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Precision Cleaning with Supercritical Carbon Dioxide for the Elimination of Organic Solvents and Reduction of Hazardous Waste

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Abstract

Private and governmental industrial facilities are accustomed to using chlorofluorocarbons and chlorocarbons for the cleaning of a variety of items. The Montreal Protocol (1987) and amendments to this act will phase out the use of chlorofluorocarbons, or CFCs, by the year 2000 because they are toxic, carcinogenic, and implicated in the depletion of the Earth's ozone layer. The United States has pledged to eliminate these substances by 1995. To stay competitive in the global market, US industries require an economical replacement. Supercritical fluids, which have been used in food, fragrance, and petroleum processes for years, are attractive replacement solvents because of their low environmental impact, high diffusivities, low viscosities, and temperature-pressure dependence of solvent strengths. In the case of nontoxic and nonflammable carbon dioxide (CO₂), its critical temperature and pressure are readily accessible with well-established process technology and equipment. In addition, applications using a supercritical fluid such as CO₂ are generally safer and environmentally benign. Extractions using supercritical CO₂ use less energy than distillation and incineration processes and are less expensive than liquid extraction processes using toxic and costly organic solvents. Finally, CO₂ has a very high volatility compared to virtually any organic extractant which facilitates its separation from extract solutions for extract recovery and CO₂ recycle. Data will be presented on the successful removal

of cutting and machine oils, silicone oils, body oils, and hydraulic fluids from a variety of industrial substrates with supercritical CO₂ to, at, or below precision cleaning levels (less than 10 micrograms of contaminant per square centimeter of surface). The applicability of this technique to commercial operations was evaluated in the areas of contaminant removal, surface interactions, operational costs, and waste reduction and elimination.

Introduction

The importance of product cleaning in many industrial operations is obvious. Current parts cleaning processes can be broadly divided into aqueous and non-aqueous based cleaning systems. Aqueous based cleaning systems can basically be considered a soap and water approach to parts cleaning, and are quite effective for many cleaning applications. However, aqueous cleaning has some disadvantages. The most obvious is that many parts are not amenable to water cleansing, and this can be compounded by long drying times and flash rusting which are often associated with aqueous cleaning. In addition, the user can be faced with expensive water treatment processes both prior to actual use in the cleaning system and prior to waste water disposal. These problems lead to non-aqueous or organic solvent based cleaning systems. Many industrial facilities currently employing non-aqueous cleaning technology are accustomed to using chlorocarbons and chlorofluorocarbons (CFCs) for the cleaning of a variety of items. Unfortunately, the Montreal Protocol (1987) and amendments to this act will phase out the use of CFCs by the year 2000 because they are toxic, carcinogenic, and implicated in the depletion of the Earth's ozone layer. For these reasons, the United States has pledged to eliminate these substances by 1995. To stay competitive in the global market, US industries require an economical replacement. Any cleaning solvent replacement must be discussed in terms of a definition of what type of item is being cleaned and what cleanliness level is required.

Most cleaning specifications are based on the amount of specific or characteristic compounds or contaminants remaining on the surface being cleaned. Potential common contaminants can include machining oils and greases, fingerprints, body oils, hydraulic and damping fluids, adhesives, waxes, and particulates. **Table 1** presents a simplified contamination scale for oil and

can be regarded as a reasonable estimate of cleanliness levels.¹ For the purposes of this paper, precision cleaning is defined as a contaminant level of less than 10 micrograms of contaminant per square centimeter. This $10 \mu\text{g}/\text{cm}^2$ level of cleanliness is either very desirable or required by the function of parts such as electronic assemblies, optical and laser components, electromechanical elements, hydraulic items, computer parts, ceramics, plastics, and many cast or machined metals.¹ It should be noted, however, that the goal for most precision cleaning levels is less than $1 \mu\text{g}/\text{cm}^2$, with the most stringent military specification being $0.4 \mu\text{g}/\text{cm}^2$.² Now, any CFC replacement solvent under consideration should be able to remove commonly encountered soils to these levels from a variety of surfaces, including printed circuit boards, plastics, metals, rubbers, composites, and glasses. Supercritical fluids, which have been used in food, fragrance, and petroleum processes for years, are attractive replacement solvents since they can remove many of these common contaminants from a variety of surfaces.

Cleaning with Supercritical Fluids

In order to appreciate the unique properties of supercritical fluids that make them ideal solvents for many cleaning applications, it is helpful to define a supercritical fluid. The physical states of all pure substances can be represented using a phase diagram, which is a representation of the states of the material as a function of temperature and pressure or of other properties of the material. In order to define a supercritical fluid, it is helpful to use a phase diagram based on temperature and pressure, and a temperature-pressure phase diagram of a pure substance is shown in **Figure 1**. The lines in the phase diagram depict the conditions of phase changes of the material (e.g., from liquid to gas). The critical point is defined by both a pressure (P_c) and a temperature (T_c). The region beyond the critical point is called the supercritical fluid region. Once a substance attains this state, it exhibits some of the properties of both gases and liquids.

Supercritical fluids have low viscosities and nearly zero surface tensions. Diffusion coefficients of supercritical fluids are between those of liquids and gases. These properties make supercritical fluids ideal for cleaning parts having porous, intricate, or rough surfaces or confined work areas because the solvent can penetrate into these regions to remove contaminants. As a result, the

removal process is often more rapid than when using conventional liquid organic solvents. Supercritical fluids can also possess "liquid-like" densities, which leads to excellent solubilities for many compounds. With supercritical fluids, density is a selective function of temperature and pressure. Generally, density increases with increasing pressure and decreases with increasing temperature. These combined effects can provide unique sets of solvation parameters. In general, it should be noted that a large increase in compound solubility occurs when going from the gas to the supercritical state. This enhanced solubility of organic compounds in the supercritical state combined with the low viscosity, low surface tension, and high diffusion rates of supercritical fluids form the basis for using supercritical fluids as cleaning solvents.

The solvent of choice in supercritical fluid processing and cleaning applications is often carbon dioxide for several reasons. One reason CO₂ is often used is because its critical parameters (critical temperature and pressure) are easily attainable. The critical point of CO₂ occurs at 31.1 degrees Celsius and 1047 pounds-per-square-inch (psi) of pressure. In addition, CO₂ is generally safe to work with. That is, it is environmentally benign and nontoxic. For this reason, CO₂ has been used in the food industry for many years.

Extraction or cleaning apparatuses using supercritical fluids are conceptually simple, and a basic schematic diagram of such a system is illustrated in **Figure 2**. Some source of liquid CO₂ such as standard gas cylinders or a large storage vessel provides fluid flow to a pump. The pump is then used to pressurize the CO₂ above its critical pressure. At this point, the CO₂ is usually in a high pressure liquid state. This liquid can then be introduced in the extraction vessel and then heated above the critical temperature or heated prior to introduction to the extraction vessel. The cleaning action then occurs in the vessel as the supercritical CO₂ extracts the contaminants from the substrate being cleaned. The supercritical CO₂ containing dissolved contaminants then flows through the extraction cell and is then expanded into the separator. It is here that as CO₂ becomes a gas through the expansion process, the contaminants fall out of solution and are collected. The gaseous CO₂ is then passed back into the flow stream to be used again in the cleaning process. The system shown in Figure 2 and many cleaning systems run as a batch mode operation. While batch cleaning may be slow when compared to a continuous cleaning system, a

batch CO₂ cleaning process can be used to recycle the contaminant. For example, expensive oils used in the processing of beryllium metal are recovered and reused. In addition, with this type of cleaning, the solvent CO₂ is removed by releasing the pressure in the extraction chamber resulting in cleaned components that are dry and ready for immediate use.

Overall operational costs for CO₂ cleaning tend to be lower than for other cleaning processes. The low critical parameters of CO₂ make it quite cost efficient in terms of energy use during operation. It was found that the highest energy costs for our large scale cleaning operation occurred at a temperature of 40 °C and a pressure 3500 psi for a total electrical cost of about \$2.75 per hour.⁴ While energy costs are low, the elevated pressures required to attain the supercritical state can cause the cost of the cleaning vessel to be relatively high. This initial high capital cost of supercritical CO₂ cleaning equipment and has caused many potential users to opt for aqueous and semi-aqueous based cleaning systems.³ However, with more companies beginning to offer supercritical CO₂ cleaning systems and custom tailoring of the cleaning systems to actual process needs, the capital cost of CO₂ cleaning technology has decreased substantially. Other operational costs for CO₂ cleaning systems remain low. For example, when compared to various organic solvents, CO₂ is much less expensive. For example we can purchase liquid CO₂ for about \$0.03 per pound, whereas we pay \$45.00 per pound for freon-113. With all of these factors in consideration, supercritical CO₂ cleaning is a viable alternative for many cleaning applications.

Supercritical fluids are in no way an absolute solution to all cleaning problems. Many substances requiring removal in cleaning operations, inorganic or ionic contaminants, are insoluble in supercritical fluids with low polarities such as carbon dioxide. More polar supercritical fluids such as ammonia or water are capable of dissolving polar and ionic compounds, but these fluids are very reactive and cause deterioration and corrosion of the materials to be cleaned as well as the cleaning apparatus itself. It should be noted that supercritical CO₂ is best suited for the removal of organic compounds with mid-to-low volatilities. These types of compounds often occur as common contaminants encountered in precision cleaning, and it is on these compounds that our experimental studies were focused.

Supercritical CO₂ Cleaning Results

Preliminary cleaning studies were conducted on a small scale as single point extraction data. Two separate studies were conducted, one on the removal of common machine contaminants (machining, cutting, drawing, lubricating, and body oils) and one on the removal of a wide variety of chemical compounds, both from a wide variety of substrates. All in all, the removal of 14 cutting oils, 17 machining oils, SiO_x fluids, 5 water soluble cutting fluids, and 120 individual chemicals from 18 metals, glass, quartz, sapphire, and 24 polymers. A portion of the substrates cleaned using supercritical CO₂ are summarized in **Table 2**. For the chemical compound removal studies only 340 stainless steel, electrolytic grade copper sheet, glass fiber filled epoxy board, borosilicate glass, and cast magnesium were used. The contaminant compounds were applied as a dilute solution to the entire single 0.5" by 2" substrate surface using a manual pipettor for a contamination level of 2 $\mu\text{g}/\text{cm}^2$. After the application solvent had evaporated, the extraction was begun. Each substrate was placed in a 10 ml commercial extraction vessel and dynamically extracted using pure CO₂ at 300 atm and 45 °C for 15 minutes using a Suprex SFE/50 supercritical fluid extraction instrument with a supercritical fluid flow rate of 2.8 ml/min. The extracted fluid was let down directly to the inlet of an HP 5971 GCMS operated in the split mode with a split ratio of 150 to 1. The GC column was a 60m x 0.25 mm i.d. DB-5 (5% crosslinked Ph-Me silicone) column programmed from 30 to 275 °C with a temperature ramp of 7 °C/min. Areas and concentrations of the extracted compounds were calculated from the total ion chromatogram by the HP software. The data were prepared as percent of original material removed from the substrate, and have 4% relative standard deviation as determined from three trials.

Typical results for the removal of oils from a variety of substrates is illustrated in **Figure 3**. Oil removal rates from all of the smooth surfaces such as epoxies, glasses, and plastics, were near quantitative as seen from the figure. The overall removal rates of oils from all metal surfaces were quite good, averaging from about 85 to 90%. The removal rates shown are not quantitative since the cast metals investigated were highly porous. Cleaning efficiency using the described

conditions was not quite as high for porous substrates, and this tends to lower the overall cleaning average depicted in the figure. For example, cleaning ranged from removal rates as low as 75% for the removal of 3-in-1 Oil® from cast aluminum to as high as 98% from stainless steel 340. Cleaning from cast materials has the potential to be quantitative with a longer extraction time or the use of a static extraction step (substrate immersed in supercritical CO₂ with no flow through the cell) followed by a dynamic extraction (CO₂ flow through the cell). Of particular importance is the quantitative removal of fingerprints, which tends to be a commonly encountered contaminant, from most all of the substrates investigated. Again, however, using the test conditions as described, cast metals showed lower extraction efficiencies. For example, cast magnesium had a fingerprint removal rate of 56%, while stainless steel 306 had a removal rate of 97%.

A portion of the overall results for the removal of a variety of chemicals from several substrates is shown in **Figure 4**. This study investigated the removal of 120 different individual chemicals from 340 stainless steel, electrolytic grade copper sheet, glass fiber filled epoxy board, borosilicate glass, and cast magnesium. The substrates also range from polished smooth, 340 stainless steel, for example, to porous cast magnesium. In this study, the removal rates were largely dependent on the functionality of the different chemicals. For example, cleaning ranged from removal rates as low as 35% for the removal of benzoic acid from cast magnesium to as high as 99% for the removal of 2-nitroaniline from epoxy board. In general, supercritical CO₂ proved to be an effective cleaning solvent for nonpolar or lipophilic chemical contaminants, while it was not so effective in the removal of polar or hydrophilic compounds. Of particular interest is the fact that removal rates from all of the substrates tested in this case had no statistical difference. Of course this is with the exception of cast magnesium for the same reason as observed with oil removal from porous substrates. In any event, this observation implies that the removal of contaminants using supercritical CO₂ is dependent more on the contaminant itself rather than on the surface that is being cleaned.

While it appears from the results thus far presented that cleaning with supercritical CO₂ is quite effective, it is of interest to compare CO₂ cleaning with current degreasing techniques. In this

case, the removal of a typical drawing oil from a stainless steel surface using supercritical CO₂ was compared with a standard freon-113 (1,1,2-trichlorotrifluoroethane) wash. In this case, after the application of the drawing oil, the stainless steel surface was cleaned using both supercritical CO₂ at different densities and a freon wash. The CO₂ density was varied using both temperature and pressure. After cleaning with supercritical CO₂, the stainless steel surface was subjected to a freon wash so that the amount of oil remaining could be determined. All freon washes were monitored with a Buck IR total hydrocarbon analyzer to measure the amount of drawing oil in the wash solution which is determined from hydrocarbon absorption at a fixed wavelength of 2924 cm⁻¹. The results of this study are shown in **Figure 5**. As seen from the figure, once the CO₂ density reaches about 0.5 g/mL, the cleaning efficiency is equivalent to that obtained using a freon wash. As the density of the supercritical fluid is increased, the cleaning efficiency also increases to a level below that obtained using a freon wash. This observation illustrates the selective solvation capability of a supercritical fluid based on temperature and pressure. As a result, a supercritical fluid has a unique advantage in that it could be used to selectively remove one contaminant from a surface while leaving a desired coating intact.

Conclusion

Supercritical carbon dioxide is an excellent solvent for precision cleaning, particularly for porous, intricate parts or parts that are relatively accessible by conventional solvents. This has been summarily demonstrated by results presented in this paper. Furthermore, to a first approximation, cleaning with supercritical CO₂ appears to be contaminant dependent while being surface independent. In addition, the use of supercritical CO₂ as a cleaning solvent can reduce the need for washing in organic solvents, thus reducing their overall use in manufacturing process. This in turn reduces hazardous waste by minimizing the solvent required to dispose of collected contaminants. Along with the effectiveness of cleaning with CO₂, the economics of the entire cleaning process may direct the use of CO₂ in cleaning applications other than precision cleaning.

Acknowledgments

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References

1. Spall, W.D. *International Journal of Environmentally Conscious Design & Manufacturing*, 1993, 2(1), pp. 81-86.
2. McHardy, J., et al. *SAMPE Journal*, 1993, 29(5), pp. 20-27.
3. Snowden-Swan, L.J. *PNL-10044/UC-602*, 1994, Pacific Northwest Laboratory, Richland, Washington.
4. Barton, J. *LA-12786*, 1994, Los Alamos National Laboratory, Los Alamos, New Mexico.

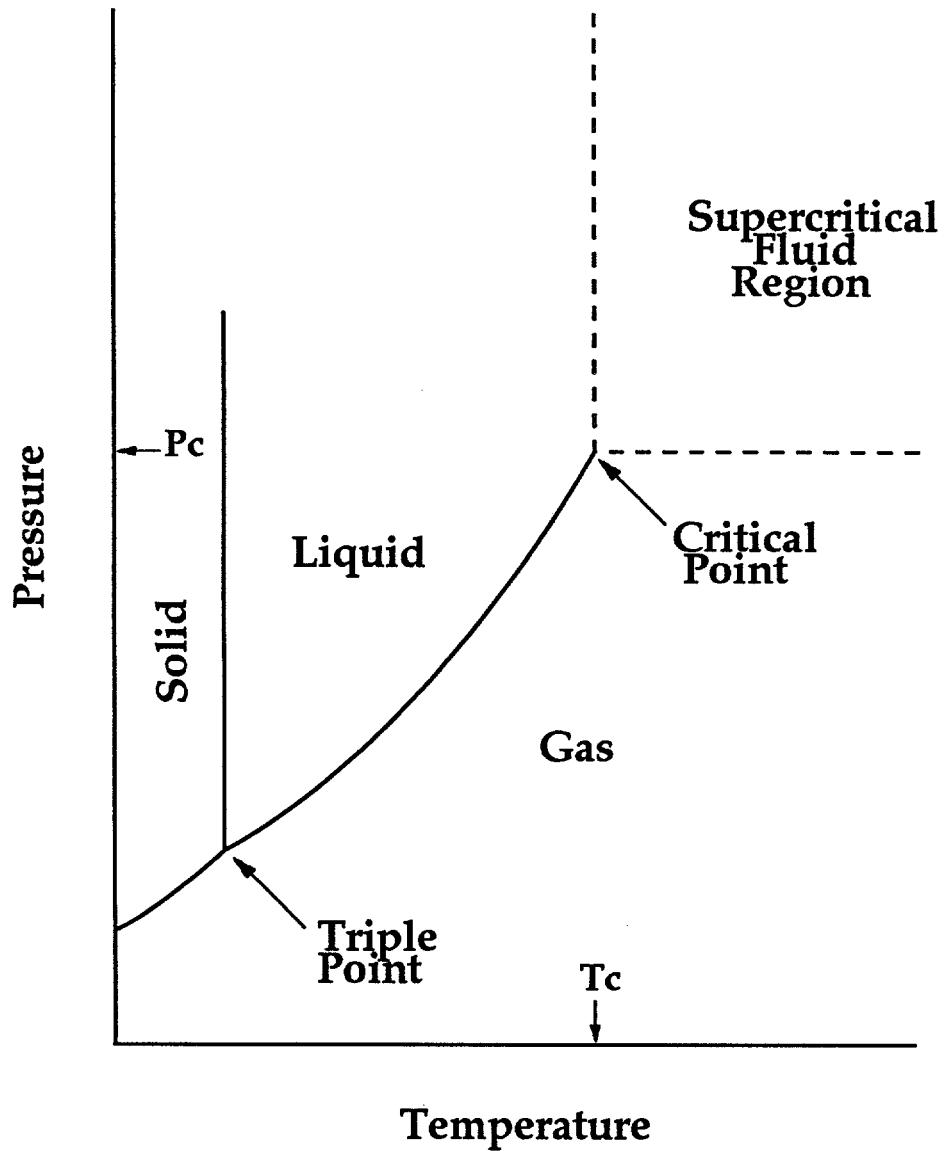
Table 1. Oil Contamination Scale

Oil Contamination Level	Surface Contamination	Cleanliness
10 mg/cm ²	Oil wet surface	Clean
1 mg/cm ²		
100 µg/cm ²	Surface absorbtion at 25 µm RMS	
10 µg/cm ²	Surface absorbtion at 1 µm RMS	
1 µg/cm ²	Interstitial absorbtion	
100 ng/cm ²	Monolayer	
10 ng/cm ²		

Table 2. Sample of Substrates Cleaned using Supercritical CO₂

Substrates Cleaned			
Metals	Glasses	Epoxies	Plastics
Machined Al	Borosilicate	Fiber filled PC board 1	Polyacrylate
Cast Al	Fused silica	Fiber filled PC board 2	Polyimide
Foil Al	Sapphire	Fiber filled PC board 3	Polystyrene
Machined Mg		Fiber filled PC board 4	Polymethylmethacrylate
Cast Mg		Fiber filled PC board 5	Polyisobutylene
Cast Fe			Polytetrafluoroethylene
SS 340			Polycarbonate
SS 316			Polyvinylidene
SS 306			High density polyethylene
Ag			Polyethylene
Au			Polyvinylchloride
Sn			Vinylchloride-acrylonitrile
Cu			Polyacrylonitrile
Brass			Polypropylene

Phase Diagram of a Pure Substance



Critical Parameters of CO₂: $T_c = 31.1$ °C, $P_c = 72.9$ atm, $\rho_c = 0.47$ g/cm²

(Triple point of CO₂ occurs at 5.2 atm and -56.6 °C)

Figure 1

Basic CO₂ Cleaning System

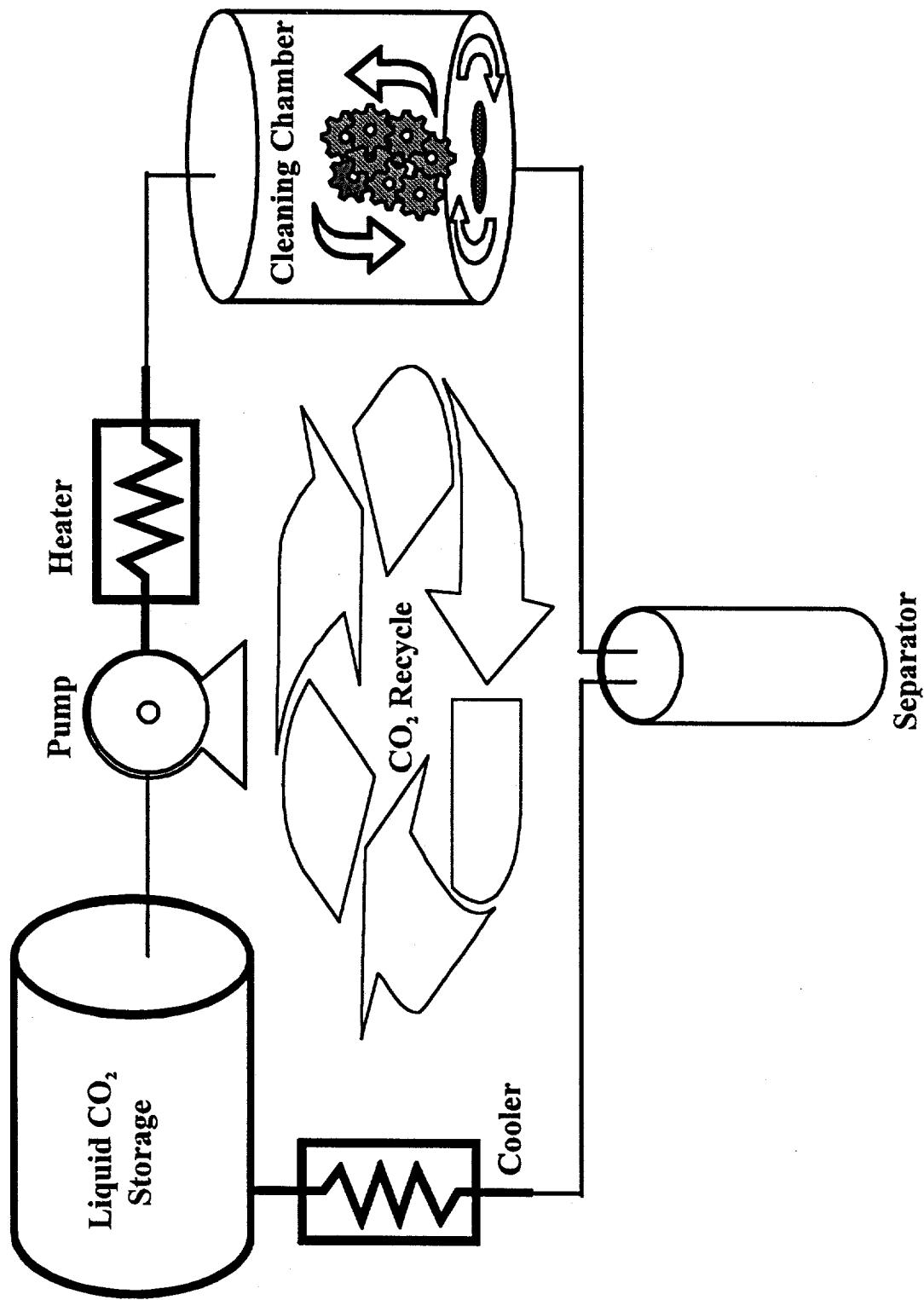


Figure 2

Removal of Oils using Supercritical CO₂

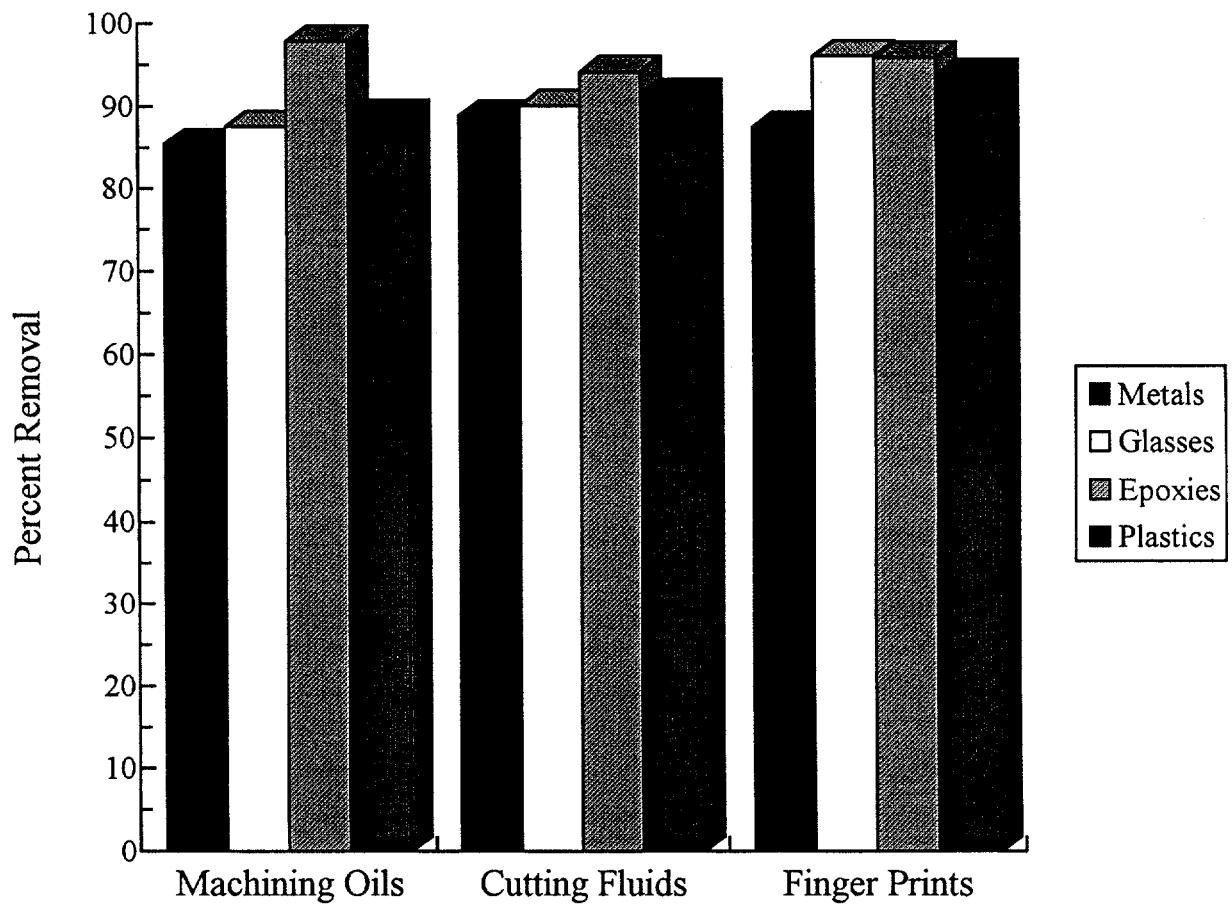
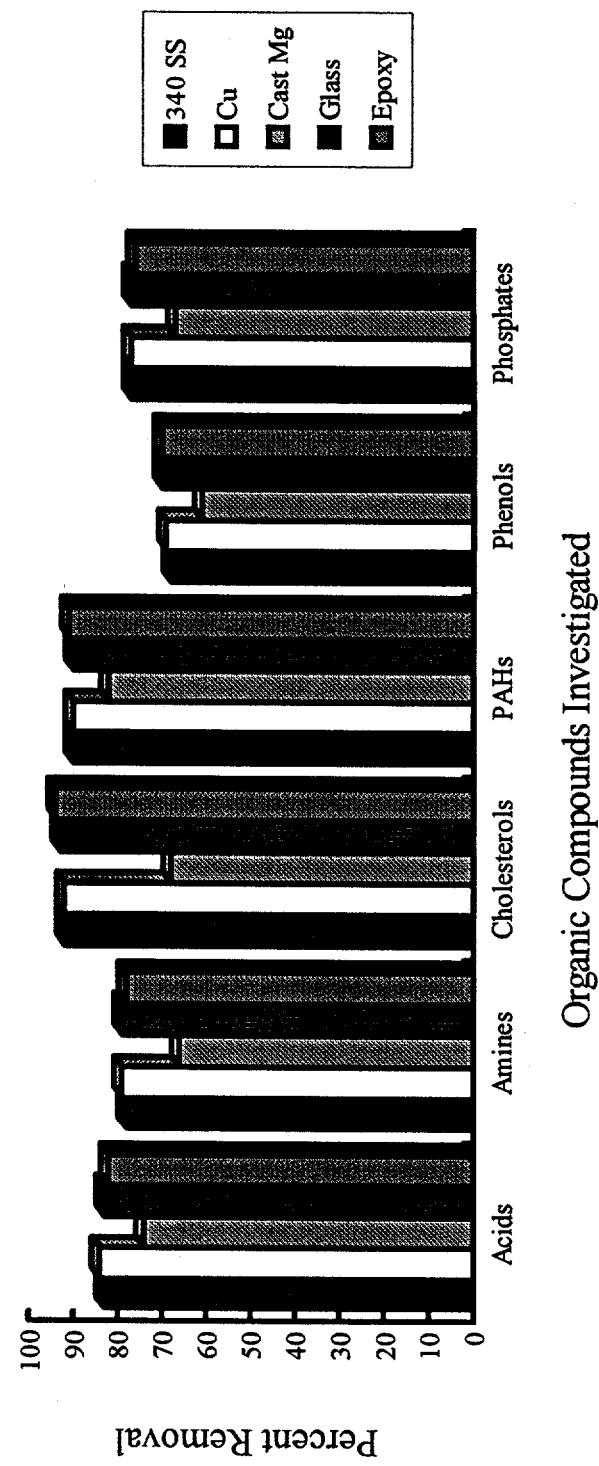


Figure 3

Figure 4

Removal of Organic Compounds using Supercritical Carbon Dioxide



Comparison of Drawing Oil Removal from Stainless Steel using CO_2 and Freon-113

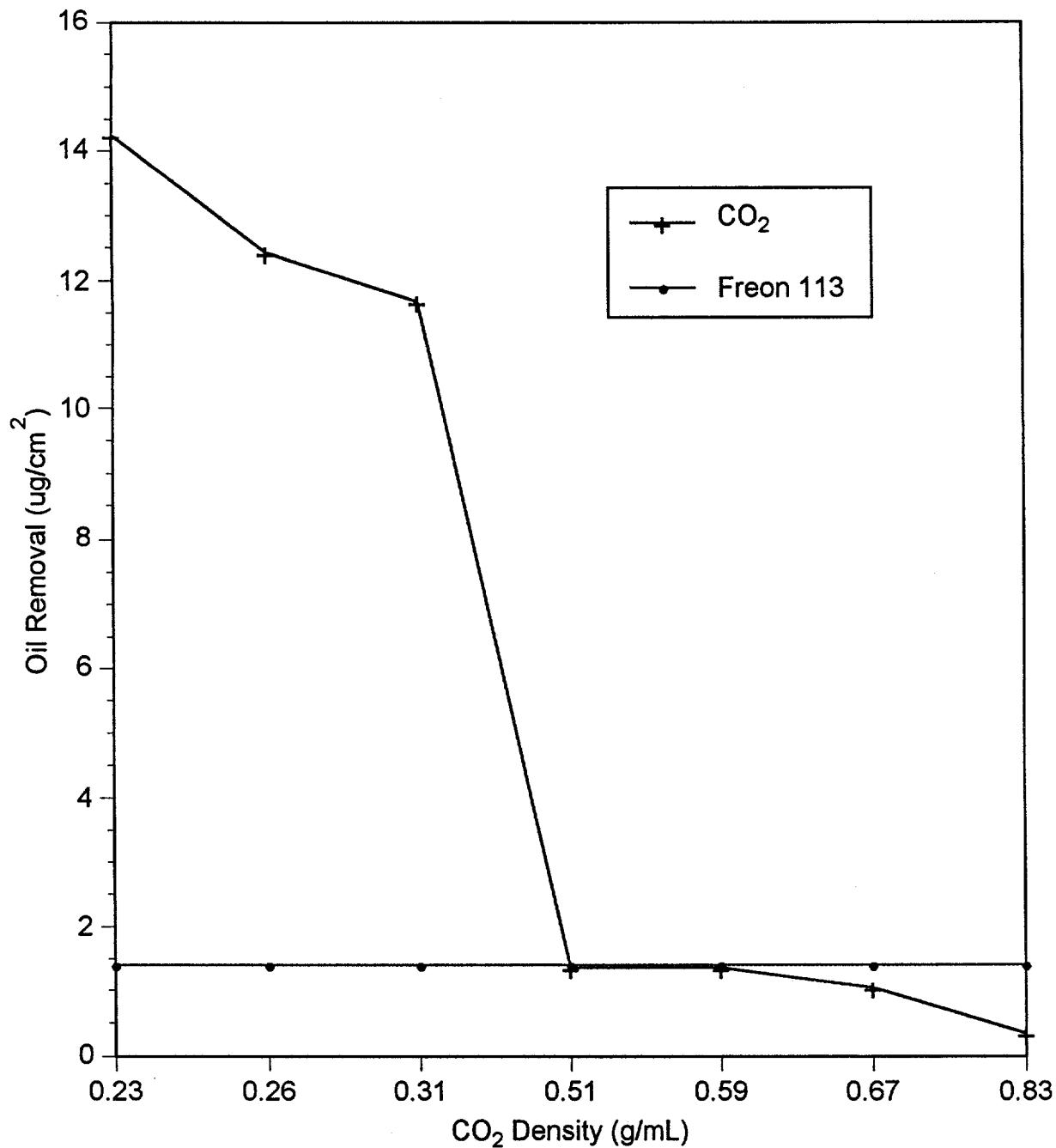


Figure 5