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DEGREASING METAL PARTS WITH LIQUID CARBON DIOXIDE

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Introduction

This paper describes a demonstration of liquid carbon dioxide (LCO_2) degreasing of metal parts from aircraft and vehicles cleaned during routine maintenance procedures. The objective of this research was to find and demonstrate innovative parts cleaning technologies to replace environmentally damaging chemicals with more benign processes. The process chosen to be replaced was vapor degreasing in 1,1,1-trichloroethane (TCA). This solvent needs to be replaced because it is an ozone-depleting compound, a hazardous air pollutant (HAP), and one of the 17 chemicals on the U.S. Environmental Protection Agency (EPA) 33/50 list of priority pollutants.[1] Carbon dioxide (CO_2) degreasing was chosen for demonstration as an alternative to TCA because it is non-ozone depleting, nontoxic, nonflammable, and on the EPA Significant New Alternatives Program (SNAP) list of approved cleaning alternatives.[2] This project was sponsored by the EPA under Cooperative Agreement No. CR818419.

Prior to the on-site demonstration, Research Triangle Institute (RTI) performed preliminary nonvolatile residue (NVR) analyses on metal parts cleaned with the LCO_2 process at the equipment manufacturer's facility. Based on favorable results from this preliminary testing, full-scale degreasing equipment was moved to the Warner Robins Air Logistics Center (ALC) at Robins Air Force Base (RAFB), GA. The ALC maintains and repairs F-15 fighters, C-130 and C-141 transport aircraft, and all Air Force helicopters, as well as electronics for airborne avionics, communications, vehicles, and radar equipment. The equipment was operated on-site for 2 weeks. During this time, samples of each type of part were cleaned and inspected, and some were sent back to RTI for NVR testing. Dirty parts and parts cleaned by current processes were also collected and tested for comparison.

The primary parts tested were fuel system tubing, brass filters, miscellaneous machined metal parts, and rags from the maintenance processes. Preliminary soaking in a warm mixture of hydrocarbon oil (spindle oil) and surfactants (hot oil process or HOP) was necessary to remove difficult contaminants from many parts. This high-boiling, nonflammable mixture was then removed by the LCO_2 process and could be recovered for reuse.

Background on CO_2 Chemistry

CO_2 is a gas at normal room temperature and pressure. It is odorless, colorless, nonflammable, and nontoxic. It is not an ozone-depleting material, volatile organic compound (VOC), or HAP. It is a greenhouse warming gas, but commercial supplies of CO_2 are obtained by recycling by-products from other processes. Therefore, its use results in no net addition of CO_2 to the atmosphere.

By increasing pressure on CO_2 and controlling the temperature, it can be changed from the gas phase to solid, liquid, or supercritical fluid phases. When the pressure is reduced, it reverts to a gas. As a liquid or supercritical fluid, CO_2 has excellent solvent properties for many oils, greases, and other common machining contaminants. Cleaning with liquid CO_2 is generally performed within the temperature range of 60-80 °F (16-27 °C) and pressures of 700-1500 psi (48-102 bar).

Liquid CO_2 is distinct from the better known *supercritical* CO_2 because it can be maintained at lower pressures and temperatures than supercritical, so cleaning equipment may be less expensive. Both liquid and supercritical CO_2 have the advantage of permeating into tiny holes like a gas and have good solvency for many oils, greases, and other contaminants. Liquid CO_2 will not remove paint, rust, conversion coatings, or most adhesives. Liquid CO_2 is not applicable for degreasing parts that will be damaged by pressure or by leaching of plasticizers from elastomers.

There is no solvent waste or other media to dispose of because CO_2 reverts to a gas after cleaning. The contaminants can be collected for reuse or disposal. Even though it can be released to the atmosphere, the CO_2 was recycled between cleaning cycles during the demonstration, so material costs also were reduced.

Process Description

For this demonstration, most parts were precleaned by immersion in HOP oil, sometimes with hand scrubbing or ultrasonics. The oil was heated in a tank to about 140 °F (60 °C). The HOP's purpose was to solubilize or mechanically remove difficult soils and materials that were not soluble in the LCO_2, such as waxes and soaps from greases. After the parts were soaked in the HOP, they were drained or spun in a centrifugal spinner loaned by Nobles Manufacturing to remove most of the oil. Then they were degreased in LCO_2 to remove the solubilized contaminants and particles carried in the HOP oil. Upon completion of the cleaning cycle, the CO_2 was automatically transferred from the cleaning vessel to the recycler, and the parts were removed clean and dry.

A typical CO_2 degreasing cycle takes about 25 minutes including loading and unloading parts. The cycle is divided into five steps: filling, cleaning, draining, purging, and venting. Parameters that can be changed by the operator are the duration of the cleaning step and the speed and direction of basket rotation. These values are chosen based on the type and amount of contamination and the complexity and fragility of the part to be cleaned. Once the unit has been programmed, these parameters are controlled by microprocessor. The operator needs only to load the parts, close the vessel, and push the start button.

Projected Costs

Equipment - LCO_2 equipment cost depends on the size of the cleaning vessel. The unit used at RAFB (supplied by DEFLEX Corporation) costs about $100,000 with the recycler. A centrifugal spinner that holds a similar sized basket (12 in. diameter x 12 in. deep) costs $3,000-5,000. A tank with a heater for HOP oil costs less than $2,000.

Materials - CO_2 costs range from about $0.20/gal for bulk to a high of about $0.85/gal for CO_2 in bottles. Each bottle used in this demonstration cost $28 and held 40 gal of CO_2, so cost about $0.70/gal. The average recovery rate of CO_2 recycled during the demonstration was 93.8%. Total CO_2 lost during the 37 cleaning batches run during the demonstration was about 24 gal. At $0.70/gal, this would mean a cost of about $17.

Spindle oil is $130/gal in 55 gal drums. It is not very volatile, so the major losses are the material dragged out on the parts. If the oil removed by the CO_2 degreasing were returned to the HOP tank, these losses would be minimal.

Parts Tested

Parts cleaned during the demonstration included:

- Aluminum and titanium tubing for F-15 fuel and breathing oxygen systems contaminated with drawing compound (tallow, fatty acids, and alkaline salts), metal chips, and shavings,
- Brass filters contaminated with black grime and used hydraulic fluid,
- Small pieces of aluminum honeycomb core contaminated with light oils,
- Steel bolts contaminated with heavy grease,
- Gears and other machined parts contaminated with oil and black carbon residue,
- Flap jack screw yokes (assemblies of machined steel parts containing a sealed bearing, used to repair F-15 aircraft) heavily crusted with dirt, grime, and oil.
- Large used aircraft bearings packed with heavy grease,
- Small precision bearing assemblies for avionics,
- An electronic test circuit board, and
- Rags contaminated with shop dirt, drawing compound, grease, and solvents.

The current cleaning processes for a few of these parts did not involve TCA, but the parts' owners were not satisfied with the current cleaners or results of the current process, and requested testing in LCO_2.

Results

Tubes - Visual inspection showed the tubes to be completely free of drawing compound after the HOP/LCO_2 process. It removed large metal chips and debris but did not remove all the fine particles. In all cases, a haze of particles or small piles like dried puddles could be seen inside the tubes. In some, these particles could be seen only with bright light pointing through the tube towards the viewer.

In one test, the HOP oil was deliberately skipped. The LCO_2 used without HOP oil removed metal chips and the oily portion of the grease, but left visible residues of white, soap-like material.

Five aluminum tubes cleaned by the HOP/LCO_2 process were sealed in a nylon bag and returned to the plating shop to be anodized. The parts were anodized inside and out and were inspected by shop personnel. They verified that the tubes were sufficiently clean for the anodizing process. The tubes also passed visual inspection after anodizing. Four of them were kept for further tests by RAFB.

Several sets of tubes were sent to RTI for NVR testing (Table 1). This included parts cleaned by the current TCA process, parts contaminated with drawing compound and cutting debris, and several batches of tubes cleaned in the HOP/LCO_2 process. Tubes from the HOP/LCO_2 batches had lower NVR than the TCA tubes and slightly less variability in standard deviations, which suggests that HOP/LCO_2 is more effective for removing this NVR.

This establishes that the HOP/LCO_2 process is a feasible alternative to the TCA process for removing drawing compound, metal chips, and shop debris from tubes. Further testing would be necessary to determine whether the process would be capable of removing small particles to the levels required for breathing oxygen equipment.

Table 1. Average Values and Standard Deviations for NVR Tests on Tubes (g/ ft²)

	Average NVR	Standard Deviation
Dirty tubes	5.462	2.471
TCA cleaned	0.009	0.009
CO_2, batch 10	0.005	0.005
CO_2, batch 36	0.008	0.004
CO_2, batch 37	0.003	0.002

Steel Bolts - Most of the heavy grease was removed by soaking in HOP oil with stirring. The most difficult areas to clean were inside the cap heads of the bolts, where grease was packed into the corners and would not come out with stirring alone. Once most of the grease was removed with the HOP, the bolts were cleaned in LCO_2. This completely removed all visible traces of oil, but some grease remained in the bottom of the cap heads. Rust and paint were not removed, but some paint was flaking off. These parts were returned for inspection by RAFB personnel who reported that the parts were cleaned as well as those from the current process and would be acceptable for use in the next process.

Brass Filters - The owners were interested in a new process because the current one takes too long and does not clean well, leaving visible black residue on the surface of the filter. They are considered clean enough when light can be seen through the mesh.

Filters cleaned with HOP/LCO_2 without hand scrubbing were still covered with crusty black residue left behind when the oil and grease were removed, and light could not be seen through the mesh. Once the process was changed to include hand scrubbing in HOP oil (with a 0-5 minute presoak), the filters came out of the LCO_2 visually clean and shiny, and light could be seen through all open portions of the mesh. Parts cleaned by the current process were brought to the demonstration site for comparison. These filters had black residue blotches on the surfaces; the HOP/LCO_2 cleaned parts did not.

Additional filters were cleaned and returned to RTI for NVR testing (Table 2). Seven filters were blown out with shop air between the HOP and LCO_2 processes to see if this would dislodge any of the contamination between the mesh screens. Seven others were not blown out. Samples of dirty parts and parts cleaned by the current process were sent to RTI for comparison. The amount of contamination on the dirty parts varied widely, from 55 to 559 mg/filter. The NVR results for the parts blown out with air were as low as for the current process. The NVR of parts not blown out was not as low as those cleaned by the current process, but were still much cleaner than the dirty parts. The results could be further improved with some minor process engineering.

Table 2. Averages and Standard Deviations for Brass Filter NVR Tests (mg/filter)

	Average NVR	Standard Deviation
Dirty filters	289.02	210.13
Current process	17.13	4.68
CO_2 cleaned, blown out	16.80	3.18
CO_2 cleaned, not blown out	24.61	9.73
CO_2 cleaned, not blown out (another batch)	25.65	15.09

Large C-130 Aircraft Bearings - This grease was not very soluble in HOP oil. After LCO_2, all of the heavy grease was gone, but a thin film of soap-like material was left under the roller bearings. The assembler said it looked clean enough to be used, but was not as clean as the current process.

Aluminum Honeycomb Core - The main concern was whether rotation of the parts in the machine would damage the core edges. There were no visible signs of contamination on the parts either before or after cleaning. There was no visual sign of damage to the core after cleaning. Further testing is in progress for these parts to determine whether the process will clean the honeycomb core well enough for bonding to aluminum skins.

Gears and Machined Parts - The hydraulic fluid and grease were completely removed, but black carbon residue remained on some pieces. The owners of this part said it did not meet their final cleanliness criterion of "no moveable contamination," but their current process includes a subsequent abrasive step to remove the black carbon.

Flap Jack Screw Yokes - The oil and grease were removed from all parts. Parts that were not hand-scrubbed had areas of black carbon residue in a few places. Soap from the grease in the bearings was visible on the outside of the seals. The owner of the parts said they were clean enough for use.

Small Avionic Bearing Assemblies - The first bearing had no signs of oil or other contamination after the HOP/LCO_2 cleaning. The engineers in charge of the avionic bearing assembly visually determined it to be cleaner than was obtained with the CFC-113 degreaser. A bearing that had already been cleaned once using a hydrofluorinated ether (HFE) solvent in a vapor degreaser was then cleaned with HOP/LCO_2. RAFB personnel inspecting the part said it was cleaner than after the HFE process.

Electronic Test Circuit Board - This was an initial test to determine if the components on a circuit board would withstand the 800-900 psi (54-61 bar) pressure of the LCO_2 process. Avionics provided a test board specifically designed to measure the effect of processes on circuitry operations. The board had both through hole and surface mount components. It was cleaned with the same HOP/LCO_2 procedure as the most rugged parts. The board was visually determined to be clean and showed no signs of damage to the components or the inks used to mark them. It was then taken back to avionics for electronic component testing where it was determined that all components still were functioning properly.

Rags - If HOP oil was used, drawing compounds were completely removed, leaving no oily feel or smell. When HOP oil was not used, the soap-like portion of the drawing compound was left behind. The HOP/LCO_2 process removed grease and oils, but not ground-in black carbon grime. There was no fraying or other visible damage, even to paper towels. If the batch was filled too full, clumps of CO_2 ice formed that left oily spots behind as they evaporated. Once cleaned in HOP/LCO_2, the rags were considered clean enough for general shop use.

Summary

The LCO_2 is similar in effectiveness to TCA vapor degreasing for many contaminants. It is capable of cleaning debris from a wide variety of substrates, including precision and nonprecision applications. It can dissolve oils and most greases, but does not have enough mechanical force to remove fine particles or carbonaceous wear products on its own. The HOP is necessary to remove fine particles and assists greatly with removal of other contaminants.

The HOP/LCO_2 process in this feasibility demonstration proved to be very effective for general cleaning applications. It removed drawing compounds from aluminum and titanium tubes used in fuel systems, heavy grease from bolts, hydraulic fluid from brass filters, and general shop dirt from aluminum, brass, and stainless steel parts. The aluminum tubes were cleaned to a lower NVR level than with the current TCA process. Brass filters were cleaned equally as well as the current process if an air blowout was used. Components from breathing oxygen systems and aluminum honeycomb core also were cleaned, but additional testing would be required to validate the LCO_2 process for these applications.

This work was the first step in establishing feasibility of the HOP/LCO_2 method for replacing chlorinated solvent vapor degreasers. As with all processes, it needs further refinement to optimize the cleaning effectiveness for specific applications.

Notices

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References

1. U.S. EPA Pollution Prevention Fact Sheet: *EPA's 33/50 Program*. Office of Pollution Prevention, Washington, D.C., August 1991.

2. Final Rulemaking (59 FR 13044), published in the Federal Register on March 18, 1994.

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16. ABSTRACT The paper summarizes the demonstration of an innovative parts cleaning technology with a more benign process to replace environmentally damaging chemicals. The process has the potential to replace 1,1,1-trichloroethane (TCA), an ozone-depleting compound, a hazardous air pollutant, and 1 of the 17 chemicals on EPA's 33/50 list of priority pollutants. Carbon dioxide (CO2), in a liquid or supercritical form, has significant surface cleaning properties. Liquid CO2 (LCO2) is distinct from supercritical CO2 because it can be maintained at lower pressures and temperatures than supercritical. Both have the advantage of permeating tiny holes (e.g., a gas) and have good solvency for many oils, greases, and other contaminants. There is no solvent waste to dispose of because CO2 returns to a gas phase after cleaning. Contaminants can be collected for reuse or disposal. In the demonstrated system, CO2 was recycled between cleaning cycles, so material costs also were reduced. The technology was demonstrated at Warner Robins Air Logistics Center at Robins Air Force Base, GA. Preliminary soaking in a high-boiling, nonflammable mixture of hydrocarbon oil and surfactants (HOP) was necessary to remove difficult contaminants from many parts. The HOP was then removed by LCO2 and could be recovered for reuse.

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Metal Products	Metal Parts	11F
Carbon Dioxide		07B
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