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CORROSION INHIBITORS FOR WATER-BASE SLURRY IN MULTIBLADE SAWING

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ABSTRACT

In the JPL Low-Cost Solar Array (LSA) Project, the use of a water-base slurry instead of the standard PC oil vehicle was proposed for the multiblade sawing (MBS) silicon wafering technology. Potential cost savings were considerable; however, significant failures of high-carbon steel blades have been observed in limited tests using a water-based slurry during silicon wafering. Failures have been attributed to stress corrosion. Plans were developed to improve blade performance by adding a corrosion inhibitor to the slurry.

A specially designed fatigue test of 1095 steel blades in distilled water with various corrosion-inhibitor solutions was used to determine the feasibility of using corrosion inhibitors in water-base MBS wafering. Fatigue tests indicated that several corrosion inhibitors had significant potential for use in a water-base MBS operation. The fatigue life of blade samples tested in these specific corrosion-inhibitor solutions were found to exhibit considerably greater lifetime than those blades tested in PC oil.

INTRODUCTION

In the Low-Cost Solar Array (LSA) Project, the use of high-carbon steel blades (with a water-base slurry) for the multiblade sawing (MBS) technique has been proposed. This cutting-base system can reduce the cost of silicon ingot wafering significantly. Until now, PC oil, fully hardened 1095-steel blades and silicon carbide abrasive have been used for MBS ingot wafering. The PC oil, cutting abrasive and blades are "expendables" in the MBS technique. Short working lifetimes of these materials have made this slicing technique costly.

Significant failures of high-carbon steel blades have been observed in limited tests (Reference 1) using a water-based slurry during silicon wafering. These blade failures were determined to have been attributed to stress corrosion. Plans were developed to improve steel-blade performance by adding a corrosion inhibitor to the slurry.

A specially designed fatigue test of 1095-steel blades was developed to determine the feasibility of using corrosion inhibitors in water-base MBS wafering. Sample blades were fatigue-tested in distilled water with various types and amounts of corrosion inhibitor solutions added.

Results of failure analyses on saw blades from water-based slurry wafering, fatigue and corrosion-inhibitor testing on 1095 high-carbon steel blade samples and present and future test plans are summarized below.

FAILURE ANALYSIS OF BLADES

The typical fracture surface of a saw blade that failed in service during water-based-slurry silicon cutting action is shown in Figure 1. Corrosion products were observed on the fracture surface and intergranular fracture features were noted near the original cutting edge (Figure 2). This type of fracture surface suggested stress corrosion, a mechanism probably induced by an oxygen concentration cell effect (Reference 2), residual blade tensioning load and cyclic cutting loads. Considering these factors, a more descriptive term for the failure mechanism is corrosion fatigue. The concentration-cell effect can usually be seen on steel surfaces, resulting from a water-drop interaction.

In environments where oxygen concentration is variable, oxygen-deprived areas become anodic to oxygen-rich areas. In-service blade cracking was found to have started at the cutting edge of blades near the worn-unworn blade boundary (Figure 3). This failure site is located at the wetted-nonwetted interface on working saws. Thus oxygen surface concentration is most variable in this area on a blade where fully aerated cathodic areas drive corrosion in air-deprived areas.

To improve the service life of 1095 high-carbon steel for MBS wafering, slurry solutions carrying corrosion inhibitors with the potential of preventing or minimizing oxygen concentration-cell effects were proposed for evaluation. Inhibitors can (1) interfere with cathodic oxygen reduction on iron surfaces by maintaining a layer of absorbed oxygen on the surface or (2) passivate the steel by forming a stable surface oxide. Oxygen-scavenger or anode-cathode inhibitors (absorbed oxygen effect) were selected for blade-screening tests.

METALLURGICAL-MECHANICAL EVALUATION OF BLADE MATERIAL

A quantitative chemical analysis was made on sample blade material; the results are presented in Table 1. Chemical analysis indicated that the blade material was indeed 1095 high-carbon steel.

Metallographic examination of a cross-section sample of a blade was made. A photomicrograph of the blade material is shown in Figure 4. Spheroidal cementite particles were found to be uniformly sized and distributed, which indicated a fully hardened steel blade.

Hardness and standard tensile tests also were performed on the blade material. Rockwell hardness (Rc) was approximately 56. Yield and ultimate tensile-strength values for reduced-section samples were 242×10^3 lb/in.^{2} and 260×10^3 lb/in.^{2}, respectively (Table 2). These were the average values from five tests.

FATIGUE TESTING OF BLADES

To determine the feasibility of using corrosion inhibitors in water-base MBS wafering, a specially designed fatigue test of 1095-steel blades was developed. The width of blade samples for fatigue tests was reduced to control failure location. Blade thickness was 0.0086 in. and original width 0.250 in. The typical configuration of a blade sample and fractured blade sample are shown in Figure 5.

Fatigue-test loading conditions are give in Table 3. The mean load applied to the samples was approximately 70%, ≈200 KSI, of determined yield stress, similar to the blade tensioning load in actual blade packs. The minimum and maximum fatigue stresses were considered to be comparable with the loading range on a blade during MBS sawing. The controlled-test environment (aqueous fluid) was applied to the test sample by enclosing it in a silicone-sealed plastic bag, as shown in Figure 6.

Baseline fatigue test results of 1095-steel blade samples in PC oil, water and air environments are given in Table 4. Considerable improvement was seen in fatigue resistance from water to PC oil and again from PC oil to air.

Seven corrosion inhibitors were selected for fatigue-test evaluation and screening. Specific inhibitors tested included:

1. Cortec VCI-309. This product combines contact and volatile corrosion inhibitors to protect the metal surface. Use over 57°C (135°F) should be avoided. Continuous exposure to temperatures above 40°C (104°F) can result in a 40% reduction in lifetime protection.

Typical Properties:

Vapor pressure at 70°F (mm Hg)	0.0007
Solubility at 70° g/100 g solvent	
in H_2O	10.0
in slushing oil (SUS 65)	<3.0
Appearance	white crystals

Recommended concentrations of VCI-309 for water or aqueous systems range from 0.5% to 2.5%.

These types of inhibitors (VCI, volatile corrosion inhibitors) are amine salts. For analysis of this compound, a sample of VCI-309 was hydrolyzed in dilute hydrochloric acid. The extracted organic acid was identified by infrared analysis to be benzoic acid. Benzoic acid is a relatively strong organic acid that volatizes with steam and sublimes at about 100°C. The amine was considered to be propylamine or hexyldiamine with an equivalent weight by titration of 177. The pH of a 1% solution was 6.3 and the conductivity was 0.0020 mho/cm, indicating ionization.

2. Wrico H-1015. This product is designed for corrosion control and scale retardation in recirculating cooling systems. It is used when pollution-control regulations require a treatment containing no heavy metal regarded as pollutant. Wrico H-1015 is a blend of organic inhibitors with molybdate, polymer, phosphonate and a specific inhibitor for non-ferrous metals. It is a straw-colored mobile liquid weighing 9.8 lb per gallon. Maintenance of 75-400 ppm of treatment is recommended.

3. Wrico H-7654. This product is classified as a non-heavy-metal inhibitor to replace chrome, zinc and phosphate formulae. It is a blend of organic inhibitors that include tolyltriazole. It has a high stability with respect to chlorine and can be used over a broad pH range. Wrico H-7654 is a light-brown liquid with a drummed pH of 12.4.

4. Wrico H-7888. This product is used as an inhibitor in open, recirculating cooling systems. It is a blend of chromate, trizaole, phosphonate and organic additives. It can provide good stability at low chromate levels. Vendor literature describes it as being totally compatible with both non-oxidizing bromides and chlorination programs. Wrico H-7988 is a brown liquid with a drummed pH of 11.9.

5. Penechrome 17. This product is designed for a broad range of water recirculation applications. Penechrome 17 is a dark-brown mobile liquid of zinc chromate and hexavalent chromium, with organic additives. It has a pH of 3.9 in a 1% tap-water solution. Temperature exposure below 0°F will solidify it.

6. Leco. Rust-inhibiting compound, Part No. 811-108. Recommended dilution of this purple liquid is 1 part to 150 parts water.

7. Water-soluble oil. "Pigeon milk," used in machining operations.

The fatigue life of 1095-steel blade samples in the corrosion-inhibiting water-base solutions cited above (using preselected inhibitor concentrations in three tests each) are given in Table 5. Blade fatigue life in PC oil is included in Table 5 for comparison. Four of the seven corrosion inhibitors were found to have potential for water-base slurry MBS wafering application: Wrico H-1015, Wrico H-7654, Penechrome 17 and water-soluble oil. The fatigue life of blade samples in these solutions was found to be greater than that in the PC oil.

The inhibitor concentrations used for initial tests was relatively high. Optimization of inhibitor concentration has continued by use of the fatigue test. Table 6 gives the optimized concentration of inhibitors found so far. Although the optimization listed in this table is not final, the corresponding cost per gallon of MBS vehicle is given (abrasive cost is not shown). The cost of PC oil per gallon is shown for comparison in Table 6. Fatigue-test results for two different inhibitor concentrations and three inhibitor types are compared in Table 7. Reducing inhibitor concentration levels by an order of magnitude from those values shown in Table 5 caused significant reduction in fatigue life.

Wafering Tests

Silicon wafering tests using aqueous-based slurry systems are planned. Further optimization efforts are expected to provide adequate SiC abrasive slurry suspension and lubricity (to minimize blade drag). The addition of methyl cellulose, a water-soluble gel, for abrasion suspension, has been contemplated.

Two Varian 686-type multiblade saws have been renovated, installed and operated at JPL. Four demonstration or learning wafering runs have been made on one rachine using standard PC oil and 400- or 600-grit SiC abrasive. Pre-pinned blade packs of 100, 43, and 25 blades have been used with 8-mil-thick blades and 14-mil spacers. Wafering yields have ranged from about 60% to 90%. The other laboratory saw has been instrumented with closed-loop linear variable differential transformer controls and load transducer for blade-head operation control and readout. This machine will be used for alternative slurry-system research.

CONCLUSIONS

Fatigue test of high-carbon steel blades in several corrosion-inhibitor and water solutions indicate that four solutions have significant potential for water-base slurry MBS wafering application. The cost of these corrosion inhibitor and water solutions is significantly lower than that of PC oil, which is the vehicle presently used in MBS wafering systems.

REFERENCES

1. Holden, S. C., and Fleming, J. R., Slicing of Silicon into Sheet Material, Eighth Quarterly Report, Varian Associates, Lexington Vacuum Division, DOE/JPL 954374-78/1, April 3, 1978.

2. Uhlig, H. H., Corrosion Handbook, John Wiley, New York, 1948.

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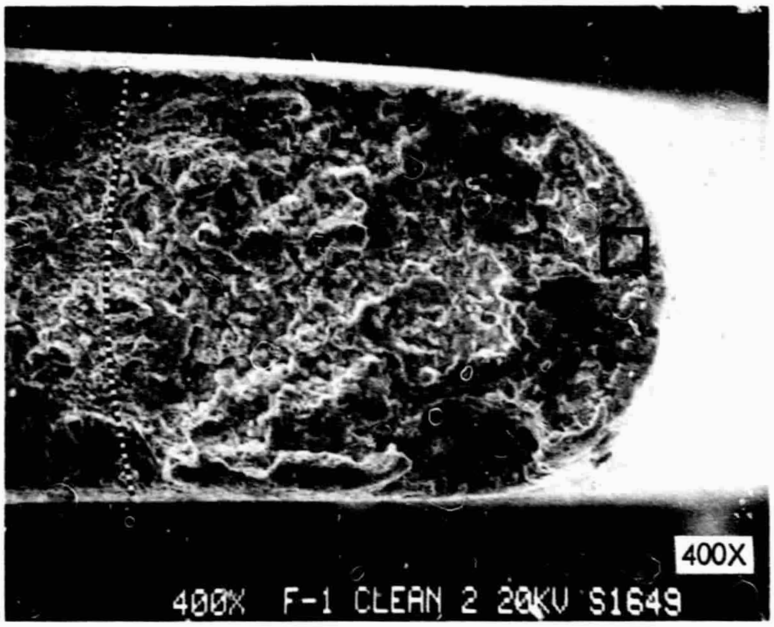

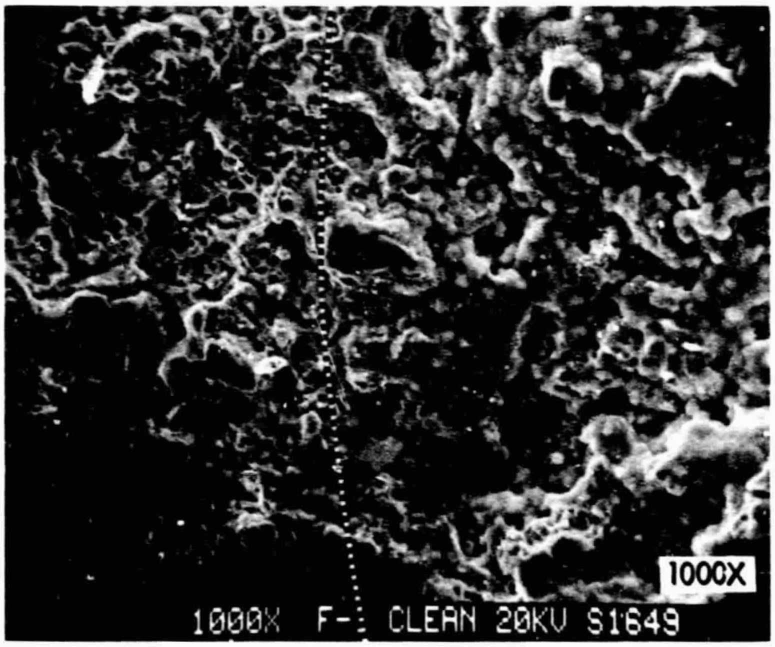

Figure 1. Scanning Electron Micrographs of Sample F-1. Corrosion-Product-Covered Area can be seen to the Left of the Dashed Line in 1(b).

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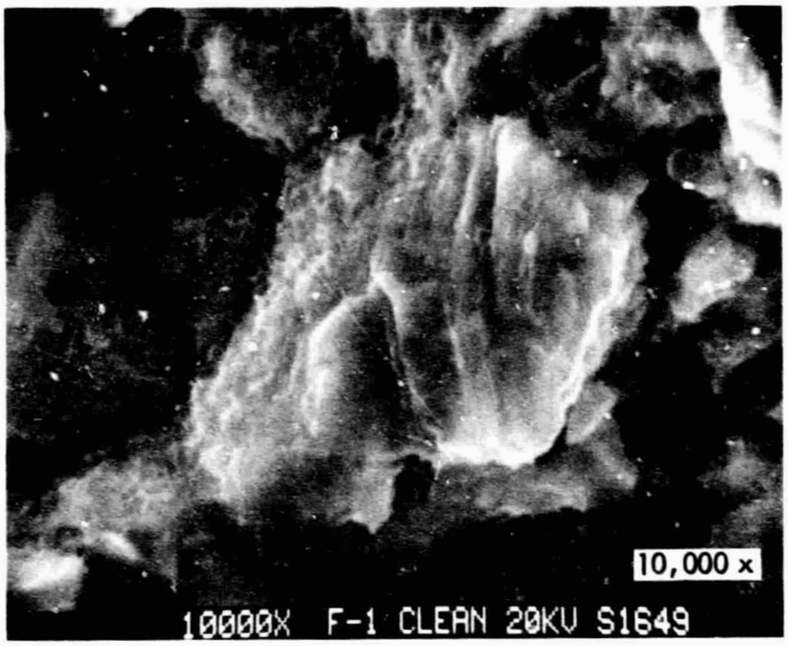

Figure 2. High Magnification Image of Fractured Blade Surface Showing Needle-Like Corrosion Products and Intergranular Nature of Cracking. Water-Base MBS Technique

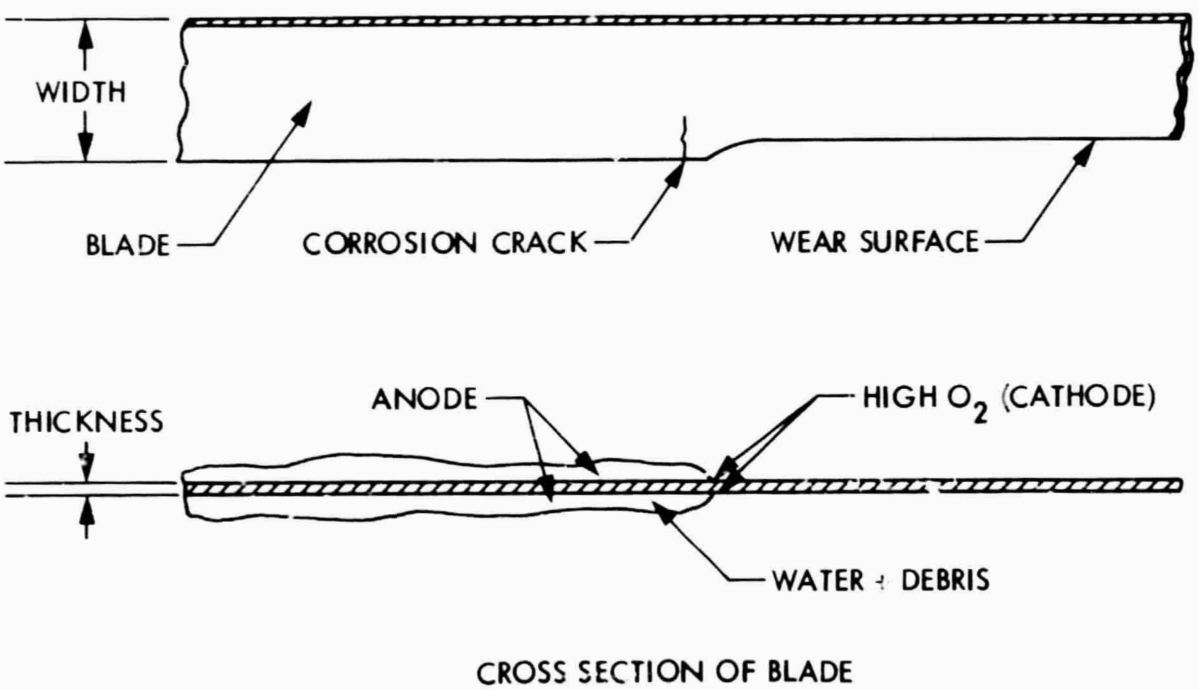

Figure 3. Blade Schematics Showing Location of In Service Failures and How the Oxygen Concentration Cell is Established

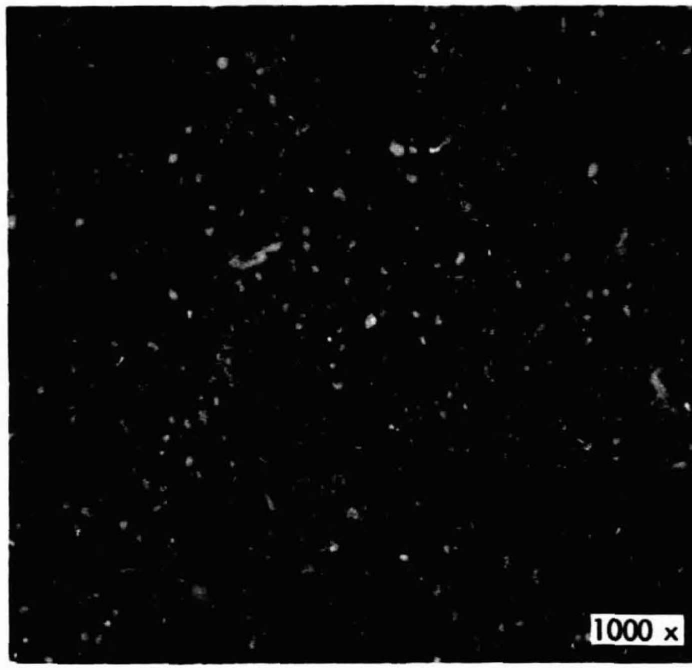

Figure 4. Micrograph of MBS Blade Material

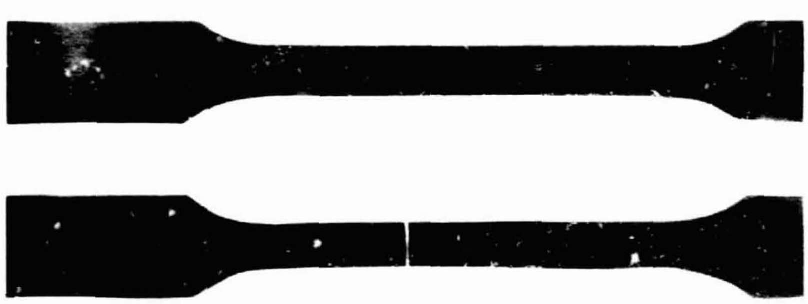

Figure 5. The Typical Configuration of Blade Sample Cross-Section Reduction and a Typical Fatigue Fracture of the Tested Blade Sample

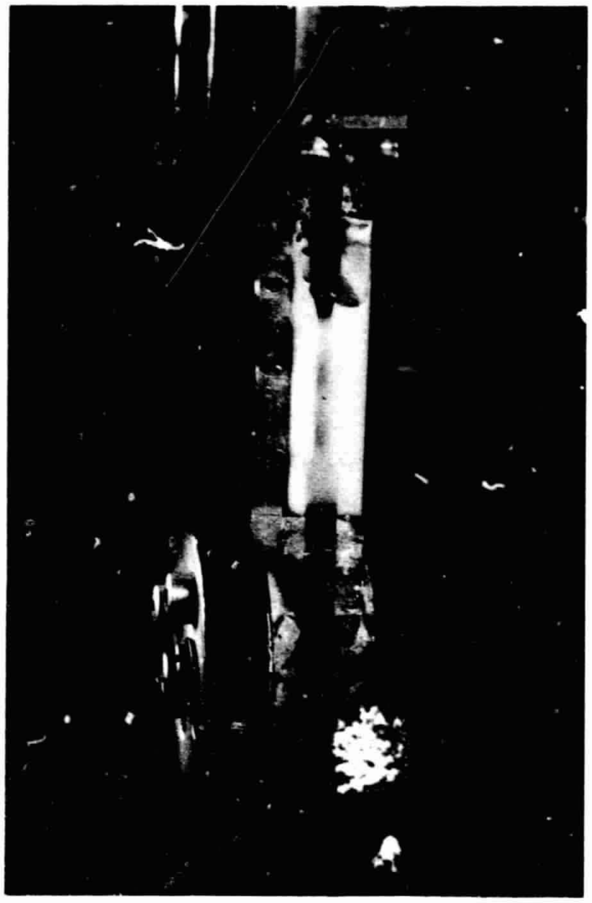

Figure 6. The Controlled Test Environment was Applied to the Test Section of Specimen by Using a Plastic Bag

Table 1. Quantitative Chemical Analysis of Varian Saw Blade by Peabody Testing Services P.O. No. GT 699592 CWO 19 2-5-80

Element	%
Mn	0.39
Si	0.21
P	0.015
S	0.011
Cr	0.15
Ni	0.07
Mo	<0.01
Cu	0.01
C	1.00
Fe	Base

Analysis Indicates Sample is 1095 Steel

Table 2. Mechanical Properties of 1095 Steel Saw Blade

	As-Received Sample	Section-Reduced Sample
Yield strength (10^3 lb/in.^{2}):	254 (250-259)*	242 (225-269)
Ultimate strength (10^3 lb/in.^{2}):	276 (267-285)	260 (246-293)
Hardness: R_c 56 (R_c [illegible] 58)		

( )* Showing minimum and maximum measured data of five samples

Table 3. Fatigue Test Conditions

$\sigma_{max} = 0.82\ \sigma_{yield}$	
$\sigma_{min} = 0.70\ \sigma_{max}$ (for fatigue test)	$\therefore R = 0.7$
Frequency = 10 Hz	
Max test duration = 10^6 cycles ($\approx$28 h)	

Table 4. Baseline Fatigue Test Results on 1095-Steel Blade Samples

Environment (or Slurry)	Number of Samples	Fatigue Life (Cycles)
PC oil*	3	242,500 203,700 357,200
Water	3	60,000 61,200 55,500
Air	5	All $>10^6$

*PC oil is a petroleum-based vehicle; it can be obtained from Process Research Corp.

Table 5. Fatigue Test Results of 1095-Steel Blade in Tap Water with Corrosion Inhibitors

Inhibitors	Fatigue Life (cycles)	Inhibitors	Fatigue Life (cycles)
PC oil	242,500 203,700 357,160	Wrico H-1015 (1% wt)	$>1 \times 10^6$ $>1 \times 10^6$ $>1 \times 10^6$
Soluble oil (2.5% Vol)	891,370 $>1 \times 10^6$ $>1 \times 10^6$	Penechrome 17 (0.3% wt)	$>1 \times 10^6$ $>1 \times 10^6$ $>1 \times 10^6$
LECO (0.67% Vol)	122,890 $>1 \times 10^6$ 37,500	Wrico H-7654 (0.4% wt)	$>1 \times 10^6$ $>1 \times 10^6$ $>1 \times 10^6$
CORTEC VCI-309 (5% wt)	49,945 $>1 \times 10^6$ $>1 \times 10^6$	Wrico H-7988 (18.1% wt)	210,600 52,700 $>1 \times 10^6$

Table 6. Cost Comparison: Selected Corrosion Inhibitors and PC Oil

Type of Inhibitor	Recommended Concentration	Cost of Slurry* $/gal
Tap water with:		
Soluble oil	2.5% volume	0.066
Penchrome #17	0.3% weight	0.023
WRICO H-7654	0.4% weight	0.046
WRICO H-1015	1.0% weight	0.156
PC oil	100%	5.00**

*Abrasive not included
**Additional wafer-cleaning solvent cost not included

Table 7. Fatigue Test Results of 1095-Steel Blade in Tap Water with Corrosion Inhibitors (Optimization Efforts)

Inhibitors	Fatigue Life (cycles)	Inhibitors	Fatigue Life (cycles)
Wrico H-1015 (1.0% wt)	>1 x 10^6 (3 tests)	Wrico H-1015 (0.04% wt)	79,090 81,700 682,110
Penechrome 17 (0.3% wt)	>1 x 10^6 (3 tests)	Penchrome 17 (0.03% wt)	62,470 166,100 410,120
Wrico H-7654 (0.4% wt)	>1 x 10^6 (3 tests)	Wrico H-7654 (0.04% wt)	73,370 72,550

DISCUSSION:

HEIT: Among the parameters for the evaluation of a suitable corrosion inhibitor, I notice the lack of any reference to concern over the effluent from those runs winding up in either a company-controlled or a municipally controlled sewage disposal plant. I would suspect some of the better performers are in the nitrite-chromate category, and they're rough as hell on the sludge.

O'DONNELL: I recognize your concern I guess several of those selected are considered non-heavy metal, non-polluting, as far as some of the requirements of EPA regulations are concerned.

DANYLUK: I'd like to make a comment about your fracture mode and the saw blades. Usually, the intergranular type of failure mechanism has almost always been related to some thermomechanical treatment of the steel. I was just wondering whether you had traced back the thermomechanical history of these individual saw blades.

O'DONNELL: We performed metallographic examination of these steel blades and essentially saw nothing abnormal. We saw the standard amount of martensitic formation, spheroidite-cementite particles. It looked like a fully hardened 1095 steel blade. Nothing abnormal appeared in the microstructure that we could ascertain. Many times some of these high-strength materials will show that type of fracture pattern when there is the evolution of hydrogen at the surface during the corrosion process. It's difficult to rule out the hydrogen embrittlement phenomenon that would also cause this fracture appearance.

DYER: The gist I got out of it was that it was very successful. You got some things that work and make it possible to use a water-base slurry.

O'DONNELL: In our fatigue test method--not real-world conditions, but as close to them as we felt we could get and be able to test a high number of blades and a high number of different corrosion inhibitors and concentrations--we did show significant results, in that four of them show very high promise and have very low cost.

ROSS: They have shown some success with regard to the problem of blade failure, but we're still a long way from water-based slurries in that we have lubricity concerns, we have grit suspension concerns, and we have a lot of drag forces in the system.

O'DONNELL: The one test that we've done in just this t week is of suspension. We didn't know if we'd have a lot of settling out, so we ran the pump system with the 2.5% by percent of volume of the soluble oil in water with silicon-carbide abrasive. I believe it was a 2 lb/gal ratio for 20 hours. Essentially we saw no more settling out of silicon carbide than we've seen in the PC oil systems.

LANE: I have question about the motivation for this work. I gather there's a real difficulty in recycling the oil that is a high cost item. Is that correct?

O'DONNELL: It is a high up-front cost per gallon. Jack (Ross) will probably comment more on trying to recycle PC oil. We haven't done any of that, but it is identified as a very high-cost consumable, which we felt we could significantly reduce.

ROSS: That's right. The initial cost of the PC oil was the concern even during the period when Varian was still working on the project. If the PC can be replaced with water, obviously cost would be radically reduced. We have since suggested that reclamation may be the ultimate answer; we've very recently embarked on an investigation of that. I'd say that we've made some significant progress in the past two weeks. We certainly haven't solved the problem yet. The cost of consumables in the MBS system is a major factor in getting the cost down. Not only the oil but the abrasive and the bladepacks also.