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OAK RIDGE Y-12 PLANT

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DEALING WITH THE CHLORINATED SOLVENT SITUATION AT THE OAK RIDGE Y-12 PLANT

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DEALING WITH THE CHLORINATED SOLVENT SITUATION AT THE OAK RIDGE Y-12 PLANT

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Recent events regarding health and environmental problems associated with the use of chlorinated solvents have prompted the Oak Ridge Y-12 Plant* to investigate substitutes for these materials. Since 1987, the purchase of chlorinated solvents at the Y-12 Plant has been reduced by 92%. This has been accomplished by substituting chlorinated solvent degreasing with ultrasonic aqueous detergent cleaning and by substituting chlorinated solvents with less toxic, environmentally friendly solvents for hand-wiping applications. Extensive studies of cleaning ability, compatibility, and effects on welding, bonding, and painting have been conducted to gain approval for use of these solvents. Toxicity and waste disposal were also assessed for the solvents.

1. Introduction

Because of health and environmental concerns, chlorinated solvents have received intense scrutiny in recent years regarding their use as cleaning agents. Both trichlorotrifluoroethane and methyl chloroform (1,1,1-trichloroethane) are considered ozone-depleting chemicals (ODCs) and are being regulated as such. Production of these chemicals is to be phased out by 1996. Perchloroethylene and methylene chloride are considered suspect carcinogens. All of these solvents are classified as Resource Conservation and Recovery Act (RCRA) wastes which require controls on the handling of the wastes and disposal only at permitted facilities. The Environmental Protection Agency (EPA) Region IV office ruled that wipes which had come in contact with F-listed RCRA wastes must also be handled as RCRA wastes; this prompted fast action at the Oak Ridge Y-12 Plant. This ruling meant that wipes which were used for cleaning uranium with CFC-113 were considered both a RCRA and a radioactive waste, or mixed waste. As recently as the late 1980s, there were no treatment facilities permitted for handling of mixed wastes in the country. Thus, the wastes accumulated and permitted storage facilities were being filled quickly. Once the facilities were full, production would have to be stopped unless permission from the EPA could be obtained to open more storage facilities. Since means were available for handling of radioactive wastes, these wastes could be disposed of if the RCRA component was removed from the process. Efforts had been ongoing for substitution of chlorinated solvents at the Y-12 Plant at that time, but this ruling accelerated the schedule.

*Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-ACO5-84OR21400.

2. Experimentation

The substitution of chlorinated solvents at the Y-12 Plant basically has been a twofold effort. First, batch processing using vapor degreasers has been replaced with ultrasonic cleaning with aqueous detergent, and secondly, chlorinated solvents used in hand-wiping operations or other specialty operations such as urethane foam spray guns or softening of adhesive bonds have been replaced with other organic solvents.

Ultrasonic Cleaning

Due to problems which had arisen with degreasing operations in the plant, evaluations began on cleaning alternatives for vapor degreasers in the early 1980s. In one particular shop, there were concerns that welding operations in the vicinity of the perchloroethylene vapor degreaser would produce phosgene. Problems had also arisen with conducting dye penetrant tests and with black spots appearing on parts when heat treated following cleaning operations. This led to a series of studies regarding ultrasonic aqueous cleaning.

Several factors were found to influence the effectiveness of the ultrasonic cleaning such as frequency, packing of the transducers, energy supplied to the transducers, liquid medium used, temperature of the liquid medium, and the coupling between the liquid medium and the transducers.

Various equipment manufacturers offer equipment at frequencies which range from approximately 20 kHz to 90 kHz. The lower the frequency, the more intense the cavitation; thus, the more mechanical cleaning action. One disadvantage with the lower frequency is that the noise levels increase at these frequencies. Ear protection or acoustic insulation is generally required for these tanks. The other disadvantage is that the number of dead zones or nodes normally increases at the lower frequencies. This is handled by dense packing of the transducers which minimizes the number of dead zones present and by slowly rotating parts through the solution.

The amount of energy supplied to the transducers is critical. Enough energy is required to obtain sufficient cavitation. However, if too much energy is used, the phenomena of surface cavitation can occur. Surface cavitation occurs when cavitation exists at the water/transducer interface and does not penetrate further into the liquid bath. This cavitation serves only to heat the bath.

The liquid medium is important in that you want a medium which will cavitate properly. Water has been shown to have the best cavitation products of any liquid [1], thus, aqueous detergent systems are an excellent choice for ultrasonic cleaning. The choice for your detergent is important in that you want a detergent which will reduce surface tension, undercut and then suspend contaminants and keep contaminants from redepositing. Because of regulations regarding disposal of phosphates, silicates, and other "builders," one may wish to avoid detergent formulations that contain these components. The cloud point is

also important in selecting a detergent for your operation. Once a detergent clouds, phase separation is occurring and your ability to solubilize and emulsify oils decreases. Oil solubilization and cleaning efficiency increase if the detergent is maintained near, but not exceeding, the cloud point. Higher temperatures may be preferred for removal of some oils or waxes as the higher temperature helps to melt the contaminants and makes solubilization and removal easier. Thus, cloud points should be considered when selecting a detergent. However, too high of a temperature can have a detrimental effect on the cavitation of certain brands of cleaners.

Proper coupling between the transducers and the liquid medium is important so that the energy is transferred efficiently from the transducers to the liquid. A quick test to determine if sufficient cavitation is present for cleaning of parts is the aluminum foil erosion test. If sufficient cavitation is present, 30 s immersion of a 1-mil-thick sheet of aluminum foil will be sufficient to erode holes in the foil. This method is also good for determining where dead zones or nodes may be located in your tank. When cleaning electronics, jewelry, or other parts which may be damaged easily, a higher frequency tank (40 kHz) should be used.

A number of studies have been conducted regarding the effectiveness of ultrasonic aqueous detergent cleaning versus vapor degreasing or ultrasonic cleaning with chlorinated solvents. The effectiveness of ultrasonic cleaning with large parts, in small diameter tubing, parts with narrow clearances, and other complex geometries has been tested. More details regarding this work can be found in the report "Solutions for the Chlorinated Solvent Debacle" [2].

There are disadvantages with ultrasonic aqueous detergent cleaning. Generally, a rinse step is required with aqueous cleaning to remove detergent residues. Hot demineralized water is generally suggested because it tends to dissolve detergent residues more readily than would cold water and will evaporate more readily. A drying step is also required with aqueous cleaning. In some cases, room temperature drying may be adequate whereas other cases may require some type of oven drying.

Solvent Cleaning

The main use of chlorinated solvents at the Y-12 Plant, other than vapor degreasing, was hand-wiping of parts after machining operations. This wiping was done to remove rust-preventative oils, coolants, and lubricants prior to or following machining or part inspection. In evaluating substitutes for solvents in this or any other area, several factors are examined. These include compatibility, effects on subsequent operations, toxicity, and cleaning ability. Toxicity of possible alternatives was generally evaluated by searches through sources such as *Sax Dangerous Properties of Materials*, *Registry of Toxic Effects of Chemicals (RTECS)*, and the *Hazardous Substance Data Bank (HSDB)*. The Industrial Hygiene Department at our plant was also included in this process.

Initially, selection of possible alternative candidates was conducted using Hansen

Solubility Parameter Theory [3]. This theory breaks down solubility into three parameters: dipole-dipole interaction, hydrogen bonding, and London dispersion forces. Solvents with similar values have similar solvent properties. Solvents were also selected from a variety of chemical families. Initially, solvents were only selected which had low toxicity and a closed-cup flash point exceeding 100°F due to fire protection concerns. Later this value was changed to 140°F to eliminate concerns with RCRA wastes. (Solvents with flash points less than 140°F are considered characteristic RCRA wastes.) These solvents were then subjected to several tests to determine their feasibility as alternatives.

Normally, cleaning ability is determined by using small sample pieces and comparing the old method of cleaning to the new. These samples are analyzed using X-ray photoelectron spectroscopy (XPS). XPS is capable of evaluating cleanliness to the monolayer level. This analytical method works by bombarding a surface with X rays and evaluating the electrons which are ejected. Each element can be identified on the basis of its binding energy signature. Thus, one can determine the elements present on the surface. For comparison purposes, a peak height ratio of the element associated with the contaminant to the base metal is calculated. This ratio is normally a carbon/chromium (C/Cr) ratio. The lower the ratio, the cleaner the surface. This type of testing has been conducted on a wide variety of hard surfaces using contaminants such as machining coolants, lubricants, drawing compounds, lapping oils, rust-preventative oils and fingerprints, and using a variety of solvents such as Solvent 140, ethyl lactate, dipropylene glycol methyl ether (DPM), propylene glycol methyl ether acetate (PMA), dipropylene glycol methyl ether acetate (DPMA), d-limonene based formulations, N-methyl pyrrolidone (NMP), anisole, isopropanol, and ethanol/acetone. For removal of the water-based machining coolants, the straight-chain hydrocarbons, the aromatic hydrocarbons, short-chain esters, and a short-chain alcohol were found to be effective cleaners. Rust-preventative oils, lapping oils, and oil-based lubricants were removed by the straight-chain hydrocarbons confirming the "like dissolves like" principle. Fingerprints were removed with the alcohols and the straight-chain hydrocarbons.

Compatibility testing was the next step in determining alternatives. Compatibility with the metals being cleaned was initially conducted using 72-hour submersion tests. This type of testing was conducted on uranium, uranium alloys, aluminum alloys, steel alloys, beryllium, and magnesium with Solvent 140, DPM, tripropylene glycol methyl ether (TPM), PMA, ethyl lactate, anisole, DPMA, and 2-pentanol. The only problems noted were that ethyl lactate stained 4330 V steel and anisole increased the oxidation of uranium. The compatibility test with uranium and Solvent 140 also showed some slight oxidation although not enough to be considered a problem. The oxidation may have been caused by the hydrocarbon trapping immiscible moisture on the surface. There were also concerns regarding how well the hydrocarbon would displace water or water-based coolants from the surface, since the hydrocarbon floats on water. This led to a formulation of a solvent blend (U. S. Patent Number 5,207,838) which contains the hydrocarbon blended with a slightly polar solvent. This blend causes the solvent to have a slight affinity for moisture and hence ability to displace

water. The addition of a polar solvent to a nonpolar solvent also increases your overall solvent power. When tested for compatibility with uranium, the uranium surface remained silver and showed no signs of oxidation. The blend has also been tested for its cleaning ability on the contaminants mentioned above and was successful.

Since the Solvent 140 and the water-displacing solvent blend appeared to give good results for cleaning a variety of contaminants and was acceptable from a compatibility standpoint, further testing was conducted in order to prove-in these solvents for production use. Long-term compatibility tests, compatibility with polymeric materials, and tests regarding effects on welding, bonding, and painting were conducted.

Long-term compatibility tests consisted of placing various materials cleaned with these solvents in a helium atmosphere and cycling it through temperatures which the parts may see. Outgassing of the parts was measured to determine if any problems were present. No problems were noted over a two-year time frame.

Weight gain tests were conducted for a variety of polymeric or nonmetallic materials that may come in contact with the candidate solvents. These materials included polymethylpentene, polyethylene, mylar, silicone rubber, polyvinyl chloride, beryllium oxide, lithium hydride, and diallyl phthalate, as well as glove materials such as nylon, butyl rubber, neoprene, nitrile, and latex. These results were compared to results from similar tests with the chlorinated solvents. The hydrocarbon-based solvents had less of an effect on the materials than did the chlorinated solvents. No major problems were noted. Compatibility and permeation tests conducted with the glove materials indicate that latex gloves work well for short-term exposures, however, if the glove will be in contact with the solvent for long periods of time, nitrile gloves are preferred.

Bonding studies were conducted for a variety of substrates using the Solvent 140 and the solvent blend with several epoxy and urethane formulations. No detrimental effects on bond strength were noted. Specimens cleaned with these solvents gave similar or better strengths than did those cleaned with the chlorinated solvents.

Welding studies were conducted on electron-beam welding and laser welding of aluminum and steel, respectively, cleaned with Solvent 140 as compared to the chlorinated solvents. Again, no major problems were noted with the samples cleaned with the Solvent 140 having statistically less porosity in the welds.

Experiments were also conducted on cleaning surfaces with Solvent 140 prior to painting operations. Steam tests indicated no problems with adhesion of the paint to the substrate following this type of cleaning.

Prior to implementation, cleaning studies were conducted on production parts using an analytical rinse technique for analysis and Fourier Transform Infrared Spectroscopy (FTIR) with a Spectropus™ attachment. With this attachment, a

hard vacuum is not required for testing. These tests confirmed the results from the XPS that the Solvent 140 and the water-displacing blend worked as well as or better than the chlorinated solvents used in the past. These solvents were also evaluated in one of the shops for a trial period of one month prior to implementation. No major problems were noted and the solvents were implemented in the remainder of the shop areas.

Solvents which have been implemented in other specialty operations include anisole for cleaning of urethane foam spray guns and N-methyl pyrrolidone for softening of urethane or epoxy bonds for debonding operations. The anisole works well for cleaning the guns but is considered a RCRA characteristic waste. Other solvents such as dibasic esters and N-methyl pyrrolidone will also work in this application; however, they tend to evaporate more slowly. N-methyl pyrrolidone will soften urethane and epoxy bonds. However, this solvent does take longer to work than does methylene chloride. There are other solvents which may be blended with the NMP that will enhance its performance.

The disadvantages of the new solvents are the slow evaporation rates compared to the chlorinated solvents and the combustibility concerns. Care must be taken to handle the solvents properly.

3. Conclusions

There are alternatives available for the use of chlorinated solvents in cleaning purposes. Ultrasonic cleaning with aqueous detergent has been found to work as well as or better than vapor degreasing with chlorinated solvents and yields more consistent results. This type of cleaning produces a waste which is handled easily. The disadvantages of ultrasonic aqueous cleaning are the requirement for a rinse and drying step, the initial capital investment, and the noise abatement issues. Both Solvent 140 and the solvent blend have been found to yield good cleaning results, no compatibility problems, and no adverse effects on production. These solvents were initially implemented in 1990 at the Y-12 Plant, and there have been no problems arising from their use.

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