LA-UR-95-3313 (1017)

TITLE: **Elimination of Solvents and Waste by Using Supercritical Carbon Dioxide in Precision Cleaning**

AUTHOR(S): Sarah B. Williams, Kenneth E. Laintz, Jerome C. Barton, and W. Dale Spall

PRESENTED AT: American Chemical Society Emerging Technologies in Hazardous Waste Management VI Conference
Atlanta, Georgia
September 19–21, 1994
Manuscript A-703

Los Alamos

NATIONAL LABORATORY

ELIMINATION OF SOLVENTS AND WASTE BY USING SUPERCRITICAL CARBON DIOXIDE IN PRECISION CLEANING

S.B. Williams, K.E. Laintz*, J.C. Barton, and W.D. Spall

Los Alamos National Laboratory

Chemical Science and Technology Division

CST-12, MS E537

Los Alamos, New Mexico 87545

ABSTRACT

Physiochemical properties of supercritical carbon dioxide make it ideally suited for removing commonly encountered contaminants found in the precision cleaning of optical components, computer parts, and electronic assemblies. Data will be presented on a survey demonstrating the successful removal of cutting and machine oils, silicone oils, body oils and hydraulic fluids from a variety of surfaces with supercritical carbon dioxide to, at, or below precision cleaning standards (less than 10 micrograms of contaminant per square centimeter of surface). Replicate studies were performed in both a small bench-scale unit (10 milliliter cleaning vessel) and in a large-scale unit (60 liter, 14 inch diameter cleaning vessel) showing the ability to scale small experiments to commercial sizes. Applicability of this supercritical fluid cleaning technique to commercial operations was evaluated in the areas of contaminant removal efficiencies, surface interactions, operational costs, and environmental waste reduction/elimination.

Los Alamos National Laboratory ID Number LA-UR-94-3313

INTRODUCTION

Current manufacturing processes for electronic assemblies, optical and laser components, precision mechanical, electromechanical, and computer parts often require the use of chlorofluorocarbons, or CFCs, as the solvent of choice for the removal of oil and fluid contaminations. The Montreal Protocol and the Clean Air Act amendments mandate the phase- out of ozone depleting solvents including CFCs by the end of 1995. Therefore, alternative cleaning methods to achieve precision cleaning will be necessitated. The physiochemical properties of supercritical fluids, high diffusivities, low viscosities, low surface tension, and temperature-pressure dependence of solvent strength, make them ideally suited for the removal of many common contaminants. The combination of both gas and liquid like properties of supercritical fluids permit penetration into porous and intricate parts of assemblies and components allowing the solubilization of common contaminants followed by their subsequent removal to very low levels.

Carbon dioxide is commonly used in supercritical fluid processing and cleaning operations for several reasons. One reason CO_2 is often used is because its critical parameters (critical temperature and pressure) are easily reached, resulting in low equipment and operational costs. The critical temperature occurs at a mild 31°C, and the critical pressure occurs at 1070 pounds per square-inch (psi). Besides its ready availability, CO_2 is safe to work with. It is environmentally benign and nontoxic in comparison to many commonly used organic solvents, including CFCs. The use of supercritical CO_2 reduces the overall use of organic solvents in industrial processes which contributes to the reduction of hazardous waste. For these reasons, CO_2 has been in use for many years as an extraction solvent in the food and flavor industries.

The physical states of all pure substances can be represented using a phase diagram. When discussing supercritical fluids as solvents it is often helpful to define such a fluid in terms of a temperature and pressure phase diagram as shown in **Figure 1**. In Figure 1 the phase diagram illustrates a substance’s three physical states (solid, liquid, and gas) as a function of both temperature and pressure. The critical fluid region is characterized by a critical pressure (P_c) and temperature (T_c) and can be defined as the P-T region at which the gas cannot be compressed into the liquid state upon increasing pressure. It is known that the solvent properties of supercritical CO_2 are related to density. The density is controlled by manipulating the pressure and temperature of the liquid. In general, as the density of CO_2 increases, the solvation power also increases, which leads to excellent solubilities for many organic compounds in the supercritical fluid phase.

The removal of organic contaminants to a level of less than 10 micrograms of contaminant per square centimeter of surface is a desired level of precision cleaning required by many manufacturers[1] and has been used as a standard cleanliness level performance specification.[2] Precision cleanliness is either very desirable or required for 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] However, the ultimate level of cleanliness is dictated by the planned end-use of the component. Of course, any CFC replacement solvent should be able to clean commonly encountered soils to at least 10 $\mu g/cm^2$ from a variety of surfaces, including printed circuit boards, plastics, metals, rubbers, composites, and glasses. In order to determine whether this level of precision cleaning could be achieved with supercritical carbon dioxide, small bench scale (10 ml cleaning vessel) and large scale (60 L cleaning vessel) studies were undertaken The ten organic contaminants and substrate materials listed in Table 1 were selected as representative of commonly encountered components found in manufacturing processes. This study was conducted as a survey to determine the general applicability of supercritical fluid cleaning technology

EXPERIMENTAL SECTION

Small, bench scale cleaning studies were conducted as single point extraction data. These studies were conducted using a Suprex SFE/50 extraction unit (Suprex Corp., Pittsburgh, PA) containing a 10 ml cleaning vessel. The small scale study investigated 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.[3] However, only those studies duplicated by the large scale tests will be discussed here. Stainless steel 340 and 316, machined and electropolished strips, reagent grade copper, epoxy fiber filled standard PC board, borosilicate glass, and cast magnesium coupons measuring 0.5 in. x 2 in. (12.9 cm^2) were contaminated with 2 $\mu g/cm^2$ of each of the substances in Table 1.

The selection of contaminant compounds listed in Table 1 are representative of larger classes of common contaminants. For example, TRIM® SOL (Master Chemical Co., Perrysburg, OH) is a water miscible cutting fluid, Tapmatic® Cutting fluid (LPS Laboratories. Inc., Tucker, GA) is a light machining oil, 3-IN-ONE® Oil (Boyle-Midway, Inc., New York, NY) is a light lubricating oil, SAE 30 Motor Oil (Quaker State, Oil City, PA) represents a heavy machining oil, silicone oil (Aldrich Chemical Co., Milwaukee, WI) is a high temperature lubricating oil, Triton® X-100 (Dow-Corning, Midland, MI) is a nonionic surfactant, hexadecane (EM Science, Gibbstown, NJ) is a component of kerosene and diesel, and mineral oil (Furrs Supermarket, Los Alamos, NM) and hydraulic fluid (Gold Eagle Co., Chicago, IL) represent common organic contaminants found on parts and components. A surrogate mixture of skin lipids (components obtained from Aldrich) was prepared based upon previous work.[4-6] This type of contamination can be found in sweat, fingerprints, and other human contamination, and is often a major constituent of organic contamination found on parts, components, and assemblies.

The contaminant materials were applied as a dilute solutions to the entire 0.5 in. by 2 in. substrate surfaces using a manual pipettor. Once the application solvent had evaporated to dryness, a contaminated substrate was placed in a 10 ml extraction vessel and dynamically extracted (solvent flow through the cell) using SFC/SFE grade CO_2 (with siphon tube and 1500 psi He head space, Scott Specialty Gases, Inc., Longmont, CO) at 300 atm and 45°C for 15 min. with a flow rate of 7.8 ml/min. After flowing through the extraction cell, the fluid was let down directly into 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 60 m 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. Peak areas and subsequent concentrations of the extracted compounds were calculated from the total ion chromatograms by the HP software. The extractions were run in triplicate which yielded and overall 7% relative standard deviation. Data were prepared as percent of original material removed from the substrate.

For the large scale study, a SUPERSCRUB™ CO_2 cleaning system, Model No. 2, manufactured by EnviroPro Technologies™ (Erie, PA) equipped with a 60 L cleaning vessel was utilized. The SUPERSCRUB™, introduced in 1991, was the first large scale, computer controlled, commercially available supercritical CO_2 cleaning apparatus. The cleaning conditions for all runs programmed into the SUPERSCRUB™ unit controller consisted of a CO_2 (food grade, TriGas, Irving, TX) flow rate of 500 lb/hr at 1500 psi. The CO_2 was heated to 40°C and the chamber impeller was set at a speed of 500 rpm. This impeller mixes the CO_2 within the cleaning chamber to provide improved contaminant solvation and removal. Complete operational specifications and details for the SUPERSCRUB™ can be found elsewhere.

The large scale supercritical CO_2 cleaning study also investigated the removal of the contaminant compounds listed in Table 1 from similar substrates. In this case 314 stainless steel was used. The epoxy board was rigid-flex, multilayer through-hole-mount board which provided a very porous surface unlike the smooth glass fiber filled epoxy board used in the small scale study. The six substrate materials used in the large scale study, aluminum, brass, copper, epoxy, glass, and 314 stainless steel, were cut into 2 in. x 2 in. (51.63 cm^2) coupons and placed in a slotted stainless steel box. This box contained six rows and twenty-five slots per row and held the coupons in a fixed position while in the cleaning chamber. The coupon holder was milled to allow CO_2 to flow around the coupons and through the box. The contaminant compounds listed in Table 1 were applied as dilute solutions in HPLC grade Freon 113 (1,1,2 trichlorotrifluoroethane, J.T. Baker, Phillipsburg, NJ) to the entire surfaces of duplicate substrates using a manual pipettor at 500 μg and 2500 μg contamination levels for total contaminations of about 10 $\mu g/cm^2$ and 50 $\mu g/cm^2$. While it can be argued that a contamination level of 10 $\mu g/cm^2$ already passes precision cleaning specifications,[2] a residue is usually still visible at this level. Since the final determination of cleanliness is often visual observation, removing contaminants to cleanliness levels below 10 μg/cm^2 is desirable. After the solvent had evaporated, the box containing 24 randomly placed contaminated coupons and 6 blank coupons was placed within the SUPERSCRUB™ cleaning vessel and the extraction carried out. At the end of the cleaning run, the box was removed from the cleaning vessel and an analytical wash was performed on each of the thirty coupons to determine the amount of contaminant remaining. The analytical wash was performed by placing the coupons into a 100 mm dia. petri dish containing 10 ml of Freon 113. The petri dish was placed into a dry sonication bath for one minute. The remaining Freon 113 was transferred to a 5 ml volumetric flask and brought to volume. The coupons were washed with Freon 113 into a 3 ml Infrasil quartz cuvette with a 1 cm pathlength. The cuvette was placed into a Buck Total Hydrocarbon Analyzer Model 404 (Buck Scientific lnc., East Norwalk, CT) and the concentration determined by comparison of the hydrocarbon absorption at a fixed wavelength of 2924 cm^{-1} (3.42 μm) to standard solutions. Standard calibration curves were linear with an r^2 of at least 0.99. The average mass detection limit for this procedure was about 8 μg, which corresponds to 0.15 μg/cm^2 for the 51.6 cm^2 substrate coupons. Although the detection limit for silicone oil with this method was about 107 μg (2 μg/cm^2), it is below the desired precision cleaning level. The overall procedure was shown to have an average RSD of 2.9% and performed in duplicate for a total of four trials for each substrate.

RESULTS AND DISCUSSIONS

Large scale cleaning or extraction systems using supercritical fluids like the SUPERSCRUB™ are conceptually simple, and a basic schematic diagram of such a system is illustrated in **Figure 2**. The component operation can be understood when a cleaning cycle is superimposed over a P-T phase diagram as shown in **Figure 3** to explain the overall operation of the system. Initially, a source of CO_2 such as a liquid storage vessel or standard gas cylinders as shown in figure 2 provides liquid at a P1-T1 to some type of pump. The pump in figure 2 compresses the CO_2 above its critical pressure to P2-T1. This liquid can then be introduced into the extraction vessel of figure 2 at P2-T1 and then heated above the critical temperature to P2-T2 or heated to P2-T2 prior to introduction to the extraction vessel. The items are cleaned by continuous displacement of the vessel's volume for some fixed period of time at P2-T2. This type of cleaning mode is referred to as dynamic cleaning. The addition of a static cleaning mode, often a better method for substances with low solubilities, does not continuously flow fresh solvent through the extraction chamber. Removal of the dissolved contaminants from the supercritical CO_2 is achieved by decompressing the carbon dioxide to P1-T2 within the separator shown in figure 2. As the CO_2 enters the gas phase at P1-T2, the dissolved contaminants precipitate from the gas and are separated from the system. The gaseous CO_2 is cooled in figure 2 to the liquid state at P1-T1 and is passed back into the flow stream to be used again in the cleaning process. The items that were in the chamber are removed, clean and dry, ready for immediate use.

Overall operational costs for CO_2 cleaning tend to be lower than for other cleaning processes when the entire cleaning process is considered.[8] The low critical parameters of CO_2 make it quite cost efficient in terms of energy use during operation. It was found that energy costs for our large scale cleaning operation for a standard run at a temperature of 30°C and a pressure of 1500 psi were about $0.90 per hour while the highest energy costs occurred at 40 °C and 3500 psi for a total electrical Cost of about $2.75 per hour.[9] Even though energy consumption costs are low, the pressures required to attain a supercritical phase can cause the cost of the cleaning vessel to be relatively high. This initial perceived high capital cost of supercritical CO_2 cleaning equipment[8] has probably caused many potential users to opt for aqueous type cleaning systems. Currently, however, more companies are offering supercritical CO_2 cleaning systems and custom tailoring these systems to process needs. These efforts have driven the capital costs of CO_2 cleaning systems down. Meanwhile, other operational costs for CO_2 cleaning systems have always been low. For example, the price of liquid CO_2 is about $0.05 per pound, while Freon 113 costs around $45.00 per pound, offsetting much of the potentially high initial costs. In consideration of these factors, supercritical CO_2 cleaning is a viable alternative for many cleaning applications.

Results for the small scale removal of machining oils and fluids from the substrates listed in **Table 1** are summarized in **Table 2**. In general, the removal rates for these fluids from all of the surfaces listed were near quantitative as seen from the table. In particular, supercritical CO_2 was quite effective in the removal of the various oils and fluids from all metal surfaces, removing, for example, from about 86 to 99% of the 3-IN-ONE® Oil. It should be pointed out that with a 7% RSD, there is no statistical difference between an 86% removal rate and a 99% removal rate at the 5% level using a standard two-tailed mean comparison *t*-test with 4 degrees of freedom. The removal rates listed for cast magnesium in Table 2 are not quantitative. Cleaning from cast or porous materials has the potential to be quantitative using more rigorous conditions such as a longer extraction time or the use of a static extraction step (substrate immersed in supercritical CO_2 with no flow through the cell) followed by a dynamic extraction, and indeed, further testing showed this to be true. Silicone oil was also not as efficiently removed as the other contaminants from the substrates investigated. This may be due to solubility or to fractionation of the oil with the higher molecular weight, less soluble components remaining on the surface.

The removal of skin lipids, Triton® X-100, and hexadecane is summarized in **Table 3**. While it was no surprise that these lipophilic organic compounds were quantitatively removed, of particular importance is the quantitative removal of skin lipids. Again, however, using the test conditions as described, cast magnesium showed lower extraction efficiencies. For example, cast magnesium had a fingerprint removal rate of 56%, while Stainless Steel 316 had a removal rate of 95%. The low removal rate from the cast magnesium sample is again believed to be due to the porosity of the substrate surface. Longer extraction times (30-45 min), however, resulted in quantitative removal of the skin lipids from the magnesium surface. In general the results of the contaminant removal studies using the SUPERSCRUB™ closely correlate with those observed in the small scale study. The overall results for the removal of machining oils and fluids at the two different contamination levels investigated in the large scale study are summarized in **Table 4**. As seen from the table, most of the machining oils and fluids, 3-IN-ONE® oil, Tapmatic® cutting fluid, SAE 30 motor oil, hydraulic jack oil, and mineral oil, were effectively removed from all substrates at both contamination levels below the precision cleaning level. On the other hand, at a contamination level of 50 μg/cm2, TRIM®, SOL and silicone oil were not removed from most or the substrates to a precision clean level below 10 μg/cm^2. In fact, there was visible silicone oil contamination remaining on the 50 μg/cm^2 contaminated coupons after the SUPERSCRUB™ run. An exception in this case was the removal or TRIM® SOL from copper, where 83% of the initial 50 μg/cm2 was removed. It is likely that those contaminants not efficiently removed at 1500 psi and 40°C would be removed at higher pressures and temperatures corresponding to increased solvation capacity of the supercritical CO_2.

In general, removal rates for the coupons contaminated at the 50 μg/cm^2 were higher than those of the coupons contaminated at 10 μg/cm^2. An example of this is shown in figure 4 with the removal of TRIM® SOL from the metal substrates cleaned using the SUPERSCRUB™. As shown in the figure, the removal of TRIM® SOL is appreciably higher from the metal coupons contaminated at 50 μg/cm^2 as compared to those contaminated at 10 μg/cm^2. It has been shown that the solubility of components within a mixture often have higher solubilities in supercritical CO_2 than the pure components themselves. This phenomenon is caused by one or more components acting as solubility enhancers for other components. With more contaminant present at 50 μg/cm^2, it is possible that the overall solubilities of the contaminants were increased to yield higher extraction efficiencies. In fact, metal coupons were placed in the SUPERSCRUB™ for cleaning that had been saturated with 3-IN-ONE® oil to the point where oil was dripping from the coupons. Following cleaning with CO_2 at 1500 psi and 40°C, the oil was removed down below the precision clean level. It should be noted that these results in suggest that CO_2 may be used as a one step bulk cleaning method in addition to its use in precision cleaning. The removal of skin lipids, Triton® X-100, and hexadecane in the large scale SUPERSCRUB™ study also correlate well to those results obtained in the small scale study, and these results are summarized in **Table 5**. As in the small scale study, these organic contaminants were quantitatively removed from all substrates at both contamination levels including the porous rigidflex, through-hole epoxy board. While the removal of these contaminants was well below the precision clean level of 10 μg/cm^2, the skin lipids left a visible film on the 50 μg/cm^2 contaminated coupons after the SUPERSCRUB™ run. This film may represent a small residual of the lower solubility components in the skin lipids mixture. Again, longer extraction times would probably remove this residual film.

Overall, the removed contaminants showed no evidence of redeposition on the blank coupons randomly placed throughout the stainless steel holder. Additionally, the coupon substrate did not effect the removal of the contaminants by supercritical carbon dioxide, except in the case of rigidflex, through-hole epoxy board which demonstrated consistently lower rates of removal due to its surface topography, analogous to the cast magnesium used in the small scale study. The large errors associated With the large scale SUPERSCRUB™ experiments are largely due to the spread of data obtained with the rigid-flex, through-hole epoxy board. However, all raw data were used to calculate the removal rates and only four data points were collected, contributing to the large RSD In some cases, results were sporadic. For example, a 50 $\mu g/cm^2$ deposited contaminant might have been removed to below the analytical detection limit one run while the duplicate run yielded a removal rate around 10 $\mu g/cm^2$. A more thorough investigation is currently being conducted to determine the cause of the spurious data.

It should be noted that the removal of the all of the contaminants was independent of the placement of the coupons inside of the stainless steel holder in the SUPERSCRUB™. Overall results have shown that the removal of organic residues with supercritical CO_2 is quite effective, however, it is important to compare CO_2 cleaning with a typical degreasing technique. While the above study was conducted as a survey to determine the general applicability of this technique, actual operating conditions need to be examined for the implementation of supercritical CO_2 cleaning in an actual process. Basically, the density of the CO_2 cleaning solvent needs to be adjusted to achieve the appropriate level of cleanliness desired. In this case, the removal of a typical drawing oil from a stainless steel surface using supercritical CO_2 was compared with a standard Freon 113 wash. After the drawing had been applied to the stainless steel surface in a uniform coating, the surface was cleaned using both supercritical CO_2 at different densities and using a Freon 113 wash. After cleaning with supercritical CO_2, the stainless steel surface was washed with Freon 113 to determine the amount of oil remaining. As before, all Freon 113 washes were monitored with the Buck IR total hydrocarbon analyzer to measure the amount of drawing oil in the wash solution. The overall results of this study are shown in **Figure 5**. As seen from the figure in this case, the cleaning efficiency of supercritical CO_2 is equivalent to that obtained using a Freon 113 wash when the density reaches about 0.5 g/ml. As the density of the supercritical CO_2 is increased, the cleaning efficiency also increases to a level better than that obtained using Freon 113. This investigation illustrates the selective solvation capability of a supercritical fluid based on temperature and pressure and demonstrates the need for careful preliminary studies to determine appropriate operating conditions. As a result, a supercritical fluid has a unique advantage in that it has the potential to selectively remove one contaminant from a surface while leaving a desired coating intact.

CONCLUSION

Cleaning with supercritical fluids is not an absolute or drop-in solution to all cleaning problems. It is best for parts that are incompatible with water or are thermally sensitive. Supercritical CO_2 has been shown and is noted for its solvation of organic compounds having mid-to-low volatilities, and these types of compounds are common contaminants requiring removal to precision clean levels. On the other hand, inorganic or ionic contaminants are insoluble in supercritical fluids with low polarities such as carbon dioxide, and alternate cleaning methods should be considered for the removal of these types of contaminants. To a first approximation, cleaning with supercritical CO_2 appears to be contaminant dependent while being surface independent. The use of supercritical CO_2 as a cleaning solvent can reduce the need for washing in organic solvents, thus reducing their overall use in manufacturing processes. This in turn reduces hazardous waste by minimizing the solvent required to dispose of collected contaminants. Furthermore, cleaning with supercritical CO_2 removes the need for energy consuming drying steps which increases the speed of the overall cleaning process since less inventory needs to be held in the cleaning and drying phases of manufacturing. Therefore, along with the effectiveness of cleaning with CO_2, the economics of the entire cleaning process may direct the use of CO_2 in cleaning applications other than precision cleaning. These studies demonstrate that waste reduction and elimination of hazardous solvents utilizing supercritical carbon dioxide at relatively low temperatures and pressures during the manufacturing processes is a viable process.

ACKNOWLEDGMENT

This work was performed under funding from the Industrial Waste Program Office, Department of Energy, Office of Industrial Technologies.

REFERENCES

1. Spall, W. D. *International Journal of Environmentally Conscious Design & Manufacturing, 1993*, 2(1) pp. 81-86.
2. American National Standards Institute. ANSI/IPC-Ch-65, 1990, 7.2.3, pp. 47-48.
3. Unpublished results, currently in preparation for publication.
4 Downing, D.T., Strauss, J.S., and Pochi, P.E. *Journal of Investigative Dermatology*, 1969, 53(5), pp. 322-327.
5. Downing, D.T., and Strauss, J.S., *Journal of Investigative Dermatology*, 1974, 62(3), pp. 228-244.
6. Strauss, J.S., Pochi, P.E., and Downing, D.T., *Journal of Investigative Dermatology*, 1976, 67(1), pp. 90-97.
7. EnviroPro Technologies, 2930 W. 22nd St., Erie, PA 16512 (814) 838-5888.
8. Snowden-Swan, L.J., PNL-10044/UC-602, 1994, Pacific Northwest Laboratory, Richland, Washington.
9. Barton, J.L., LA-12786, 1994, Los Alamos National Laboratory, Los Alamos, New Mexico.
10. Kurnik, R.T., and Reid, R.C., Fluid Phase Equilibrium, 1982, 8, p. 93.

Table 1. Contaminants cleaned from substrate materials using supercritical CO_2 in large and small scale cleaning studies.

Contaminants		Substrate Materials
Triton® X-100	Skin Lipid Mixture:	Aluminum
Hexadecane (C16)	30% Triolein	Borosilicate glass
3-IN-ONE® Oil	25% Oleic acid	Copper
Tapmatic® Cutting Fluid	25% Cetyl palmitate	Brass
SAE 30 Motor Oil	15% Squalene	*Glass fiber filled epoxy board
Silicone Oil	2.5% Cholesterol	†Cast magnesium
TRIM® SOL	2.5% Cholesterol oleate	†340 Stainless steel
Mineral Oil		†316 Stainless steel
‡Hydraulic Jack Oil		‡314 Stainless steel
		‡Rigid-flex, through-hole epoxy board

*Substrates used in small scale study only

‡Substrates and compounds used in large scale study only

Table 2. Small scale supercritical CO_2 machining oils and fluids removal results.

Substrate Materials	Contaminant Compounds (Percent Removal*)					
	3-IN-ONE® Oil	TRIM® SOL	Tapmatic® Cutting Fluid	SAE 30W Motor Oil	Silicone Oil	Mineral Oil
Stainless Steel 340	98	94	95	91	88	98
Stainless Steel 316	96	90	94	92	84	94
Copper	96	85	96	91	79	93
Aluminum	86	83	97	94	85	87
Brass	99	85	89	95	89	89
Cast Magnesium	75	72	99	80	71	70
Glass	89	84	98	91	85	88
Epoxy board	93	82	98	94	83	89

*Based on triplicate runs with an average 7% RSD

Table 3. Small scale supercritical CO_2 removal of skin lipids, Triton® X-100, and hexadecane.

Substrate Materials	Contaminant Compounds (Percent Removal*)		
	Skin Lipids	Triton® X-100	Hexadecane
Stainless Steel 340	94	98	91
Stainless Steel 316	95	97	90
Copper	95	93	92
Aluminum	94	93	95
Brass	94	98	98
Cast Magnesium	56	78	85
Glass	94	95	98
Epoxy board	96	94	96

*Based on triplicate runs with an average 7% RSD

Table 4. Results of large scale supercritical CO_2 machining oils and fluids removal study at contamination levels of 10 µg/cm² and 50 µg/cm².

Substrate Materials	Contaminant Compounds (Percent Removal*)						
	3-IN-ONE®	TRIM® SOL.	Tapmatic®	SAE 30W	Silicone Oil	Hydraulic Oil	Mineral Oil
Brass							
10 µg/cm²	> 99	64	95	92	54	45	> 99
50 µg/cm²	> 99	72	99	95	75	89	> 99
Stainless Steel 314							
10 µg/cm²	> 99	42	89	78	65	90	> 99
50 µg/cm²	> 99	77	98	88	72	98	> 99
Glass							
10 µg/cm²	98	27	94	87	60	85	98
50 µg/cm²	> 99	76	98	94	74	96	> 99
Aluminum							
10 µg/cm²	97	52	96	95	58	83	97
50 µg/cm²	99	66	99	96	73	96	99
Copper							
10 µg/cm²	99	20	54	93	55	43	99
50 µg/cm²	> 99	83	99	95	58	89	> 99
Rigid-flex Epoxy Board							
10 µg/cm²	94		65	61	< 1	< 1	94
50 µg/cm²	94		96	84	70	93	94

***Based on averages of four runs with an average 50% RSD**

Table 5. Large scale supercritical CO_2 removal of skin lipids, Triton® X-100, and hexadecane at contamination levels of 10 μg/cm^2 and 50 μg/cm^2.

Substrate Materials	Contaminant Compounds (Percent Removal*)		
	Skin Lipids	Triton® X-100	Hexadecane
Brass			
10 μg/cm^2	99	> 99	92
50 μg/cm^2	89	> 99	99
Stainless Steel 314			
10 μg/cm^2	> 99	> 99	96
50 μg/cm^2	> 99	> 99	99
Glass			
10 μg/cm^2	> 99	99	96
50 μg/cm^2	99	97	99
Aluminum			
10 μg/cm^2	98	97	96
50 μg/cm^2	> 99	> 99	99
Copper			
10 μg/cm^2	97	99	91
50 μg/cm^2	97	> 99	99
Rigid-flex Epoxy Board			
10 μg/cm^2	77	94	84
50 μg/cm^2	92	93	94

*Based on averages of four runs with an average 60% RSD

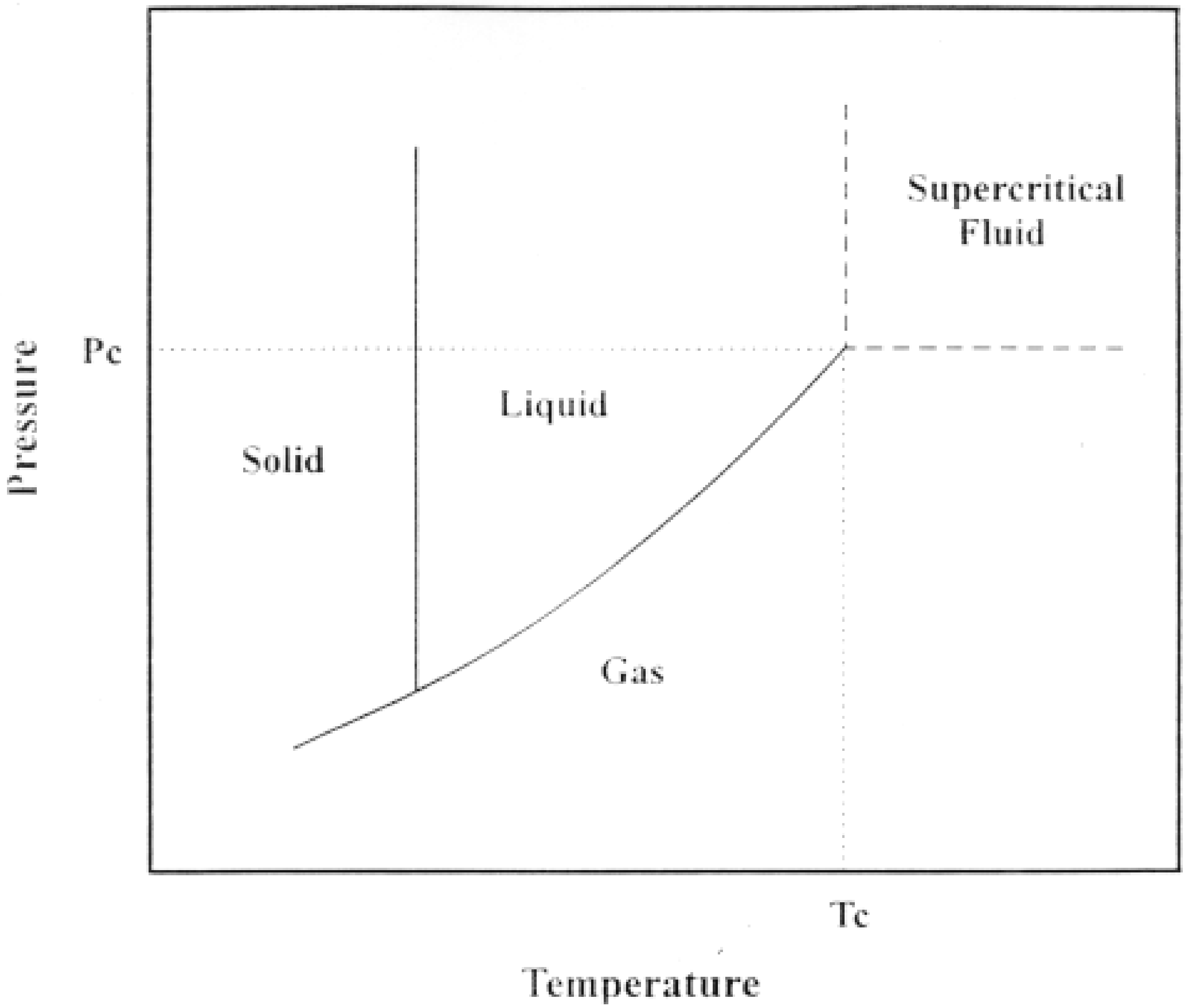

Figure 1. Generic pressure-temperature phase diagram of a pure compond.

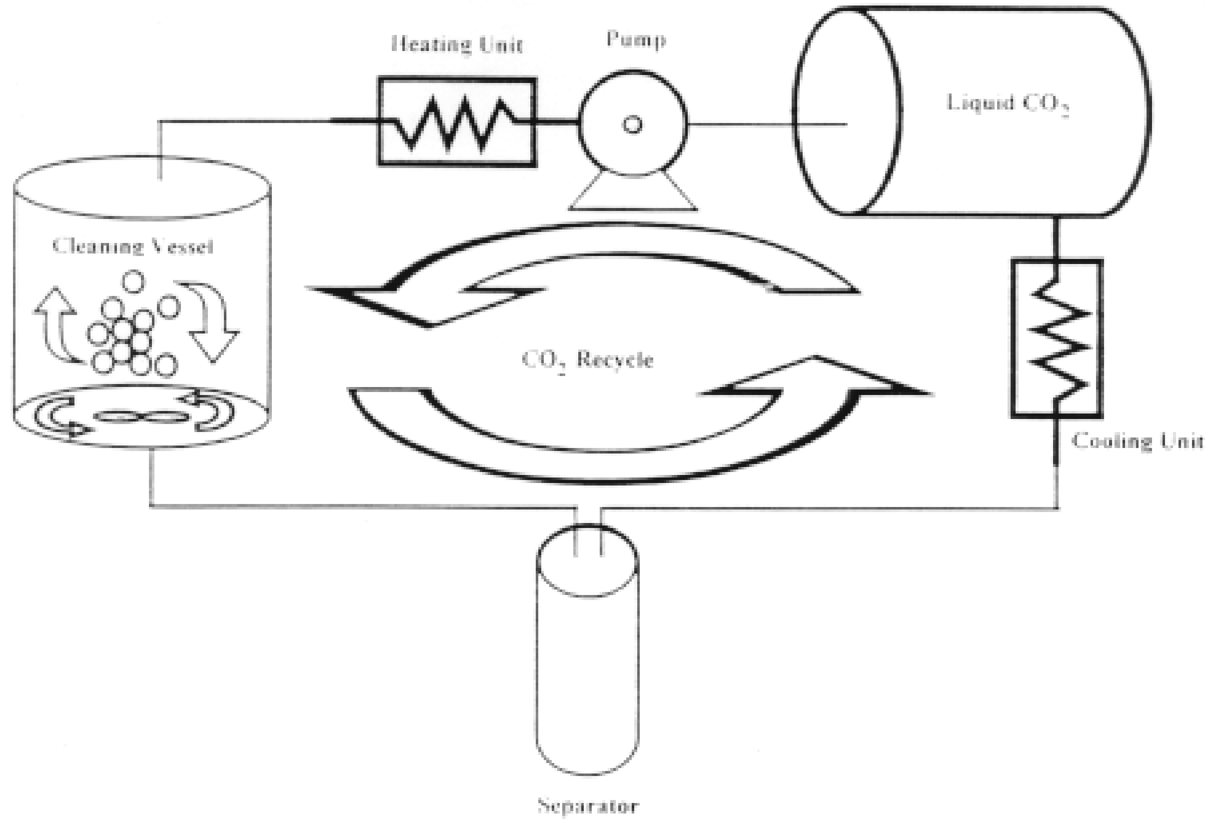

Figure 2. Basic schematic diagram of a CO_2 cleaning system.

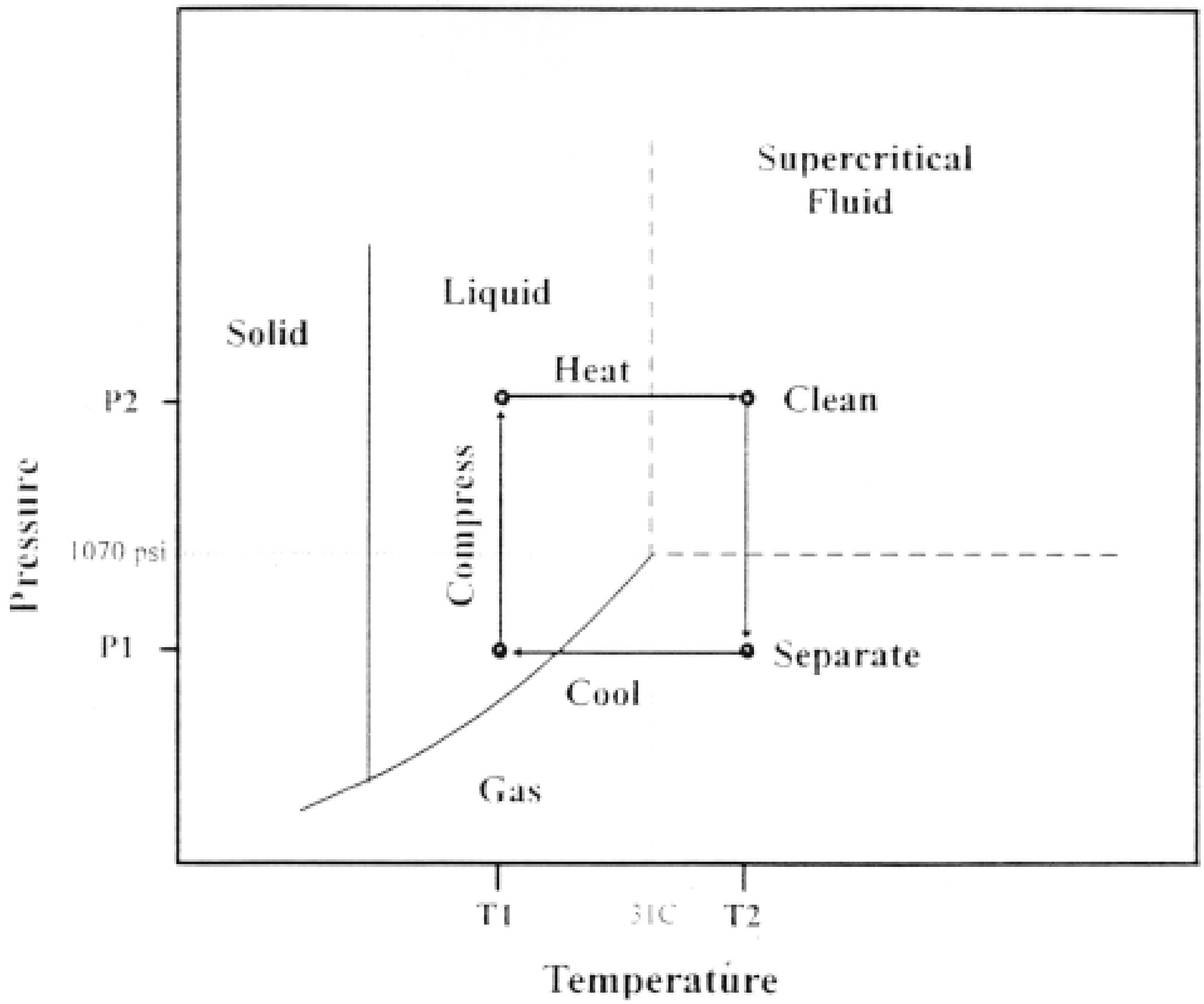

Figure 3. Phase behavior of CO_2 in cleaning cycle.

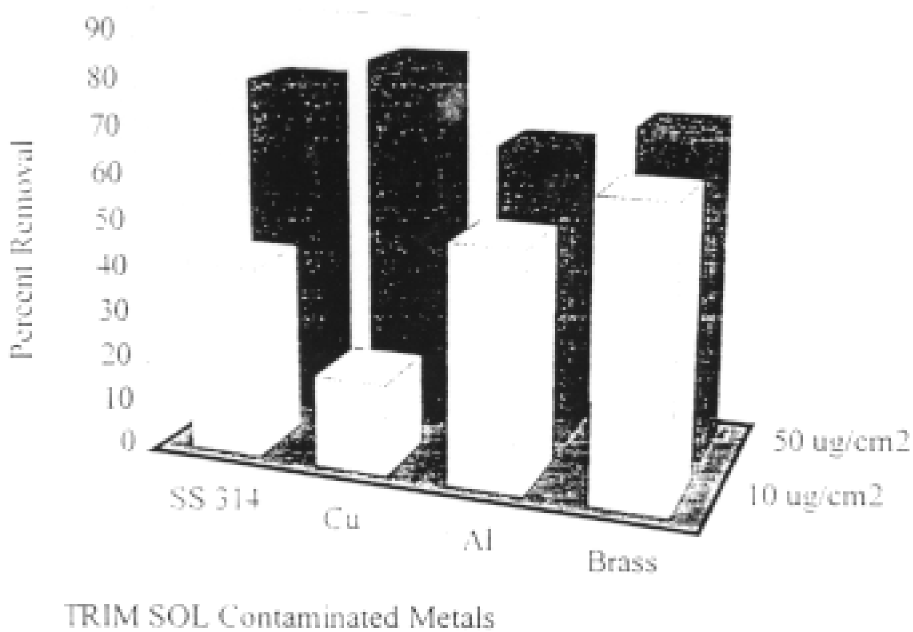

Figure 4. Comparison of the cleaning efficiency of supercritical CO_2 for the removal of TRIM[4] SOL from metal surfaces contaminated at 10 and 50 $\mu g/cm^2$.

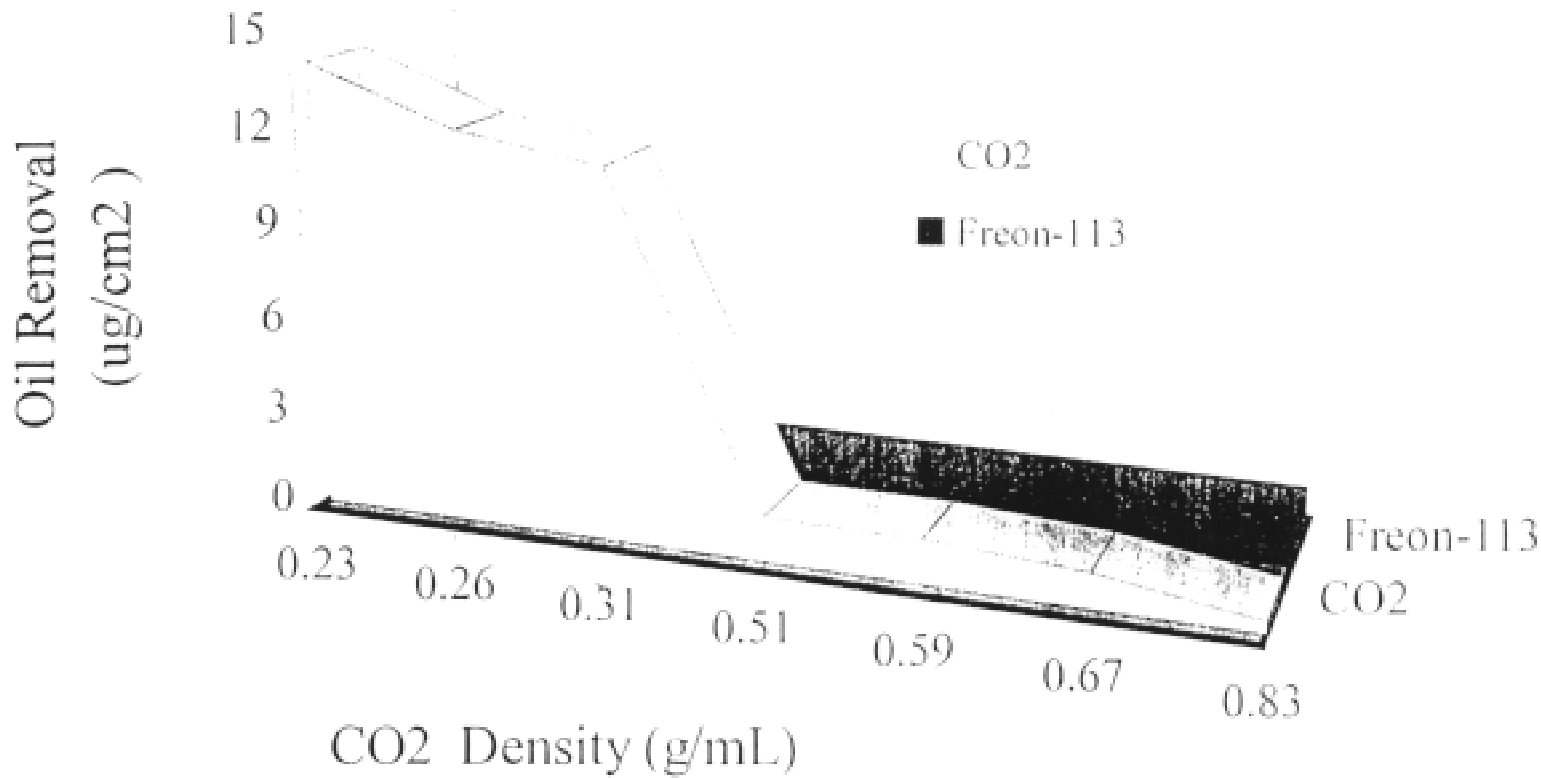

Figure 5. Comparison of the cleaning efficiency of CO_2 as a function of density with Freon-113 for the removal of drawing oil.