Current Status & Technical Challenges of Liquid Carbon Dioxide Dry Cleaning

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INTRODUCTION

Liquid carbon dioxide dry cleaning is a high-pressure carbon dioxide process that is emerging in 1999 as a viable commercial alternative to conventional dry cleaning technologies utilizing perchloroethylene (PERC), petroleum derivatives, and (aqueous) wet cleaning. Two U.S. based organizations, Micell Technologies and Global Technologies are currently introducing the first commercial, liquid carbon dioxide dry cleaning systems. Other organizations in Japan and Western Europe are reportedly in earlier stages of developing their own liquid carbon dioxide dry cleaning technology.

Liquid carbon dioxide is the only new dry cleaning solvent that can potentially meet all of the criteria of many dry cleaners for the dry cleaning solvent that will replace PERC:

1. It must not weaken, dissolve or shrink ordinary textile fibers or damage buttons.
2. It must not bleed the common dyes from fibers.
3. It must be an excellent solvent for fats and oils.
4. It must not impart any objectionable odor to the dry cleaned garments.
5. It should be sufficiently volatile to permit reclamation by distillation and to permit the garments to be dried without prolonged heating at excessive temperatures.
6. It must be non-corrosive to metals.
7. It must be non-toxic.
8. It must be non-flammable and comply with fire regulations.
9. It must be inexpensive.
10. It must work in a reliable, cost effective and easy to operate dry cleaning machine.

The most common dry cleaning solvents in use at the present time are Stoddard solvent and perchloroethylene. These have been considered acceptable until recently with reference to the above-listed standards, but they are compromises at best in respect to either flammability, toxicity, residual odor, excessive drying temperature, length of drying time, and solvent loss

Supercritical Technology Consultants (STC) has researched the patent and technical literature to document the multi-disciplined, high-pressure technology development that was required for liquid carbon dioxide dry cleaning to begin to compete commercially with the conventional technologies. We have divided the technical development of liquid carbon dioxide dry cleaning into three major areas: 1) the development of the liquid carbon dioxide dry cleaning equipment, 2) the development of surfactants and chemical additives for liquid carbon dioxide dry cleaning, and 3) the development of unique technical infrastructures, such as additive and surfactant distribution and recycle systems, to handle the unique technical needs of the liquid carbon dioxide dry cleaning process.

TECHNICAL DEVELOPMENT OF LIQUID CARBON DIOXIDE DRY CLEANING EQUIPMENT

(1) Raymond L. Maffei filed the first patent (U.S. Patent # 4,012,194) pertaining to liquid carbon dioxide as a dry cleaning solvent on August 2, 1973. The patent was issued with the following claim allowed: "A garment cleaning process consisting essentially of passing liquid carbon dioxide through garments to be cleaned by placing the garments within a closed container. Admitting liquid carbon dioxide from the container to an evaporator and removing the dissolved garment soil material from the carbon dioxide by converting the liquid carbon dioxide to gaseous carbon dioxide in the evaporator. Collecting the garment soil material in the evaporator and discarding it, and transferring carbon dioxide from the evaporator to a refrigerated condenser and then to the refrigerated storage container."

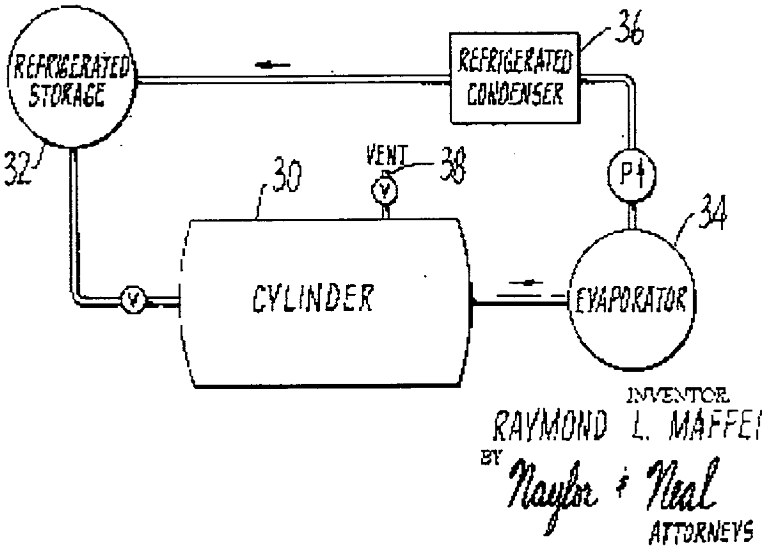


Figure 1: Maffei Dry Cleaning Process

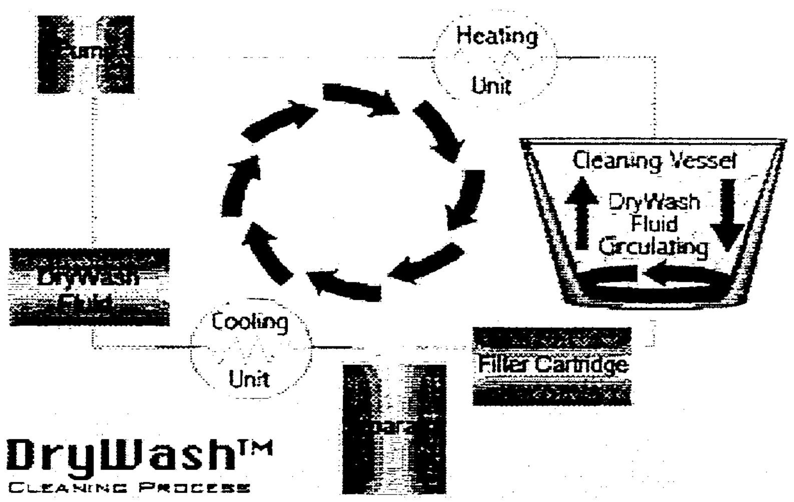
With reference to **Figure 1**, garments or other objects to be cleaned are placed within the cylinder 30 . Liquid carbon dioxide is admitted to the cylinder from refrigerated storage tank 32, and passed through the garments. The liquid carbon dioxide is then transferred to evaporator 34 and removed as gaseous carbon dioxide to refrigerated condenser 36 and then on to refrigerated storage unit 32. After recovery of the main body of gaseous carbon dioxide from cylinder 30, as by cryogenic condensation, the small amount of vapor left is vented to atmosphere through vent line 38.

Raymond Maffei never attempted to build a working prototype of his dry cleaning system. If he had, however, he would have found that more development of the liquid carbon dioxide dry cleaning equipment (to create agitation in the cleaning vessel, etc) and solvent chemistry (surfactants and additives) would be required to clean clothes adequately. Mr. Maffei should be credited as the inventor of the basic concept of liquid carbon dioxide dry cleaning. Also, Mr. Maffei taught in the specifications of the patent, for the first time, that a major advantage of liquid carbon dioxide dry cleaning (compared to all other liquid dry cleaning solvents), is that the garments do not need to be subjected to a heated drying cycle (that has the potential to damage them).

The Clorox Company worked on liquid carbon dioxide dry cleaning technology during the late 1980's, and developed a series of five patents that were issued from 1992 through 1996 (U.S. Patents: 5,370,742; 5,267,455; 5,486,212; 5,412,958; and 5,279,615). These patents claimed (among other innovations): 1) a method of decreasing polymer damage by substituting a compressed gas, such as air or nitrogen, for the liquefied carbon dioxide prior to depressurizing a cleaning vessel; 2) a sealed magnetically coupled cleaning vessel containing a rotatable drum for holding garments during the cleaning cycle, and; 3) increased energy efficiency by channeling heating and cooling effects associated with carbon dioxide gas condensation and expansion to various parts of the system. To date, the Clorox Company has chosen not to directly pursue commercialization of their liquid carbon dioxide dry cleaning technology.

Hughes Aircraft Company was issued a series of patents in the early to mid-1990's related to the design of cleaning equipment utilizing liquid carbon dioxide (U.S. Patents: 5,467,492; 5,651,276; and 5,669,251). These patents are now assigned to Global Technologies. U.S. Patent 5,467,492 claims a "means (gas, sonic, and/or liquid) for directly agitating the liquid carbon dioxide in the walled vessel to thereby agitate the garments and fabrics in the perforated lidded drum." This claim would become the basis of the DryWash™ cleaning process shown below in **Figure 2** and **Figure 3**.

Figure 2: Simplified DryWash™ Process Schematic



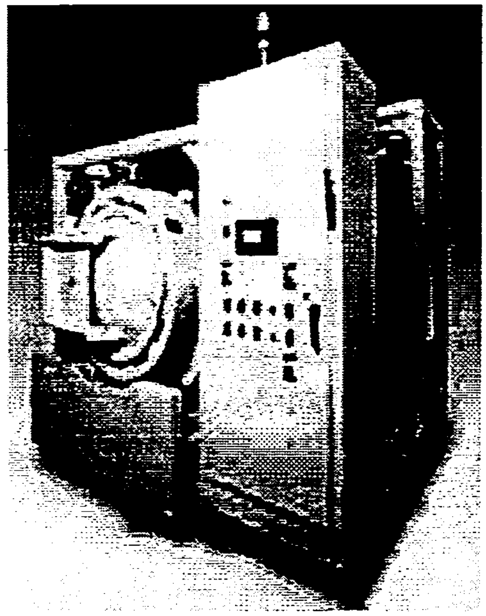
Three distinct types of stains/soils are present in the garments: 1) solvent soluble (e.g. fats, oils, and greases), 2) water-soluble (e.g. sugars and salts) and 3) insoluble particles (e.g. pigments and some inorganic particles). The mechanism of solvent soluble soil removal is dissolution in the liquid carbon dioxide solvent. The mechanism for removing water-soluble soils is secondary dissolution in water (ionic soils) and/or surfactants (polar soils) that are added to the liquid carbon dioxide solvent as co-solvents. Pre-spotters are also utilized to facilitate the removal of polar and ionic soils, just as they are used with conventional dry cleaning solvents. The insoluble particles are bound to the garment surfaces by either surface forces such as surface tension, electrostatic forces and/or Van der Waals forces. Sometimes, they are physically bound by being imbedded between two adjacent fibers. To remove the insoluble particles, shear forces must be applied, which exceed the binding forces between the particle and the garment. The liquid carbon dioxide cleaning process must impart the required sheer forces without damage to the garments.

In the DryWash™ system, the load is set in motion and agitated by high velocity fluid jets. These jets are located in manifolds within the cylindrical perforated basket with the cleaning vessel. The cleaning zone is located near the jet source, on the outermost periphery of the rotating load. The high velocity fluid jets entrain the garments by a Venturi effect. As they enter the high velocity jet-cleaning zone, the garments experience a stretch as a result of acceleration. As the garments exit the cleaning zone, they snap back into their original shape. This stretch/relax cycle in the cleaning zone is responsible for dislodging pigment soil from garments.

The jets also perform a dual function in creating a vortex/spiral of liquid carbon dioxide that entrains and carries insoluble particles through the perforated drum and out of the cleaning vessel through an exit port (so the particles do not adhere to another garment).

Figure 3: Commercial DryWash™ Dry Cleaning Unit

Micell Technologies has developed the Micare™ system of liquid carbon dioxide dry cleaning. It utilizes a specially designed, horizontally oriented, 60-pound capacity cleaning vessel $MICO_2$™ machine, shown in **Figures 4 & 5**. The cleaning vessel is a rotating drum with a sealed drive, which holds both liquid and gaseous carbon dioxide. On a volume basis, one third of the capacity of the vessel is filled with liquid and two thirds are filled with gaseous carbon dioxide. It is similar to today's front-load, mechanical action conventional solvent dry cleaning machines, where garments travel upwards via the rotating drum out of the liquid phase and are dropped at the eleven o'clock position. As garments are dropped into the liquid carbon dioxide phase, they descend to the bottom of the rotating drum in a sequential fashion until they are picked up by the rotating drum to ascend back into the gas phase for another drop into the liquid phase. The garments are pulled through the liquid/gas interface within the cleaning vessel on the way up the mechanical drum and are dropped through the gas back into the liquid phase. Much of the mechanical cleaning on insoluble particles occurs when the garments are forced from gas to liquid phase and back. The rotating drum is designed to alternate between clockwise and counterclockwise modes during the cleaning cycle every thirty seconds to assure random motion of the garments, (so that they do not get wound). The $MICO_{2}$™ machine can be programmed by the operator for gentle through aggressive wash and extraction cycles. During the first three minutes of the cleaning cycle, a portion of the liquid carbon dioxide solvent is constantly being removed from the cleaning vessel and passed through a lint filter in the wash cycle loop. During the next five minutes of the cleaning cycle a carbon filter is added to the wash cycle loop. The final stage of the cleaning cycle is an extract cycle comparable to a traditional dry cleaning solvent extract cycle to remove residual solvent from the garments. After the cleaning cycle, the machine pulls both the liquid and gaseous carbon dioxide to the working tank, a portion of the cleaning fluid is sent to the still, which separates the carbon dioxide from a residue composed of surfactants, additives, and soils. The residue is sent back to Micell Technologies for recycling.



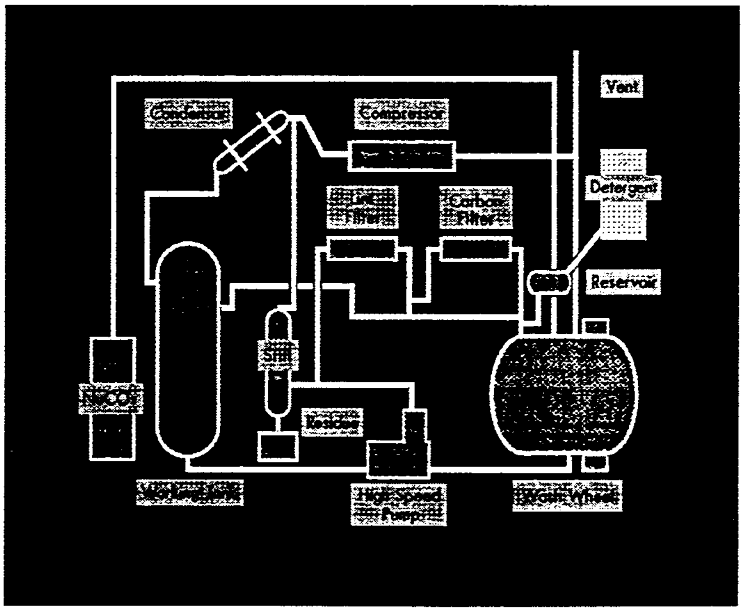


Figure 4 Commercial $MICO_{2}$™ Unit Figure 5 $MICO_{2}$™ Process Schematic Unit

TECHNICAL DEVELOPMENT OF SURFACTANTS AND CHEMICAL ADDITIVES FOR LIQUID CARBON DIOXIDE DRY CLEANING

Surfactants are required in liquid carbon dioxide cleaning systems to clean polar soils, and to increase the loading of water in the liquid carbon dioxide for removal of ionic salts. Much research has been directed towards finding surfactants, which are highly soluble in carbon dioxide and have a great affinity for specific polar compounds.

Additionally, liquid carbon dioxide surfactants should be non-toxic, inexpensive and easily separate from the carbon dioxide in a separator vessel or distillation column.

The two basic criteria used to evaluate carbon dioxide surfactants are: (a) how much surfactant is required to do the cleaning job (i.e., what concentration is needed to do the cleaning) and, (b) what pressure is required to put sufficient concentrations of surfactant into solution. In general, more nonionic surfactant is needed to perform an equivalent cleaning job than an ionic one. Ionic surfactants often use concentrations in the 1% range, while nonionics are used at much higher concentrations.

A liquid carbon dioxide cleaning surfactant must dissolve in CO_2 at sufficient concentrations at a pressure which is low enough to solublize at the pressures of commercial liquid carbon dioxide dry cleaning equipment. The University of Pittsburgh has generated simple fluoroether-functional sulfonates and sulfate surfactants that would likely be ideal in a cleaning application and would dissolve at low pressures, yet these surfactants would be too expensive for application in liquid carbon dioxide dry cleaning. Similarly, Micell Technologies originally used fluorinated polymeric surfactants, which they apparently have found to be too expensive. Micell Technologies is now reportedly using silicone based surfactants with side chains made of ethylene and propylene oxide.

US Patents related to surfactants in liquid carbon dioxide include a series of Battelle Memorial Institute patents of the early 1990's (US Patents 4,933,404, 5,158,704, 5,266,205). These patents have been licensed by Micell Technologies. A comprehensive series of patents was also filed by Unilever/Lever Bros. in the mid 1990's (US Patents 5,676,705, 5,683,977, 5,683,473). Unilever/Lever Bros. has signed an agreement to exclusively offer their surfactants to the Global Technologies consortium members. Recently, in 1998, two US patents were issued to Air Products and Chemicals pertaining to surfactants for liquid carbon dioxide (US Patents 5,733,964 and 5,789,505), and one patent related to an anti-static additive (US Patent 5,784,905) to Global Technologies.

TECHNICAL DEVELOPMENT TO SUPPORT UNIQUE BUSINESS INFRASTRUCTURES

The DryWash™ consortium plans to offer dry cleaners carbon dioxide in which additives and surfactants are already incorporated. Micell Technologies introduces additives and surfactants into the CO_2 inside the dry cleaning unit. Additionally, Micelle Technologies plans to collect and recycle their additives and surfactants. These unique additive and surfactant distribution and recycle systems provide special technical concerns to be addressed in commercial operations.

CONCLUSION

Liquid carbon dioxide dry cleaning has undergone significant technical development since it was invented in 1973. STC predicts that significant ongoing development activity will be occurring over the next several years. Especially intense will be development activity to finding inexpensive, high soluble, and high performing surfactants for liquid carbon dioxide dry cleaning.

REFERENCES

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