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Materials Compatibility Issues Associated With Aqueous Alkaline Cleaners*

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Abstract

As part of the Environmentally Conscious Manufacturing (ECM) technology, and in support of various mechanical assembly applications, several aqueous alkaline cleaners were studied as potential candidates for cleaning mechanical piece parts. Historically, ozone depleting and hazardous chlorinated cleaners have been used to degrease mechanical assemblies. In an effort to replace these chemicals, several cleaning processes, including aqueous alkaline cleaners, were screened as potential candidates using a variety of criteria, including: cleaning efficiency, materials compatibility, etch rate, corrosion, immersion tests, temperature/humidity exposure, and an exposure to a simulated indoor industrial environment. Cleaning efficiency was determined using visual examination, Auger electron spectroscopy, X-ray photoelectron spectroscopy, MESERAN, and goniometer/contact angle measurements. Several cleaners were identified as potential alternatives based solely on the cleaning results. Some of the cleaners, however, left undesirable residues. This paper will focus on materials compatibility issues of these aqueous cleaners after immersion tests, an etch rate study, and exposures to temperature/humidity and a standard industrial environment.

1. Introduction

With the push toward more environmentally conscious manufacturing, the use of acceptable materials and processes is essential. In support of this effort, an environmentally responsible cleaning process must be qualified for cleaning mechanical piece parts and assemblies. Traditionally, ozone depleting chemicals (ODC's) and other hazardous chemicals, such as trichloroethylene (TCE) and methylene chloride (MC), have been used as primary degreasers for removing machining lubricants and other contaminants. Several aqueous based formulations used with ultrasonics were studied as potential replacements for TCE, MC and ODC's. In qualifying these processes, the following criteria had to be fulfilled: 1) the cleaner had to clean as well as or better than the existing process, 2) the cleaning process could not leave undesirable residues behind, 3) the candidate cleaners could not affect the material in any deleterious manner (ex. swell, dissolve, corrode), 4) the cleaner could not etch the material to the point where it might affect tolerances, and 5) the cleaning process should meet Environmental, Safety and Health criteria. This paper will focus on how different metals were affected by immersion in the cleaners, etch rate, exposures to temperature and humidity, and exposures to a simulated standard indoor industrial environment after deliberate residues of cleaner were left on the surface.

2. Experimental

Four experiments were performed to determine the effect of the candidate aqueous cleaners on various metals. To provide an initial, uniform, reproducible, baseline surface, all samples were pre-cleaned by degreasing in TCE, rinsed with isopropyl alcohol and blown dry with filtered nitrogen. Depending on the surface to be tested some metals received additional processing. For example, before the etch rate study was performed, aluminum alloy 1100 received an additional alkaline non-etch cleaning step, followed by an acid deoxidize cleaning step.

In the first experiment, metals particular to the Switch Tube Assembly were immersed in concentrated and 10% by volume Brulin 815GD and Oakite NST for up to 17 hours. These two aqueous cleaners were selected for further materials compatibility evaluations based on initial screening test results. Additionally, in support of the neutron tube and neutron generator development, as well as other component evaluation studies, several metals were immersed in candidate cleaning solutions. To determine the effect of the aqueous cleaners on the metal substrates, weight measurements were taken before and after immersion with a Mettler balance, sensitive to 0.1 mg. If significant weight changes were measured, this normally indicated that a reaction had taken place between the substrate and the cleaner, such as etching of the metal surface.

The second experiment performed was an etch rate study, whereby seven aqueous alkaline cleaners were tested on aluminum alloy 1100. Of the metals particular to the switch tube, the selected alloy was considered the most susceptible to etching. The aqueous alkaline cleaners that were studied ranged in pH from ≈ 7.5 to 12.0. Concern was expressed that the higher pH cleaners would etch the aluminum. After the metal was degreased and prepared, coupons were placed in the various solutions and ultrasonically cleaned for 30 minutes at 135°F. The solutions were cooled to room temperature and analyzed for aluminum content using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). ICP-AES is sensitive to 1 ppm.

The third experiment performed involved exposure of different metals to a 40°C/70% relative humidity environment for 12 days. The test is designed to show materials compatibilities or incompatibilities. In this case, each metal was immersed in a candidate solution and then hung in the temperature/humidity chamber. Visual observations were performed before and after exposure.

The fourth experiment performed, involved exposure of metals (which had been dipped in the candidate solutions), to the Facility For Atmospheric Corrosion Test (FACT) Lab for 11 days. The FACT environment contains 10 ppb H_2S, 10 ppb Cl, 200 ppb NO_2, 35°C and 70% RH and simulates an uncontrolled indoor standard industrial environment. Visual observations were performed before and after exposure in the flowing mixed gas test cell.

3. Results and Discussion

3.1. Immersion Test Results

Weight measurements taken for the metals particular to the switch tube assembly (gold, Sn60-Pb40 solder, copper, Kovar (Fe-Ni-Co), Palco (Pd-Co), molybdenum, and niobium) after immersion for 17 hours, indicated negligible weight changes. The only real effect seen was a dulling appearance after Sn60-Pb40 solder was immersed in Brulin 815GD and Oakite NST. Weight loss measurements were also taken for copper, Kovar, 13-8, 15-5, and 17-4 precipitation hardened stainless steel (PH SS) materials, Aluminum Alloy 7075 and Aluminum Alloy 6061 after immersion for 10 days in 10% by volume Brulin 815GD, 10% by volume Oakite Citridet and 2.73 weight % Dirlum 603. A small weight change was noted on copper after immersion in Brulin 815GD. The weight change differences for the aqueous alkaline cleaners were compared to TCE, which served as the baseline cleaner.

3.2. Etch Rate Results

Table 1 shows the results of the etch rate study after ICP-AES analysis. The first two columns of the table show the results for each cleaning solution before exposure (virgin solution) and after exposure, as parts-per-million. The quantity of aluminum etched per coupon was then calculated from the solution volume, and the etch rate was calculated as mils/minute based on a 2 cm^2 surface area and 30 minutes exposure. As shown, the aluminum concentrations, determined in the majority of the cleaners after 30 minutes, were less than 1-part-million. Measurable values were determined for two of the cleaners (10% Micro Cleaner and 10% Oakite NST). The measurable values obtained for both cleaners were considered insignificant. These results can be considered as semiquantitative with uncertainties on the order of 100% (2X).

3.3. Temperature/Humidity Results

The following visual observations were noted for the different metals tested, after exposure to the temperature humidity environment: 1) copper revealed a greenish-blue corrosion product (which is normally indicative of copper chloride) mostly in the areas where the residue was concentrated, after intentional residues of Brulin 815GD, Oakite Citridet and Dirlum 603 were left on the surface. The Oakite Citridet samples also showed a blackening of the surface, 2) the PH SS materials showed no effect as a result of leaving cleaner residues behind, 3) aluminum alloy 7075 and 6061 for the most part looked good. Some pitting was observed on the surfaces and requires further examination with SEM and, 4) a brown-orange corrosion product was observed on the Kovar surfaces, which is normally indicative of iron oxide. A slight pitting was also observed on the Kovar surfaces. On

Kovar, Oakite Citridet appeared to be more aggressive than Brulin 815GD, which in turn appeared to be more aggressive than Dirlum 603. On the other hand, a black film and white crystal residue was observed on some of the Dirlum 603 surfaces.

3.4. FACT Exposure Results

The following visual observations were noted for the metals subjected to the FACT environment: 1) very little reaction was noted on copper, which had residues of TCE (copper generally has a native oxide which protects it from sulfidation). On the other hand, the aqueous alkaline cleaners etched the copper surface slightly, exposed bare metal, and left the surface black, 2) the PH SS materials revealed definite incompatibilities to Oakite Citridet. Additionally, all of the PH SS materials subjected to Brulin 815GD and Dirlum 603 showed increased activity on the surface, as compared to TCE, 3) very slight pitting was observed on both aluminum alloy 7075 and 6061 surfaces for all three aqueous cleaners and, 4) as compared to TCE, substantial corrosion was seen on Kovar for Oakite Citridet and Brulin 815GD. Oakite appeared worse than Brulin 815GD. Dirlum 603, on the other hand, may be slightly better than TCE.

Summary

Several tests were performed to determine the effect of leaving cleaner residues on metal surfaces. For the most part, insignificant weight changes were noted after the immersion tests. Two of the aqueous alkaline cleaners showed a measurable etch rate as determined by ICP-AES. The etch rates, however, were considered insignificant. Some materials incompatibilities were noted after exposures to a temperature/humidity environment and to the FACT which simulates an uncontrolled indoor industrial environment. Rinsing of these aqueous cleaners is critical, otherwise long-term reliability may be affected.

Table 1 - Etch Rate Study

Cleaner	Al Concentration			
	pre-clean (µg/ml)	30 minutes, 135°F (µg/ml)	(µg/coupon)	(mil/min.)
TCE	<1	<1	<20	<5.00E-05
0.5% Igepal 710	<1	<1	<20	<5.00E-05
10% Daraclean 212	<1	<1	<20	<5.00E-05
20% Daraclean 235	<1	<1	<20	<5.00E-05
10% Daraclean 282	<1	<1	<20	<5.00E-05
10% Brulin 815 GD	<1	<1	<20	<5.00E-05
10% Microclean	<1	170	3400	8.00E-03
10% Oakite NST	<1	50	1000	2.50E-03

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