THE ELIMINATION OF CHLORINATED, CHLOROFLUOROCARBON, AND OTHER RCRA HAZARDOUS SOLVENTS FROM THE Y-12 PLANT'S ENRICHED URANIUM OPERATIONS

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INTRODUCTION

The Oak Ridge Y-12 Plant* is one of several plants which make up the Department of Energy's manufacturing facilities for production of nuclear weapons components and subassemblies. The plant is a comprehensive manufacturing facility with operations encompassing material manufacture, component fabrication and subassembly generation. All associated inspection and certification functions are performed in the plant. The plant's two primary products are uranium and lithium materials.

A major driving force in waste minimization within the plant is the reduction of mixed radioactive wastes associated with operations on highly enriched uranium. High enriched uranium has a high concentration of theuranium-235 isotope (up to 97.5% enrichment) and is radioactive, giving off alpha and low level gamma radiation. The material is fissionable with as little as two pounds dissolved in water being capable of producing a spontaneous chain reaction. For these reasons the material is processed in small batches or small geometries. Additionally, the material is completely recycled because of its strategic and monetary value.

Since the early eighties, the plant has had an active waste minimization program which has concentrated on substitutiion of less hazardous solvents wherever possible. The following paper summarizes efforts in two areas--development of a water-based machining coolant to replace perchloroethylene and substituion of an aliphatic solvent to replace solvents producing hazardous wastes as defined by the Resource, Conservation, and Recovery Act (RCRA). A summary of the plant's overall solvent substitution and reduction program can be found elsewhere[1].

A WATER-BASED MACHINING COOLANT FOR USE WITH ENRICHED URANIUM

A 50% mixture of perchloroethylene (tetrachloroethylene) and mineral oil had been used in Y-12 for machining enriched uranium for nearly twenty years, but changing regulatory conditiions made its use very difficult. Both the Clean Water Act and the Toxic Substance Control Act listed perk as a hazardous substance and RCRA declared waste sludge of perchloroethylene to be hazardous. For these reasons, a new coolant was developed.

Perchloroethylene has several properties which make it ideal for use as a machining coolant for uranium. It is non-reactive with uranium and all known machine tool materials, it can extinguish small uranium chip fires, it enhances nuclear criticality safety due to the presence of the chlorine-35 isotope which is a neutron poison, and it facilitates recycle of chips due to the ease with which it evaporates. Any new coolant has to maintain these characteristics. Additionally it has to be safe

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*Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400 for humans and generate no RCRA hazardous wastes with the over-riding issue being nuclear criticality safety at the expense of any other desirable characteristics.

A secondary issue was an operating philosophy based on best management practices which encourages the use of generic rather than proprietary chemicals. Examination of available literature shows a number of commercial, water-based coolants are available which can be used with uranium after modification to insure nuclear criticality safety. However, formulations are not specified, are subject to change, and vary from lot-to-lot; all of which conditions are unacceptable conditions in nuclear operations and support a decision to utilize a specified formulation.

The coolant formulation selected consists of a 50/50, by volume, mixture of water and propylene glycol to which is added 90 g/L sodium borate, 1000 ppm sodium nitrate, and a few drops of Azure Blue dye. The sodium borate is a neutron poison and provides the necessary criticality safety margins for the coolant. The sodium nitrate is a corrosion inhibitor and the dye is a coloring agent added to facilitate quick visual verification that the coolant in use is nuclear safe.

The new coolant was implemented in January, 1985. Perchloroethylene usage in Y-12 dropped from 1,200,000 pounds in 1984 to less than 130,000 pounds in 1986; however, all chlorocarbons or chlorofluorocarbons were not eliminated since degreasing agents and water removal chemicals were still required. Any residue of sodium borate left on the machining chips must be removed prior to chip recycle in order to maintain the required nuclear characteristics of the material stream. The chips are washed in distilled water to clean off the borate residue which leaves absorbed water on the chips. This water is displaced by dipping the chips in Freon-113 which is immiscible with water. The displaced water then floats on the Freon-113 and is skimmed off for recovery of any residual uranium or disposal. These operations led to an increase in Freon-113 usage in-plant of about 60,000 pounds, yielding a net reduction in controlled substance usage of approximately 1.1 million pounds.

ELIMINATION OF THE GENERATION OF RCRA HAZARDOUS WASTES FROM SHOP FLOOR OPERATIONS

Background

On December 20, 1989, Region IV of the United States Environmental Protection Agency (EPA) issued a regulatory interpretation memo[2] concerning solvent wipers which said that solvent wipes and rags "used in cleaning and degreasing operations with any solvent or mixture of solvents identified under the RCRA hazardous waste codes, F001-F005, at 40 CFR $261.31" are "considered to be a listed hazardous waste (i.e., a spent solvent)."

On April 12, 1990, in the U.S. District Court for the District of Colorado, Judge Lewis T. Babcock issued a Memorandum Opinion and Order[3] in a civil suit between the Sierra Club, Plaintiff, versus the U.S. Department of Energy and Rockwell International Corporation which stated 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.

These two rulings required an immediate change in the way Y-12 was doing business. Firstly, all shop floor cleaning operations which used Freons, methyl chloroform, or any volatile organic compound (VOC) which produced wastes classified as RCRA characteristically hazardous had to be treated as RCRA hazardous wastes and were now subject to manifesting and associated control requirements prior to disposal. Since these wastes were incinerated to recover any uranium residues, treatment facilities for such wastes now had to be permitted as hazardous waste treatment facilities, almost an impossibility for such "land-banned" wastes. Therefore, an immediate program was undertaken to eliminate generation of all RCRA wastes from enriched uranium operations.

SELECTION OF A NEW SOLVENT SYSTEM CALLED WATERCHASER 140 FOR SHOP FLOOR USE

Several criteria were considered in selecting a substitute solvent system. They included requirements that the new solvent should clean as well as the solvent it was replacing, yield non-hazardous wastes as defined by RCRA, have low or minimal toxicity, be a non-air pollutant, be compatible with all weapons materials, and require minimal changes in the plant's operational areas in order to comply with applicable safety and fire codes. Additional considerations were the universality of the solvent and potential costs.

Examination of these requirements drives one to the conclusion that the solvent should have a flash point greater than 139°F to meet Occupational Health and Safety Act (OSHA) requirements and be a Class III liquid as defined by the National Fire Protection Association (NFPA) in order to allow open shop usage. A study of Y-12's production operations showed that the primary solvent in use for part and component cleaning was Freon-113 with lesser amounts of methyl chloroform, naphtha and various low flash point alcohols. Comparison of the characteristics of these solvents with available materials using Hansen Solubility theory[4,5] led to the conclusion that a medium weight aliphatic hydrocarbon mixture with a small amount of a polar co-solvent additive would meet the cleaning requirements as well as code requirements. Figure 1 shows a comparison of cleaning characteristics of a number of solvents and methods using electron spectroscopy for chemical analysis (ESCA) methodology to determine cleanliness. As can be seen Water Chaser 140 fulfills the stated needs.

A survey of available commercial solvents shows that a number of blends are available which meet these general needs. Usually they are called hydrocarbon blends or "varsols," and are almost always refinery fractions. As such, they are subject to the variability inherent in these operations. To prevent regulatory liability due to the presence of uncontrolled or unknown (primarily aromatic) chemicals in the solvent due to lot-to-lot variability, generic specifications requiring certification of contents were generated and used for procurement.

The solvent selected for general shop usage consists of a mixture of aliphatic hydrocarbons with 5% dipropylene glycol monomethyl ether (DPM) which Y-12 calls Water Chaser 140. The DPM has alcoholic functional groups as part of its structure which lends some polar character to the solvent and causes water to bead up on uranium surfaces. Because of the strong hydrophilic nature of the surface oxide film which forms when uranium is exposed to air, water forms a tightly bonded film on uranium. The DPM acts as a surfactant which breaks the bonds, causing the water to bead so that it can be easily wiped from the part or component. Table 1 gives a summary of the procurement specifications for the solvent and Table 2 gives a summary of the pertinent characteristics of the material.

Based upon the data shown, Water Chaser 140 meets the majority of the characteristics desired when the study started; however, some obvious problems arise. The flash point causes the material to be classed as combustible, leading to increased potential fire loads in shops where either chlorocarbons or chlorofluorocarbons were previously used. Secondly, the material has a toxicity rating of 2 based upon the TLV-TWA. For these reasons, best management practices would indicate that the solvent wipes and rags should be stored in closed, nuclear-safe, approved containers. The low vapor pressure increases drying time, but also prevents exceeding the TLV if any ventilation at all is present. The increased drying time is not a problem in practice if operators wipe parts to remove excess liquid and, in fact, leads to cleaner parts because wiping is a much better cleaning method than air drying which is the general practice with highly volatile solvents.

Procurement was accomplished via standard bid processes with bids received from three chemical companies. In-house certification of the material indicated all specifications had been met by the low bidder and the material was accepted for use as a weapons-approved cleaning agent.

Implementation occurred during June, 1990. No major problems surfaced. To-date, no use related health incidents have occurred; i.e., no dermatitis, allergic reactions, or skin irritations have been reported. Industrial hygiene monitoring has been on-going and to-date no incidence in which the TLV was exceeded has occurred. On one occasion, a worst case scenario for exposure was mocked-up in which a two-gallon bucket of solvent was poured onto a machine; the maximum measured air concentration was 25ppm. With wiping, part cleaning times are comparable to previous experience.

CONCLUSIONS

Two major generators of RCRA wastes in the Y-12 Plant have been eliminated. A water-based machining coolant has been implemented to replace a perchloroethylene based coolant and an aliphatic hydrocarbon based solvent has been implemented to replace previous solvents which produced RCRA hazardous wastes when used in shop floor degreasing and cleaning operations.

REFERENCES

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4. Hansen, C.M.; "The Universality of the Solubility Parameter," IE & C Product Research and Development; ACS Publication Volume 8, Number 1; 1969.

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TABLE 1
SUMMARY OF PROCUREMENT SPECIFICATIONS FOR WATER CHASER 140

Flash Point	141°F Minimum per ASTM-D-56 TCC Method
Specific Gravity	0.777 - 0.827 @ 60°F
Evaporation Residue	<200 micrograms per gram
Acidity	Neutral per ASTM-D-1093
Volume % Aromatics	5% maximum per NMR Methodology
Doctor Test (for Sulfur)	Negative per ASTM-D-235
DPM	5 +/- 1% per G C Mass Spec or NMR
Aliphatic Hydrocarbons	> 90% per G C Mass Spec or NMR

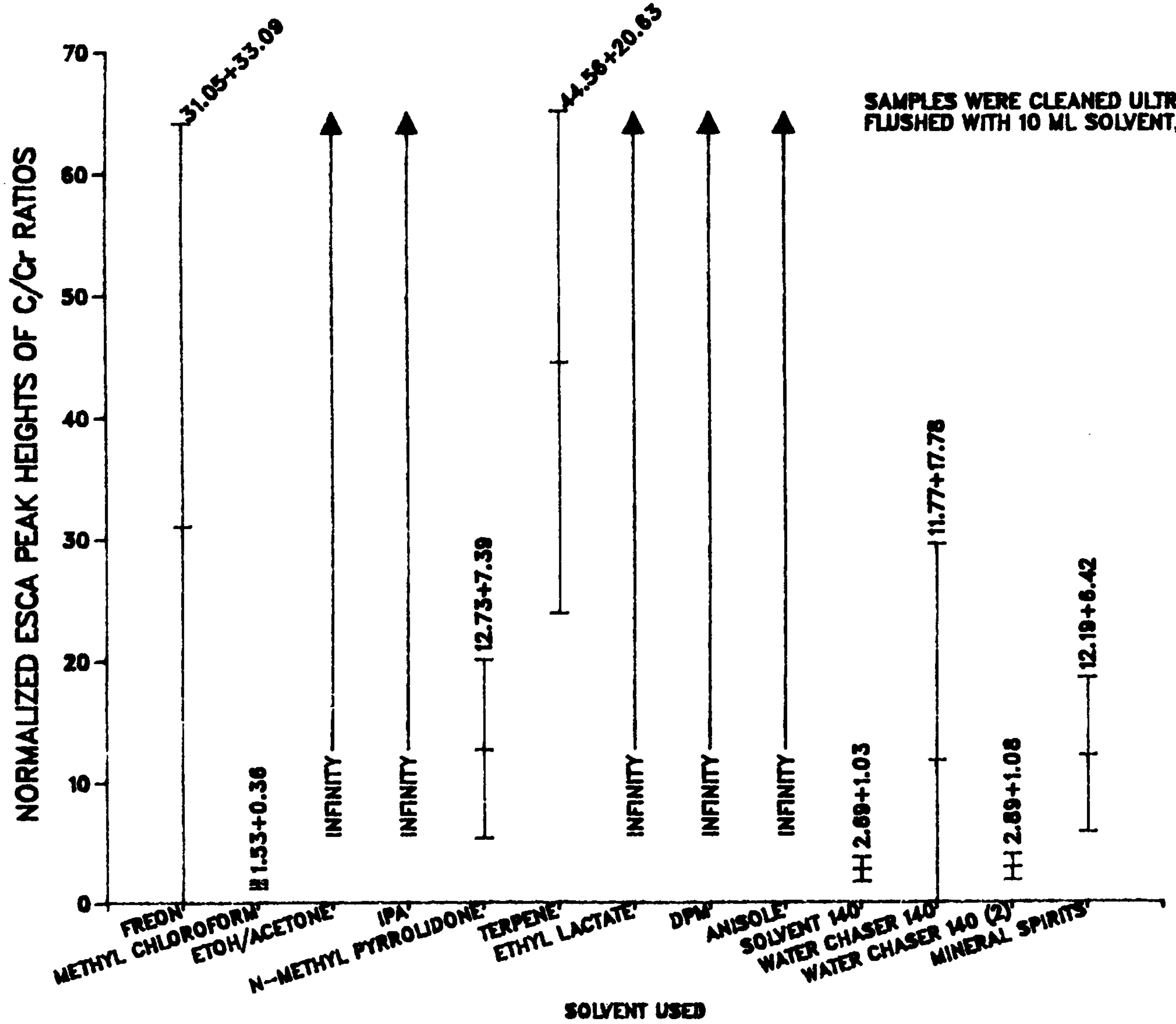
TABLE 2
APPLICATION CHARACTERISTICS OF IMPORTANCE FOR WATER CHASER 140

Flashpoint	142°C
NFPA Class III Liquid	Allows open usage without necessity to store in a flammable storage cabinet during off shift
TLV-TWA	100 ppm

* Can cause irritation to eyes
* Prolonged exposure to skin can cause dermatitis
* Excessive inhalation can cause irritation, headaches, or asphyxiation

Vapor Pressure	0.50 mm Hg

FIGURE 1 – ABILITY OF SOLVENTS TO REMOVE LIGHT OILS FROM 304L SS



SAMPLES WERE CLEANED ULTRASONICALLY, CONTAMINATED,
FLUSHED WITH 10 ML SOLVENT, AND WIPED DRY