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CLEANING WITHOUT CHLORINATED SOLVENTS

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CLEANING WITHOUT CHLORINATED SOLVENTS

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ABSTRACT

Because of health and environmental concerns, many regulations have been passed in recent years regarding the use of chlorinated solvents. The Oak Ridge Y-12 Plant* has had an active program to find alternatives for these solvents used in cleaning applications for the past 7 years. During this time frame, the quantity of solvents purchased has been reduced by 92%. The program has been a twofold effort. Vapor degreasers used in batch cleaning operations have been replaced by ultrasonic cleaning with aqueous detergent, and other organic solvents have been identified for use in hand-wiping or specialty operations.

In order to qualify these alternatives for use, experimentation was conducted on cleaning ability as well as effects on subsequent operations such as welding, painting and bonding. Cleaning ability was determined using techniques such as X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) which are capable of examining monolayer levels of contamination on a surface. Solvents have been identified for removal of rust preventative oils, lapping oils, machining coolants, lubricants, greases, and mold releases. Solvents have also been evaluated for cleaning urethane foam spray guns, swelling of urethanes and swelling of epoxies.

Introduction

Recently many regulations have come to pass regarding the use of chlorinated solvents. Not only are solvents such as 1,1,1-trichloroethane (TCA) and 1,1,1-trichlorotrifluoroethane (CFC-113) considered ozone depleting substances and will no longer be produced in 1996, but others such as methylene chloride and perchloroethylene are also being stringently regulated. Methylene chloride and perchloroethylene are considered suspect carcinogens. Stringent emission controls are currently being proposed under the Clean Air Act for these chemicals, and their wastes are controlled under the Resource Conservation and Recovery Act (RCRA). This became a particular problem for the Oak Ridge Y-12 Plant.

*Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

The regional Environmental Protection Agency (EPA) office ruled that wipes that had come into contact with F-listed RCRA wastes must also be handled as RCRA wastes. The Y-12 Plant handles uranium and any wipe which comes into contact with uranium is regarded a low level radioactive wastes. If one of these solvents are used to wipe uranium, the wipe is then classified as a mixed waste because it is considered both RCRA and radioactive. Currently, handling of mixed waste is very difficult. Thus, the desire of the plant was to find a substitute for the solvents being used so that the wipes would only be classified as a radioactive wastes. Since 1987, personnel at Y-12 have been active in a chlorinated solvent substitution program.

Initially, steps were taken to determine the amount of these solvents being used and how they were being used. This was done by first compiling purchase records from the plant stores for a three year time frame. Surveys were also issued to each of the areas in the plants asking for their usage. After this data were obtained, visits were made to each of the facilities to observe the operations and talk to the personnel using the solvents. The usages throughout the plant included cleaning parts prior to and after machining, inspection or operations such as welding, bonding, plating, painting, and heat treating; drying metal chips; cleaning urethane foam spray guns; and cleaning meter mix machines. A priority list was established for attacking these usages and work began.

To determine levels of cleanliness obtained from solvents or aqueous cleaning, comparative studies were conducted using coupons which are prepared, cleaned and analyzed using X-ray photoelectron spectroscopy (XPS). This technique is capable of looking at monolayer levels of a surface. The surface is bombarded with X-rays and the electrons which are ejected are then measured. The energies at which these electrons are ejected differ for various elements or elements in different binding states. Thus, one can determine the elements present on the surface. When conducting cleaning studies, the ratio of the element most associated with the contaminant, generally carbon, to the base metal, such as iron or chromium is calculated. The lower this ratio, the cleaner the surface.

Not only does the cleaning ability have to be assessed in order to determine possible alternatives but other factors such as compatibility and effects on subsequent operations must also be addressed. Generally, compatibility tests are conducted by submerging metals to be cleaned into the cleaner for a given period of time and then examining the metal to determine if any corrosion is evident. Compatibility tests can also be conducted on nonmetallic materials using submersion techniques and recording weight gain as a function of time. Compatibility issues must be addressed not only with materials being cleaned but the materials used to handle the cleaning materials such as gloves and squirt bottles. Some solvents may not be compatible with handling materials and will leach out or partially dissolve these materials, leaving a residue upon the part being cleaned. Effects upon subsequent operations are typically measured by cleaning the part and then performing the operation. Some type of physical testing is then conducted to determine if any deleterious effects are noted.

Aqueous Cleaning

As early as 1984, personnel at Y-12 had begun testing aqueous cleaning systems as a replacement for vapor degreasers using chlorinated solvents due to concerns such as the possibility of formation of phosgene gas from welding operations in the vicinity of the

degreasers. Initially, a pressure spray washer was obtained by this particular area. However, the cleaning obtained with this system was not adequate and other systems were then pursued. One aqueous cleaning technique which was found favorable was ultrasonic aqueous cleaning.

Ultrasonic cleaning works by using high frequency sound to cavitate a liquid medium. Cavitation creates micro bubbles which burst on the surface of the part being cleaned mechanically scrubbing the part. This mechanical action combined with the chemical cleaning action of the solution provides a powerful cleaning technique. There are several factors which can influence the effectiveness of ultrasonic cleaning such as frequency, liquid medium, and the coupling action between the liquid and the equipment.

Frequencies for ultrasonic equipment range from approximately 20 kHz to 90 kHz. A minimum frequency of approximately 18 kHz is required to cavitate a liquid medium. The cavitation energy is inversely proportional to the frequency. Thus, the lower the frequency, the greater the amount of cavitation energy which in turn increases cleaning ability. However, some delicate parts may not be able to withstand the cavitation forces at the lower frequencies. Electronic components are normally cleaned at higher frequencies.

The liquid medium also affects cleaning performance. The viscoelastic properties of the liquid affect its ability to cavitate. Water has been shown to cavitate more intensely than organic solvents, thus aqueous systems are an ideal choice for use in ultrasonics. Properties such as surface tension and vapor pressure play an important role in cavitation. The addition of detergent to water will lower the surface tension and increase cavitation. Heating the water to raise the vapor pressure will also increase cavitation. Optimum operating temperatures for ultrasonic aqueous detergent systems generally range from 50 to 60°C.

There are several considerations which should be taken into account when selecting a detergent for use in ultrasonics or in other aqueous cleaning techniques. If the intent is to discharge to local sanitary sewer systems, determine what the local requirements are for discharge. Many areas have limits on phosphates, silicates or other chemicals which may be found in detergents. Thus, those type detergents may not be an appropriate choice. The detergent selected must also be compatible with the parts being cleaned. For instance, highly alkaline solutions such as sodium hydroxide or sodium ethylenediaminetetraacetic acid (EDTA) are not compatible with aluminum. The pH of the solution may also affect ability to discharge to the sanitary sewer. Many detergents may leave a slight residue upon the surface. Ability to rinse the detergent could be a concern. Sodium compounds are very tenacious and difficult to rinse. If this type of residue could present a problem in subsequent operations then that type detergent should be avoided. The type of surfactant used is an important consideration and is dependent upon your particular application. Nonionic surfactants such as ethoxylates are generally better for oil removal. These type surfactants also tend to foam more so caution should be used in implementing these detergents. Detergents which foam should not be used in spray systems. Anionic surfactants such as sulfonates are better for particulate removal and generally do not foam.

As stated earlier, the operating temperature is an important factor. Higher temperatures (50-60°C) are optimal for cavitation properties and will soften or dissolve contaminants more readily. However, one must be careful not to exceed the cloud point of

the detergent. At the cloud point or the point at which the detergent becomes cloudy, the detergent micelles break and are no longer capable of attracting or sequestering the contaminant. Some detergents are considered high temperature detergents and are cloudy at low temperatures but will clear upon heating while other detergents are clear at low temperatures and become cloudy upon heating.

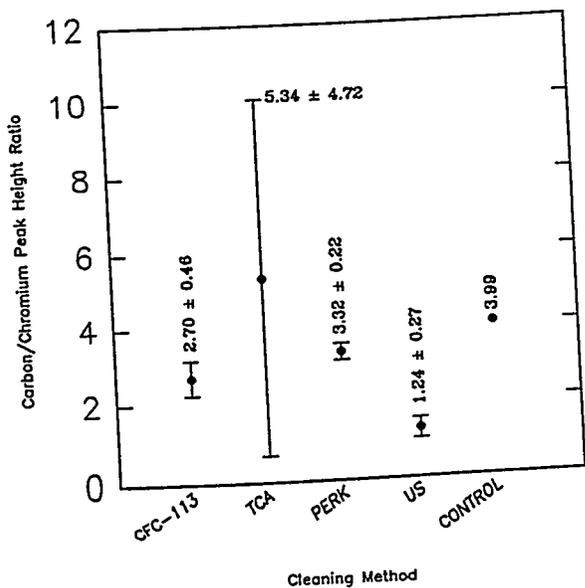
Rinsing is another important consideration for aqueous cleaning system. Demineralized water is preferred not only for rinsing but in making up the cleaning bath. Salts or chlorine found in tap water can cause corrosion of some metal surfaces. A portion of the detergent will also be used in capturing these contaminants found in the tap water thus decreasing the amount of detergent available to sequester the contaminants on the parts. Calcium present in tap water has also been shown to react with metasilicates or pyrophosphates found in some detergents to form calcium metasilicate or calcium phosphate. These substances are opalescent gels that are difficult to filter out and could deposit upon parts. Rinsing with hot water is also advisable because hot water tends to dissolve detergent residues more readily and evaporates more quickly decreasing the possibility of corrosion. If the part is rinsed until it becomes warm, the water will evaporate very readily. Agitation also plays a role in rinsing. More aggressive agitation such as ultrasonics will tend to knock off residues more readily than gentle spraying or submersion. However, minimal amounts of detergent residue may not affect your subsequent processes. Thus, it would not be necessary to use the more aggressive agitation.

If highly active metal is to be cleaned using aqueous methods, precautions can be taken to prevent corrosion. Use of demineralized water is a must to prevent corrosion. A thoroughly cleaned part which does not have salt deposits or chlorine present does not corrode. One can also use rust inhibitors in the rinse water to prevent corrosion. A wide variety of these are available on the market. A rust inhibitor should be chosen which will not affect subsequent steps. For instance, some inhibitors may prevent coatings from adhering properly and should not be used in applications where parts will be coated.

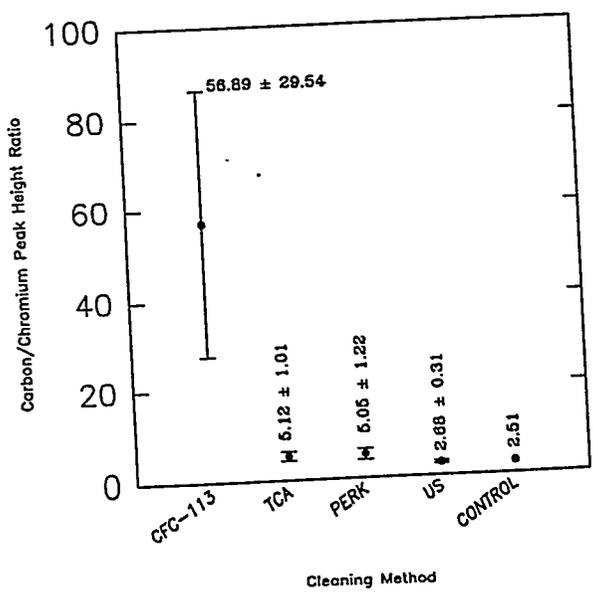
When using aqueous cleaning systems, drying must be considered. This step could be as simple as leaving parts out in the air to dry to as complex as a vacuum drying application. Drying is very dependent upon the type of part being cleaned. If there are nooks and crannies that water can be trapped in then vacuum drying may be required. Forced air drying may be adequate for drying many parts which do not have complex geometries.

Many studies have been conducted to determine the effectiveness of ultrasonic aqueous cleaning. Figure 1 shows the results of three coupon studies conducted to compare ultrasonic aqueous cleaning to vapor degreasing with chlorinated solvents. In each of these studies, metal coupons were initially cleaned to establish a baseline level of cleanliness. One sample was retained as a control sample. The remaining samples were contaminated with the various contaminants and allowed to sit overnight. The samples were then cleaned by vapor degreasing in either perchloroethylene (perk), 1,1,1-trichloroethane (TCA) or trichlorotrifluoroethane (CFC-113) for 15 min or were ultrasonically cleaned (US) in 5 vol% Oakite NST Aluminum Cleaner (NST) for 15 min at $\sim 55^{\circ}\text{C}$, rinsed by flushing in demineralized water and blown dry with argon. The samples were analyzed using XPS with the results shown in Figure 1. As shown the ultrasonic cleaning yielded samples which were as clean or cleaner than the vapor degreasing and were more reproducible.

Removal of Rust Preventative Oil From 304L Stainless Steel



Removal of Machining Coolant From 15-5 PH Steel



Removal of Lapping Oil From 4330V Steel

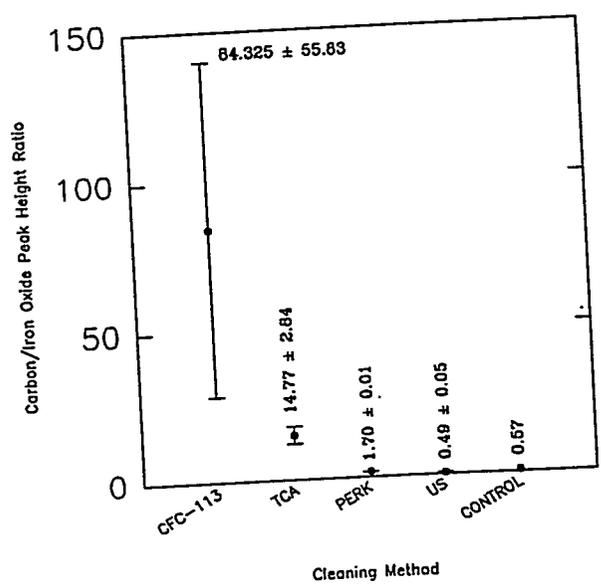


Figure 1 - Effectiveness of Ultrasonic Cleaning Versus Vapor Degreasing

Ultrasonic aqueous cleaning has been in use in the Y-12 Plant since 1984. The technique cleans well, is reproducible and generates low toxicity water waste which is treated easily. The drawbacks associated with this type of cleaning technique include noise and cost. At the 20 kHz level, irritating subharmonics are produced that require soundproof insulation and/or ear protection. Capital equipment cost is another consideration which should be taken into account.

Solvent Cleaning

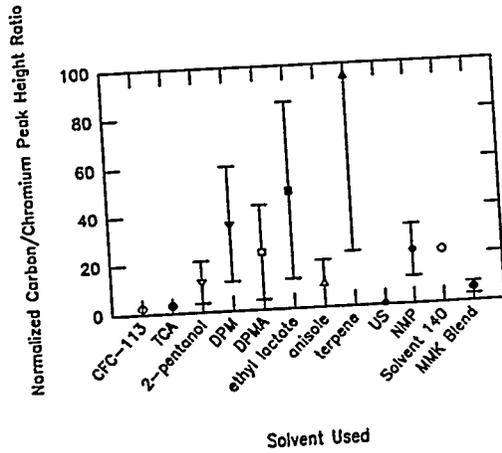
Although aqueous cleaning is an attractive alternative, some cleaning requirements do not lend themselves to the batch cleaning mode or aqueous cleaning. For instance, cleaning parts at the machine or removal of materials which are not water soluble can be a problem. Personnel at Y-12 have investigated solvent alternatives for these type applications. When evaluating solvent alternatives to chlorinated solvents, the only options are other halogenated solvents which are nonflammable or combustible solvents. In order to avoid characterization as a RCRA characteristic waste, the solvent must have a flash point greater than or equal to 140°F. This was a major consideration in certain areas of the Y-12 Plant.

Several studies including cleaning efficiency, compatibility, and effects on subsequent production operations have led to the selection of two solvents for use in the plant for general cleaning purposes. These solvents are Solvent 140, a high flash mineral spirits composed mainly of C10-C13 branched and straight chain hydrocarbon molecules, and a solvent blend developed, patented and licensed by personnel at the Y-12 Plant hereafter referred to as MMK Blend. The Solvent 140 is used in moisture sensitive areas of the plant because slight amount of moisture absorbed in the MMK Blend and the presence of an -OH group in this blend can react with materials in these areas. The MMK Blend is used in the remaining areas of the plant. Solvent 140 is very effective in removing oils and hydrocarbon contaminants since it is a hydrocarbon. However, it tends to float on the surface of water and water based coolants. The MMK Blend addresses this problem and will undercut water or water based coolants. The blend also gives the added advantage of having a hydrocarbon solvent to remove hydrocarbon contaminants with a polar solvent which aids in the removal of more polar contaminants.

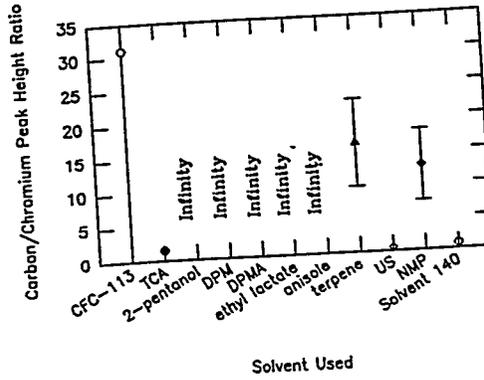
Several studies were conducted to determine if Solvent 140 and the MMK Blend are effective in removing substances commonly used in the Y-12 Plant for processing including rust preventative oils, lapping oils, machining coolants and fingerprints. Figure 2 shows the results of some of these studies. The studies were conducted by initially cleaning samples of various steels using ultrasonic aqueous cleaning in order to establish a baseline level of cleanliness. The samples were smeared with the contaminant until a visible layer was seen. A given amount of solvent such as CFC-113, TCA, 2-pentanol, dipropylene glycol methyl ether (DPM), dipropylene glycol methyl ether acetate (DPMA), ethyl lactate, anisole, terpene, N-methylpyrrolidone (NMP), Solvent 140 or MMK Blend was sprayed onto the sample using a squirt bottle. The sample was then wiped dry and analyzed using XPS. Solvent 140 and the MMK Blend gave the best overall results of the solvents tested.

Some concern had arisen regarding these cleaning studies since they were performed on coupons and not on actual parts. To alleviate these concerns, an analytical rinse study was

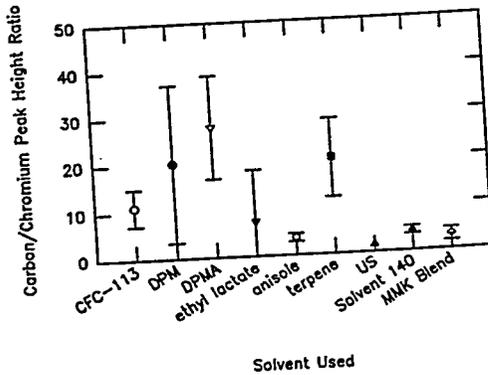
Removal of Lapping Oil



Removal of Rust Preventative Oil



Removal of Machining Coolant



Removal of Fingerprints

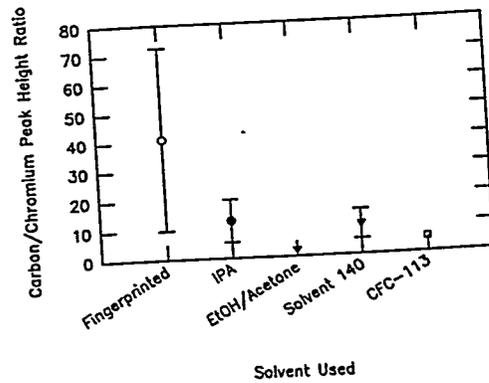


Figure 2 - Effectiveness of Solvents on Cleaning Various Contaminants

conducted on three different part types of different sizes. Four uranium parts of each type which had been coated with rust preventative oil and had been sitting on the shelf for a long period of time were randomly selected and cleaned by hand using current production processes with either CFC-113, which had currently been used in the area, or the MMK Blend. The MMK Blend was the solvent which would be implemented in this particular area. The parts were then rinsed in distilled methyl chloroform to extract any remaining oil left on the part. The rinse solution was evaporated to dryness, dissolved in distilled carbon tetrachloride and analyzed using infrared absorbance. The results of this experiment are shown in Table One. The parts cleaned in the MMK Blend had much less oil present than those cleaned in CFC-113.

Table One - Results of Analytical Rinse Experiment

Part Type	CFC-113 Cleaned µg Oil Remaining	MMK Blend Cleaned µg Oil Remaining
1	1922 ± 868	674 ± 189
2	2413 ± 1067	1419 ± 355
3	609 ± 206	387 ± 107

Compatibility experiments were conducted on the materials on which the solvent would be used as well as materials which are used to handle the solvent or may have incidental contact with the solvent to determine if there would be any problems related to the solvent use. Metal compatibility tests were conducted using a 72 hour immersion test with an artificial crevice. Both Solvent 140 and the MMK Blend were tested in this matter on depleted uranium (D-38) and its alloys, uranium-6% niobium and uranium-0.8% titanium; the aluminum alloys 1100, 7075 and 5083; iridium; the steel alloys 15-5 PH, 4330V, 1010, and HP 9-4-20; and beryllium. Slight oxidation was noted on the D-38 sample in Solvent 140 but was not perceived to be enough to be of concern. No corrosion was observed on the other metals and the solvents were approved for use. Other nonmetallic materials such as lithium hydride and beryllium oxide (BeO) were submerged in Solvent 140 with no effects noted.

Compatibility studies were also conducted on several polymeric materials such as polymethylpentene, polyethylene, mylar, silicone rubber, polyvinyl chloride, and diallyl phthalate which may come into contact with the solvent. These tests were conducted on Solvent 140 since it would be the solvent of choice in these areas as compared to methyl chloroform which was the solvent that was being used. The Solvent 140 had much less effect on the materials than did the methyl chloroform which was being used.

Long term compatibility issues were also addressed using two different means. A test unit was built using Solvent 140 for cleaning purposes replacing the methyl chloroform and CFC-113 which was being used in this area. This unit was subjected to temperature cycles under standard operating conditions. The unit exhibited no ill effects from the use of Solvent 140.

Compatibility of gloves used in handling the solvent was also addressed due to workers' health concerns and to possible contamination resulting from the use of the gloves. Weight gain studies were initially conducted on polyethylene, neoprene, butyl, latex, nylon, nitrile and vinyl gloves. Permeation studies were conducted on nitrile and latex gloves which had the best compatibility results. Tests were also conducted to determine possible contamination which may result from use. From these tests, nitrile gloves were recommended for long term or submersion use while latex was recommended for use in short exposure conditions.

Another major concern with changing solvents used in cleaning applications was the effect on subsequent production operations. Several evaluations have been conducted to determine effects on bonding, welding and painting.

Bonding studies were initially carried out that evaluated the effect on bonding of Solvent 140 or the MMK Blend when used to clean certain substances from surfaces to be bonded. Initially steel butt tensile specimens were ultrasonically cleaned in aqueous detergent, rinsed and allowed to dry in order to establish a baseline level of cleanliness. Three sets each of these samples were retained as controls. The remaining samples were coated with the substance which was to be removed and the substance was allowed to dry. Three sets each of the samples were cleaned with a given amount of solvent and bonded. The specimens were allowed to cure and tested for ultimate tensile strength. The Solvent 140 and the MMK Blend gave strengths in the same range as the CFC-113, methyl chloroform or other solvents typically used except in one instance. In this particular case, there was not adequate adhesive to cover the surface on one specimen which caused the strength to be lower than the remaining specimens and caused the average strength to be lower. If this data point were neglected, strengths were in-line with other strengths obtained.

Bonding studies were also conducted to determine the effect of Solvent 140 for a final cleaning on certain substrates. Butt tensile specimens of BeO and beryllium were initially cleaned ultrasonically in aqueous detergent, rinsed and allowed to dry. Five sets of these specimens were retained as control samples. Five sets each of the remaining specimens were cleaned with Solvent 140 or methyl chloroform which was the solvent being used in the area. The BeO specimens were bonded with an epoxy formulation while the beryllium specimens were bonded with a urethane. All of the test specimens were cured, and tested for ultimate tensile strength. No negative effects were seen from the use of Solvent 140.

Two bonding studies were also conducted on aluminum substrates using adhesives which had not been used in prior studies. These adhesives were Epon 828/Epon 871/N-aminoethylpiperazine and Accrabond PR14368. The specimens were initially treated using a standard Forest Product Laboratories (FPL) chromic acid etch. Five sets of samples were retained as control specimens while five sets each of the remaining specimens were cleaned with Solvent 140 or methyl chloroform. The samples were bonded, cured and tested for ultimate tensile strength. No deleterious effects were noted from the cleaning medium.

Welding is another operation which follows cleaning that was of concern. In order to address this concern, a study was conducted on electron beam (E-beam) welding of aluminum. Aluminum was chosen because it is known for being sensitive to hydrocarbon contamination when welding. E-beam welding is also one of the welding techniques which

is more susceptible to problems due to contamination. The major concern was that since Solvent 140 evaporates slowly that some residual solvent may be present on the surface during welding. This would increase pumpdown rates and the hydrocarbon contamination from the solvent may cause blow-outs in the weld or lead to weld porosity. A total of 30 aluminum alloy 5086 weld rings with a square butt joint with an alignment step were used for the study. A narrow weld was chosen to increase the probability of retaining any porosity in the weld. Root voids are common in narrow aluminum welds and were anticipated in this experiment. Half of the rings were to be cleaned using methyl chloroform which is the solvent that was currently in use in the production area. The remaining rings were cleaned with Solvent 140. No difference was seen in the pumpdown rates due to the cleaner used and no blow-outs were noted. The rings which were cleaned with Solvent 140 had significantly less porosity (6.47 ± 7.07 pores) than those cleaned with methyl chloroform (21.53 ± 22.488 pores).

A laser beam welding study was also conducted on stainless steel parts by personnel at Lawrence Livermore National Laboratory which compared Solvent 140 to CFC-113 for cleaning of welds. Hydrostatic burst pressure tests of weld qualification coupons were performed to verify the integrity of the welds for each cleaning method. The burst pressure values were independent of cleaning procedures for the welds.

Painting studies have been conducted on two different substrates, aluminum and nickel. Aluminum test panels were cleaned with Solvent 140 and a urethane coating applied. The panels were then submitted to a steam test. No loss of adhesion was noted due to cleaning with Solvent 140 as compared to prior cleaning techniques using methyl chloroform. Nickel panels were also cleaned with Solvent 140 and then coated with an epoxy primer followed by a urethane topcoat. Steam tests were again conducted with no differences noted in adhesion.

Due to the success of these tests, these solvents were implemented at the Y-12 Plant and have been successfully utilized since 1991. No major problems have been noted with their use. As with any alternative, there are some drawbacks associated with these solvents. These are higher flash point solvents and they do evaporate much slower than the chlorinated solvents. This requires adjustments in handling. These solvents are also combustible and require different handling techniques to comply with Occupational Safety and Health Administration (OSHA) regulations. However, these drawbacks can be overcome.

Summary

In implementing alternatives, consideration should be given to levels of cleanliness, compatibility issues, effects on subsequent production operations and compliance with various regulations. Testing should be conducted for specific applications as one technique may not work for all applications or contaminants present. Personnel at the Oak Ridge Y-12 Plant have been able to successfully implement ultrasonic aqueous cleaning and cleaning with alternative solvents in a production environment. Some drawbacks are associated with the alternatives but these drawbacks can be overcome and a successful substitution program can result.