CHLORINATED SOLVENT SUBSTITUTION PROGRAM AT THE OAK RIDGE Y-12 PLANT

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ABSTRACT

Due to the many regulations concerning chlorinated solvents, the Oak Ridge Y-12 plant has been actively seeking replacements for these solvents for the past seven years. In seeking these replacements, many factors were considered. Among these factors were toxicity, flammability, means of disposal, compatibility, effects on production, and cleaning ability. Using these factors as guidelines, the replacement program at Y-12 has been a two-fold effort. Large vapor degreasers operated in a batch mode have been replaced with ultrasonic cleaning with aqueous detergent. This cleaning method uses a low toxicity detergent which works as well if not better than vapor degreasing and yields a biodegradable waste which is handled easily. The second effort involved finding organic solvents which could be used as replacements for small squirt-bottle-type operations or specialty operations such as cleaning meter mix equipment or dissolving adhesive bonds. Currently, the Y-12 plant is in the process of changing the small cleaning operations to a solvent system which uses a high flash mineral spirits in areas where moisture sensitivity is a concern and a blend of this mineral spirits with dipropylene glycol methyl ether in other areas. There are some problems associated with replacements for chlorinated solvents such as slow evaporation rates and flammability. However, due to the regulations on chlorinated solvents, replacement is still an attractive option.

INTRODUCTION

In recent years, several regulations regarding chlorinated solvents have been established. The Montreal Protocol, which has been ratified by the United States, calls for a ban on production of chemicals such as methyl chloroform and trichlorotrifluoroethane due to their association with the depletion of the ozone layer. Other chlorinated solvents such as perchloroethylene and methylene chloride have been identified as suspect carcinogens. All of these solvents mentioned above are listed wastes under the Resource Conservation and Recovery Act (RCRA) which strictly restrains handling and disposal. The Environmental Protection Agency (EPA) Region IV office has also mandated that any wipes or rags used for cleaning or degreasing with one of these solvents must also be treated as RCRA wastes. This mandate along with a ruling by a federal court judge that "Atomic Energy Act" process residues are regulated under RCRA as mixed radioactive waste until the radioactive components are separated from the RCRA waste components gave Y-12 a problem of mixed radioactive and RCRA waste. Currently, there is not a facility in the country permitted to handle mixed radioactive wastes. These regulations make substitution of these solvents very appealing. Y-12 has been actively seeking substitutions for these solvents for the past seven years.

The first step in our substitution program was to determine the uses of the chlorinated solvents. This step was done by conducting usage surveys in the plant and by compiling information of purchases from the Y-12 stores and other purchasing systems. The main uses of these solvents were determined to be for cleaning purposes. The uses included cleaning parts after machining and prior to inspection, cleaning chips in the chip cleaning facility, cleaning urethane foam guns, cleaning meter mix machines, and dissolving adhesives.

EVALUATION OF SUBSTITUTES

In looking for substitutes for chlorinated solvents, there are several pitfalls one must avoid. Large problems can result from overlooking small details. Factors which we take into consideration include compatibility, toxicity, flammability, means of disposal, effects on production, and cleaning ability.

Compatibility issues concerning the material to be cleaned are usually addressed by conducting submersion tests and looking for signs of corrosion. When addressing compatibility issues, one must look not only at the material to be cleaned but at the handling materials such as gloves, wipes, and dispensers. Degradation of these materials can transfer unwanted contamination to the part as well as risk personnel exposure. This issue is usually addressed by conducting submersion tests with the materials in the potential solvent substitute or conducting surface analysis studies on a sample which has been cleaned while using these materials.

Toxicity issues are addressed by searching for health properties of the solvent in sources such as Sax Dangerous Properties of Industrial Materials (1), Registry of Toxic Effects of Chemicals, and the Hazardous Substance Data Bank. Our Industrial Hygiene Department also evaluates the solvent and/or cleaning operation for health concerns and determines if monitoring is needed or the personal protective equipment to be used.

When it is necessary to replace a halogenated solvent with another organic solvent, one must begin looking at the flammability of solvents. Due to stringent requirements by the Occupational Safety and Health Administration (OSHA) regarding highly flammable solvents, our approach has been to use solvents with a flash point of 140°F or higher. This also enables you to be above the 140°F limit given as a characteristic RCRA waste. Other concerns which must be addressed concerning flammable solvents deal with the proper use of these solvents which includes storage, use, and dispensing. In addition, the ability of the solvent to form peroxides is examined so that the solvent could be handled safely.

The means of disposal must be examined to prevent generation of a waste which cannot be handled. Generally, a biodegradable solvent is desirable although incineration is acceptable. Bacteria from our biodegradation pond is placed in a given amount of solvent. This mixture is then tested to determine if and when the solvent is degraded.

Effects on production include several items depending upon the next operation involved. When using a solvent with a high flash point, the evaporation rate is much slower than a chlorinated solvent. This results in changes in production whether it be simply waiting longer before doing the next step or drying with a paper towel. Other effects include effects on bond strength, effects on welding, or effects on handling.

In testing the ability of a substitute solvent or cleaning method, comparative studies between possible substitutes and the current cleaning method are first conducted on small samples. Surface analysis is conducted using X-ray Photoelectron Spectroscopy (XPS/ESCA). Using this technique, a surface is bombarded with x-rays and the energy of the electrons emitted from the surface is measured. The electrons from different elements or elements in specific bonding states have different binding energies. Thus, one can determine the specific elements or combination of elements on a surface from the measure of these different energy levels. XPS/ESCA is capable of examining microlayers of a surface. Data is recorded for a contaminated surface to get a feel for what elements are present due to the contamination. Peak height ratios of the main element associated with the contamination to the base metal are calculated from this data. These ratios are compared to determine the effectiveness of the solvent and/or cleaning operation. The lower this ratio, the cleaner the surface. The ability to remove other elements associated with the contamination is also examined. After conducting these studies, the solvent and/or cleaning operation is tested on a larger scale to determine if there are any problems associated with its use.

ULTRASONIC CLEANING

Substitution efforts at Y-12 have been divided into two main efforts. The first effort was the replacement of large vapor degreasers utilizing chlorinated solvents with ultrasonic cleaners using aqueous detergent and water. Ultrasonic cleaning works by cavitating a liquid and forming small micro bubbles which burst on the surface to be cleaned. This provides mechanical as well as chemical cleaning action. Three variables can influence the effectiveness of ultrasonic cleaning: 1) the frequency of the ultrasonic cleaner, 2) the liquid medium, and 3) the coupling between the cleaner and the liquid. In order to cavitate the liquid, a frequency of at least 18 kilohertz is required.

Ultrasonic cleaning has been shown to perform as well as, if not better than, cleaning with vapor degreasers, as shown in Figs. 1 through 3. Fig. 1 shows the results of a study where samples of Type 304L stainless steel (SS) were coated with a rust preventative oil and then cleaned by vapor degreasing or by ultrasonic cleaning. Initially, the samples were cleaned ultrasonically in detergent and water to provide a sample baseline. One of these samples was retained as a control sample. The remaining samples were coated with a rust preventative oil and allowed to sit overnight. Three samples each were vapor degreased in 1,1,2-trichlorotrifluoroethane (CFC-113), methyl chloroform (TCA), or perchloroethylene (perk) for fifteen minutes. Three samples were also cleaned ultrasonically (US) in aqueous detergent and water for 15 minutes at 54°C, rinsed in demineralized water, and blown dry with argon. The ultrasonically cleaned samples were much cleaner than the samples vapor degreased in a chlorinated solvent. The samples degreased in methyl chloroform yielded the dirtiest surfaces.

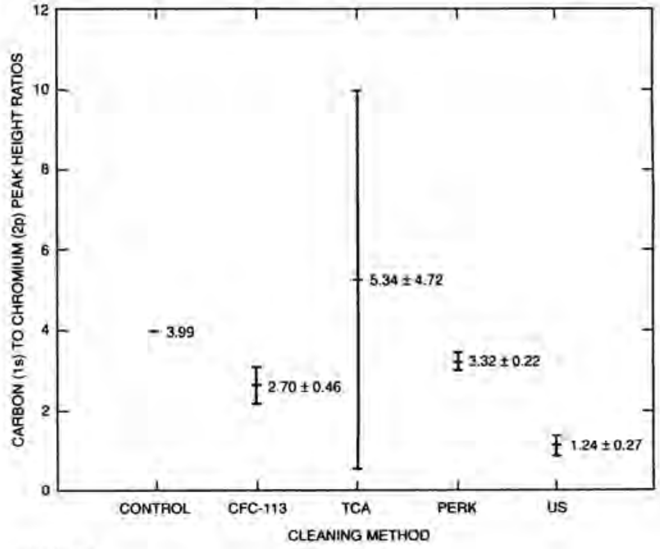

Fig. 1. Effectiveness of vapor degreasing versus ultrasonic cleaning for removal of rust veto.

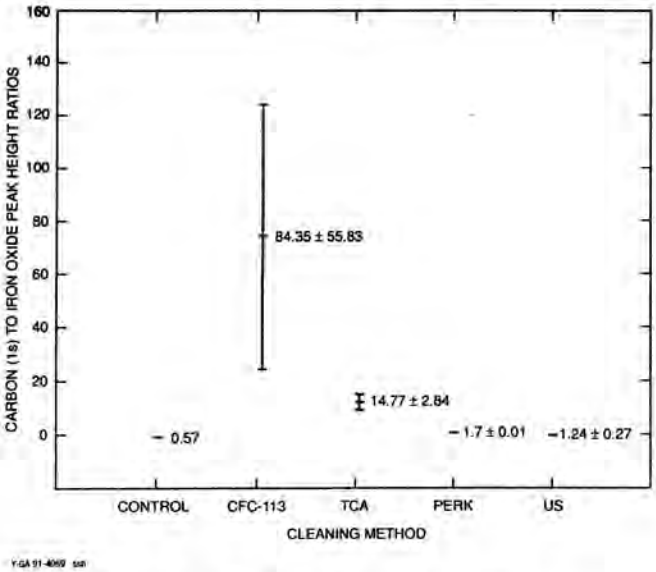

Fig. 2. Effectiveness of vapor degreasing versus ultrasonic cleaning for removal of lapping oil.

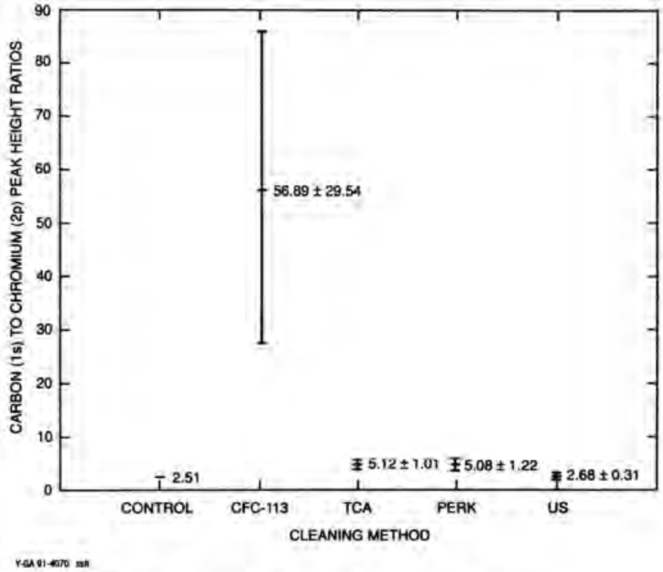

Fig. 3. Effectiveness of vapor degreasing versus ultrasonic cleaning for removal of trim sol.

Figure 2 shows the results of a similar study conducted on 4330 V steel which was coated with lapping oil. Again, the ultrasonic cleaning yielded cleaner surfaces with CFC-113 giving the worst cleaning results.

Figure 3 shows the results of another study which was conducted using the same methods as above. This study was conducted on 15-5 PH stainless steel which was coated with a machining coolant known as Trim Sol. Again, ultrasonic cleaning yielded the cleanest surfaces and vapor degreasing with CFC-113 yielded the dirtiest surfaces.

Ultrasonic cleaning has been shown to yield cleaner surfaces than vapor degreasing and the results are more reproducible. No compatibility problems have been observed with the ultrasonic cleaning. The detergents used have low toxicity and are nonflammable and the waste produced is biodegradable.

There are some drawbacks with ultrasonic cleaning. The equipment requires an initial capital investment, a rinse step must be included in the process, and a drying step is also necessary.

SOLVENT CLEANING

The second phase of the substitution program has been the replacement of squirt bottle or specialty type operations with other organic solvents. The main application was the cleaning of parts after machining or prior to inspection by wiping. The contaminants being cleaned from the surface were the usual machine shop contaminants such as machining coolant, rust preventative oil, lapping oil, lubricants, and fingerprints. Initially, possible solvent substitutes were chosen using Hansen Solubility Parameter Theory.(2) Using this theory, solvents which have similar parameters have similar solvent properties. A wide range of solvent types have been tested for the different contaminants which are present. The experimental procedure used was to initially clean samples of 304L stainless steel ultrasonically in aqueous detergent and water in order to establish a baseline level of cleanliness. A sample was retained as a control sample. The remaining specimens were coated with the contaminant and allowed to dry overnight. One contaminated sample was also retained to determine what elements are present due to contamination. Each sample was then squirted with a given amount of solvent being tested and wiped dry. The samples were submitted to XPS/ESCA for analysis. The main element present due to the contamination was carbon. Therefore, a peak height ratio of carbon to chromium (which represents the base metal) was calculated and comparisons were made of this ratio. The lower this ratio the cleaner the surface.

Figure 4 shows the results of the study comparing solvents for the cleaning of rust preventative oil. Solvents such as dipropylene glycol methyl ether (DPM), ethyl lactate, anisole, propylene glycol methyl ether acetate (pm acetate), ethanol denatured with acetone (EtOH/acetone), and isopropanol did not remove the rust preventative oil sufficiently enough to enable the ESCA to see the metal surface. A terpene based cleaner and N-methyl pyrrolidone (NMP) worked as well as CFC-113. Solvent 140, which is a high flash mineral spirits, worked as well as the methyl chloroform and better than CFC-113. Ultrasonic cleaning with aqueous detergent yielded the cleanest surfaces.

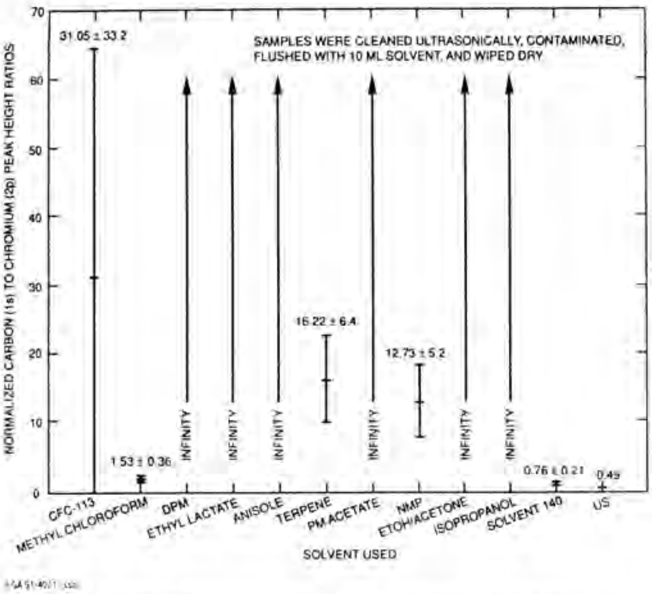

Fig. 4. Ability of solvents to remove rust veto from 304L SS.

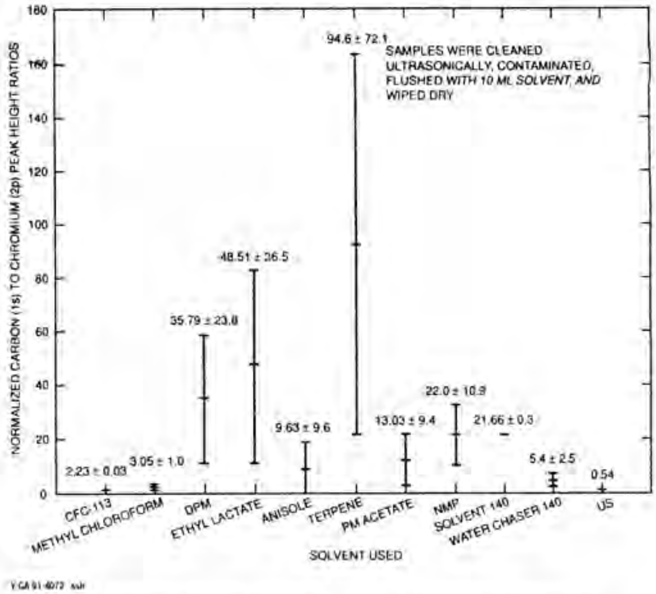

Fig. 5. Ability of solvents to remove lapping oil from 304L SS.

Figure 5 shows the results of a study comparing the ability of solvents to remove lapping oil. DPM, ethyl lactate, and a terpene based solvent yielded the dirtiest surfaces followed by anisole, pm acetate, NMP, and Solvent 140. A solvent blend, which consists of 95% Solvent 140 with 5% DPM, yielded the best results of the possible solvent substitutes compared to methyl chloroform and CFC-113. Ultrasonic cleaning with aqueous detergent again yielded the cleanest surfaces overall.

Figure 6 shows the results of a study comparing the ability of solvents to remove a water based machining coolant known as Trim Sol. Solvents such as anisole, pm acetate, isopropanol, Water Chaser 140, and Solvent 140 yielded surfaces comparable to those cleaned with CFC-113. Surfaces cleaned with DPM, ethyl lactate, and a terpene based cleaner were somewhat dirtier and the ethanol/acetone blend yielded the dirtiest surface overall. The cleanest surface was found by cleaning with ultrasonic cleaning with aqueous detergent.

Figure 7 shows the results of a study comparing the ability of solvents to remove fingerprints. The ethanol/acetone solvent mixture and the ultrasonic cleaning yielded the best results overall. Methyl chloroform, isopropanol, and Solvent 140 gave the next best results followed by Water Chaser 140. CFC-113 yielded the worst results and did not appear to remove the fingerprint oils. All of the organic solvents left behind inorganic contamination from the fingerprints such as sodium, nitrogen, sulfur, potassium, chlorine, and calcium.

Due to these results, the Y-12 Plant is currently in the process of changing to a strategy using Solvent 140 and

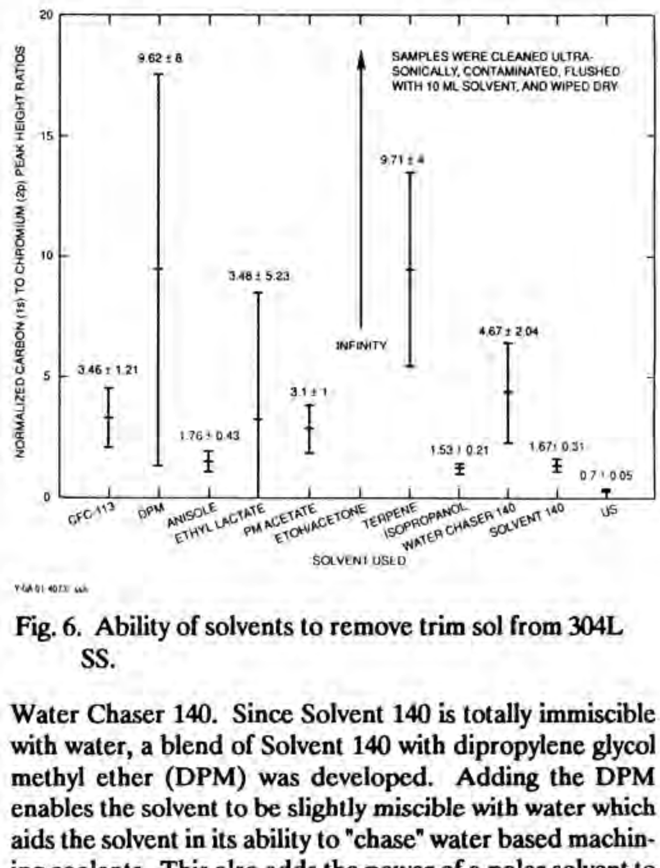

Fig. 6. Ability of solvents to remove trim sol from 304L SS.

Water Chaser 140. Since Solvent 140 is totally immiscible with water, a blend of Solvent 140 with dipropylene glycol methyl ether (DPM) was developed. Adding the DPM enables the solvent to be slightly miscible with water which aids the solvent in its ability to "chase" water based machining coolants. This also adds the power of a polar solvent to that of a non-polar solvent. These solvents have low toxicity, are non-RCRA, are easily handled under fire code considerations, and are compatible with materials used at Y-12. Solvent 140 will be used in moisture sensitive areas of the

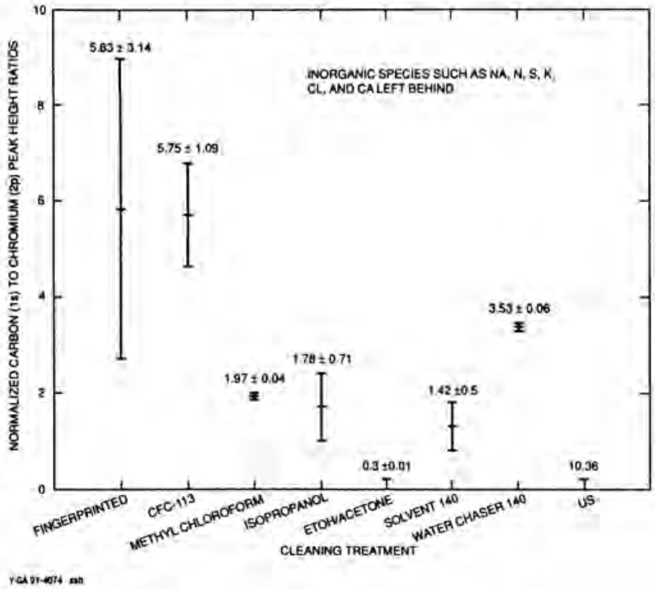

Fig. 7. Ability of solvents to remove fingerprints from type 304L SS.

plant while Water Chaser 140 will be used in the remainder of the plant. The drawbacks of these solvents are that they are flammable and are slow evaporators which require a change in production operations.

CONCLUSIONS

Chlorinated solvents are widely used throughout industry for cleaning purposes. However, because of health and environmental problems associated with their use, substitution of these materials have become desirable. The Y-12 Plant has successfully substituted ultrasonic cleaning with aqueous detergent as a substitute for large vapor degreasers and Solvent 140 and Water Chaser 140 for chlorinated solvents used in squirt bottle type operations. There are drawbacks associated with the use of these substitutes but these drawbacks can be overcome.

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