

# Review

## Environmentally friendly coatings using carbon dioxide as the carrier medium

J. N. HAY

*Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 7XH, UK*  
*E-mail: j.hay@surrey.ac.uk*

A. KHAN

*School of Engineering, University of Surrey, Guildford, Surrey, GU2 7XH, UK*

The use of supercritical or liquid carbon dioxide as a medium for delivering coating systems is attracting much interest because of concerns over the environmental effects of volatile organic compound (VOC) emissions from conventional coatings. Significant reductions in VOC emissions can be achieved by replacing some or all of the organic solvent by CO<sub>2</sub> in spray coatings. Technical and commercial benefits are also claimed for these systems, including improved coating efficiency and operating cost savings. In this review, the range of current and potential applications achievable using CO<sub>2</sub>-based coatings is discussed. In addition to spray coatings onto a variety of substrate surfaces, CO<sub>2</sub> processes can be used to produce controlled particle size powders for use in powder coatings and also for the coating of preformed particles such as metal powders and pharmaceuticals for controlled release in drug delivery. Use of CO<sub>2</sub> in spin coating and microlithography offers the potential for significant waste reduction. Specific substrates where use of CO<sub>2</sub> can be beneficial include the treatment of building stone and wood treatment. CO<sub>2</sub> can aid surface impregnation of substrates because of its high diffusivity and the potential for substrate swelling. © 2002 Kluwer Academic Publishers

### 1. Introduction

In coating applications, increasingly stringent pollution controls have forced moves away from the use of organic solvents towards alternative coating technologies. Volatile organic compound (VOC) emission limits are being reduced in many industrialised countries, for example new European Union (EU) legislation came into force in 2000. It has been estimated that *ca.* 6% of man-made VOC emissions across the EU emanate from coating operations [1]. Moves to reduce VOC emissions have accelerated the development of aqueous and powder coating systems. Although water is an attractive alternative, it does have drawbacks. The properties of waterborne polymers are often inferior to those of their solvent-cast analogues. The high latent heat of vapourisation leads to high drying costs and, where natural drying is required, this can be problematic in cold climates or those of naturally high relative humidity. A further problem is that of waste-water clean-up where ever lower limits are being set by regulatory authorities on contamination levels. Powder coatings can overcome these drawbacks, but significant reformulation of the corresponding solvent-based system may be required, leading to changes in coating properties. Control of the rheology of the systems in order to promote effective coalescence of the powder particles to form a coherent

film is of crucial importance. Alternative solutions to the solvent problem have therefore been sought.

Supercritical fluids (SCFs) have unique characteristics that make them potentially useful solvents and processing aids in many chemical processes and operations [2–4]. A material exists as an SCF above its critical temperature and pressure, where it can no longer be liquefied by increasing pressure. This can be seen in Fig. 1 [5]. At extremely high pressures, an SCF can solidify. For a pure substance, the critical point is the highest temperature and pressure where a gas can be liquefied. There is no apparent distinction between a high-pressure gas and a supercritical fluid, as a supercritical fluid will occupy the full volume of the container in which it is stored, like other gases. For a supercritical fluid above its critical temperature and pressure, no phase separation occurs and therefore no meniscus can be seen.

Supercritical carbon dioxide (scCO<sub>2</sub>) is the most widely used supercritical fluid and is becoming an attractive choice for replacing organic solvents in a number of chemical processes, including coatings. It is already in widespread commercial use for the decaffeination of coffee beans and there are large new emerging markets in chemicals manufacture, dry cleaning and other extraction processes. CO<sub>2</sub> is available

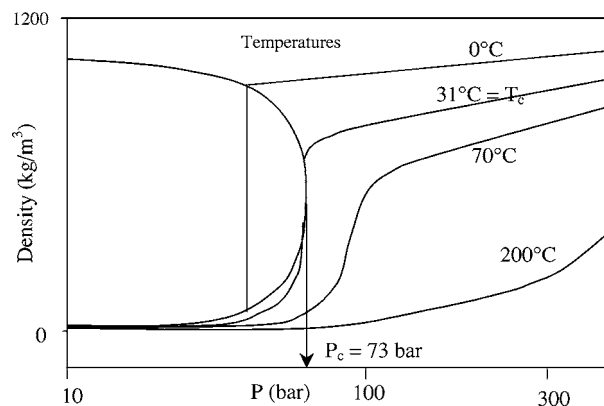


Figure 1 Liquid-vapour phase diagram of carbon dioxide showing critical temperature ( $T_c = 31^\circ\text{C}$ ) and critical pressure ( $P_c = 73\text{ bar}$ ) [5]. Also shown in the figure are three other isotherms at  $0^\circ\text{C}$  (below critical temperature) and at  $70^\circ\text{C}$  and  $200^\circ\text{C}$  (above critical temperature).

in abundance and is non-toxic, non-flammable, relatively cheap and has zero ozone-depletion potential. Vast quantities of  $\text{CO}_2$  are produced as a by-product in ammonia, hydrogen, and ethanol plants, from burning fossil fuels in power stations and in fermentation processes. Despite concerns over the greenhouse effect of  $\text{CO}_2$ , it can be considered as an environmentally friendly alternative to existing organic solvents, since the  $\text{CO}_2$  used in this way is already recycled and so the net load on the atmosphere is unchanged. Carbon dioxide is a gas under ambient conditions and therefore its removal from coatings in the post processing operation is very easy and no complicated drying and solvent removal operations are involved.

In the last 10 years, supercritical  $\text{CO}_2$  has attracted increasing interest as a replacement for organic solvents in polymer processing, in particular as a polymerisation medium [4–10]. Free radical polymerisation is the most common polymer technology using supercritical  $\text{CO}_2$ , where reaction is often carried out by dispersion polymerisation. In dispersion polymerisation, the morphology of the particles that nucleate during the reaction is controlled by a surfactant. To stabilise these polymer latexes fluorocarbon and siloxane based homopolymers and copolymers have been developed which are soluble in  $\text{scCO}_2$  [11–14].

## 2. Supercritical coatings

In comparison with activity on polymerisation in  $\text{scCO}_2$ , relatively little research work has been directed towards the application of supercritical carbon dioxide in the coatings area. However, an increasing number of publications have appeared in the recent literature, reporting use and/or proposing the use of supercritical carbon dioxide as a replacement for conventional organic solvents [15–21]. Some commercial processes use supercritical carbon dioxide for spray coating of substrates, for example the UniCarb<sup>TM</sup> process. Dip coating provides an alternative approach to the coating and impregnation of a range of substrates. The possibility of swelling of the substrate with enhanced penetration depth of the coating offers a potential advantage in the use of  $\text{CO}_2$  in addition to the environmental benefits outlined above. Other processes such as rapid expansion of supercritical solutions (RESS) are used to coat

polymer/solute layers onto particles. The latter process is also used to synthesise particles of different morphologies. These processes are described below, along with other supercritical systems which have been used or have potential use in coatings. It should be noted that the presence of other soluble materials (e.g., a coating formulation) in a supercritical fluid can change its critical parameters, and the extent of the change depends upon the concentration of the other substance. What this means in practice is that a ‘supercritical’ coating system may vary between supercritical and sub-critical during different parts of the process. From the point of view of much of this review, the key factor is the use of environmentally friendly  $\text{CO}_2$  rather than the precise state of the coating system. Thus, where the term ‘supercritical’ is used, this means only that the  $\text{CO}_2$  is in this state at some stage during the process.

The areas where supercritical coatings have been used or proposed include the following [15–18].

- Metal primers and coatings.
- Textiles, fabrics and fibres.
- Pharmaceutical particle coatings.
- Coating/impregnation of porous materials: brick, cement, stone, wood.
- Metal particles and solid propellant fuel particles.
- Biomedical devices.
- Food coatings.
- Leather and paper coatings.
- Coatings for polymers and elastomers.
- Glass coatings.

A further major advantage of  $\text{CO}_2$  over organic solvents in applications in the food, medical, healthcare and pharmaceutical industries is the lack of toxicity and the absence of any taint or odour caused by residual solvent in the final product.

### 2.1. The UniCarb<sup>TM</sup> process

Union Carbide and Nordson developed a process (the UniCarb<sup>TM</sup> process) for spray coating substrates from a medium such as carbon dioxide [15–17]. Following the recent acquisition of Union Carbide by Dow Chemical Co., this technology is now proprietary to Dow. For polymer coatings, the use of a SCF-organic solvent system has been claimed to have a number of advantages over the alternative approach of powder coatings, for example improved film coalescence and quality and no need to re-formulate the resin from that used in solvent-based coating. The UniCarb<sup>TM</sup> process uses a new type of spraying process called a decompressive atomisation [15–17] to produce the droplets. The coating material (or concentrate in a solvent such as methanol) is mixed with the carbon dioxide and subsequently discharged from the machine as an atomised spray. Whereas conventional airless and air sprays atomise the coating material through external shear forces, the rapid decompression and evaporation of the  $\text{CO}_2$  within the coating material produces high internal forces which overcome surface tension and cohesive forces and produce a highly uniform spray [15–17], even for highly viscous coatings (up to *ca.* 500 P). The spray has a narrow

droplet size distribution with an average diameter typically of the order of 20–50  $\mu\text{m}$ . The use of  $\text{CO}_2$  as the coating carrier medium and the production of a highly uniform spray result in a number of claimed benefits for the UniCarb™ process compared to conventional coating processes [15–17]:

- Significant reductions in VOC emissions.
- Reduced worker exposure to organic solvents.
- Improved coating appearance and performance.
- Higher transfer efficiency.
- Reduced operating and capital costs.
- Reduced maintenance costs.

## 2.2. Polymer coatings

A supercritical carbon dioxide polymer coating system may be a true solution of the polymer in  $\text{CO}_2$ , a solution of  $\text{CO}_2$  in the polymer (as can occur in the UniCarb™ process) or a dispersion. Pure carbon dioxide solution systems are limited by the solubility of the polymer in carbon dioxide. There are few polymers that are appreciably soluble in carbon dioxide, silicones (siloxanes) and amorphous fluoropolymers representing the two most common examples (Fig. 2) [22–25]. A co-solvent can be used in a coating system where the amount of organic solvent used is greatly reduced compared to the conventional solvent-borne system. In the case of thermosetting polymers, monomeric coating formulations may show reasonable solubility in  $\text{CO}_2$ . To overcome the problem of the limited solubility of polymers in carbon dioxide, the use of dispersion coatings offers a potential solution, which could help to broaden the applicability of carbon dioxide coating systems and furthermore produce essentially 100% VOC-free systems [18, 21]. The quality of the dispersion will depend on the availability of  $\text{CO}_2$ -compatible stabilisers. The choice of these stabilisers has been mostly limited to either fluoropolymers (e.g., **I**) [26, 27] or silicone polymers (e.g., **II**) [8, 10, 14, 28], which are relatively expensive; however, the recent development of comparatively cheaper  $\text{CO}_2$ -compatible polymers (e.g., **III**) [29] may open the way to development of cheaper stabilisers and more widespread use of supercritical carbon dioxide polymer coatings technologies.

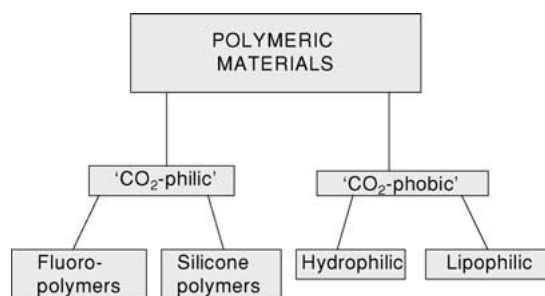
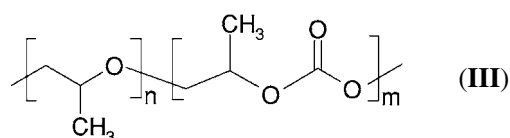
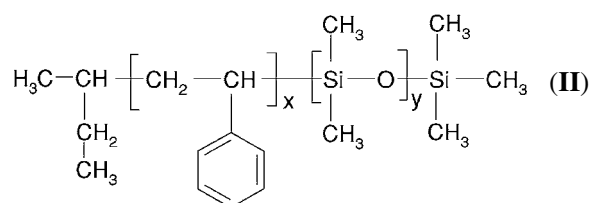
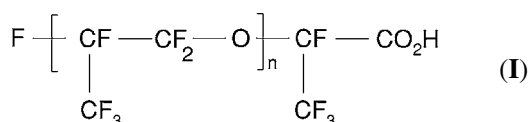


Figure 2 Polymer compatibility with supercritical  $\text{CO}_2$ .

To date, limited work has been reported on the use of  $\text{scCO}_2$  for the delivery of coatings based on polymer dispersions [30]. Shim *et al.* [21] used a dispersion of poly(2-ethylhexyl acrylate) in  $\text{scCO}_2$  and investigated the effects of various parameters (nozzle size, spray distance and time, fluid viscosity) on resultant film quality after spraying of the dispersion onto a substrate. A siloxane based surfactant was used and the authors investigated both the use of a preformed polymer dispersion and re-dispersion of partially coalesced polymer. The work clearly demonstrated the importance of the presence of surfactant in the dispersion if good quality coatings were to be obtained. It was reported that the spray nozzle size had little effect on the spray pattern, whereas the spraying distance and fluid (suspension) spray velocity had a significant effect on the spray pattern. It was also noted that the  $\text{CO}_2$  may remain dissolved in the polymer for a finite period of time after atomisation, but the authors proposed that large droplets (*ca.* 70  $\mu\text{m}$ ) were necessary to retain the  $\text{CO}_2$  for a sufficient period of time to aid coalescence.

In our own laboratories, we have recently studied supercritical coatings using the UniCarb™ process [30]. We have found that the concentration of carbon dioxide, temperature, pressure, nozzle orifice size, all affect the spray pattern (see Fig. 3). The equipment has been modified to measure *in situ* viscosity of the coating systems. Work on relating the viscosity to the nature of the droplets and the spray pattern formed during spraying is underway and will be reported separately.

$\text{CO}_2$  can act as a plasticiser for polymers [10, 31], dramatically reducing the glass transition temperature ( $T_g$ ) of the polymer in some cases [31]. For polystyrene (PS), for example, a minimum was observed in the polystyrene  $T_g$ -pressure (of  $\text{CO}_2$ ) curve at a  $T_g$  of 36°C, well below the normal PS  $T_g$  of *ca.* 100°C.  $\text{CO}_2$  lowers the  $T_g$  of syndiotactic polystyrene at the rate of  $-0.92^\circ\text{C}/\text{bar}$  [32]. It has also been demonstrated that PS melt viscosity can be lowered by 25–80% by  $\text{CO}_2$  [33]. Consequently, in  $\text{CO}_2$ , a normally glassy polymer may behave as though it is a rubber above its  $T_g$ , with a possible improvement in the coalescence properties of a resultant dispersion coating using this polymer. In supercritical spray coating, the rate at which the  $\text{CO}_2$  ‘evaporates’ from the polymer particles following the decompressive atomisation process will determine to what extent this will facilitate the coalescence, so long as continued degassing does not damage ultimate coating quality. Another possible

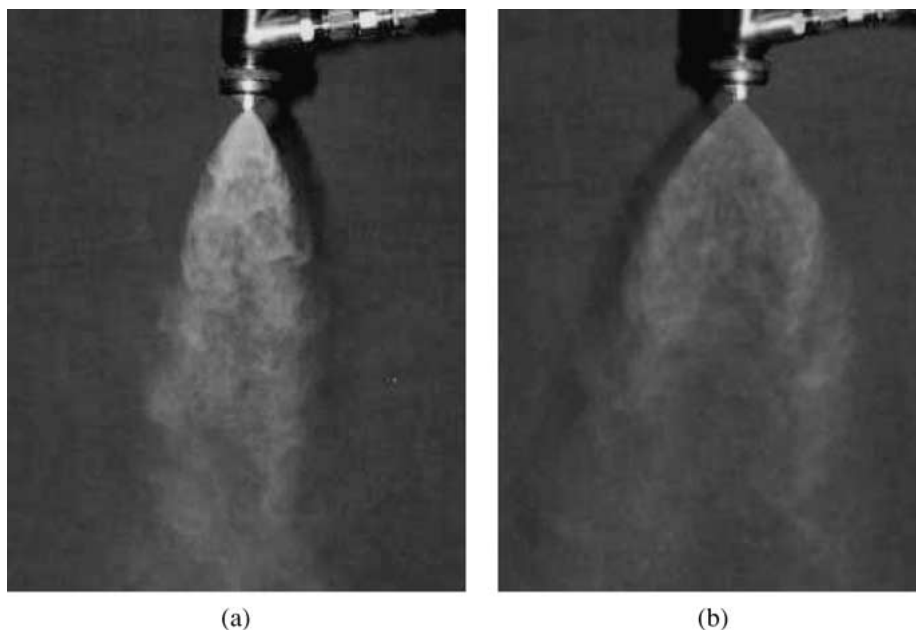


Figure 3 Effect of carbon dioxide temperature on the shape of the spray at relatively low CO<sub>2</sub> concentration and 7 MPa pressure, temperature (a) 40°C and (b) 23°C.

consideration is the effect of any dissolved CO<sub>2</sub> on ‘rebound’ of the coating droplets or particles—this will have an important effect on both coating efficiency and quality [34].

The effect of the stabiliser on the particle coalescence process is also relevant to the potential use of polymer dispersion coatings. In styrene dispersion polymerisation using a siloxane diblock copolymer (II), it was found that multi-particle polymer aggregates formed during the CO<sub>2</sub> venting process [14]. The authors suggested the aggregates formed as the solvent-swollen, extended PDMS chains collapsed during venting. It was noted, however, that spraying the polymer product from the reactor prevented secondary aggregate formation. Further studies of CO<sub>2</sub> dispersions of poly(2-ethylhexyl acrylate) (PEHA) stabilised by fluorinated block copolymers have helped to clarify the processes resulting in particle flocculation [35,36]. Above the critical flocculation density (CFD), steric stabilisation by the CO<sub>2</sub>-philic blocks hinders flocculation (Fig. 4). Decreasing the CO<sub>2</sub> density to below the CFD causes the CO<sub>2</sub>-philic chains to collapse and flocculation

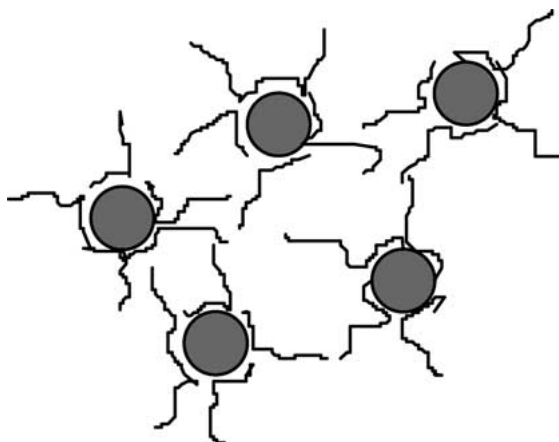


Figure 4 Polymer dispersion stabilised by a block copolymer.

occurs; however, even in the collapsed state, the fluorinated CO<sub>2</sub>-philic blocks provide sufficient repulsive force to inhibit coalescence [35]. Only relatively low shear is required to re-disperse the polymer particles in scCO<sub>2</sub> above the CFD. Re-dispersion becomes more difficult with time as the stabiliser molecules desorb from the polymer particles and migrate from the inter-particle region, resulting in coalescence.

### 2.3. Coatings using rapid expansion of supercritical solutions (RESS) and related processes

RESS is one of a number of supercritical fluid processes which have been used to produce fine particles with potential applications in pharmaceuticals and catalysis [3, 4, 37–39], but also with extensions to coatings technologies. In a RESS process, a supercritical fluid at high pressure dissolves a polymer or some other substance. Subsequent rapid depressurisation of this solution causes a decrease in the density of the fluid, reducing the solubility of the dissolved material, so that depressurisation of this supercritical fluid solution through a nozzle leads to a rapid nucleation of the dissolved material. Fig. 5 represents a schematic concept of the principle used in RESS [4].

The basic concept of the RESS process is over a century old, since Hannay and Hogarth [40] first described the process in their pioneering work. However, it was

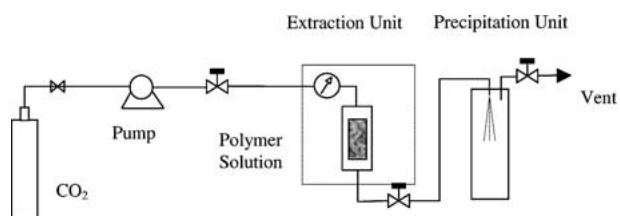


Figure 5 Schematic diagram of RESS principle [4].

not until the 1980s that the process was investigated in much more detail and the flow pattern and nucleation processes were modelled [41–47]. There have been a number of studies dealing with particle formation by this and related processes such as use of supercritical anti-solvents (SAS) or particles from gas saturated solutions (PGSS) [4, 38, 39]. The RESS technique has been extended to the formation of droplets of perfluoropolyethers for application as coatings for the protection of buildings and other structures [48]. This approach can avoid the undesirable use of VOC-producing solvents.

### 2.3.1. Powder coatings

The processes described in the previous section provide a possible route to polymer powders for use in conventional powder coating applications. Ferro Corp. has developed a process for production of powders using a variant of the PGSS process [49–52]. This process, termed the *SF MicronMix*<sup>TM</sup> process, is claimed to produce products suitable for powder coating directly, thus reducing the number of processing steps required compared to conventional powder coating production processes [52]. Weidner *et al.* have reported a related process which uses continuous rather than batch processing to produce the powder coating material [53]. Typical particle sizes are  $<40\ \mu\text{m}$ . Messer Griesheim in Germany have recently developed a low temperature process for producing powders in liquid  $\text{CO}_2$  based on the PGSS process [54]. The so-called VarioSol process has been used initially for formation of food additive powders, but could perhaps also be applied to the production of certain powder coating systems.

### 2.3.2. Aqueous coatings

Aqueous polymer emulsions (latexes) represent a hugely important part of the coatings industry. Recently, it has been shown how aqueous latexes can be formed from suspensions of a polymer in  $\text{CO}_2$  to produce latexes completely free of organic solvent residues [55]. The three different types of process were evaluated for their ability to produce a stable emulsion. These were:

- (a) Formation of a polymer dispersion in  $\text{scCO}_2$ , in the presence of both a  $\text{CO}_2$ -compatible stabiliser and a hydrophilic surfactant chosen to stabilise the final emulsion. This dispersion was expanded into water *via* a RESS process.
- (b) Precipitation of the polymer from (a) by depressurisation of the  $\text{CO}_2$ , followed by transfer of the polymer precipitate to water.
- (c) Re-dispersion of the polymer in  $\text{CO}_2$  by increasing the pressure, followed by RESS into water.

It was found that the two RESS routes (a) and (c) led to the formation of stable emulsions, whereas route (b) did not. The resultant latex was totally free of organic solvent residues. While this approach is likely

to be too complex for widespread applicability, it offers possible advantages in cases where an aqueous emulsion cannot be formed directly by conventional means.

## 2.4. Particle coatings

### 2.4.1. Coating of metal powders

Metal powders are used quite commonly in pyrotechnic and solid propellant compositions [56]. Polymer coating of the metal particles is used to reduce deterioration resulting from corrosion and aggregation caused by water and other aggressive environments [57]. Coated particles have lower flammability and are relatively safer to handle than uncoated [58]. Glebov *et al.* [59] studied the use of supercritical  $\text{CO}_2$  for the coating of aluminium spherical particles of approximately  $20\ \mu\text{m}$  diameter and magnesium particles of 325 mesh. They also coated polymer layers onto fused silica plates of 1 mm thickness. The polymers used to coat the particles were poly(vinylidene fluoride) (PVDF) and poly(4-vinylbiphenyl) (PVB). A schematic diagram of the apparatus used is shown in Fig. 6.

Metal particles and/or silica plates were placed in the sampling vessel, which was connected to the reactor (where the polymer is dissolved in supercritical  $\text{CO}_2$ ) *via* a sampling valve. After transfer of the polymer- $\text{CO}_2$  solution to the sampling vessel, cooling to  $40\text{--}70^\circ\text{C}$  (from the initial reactor temperature of up to  $300^\circ\text{C}$ ) and depressurisation caused the dissolved polymer to precipitate onto the particles. Uniform layers of polymer were found to be deposited on the surfaces of the particles, suggesting that fluidisation of the metal particles occurred during filling and discharge. Such fluidisation assisted coating of the particles from all sides, evenly and uniformly. Under the experimental conditions, the solubility of PVB in supercritical  $\text{CO}_2$  is  $(1.5 \pm 0.3)\ \text{kg}/\text{m}^3$ . Although the solubility is very low, it is sufficient to produce films on the metal particles which alter their properties and prevent aggregation and other adverse effects. The thickness of the polymer film formed on the particles depended on the pressure and temperature of the  $\text{CO}_2$ , as temperature and pressure also affect polymer solubility in  $\text{CO}_2$ . A typical average thickness of the deposited films on the metal particles was observed to be in the range of 1–30 nm [59].

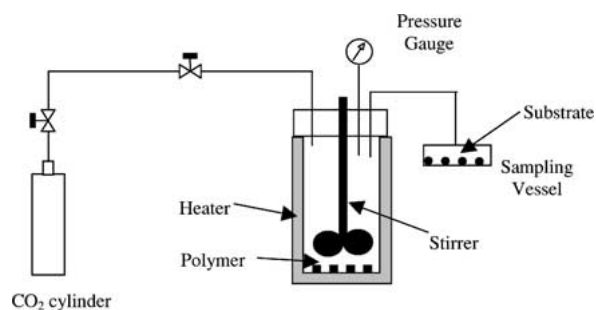


Figure 6 A schematic diagram of the (metal) particle coating apparatus [59].

### 2.4.2. Pharmaceutical coatings

The use of supercritical CO<sub>2</sub> for particle coating also has possible applications in the pharmaceutical industry, particularly in the field of controlled release for drug delivery. The RESS process can be used in this way [60]. Controlled depressurisation of the coating material in scCO<sub>2</sub> has also been described for drug coating [61], in a similar way to that described above for metal particle coating. Glycerides and fatty acid esters of poly(ethylene glycol) were among the materials used in this way to coat paracetamol particles [61]. It was shown that the resultant microcapsules demonstrated sustained release of the active constituent *in vitro* and that the release rate was dependent on the CO<sub>2</sub> depressurisation rate used to form the particles. Preliminary studies of the formation of possible controlled release coatings using scCO<sub>2</sub> and a co-solvent have also been reported [62].

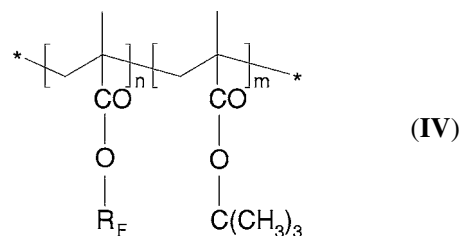
### 2.5. Spin coating and photolithography

In the manufacturing of integrated circuits (IC), two key steps are involved, (1) spin coating of a photoresist layer and (2) development of the image after exposure to light of a suitable wavelength. During these two steps a vast amount of environmentally polluting solvent is used, since the steps are repeated again and again for each layer in the IC, perhaps as many as 30 times or more in the processing of a wafer [63]. Therefore, this overall process creates large amounts of solvent waste, typically about 7.5 m<sup>3</sup> of waste developing solution and a similar volume of contaminated water per day in a semiconductor processing line producing 5000 wafers per day [63, 64]. As supercritical carbon dioxide behaves like a dense gas and has a very low viscosity and surface tension compared with other organic solvents and water, it is likely to be able to penetrate and transport material to and from very small crevices. Since the trend in semiconductor technology is for feature sizes to become ever smaller, to below 0.13 μm, these properties of carbon dioxide are likely to prove invaluable and offer genuine benefits over conventional solvent-based approaches.

Hoggan *et al.* noted that fluorinated acrylate and methacrylate base polymers provided suitable resists for use with carbon dioxide (both liquid and supercritical) [6, 20]. They synthesised a series of random copolymers of 1H,1H-perfluorooctyl methacrylate (FOMA) and *t*-butyl methacrylate (TBM) (IV) for use as a negative resist in deep UV lithography. Removal of the acid sensitive *t*-butyl groups using a fluorinated (hence soluble in CO<sub>2</sub>) photoacid generator (PAG) results in a polymer which is much less soluble in carbon dioxide. Irradiating the PAG produces an acid which catalyses the elimination of isobutylene from the TBM moiety, leaving an insoluble methacrylic acid unit. The combination of the random copolymer, poly(FOMA-TBM), with a PAG thus provides a possible photoresist for use in CO<sub>2</sub>.

Polymer (IV) was used to spin coat silicon wafers in a pressure chamber which could withstand pressures up to 200 bar. Film thicknesses of very good uniformity,

ranging from 1–10 μm, were produced when solutions of suitable concentration and viscosity were used [20].



### 2.6. Historical building protection

Perfluoropolyethers are transparent, colourless and highly water repellent (hydrophobic) polymers, and are capable of reducing water absorption into stone by 80 to 90% for at least 30 months. These properties of perfluoropolyethers make them good candidates for the coating and protection of historic buildings and monuments made of stone [65]. The polymers have low surface energies and can tolerate hostile environments such as high temperatures, oxidising agents, corrosive acids and UV radiation [66]. The common solvents for these polymers are chlorofluorocarbons (CFCs), which are environment damaging and whose use was phased out following the Montreal protocol of 1992. Fortunately, perfluoropolyethers are soluble in carbon dioxide, which makes use of carbon dioxide solutions of these polymers for stone protection a viable option, with a number of advantages over CFCs [67]. Carbon dioxide is suitable for spray coating polymers onto the surfaces of stones. This application method is potentially faster than brush application and is able to produce a much more homogeneous coating. As in RESS, the atomisation of the coating product is achieved by rapid expansion of a supercritical solution. This same polymer coating technique can be applied to a variety of porous substrates, including bricks, cement, wood etc. Cloud point and spray-coating tests on various perfluoropolyethers using carbon dioxide have demonstrated that supercritical carbon dioxide is a viable solvent for spray application onto stone surfaces and is a good alternative to the currently used solvents [48, 67, 68].

Similarly, silicones can be used as protective coatings for stone and brickwork, because of the hydrophobicity and water repellence displayed by the polymer [69]. Like the fluorocarbons, the reasonable solubility of silicones in CO<sub>2</sub> (Fig. 2) makes use of CO<sub>2</sub>-based formulations a genuine alternative to existing solvent-based systems. It is worth noting that carbon dioxide can have the additional effect of accelerating the formation of carbonate in cementitious material [70], which may have either a beneficial or deleterious effect on the surface of the object; however, for historic stone which may be fully carbonated already, this is unlikely to be a problem.

### 2.7. Dip or free meniscus coating

Dip coating is used industrially to coat irregularly shaped objects. For example, auto bodies or frames have been completely coated by immersion for rust protection. In the simplest form of dip coating, objects

are immersed in a coating composition, removed, drained and dried or baked. There are many variations of this method of coating [71], which is also called free meniscus coating. Any film-forming material which can be dissolved or made into a suspension, with or without dispersant, can be used as a coating material to form a thin layer coating on a substrate. Carbon dioxide has been reported as a benign solvent for dip or free meniscus coating by Carbonell *et al.* [72]. They noted that free meniscus coating can be subdivided into three processes, namely, withdrawal processes, drainage processes and continuous processes. Their method consists of immersing a surface portion of a substrate into carbon dioxide containing some film forming polymer [72]. The next step is withdrawal of the immersed substrate through a meniscus which exists at the interface of the first phase, into a distinct (gaseous) second phase. In the second phase the solvent (in this case carbon dioxide) evaporates leaving a thin film coating on the solid substrate. The pressure in the second phase is maintained such that a differential pressure exists between the first and the second phases. Different substrates such as solid articles, fibres and textiles have been claimed to be suitable for coating. The thickness of the film was reported to be very uniform.

## 2.8. Impregnation of polymers

Impregnation can also be considered as a form of coating. Supercritical fluids have been studied in some detail for the impregnation of polymeric materials, because of their high diffusivity, low surface tension and easy recovery from the polymer matrix. A comprehensive review of this subject has been written by Kazarian [5]. The pioneering work of Sand [73] and Berens [74] stimulated the original interest in this field. A very wide range of polymers have been impregnated using  $scCO_2$ , including polystyrene [74, 75]; poly(methyl methacrylate) (PMMA) [74–80]; poly(vinyl chloride) (PVC) [74, 81]; polycarbonate [74, 75, 81–83]; polyethylene [73, 83–87]; poly(tetrafluoroethylene) (PTFE) [81]; poly(chlorotrifluoroethylene) (PCTFE) [81, 83, 88]; poly(4-methyl-1-pentene) (PMP) [83]; poly(oxyethylene) [83]; poly(ethylene terephthalate) (PET) [89–93]; poly(dimethylsiloxane) (PDMS) [76, 94–97] and polyamides [98, 99]. A wide range of impregnating solutes can be used [5]. A specific example of impregnation (arguably not really a coating, however) which could be of considerable importance in the future is that of textile dyeing, which has been discussed by Kazarian *et al.* [89]. This has the potential to overcome the problem of waste water in conventional dyeing processes. In addition to acting as the polymer to be impregnated, polymers may also be used as the impregnant, as noted above for building stone and also for wood coatings (*vide infra*).

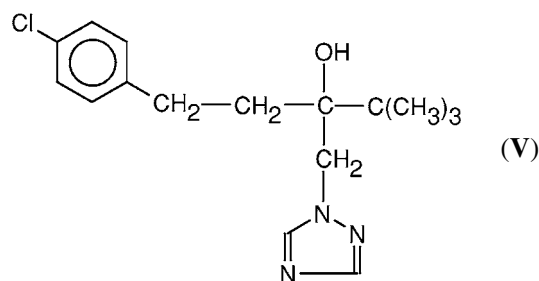
## 2.9. Wood coatings

Wood is a difficult material to coat for long-term environmental resistance. VOC legislation has been applied specifically to wood products [100] and the regulations

are making use of traditional coating systems more difficult and accelerating the development of alternatives such as aqueous systems; however, these suffer from the disadvantages noted earlier as well as the problem of incompatibility with wood, which will swell and inhibit penetration [101]. The effect on coating quality remains uncertain and there is room for improved products for wood coating [102]. There is also a need for improved coating penetration into wood [103].

Supercritical fluids offer advantages for the impregnation of porous substrates such as wood, including low viscosity and very high diffusivity compared to conventional liquids, both of which aid penetration and impregnation [87, 104, 105]. A further benefit of  $scCO_2$  in impregnation of wood is its extraction capability, since extraction of resin and fatty acids can increase the permeability of wood in a  $scCO_2$  medium [104].

The use of supercritical [106] or liquid  $CO_2$  for the impregnation of wood biocides, such as tebuconazole (V), may offer advantages in terms of elimination of VOCs, allow a greater depth of impregnation, more efficient impregnation and perhaps allow use of water insoluble active components. Since the requirements for controlled leaching of the biocide in an aqueous environment and those for compatibility with the solvent are completely different when  $CO_2$  is used as the application medium, it might be expected that such an approach would lead to significantly improved durability relative to aqueous treatment.



In the use of supercritical carbon dioxide as an impregnating medium for biocide application, the solubility of the biocides in  $scCO_2$  can be increased by increasing the pressure, which provides a driving force for flow into the solid wood [104, 107], resulting in more efficient impregnation from SCFs than in conventional treatments.  $ScCO_2$  has been found to be effective in impregnating non-permeable woods such as spruce with biocides, increasing resistance to fungi and insects [101, 106]. Unused impregnating agent can be readily recycled and a  $scCO_2$ -co-solvent solution can be used for impregnating difficult woods [108]. No adverse effect of  $scCO_2$  treatment on wood composites has been found [109] and little effect on the mechanical properties of wood was noted [110], although some reaction between the  $CO_2$  and the cell wall constituents has been found to occur [111].  $ScCO_2$  may also offer benefits in the application of water repellents to wood, since the most common substances used are silicones or polyfluorocarbons, both of which have significant compatibility with  $scCO_2$  (Fig. 2). It is believed that there is currently some commercial activity in Denmark in impregnation of wood products, but

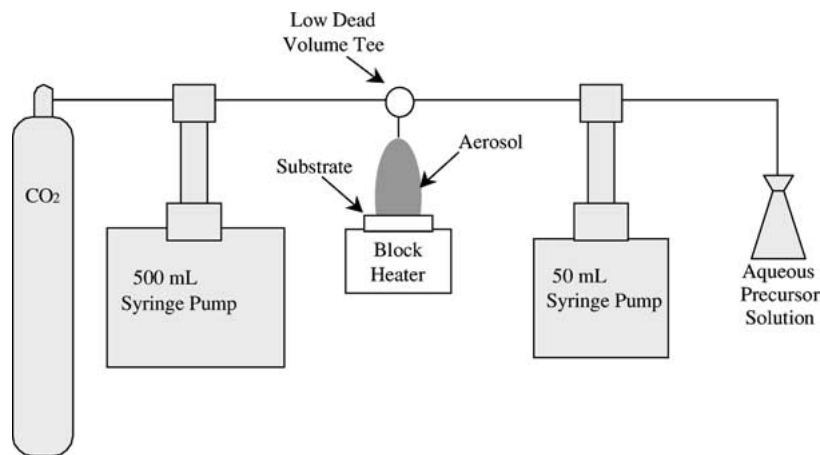


Figure 7 Application of carbon dioxide to deposition of water-based thin film coatings [110]. Diagram courtesy of Prof. R. E. Sievers.

this overall area of supercritical wood treatment is still very much in its infancy, with more work needing to be done to demonstrate the benefits and limitations of the approach.

## 2.10. Miscellaneous coating applications

### 2.10.1. Water-based coatings

Carbon dioxide can also be used as a means of delivering aqueous-based coating systems [112] (Fig. 7). This may be done by mixing the carbon dioxide with an aqueous solution of the coating or its precursor immediately prior to spraying. The coating/precursor is delivered as a fine aerosol to the substrate. Examples of the use of this technique include:

- Spraying of an aqueous solution of mixed cobalt, iron and chromium nitrates onto a hot glass or quartz substrate forming a crystalline spinel film.
- Deposition of crystalline zinc oxide films on silicon wafers or glass by spraying zinc acetate solution onto the hot substrate.
- Synthesis of phosphor thin films.

Although this approach was applied to metal oxide thin films, it could probably also be adapted to a wide range of water-based coating systems.

### 2.10.2. Foamed coatings

Recent work on foaming of polymers using carbon dioxide suggests wider application in a range of foamed coatings. Nitto Denko has patented the production of foamed pressure sensitive adhesive tape using liquid or supercritical CO<sub>2</sub> [113, 114]. Adhesives used were typically acrylic or natural rubber-based systems. In the UK, RAPRA has been developing technology for extrusion foaming using CO<sub>2</sub> [115]. A modified extruder was used and a range of foams produced successfully from thermoplastics such as polyolefins, polystyrene, poly(ether ether ketone) [PEEK], polyphenylsulfone and poly(ester carbonate).

### 2.10.3. Coating removal

Interestingly, workers at Colorado State University and Los Alamos have described the application of scCO<sub>2</sub> for the removal of polymer coatings [116], thus providing a potentially environmentally friendly approach to recycling and re-use of waste coated products. Use of a co-solvent may be beneficial.

## 3. Conclusions

Concerns over the environmental effects of VOC emissions, coupled with increasingly stringent legislation, are stimulating interest in the use of carbon dioxide (both supercritical and liquid) as a replacement for organic solvents in coating operations. Spray coating processes have been studied, where the use of VOC-emitting solvents can be greatly reduced or eliminated. These processes are claimed to have other benefits, including improved transfer efficiencies and reduced operating costs compared to conventional spray coating. Processes such as RESS and PGSS which were developed originally for the formation of controlled morphology particles using (supercritical) CO<sub>2</sub> have been adapted for the formation of controlled particle size powder coating products and also for the coating of preformed particles, including metal powders used in pyrotechnics and pharmaceutical powders for controlled release during drug delivery. Solvent-free aqueous polymer latexes can be made by a RESS process using an initial CO<sub>2</sub>-polymer dispersion. The use of CO<sub>2</sub> in spin coating and microlithography has the potential to greatly reduce the volume of waste produced during microelectronics fabrication processes. Coating of building stone (such as ancient monuments) and wood products can both benefit from the use of CO<sub>2</sub> technology. The materials used for the treatment of building stone are often conveniently soluble in CO<sub>2</sub>. The ability of CO<sub>2</sub> to swell substrates and also its high diffusivity make it highly effective in impregnating a wide range of substrates, including wood and many polymers. A variety of metal oxide coatings have also been produced successfully by CO<sub>2</sub>-assisted spraying of aqueous precursor solutions. The range of coating processes amenable to the use of CO<sub>2</sub> technology



is thus very broad and being expanded all the time. If environmental factors can be coupled with genuine technical benefits arising from the use of CO<sub>2</sub>, then the technology becomes even more attractive to the potential end-user. There seems little doubt that the coming years will see increasing commercialisation of coating processes based on use of CO<sub>2</sub>. Concerns over the use of high pressure equipment are likely to provide some hindrance to this, but increasing evidence (e.g., from decaffeination plant) that this does not create insuperable practical problems should help alleviate these concerns.

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