Green Engineering for Steel Cleaning

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Abstract

An analysis of the cleaning solutions and methods utilized on steel has been conducted. The effectiveness and environmental impact of these cleaning solutions and methods has been analyzed. One found that most volatile organic compounds have a negative impact on the environment and humans. There are many effective and non-toxic cleaning methods that should be employed. These methods include soy methyl ester solvents, carbon dioxide dry ice cleaning, carbon dioxide snow cleaning and supercritical carbon dioxide fluid cleaning.

Executive Summary

One conducted an analysis of the hazardous solutions that are currently employed to clean steel. Typically the most harmful chemicals are solvents. The Environmental Protection Agency and the Occupational Safety and Health Administration regulate many cleaning solvents. Many cleaning solvents deplete the ozone layer, are carcinogenic, and highly flammable.

There are numerous cleaning methods that are non-toxic to the environment and humans. One discovered that soy methyl esters exhibit excellent solvent properties, are non-toxic and are cost effective. However, soy methyl esters leave a film on the material being cleaned. Vertec Gold^{TM} by Vertec BioSolvents is a soy methyl ester and ethyl lactate (a derivative of corn oil) solution. Vertec Gold^{TM} does not leave a film on the surface of the material being cleaned. The reason for this is that ethyl lactate has a high evaporation rate. Furthermore, Vertec Gold^{TM} has a low volatile organic compound content. Therefore, this product is non-toxic to the environment and humans. Vertec Gold^{TM} is biodegradable in twenty eight days. Vertec Gold^{TM} is an excellent alternative cleaning solution due to its great solvent properties, low volatile organic content, ability to biodegrade and low cost. In addition, one found that carbon dioxide dry ice cleaning, carbon dioxide snow cleaning and supercritical carbon dioxide fluid cleaning are other cleaning alternatives. In carbon dioxide dry ice, snow and supercritical fluid cleaning the carbon dioxide is recycled. If workers in the plant use carbon dioxide cleaning they could consume too much carbon dioxide. The consumption of too much carbon dioxide could be hazardous. Furthermore, soy methyl ester based solvents are more cost effective than carbon dioxide cleaning methods. Therefore, one believes that a soy methyl ester and ethyl lactate solution is the best cleaning alternative.

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Introduction

Throughout time numerous cleaning methods have been utilized to remove contaminants from steel. Unfortunately, many of the commonly used cleaning methods are hazardous to the environment and human health. For instance, some of the chlorofluorocarbons that are used as cleaning agents deplete the ozone. Additionally, the primary role of ozone is to absorb some of the harmful ultra violet radiation. Furthermore, “The absorption of UV-B radiation by ozone is a source of heat in the stratosphere. This helps maintain the stratosphere as a stable region of the atmosphere, with temperature increasing with altitude. As a result, ozone plays a key role in controlling the temperature structure of the Earth’s atmosphere” (United Nations Environment Program). As a result, chlorofluorocarbons have contributed to the global warming crisis. In response to the rise of the global warming crisis the United Nations formed the Montreal Protocol in 1987. The Montreal Protocol is an international treaty that was put into effect in order to decrease the production and use of ozone depleting substances. In order to decrease the production and use of ozone depleting substances the industrial sector should use alternative cleaning methods that are better for the environment and human health.

Within the past couple of years many green alternative cleaning methods have been discovered. In order for a cleaning method to be acknowledged as green the product must adhere to certain guidelines. For example, the cleaning method must be non-toxic to humans and aquatic life. The cleaning method must also not be highly reactive with certain chemicals (i.e. gases prevalent in the atmosphere). Lastly, the cleaning method must be cost effective for the producer and the consumer. There are many hydrochlorfluorocarbons that are used in place of chlorofluorocarbon cleaning solvents. Hydrocholorfluorocarbons contain chlorine which deplete the ozone. HCFCs do not deplete the ozone to the degree that CFCs do; however, there are other cleaning methods that are better for the environment. For example, carbon dioxide dry ice blasting is used to remove rust from steel. Supercritical carbon dioxide fluid is utilized to remove lubricants, grease, cutting fluids, and other contaminants from steel. Carbon dioxide is non-toxic and non-flammable; therefore, carbon dioxide is an exceptional alternative cleaning agent. Methyl esters are an effective cleaning alternative due to their low volatile organic compound and excellent solvent properties.

In the following chapters one will explain the reasons why many cleaning methods should be discontinued. Additionally, one will describe why certain green cleaning methods should be put into effect. "The Montreal Protocol plans to reduce production and use of HCFCs by 65% by 2010, 90% by 2015, and 99.5% by 2020." (United Nations Environment Program). Therefore, the industrial sector should consider using cleaning methods that do not involve CFCs or HCFCs.

1.0 Pigmented Drawing Compounds

There are numerous cleaners utilized to remove pigmented drawing compounds from steel. Pigmented drawing compounds are used to lay out steel. Zinc oxide, graphite, and stearates are examples of pigmented drawing compounds.

1.1 Alkaline Cleaning

Alkaline cleaners are effective at removing soils that contain pigmented drawing compounds. The three major components of alkaline cleaners are alkalinity builders, organic or inorganic additives and surfactants.

The alkalinity builders penetrate the soil deposits by increasing the alkalinity of the cleanser. Additionally, alkalinity builders hydrolyze the soils (i.e. animal fat/vegetable oils) in order to produce water soluble soap. The most common alkalinity builders are sodium metasilicate, sodium or potassium hydroxide, sodium bicarbonate and many forms of sodium phosphate. Sodium bicarbonate and sodium phosphate act as buffers in order to maintain the alkalinity at steady state levels. In addition, sodium metasilicate and sodium phosphate are utilized to protect aluminum, brass, bronze and iron from the corrosiveness of alkali salts. Furthermore, sodium metasilicate and sodium phosphate do this by binding to the etched ionic surface of the metal.

Surfactants provide detergency, emulsification and wetting action. For instance, surfactants reduce the surface tension of the soils. Therefore, the soils are emulsified and removed from the material. The surfactant molecules that are dissolved in water are in free or aggregate forms. Micelles are surfactant aggregates. If the aqueous surfactant mixture is cloudy then there is a high concentration of micelles. Additionally, if a surfactant mixture is cloudy at room temperature then the surfactant level is above its critical micelle concentration. If a surfactant solution is clear at room temperature and becomes cloudy when the temperature is elevated; the solution has reached its designated cloud point. The cloud point is the temperature at which a surfactant becomes insoluble in water. Furthermore, "Most cleaners are used at a temperature around their cloud point. Therefore, the amount of foaming is minimized and there is more effective cleaning activity." There are anionic, cationic, and non-ionic surfactants. Anionic surfactants are water soluble and are effective detergents. "Hard water metal ions can make anionic surfactants insoluble" (Research Triangle Institute). Calcium and magnesium are example of hard water metal ions. Chelating agents are utilized in alkaline cleaners in order to prevent hard water metal ions from making anionic surfactants insoluble. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. For instance, "EDTA is frequently used in soaps and detergents, because it forms a complex with calcium and magnesium ions. The EDTA binds to them, sequestering them and preventing their interference" (University of Wisconsin-Madison). Cationic surfactants are poor detergents. Non-ionic surfactants are synthetic surfactants. For example, ethylene oxide molecules are added to a water insoluble molecule in order to synthesize non-ionic surfactants. The number of ethylene oxide molecules and carbon atoms determine whether the non-ionic surfactant is a wetting agent, detergent or an emulsifier. Anionic and non-ionic surfactants are used in formulations for immersion cleaning baths. Non-ionic and amphoteric surfactants are used in solutions for spray cleaners.

Inhibiting agents are added to alkaline solvents in order to minimize the effect that the cleaners have on certain metal substrates. In addition, inhibiting agents are added to prevent oxidation. For instance, strong alkaline cleaners can tarnish brass; therefore, inhibiting agents are added to prevent this. Tin is sensitive to strong alkaline solvents. Silicate chromate can be used as an inhibiting agent. Alkaline cleaners that have a high pH have effects on non-ferrous materials; therefore, inhibiting agents are added to alkaline solvents with a high pH.

Alkaline cleaners are replacing many cleaners because they are better for the environment. However, the chelating agent EDTA used in alkaline cleaners poses wastewater treatment difficulties. For example, "When chelating agents ethylene diamine tetra-acetic (EDTA) are used, high concentrations of heavy-metal ions are found in the waste water. This creates problems at the treatment plant, so use of EDTA as a chelating agent should be avoided" (Bird and Donohue). Alkaline cleaners can cause eye and skin irritation due to their high alkalinity. Alkaline cleaners do not have a flash point; therefore, there is no potential for a fire or explosion. Typical alkaline cleaning processes are batch operations. The soils accumulate in the cleaner holding tank; therefore, the cleaner will not be able to work effectively. Membrane filtration can be used to recycle alkaline cleaners. For instance, "The membrane prevents the free floating and emulsified oil phases from passing through. The membrane allows the free surfactants, alkalinity builders and water to pass through its pores. As a result, the alkaline cleaner can be reused" (GE Water Division). Alkaline cleaners exhibit excellent solvent properties. The types of surfactants and builders added to alkaline cleaners depend on the cleaning application. One needs to take in to consideration if the surfactants and builders are hazardous to the environment.

1.2 Glycol Ethers

Glycol ethers are semi-aqueous cleaning solvents. Glycol ethers are also used to remove unpigmented oil and grease. Additionally, glycol ethers are commonly used to remove contaminants from semiconductors and from glass. Glycol ethers emulsify well during cleaning and can be separated easily during recovery.

Glycol ethers are volatile organic compounds. The two types of glycol ethers are ethylene glycol ether and propylene glycol ether. Ethylene glycol ethers have a higher toxicity profile than propylene glycol ethers. For example, "Tests indicate that propylene glycol butyl ether cleans as well or better than ethylene glycol butyl ether, cuts grease better, is compatible with many components of cleaning products, and has a lower toxicity profile" (The Research Triangle Institute). Propylene glycol methyl ether (PM) and propylene glycol methyl ether acetate (PMA) are good substitutes for methylene chloride in paint and foam removal. Propylene glycol methyl ether and propylene glycol methyl ether acetate have low toxicity, high solvency and low odor. In addition, PM and PMA can be used by themselves or contain additives. Propylene carbonate, n-methyl pyrrolidone and acetaphenonel are some of the additives used in PM and PMA. Furthermore, these additives enhance the solvent properties. According to the U.S. Environmental Protection Agency propylene glycol ethers are practically non-toxic.

For instance:

> Although widespread use of these compounds, primarily as solvents, can lead to dispersive entry into the environment, their physical and toxicologic properties make each unlikely to cause harm to the environment. PGE's do not

bioconcentrate. Their half-lives in air range from 6 to 34 hours, and their biodegradation half-lives in wastewater treatment plants, surface water and soil range from 5 to 25 days. Toxicity data show PGE's are "practically non-toxic" to fish, invertebrates and algae (Propylene Glycol Ethers Panel).

Propylene glycol ether exhibits excellent solvent properties and is non toxic; therefore, one should use propylene glycol ether in place of ethylene glycol ether.

1.3 Dibasic Esters

Dibasic esters (DBE) are commonly used to remove paint. In addition, dibasic esters exhibit excellent solvent properties. Dibasic esters are typically used in blends with other solvents in place of glycol ethers. Furthermore, dibasic esters have a high flash point of 100 degrees Celsius; therefore, they are not classified as flammable. DBE is stable at normal temperature, humidity and pH. In addition, "DBE has a low vapor pressure (0.1 torr or less); therefore, air emissions are low" (The Research Triangle Institute). Dibasic esters are not classified as toxic. For example, "Toxicity tests on DBE as well as on the individual components show no reproductive or developmental toxicity. No organ damage except mild nasal lesions, indicative of irritation, was seen in 90-day tests" (The Research Triangle Institute). Additionally, dibasic esters can be incinerated or can be recycled by vacuum distillation. Many experts report that dibasic esters may be biodegradable. For instance, "Dupont reports that DBE tested in a batch, aerated reactor, and electrolytic respirometer, is biodegradable and non-inhibitory up to 300 ppm" (The Research Triangle Institute).

2.0 Removal of Unpigmented Oil and Grease

Lubricant oils, quenching oils, shop oils, greases and unpigmented drawing lubricants are all classified as unpigmented oils. Unpigmented oils and greases are used to protect steel during manufacturing processes (i.e. rolling). They also provide more efficiency during machining.

2.1 Terpenes

Terpenes are organic solvents derived from pine trees or citrus fruit. The two common types of terpenes are d-limonene (citrus based terpene) and a-pinene (pine based terpene). Electrical components are typically cleaned using terpenes. In addition, they are strong solvents; therefore, they are effective cleaning solvents and they are not compatible with some elastomers. Silicone rubber and PVC are elastomers that are not compatible with terpenes. In addition, citrus based terpenes can dissolve heavy petroleum grease (i.e. cosmolene). Terpenes work at low temperatures; therefore, it is not necessary to heat the cleaning bath. "Citrus and pine based terpenes can clean cosmolene in about 30 minutes at relatively low temperatures" (The Research Triangle Institute). According to the Research Triangle Institute, a surfactant is added to commercial terpene in order to allow the use of water as a rinse agent. Futhermore, "When mixed with water, terpene forms an emulsion. The emulsion can be separated and the terpene can be reused" (The Research Triangle Institute). Additionally, "Terpenes have low vapor pressure; therefore, there is slower cleaner evaporation. There is longer cleaning time due to the slower cleaner evaporation" (The Research Triangle Institute).

Terpenes are volatile organic compounds; therefore, they are flammable and combustible. Furthermore, the material safety data sheet for d-limonene (orange based terpene) states that the volatile fraction by weight is one hundred percent. For instance, when terpenes are sprayed they are highly flammable. When one sprays terpene one should handle the terpene spray with care. Additionally, the University of California at Berekely conducted a study on the effect of terpenes on the ozone. They conducted an experiment that involved using a terpene in a room sized chamber with and without the presence of ozone:

> Some terpenes can react with ozone. Ozone-terpene chemistry produces the hydroxyl radical, which triggered an array of indoor chemical reactions, and formaldehyde, a TAC with a low acceptable exposure limit. This chemistry also converts some of the gaseous species into organic particulate matter, raising possible concerns because of the strong association between ambient particulate matter levels and a host of adverse health effects (University of California Berkeley, 2006).

Furthermore, a TAC is a toxic air contaminant. In addition, terpene-ozone reactions can cause a hydroxyl radical to generate. A hydroxyl radical is an extra electron added to an OH group; therefore, the TAC levels alter. For instance, "The OH yield for ozone-terpene reactions is high: 0.85 for alpha pinene and 0.86 for d-limonene" (University California Berkeley). This is significant because OH reacts rapidly with a broad spectrum of volatile organic compounds and the presence of OH in air can influence pollutant concentration. Additionally, "The use of terpene-containing cleaning product in the presence of ozone increased the fine particulate matter concentrations by approximately 30-90 micrograms per cubic meter. California's standard for ambient fine particulate matter ($PM_{2.5}$) is twelve micrograms per cubic meter on annual average basis." (University of California Berkeley). The material safety data sheet states that d-limonene is stable under normal conditions. However, if one burns d-limonene carbon monoxide and carbon dioxide will form. The material safety data sheet for d-limonene also advises one to not mix the solvent with strong oxidizing agents. D-limonene is reactive with strong oxidizing agents. Terpenes should not be stored in plastic containers because they could react with the plastic. Dermatitis can arise if one comes into contact with terpene. According to the material safety data sheet d-limonene does not pose a global warming threat and is non-carcinogenic. Additionally, d-limonene is one hundred percent biodegradable in twenty eight days according to the material safety data sheet. Terpenes exhibit good solvent properties; therefore, terpenes are excellent cleaning agents for heavy grease and oil. However, one must be cautious when utilizing terpene due to the volatile organic behavior of terpene.

2.2 Alkaline Cleaning

Alkaline cleaners are effective at removing soils that contain pigmented drawing compounds. Alkaline cleaners are used in place of toxic cleaners (i.e. trichloroethylene). Furthermore:

> Manufacturers claim that alkaline cleaners are non-toxic. But in concentrated form, most alkaline cleaners contain a solvent (approximately nine percent by weight) that helps the cleaner in oil emulsification. Typical solvents used are n-Butoxyethanol and Dipropylene Glycol Methyl Ether. In a typical operation, alkaline cleaners are diluted before use (approximately one part

degreaser in eight to twenty parts water). As a result, the solvent present would make up a very small part of the bath solution (less than 0.01 percent after bath solution). Due to the solvent's low concentration, it should not pose a threat to personnel or the environment (Bird and Donahue). For further information on alkaline cleaning refer to section 1.1.

2.3 Trichloroethylene

Trichloroethylene (TCE) exhibits excellent solvent properties; therefore, trichloroethylene is commonly utilized as a vapor degreaser. Trichloroethylene is a man made solvent.

Trichloroethylene is highly toxic to humans; therefore, many health and environmental agencies have instituted a set of laws that regulate the amount of exposure to trichloroethylene.

For example:

> Trichloroethylene levels in the workplace are regulated by the Occupational Safety and Health Administration. The occupational exposure limit for an eight hour work day, 40 hour workweek, is an average concentration of 100 ppm in air. The OSHA standards are based on preventing central nervous system effects after trichloroethylene exposure (The Agency for Toxic Substances and Disease Registry).

Trichloroethylene is classified as a possible carcinogen by most health agencies.

For instance:

> In its 9th Report on Carcinogens, the National Toxicology Program (NTP) determined that trichloroethylene is "reasonably anticipated to be a human

> carcinogen." Additionally, the International Agency for Research on Cancer (IARC) has classified trichloroethylene in group 2A, as a substance considered "probably" carcinogenic to humans. IARC, following its own restrictive classification scheme, concluded that there is "limited" evidence of carcinogenicity in humans on the basis of a combination of the results of some of the available epidemiological studies (Agency for Toxic Substances and Disease Registry, 2003).

Trichloroethylene can affect the heart, liver, kidney and the brain. According to the Toxics Use Reduction Institute at the University of Massachusetts Lowell TCE can affect the heart, liver, kidney, brain and skin.

For instance:

> TCE can affect the heart by causing irritability and possible sudden death. Secondly, TCE can affect the liver by causing acute chemical hepatitis cirrhosis. Tubular injury to the kidney can be caused by TCE. Lastly, TCE can cause headache, depression, and coma (Wilcox).

Trichloroethylene is also known to cause dermal effects. For example, "Skin irritants, burns and rashes such as generalized dermatitis, have resulted from occupational exposure to trichloroethylene" (EPA 1985). Degreasing methods contribute to the majority of the trichloroethylene emissions. For instance, "In a comprehensive study of trichloroethylene emission sources from industry conducted for the EPA, the major source was degreasing operations, which eventually release most of the trichloroethylene used in this application to the atmosphere" (EPA 1985).

TCE is volatile and evaporates quickly into the air during cleaning processes. Furthermore, “When trichloroethylene is broken down in the air, phosgene, a lung irritant, can be formed” (Wilcox). The atmospheric lifetime of TCE is one to two weeks. Additionally, “Precipitation carries TCE to groundwater and is listed as the number one contaminant of ground water. Persistence in soil and ground water is longer and can have a half life up to ten months” (Wilcox). TCE is environmentally benign; the industrial sector should replace TCE with cleaners that are better for the environment.

2.4 Aliphatic Hydrocarbons

Aliphatic hydrocarbons are semi-aqueous solutions that are used to remove heavy oil and grease. Petroleum distillates and synthetic paraffinic hydrocarbons are two types of aliphatic hydrocarbons. Petroleum distillates are produced from crude oil. “These products typically have low liquid surface tensions (22 to 28 dynes/cm). This allows them to penetrate and clean small spaces” (The Research Triangle Institute). Stoddard solvent is a petroleum distillate. Stoddard solvent contains volatile organic compounds. In addition, stoddard solvent is toxic to the lungs and the nervous system.

Furthermore:

> Data from acute studies in cats, dogs, mice and rats from intermediate studies in guinea pigs, rats and dogs that demonstrate toxicity are shown in Table 2-1 and Figure 2-1. One of the intermediate studies (Rector et al 1966) used a mixture of chemicals called mineral spirits, but authors stated that this particular mixture was similar to stoddard solvent. (Agency for Toxic Substances and Disease Registry, 1995).

Refer to Table 2-1 for further information about this study conducted by the U.S Department of Health. Paraffinic hydrocarbons have lower toxicity, lower flammability, higher solvency, lower aromatic content, and a narrow boiling range than petroleum distillates.

2.5 Glycol Ethers

Glycol ethers are also used to remove unpigmented oil and grease. Refer to section 1.2 for further information.

2.6 Acids

Acids are used to remove unpigmented oil and grease. According to the Research Triangle Institute acids are poor at removing oil and grease. "Acids are not commonly used on alloy steel sand high carbon grades of steel because acids cause hydrogen embrittlement" (Research Triangle Institute).

3.0 Removal of Chips and Cutting Fluids

Cutting and grinding fluids are categorized into three groups. The first group consists of plain or sulfurized mineral and fatty oils, chlorinated mineral oils and sulfurized chlorinated mineral oils. The second group consists of conventional or heavy duty soluble oils with sulfur or other compounds added and soluble grinding oils with wetting agents. The third group contains chemical cutting fluids, which are water soluble and generally act as cleaners (Xiaolan Wang).

3.1 Acids

Acids are used to remove cutting fluids. For example, phosphoric and chromic acid are commonly used to remove cutting fluids. Phosphoric acid can affect the respiratory tract, the eyes and skin. According to the Occupational Safety and Health Administration (OSHA) phosphoric acid can be corrosive to the eyes. Phosphoric acid can also cause permanent burns to the skin. Chromic acid is regulated by OSHA and the EPA because of the high toxicity of chromic acid. The acute health effects of chromic acid are skin, eye, nose and throat irritation. The possible chronic health effects of chromic acid are cancer, skin allergies and damage to a fetus.

3.2 Trichloroethylene

Vapor degreasing solvents are also utilized to remove cutting fluids. Trichloroethylene is a commonly used vapor degreaser. "Vapor degreasing will remove the first group of fluids easily and completely, but the fluids from the second and third groups can not be completely removed. Perchloroethylene is preferred to remove water containing soils" (Xiaolan Wang). For further information on trichloroethylene refer to section 2.3.

3.3 Alkaline Cleaning

Alkaline cleaners are used to remove cutting fluids. Refer to section 1.1 for further information on alkaline cleaners.

4.0 Removal of Rust and Scale

4.1 Abrasive Blasting

Abrasive blasting is used to remove rust and scale. Sand, metal pellets or plastic pellets are typically used as the media in this process. This process is effective at removing rust from steel. Abrasive blasting is not hazardous to the environment or to the health of the public. This method can cause dust; therefore, the dust is typically blown off utilizing pressurized air.

4.2 Acids

Acids are commonly used to remove rust and scale. For further information refer to the section 3.1.

5.0 Supercritical Carbon Dioxide Fluid Cleaning

5.1 Supercritical Fluids

A supercritical fluid forms above the critical temperature. A supercritical fluid is not a fluid or a gas. The supercritical fluid exhibits some of the liquid and gas properties. In addition, no matter how much pressure is applied this phase does not condense. In addition, at the supercritical state the fluid can not vaporize.

5.2 Supercritical Fluid Cleaning

For maximum efficient cleaning with supercritical fluid one needs to consider supercritical solvating power and the volatility of the contaminant. As the pressure increases the density increases. The higher the density, then the solvating power is higher. At constant pressure the solubility of a solute decreases as the temperature increases. This is a result of the density of the supercritical fluid decreasing. Therefore, the solvating power decreases. However, as the temperature increases the volatility of the contaminant increases. The effect from the increase of the volatility of the contaminant overcomes the decrease in the density of the supercritical fluid. Therefore, the contaminant removal is better. The addition of other compounds can increase the solubility.

For example:

> Perhaps a classic example was first reported by Kurnik and Reid. In their study, they observed that the solubilities of both naphthalene and benzoic acid in supercritical carbon dioxide were enhanced by 107% and 280% respectively, when both species were present. It also has been shown that there needs to be enough of a secondary component present in a solution about the local

contaminant environment to enhance the solubility of another compound (McHardy and Sawan).

According to McHardy and Sawan, the addition of fluorosurfactants to carbon dioxide increases the solubility of carbon dioxide. Furthermore, “The fluorinated tails have a longer chain length; therefore, they extend farther than the hydrocarbon tails. As a result the solubility increases” (McHardy and Sawan).

5.3 Supercritical Carbon Dioxide Fluid

Supercritical carbon dioxide fluid cleaning is better for the environment and the public health. Carbon dioxide is non-toxic and non-flammable. The supercritical carbon dioxide fluid has a very low viscosity (low surface tension) and good solvent properties compared to the liquid phase. This cleaning method is appropriate for small and delicate parts.

5.4 Supercritical Carbon Dioxide Fluid Cleaning

According to McHardy and Sawan, supercritical carbon dioxide is best at removing organic compounds. In Supercritical Fluid Cleaning a study that included the removal of six human based organic contaminants, five adhesives, seven different hydrocarbons, waxes, high molecular weight compounds, and thirteen different machining oils, fluids, and lubricants from fifteen different metals, nineteen polymeric, five rubber, five cables, three glasses and two fabric substrates. In addition, the contaminants were applied as dilute solutions to a half by two inch coupons using a pipettor. The contaminants were placed on many different types of coupons (i.e. steel). Once the coupon was dry it was placed in a ten milliliter cleaning vessel. There was a continuous flow of the SCF in the cell. Human organic contaminants (i.e. fingerprints) were used on the coupons. Fingerprints generally consist of skin lipids and oils. Therefore, in the study they created a sample of skin lipids that consisted of squalene, triglycerol, diglycerol, cholesterol and palmityl palmitate. For example, "The components of the surrogate fingerprints consisted of 30% triolein, 25% oleic acid, 25% cotyl palmitate, 15% squalene, 2.5% cholesterol oleate (components obtained from the Aldrich Chemical Company, WI)" (McHardy and Sawan). From the study on supercritical carbon dioxide as a cleaning solvent:

> Cast magnesium has a synthetic fingerprint removal rate of 56% while stainless steel 306 had a removal rate of 97%. The low removal rate from the cast metals were easily accomplished through parametric changes. For example, longer extraction times of thirty to forty five minutes resulted in quantitative removal of the synthetic fingerprints from the cast magnesium surface (McHardy and Sawan).

Therefore, supercritical carbon dioxide is excellent at removing human organic contaminants from steel. The study also discussed the removal of different organic chemicals (i.e. PAHs, amines, substituted phenols, substituted benzenes, phosphates, acids, and acid esters.

For instance:

> In general, the twenty three PAHs listed in the table averaged removal rates around 90% from the smooth surfaces and over 80% for the porous cast magnesium surface. Compounds such as N-nitrosophenylaniline had low removal efficiencies ranging from 30 to 40% from the smooth surfaces and only 21% removal from cast magnesium. All in all, the organic amines had a general

> average removal rate near 80% which still shows fairly effective supercritical carbon dioxide cleaning (McHardy and Sawan).

In addition, the study of the removal of phenols (organic compounds) using supercritical carbon dioxide cleaning was also conducted in this study.

For example:

> Phenols are polar organic compounds primarily soluble in polar organic compounds, and in some cases, water. For this reason, it was expected that removal rates for these types of compounds from the five substrates in the chemical removal survey would be rather low. Several of the substituted phenols, the cresols, for example, had very effective removal rates, averaging above 90% removal using supercritical carbon dioxide at 40 degrees Celsius and 350 atm despite the fact that carbon dioxide is a non-polar solvent. It is possible that the high removal rates of these compounds could be attributed to the fact that they are liquids at 40 degrees Celsius, thus facilitating extraction due to faster kinetics (McHardy and Sawan).

The removal of cutting fluids using supercritical carbon dioxide solvent was also studied in this particular study.

For instance:

> Of particular note, as seen in Table 4, is that supercritical carbon dioxide was quiet effective in the removal of the various oils and fluids from all smooth metal surfaces, removing, for example, from about 89 to 99% of the Tapmatic cutting fluid. These results show the applicability of supercritical carbon dioxide

cleaning to machined and precision metal parts and components (McHardy and Sawan).

Supercritical carbon dioxide is excellent at removing organic compounds and cutting fluids

5.5 Costs of Supercritical Carbon Dioxide Cleaning Systems

There are numerous considerations that one must take into account when purchasing a supercritical carbon dioxide fluid cleaning system. For instance, the types of supercritical carbon dioxide fluid cleaning systems must be considered. The direct system is the least expensive. The single cycle system consists of a process in which a cosolvent is added to the cleaning vessel before or during carbon dioxide processing. In addition, "The cosolvent, the contaminant, and the carbon dioxide are returned to the condenser for recycle. The cosolvent can usually be separated from the contaminant and reclaimed. If not, the cosolvent is disposed of (along with the contaminant) as a hazardous waste, adding to the operating cost" (McHardy and Sawan). The disadvantage of the single cycle system is that there is difficulty predicting the cleaning efficiency of the cosolvent and carbon dioxide mixture at various operating conditions. The single cycle system is moderately priced. The dual cycle system is the most expensive; however, it is the most effective and versatile. Each step in this cleaning process takes place in a single vessel. First the cosolvent is transported from a separate module to the cleaning vessel. During this step the cosolvent dissolves the contaminant. Then the cosolvent and the contaminant are removed from the cleaning vessel. The contaminant and the cosolvent are returned to the cosolvent processing module. "The cosolvent can be filtered and/or distilled in the cosolvent module to separate the contaminant and recycle the cosolvent. Then the contaminant is disposed. Lastly, the carbon dioxide is added to the cleaning vessel in order to remove any remaining residual solvent. The dual system is the most effective and efficient because the cosolvent is distilled and recycled.

One must consider the operating costs of supercritical carbon dioxide fluid cleaning systems. Liquid carbon dioxide is less expensive than gaseous carbon dioxide. For example:

> Bulk liquid carbon dioxide is supplied at approximately 300 PSIG. The minimum pressure in the carbon dioxide recycle system of a precision cleaning system is approximately 500 PSIG, therefore the pressure of the bulk liquid carbon dioxide must be increased when it is transferred to the cleaning system. Although this pressurization adds capital cost to the system, the lower price of bulk carbon dioxide will rapidly pay for the initial investment. Currently, the bulk cost is less than ten cents per pound as compared to 50-70 cents per pound for other forms (McHardy and Sawan).

One should consider the types of control systems utilized. An automatic control system consists of flow sensors, pressure and temperature sensors, programmable logic controllable (PLC) and an operator interface device. Furthermore:

> The operator interface control device can be as simple as a stop-go for totally dedicated systems, or a personal computer. A personal computer connected to the PLC to provide operator interface, data collection, and analysis compatibility is recommended especially if the system parameter and/or the parts being processed will be changing (McHardy and Sawan).

Internal agitation which is also referred to as forced circulation should be considered. For example, "In addition to assuring uniform temperature and density in the solution it helps to assure an even flow of solvent around the work parts and rapid removal of the contaminant. This results in a shorter cleaning cycle. In addition, forced circulation assures uniform heating and cooling of critical parts during the process cycle" (McHardy and Sawan). An external magnetic coupled rotor and internal electronic motors have been used to provide internal agitation. These components can be costly; however, they ensure process consistency. One needs to take into account the pump capacity. "The pumping system is dependent on the pressures and the flow capacity required to meet the process production rate and cleanliness criteria" (McHardy and Sawan). According to Supercritical Fluid Cleaning, liquid carbon dioxide pumps are smaller, simpler to operate, more reliable, and less expensive than gas compressor systems. One should consider the materials that are used to construct the process vessels. The process vessels include valves, heat exchangers, separators, filters, and pipes.

For example:

> Process vessels with internal diameters larger than twelve inches may be fabricated using alloy steel, lined with 316 stainless steel to reduce the vessel cost, and still protect the vessel wetted surface from carbon acid attack. The use of alloy steel for the larger vessels can lower the costs to 30 to 50% of the figure for stainless steel vessels (McHardy and Sawan).

According to the Supercritical Fluid Cleaning the operating pressure and vessel diameter have the largest effect on cost. The recycle of carbon dioxide also has an effect on the supercritical carbon dioxide cleaning process.

For example:

> A production process rated for 500 pounds or carbon dioxide per hour that required five free volume exchanges of one cubic foot (carbon dioxide density equal to 50 to 60 pounds per cubic foot at operating conditions) to reach the desired cleaning level would consume up to 300 pounds or carbon dioxide per cleaning cycle or approximately thirty dollars per cleaning cycle if the carbon dioxide is not recycled. If the system is run twenty cycles per day for 250 days per year then the carbon dioxide cost approaches $150,000 per year. Recycling and only losing five percent per cleaning cycle would reduce this cost to less than $10,000 (McHardy and Sawan).

Therefore, the recycle of carbon dioxide reduces the operating costs. The recycle carbon dioxide should be meet the cleanliness level desired. Separators are utilized in supercritical carbon dioxide cleaning systems in order to ensure optimum cleanliness. For instance:

> Some of the contaminant that is removed from carbon dioxide in the separator will fractionate as a function of its vapor pressure at operating temperature and will be carried with the carbon dioxide vapor into the system, posing a recontamination risk. Since the vapor pressure of the contaminant is a function of the separator operating temperature, it is desirable to operate the separator at the lowest reasonable temperature consistent with the process requirements (cleanliness level desired and vapor pressure of the contaminants) (McHardy and Sawan).

In addition, refrigeration systems can provide the recirculation of carbon dioxide that meets the desired cleanliness level. This is evident in Supercritical Fluid Cleaning: Refrigeration systems are initially more expensive than chilled water systems (assuming that chilled water is available) but a direct refrigerated system will provide more assurance of clean recirculating carbon dioxide. When purchasing a supercritical carbon dioxide fluid cleaning system one must consider the phase of the carbon dioxide that is purchased, the materials of construction for the process vessels, the type of control system, recycle of the supercritical carbon dioxide and the desired level of cleanliness of the supercritical carbon dioxide.

6.0 Carbon Dioxide Snow Cleaning

Carbon dioxide snow cleaning is another excellent cleaning alternative. This cleaning method is non-abrasive, does not produce any chemical waste, non-flammable and non-toxic. Applied Surface Technologies produces a carbon dioxide snow cleaning unit that has an asymmetric venturi nozzle design. "The carbon dioxide expands through the orifice. The orifice of the venturi nozzle produces a high velocity stream of carbon dioxide snow. As a result of this nozzle design the snow stream can remove particulates and organic residues" (Applied Surface Technologies). Carbon dioxide snow cleaning removes paint, oil, grease, ink resins and adhesives. According to Applied Surface Technologies, carbon dioxide snow cleaning removes particulates by colliding with them, impacts momentum and then frees them. In addition, organic residue is removed by solvency and freeze fracture. Furthermore, "When the snow strikes the surface the pressure increases between the snow and surface. When the pressure exceeds 78 psi (the triple point pressure) the solid phase reverts into the liquid phase. The liquid carbon dioxide is a great solvent for organic residue (i.e. hydrocarbons)" (Applied Surface Technologies). In addition, the mechanism for hydrocarbon removal by carbon dioxide cleaning is based upon the excellent solvent properties of liquid carbon dioxide. "When the snow impacts the surface, the force on the solid carbon dioxide snow can exceed the yield stress, causing formation of a transient liquid phase at the snow-particle-surface interface. Surface hydrocarbons are absorbed by the liquid carbon dioxide and are removed when trapped during resolidification by the rebounding snow particle (Applied Surface Technologies). Furthermore, "Carbon dioxide is the only carbon dioxide method that removes particles and organic residue without any other assistance" (Applied Surface

Technologies). Carbon dioxide cleaning is not a batch process like liquid carbon dioxide cleaning systems; therefore, the carbon dioxide snow cleaning process is continuous. The carbon dioxide source can be in a liquid or gaseous phase.

Additionally:

> Gas fed systems tend to be cleaner (easier to filter a gas than a liquid), have less heavy hydrocarbon contamination, and have less consumption per unit time. Liquid fed systems produce more snow, allow for faster cleaning, but at a higher consumption rate. If the cleaning is occasional or a "small" area, a gas feed system is recommended, while for continuous high speed cleaning or large areas, a liquid source is recommended (Applied Surface Technologies).

The stream of carbon dioxide utilized in this specific cleaning process is at -80 degrees Celsius; therefore, one needs to be a cautious when utilizing carbon dioxide. One also should regulate the carbon dioxide consumption. Applied Surface Technologies recommends that one should keep the carbon dioxide concentration below 0.1%. A sensor should be installed in order to regulate the concentration. According to Applied Surface Technologies, carbon dioxide snow cleaning systems are ten times less expensive than other carbon dioxide cleaning systems. Carbon dioxide snow cleaning is an excellent cleaning alternative due to its great solvent characteristics, non-toxicity and low cost compared to other cleaning systems.

7.0 Carbon Dioxide Dry Ice Cleaning

Carbon dioxide dry ice cleaning involves forming liquid or gaseous carbon dioxide into dry ice pellets. This cleaning method is comprised of three steps:

> The first step involves the dry ice pellets traveling at a high velocity and impacting the surface of the material being cleaned. Therefore, the impact causes the contaminants to fall off. Secondly, the cold temperature during dry ice blasting of the dry ice pellets hitting the contaminant creates a micro-thermal shock (caused by the dry ice temperature of negative seventy nine degrees Celsius) between the surface contaminant and the substrate. Cracking and delamination of the contaminant occurs furthering the elimination process. The final phase of dry ice blasting has the dry ice pellet explode on impact, and as the pellet warms it converts to a carbon dioxide gas which expands rapidly underneath the contaminant surface. This forces the contaminant to fall off the surface. (RSG Technologies Inc.).

7.1 Advantages of Carbon Dioxide Dry Ice Cleaning

Carbon dioxide dry ice cleaning is non-toxic and non-flammable. The carbon dioxide dry ice evaporates completely as a gas. Therefore, the only waste that is generated from carbon dioxide dry ice cleaning is the contaminant material that was removed. Dry ice cleaning can replace hazardous chemical cleaners; therefore, there are not any expenses for hazardous chemical waste disposal. Additionally, dry ice cleaning eliminates scrubbing and manual cleaning. As a result, this reduces labor time. Dry ice cleaning does not erode or damage equipment; therefore, there is longer equipment life. This cleaning method is known to be better than sand blasting. Dry ice is softer than sand; therefore, dry ice does not damage the underlying surface. Dry ice cleaning is an excellent cleaning alternative; however, the material that is being cleaned must be able to withstand the impact from the dry ice pellets. Carbon dioxide dry ice cleaning is an excellent cleaning alternative for removing rust from steel.

8.0 Soy Methyl Ester

Soy methyl ester is made from the transesterification of soybean oil in order to remove the glycerin from the oil. In the transesterification of soybean oil, methanol is utilized as a raw material and sodium or potassium is used as a catalyst. The soy methyl ester goes through a water-wash process. Furthermore, "The water adheres to any impurities, causing the impurities to be filtered from the soy methyl ester" (Vertec BioSolvents^{TM}). Lastly, the soy methyl ester is dried through a vacuum drying system.

8.1 Utilization of Soy Methyl Ester as a Solvent

Soy methyl ester is utilized as a solvent to remove oil, grease, paint, cutting fluid and adhesives. According to the United Soybean Board, the Kauri-butanol (Kb) value for soy methyl ester is 58. The Kauri-butanol value is a standardized measure of the solvent power for a hydrocarbon solvent. The Kauri-butanol value represents the maximum amount of a hydrocarbon solvent that can be added to a kauri resin in butyl alcohol solution without causing cloudiness. If a surfactant solution is clear at room temperature and becomes cloudy when the temperature is elevated; therefore, the solution has reached its designated cloud point. The cloud point is the temperature at which a surfactant becomes insoluble in water. Furthermore, "Most cleaners are used at a temperature around their cloud point. Therefore, the amount of foaming is minimized and there is more effective cleaning activity." When the solution becomes cloudy then the solvent is inactive. Kauri resin is readily soluble in butyl alcohol and not in most hydrocarbon solvents; therefore, the resin solution will only tolerate a certain amount of dilution. A higher Kb value indicates that the solvent is more active. The Kb value for soy methyl ester compares favorably to the other common solvents (i.e. Stoddard solvent and d-limonene). For further information on the Kb values of soy methyl ester and other common solvents refer to the table. Soy methyl ester is used to clean up oil spills.

For example:

> Soy methyl ester is the basis for the CytoSol process which allows the removal and recovery from coastal and inland spill sites. The CytoSol Biosolvent™ dissolves and extracts crude oil which is then washed from contaminated soil with cold water and recovered for use as a bunker fuel. This product has been listed by the EPA on the National Contingency Plan for oil spill cleanups (University of Illinois, 2000).

In addition, many companies are replacing chlorinated hydrocarbon and fluorocarbon solvents with soy methyl ester. For instance, "Vertec Gold™ is an industrial cleaning solvent intended to replace mineral spirits, lacquer thinner, xylene, methyl ethyl ketone, and other hydrocarbon degreasing solvents. Vertec Gold™ is a blend of soy methyl ester and corn-derived ethyl lactate (Vertec BioSolvents™, 2000). Soy methyl ester exhibits excellent solvent characteristics. However, soy methyl ester leaves a film on the surface of the material being cleaned. This film is not desirable by some companies.

Vertec Gold™ by Vertec BioSolvents™ is a solvent that does not leave a film on the surface of the material being cleaned:

> The United Soybean Board has funded the research and development of several successful methyl soyate-based products. One of the most successful is Vertec Gold™, developed by Vertec BioSolvents™ and Henneberry Marketing. Because of the slow evaporation rate of methyl soyate, a film is left behind on the surface that is being cleaned. This characteristic is not desirable by all industrial-

cleaning markets. Vertec Gold^{TM} is a combination of methyl soyate and ethyl lactate, a derivative of corn that has a very quick evaporation rate. As a result, do Vertec Gold^{TM} does not leave a film on the surface of the material being cleaned. This combination offers the ideal cleaning and degreasing characteristics of soy methyl ester and the quick evaporation rate of ethyl lactate (United Soybean Board).

8.2 Advantages of Soy Methyl Ester

Soy methyl ester is non-carcinogenic, non-ozone depleting, non-flammable and biodegradable. The VOC content of soy methyl ester is very low in comparison to other cleaning solvents. The percentage of VOCs in soy methyl ester is thirty three percent. The percentage of VOCs in Stoddard solvent and d-limonene is, one hundred percent and ninety five percent. For further information concerning the VOC content of other cleaning solvents refer to table. In addition, the flash point of soy methyl ester is higher than most cleaning solvents. Therefore, soy methyl ester is non-flammable. The flash point of soy methyl ester is greater than 182 degrees Celsius. The flash point of Stoddard solvent is 38 degrees Celsius. For further information concerning the flash points of common cleaning solvents refer to table. Soy methyl ester is not a HAP (Hazardous Air Pollutant) or SARA (Superfund Amendment Reauthorization Act) 313 reported chemical. Soy methyl esters are biodegradable. "Biodegradability testing by an independent research laboratory determined that 95 percent of soy methyl ester samples biodegraded in 28 days" (United Soybean Board, 2002). Soy methyl ester has exceptional solvent characteristics and is non-hazardous to the environment and public health.

8.3 Costs of Soy Methyl Ester

Soy methyl ester is a cost effective cleaning solvent. Soy beans are very plentiful and are grown throughout numerous U.S states. Additionally, soy beans are harvested during many times of the year. This year, the U.S. will produce almost 3 billion bushels of soybeans that will generate about 4.5 billion gallons (over 31 billion pounds) of soybean oil, according to the United Soybean Board. Soy methyl ester does not generate hazardous waste. Therefore, one does not have to pay for the disposal of hazardous waste. Soy methyl esters are an exceptional alternative due their low cost.

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