

## Demonstration of Liquid CO<sub>2</sub> as an Alternative for Metal Parts Cleaning

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### Introduction

The use of carbon dioxide (CO<sub>2</sub>) in its supercritical state is an established technology for solvent extraction in processes such as decaffeinating coffee, wastewater treatment and chemical analysis.<sup>1-3</sup> Several studies have been conducted with supercritical CO<sub>2</sub> for surface cleaning.<sup>4,5</sup> However, the potential for liquid CO<sub>2</sub> (LCO<sub>2</sub>) as a surface cleaning agent has remained largely unexplored. This may be due to supercritical CO<sub>2</sub>'s greater solvency for some contaminants compared to LCO<sub>2</sub>.<sup>6</sup> The difference in cleaning capability can be offset in a liquid system with the addition of process enhancements such as ultrasonics or megasonics, techniques that have not been very effective with CO<sub>2</sub> in the supercritical state.

In early 1995, a program was initiated by the Environmental Protection Agency to investigate new and innovative surface cleaning and degreasing technologies as alternatives to ozone-depleting compounds including 1,1,1-trichloroethane (TCA), methylene chloride, and Freon 113™ [1,1,2-trichloro-1,2,2-trifluoroethane, chlorofluorocarbon (CFC)-113]. One promising candidate identified during the investigation was LCO<sub>2</sub>. The United States Air Force at the Warner Robins Air Logistics Center (WR-ALC), Robins AFB, GA, was requested to participate in the demonstration and served as the demonstration site. The WR-ALC uses several surface cleaning processes at the facility during aircraft systems maintenance. These processes generate a broad range of air, water and solid waste environmental contaminants. The volume of these wastes could be reduced by the use of LCO<sub>2</sub> cleaning.

LCO<sub>2</sub> is of interest as a potential solvent degreasing substitute largely because of what it is not. First of all, it is not an ozone-depleting compound (ODC). Therefore, it does not present a threat to the earth's ozone layer as found with typical chlorofluorocarbon (CFC) solvents. It is nonflammable and has low toxicity. Thus, it does not present a safety hazard when used properly. Finally, LCO<sub>2</sub> is not expensive when compared to CFCs and equivalent substitutes. This is important to its viability as an industrial surface cleaning and degreasing solvent.

The objective of the project was to demonstrate the viability and efficiency of the LCO<sub>2</sub> cleaning as an alternative to current cleaning and degreasing technologies. The study was designed to show that LCO<sub>2</sub> cleaning, when properly integrated into the manufacturing process, could remove various organic and solid contaminants typically removed during vapor degreasing with ozone-depleting solvents.

### Liquid CO<sub>2</sub>

Carbon dioxide is a gas at standard temperature and pressure, 32°F (0°C) and 14.7 psi (1 bar). By increasing the pressure and temperature of the CO<sub>2</sub>, it can be converted from the gaseous phase to the liquid and supercritical phases. As a liquid

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or supercritical fluid, CO<sub>2</sub> has good solvent properties for oils, greases, and other common machining contaminants. Changing the operating pressure and temperatures within the defined state boundaries will allow selective removal from a surface and separation of a variety of metal finishing and fabrication contaminants. Although solubility is not the sole property that defines the acceptability of a potential solvent substitute, LCO<sub>2</sub> compares favorably with other typical degreasing solvents. Two other physical properties shown in Table 1 that affect cleaning are surface tension and viscosity. LCO<sub>2</sub> has low surface tension and very low viscosity, which improves the likelihood that the solvent will wet the surface to be cleaned and penetrate into small crevices and blind holes in the parts.

TABLE 1. Chemical and Physical Properties of Degreasing Solvents

Solvent	Solubility Parameter (MPa <sup>1/2</sup> ) <sup>7</sup>	Viscosity at 20 °C (Centipoise) <sup>8</sup>	Surface Tension at 20 °C (Dynes/cm) <sup>9</sup>
TCA	17.7	1.2 <sup>b</sup>	25.5 <sup>c</sup>
Methylene chloride	20.3	0.5	26.5
Acetone	20.0	0.4	23.7
Liquid CO <sub>2</sub>	20-22 <sup>a</sup>	0.07	5.0

(a) Calculated from Giddings equation, page 224 of Reference 7.

(b) From Reference 9.

(c) Value at 25 °C, from supplier literature.

#### Liquid CO<sub>2</sub> Cleaning and Degreasing Process

The LCO<sub>2</sub> cleaning process is primarily a degreasing process consistent with vapor degreasing. Similar to vapor degreasing, it has only limited capability to remove particulate matter from a surface without additional mechanical enhancements such as ultrasonics or sprays. The process will remove most light and medium weight hydrocarbon oils, gross particulate contamination, drawing compounds, and other machining fluids. A typical LCO<sub>2</sub> degreasing cycle takes approximately 20 to 25 minutes, including loading and unloading parts. The best applications are those where organic vapor degreasing solvents will work. Similar to CFCs and aqueous solvent systems, LCO<sub>2</sub> will not remove rust, paint, coatings or most adhesives. These are typically removed by other surface preparation techniques such as abrasive blasting or surface stripping. An illustration of the LCO<sub>2</sub> equipment used during this demonstration is shown in Figure 1. It consists of a sealed pressure vessel, associated vacuum pumps and compressors, and a CO<sub>2</sub> capture and recycle tank. During the evaluation period, a centrifuge and a hot oil process (HOP) tank with ultrasonic generator were included and used to enhance the capability of the cleaning process. HOP oil is a proprietary formulation of a lightweight, low volatility hydrocarbon oil and surfactants. If heavily contaminated with soils, the item to be cleaned is first

submerged in the HOP oil tank. Ultrasonic agitation can be incorporated in the HOP tank to further break the soils from the part's surface. The HOP oil is subsequently removed during the LCO<sub>2</sub> degreasing step.

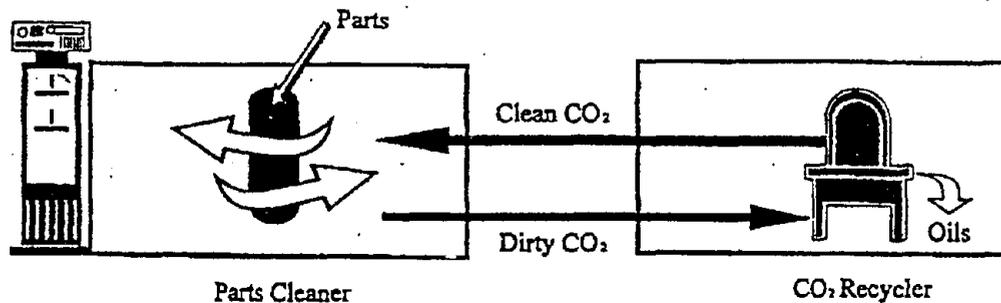


Figure 1. Illustration of LCO<sub>2</sub> Equipment.

#### Laboratory Feasibility Tests

Prior to conducting the site demonstration, preliminary laboratory evaluations were conducted by cleaning parts similar to those anticipated during the demonstration. These tests were performed in a prototype of the equipment planned for use at RAFB. The prototype was functional but not as fast or effective as the next generation of LCO<sub>2</sub> cleaning equipment to be produced. During these tests, contaminated aluminum fuel line tubing of varying lengths, diameters and shapes were cleaned. The parts were cleaned with the HOP oil first, followed by LCO<sub>2</sub>. The HOP process was used because the drawing compound contained a combination of soaps and oils. LCO<sub>2</sub> by itself removed the oils, but not all of the soaps. The HOP/LCO<sub>2</sub> process removed the drawing compound as effectively as the TCA process from some of the tubes but not all of them. Tubes with smaller diameters or more bends were not cleaned as well as larger diameter, straight tubes. A summary of the results for these tests are shown in Table 2.

Because some tubes were cleaned as well as with TCA even using the prototype equipment, it was decided that the LCO<sub>2</sub> results were good enough to warrant further testing and demonstration at RAFB once the improved LCO<sub>2</sub> equipment was available.

TABLE 2. SUMMARY OF LABORATORY EVALUATIONS OF NVR FOR TUBES

Soiled/Cleaned	Average NVR (g/ft <sup>2</sup> )	Range of NVR Values (g/ft <sup>2</sup> )	Standard Deviation (g/ft <sup>2</sup> )
Contaminated tubes	2.311	1.612 - 2.808	0.623
TCA-cleaned	0.007	0.005 - 0.008	0.002
HOP/LCO <sub>2</sub> -cleaned	0.035	0.006 - 0.181	0.050

**Site Demonstration and Evaluation**

The demonstration and evaluation was conducted at WR-ALC, GA during August 1995 to show the feasibility and capability of the LCO<sub>2</sub> process. Actual aircraft parts, including scrap parts and non-flight tools were cleaned during the demonstration. These parts were not placed back in the maintenance inventory after the cleaning tests because this cleaning process is not currently included in the parts specifications. A great variety of parts were selected for cleaning, including bearings, fuel system tubing, filters, bolts, and other mechanical and structural aircraft parts. The demonstration incorporated HOP oil and ultrasonics to enhance and maximize the efficiency of the process.

The evaluation procedure to define the capability of the system was a combination of laboratory analytical testing and visual inspections conducted by the facility maintenance personnel. The final level of surface cleanliness achieved was quantified by measuring and comparing the amount of nonvolatile residue on parts cleaned by the TCA and LCO<sub>2</sub> processes. All NVR tests were performed by sonicating the cleaned or dirty parts in solvents that had been proven to be effective in removing the contaminants from the parts, followed by evaporating the solvents and weighing the residue. Because cleaning effectiveness was to be defined by comparison between parts cleaned by the two processes, it was not necessary to quantitatively determine the amount of contamination present on the surface of the parts before they were cleaned. This was important in the test evaluations since the many of the parts provided were of various sizes, shapes, and diameters.

**Fuel Line Tubes**

The fuel line tubes cleaned were contaminated with drawing compound with an average NVR of 5.462 g/ft<sup>2</sup>. The HOP process was used prior to LCO<sub>2</sub> on the tubes since it was determined that the drawing compound was soluble in the HOP. Table 3 summarizes the results of the fuel line samples cleaned during the on-site evaluation. These tubes were cleaned as well by the HOP/LCO<sub>2</sub> process as those by the current TCA process.

TABLE 3. AVERAGE NVR LEVELS FOR FUEL LINE CLEANING USING LCO<sub>2</sub>

Soiled/Cleaned	Average NVR (g/ft <sup>2</sup> )	Standard Deviation (g/ft <sup>2</sup> )
Contaminated tubes	5.462	2.471
TCA cleaned	0.009	0.009
LCO <sub>2</sub> batch 10	0.005	0.005
LCO <sub>2</sub> batch 36	0.008	0.004
LCO <sub>2</sub> batch 37	0.003	0.002

#### Steel Bolts

Steel bolts are typically removed from aircraft during maintenance and repair. The bolts normally are cleaned, inspected, and reintroduced into the inventory. When removed, they are encrusted with heavy grease and embedded soils. The current cleaning process used at the depot includes a pre-soak in a petroleum distillate similar to the hydrocarbon oil of the HOP process. The bolts are scrubbed with a brush to remove visible grease, then placed in a vapor degreaser containing TCA to remove the petroleum distillate and any grease residue. Finally, the bolts undergo an abrasive blasting process to remove rust and carbon deposits.

The LCO<sub>2</sub> process steps used were similar to the current process. The bolts were cleaned in HOP oil with ultrasonics followed by degreasing with LCO<sub>2</sub>. Table 4 shows the average NVR level remaining on the samples after cleaning with HOP and LCO<sub>2</sub>. No bolts cleaned by the current process were available for comparison.

TABLE 4. NVR RESULTS FOR BOLT CLEANING WITH HOP/LCO<sub>2</sub>

Part Description	Average NVR/bolt (mg)
Contaminated	788.08
Cleaned by HOP/LCO <sub>2</sub>	70.17

The results of the bolt cleaning evaluation by NVR and visual examination indicate that the bolts cleaned by the HOP/LCO<sub>2</sub> process were clean enough to be sent on to the next step, abrasive blasting. The HOP/LCO<sub>2</sub> process requires approximately the same steps as the current process, however, the LCO<sub>2</sub> process eliminates the use of TCA.

#### Brass Filters

The brass filters evaluated are used in aircraft propeller assemblies to filter hydraulic fluid. The filter contaminants included hydraulic fluid, aircraft grease, and heavy carbon deposits. A picture of brass filters is shown in Figure 2. The current process to clean these parts includes soaking them

overnight in a petroleum distillate (PD) formulation, then hand scrubbing with a brush, washing in water-based general purpose detergent, rinsing with water, and drying in an oven. Due to the prolonged soaking and hand scrubbing, cleaning of this part is labor intensive and time consuming. Although the cleaning of the filters does not require the use of a CFC solvent, it does result in the generation of contaminated water stream. In addition, the process leaves visible black carbon deposits on the surface of the filter.



Figure 2. Brass Filters.

The HOP/LCO<sub>2</sub> cleaning process consists of three steps compared to five for the current process. Hand scrubbing in HOP oil with no pre-soak replaces the overnight soak and hand scrubbing in the PD; and LCO<sub>2</sub> cleaning replaces washing in water and detergent, water rinsing, and oven drying. An added blow-out technique using compressed shop air to dislodge particles trapped within the filter mesh improved the NVR of the filters. In addition, the filters cleaned with the HOP/LCO<sub>2</sub> process were visually much cleaner and shinier than those cleaned with the current process. Table 5 compares the NVR levels for the filters cleaned by the various methods.

TABLE 5. SUMMARY OF NVR LEVELS FOR BRASS FILTERS

Filter Sample	Average NVR (mg/filter)	Standard Deviation (mg/filter)
Contaminated filters	289.02	210.13
Current process	17.13	4.68
LCO <sub>2</sub> without blow out	25.13	11.98
LCO <sub>2</sub> with blow out	16.80	3.18

### Processing Cost

During the two week evaluation period a total of 37 experimental batches were run. The LCO<sub>2</sub> recovery rate over the two week period was 94 percent. A total of 24 gallons of LCO<sub>2</sub> was lost during this time. At an average cost of approximately \$0.70 per gallon, the total LCO<sub>2</sub> cost was \$16.80. The spindle oil, which constitutes the major HOP cost, averages \$490.00 for 55 gallons. The HOP oil recovered during the LCO<sub>2</sub> degreasing step is recycled to the HOP tank. The spindle oil in the HOP tank can be reused indefinitely with disposal required only after it becomes saturated with contaminants to a point where it cannot complete its function. This contamination level was not achieved during the two week evaluation period.

The capital cost of the LCO<sub>2</sub> equipment will vary significantly depending on its configuration. It can be relatively high when compared to conventional vapor degreasing or aqueous cleaning. Equipment cost will depend on the size of parts to be cleaned, since it requires pressure vessels fabricated to hold the range of parts to be cleaned, and the ultimate configuration of the system. A realistic estimate of capital costs for a LCO<sub>2</sub> cleaning system and recycler is \$175,000 to \$350,000. However, the return on investment of the system should be weighed against the savings achieved in material costs, disposal costs, elimination of regulatory compliance costs, and pollution abatement costs.

### Conclusions

The LCO<sub>2</sub> process was shown to be equivalent to TCA in performance for cleaning the parts evaluated during this project. Successful introduction of the LCO<sub>2</sub> process into a facility will require a detailed knowledge of the contaminant to be removed, the desired surface cleanliness level, and the configuration of the part. This knowledge will permit the LCO<sub>2</sub> process to be effectively integrated into the production operation to achieve the required cleanliness level.

### References

1. R. P. de Fillipi and M.E. Chung, "Laboratory Evaluation of Critical Fluid Extraction for Environmental Applications," EPA Report EPA-600/2-85-045, April 1985.
2. Katauskas, T. and H. Goldner, "SFE: Will it Solve Your Lab's Solvent Waste Problems?" R & D Magazine, March 1991, pp. 40-44.
3. Stahl, E., et. al, "Extraction of Seed Oil with Liquid and Supercritical Carbon Dioxide," J. Agric. Food Chem., Vol. 28, 1980, pp. 1153-1157.
4. Bok, Edward, K. Dieter, and K.S. Schumacher, "Supercritical Fluids for Single Wafer Cleaning," Solid State Technology, June 1992, pp.117-120.
5. McHardy, J., T.B. Stanford, L.R. Benjamin, T.E. Whiting, and S.C. Chao, "Progress in Supercritical CO<sub>2</sub> Cleaning," SAMPE Journal, Vol. 29, No. 5, September/October 1993, pp.20-27.
6. Phelps, M.R., M.O. Hogan, and L.J. Silva, "Fluid Dynamic Effects on Precision Cleaning with Supercritical Fluids,"

In: Conference Proceedings for 1994 International CFC and Halon Alternatives Conference, October 24-26, Washington, DC, pp.540-549.

7. Barton, A.F.M., Handbook of Solubility Parameters and other Cohesion Parameters, CRC Press, Boca Raton, 1983, pp 153-158.
8. Determined from Figure 3-45 and Table 3-283 of: R. H. Perry and C.H. Chilton, Chemical Engineer's Handbook, 5th Edition, McGraw-Hill Book Company, 1973.
9. Handbook of Chemistry and Physics, 56th Edition, CRC Press, Boca Raton, FL, 1975.

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