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ABSTRACT

The U.S. Department of Energy's (DOE) Industrial Waste Program (IWP) has been sponsoring the research, development, and commercialization of supercritical fluid cleaning technology for replacement of traditional solvent cleaning processes. The Joint Association for the Advancement of Supercritical Technology (JAAST), a research consortium consisting of industry, university, and National Laboratory partners was formed to facilitate teaming and communication and to specifically address issues inhibiting the growth and acceptance of supercritical fluid cleaning. The IWP/JAAST effort has helped to stimulate the successful commercialization of supercritical carbon dioxide cleaning for very specific applications and, as a result, this technology is steadily gaining more widespread acceptance.

Los Alamos National Laboratory and Pacific Northwest Laboratory have been working through this collaborative effort to test the efficacy of carbon dioxide (CO_2) cleaning. Tests were performed on a variety of substrates at various solvent conditions for a large number of common contaminants to characterize cleaning performance. Cleaning efficiencies with respect to system dynamics were also studied.

Results of these tests show that supercritical and near-critical carbon dioxide is not only an effective solvent for precision cleaning applications of parts such as gyroscopes, bearing assemblies, and machine tools but is also feasible for bulk cleaning operations for a variety of industrial needs. It has been tested and shown to be effective for a range of substrates including laser optics components, computer disk drives, and cloth rags (Wright Laboratory 1992; Novak et al. 1993; Smith et al. 1994). Metals, including stainless steel, beryllium, gold, silver, copper and others; ceramics; and elastomeric seals such as Teflon, silicone, and epoxy potting compounds are highly compatible with SuperCritical CO_2 ($SCCO_2$) (Wright Laboratory 1992). Many contaminants, including silicones, Krytox, hydrocarbons, esters, fluorocarbons, gyroscope damping and fill fluids, and machining oils and lubricating oils, will dissolve in $SCCO_2$ (Wright Laboratory 1992). In general, nonpolar, hydrophobic contaminants such as oils dissolve well, while hydrophilic contaminants such as inorganic salts do not (Novak et al. 1993).

The parts and contaminants mentioned here are not the only applications for $SCCO_2$ cleaning, as the full range of possibilities is still being defined by developers and users of the technology. The many advantages of $SCCO_2$ indicate that it is a technology that should carry industrial cleaning operations into the future.

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BACKGROUND

Scope

Alternative solvents such as perfluorocarbons, hydrochlorofluorocarbons, and other new hydrocarbon solvents, have been investigated and implemented for certain applications in industrial cleaning. However, many of these alternatives still pose environmental and/or health concerns and are likely to be significantly regulated and possibly banned in the future. Water-based cleaning has gained popularity as the alternative of choice for many applications because it is considered "environmentally friendly." However, chemicals employed with aqueous emulsion systems, such as detergents, and especially ethanolamines and terpenes, still require safety and health precautions due to known or uncertain human and aquatic toxicity associated with them. In particular, the U.S. Environmental Protection Agency (EPA) has expressed concern over the aquatic toxicity of the terpene family (Wolf 1994). In addition, water (especially for rinsing) and energy usage (especially for drying) and the treatment and disposal of spent bath and/or sludges associated with water-based cleaning add to the environmental and financial burdens.

Since 1990, the U.S. Department of Energy's (DOE) Industrial Waste Program (IWP) has been sponsoring the research, development, and commercialization of supercritical fluid cleaning technology for replacement of traditional solvent cleaning processes that contribute to stratospheric ozone depletion or have other environmental consequences. Research activities under this program have focused on development of technologies built upon years of fundamental supercritical fluid extraction research for the practical application of supercritical fluids as an alternative cleaning process.

The Joint Association for the Advancement of Supercritical Technology (JAAST), a research consortium consisting of industry, university, and National Laboratory partners was formed to facilitate teaming and communication and to specifically address issues inhibiting the growth and acceptance of supercritical fluid cleaning. The IWP/JAAST effort has helped to stimulate the successful commercialization of supercritical fluid cleaning for very specific applications and, as a result, this technology is steadily gaining more widespread acceptance.

Technology

A supercritical fluid is a pure compound or mixture, which is at a temperature and pressure at or above the critical temperature and pressure of the compound (see Figure 1). A fluid in this state possesses physical properties such as density and viscosity that are intermediate between the properties of the liquid and gas states, giving a solvent with high rates of mass transfer while maintaining excellent solubilization characteristics. These properties also result in a fluid with very low surface tension and, consequently, the ability to penetrate small pores and crevices very effectively. CO_2 is especially attractive as a solvent for Supercritical and near-critical Fluids Parts Cleaning (SFPC). While CO_2 in the liquid phase is an excellent solvent, it is not especially suited for penetrating small pores and crevices. That is why present systems generally allow for cleaning with either the liquid or supercritical states of CO_2. The attractiveness of CO_2 as a commercial solvent is tied to its chemical and physical properties; it exists naturally as a non-flammable, virtually inert gas which is readily available and inexpensive. The low critical point of CO_2 at 31°C and 73.8 bar [1070 psi] makes for a relatively safe working environment.

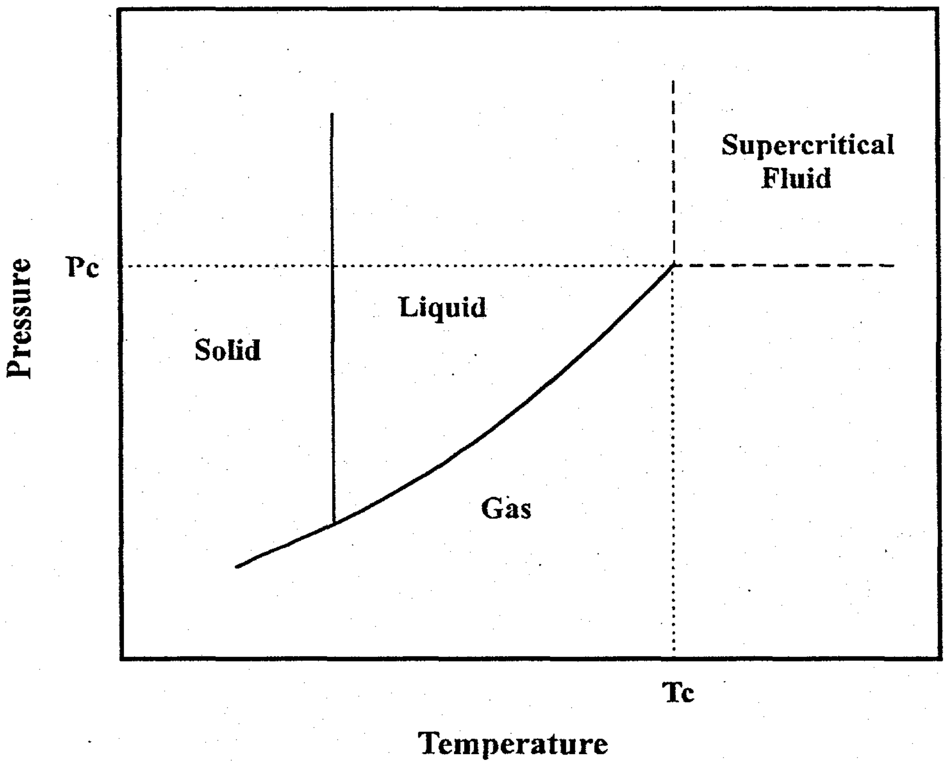

Figure 1. Generic pressure-temperature phase diagram of a pure compound.

CO_2 is fairly well established for precision cleaning applications of parts such as gyroscopes, bearing assemblies, and machine tools but is also feasible for bulk cleaning of a variety of substrates. It has been tested and shown to be effective for a range of parts and materials which include laser optics components, computer disk drives, and cloth rags (Wright Laboratory 1992; Novak et al. 1993; Smith et al. 1994). Metals, including stainless steel, beryllium, gold, silver, copper and others; ceramics; and elastomeric seals such as Teflon, silicone, and epoxy potting compounds are highly compatible with CO_2 (Wright Laboratory 1992). Many contaminants, including silicones, Krytox, hydrocarbons, esters, fluorocarbons, gyroscope damping and fill fluids, and machining oils and lubricating oils, will dissolve in CO_2 (Wright Laboratory 1992). In general, nonpolar, hydrophobic contaminants such as oils dissolve well, while hydrophilic contaminants such as inorganic salts do not (Novak et al. 1993).

INTRODUCTION

The removal of organic contaminants to a level of less than 10 $\mu g/cm^2$ (that is, 10 μg of contaminant per cm^2 of the surface that the contaminant is occupying) is a desired level of precision cleaning required by many manufacturers (Spall 1993) and has been used as a standard cleanliness level performance specification (American National Standards Institute 1990). 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 (Spall 1993). However, the ultimate level of cleanliness is dictated by the planned end-use of the component. Of course, any chlorofluorocarbon (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 $SCCO_2$, small bench scale (10 mL cleaning vessel) and large scale (60 L cleaning vessel) studies were undertaken. Los Alamos National Laboratory has demonstrated the successful removal of cutting and machine oils, silicone oils, body oils and hydraulic fluids from a variety of surfaces with $SCCO_2$ to, at, or below precision cleaning standards (less than 10 $\mu g/cm^2$). The ten organic contaminants and substrate materials listed in Table 1 were selected as representative of commonly encountered components found in manufacturing processes.

Table 1. Contaminants cleaned from substrate materials using $SCCO_2$ 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% Cotyl 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

Replicate studies were performed in both a small bench-scale unit (10 mL cleaning vessel) and in a large-scale unit (60 L, 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.

In a similar effort, Pacific Northwest Laboratory has assembled a small supercritical fluids parts cleaning test stand to characterize how system dynamics affect the efficacy of precision cleaning with CO_2. A soiled stainless steel coupon, loaded into a "Berty" autoclave, was used to investigate how changes in system turbulence and solvent temperature influenced the removal of test contaminants.

EXPERIMENTAL SECTION: LOS ALAMOS NATIONAL LABORATORY

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 (Unp. Spall). 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 (Downing et al. 1969, Downing and Strauss 1974, Strauss et al. 1976). 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 [103 bar] He head space, Scott Specialty Gases, Inc., Longmont, CO) at 300 atm [304 bar] and 45°C for 15 min. with a flow rate of 2.8 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 an 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 $SCCO_2$ 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 [3.8 kg/min.] at 1500 psi [103 bar]. 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 (EnviroPro Technologies).

The large scale $SCCO_2$ 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 (American National Standards Institute), 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 $\mu g/cm^2$ 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 path length. The cuvette was placed into a Buck Total Hydrocarbon Analyzer Model 404 (Buck Scientific Inc., 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-squared value of at least 0.99. The average mass detection limit for this procedure was about 8 μg, which corresponds to 0.15 $\mu g/cm^2$ for the 51.6 cm^2 substrate coupons. Although, the detection limit for silicone oil with this method was about 107 μg (2 $\mu g/cm^2$), 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 Discussion

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 cleaning 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 cleaning 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 cleaning vessel. Removal of the dissolved contaminants from the $SCCO_2$ is achieved by decompressing the CO_2 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 cleaning chamber are removed, clean and dry, ready for immediate use.

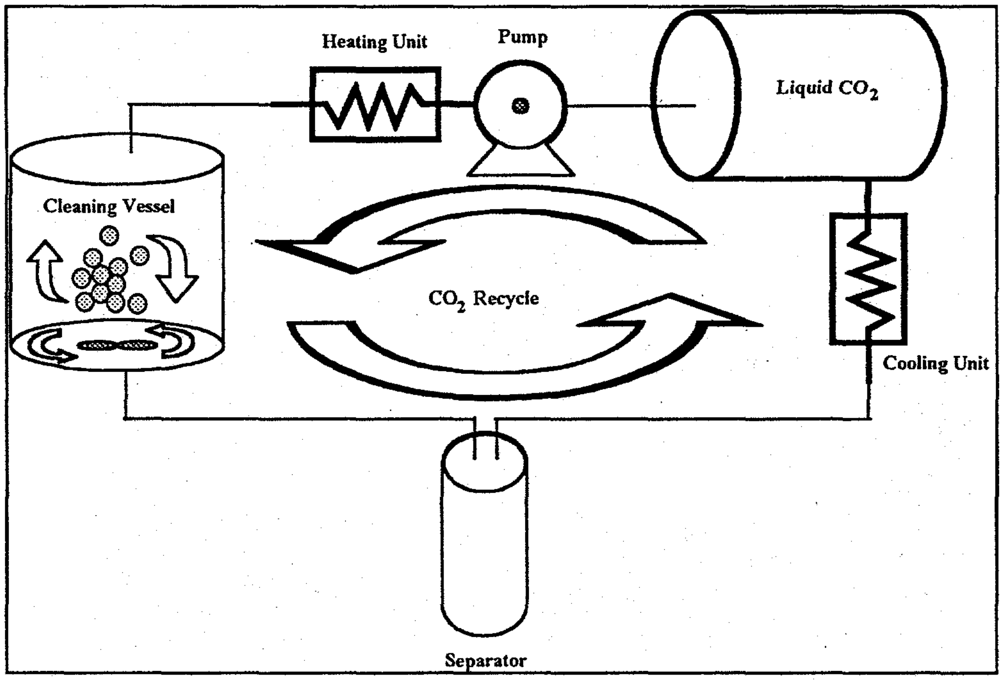

Figure 2. Basic schematic diagram of a CO_2 cleaning system.

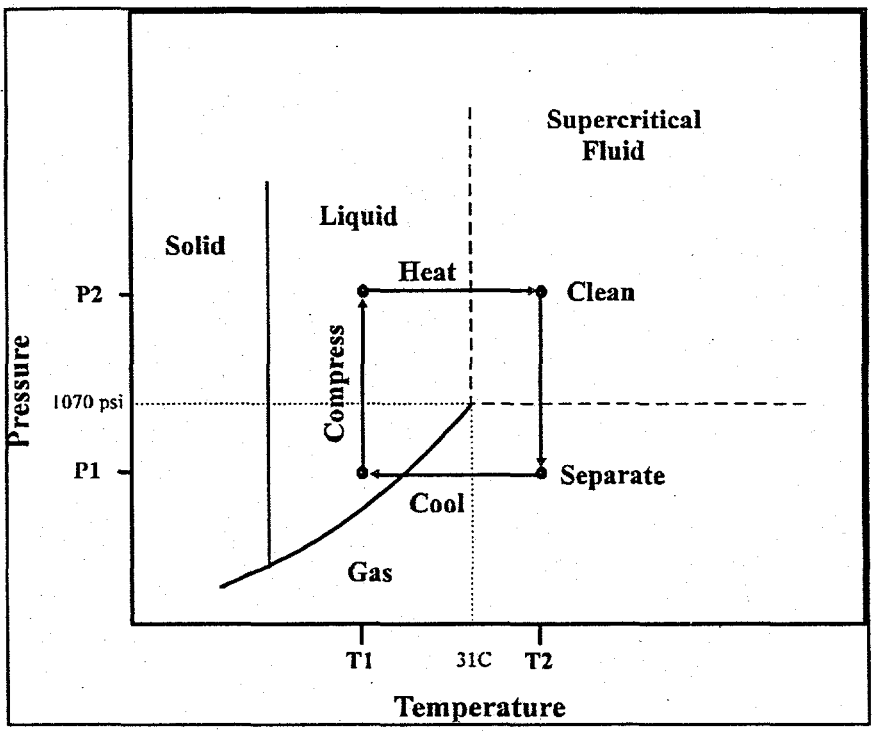

Figure 3. Phase behavior of CO_2 in cleaning cycle.

Overall operational costs for CO_2 cleaning tend to be lower than for other cleaning processes when the entire cleaning process is considered (Snowden-Swan 1994). 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 [103 bar] were about $0.90 per hour while the highest energy costs occurred at 40°C and 3500 psi [241 bar] for a total electrical cost of about $2.75 per hour (Barton 1994). 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 $SCCO_2$ cleaning equipment (Snowden-Swan 1994) has probably caused many potential users to opt for aqueous type cleaning systems. Currently, however, more companies are offering $SCCO_2$ 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, $SCCO_2$ 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, $SCCO_2$ 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 $SCCO_2$ 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.

Table 2. Small scale $SCCO_2$ 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

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 of the substrates to a precision clean level below 10 μg/cm². In fact, there was visible silicone oil contamination remaining on the 50 μg/cm² contaminated coupons after the SUPERSCRUB™ run. An exception in this case was the removal of 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 [103 bar] and 40°C would be removed at higher pressures and temperatures corresponding to increased solvation capacity of the $SCCO_2$.

Table 3. Small scale $SCCO_2$ removal of skin lipids, Triton® X-100, and hexadecane.

	Contaminant Compounds (Percent Removal*)		
Substrate Materials	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 $SCCO_2$ machining oils and fluids removal study at contamination levels of 10 μg/cm^2 and 50 μg/cm^2 .

	Contaminant Compounds (Percent Removal*)						
Substrate Materials	3-IN-ONE®	TRIM® SOL	Tapmatic®	SAE 30W	Silicone Oil	Hydraulic Oil	Mineral Oil
Brass							
10 μg/cm^2	> 99	64	95	92	54	45	> 99
50 μg/cm^2	> 99	72	99	95	75	89	> 99
Stainless Steel 314							
10 μg/cm^2	> 99	42	89	78	65	90	> 99
50 μg/cm^2	> 99	77	98	88	72	98	> 99
Glass							
10 μg/cm^2	98	27	94	87	60	85	98
50 μg/cm^2	> 99	76	98	94	74	96	> 99
Aluminum							
10 μg/cm^2	97	52	96	95	58	83	97
50 μg/cm^2	99	66	99	96	73	96	99
Copper							
10 μg/cm^2	99	20	54	93	55	43	99
50 μg/cm^2	> 99	83	99	95	58	89	> 99
Rigid-flex Epoxy Board							
10 μg/cm^2	94		65	61	< 1	< 1	94
50 μg/cm^2	94		96	84	70	93	94

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

In general, removal rates for the coupons contaminated at the 50 μg/cm² were higher than those of the coupons contaminated at 10 μg/cm². 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/cm² as compared to those contaminated at 10 μg/cm². It has been shown that the solubility of components within a mixture often have higher solubilities in $SCCO_2$ than the pure components themselves (Kurnik and Reid 1982). This phenomenon is caused by one or more components acting as solubility enhancers for other components. With more contaminant present at 50 μg/cm², 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 [103 bar] and 40 °C, the oil was removed down below the precision clean level. It should be noted that these results suggest that CO_2 may be used as a one step bulk cleaning method in addition to its use in precision cleaning.

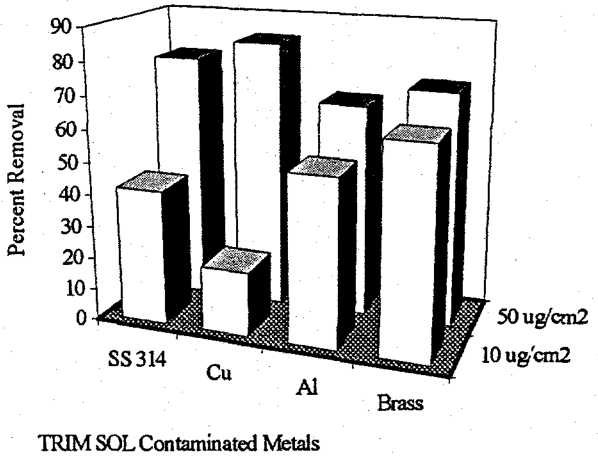

Figure 4. Comparison of the cleaning efficiency of $SCCO_2$ for the removal of TRIM® SOL from metal surfaces contaminated at 10 and 50 μg/cm².

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 rigid-flex, through-hole epoxy board. While the removal of these contaminants was well below the precision clean level of 10 μg/cm², the skin lipids left a visible film on the 50 μg/cm² 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 affect the removal of the contaminants by $SCCO_2$, except in the case of rigid-flex, 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 µg/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 µg/cm^2. A more thorough investigation is currently being conducted to determine the cause of the spurious data.

Table 5. Large scale $SCCO_2$ removal of skin lipids, Triton® X-100, and hexadecane at contamination levels of 10 µg/cm^2 and 50 µg/cm^2 .

	Contaminant Compounds (Percent Removal*)		
Substrate Materials	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

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 $SCCO_2$ 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 $SCCO_2$ 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 $SCCO_2$ was compared with a standard Freon 113 wash. After the drawing oil had been applied to the stainless steel surface in a uniform coating, the surface was cleaned using both $SCCO_2$ at different densities and using a Freon 113 wash. After cleaning with $SCCO_2$, 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 $SCCO_2$ is equivalent to that obtained using a Freon 113 wash when the density reaches about 0.5 g/ml. As the density of the $SCCO_2$ 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.

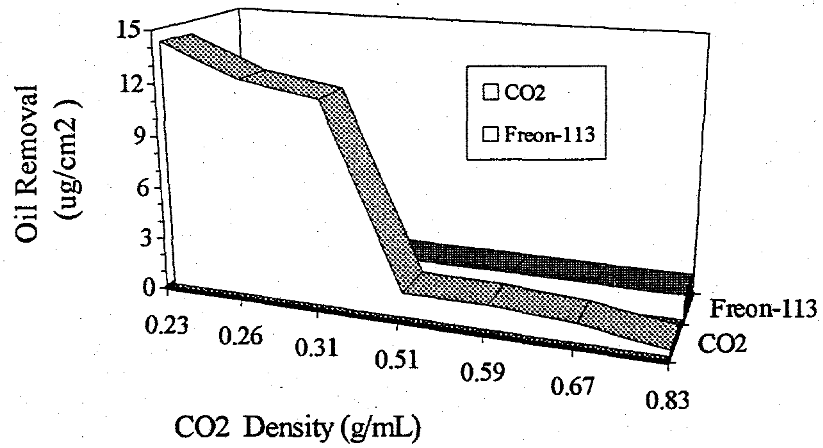

Figure 5. Comparison of the cleaning efficiency of CO_2 as a function of density with Freon-113 for the removal of drawing oil.

EXPERIMENTAL SECTION: PACIFIC NORTHWEST LABORATORY

Equipment

For Supercritical and near-critical Fluids Parts Cleaning (SFPC) studies, a test stand consisting of a medium pressure, high-temperature autoclave constructed by Autoclave Engineers (a "Berty" autoclave) was used. This autoclave is a bolted-closure, 3-inch I.D., fixed bed catalytic reactor with an internal volume of 433 mL. Agitation in the autoclave is supplied by an impeller attached through the bottom of the autoclave to a MagnaDrive assembly. The autoclave rests in a ceramic heater assembly which is capable of heating the autoclave to over 500°C. Rated pressure of the autoclave is 5800 psi [400 bar] at 340°C. Power to the heaters is supplied through a variac which was manually adjusted during testing to control temperature. Impeller speed is controlled by a variable speed controller that is part of the MagnaDrive unit. The only modifications to the autoclave necessary for our testing was to change the MagnaDrive bushings from carbon to nylon, perform a complete polishing of all the interior surfaces of the autoclave, and to fashion a coupon holder to position the coupon in the autoclave in the same orientation for every test run.

CO_2 is supplied to the system from standard compressed gas bottles and enters the system through a constant-temperature water bath where condensation occurs at 15°C. A refrigeration cooler maintains the temperature at the pump head and in the line from the constant-temperature bath to the pump head. Temperature at the pump head must be maintained in order to insure that fluid entering the pump is in liquid form. Liquid CO_2 is then fed through the top and into the autoclave where it is pumped to operating pressure by a high pressure liquid chromatography (HPLC) precision metering pump. Pressure in the autoclave is controlled by a back pressure regulator located downstream of the autoclave. Flow through the autoclave is from top to bottom. A separator vessel collects the contaminant as it disengages from the CO_2 on pressure letdown. A dry test meter measures the total flow of gas through the system.

A Mettler AE200 analytical balance was used to perform gravimetric analyses for the various experiments. Reproducibility for this balance is specified at ±0.1 mg.

Tests were designed to investigate the possible effects of system turbulence on the degree of cleaning of contaminants from parts. To do this, stainless steel coupons were selected as the parts from which removal of test contaminants could be measured.

Procedure For Analytically Contaminating Parts

For each series of experiments, the same stainless steel coupon was cleaned conventionally, coated with a test contaminant, and then placed in the autoclave for cleaning. Before each run, the coupon was either cleaned first in a chloroform bath, rinsed with acetone, and then dipped in an acetone bath, or cleaned in a 1,1,1-trichloroethane bath and then wiped with a tissue to remove any residue. After cleaning, the coupon was weighed to ensure that cleaning had been accomplished to within the limits of our analytical balance. The coupon measured 4 cm x 3.5 cm x 0.1 cm.

For the turbulence dependence studies, the coupon was coated with one of two test contaminants by completely submerging the coupon in the respective test contaminant, patted lightly with a Kim Wipe to remove excess material, and then weighed. Two different test contaminants were used: Dow Corning® 200 fluid and Castle/Sybron X-448 High-temperature Oil. The Dow Corning Fluid is poly(dimethylsiloxane) with an average molecular weight of 5000 g/mol and a viscosity of 100 cSt. The X-448 Oil is a polybutene/mineral oil mixture.

Experimental Procedures:

After applying the test contaminant, the coupon was loaded into the preheated autoclave where it was held vertically in place by a special holder. The autoclave's top was then bolted on and the test started.

Testing proceeded by filling the autoclave vessel and system with CO_2 to the first backpressure regulator and venting residual air from the system through a valve at the top of the autoclave. Once the system was filled, the pump was started at an average feed rate of 57 mL/min of liquid CO_2. For testing at supercritical conditions, timing began when the pressure gauge located at the top of the autoclave reached 1100 psi [77 bar].

When pressure in the autoclave reached 1100 psig [77 bar], the impeller was turned on to a predetermined speed. The autoclave pressure was allowed to reach and maintain operating pressure for the remainder of the test run. Approximately 15 seconds before the end of the run, the CO_2 supply was turned off and the system vented. When the system pressure dropped to 1100 psig [77 bar], the impeller was turned off. Pressure letdown typically took 15 seconds. One volume turnover for the autoclave (internal volume = 433 mL with baffles and basket in place) is estimated at 7.5 minutes.

After pressure letdown, the coupon was removed from the system and immediately reweighed on the same analytical balance that was used for contaminant loading. Weight differentials were used to determine mass flux of the test contaminant from the coupon.

Results and Discussion

A definite relationship between mass flux of contaminant and system turbulence can be seen in Figure 6 which represents data taken from the first two sets of experimental runs. For equal cleaning intervals, contaminant removal increases as the impeller speed increases up to a maximum efficiency, which depends on the contaminant. The maximum efficiency was reached for silicone oil at a lower impeller speed than for high-temperature oil. Increasing system turbulence beyond this point does not improve mass flux, and would be a waste of energy.

Another set of experiments was performed in order to establish cleaning efficacy by $SCCO_2$ in comparison with conventional solvent cleaning. Optically Stimulated Electron Emission (OSEE) analysis relates the difference between a clean surface and a contaminated one. The plot, shown in Figure 7, relating results of the OSEE analysis of coupons cleaned by SFPC to Boeing's conventional critical cleaning method shows that surface cleanliness for coupons cleaned by $SCCO_2$ compare very favorably to coupons cleaned by conventional critical cleaning methods.

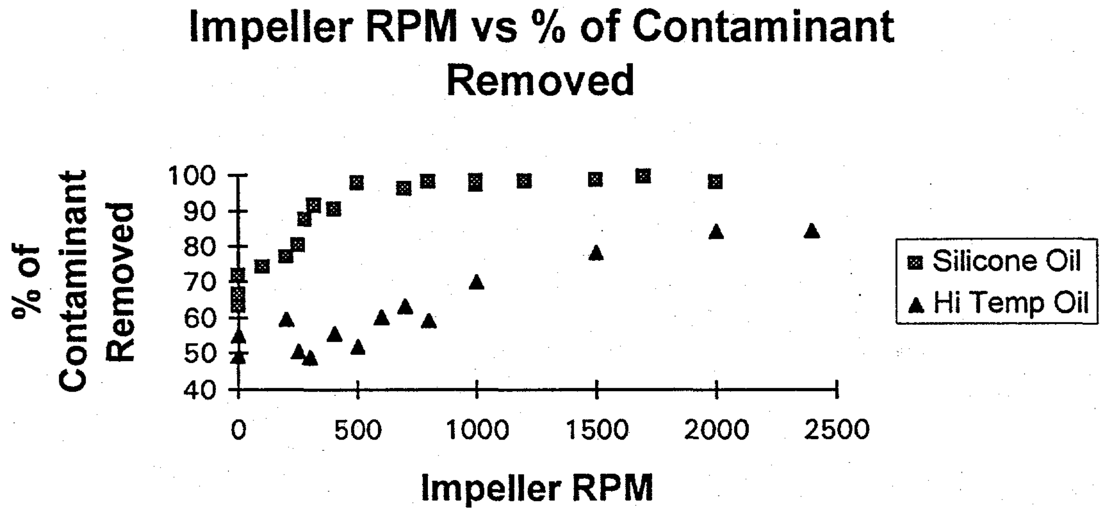

Figure 6. Plot showing contaminant removal as a function of impeller speed. System conditions: 1400 psig, 35-45°C, 5-minute cleaning cycle.

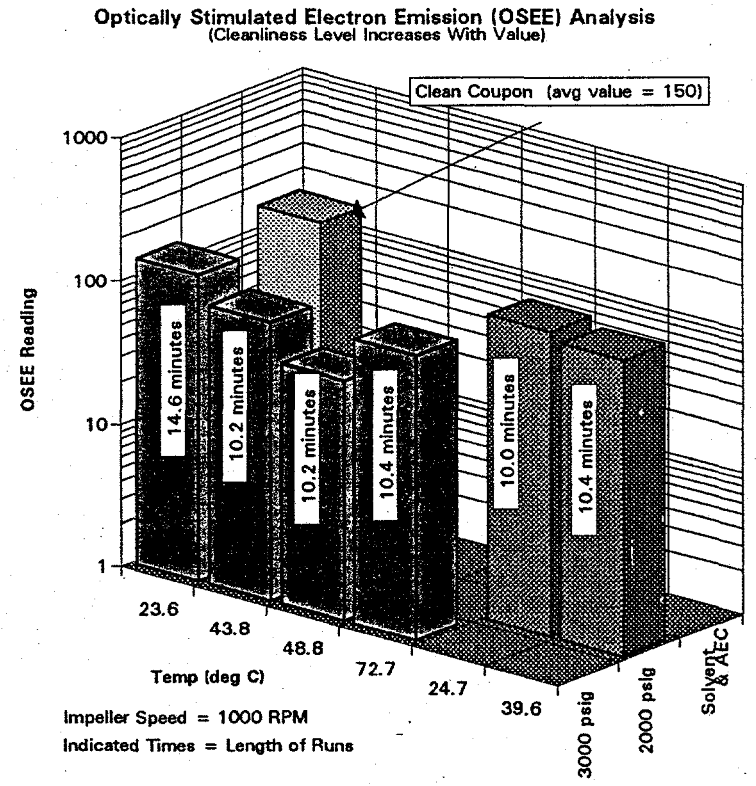

Figure 7. OSEE analysis of contaminated coupons cleaned in $SCCO_2$.

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. $SCCO_2$ 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 CO_2, and alternate cleaning methods should be considered for the removal of these types of contaminants. To a first approximation, cleaning with $SCCO_2$ appears to be contaminant dependent while being surface independent. The use of $SCCO_2$ 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 $SCCO_2$ 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 $SCCO_2$ at relatively low temperatures and pressures during the manufacturing processes is a viable process.

Because results from these experiments also show that system agitation has a pronounced effect both on overall contaminant removal and the mass flux from the contaminated surface [Phelps, et al. 1994], the use of agitation in commercial cleaning systems should, wherever possible, be used. It is well known that many substances exhibit a marked increase in solubility in the higher pressure regions [Pressure Products Industries]. However, since comparable cleaning can be achieved at lower pressures by taking advantage of increased solvent flow around the part and/or system agitation [Phelps, et al. 1994], the cost of SFPC systems can be greatly reduced.

As has been previously shown, agitation levels, temperatures, and densities needed for optimal cleaning are largely contaminant dependent. Using proper system dynamics, the levels of cleanliness achieved with $SCCO_2$ compare favorably with conventional precision cleaning methods. The correlations derived from the findings obtained in these studies can be used to optimize cleaning performance, system design, and time and energy consumption for particular parts cleaning applications.

ACKNOWLEDGEMENT

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