EPA/600/A-97/095

High Performance Metal Cleaning Using Liquid CO_2 and Surfactants

by

Charles H. Darvin
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Research Triangle Park, NC 27711

Brad Lienhart
MiCELL Technologies Inc.
NCSU Centennial Campus
1017 Main Campus Dr., Suite 3500
Raleigh, NC 27606

Introduction

The landmark treaty, the Montreal Protocol signed in 1987, and the U.S. Clean Air Act Amendments of 1990 mandated the end to production and use of substances that deplete the Earth's ozone layer, sometimes called ozone depleting substances (ODSs). Since that time the developed industrial world has been struggling to find suitable and effective alternatives for these critical industrial chemicals. Two of the more widely used ODSs are the chlorinated solvents 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE), both used for surface cleaning of metal components and parts.

Many industrial operators have dealt with the challenge of surface cleaning by pushing the problem off onto their suppliers, by utilizing "no-clean" options where possible, and to a large extent by attempting to find workable aqueous cleaning processes. While much improvement has been made to the aqueous cleaning technology, from improved detergents, to new agitation techniques, it is clear that a growing number of users are still looking for solvents that perform like the chlorinated solvents TCE and TCA. One potential option, still in the developmental stage, is the use of carbon dioxide (CO_2) in either the liquid (LCO_2) or the supercritical ($scCO_2$) state. These two states differ only in their containment pressures. CO_2 is a plentiful, non-ozone-depleting compound, that is non-toxic, non-flammable, and easily recyclable. Unfortunately, CO_2 alone in either state is not capable of precision cleaning for most applications without some type of enhancement to improve its solvency capability.

Background

The solvency capability of CO_2 has been known and used in the food processing industry and in wastewater treatment for a number of years. Since the early 1980s, research has been underway to investigate the use of supercritical carbon dioxide ($scCO_2$) as a solvent substitute in the polymerization of hydrocarbon monomers. This work also generated an interest in the potential use of CO_2 as a surface cleaning agent. The use of $scCO_2$ as a surface cleaning agent, however, has not been a totally satisfactory solution by itself. Since it is not a true liquid, $scCO_2$ does not possess the capability that a liquid system might provide in washing the surface to allow removal of particles from the surface that is being cleaned. For cleaning beyond removal of light oils, it has been found to be generally ineffective. Even LCO_2 does not provide a significantly greater surface cleaning capability other than for general surface cleaning.

Beginning in 1990 and working under the leadership of Dr. Joseph DeSimone of the chemistry department at the University of North Carolina at Chapel Hill, a group of 25 research colleagues at major universities, made a major breakthrough in the development of a CO_2 compatible surfactant chemistry.[1] The research to polymerize hydrocarbon monomers in $scCO_2$ led to the development of a group of unique CO_2 compatible phillic surfactants. The key to both polymerization and surface cleaning is the surfactant used which adds functionality and enhances the efficiency of the solvent. This development of a class of CO_2 compatible surfactant results in significant improvements in the potential of CO_2 as a solvent and thus as a cleaning agent. This work was supported by the U.S. EPA and a consortium of eight chemical companies: DuPont, Hoechst Celanese, Eastman Chemical, General Electric, Xerox, Air Products, BF Goodrich, and Bayer.[2]

General and Precision Cleaning

The key to the eventual use of CO_2 for general cleaning applications must be the improvement of its cleaning efficiency for a broad range of contaminants and surfaces. In chlorinated and aqueous based solvent systems, this is accomplished by the addition of surfactants and other chemicals to the cleaning system. However, conventional solvents are not compatible with CO_2. The newly developed CO_2 compatible surfactants will serve the same purpose in the LCO_2 system as conventional surfactants in chlorinated or aqueous based surface cleaning systems. They will make it possible to clean the parts of contaminants that up to now have not been affected by CO_2 in any state including heavy oils, greases, and waxes. Being in a liquid state, it will also allow for washing of the surface as in conventional liquid systems. In addition, in the liquid state the process will operate at ambient temperatures and at pressures of only 800 to 1200 psi (81×10^6 to 122×10^6 Pa), which most components can withstand without any damage.

LCO_2 has been shown to be capable of cleaning some metal surfaces where precision cleaning is not of great concern.[3] However without the enhancement provided by the surfactants, LCO_2 has limited application for precision cleaning. With a density close to that of water, and a viscosity more like a gas, LCO_2 has the capability to remove particulate matter to a greater degree than $scCO_2$. Laboratory testing at MiCELL Technologies Inc., and at North Carolina State University's Chemical Engineering Department, have demonstrated significant cleaning performance improvement when using LCO_2 and the new surfactants on various contaminants and material surfaces. MiCELLTechnologies Inc. has been licensed to produce and market CO_2 surfactants for use in cleaning systems.

Potential of the LCO_2 Cleaning Technology

The application of LCO_2 with the surfactant additives technology is one of the most promising surface cleaning options since the development of chlorinated solvent cleaners. A LCO_2 system will function similar to most present liquid systems and preserve all of the functional advantages of those systems. Since it is liquid, it can penetrate surface depressions, holes, and surface imperfections, and evaporates from the surface without leaving a residue.

Finally, with the proper surfactant package, it will remove the surface contaminants removed by CFC and aqueous based solvents including oils, greases, and particulates.

CO_2 is not an ozone depleting compound and can be acquired as a by-product from ammonia fermentation and petrochemical processes. This eliminates a requirement to manufacture CO_2 which would add to the discharge of additional greenhouse gas into the atmosphere. The material cost of CO_2 and the surfactant package is relatively low when compared to typical chlorinated solvents or equivalent substitutes used for surface cleaning.

There are no applicable regulations for the LCO_2 process. The process residue stream could be deemed hazardous depending on the nature of the contamination removed from the surface. The Occupational Safety and Health Administration (OSHA) has guidelines for CO_2 exposure which encourage monitoring to ensure that CO_2 concentrations do not exceed 10 percent by volume of the average daily air intake.[4]

Conclusions

The development of a viable surfactant system for use with LCO_2 offers an environmentally safe and efficient system. The development of a compatible surfactant allows the potentials of CO_2 to be fully realized as a clean environmentally safe and non-polluting surface cleaning process . Since CO_2 can be recycled and reused, the only waste product from the process is the contaminant itself. With the development of viable surfactant additives, the major remaining developmental activity for this technology is the design of a fully integrated and economical system for industrial application.

References

1. McClain, J.B., Betts, D.E.,Canelas, D.A., Samulski, E.T., Desimone, J.M., Londono, J.D., Cohran, H.D., Wignall, G.D. , Chillura-Martino, D., and Triolo, R., "Design of Nonionic Surfactants for Supercritical Carbon Dioxide," Science 1996, 274, 2049-2052.

2. Black, Harvey, "Supercritical Carbon Dioxide: The Greener Solvent." Environmental Science and Technology/News, Vol 30, No 3, 1996: 124-127.

3. Darvin, C. H., and Hill, E.A., "Demonstration of Liquid CO_2 as an Alternative for Metal Parts Cleaning," Precision Cleaning, IV, 9: 25, 1996.

4. Department of Labor, Occupational Safety and Health Administration, 29 CFR, 1910.1000, Subpart Z, "Toxic and Hazardous Substances," 1987.

NRMRL-RTP-P-267

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/A-97/095	2.	3. RE(
4. TITLE AND SUBTITLE High Performance Metal Cleaning Using Liquid CO_2 and Surfactants		5. REPORT DATE 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Charles H. Darvin (EPA) and Brad Lienhart (MiCELL)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS MiCELL Technologies, Inc. North Carolina State University Centennial Campus 1017 Main Campus Drive, Suite 3500 Raleigh, North Carolina 27606		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. NA (Inhouse)
12. SPONSORING AGENCY NAME AND ADDRESS **EPA, Office of Research and Development** **Air Pollution Prevention and Control Division** **Research Triangle Park, NC 27711**		13. TYPE OF REPORT AND PERIOD COVERED Published paper; 1990-1997 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES APPCD project officer is Charles H. Darvin, Mail Drop 61, 919/541-7633. For presentation at International Conference on Ozone Protection Technologies, Baltimore, MD, 11/12-13/97.

16. ABSTRACT The paper discusses high-performance metal cleaning using liquid carbon dioxide (CO2) amd novel surfactants. (NOTE: The chlorinated solvents 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE), both used for surface cleaning of metal components and parts, are two of the more widely used ozone depleting substances.) While much improvement has been made to the aqueous cleaning technology, from improved detergents to new agitation techniques, a growing number of users are still looking for solvents that perform like TCA and TCE. A potential option, still in development, is the use of CO2 in either the liquid (LCO2) or supercritical (scCO2) state. There has been a major breakthrough in developing a CO2-compatible surfactant chemistry. Research to polymerize hydrocarbon monomers in scCO2 led to the development of a group of unique CO2-compatible phillic surfactants. The key to both polymerization and surface cleaning is the surfactant used which adds functionality and enhances the efficiency of the solvent. This development of a class of CO2-compatible surfactants results in significant improvements in the potential of CO2 as a solvent and thus as a cleaning agent. This work was supported by the U.S. EPA and a consortium of eight ehcmical companies: DuPont, Hoechst Celanese, Eastman, G.E., Xerox, Air Products, B.F. Goodrich, and Bayer.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Prevention	13B
Metal Cleaning	Stationary Sources	13H
Carbon Dioxide		07B
Surfactants		11K
Solvents		
Ozone		

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)