

# Application of Near Critical/Supercritical Solvent Cleaning Processes

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## Abstract

Carbon dioxide can be used in its liquid (near critical) or supercritical fluid state as a replacement for conventional cleaning solvents, reducing the pollution associated with the operations that would otherwise require significant amounts of volatile organic compounds, ozone depleting substances, or hazardous air pollutants.

The results of several near critical/supercritical parts cleaning and treatment studies performed at the Applied Research Laboratory are discussed. Near critical/supercritical processing is a commercially viable process for many industrial, electronic and medical device cleaning applications. This applications note will focus on industrial applications such as oxygen-service pressure gauges, fuel and transmission oil filters, and bearings.

## Background:

The supercritical fluid solvent phenomenon was first described by Hannay and Hogarth (1879), who reported on the solubility of cobalt chloride in supercritical ethanol. Industrial use of supercritical fluids as solvents began in the 1950s.<sup>1</sup> Today supercritical fluids, primarily supercritical carbon dioxide (SCCO<sub>2</sub>), are used in a number of analytical, industrial, and cleaning processes. Because it replaces or reduces the use of "conventional" solvents such as alcohols or ketones, SCCO<sub>2</sub> processing is a Pollution Prevention (P<sup>2</sup>) technology. The following discussion describes some applications with significant P<sup>2</sup> implications.

## Replacement for Cleaning Solvents:

The use of NC/SCCO<sub>2</sub> for parts cleaning is a natural outgrowth of the analytical and production scale extraction processes discussed above. This technique has significant potential as P<sup>2</sup> replacement technology.

Precision cleaning of surfaces is a crucial step in many manufacturing activities. Removal of contaminants, including oils, greases, inorganic residues and particulates, is needed to prepare surfaces for subsequent operations such as coating, plating, or final assembly.<sup>2</sup> In addition, removal of residues from piping and fluid handling equipment is essential when these contaminants are incompatible with process fluids. An important example is the cleaning of parts used in equipment which exposes the parts to high pressure oxygen gas. Even minor traces of grease or oils can react violently with high pressure O<sub>2</sub> gas or liquid oxygen. As a result of these considerations, cleaning operations can be a very significant component of the manufacturing and remanufacturing costs.<sup>3</sup>

Currently, many critical cleaning/degreasing operations require the use of chlorofluorocarbon solvents, most notably CFC 113 (1,1,2-trichloro-1,2,2-trifluoromethane) and methyl chloroform (1,1,1-trichloroethane). The EPA estimates that approximately 170 million pounds of CFCs were used in the USA for industrial cleaning operations in 1980.<sup>4</sup> Unfortunately, these chemicals are believed to participate in the catalytic destruction of stratospheric ozone.<sup>5</sup> Under the Montreal convention, these species have been banned from United States production or import since December 31, 1995.

A number of alternative cleaning agents and processes have been proposed. Aqueous solutions of detergents and/or emulsifiers can be used in many instances. Drawbacks to this approach include the production of large quantities of contaminated wash solution which, in most cases, must be handled as hazardous waste. In addition, the surface tension and wetting properties of water make it difficult to remove contaminants from small interstices and crevices in parts. In certain instances, existing, more environmentally benign, solvents such as alcohols or ketones can replace CFC cleaning agents. In many cases, these alternatives present material compatibility or health and safety problems.

Contrastingly, NC/SCCO<sub>2</sub> is an environmentally benign cleaning technology that is very effective at removing contaminants from parts, including those with complex geometries. The use of near critical (i.e. liquid) or supercritical fluid cleaning has been proposed as a solution to this problem. Supercritical carbon dioxide is an excellent solvent for precision cleaning, particularly for porous, intricate parts<sup>6</sup>. Some of the factors that must be considered in order to determine if near critical/supercritical carbon dioxide (NC/SCCO<sub>2</sub>) cleaning is suitable for a particular part are discussed below:

*Current Cleaning Practices:* NC/SCCO<sub>2</sub> cleaning is indicated for parts that are currently cleaned with solvents such as Freon-113 that are in limited supply, or with hazardous solvents, or for which no acceptable cleaning processes exist.

*Part size:* Because the process occurs at elevated pressures (1100 psi or greater), parts that can fit within a moderately sized pressure vessel are best candidates for NC/SCCO<sub>2</sub> cleaning.

*Part geometry:* Components that incorporate blind holes, or other surface features that can prevent aqueous cleaning solutions from effective contact with contaminants, may be strong candidates for NC/SCCO<sub>2</sub>.

*Materials of Construction:* NC/SCCO<sub>2</sub> cleaning is well suited to parts that are sensitive to corrosion, since carbon dioxide is compatible with all metals and evaporates completely, leaving no residue. As with many traditional solvents, NC/SCCO<sub>2</sub> can swell certain elastomers and damage some polymeric materials.

*Type(s) of Contaminant(s):* Although NC/SCCO<sub>2</sub> is most effective at removing nonpolar contaminants such as greases or oils. Introducing a small quantity of a “co-solvent” such as methanol can effectively dissolve polar soils such as fingerprints or soldering flux. In some cases, NC/SCCO<sub>2</sub> is effective as one component of a multistage cleaning process.

*Degree of Cleanliness Required:* Although NC/SCCO<sub>2</sub> can clean components to very exacting standards it may be a cost effective solution even for routine cleaning problems. In some cases, lower pressure and temperature processes using subcritical liquid carbon dioxide (NC), rather than SCCO<sub>2</sub> may be more effective.

## **Near Critical/Supercritical Carbon Dioxide Processing Equipment**

The review above shows that there is a considerable amount of interest throughout the research community in NC/SCCO<sub>2</sub> cleaning processes for solvent replacement and treatment. One potential end-user of this technology is the Department of Defense. Because the DoD operates many high performance weapons systems and platforms that require frequent maintenance and re-work operations, it uses large quantities of chemical solvents such as Freon-113 and 1,1,1,-Trichloroethane. In addition, many DoD installations produce hazardous waste streams that must be treated before discharge.

The Applied Research Laboratories (ARL) of the Pennsylvania State University has acquired a NC/SCCO<sub>2</sub> system in order to evaluate the effectiveness of NC/SCCO<sub>2</sub> technologies for environmental problems of interest to the Department of Defense.

The system used for most ARL NC/SCCO<sub>2</sub> studies is an SFT-1000 SFE/SFR Processing Unit manufactured by Supercritical Fluid Technologies, Inc of Newark Delaware, USA. [www.supercriticalfluids.com](http://www.supercriticalfluids.com). Figure #1 shows a view of the apparatus while Figure #2 is a schematic diagram.

Rather than developing the components for the NC/SCCO<sub>2</sub> system at ARL, Supercritical Fluid Technologies, Inc. acted as the system integrator as well as brought several fundamental patented technologies, such as specialized equipment designs and controls for pumping carbon dioxide in a tightly controlled and efficient manner.<sup>7 8</sup>

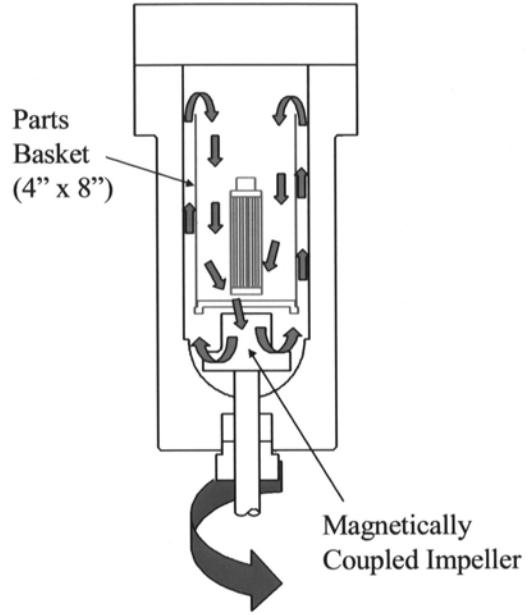


Figure #1: ARL General Purpose SFT-1000 SFE/SFR NC/SCCO<sub>2</sub> Processing System

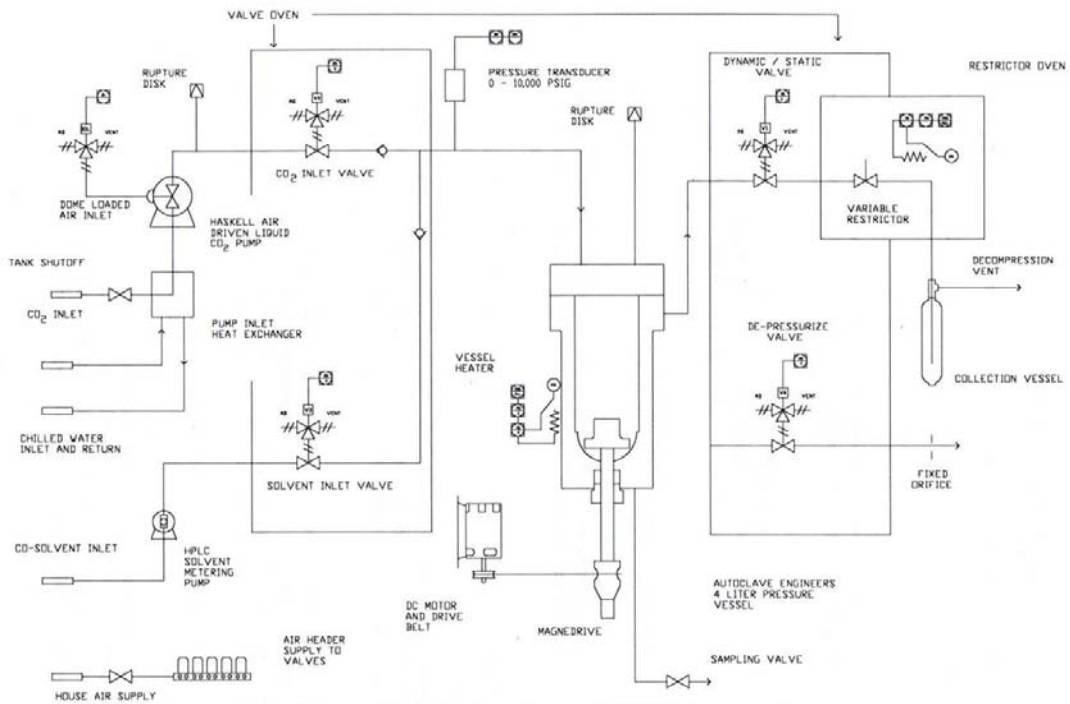


Figure #2: Schematic of ARL SFT-1000 SFE/SFR General Purpose NC/SCCO<sub>2</sub> Processing System

The system had the following features:

- The system is capable of operation at pressures up to 6,000 psi (41.4.MPa) at temperatures of 392°F (200°C). The extraction vessel itself is ASME Code-Stamped for 5,500 psi (37.9 MPa) at 650°F (343°C) operation.
- The extraction vessel has an interior volume of one gallon (3.785 L). It is fabricated from 316SS and features a bolted closure. In operation at relatively low pressures (3,300 psi), the solid metal seal can be replaced with an elastomer o-ring.
- The extraction vessel contains a magnetically driven impeller to provide agitation of the fluid bath.
- Mechanical safety components including rupture disc assemblies and relief valves are included to protect the equipment and operators from potential over pressurization conditions.
- The CO<sub>2</sub> pump is capable of sustaining a continuous flow of 350 cm<sup>3</sup> of liquid CO<sub>2</sub> per minute at the maximum operating pressure.
- Carbon dioxide is delivered to the pump under its own vapor pressure (nominally 850 psi at Room Temperature). In order to prevent cavitation, a refrigerated chiller is used to circulate a water/ethylene glycol mixture through a heat exchanger attached to the pumping head.
- All valves and lines downstream of the extraction vessel are heated to prevent formation of solid CO<sub>2</sub> deposits. A heated back pressure regulator (variable restrictor in Figure #2) is used to control the rate of carbon dioxide flow. A solid state mass flow meter can be installed downstream of the “decompression vent” of Figure #2 in order to measure CO<sub>2</sub> flowrate.
- A co-solvent delivery system is included to add small amounts of additional solvents (alcohols etc.) to the carbon dioxide feed, as required for specific extraction processes.
- All process parameters (pressure, temperature, impeller speed, co-solvent delivery rate) are governed by a Programmable Logic Controller (PLC) with software developed at Supercritical Fluid Technologies, Inc. This device is capable of storing a number of process methods, each of which can incorporate a number of discrete pressure/temperature ramps and dwells. The PLC is programmable by a keypad located on the front panel of the unit.

- The system can be monitored by the Data Acquisition Package on a PC attached to the NC/SCCO<sub>2</sub> system by an RS-232 link. The software displays a graphical process monitor showing the status of all the valves and other mechanical components, while real-time data traces track parameters such as temperature, pressures, and impeller speed.

## **NC/SCCO<sub>2</sub> Parts Cleaning Investigations**

ARL has performed a series of experimental studies to evaluate the effectiveness of NC/SCCO<sub>2</sub> solvent processes for a variety of cleaning tasks. In each case, the NC/SCCO<sub>2</sub> would replace an existing “conventional” solvent such as Freon-113 or methyl chloride.

### Case 1: Cleaning of Oxygen System Instrumentation:

Components of oxygen systems must be cleaned to very stringent standards to ensure safe operation. Even traces of oils, greases, or particulates can react with high-pressure oxygen gas or liquid and lead to catastrophic fires or explosions.<sup>9</sup> Aqueous cleaners such as Tribasic Sodium Phosphate (TSP) or the new Naval Oxygen Cleaner (NOC) formulation have been used as alternatives to Freon-113 in oxygen piping systems. Unfortunately, these water-based solutions are not acceptable for cleaning instrumentation such as pressure transducers or gauges.<sup>10 11</sup>

Figure #3 shows a typical pressure gauge that incorporates a curved bourdon tube. This tube deflects under internal pressure, driving an indicator needle through a mechanical linkage. Because the bourdon tube is flattened and sealed at one end, it is difficult for an aqueous cleaner, with its relatively high viscosity and surface tension, to penetrate into the recesses of the tube to remove contaminants. In addition, it is impossible to ensure that all of the water and cleaner residues are removed from the tube. For these reasons, ship[yard and depot level oxygen gauge cleaning operations still use Freon-113, which is in increasingly short supply due to a production ban put in place in late 1995.

Supercritical carbon dioxide offers a viable solution to these problems. Because of the exceptional penetrating power, SCCO<sub>2</sub> should be able to reach contaminants throughout the bourdon tube, even in “direct drive” gauges, which have tubes as small as 1/8” in diameter. Since residual CO<sub>2</sub> evaporates completely to form an inert gas that can easily be flushed from the gauge, there is no concern about cleaner residue remaining behind within the part to react with oxygen (gas or liquid) while the Bourdon tube pressure gauge is in service.

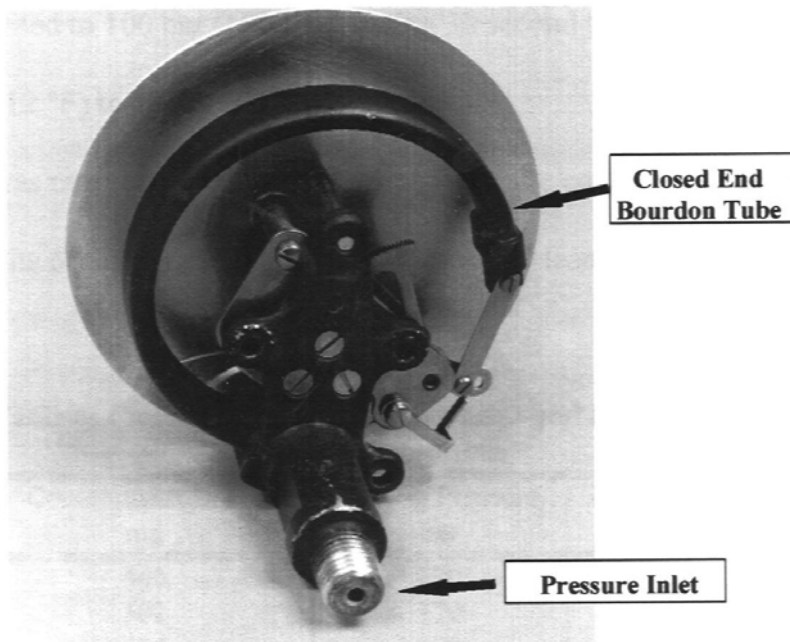


Figure #3: Typical Bourdon Tube Pressure Gauge

The program used a test protocol for oxygen gauge cleaner qualification developed by the NASA White Sands Test Facility, and accepted by NAVSEA.<sup>12</sup> Simulated gauges were constructed from 16-inch lengths of 1/8" OD tubing and bent into 4" diameter circles. These gauges were then doped with a test mixture containing five contaminants; including synthetic and petroleum based hydraulic fluids, lubricating oil, a gauge calibration fluid, and perfluoralkylether grease.

The gauges were pressurized with supercritical CO<sub>2</sub> to approximately 200 bar (3000 psi), and then vented to 100 bar (1500 psi) over a 30 second time period. The fluid temperature ranged from 100°C (212°F) to 130°C (266°F). The pressure was raised and lower five times over the course of a five-minute cleaning cycle. Cleaning efficiencies as high as 97% were achieved with this procedure that is equivalent to that obtained with Freon-113 cleaning techniques.

Although the results of this test showed that pulsed SCCO<sub>2</sub> technique can be very effective for cleaning gauges that are rated for operation above 3000 psi, this process was not suitable for gauges with pressure ratings below 3000 psi. Since approximately 40% of the oxygen gauges processed at Puget sound Naval Shipyard are rated for the lower pressures, it was necessary to identify an alternative approach that will work for all gauges. An apparatus was developed at ARL that allowed the pressure pulse technique to be applied to any gauge, regardless of pressure rating. Figure 4 is a schematic of this device. The gauge to be cleaned is placed in the main pressure vessel. The vessel headspace is pressurized with an inert gas (nitrogen or argon). At the same time, liquid carbon dioxide is delivered to the gauge via a dome loaded regulator, which tracks the

vessel pressure, automatically admitting CO<sub>2</sub> as needed to equalize the pressures inside and outside of the bourdon tube. The system is held at the desired pressure for a period of time to allow contaminants to dissolve in the carbon dioxide, which is either near critical or supercritical

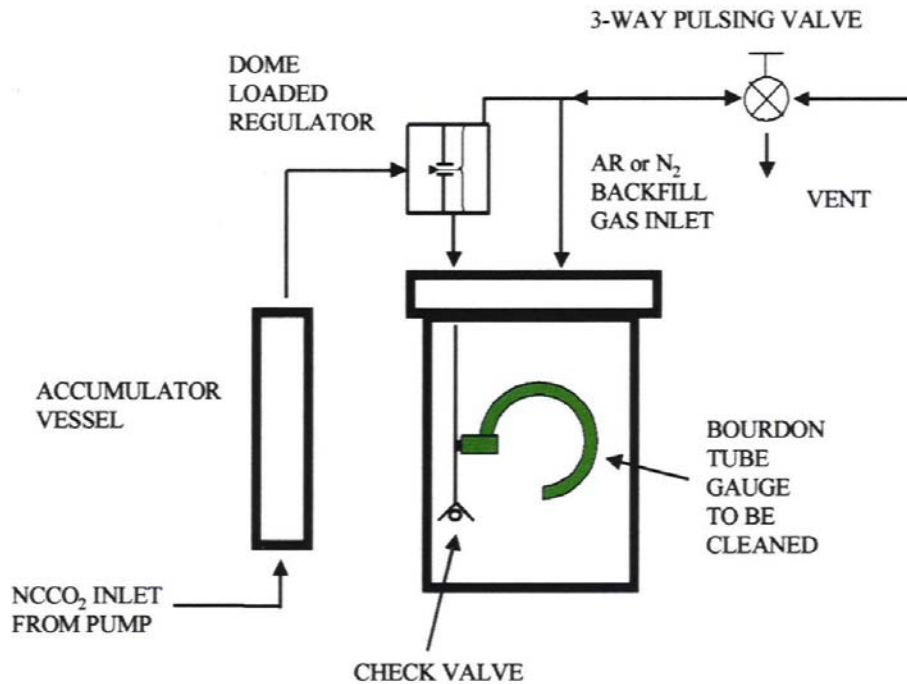


Figure #4: Pressure Pulse Cleaning Apparatus

state, depending on the temperature of the pressure vessel. After a suitable interval, the 3-way inert gas valve is switched to the “vent” position. Carbon dioxide flows out of the gauge through the check valve, then the CO<sub>2</sub> and inert gas are vented from the pressure vessel. In this manner, large pressure pulses can be applied but the differential pressure across the gauge remains small, allowing even low pressure gauges to be cleaned. A 92% cleaning effectiveness with a standard deviation of 5% was achieved with this method. It appears likely that the NC/SCCO<sub>2</sub> pressure pulse technique can be further improved and optimized, replacing Freon-113 in this gauge cleaning application.

Case 2: Cleaning of Fuel and Oil Filters:

Another example for replacement of traditional cleaning methods with NC/SCCO<sub>2</sub> is found in Fuel and Oil Filters. Figure #5 shows three aviation fuel and lubrication system components for which NC/SCCO<sub>2</sub> cleaning has been evaluated. The “Hydraulic Valve Bellows” cannot be cleaned with this technique because the smaller bellows are sealed and will not withstand high external



pressures. NC/SCCO<sub>2</sub> cleaning has, however, been successfully demonstrated for the transmission oil and fuel filters shown in the figure.

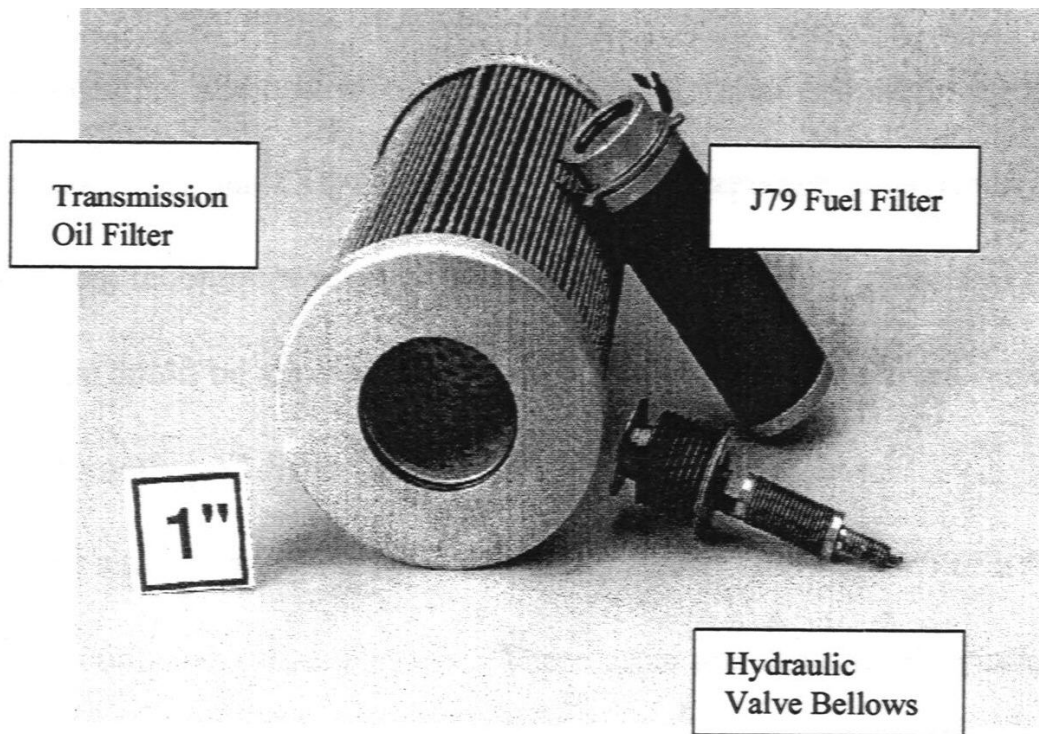


Figure #5: Aviation Fuel and Lubrication System Components

The transmission oil filter is currently discarded after a single use. It contains a polymer element supported by a wire mesh structure. As received, the filter was saturated with hydraulic fluid residue, which held a number of metallic particles in place on the outer surface of the elements.

The filter was cleaned in the laboratory scale NC/SCCO<sub>2</sub> system shown in Figure #1. For this initial test, processing conditions of 4000 psi (27.6 MPa) and 122°F (50°C) were used. A total of 93 grams of oily residue was recovered from the filter; this represented approximately one quarter of the gross weight of the filter before cleaning. The metallic particles were also removed, either by action of the carbon dioxide or because the sticky oil residue that originally held them in place was eliminated. Figure # 6 shows the filter, along with the parts basket from the NC/SCCO<sub>2</sub> extraction system, and a flask containing the recovered oil. In order to successfully implement NC/SCCO<sub>2</sub> cleaning for recycling this filter in an industrial environment, it will be necessary to optimize the process conditions (temperature and pressure) for more efficient and cost effective cleaning.

This technique could be applied to remove hazardous materials from other types of oil soaked components, such as automotive oil filters, prior to recycling or landfilling.

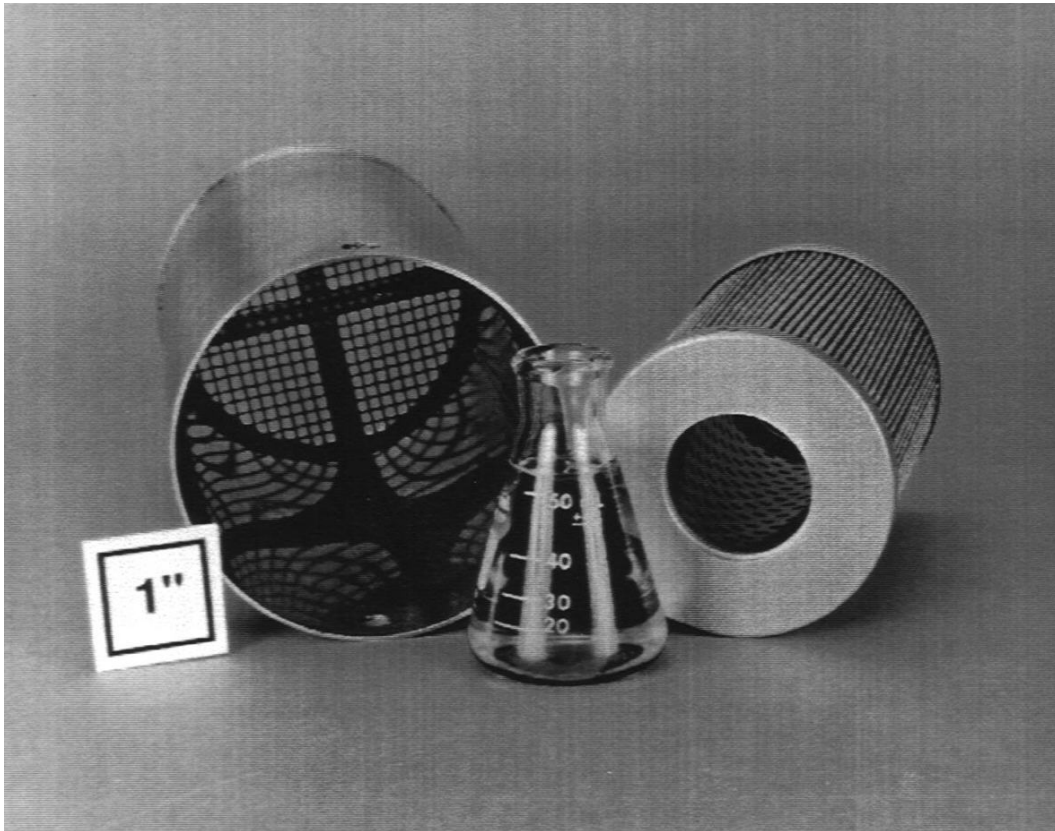


Figure # 6: Filter and Basket Assembly

The smaller filter shown in Figure #5 is a J79 Fuel Filter. This filter consists of a folded metal mesh structure and does not have a polymeric element. These units are currently degreased with perchloroethylene (PCE), followed by ultrasonic agitation with MIL-C-25107 “carbon remover,” which contains ortho-dichlorobenzene. Implementation of NC/SCCO<sub>2</sub> cleaning, therefore, has potential to reduce or eliminate the use of two relatively hazardous chemical solvents.

The J79 fuel filter was coated with a black “grime” that was very tenaciously adhered to the surface. Supercritical carbon dioxide treatment recovered a surprisingly large (5 ml) quantity of a viscous oily fluid. The total weight of the contaminant extracted was 3.31 grams. Removal of this sludge loosened the particulate contaminant; the original grimy residue was replaced with a loose, fluffy gray powder, electrostatically attached to the surface of the filter. Attempts to use near-critical liquid carbon dioxide with its higher viscosity, to dislodge the residue were largely unsuccessful. Finally, a soft bristle brush was used to manually remove the powder. Approximately 0.42 grams of powder were easily removed, leaving the surface of the filter quite clean.

As with the transmission oil filter, it will be necessary to optimize the NC/SCCO<sub>2</sub> process conditions, improve particulate removal efficiency, and develop QC/QA procedures in order to implement the technique as an alternative to the current practice. Figure #7 shows three photomicrographs of the surface of the filter before cleaning (A), after NC/SCCO<sub>2</sub> extraction (B), and after physical removal of residual particulate material (C).

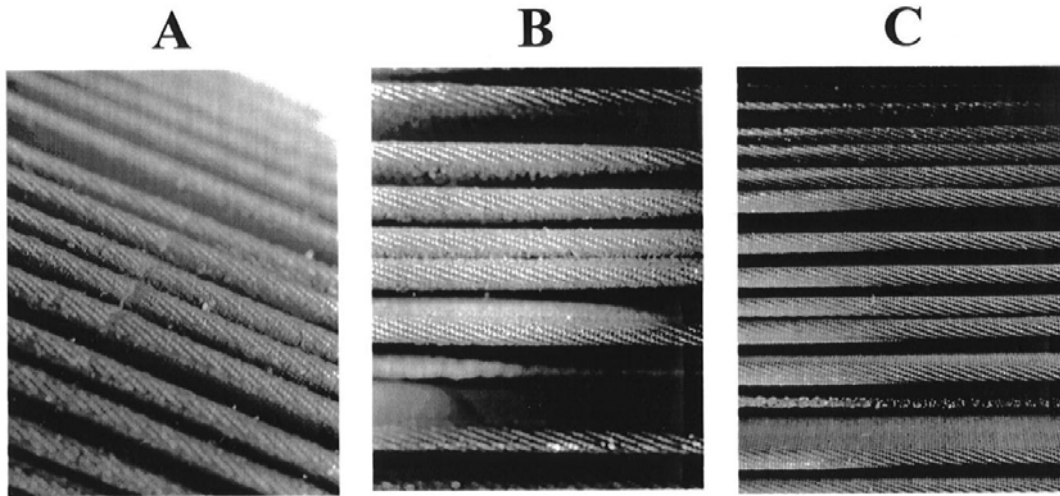


Figure #7: Photomicrographs of Filter Surface

#### Cleaning of Ball and Roller Bearing Assemblies:

Ball and roller bearing assemblies have always presented a particularly difficult cleaning challenge. Bearings inevitably incorporate many small crevices between the curved surfaces of the balls or rollers and the races. Grease and particulate material can become trapped in these interstices.

On the surface, it appears that NC/SCCO<sub>2</sub> cleaning technology offered a solution to this problem, since the solvent should easily penetrate into these spaces to dissolve contaminants. While it was recognized that greases typically contain inorganic binders and fillers that are not themselves soluble in dense carbon dioxide, it was assumed that removal of the organic fraction would loosen the insoluble residue, allowing these inorganic binders and fillers to be removed manually. This, in fact, was the experience of Farncomb and Naufflett,<sup>13</sup> who able to degrease bearing assemblies in supercritical carbon dioxide. Residual metal salts were removed through “tapping” and vacuuming.

There may be some cases where the disadvantages associated with aqueous cleaners and other chemical solvents may make NC/SCCO<sub>2</sub> cleaning a viable technology for cleaning bearings. First, some types of greases are adequately removed by NC/SCCO<sub>2</sub> cleaning, followed by vacuuming, blowing or brushing to remove particulate material. If compatible greases were substituted for existing

materials, the NC/SCCO<sub>2</sub> technique could be implemented. Second, as discussed in a previous section, new surfactants have recently been introduced that enable carbon dioxide to dissolve otherwise insoluble chemicals.

### **Results and Discussion:**

When used as a replacement for conventional solvents, NC/SCCO<sub>2</sub> has significant potential to reduce the environmental impact of certain manufacturing processes. In particular, parts cleaning operations that cannot be performed with other replacement technologies (such as the use of aqueous cleaners) may benefit from this technology.

NC/SCCO<sub>2</sub> treatment technologies may also be useful in cases where other chemical solvent processes are not applicable or efficient. In particular, when contaminant must be recovered in a highly concentrated form (either because of its intrinsic value or because it is particularly hazardous), NC/SCCO<sub>2</sub> extraction should be considered. The use of NC/SCCO<sub>2</sub> regeneration of adsorbents is an area that shows promise and should be pursued.

New surfactants and chelating agents allow NC/SCCO<sub>2</sub> to dissolve chemical species (in particular inorganic compounds and metal ions) that would otherwise be insoluble. This relatively new development promises to greatly expand the scope of solvent replacement and treatment applications of this technology. In particular, NC/SCCO<sub>2</sub> dry cleaning represents the first commercial application for which this technology is becoming widespread.

In conclusion, while SC/SCCO<sub>2</sub> processing is not a universal “drop in” solution to all cleaning and treatment problems, it should be evaluated and investigated along with other technologies when a new manufacturing process or cleaning problem arises.

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