgon Geo-Guard 3015	1.7	2.43	0.68
Calgon AC-8015	2	3.66	0.21
Mirachem 250	0.8	6.43	0.75
Oakite Inproclean 4000T	7	3.72	0.29
Sun Products Cleaner and Degreaser	12.3	0.21	0.21

ADDENDUM TO TESTING:

On August 22nd, Samples of Bioact 50 and Citra-Safe were received in the lab from Petroferm Inc. and Inland Technologies respectively. Since the samples were received in the middle of testing, I decided to test each cleaner's ability to remove the copper oxide. If a cleaning chemistry proved successful, then I'll backtrack and perform cleaning efficiency tests and base metal attack tests.

Two liters of Petroferm Bioact 50 was diluted to 10 percent and heated to 150 F. A fewoxidized copper parts were placed in the solution and immersed for one hour. It appeared that some parts of the copper was brighter, but some spots were untouched. Although the Bioact shows some potential, there are other chemistries that I am currently testing that are more effective. Due to this I will only test out the Bioact 50 further if all other alternatives prove inadequate.

Oxidized copper parts were placed in an ambient full strength solution of Inland Tech Citra-Safe for two hours. After the immersion time was up, no visual effect on the copper oxide was noticed so the Citra-Safe will not be tested further.

Summary:

Substrates:	Copper

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Contaminants:	Cutting/Tapping Fluids, Lubricating/Lapping Oils, Oxides, Oil				
Company Name:	**Product Name:**	**Conc.:**	**Efficiency:**	**Effective:**	**Observations:**
Inland Technologies Inc	Citrasafe	5	0.00	☐	
Oakite Products	Inproclean 4000 T	5	64.00	☑	
Petroferm Inc	Bioact 50 (no longer available)	5	37.50	☐	
Kester Products	# 5520 cleaner	5	15.03	☐	
Sun Products Corporation	Grease Release Degreaser	5	54.34	☐	
Valtech Corporation	Valtron SP 2700 KB	5	48.20	☐	
Blue Coral Inc	Mag Wheel Cleaner	5	42.47	☐	
Calgon Corporation	Geo Guard 3015	5	14.30	☐	
Calgon Corporation	AC 8015	5	37.74	☐	
Mirachem Corporation	Mirachem 250	5	40.96	☐	

Conclusion:

CONCLUSIONS:
On the basis of cutting oil removal, copper oxide removal, pH and base metal attack, it seems that the Oakite Inproclean 4000T would be the best chemistry to use. It appears to remove oils better than the products that E-Beam Equipment Manufacturer currently uses and is less corrosive than all effective acidic chemistries. The one downside to the Inproclean 4000T is that it does not remove copper oxide as quickly as any of the acidic chemistries tested (a 30 min immersion in a 5-10% solution should give excellent results). Due to the rate at which E-Beam Equipment Manufacturer needs to clean these parts, this should not be a factor.

RECOMMENDATIONS
From the testing conducted it appears that the Oakite 4000T would be a successful alternative to their current cleaning chemicals with the following cleaning modifications:

1) Steel parts could be cleaned in a similar manner that E-Beam Equipment Manufacturer currently uses. This involves applying on with a spray bottle, brushing and rinsing.
2) The Oakite 4000T needs an increased time to remove the copper oxide. This could be easily accomplished by immersing the copper grids into a ten percent ambient solution for 30 minutes. Some agitation of the bath might be necessary to ensure fresh solution is in constant contact with the copper oxide. This can be accomplished either by sparging with compressed air or by stirring the solution every ten minutes or so.
3) Since copper oxide is being removed, there will be copper in the spent cleaning solution which will be over the 1.5 ppm limit. Due to this E-Beam Equipment Manufacturer should evaporate their waste stream. The substitution of Oakite 4000T for the currently used chemicals will alleviate both of the problems that E-Beam Equipment Manufacturer would have with evaporating their current waste stream. Prior to purchasing the evaporator, E-Beam Equipment Manufacturer should have the vendor test out the composition of the effluent stream to make sure it will be in compliance with all applicable regulations (Samsco, Inc. performs this service to its customers).

With the above modifications implemented, E-Beam Equipment Manufacturer should be able to maintain their current cleanliness standards while meeting all pertinent regulations.