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TITLE: Supercritical Fluids Cleaning

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MASTER

Supercritical Fluids Cleaning

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Problem

The aerospace industry and related supporting industries rely on halons, chlorofluorocarbons (CFCs), carbon tetrachloride, and other fully halogenated alkanes to clean metals, plastics, composites, ceramics, electronic components, and other materials of organic contaminants and particulates. These solvents are being eliminated from use because they are suspected to be stratospheric ozone depleting agents. Alternative cleaning technologies, such as aqueous cleaning, can replace halogenated solvents in some applications, but in others, viable replacements have yet to be found.

This paper discusses a proposed multi-party research and development program which seeks to develop supercritical fluid cleaning technology as an alternative to existing solvent cleaning applications. While SCF extraction technology has been in commercial use for several years, the use of these fluids as cleaning agents poses several new technical challenges. Problems inherent in the commercialization of SCF technology include:

- The cleaning efficacy and compatibility of supercritical working fluids with the parts to be cleaned must be assessed for a variety of materials and components.
- Process parameters and equipment design have been optimized for extractive applications and must be reconsidered for application to cleaning.
- Co-solvents and entrainers must be identified to facilitate the removal of polar inorganic and organic contaminants, which are often not well solvated in supercritical systems.

The proposed research and development program would address these issues and lead to the development and commercialization of viable SCF-based technology for precision cleaning applications. This paper provides the technical background, program scope, and delineates the responsibilities of each principal participant in the program.

Background

Surface cleaning of metal, plastic, and composite parts is a critical operation in most manufacturing processes. Parts must be cleaned to remove surface contamination (oils, grease, inorganic residues, flux, etc.) prior to painting, plating, or final assembly. Electronic assemblies must be cleaned to remove surface contamination such as soldering flux and fingerprint residues to ensure their reliability. While these needs are present in nearly all manufacturing applications, they are especially critical in the aerospace industry, where component integrity, reliability, and performance are crucial.

Presently, surface cleaning is done using a variety of methods, but primarily with the use of volatile, often halogenated solvents. These methods result in the release of significant amounts of solvent vapor, and production of solvent-bearing wastes which must be treated prior to disposal. Aqueous cleaning methods promise some relief from these concerns, but are not applicable to many cleaning problems.

Numerous U.S. aerospace industry firms have instituted aggressive corporate timetables for replacing halogenated solvents in manufacturing processes. However, replacement solvents or alternative cleaning processes have not been identified for all current solvent applications. Technology development in these areas offers a unique opportunity for industry-government cooperation because of the environmental and energy benefits that can accrue.

A collaborative project has been initiated between Boeing, Los Alamos National Laboratory (LANL), Pacific Northwest Laboratory (PNL), and a third party vendor to evaluate and develop a commercial supercritical fluid cleaning system. The Hughes Aircraft Company also has experience in this area and they have expressed interest in joining this project.

The proposed use of supercritical fluid solvents as a cleaning agent for manufacturing is an outgrowth of developments in supercritical fluid extraction technology. After a flurry of research interest in the late 1970's and early 1980's, the novel solvent properties of supercritical fluids (especially supercritical CO_2) have been exploited in many commercial applications throughout the synfuels, polymers, foods, and pharmaceuticals industries. It is only recently, however, that the potential applications of SCF technology to parts cleaning have generated significant interest.

Along with the potential for new applications, the concept of supercritical parts cleaning raises some new technical issues. Whereas extraction generally involves the selective removal of a single constituent from a bulk phase (for example, the removal of caffeine from coffee beans), cleaning requires the complete removal of all contaminants from the surface. Other issues related to integrating SCF cleaning equipment into the workplace must also be addressed.

Objective

The objective of this collaborative program is to develop and evaluate the use of a SCF cleaning system for use in industrial manufacturing operations. This project will attempt to solve remaining problems that prevent commercialization of SCF by demonstrating at both the laboratory level and in a production scale-up evaluation the feasibility of such a process for a number of cleaning applications. Process variables affecting the cleaned parts will be correlated to end use requirements. The work will demonstrate if the use of SCF is practical and develop basic cost and energy data for possible comparison to competing cleaning systems. These problems are discussed in more detail in a later section which describes our approach.

Potential Benefits of Commercializing SCF Cleaning

Current estimates are that approximately 20% of the world usage of 2.5 billion pounds of CFCs are used for cleaning. The majority of the material is eventually released to the atmosphere. It is not yet known how much of the CFCs used for cleaning could be replaced by supercritical carbon dioxide (SCCO2) cleaning. Informal estimates have ranged from 5% to 50% replacement of CFCs by SCCO2. Assuming that 20% of the CFCs used for cleaning could be replaced by supercritical carbon dioxide (SCCO2) cleaning, there would be a reduction of 0.1 billion pounds of CFCs. This represents roughly $500 million/year in solvent costs. These figures do not include any reduction from the use of chlorocarbons such as tetrachloroethylene.

In addition, SFC is expected to require less energy than conventional vapor degreasing. Solvent behavior of supercritical fluids can be changed by making only small changes in the fluid pressure. Preliminary estimates indicate that SCCO2 processes would require roughly half the energy of conventional vapor degreasing. The energy impact of SFC will be evaluated more thoroughly as part of the proposed research. Based on the energy requirement for a typical degreaser at Boeing Aerospace Company and the total virgin solvent used in the U.S., we estimate that the energy used to produce chlorinated solvents and operate vapor degreasers in the U.S. is approximately 2×10^{13} Btu/year.

Some of the halogenated cleaning agents that will be eliminated could be replaced with solvents and surfactants other than supercritical fluids. Many of these cleaning alternatives are aqueous-based systems. However, aqueous-based cleaning processes are not likely to meet cleaning requirements for all applications. In addition, most of these cleaners either contain volatile organic compounds, are flammable, contain toxic components, or presents a waste disposal problem. Detergents and soaps will contribute to the biological oxygen demand (BOD) and chemical oxygen demand (COD) of a plant's waste streams.

The use of supercritical carbon dioxide as a cleaning agent eliminates many of these environmental and safety liabilities. Carbon dioxide is non-toxic, and its principal health effects are limited to its role as an asphyxiant. It is also not flammable and can be easily separated from the removed contaminants. Its potential environmental impact as a greenhouse gas is well documented; however, commercial quantities of carbon dioxide are typically derived from sources that do not significantly impact the carbon balance of the globe. As a result, its use would not increase global warming.

Scope of Studies

SCF cleaning of parts is not expected to be applicable to all surface cleaning applications. The niche for SCF cleaning appears to lie in the area of precision cleaning of small metal parts, electronic components and assemblies, and optical components. The solvent and transport properties of SCCO2 are well matched to these applications, and the environmental and energy benefits of replacing the CFC-based solvents typically used in these applications are significant. SCF cleaning is not expected to be widely applicable to gross cleaning (such as engine degreasing), or final cleaning of large components (such as wing sections, etc) where the size of the required pressure vessels would be prohibitive. SCF cleaning technology is also not expected to impact relatively small-scale, low-technology cleaning applications such as the use of acetone as a clean-up solvent in the fiberglass fabrication industry.

The proposed program will focus on the use of SCF for precision cleaning applications, specifically the precision cleaning of small metal, composite, and polymer components, electronic components and assemblies, and optical components. These applications are believed to offer the most immediate potential for commercialization of the SCF cleaning technology. Particular attention will be given to applications where alternative cleaning processes such as aqueous cleaning are least likely to meet cleaning requirements. Cleaning tests will be conducted on actual parts and assemblies provided by the industrial participants in the program.

Experimental Objectives and Technical Approach

The proposed strategy will be to use the individual technical strengths of each of the partners to greatest advantage, and to communicate results effectively between partners and with potential users and vendors of the technology.

The initial application of SCF cleaning technology in metals parts cleaning will be principally for small precision machined parts, fasteners, and similar components on a laboratory scale. Cleaning requirements vary, but typically require removal of both surface organics and particulate matter. Several aspects of metal parts cleaning will be investigated. The following efforts will be conducted by PNL:

- Determine the cleaning efficacy of a SCF-based cleaning system, especially for complex geometries. Actual aerospace components will be used for testing. The role of solvent parameters, as well as the effects of physical cleaning phenomena (eg., use of spray nozzles to create high fluid impingement forces) will be examined.

- Determine the effect of SCF solvents and entrainers on corrosion and integrity of surface coatings. A variety of surface analytical tests will be conducted on actual components.

- Characterize the effects (if any) of SCF processing on functional properties of parts to determine whether embrittlement or other phenomena occur. These tests will be largely to assess whether the parts continue to meet functional requirements.

Test components, surface analytical support and functional parts testing will be provided by Boeing.

SCF technology may also be applied to the cleaning of electronic and optical components. In addition to removing organic and particulate matter, removal of inorganic or polar organic contaminates is an essential requirement for this application. Investigations will be conducted by LANL to determine:

- Compatibility of electronic components with SCF environments. Working circuit assemblies will be cleaned and then tested to determine whether they can undergo SCF cleaning without harming the components.

- Ability of SCF systems to efficiently remove solder flux and flux decomposition products.

- Ability of SCF solvents to remove fingerprints and residual inorganic material that may affect the cleaning performance of cleaned components. The role of physical cleaning and co-solvents will be investigated.

The assemblies will be provided by Boeing. Boeing will also provide pos-cleaning testing and evaluation of the cleaned components.

In measuring the efficacy of any type of cleaning operation, it will be important to have an array of surface analytical capabilities available to determine whether target contaminants are removed from the cleaned part. It will also be important to conduct functional cleanliness tests which do not look for specific contaminants, but rather determine the effect of cleaning on the part of component's ability to meet its intended purpose. LANL will have lead responsibility for the development of these testing methods, working in close partnership with Boeing, particularly on the functional aspects of the work.

Engineering design activities, in which PNL will have the lead role, are required to make the transition from laboratory scale to full scale commercial SCF parts cleaning applications. Major issues which will be addressed include the following:

- Adaptation of SCF extraction technology to the manufacturing environment. Designing equipment which meets the needs of the factory floor is an essential step in bringing this technology to market. Issues such as minimizing floor space requirements, improving parts loading/unloading technology, and insuring workplace safety will be addressed through close interaction with Boeing and other manufacturers.

- Supercritical solvent recycle and recovery. Unlike typical SCF extraction processes, the extracted material (dirt, oil and grease) is not of high value. This imposes an even greater need to recycle and recover solvent, ideally at the highest practical pressure.

- Economic and technical evaluation. Continual process evaluation, and use of these evaluations to direct the ongoing research towards addressing the technology user's needs, will be an important aspect of this program. SCF cleaning technology will be compared with existing cleaning processes such as vapor and aqueous degreasing.

PNL will work closely with Boeing, and with other manufacturers and users (such as the U.S. Army) to resolve engineering issues. LANL will make key contributions in the analytical support and sensor development required to develop an effective solvent recycle system, and will consult on other aspects of system design and evaluation.

Commercialization Strategy

A significant complication inherent in introducing a new technology such as SCF cleaning, is that many existing commercial manufacturing and Military Specification (MilSpec) Standards require the use of CFCs and halogenated alkanes. The majority of MilSpec testing for the cleanliness of parts relies on the flushing of the part with an appropriate solvent, followed by some sort of measurement on the recovered solvent. Many of the current MilSpec tests will not be functional with the new types of cleaning agents and procedures being developed. More sophisticated testing procedures will need to be developed to meet the specification needs of the military and to achieve industry acceptance. Although many of these techniques currently exist, they tend to be more expensive to implement and more equipment intensive to use than current standards. One of the most pressing needs to facilitate commercialization is for the implementation of new testing methods to be able to determine the efficiency of the cleaning process.

Commercial specifications and standards also affect the technology choices of the private sector. A large firm such as Boeing provides manufacturing specifications to its subcontractors. These specifications influence the technology choices made by the smaller firms, which rely on larger corporate customers such as Boei for their business. As the results of cleaning with SCFs become available, they will be incorporated into corporate specifications resulting in extensive dissemination of this new technology throughout the aerospace industry.

Commercialization will also be facilitated through the involvement of potential equipment and technology vendors who are positioned to invest in bringing this technology to the market. In addition to the research and development collaboration between Boeing, LANL, and PNL, at least one third party vendor has already been enlisted for the commercial development of SCCO2 cleaning systems. Additional firms have been contacted concerning supplies of high purity CO_2 to enhance cleaning efficiency. Thus, the proposed collaboration will facilitate the rapid transfer of SCF cleaning technology to U.S. industry.

The proposed project will be executed under Cooperative Research and Development Agreements (CRADAs) as permitted under the National Competitiveness Technology Transfer Act of 1989. In addition to the CRADA mechanism, additional technology transfer options of licensing, personnel exchanges, User Facility Agreements, and contract research will be utilized wherever appropriate.