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Supercritical Fluids for Coatings–From Analysis to Xenon
A Brief Overview

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3.1. INTRODUCTION

Supercritical fluids (SCF) systems, though already established for some applications,[1] may represent more important technologies in the future. The primary motivation for adoption of such processes was concern about and legislation against conventional solvents.

SCFs are widely used in small-scale laboratory extraction and analysis[2] and are already established for large-scale extraction of caffeine from coffee, flavors from hops, and many other such uses[1] with plant sizes up to 50,000 tons per year throughput. A Philip Morris semicontinuous denicotinization plant is said to employ pressure chambers of 1.5-m diameter and 5-m height. The outlet gas is passed through activated carbon and recycled.[1]

3.2. SUPERCRITICAL FLUIDS

When fluids and gases are heated above their critical temperatures and compressed above their critical pressures they enter a supercritical phase in which some properties, such as solvent power, can be altered dramatically.

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Table 3.1. Factors Affecting Solubility of Polymers/Resins
in $scCO_2$

Solvent system	Polymer
Supercritical fluid	Amorphous or crystalline
Temperature	Structure
Pressure	Molecular weight
Cosolvents	Functionality
Surfactants	Molecular weight/functionality ratio

Water is supercritical at temperatures above 374°C and pressures above 220 bars. It changes more than many other substances on becoming supercritical, because the hydrogen-bonded structure breaks down—becoming less polar—and can become homogeneous with relatively large amounts of organic compounds as well as permanent gases such as oxygen, making them available for chemical reaction. Diffusion rates are over a hundred times faster than in water at ambient temperature. The most spectacular demonstration of its unusual characteristics, shown originally by Franck and his colleagues in Karlsruhe, is that flames can be produced in dense supercritical water at pressures of up to 2000 bars.[2]

Suitable gases in the form of supercritical fluids represent clean solvents/carriers, which neither leave residues nor impose an environmental load. A number of factors determine the solubility of polymers in supercritical carbon dioxides ($scCO_2$) and these are given in Table 3.1.

Comparison of the supercritical temperature and pressure conditions of some candidate fluids for industrial exploitation (Figure 3.1) may exclude those requiring extreme conditions, such as water, and others on environmental (SF_6) or cost grounds (xenon).

Supercritical CO, offers an acceptable combination of pressure and temperature to achieve supercritical conditions, but is not a good solvent for most materials, which are $scCO_2$-phobic. However, both silicone and fluoro products can be regarded as CO_s-philic and, therefore, potentially more soluble.

It must be made clear that while the 100% fluoropolymers, such as PTFE, may be soluble to some degree in $scCO_2$, the temperature and pressure conditions are so extreme as to render them impractical for conventional coating procedures. Nevertheless, there are some applications demanding deposition of partially fluorinated materials from low concentration solutions:

- Coating process requiring the deposition of 0.5 to 2% solutions of functionally end-capped partially fluorinated hydrocarbons or silicones may be feasible.
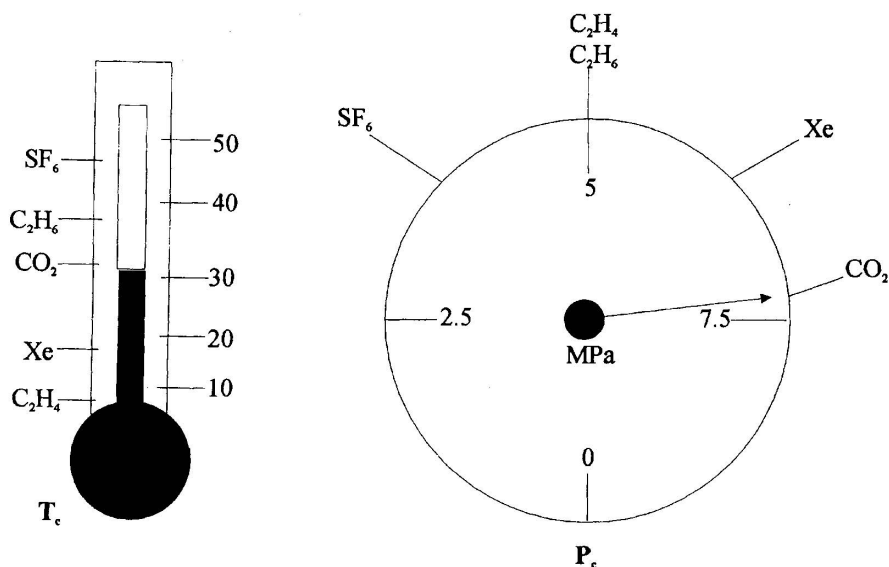- Acrylate may be the most appropriate functionality.

Figure 3.1. Critical temperature and pressure for selected gases highlighting CO_2 .

- Oxygen-containing perfluoropolyether derivatives, which are related to the preferred surfactant compatibilizers, could be important.
- The use of cosolvénts and designed surfactants (amphiphiles/stabilizers) can improve solubility.

3.3. SOLUBILITY OF SILICONE AND FLUORO COMPOUNDS

The solubility of PDMS in CO_2 /toluene mixtures has been attributed to comparable solubility parameters and the interaction between CO_2 (a weak Lewis acid) and the strong electron donor capacity of the siloxane group. The oxygen in perfluoropolyethers also has an electron donor capacity. The solubility parameter of CO_2 at the critical point is 5.5–6.0 $(cal/cc)^{1/2}$, which makes it comparable with pentane, but it can be raised as high as 9–9.5 $(cal/cc)^{1/2}$ by increasing the pressure when solvent power is more akin to that of benzene or chloroform. Fluorinated oils have the lowest solubility parameter of any known liquid at 4.5–5.0 $(cal/cc)^{1/2}$ These figures indicate that CO_2 should exhibit miscibility with fluorinated oils. Solubility in CO_2 may rise upon replacement of $-CH_2$ with $-CF_2$ or $CF (CF_3)O$.[3–8]

Table 3.2. Typical Modifiers

Modifier	T_c (°C)	P_c (atm)
Methanol	239.4	79.9
Ethanol	243.0	63.0
1-Propanol	263.5	51.0
2-Propanol	235.1	47.0
1-Hexanol	336.8	40.0
2-Methoxy ethanol	302	52.2
Tetrahydrofuran	267.0	51.2
1,4-Dioxane	314	51.4
Acetonitrile	275	47.7
Dichloromethane	237	60.0
Chloroform	263.2	54.2

The addition of small quantities of cosolvents, also known as modifiers or entrainers, can enhance the solubility characteristic further. Even though in earlier years attention was focused primarily on single-processing fluids such as CO_2 and extractions as the primary mode of application, in recent years emphasis has been shifting to binary and multicomponent fluids and processes with a greater degree of complexity, which can include either physical or chemical transformations. Some modifiers with their relevant properties are listed in Table 3.2.

3.4. POTENTIAL APPLICATIONS

Potential applications for coatings include: adhesives · analysis/extraction of paint film · cement hardening · conformal coatings · dry cleaning · dyeing · fractionation of silicone and fluoro fluids · impregnation · liquid spray · micro-emulsions · mixing/blending · polymerization · powder coating · powders from organometallics · purification · sterilization · surface cleaning · surface engineering of polymers by infusion · tetrafluoroethylene handling · waste water treatment.

Adhesives. Supercritical fluids might also be used to deposit adhesive films[9] without the use of solvents. They have even been suggested for ungluing at the time of final disposal/recycling of the bonded product.[10]

Analysis. Extraction of paint film.[11–19]

Cement hardening. Cement does not achieve its full theoretical mechanical strength. It hardens so slowly because water seals its pores and prevents ingress of CO_2. Hardening requires reaction of calcium compounds with CO_2 to form limestone and other minerals that may be stronger than concrete. Supercritical CO_2 might be employed to accelerate the hardening reactions.[20]

Conformal coatings. Deposition of a thin film that uniformly coats all exposed parts of a three-dimensional structure is known as conformal film growth. Conformality is a common requirement for dielectric films. Penetration and uniform coverage of all topography and interstices are vital and depend upon low viscosity, as well as low surface and interfacial energies.[21] Fluoropolymer in supercritical solution might provide the required characteristics.

Dry cleaning. Supercritical CO_2 fluids technology is proposed for dry cleaning wool by Global Technologies.

Dyeing. Supercritical fluid can be used to provide a water and solvent-free method of textile dyeing. Fluoro-modified dyestuffs have been developed in order to provide improved light-fastness etc. and are readily available.[22] It might be interesting to research the supercritical fluid solubility of these products.[23-27]

Fractionation of silicone and fluoro fluids. Since solubility depends on molecular weight and temperature/pressure it is possible, particularly with products such as silicone oils[3] and fluorinated liquids[4] to separate fractions by solubilization and then pressure-reduction steps.

Impregnation. In-depth penetration of additives such as biocides, fire retardants, and hydrophobes is possible for porous substrates, and $scCO_2$ solubility is not necessary for some porous substrate impregnation.[28-31]

Liquid spray. Viscous fluids can be torn apart into an efficient spray by the decompression of a supercritical fluid. Both one- and two-component systems can be handled.[32,33] This process has been loosely described as "liquid powder coating." The Union Carbide spray process (Figure 3.2) relies not on solubility of the solvent-reduced paint but on a combination of rheology modification and decompressive spray energy. In the commercial application of a silicone nonstick coating to metal bakeware using electrostatic automatic spray guns, solids in the coating concentrate were increased from 20 to 64% together with the accrual of a number of other benefits, as shown in Table 3.3

Table 3.3. Supercritical Spray Benefits Silicone Nonstick Coating

VOC level fell from 6.3 to 3.4 lb/gal
Material utilization increased by 23%
Coverage per gallon increased fourfold
Solvent emissions reduced by 89%
Overspray collected and recycled
No incineration required
Appearance of the finish was improved
Nonstick performance was improved
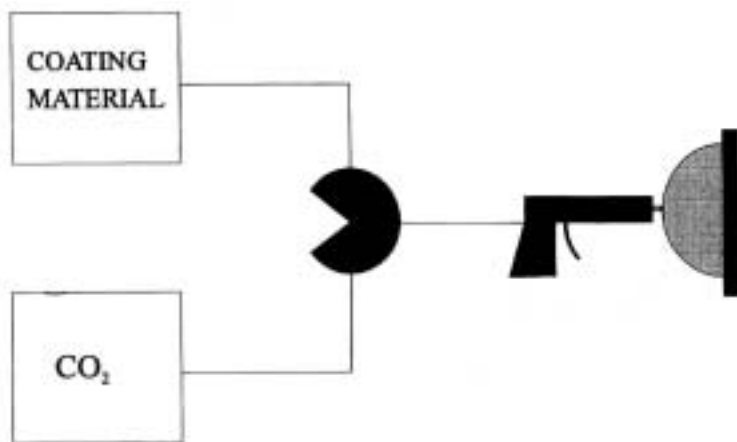
Carbon dioxide gasification gives vigorous atomisation

Sprayed material & deposited coating are identical if no
solvent is lost in the spray

Supercritical spray conditions:
            1200 - 1600 psi pressure
            40-60 degrees Celsius

Figure 3.2. Supercritical spray system outline,

Microemulsions. Systems comprising microwater droplets suspended in an
$scCO_2$ [34] "oil phase" can be achieved with the use of appropriate surfactants, of
which the best appear to be fluorinated.[35] Microemulsions in supercritical
hydrofluoro carbons are also possible.[36] Potential may also exist for speciality
coatings via low concentration solutions of fluorinated products in supercritical
fluid for, e.g., thin-film deposition, conformal coatings, and release coatings.
Supercritical CO_2 will dissolve in formulated systems to improve flow and
plasticize melt-processable materials to improve melt-flow characteristics and
lower the glass transition temperature.

Mixing/Blending. Work on powder coating indicates successful blending of
components into homogeneous systems.[37]

Polymerization. Since fluorinated products are $scCO_2$-philic, CO_2 can be
used as a substitute for CFC solvents in the production of fluoropolymers.[5-7,38,39]
Selection of fluorosurfactants has enabled polymerization of $scCO_2$-phobic
polymers such as polymethyl methacrylate.[8,40-46]

Powder coating.[47] The search is on for thin-film uniform coatings from powder with the ultimate prize being automotive clear topcoats.[48] General Motors, Ford, and Chrysler cooperate in a "low-emission paint consortium," which is spending $20 million on a test site to study clear powder coatings for full-body automotive topcoat use. In 1996 BMW (Germany) opened the world's first full-body automobile powder clear-coat line. Applications in areas such as cookware are also of interest.[49] Thin films depend on particle size, morphology, and size distribution; rheology control; and the charging system. Powder coatings are progressing fast because they represent "clean" technology. Potential now exists for marriage with another clean technology—supercritical fluids—with the combination reducing the deficiencies of both individual processes. Supercritical-fluid technology may yield chemically homogeneous powders, controlled in morphology and size distribution and produced at relatively low temperatures,[49] allowing a wider range of chemistries to be utilized. Rapid expansion spraying from supercritical solution can yield submicronic powders and fibers.[50–58] Fluorinated powder-coatings exist and might be very suitable for supercritical powder-coating development.[59–69] Silylated clear coats are already established in the auto industry.[92]

Powders from organometallics.[70–73] Fine pigment powders are also possible. Metal alkoxides such as titanium isopropoxide, which is soluble in supercritical ethanol, can undergo rapid expansion spraying to form submicronic titanium dioxide powders.[74–77]

Purification. Where an aqueous system or aqueous purification is employed, water can be left with traces of organic solvents, such as toluene, which may prohibit river disposal. Supercritical-fluid techniques can be used for final purification.[78]

Sterilization. A report suggests that $scCO_2$ may exhibit a sterilizing effect, which can be enhanced by the use of acetic acid as a cosolvent.[79]

Surface cleaning. Potential may exist for cleaning of microelectronic components, and the technique is already being used for cleaning of micromechanical devices.[80-81] Los Alamos National Laboratories had, in 1993, the largest commercially available supercritical-fluid cleaning facility at 60 liters.[82] Supercritical fluids alone cannot remove ionic contaminants although developments in reverse microemulsions might change this by allowing the incorporation of water into the system.

Surface engineering of polymers by infusion. Supercritical-fluid contact can reversibly swell some polymer surfaces and films thus helping to enhance impregnation by monomers with subsequent polymerization to form nanocomposite anchored layers.[83-85]

Tetrafluoro ethylene handling. TFE is a difficult product to handle since trace amounts of oxygen can lead to catastrophic explosion. The pure product has been shipped in cylinders but these are very expensive. Current regulations demand

dilution with nitrogen to a degree that precludes practical use. Essentially this means that this important monomer can only be used on-site where it is produced. Work has indicated that pressurizing with CO_2 can lead to a pseudoazeotrope and improved safety in handling,[86] thus enabling safe shipping to any site.

   Waste water treatment. Supercritical CO_2 has been put to use in a variety of industrial waste treatment applications. Clean Harbors Environmental Services, Inc., has used $scCO_2$ in Baltimore since 1989 to treat wastewater from chemical and pharmaceutical manufacturers. In the process the wastewater is pumped into the top of a 32-ft-high, 2-ft-diameter column, while the CO_2 is pumped in from the bottom and percolates up. As the CO_2 trowels up it dissolves the organics. CO_2 contaminated with organics is at the top of the column, and clean water is at the bottom.[78] The contaminants are incinerated off-site after separation from the CO_2 which is recycled.

3.5. XENON AND RECYCLING

   Xenon is technically an interesting supercritical fluid since the critical temperature is about 17°C (cf. 31°C for $scCO_2$) and critical pressure is about 55 atm (cf. 70 for $scCO_2$).[87] We have not considered this previously because xenon is more expensive at present, but the price could fall dramatically if there
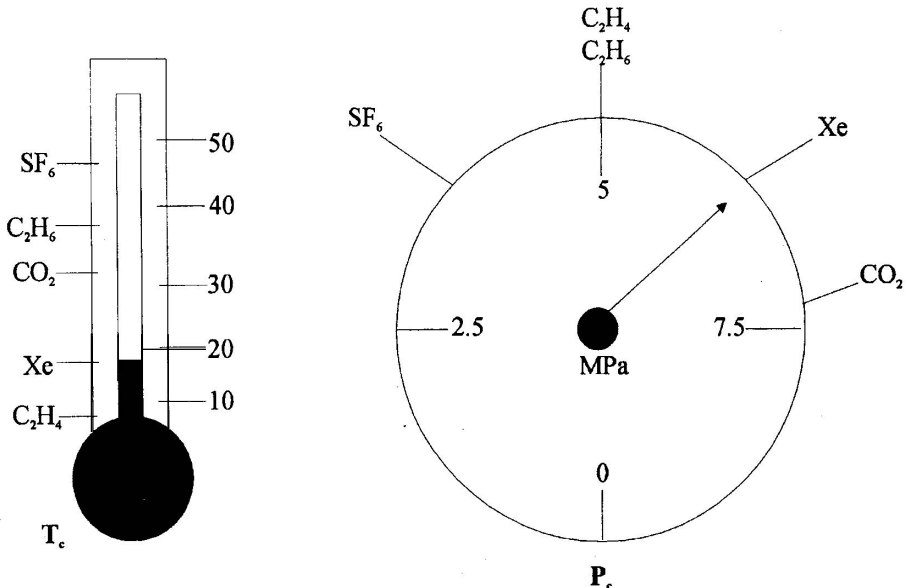

Figure 3.3. Critical temperature and pressure for selected gases highlighting xenon.

was a demand for it. Xenon is possibly a better solvent and it is possible that scXe would be a technically better candidate for wood impregnation with the higher cost being offset by lower pressure, less expensive equipment, and the possibility of simple recycling. We would suggest some basic investigation of xenon to compare against carbon dioxide (see Figure 3.3).

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