Conf-9503119--4

SAND95-0855C

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Qualification of Environmentally Friendly Cleaners

Introduction

Sandia National Laboratories (SNL) has traditionally used chlorinated and fluorinated organic solvents for general degreasing applications. Many of these solvents have been labeled by the Federal Government as ozone depleting chemicals and as toxic and/or suspected carcinogens. As a result, these solvents will no longer be recommended for use within the DOE weapons complex. There are three major classes of materials that are of concern for cleaning: organics, metals and ceramics. Each of these materials has its own special cleaning problems. Solvents that were used in the past, such as 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE), were extremely efficient at removing everything from oils and greases to salts without leaving corrosive residues or permanently absorbing into the materials. These traditional degreasing solvents were essentially "all-in-one" cleaners: quick, reliable, and easy to use. Unfortunately, a "drop-in" cleaner for such a wide variety of materials and contaminants will probably never be identified. So far, it has been difficult to identify environmentally conscious cleaners that clean as well as TCE and TCA. Most alternative cleaners require more volume to do the job, and also require longer exposure to get the job done. With these things in mind, we are hoping to identify and qualify new cleaners that will take care of general classes of materials.

New cleaners are normally qualified for a process in three phases. Phase 1 is the initial screening study to select potential candidates. Phase 2 involves more extensive testing and evaluation of the candidates with the goal to select the top performers and recommend them for possible implementation into production after conducting compatibility and long-term aging tests. (Long-term aging experiments are of particular importance to SNL due to the extensive shelf-life requirement that the DOE has on its products.) Criteria such as the following were used to select the most promising nonhalogenated candidate cleaner: (1) the new cleaner must adequately remove a large profile of soils, (2) the new cleaner must not leave residues that would disrupt subsequent processes, (3) the new cleaner must not degrade materials (or corrode) to the point where subsequent processes are disrupted, (4) adhesion shear strengths of bonded substrates cleaned with the new cleaner should be comparable to baseline strength, and (5) (for electronics) high-voltage testing of samples cleaned with the new cleaner should be comparable to baseline voltage breakdown. Other important considerations when selecting environmentally conscious cleaner candidates are worker safety, recycling capability, waste disposal and cost. Phase 3 is the actual implementation of the new, environmentally safe cleaning solvents and processes into production.[1,2]

Experimental Protocol

Trichloroethylene (TCE) followed by an isopropyl alcohol (IPA) rinse was used as the baseline cleaning process for studies of precision mechanical devices and electronic assemblies. Common soils that the organic materials could be exposed to during

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

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production processes are Apiezon Grease M, Carnauba Wax, Dioctyl Phthalate, Epon 828, Krylon Acrylic Overcoat, OSR Mold Release, RAM 225 Mold Release, Starrett M1 Oil, Thalco 550 Mold Release, various solder fluxes, Vaseline, Velva Sheen, Versamid 140 Resin, WD-40, and Zinc Stearate Mold Release. Common soils (machining lubricants) that the metal and ceramic parts might see during production are Cook's 4625, Cook's 4639D, Cook's S697, 3-Boil, H&B 50% Lard/50% Mineral Oil, Ivory Snow/Lanolin, Cimtap, and Boelube. To determine the cleaning efficacy of the alternate cleaners, Oxygen Free High Conductivity Copper (OFHC Cu), aluminum 6061, 17-4 stainless steel (SS), eutectic solder (63Sn-37Pb, wt.%), and printed wiring board, PWB (polyimide quartz) were selected as substrates. Metal coupons were used for the initial cleaning efficacy screening to determine which cleaners did a good job without compromising materials compatibility. Materials compatibility was addressed after the cleaning efficacy issues were examined.[1,2]

Gross contaminants such as body oils and salts were removed through a precleaning step. The substrates were precleaned by degreasing in TCE, rinsed with IPA and blown dry with filtered dry nitrogen. An additional cleaning step, unique to each type of substrate, was performed after the degreasing process to provide uniform, reproducible, baseline surfaces for analysis. The Cu samples were etched with concentrated sulfuric acid, rinsed with flowing deionized water, and rinsed with IPA before blow drying with filtered dry nitrogen. The aluminum 6061 was taken through an alkaline non-etching cleaning step using an aqueous solution of $NaSiO_3$ and Na_2CO_3 at 149°F, rinsed with flowing deionized water, acid reduced with a solution of NH_4HF_2 and HNO_3 followed by a final deionized water rinse and a final filtered N_2 blow dry. The stainless steel samples were passivated in a 10% (by volume) HNO_3 solution and rinsed with deionized water. The PWB's were not treated any further.[1,2]

After these substrates were "cleaned", they were contaminated with a known amount of each soil. In the case of the precision mechanical devices, the aluminum and copper samples were placed on a hot plate for 5 minutes at ~150°F (except in the case of Ivory/Lanolin), to simulate the heat that the part might see during a machining process, and air-dried for 1 hour before cleaning. Substrates used in the electronic assemblies study were Cu, SS, PWB, and Al. Samples fluxed and solder dipped or contaminated with silicone mold release, were allowed to dry for 1 hour before cleaning. Removal of general contaminates were evaluated on aluminum panels for the electronic assemblies. The oils, greases, mold releases, and resins, normally encountered for the organics in production are listed above. These contaminants were applied to the aluminum substrates and allowed to air dry for 3 days prior to cleaning.[1,2]

The contaminated substrates were cleaned using potential candidates for aqueous and non-aqueous cleaners to determine cleaning efficacy for these soils. The "cleaned" substrates were then analyzed using a variety of techniques including visual examination, surface wettability with a contact angle goniometer, residual surface composition by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Meseran surface analysis (a measure of residual organic surface contamination) and Omega Meter (a measure of residual ionic surface contamination). Based on the results gathered after the initial screening, the top performers were recommended for phase two (materials compatibility and long term aging). At this point, the electronic assemblies study diverges somewhat from the precision mechanical devises study so they will be discussed separately below.

A considerable amount of work was done within the complex in the late 80's and early 90's, using the procedure described above, that led to the choice of d-limonene (a citrus based product) as the primary cleaner for electronics assemblies. Once d-limonene was chosen as the final candidate cleaner, a materials screening test was performed on all of the materials that were of concern. The types of organics that were addressed in this Environmentally Conscious Manufacturing (ECM) study were polystyrene foams, polysulfones, polyurethane elastomers, silicones, polyolefins, polyimides, and acrylics. Coupons of these materials were submitted to a "worst case scenario" d-limonene exposure (15 min. immersion in d-limonene at 50°C, rinsed with IPA, N_2 blow dried followed by a 45 min. vacuum bake at 71°C) to determine materials compatibility. If there was a weight gain/loss or change of appearance in the material at any step of the test, further investigation was required. Phase 2 also addressed long-term aging issues. Almost every conceivable situation associated with bonding and encapsulating electronic parts after any cleaning step was investigated in long-term aging studies. These studies simulated the aging process so that bond strength and encapsulation integrity were determined. Once the long-term aging and compatibility concerns were satisfied, Phase 3 began. At SNL and Allied Signal Kansas City Division, d-limonene was qualified for electronic components in new weapons and is in the process of being qualified for existing weapons.[1]

As part of a sister ECM program at SNL, aqueous cleaners are being considered as potential replacements for cleaning mechanical piece parts (metals and ceramics). Some of the metals that have been studied at SNL are gold, Sn/Pb, aluminum, copper, Fe-Ni-Co, Pd-Co, molybdenum and niobium. This research indicates that aqueous cleaners are the alternatives of choice for metals; however, at this time, no single cleaner has been recommended for metal piece part cleaning. Brulin 815GD has been recommended for the manufacture of several components (Switch Tubes, Smoke Generators, and Exploding Bridgewire Detonators), however, it has not yet been fully qualified for War Reserve (WR) use. Aqueous cleaners have the advantage of being non-combustible, non-VOC's, and some clean as well as TCE; however, compatibility issues (such as corrosion and etching) must also be considered. The metals listed above were all subjected to various compatibility tests for corrosion activity when submitted to new cleaners. The new cleaners were also evaluated for cleaning efficacy of common soils found in production situations. The same analytical techniques were used, as listed for the electronic assemblies (above), to determine cleaning efficacy for common soils seen during production. Efforts are underway to select a general "metals cleaner" and WR qualification will begin as in the case of d-limonene.[2]

Conclusions

Sandia National Laboratories has been in the business of replacing halogenated solvents with environmentally friendly cleaners for many years now. This year, a special effort has been made to combine the cleaning work that has been underway for several different projects so that lessons learned in each study can be broadly applied. To date, we have found that there are no simple "drop-in" alternative cleaners that will perform as an "all-in-one" cleaner as did TCE and TCA. However, through the joint ECM study, environmentally friendly cleaners have been identified and new cleaning processes have been qualified for WR production for some products. Our goal is to qualify general alternative cleaners that can be used on components and systems so that all ozone depleting, toxic and/or suspected carcinogenic cleaners are replaced at SNL.

References

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