Supercritical fluids – A potential revolution in wood treatment and coating

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Introduction

Wood can be a difficult material to coat successfully for long-term resistance to exterior degradation. Resistance to microbiological degradation can be improved by the use of biocides, which must remain effective over the lifetime of the timber construction. However, by definition this creates an environmental problem on ultimate disposal. The increasing severity of modern volatile organic compound (VOC) regulations mitigates against the use of traditional double vacuum solvent-based coating systems and, therefore, change is essential. Legislation is accelerating the development of alternatives such as aqueous systems. Whilst the move to water-borne systems offers advantages in terms of environmental pollution, concomitant disadvantages may be introduced. Removal of the water carries a cost penalty in terms of the energy required for its evaporation. Complete removal of residual organic material from any waste water is extremely difficult and costly. The main problem of aqueous systems may be the incompatibility with wood, which will swell and inhibit penetration.

As a result of these concerns, work is underway on a variety of alternative coating approaches, including:

- high solids systems
- radiation curing
- powder coating
- microporous (breathable) coatings

One possiblity would be to improve European softwoods by increasing the durability in order that they might better replace imported hard wood. Durability might be improved by increasing hydrophobicity and minimising biodegradation. Safety can be increased by the efficient use of more appropriate biocides, coupled with the ability to remove these prior to wood disposal/recycling. Integrated systems for the infusion of biocides, impregnation of hydrophobes and final protection by long-life coatings would be desirable. Safety also includes environmental protection during treatment and coating in order to eliminate VOC emissions and water contamination. Supercritical fluid technologies may offer the potential to satisfy all of these stringent requirements.

Considering first biocides, it is important to note that the biocides used are generally selected from those which have already undergone the very expensive registration procedure for approval for agricultural use. However, the requirements for agricultural applications and wood protection differ greatly, so that the current biocidal products used in wood may not be ideal (Table 1).

Table 1: Requirements for biocide application

Wood	Agriculture
Persistent	Temporary
Low water solubility	High water solubility
Factory applied	Field applied
Deeply embedded	Surface coverage
Low volume	High volume

Biocides for wood should be easy to impregnate deeply, uniformly and sparingly. They should be substantially insoluble in water, but retain some degree of water solubility to allow low level leaching and hence activity. The use of aqueous impregnation may thus be eliminated on the dual grounds of timber swelling and the low solubility of the biocide. Current thinking is to minimise biocide usage in wood by impregnating hydrophobes such as silicones and fluorinated materials, since it is recognised that if the moisture content can be kept below certain levels, then microbial attack can be inhibited.

An ideal biocidal system might therefore exhibit the following features:

- minimal VOC emissions
- non-aqueous
- minimum biocide content
- more appropriate biocide selection
- more efficient biocide impregnation
- high hydrophobicity to minimise biocide usage
- water repellancy
- dirt shedding
- weather resistance

Summaries

Supercritical fluids – A potential revolution in wood treatment and coating

The paper deals with the possiblities of using supercritical fluids to improve the treatment and coating of wooden components.

Überkritische Flüssigkeiten – eine eventuelle Revolution im Bereich der Holzbehandlung und des Beschichtensverfahrens.

Der Vortrag behandelt sich mit den Möglichkeiten die Anwendung Überkritischer Flüssigkeiten um die Behandlung und das Beschichtensverfahren zu verbessern.

Fluides surcritiques – une éventuelle révolution dans le domaine du traitement et du revêtement des éléments en bois.

L'article traite des possibilités d'utiliser les fluides surcritiques pour améliorer le traitement et le revêtement des éléments en bois.

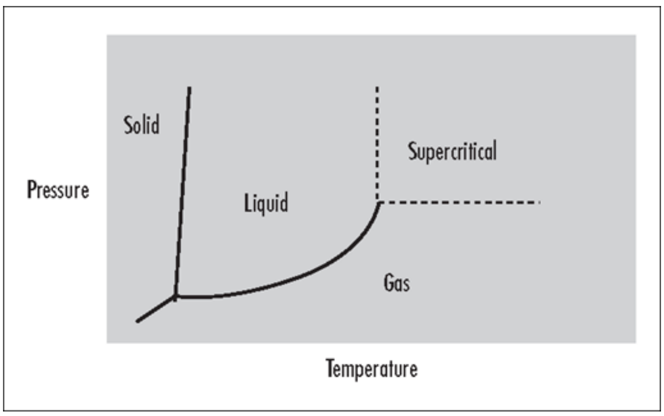
- long life
- minimise ultimate disposal/recycling problems
- possible usage in high solids/powder coating

This is a daunting wish list, but it is hoped to demonstrate in this paper that many, or even all, of these requirements might be met by the use of supercritical or near-critical fluid technologies.

Supercritical fluids

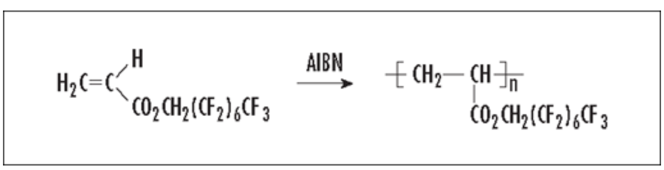
The use of supercritical carbon dioxide (scCO_2) as a carrier for coating and impregnation systems is particularly attractive because of its potential for use in truly environmentally benign systems. The CO_2 is extracted from the atmosphere or from flue gases and fermentation processes and subsequently either recycled or returned to the atmosphere, with a resultant net zero emission of polluting or greenhouse chemicals. Carbon dioxide may be produced readily in the supercritical state simply by the application of heat and pressure – above about 31°C and 73 bar pressure (the critical point), supercritical CO_2 forms. This is illustrated by the phase diagram (Figure 1). At slightly lower temperatures and pressures, liquid or near-critical carbon dioxide is formed.

Figure 1: Phase diagram showing the supercritical region



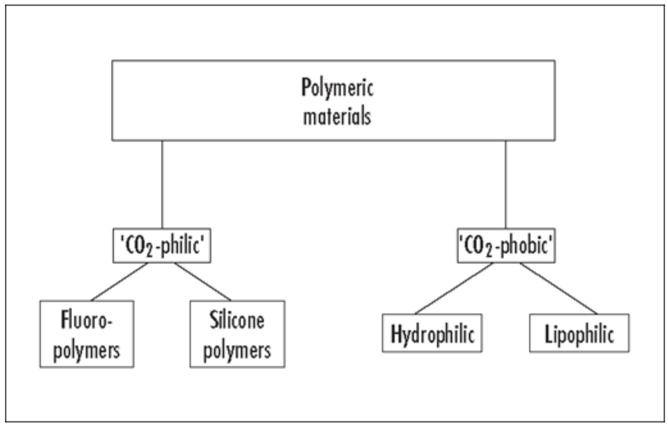
Supercritical CO_2 behaves like a dense gas, but can be used as a solvent in a number of processes. The best known application of scCO_2 is for the decaffeination of coffee beans. In the area of plastics technologies, scCO_2 has attracted interest as a medium for extraction[1] and impregnation[2] of polymers. In recent years, there has been an explosion of interest in the use of scCO_2 as a polymerisation medium, triggered by the publication by DeSimone in 1992 of a paper describing the formation of a fluoropolymer by homogeneous polymerisation in scCO_2 (Figure 2).[3]

Figure 2: Homogeneous synthesis of a fluoropolymer in scCO_2



Limitations on the solubilising power of scCO_2 limit its applicability as a medium for solution polymerisation, since fluoropolymers and silicone polymers represent the most common polymer types which show reasonable solubility in scCO_2 (Figure 3).[4,5] Many small molecules, however, exhibit good solubility in scCO_2 thus broadening the potential range of non-polymeric applications of supercritical fluids. The solubility characteristics of polymers in scCO_2 are important and will be discussed further.

Figure 3: Polymer compatibility with supercritical CO_2



Impregnation

Supercritical fluids (SCFs) offer a number of potential advantages for the impregnation of porous substrates such as wood. The SCF has low viscosity and very high diffusivity compared to conventional liquids, both of which aid penetration and impregnation.[2,6,7] Some substrates can be swollen reversibly in a SCF, further aiding penetration. Unlike normal liquids, a considerable degree of control can be exercised over the solvating and physicochemical properties of a SCF, since pressure provides an additional parameter by which to control these properties, rather than just use of temperature alone. Some examples of supercritical impregnation systems which have been studied are summarised below (Table 2).[6]

Table 2: Some supercritical impregnation systems [adapted from reference 6]

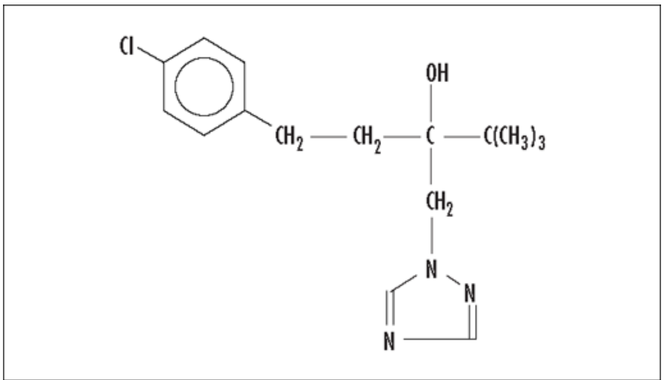
Chemical	Solid matrix	Supercritical fluid
Organometallic compound	Polethylene	Carbon dioxide [ref 2]
Polymeric substrate	Polymer	Carbon dioxide
Methyl methacrylate	Wood	Carbon dioxide
Polyethylene	Wood	Pentane
Dyes	Wood	CO_2 – co-solvent

Efficient impregnation of wood may also be aided by the extractive capacity of scCO_2. Removal of extracts such as resin and fatty acids can increase the permeability of wood in a scCO_2 medium.[6] Wood can also be delignified in scCO_2 systems, including use of binary and ternary mixtures with acetic acid and acetic acid/water.[7,8] The delignification induces chemical and morphological changes in the cell wall structure.[7]

Biocides

The biocides used are commonly small molecules such as tebuconazole (1) which are expected to have a high degree of solubility in supercritical[9] or even sub-critical (liquid) CO_2. Use of the latter would offer advantages in terms of ease of use and capital equipment costs, since lower pressures could be used. In terms of the list above, use of CO_2 should eliminate VOCs, allow the selection of a wider variety of substantially water insoluble active components, allow a greater depth of penetration and more homogeneous and efficient impregnation. Durability may also be improved relative to aqueous systems, since the requirements for controlled leaching and those for compatibility with the solvent can be kept completely distinct.

1 Tebuconazole



Various studies have been published on the use of supercritical carbon dioxide as an impregnating medium for biocides. Studies have shown that the solubility of biocides in $scCO_2$ can be improved by increasing the pressure, which also increases the flow into the wood.[6,10] Deposition rates are increased at higher pressures resulting in more efficient impregnation from supercritical fluids than in conventional treatments. Other work using conventional solvents has shown that a precompression treatment increases liquid penetration into refractory woods.[11] Using $scCO_2$, of course, precompression and penetration are in a sense simultaneous. $scCO_2$ has been shown to be an efficient medium for impregnating non-permeable woods such as spruce with biocides, increasing the resistance to fungi and insects.[9,12] Unused impregnating agent can be recycled easily. If necessary, a $scCO_2$-co-solvent solution can be used when impregnating difficult woods.[13] The phase behaviour of CO_2-biocide binary systems and CO_2-biocide-co-solvent (methanol, acetone) ternary systems has been determined.[14] This kind of data can provide valuable information for optimising treatment conditions. One important question is whether the treatment of wood with biocide in a supercritical medium affects the physical and mechanical properties of the wood since high pressures are used. In a study of the effect of this treatment on certain wood composites, no adverse effect was found.[15] A separate study also reached the conclusion that supercritical treatment had little effect on the mechanical properties of wood.[16] The results of a study on diffusivity of dissolved carbon dioxide gas in wood and the corresponding activation energy for diffusion suggested that some reaction occurred between the CO_2 and the cell wall constituents,[17] but this obviously has little adverse consequence on the mechanical behaviour of the wood.

A further benefit of $scCO_2$ in relation to biocides for wood is its capacity to extract environmentally toxic biocides from spent wood and wood products prior to disposal thus reducing pollution from such sources. As an example, using a continuous flow extractor,[18] $scCO_2$ was used to extract pentachlorophenol from wood. The rate of extraction was found to increase with increasing pressure. Another possible opportunity for $scCO_2$ is in the recovery of wood preservatives from wood pyrolysis tar, where conventional solvent extraction has been shown to be effective.[19]

The versatility offered by the use of supercritical treatment may offer some benefits once the new EC Biocidal Products Directive (98/8/EC) is introduced into Member States in May 2000.

Hydrophobes

The most effective water repellents tend to be either members of the silicone family or (poly)fluorocarbons. Both types are used widely as dirt, stain, oil and water repellents in the textile industry, while Teflon is well known as a non-stick finish for domestic utensils such as frying pans. By a remarkable coincidence, both classes of materials are those with a high degree of compatibility with $scCO_2$ (Figure 3). Thus it should be possible to impregnate efficiently porous substrates with silicone and fluoro compounds using $scCO_2$ alone. There are other relevant developments in both fluoro- and silicone-based dyestuffs.

Certain silicone products are promoted as fire retardants in polymer or coating systems.[20] Other silicones have been shown to have anti-microbial properties.[21] Although that report did not specifically mention wood substrates, it is possible to envisage a modified silicone retaining its hydrophobicity while contributing to microbial/fungal resistance. The most widely recognised fluoropolymer, PTFE, is one of the few organic materials that is resistant to microbial attack. It is not impossible to visualise the development or selection of a fluoro-, a silicone or a fluorosilicone product that is designed to provide a combination of water, fire, microbial and weather resistance and the application of this by a supercritical fluid system.

Coatings

As indicated earlier, legislation is forcing a move away from conventional solvent-borne coating systems to alternatives where the effect of VOCs is reduced.[22,23] Also such legislation has been applied specifically to wood products.[24] While a move towards water-based coating systems can solve some of the problems, the effect on coating quality remains uncertain and there is further room for improved products for wood coating.[25] There is also a need for improved coating penetration into wood.[26] To date little work has been directed towards the use of supercritical CO_2 in the coatings field, although it is clear from the above discussion that a $scCO_2$ coating system has the potential to solve many of the problems surrounding wood coatings.

That this is an area of still largely untapped potential is in part a consequence of a lack of knowledge of, or confidence in, the technology. Union Carbide has developed a process (the UniCarb process) for spray coating substrates from a supercritical fluid medium such as carbon dioxide.[27] This allows an efficient spray coating so that the decompressive nature of the process provides improvements over conventional spray systems, particularly in the control of:

- feathering
- droplet size
- droplet distribution range

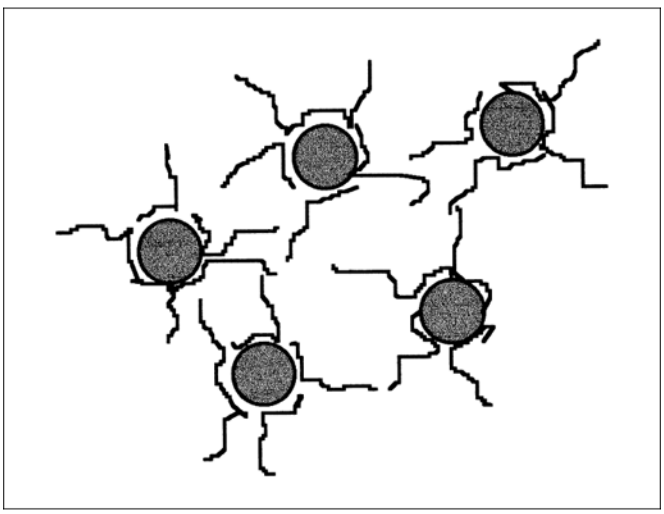
For polymer coatings, the use of a SCF-organic solvent system has been claimed to have a number of advantages over the alternative of powder coatings, for example improved film coalescence and quality and no need to re-formulate the resin from that used in solvent-based coating. Dip coating provides an alternative method for the coating and impregnation of a range of substrates. The possibility of improved penetration of the coating offers a potential advantage in the use of $scCO_2$ in addition to the environmental benefits outlined previously.

Polymer coating systems may be true solutions or dispersions. The former may be obtained by the use of:

(i) monomeric coating formulations,
(ii) use of selected soluble polymer systems or
(iii) formulation of co-solvent systems where the amount of organic solvent used is reduced greatly as compared with conventional solvent-borne systems.

For pure CO_2 systems, the use of genuine coating solutions is limited by the solubility characteristics mentioned above; however, $scCO_2$ can be used to apply top-coats, with particular advantages in the use of silicone and fluoro-types, of polymers. The use of dispersions offers a potential solution to the solubility problem and this should help to broaden significantly the applicability of $scCO_2$ coating systems. Progress in the development of practical dispersion-based coating systems is facilitated by the development of supercritical dispersion polymerisation methods, in particular, the production of new efficient stabilisers such as the fluorinated acrylate polymer product shown in Figure 2.[28] Powders made by conventional polymerisation could be re-dispersed in $scCO_2$ with the aid of an appropriate stabiliser. The stabiliser acts by adsorbing on polymer particles via the acrylic backbone while the pendant fluorinated grafts project into the CO_2 phase with which they are miscible. Suitable stabilisers may be either fluoropolymer or siloxane-based block or graft copolymers.[5,29-31] The colloidal polymer particles are stabilised by a steric stabilisation mechanism, which is illustrated below for a diblock copolymer stabiliser (Figure 4). The potential use of siloxanes (silicones) as stabilisers for supercritical coating systems has been discussed recently by one of the authors.[32]

Figure 4: Polymer dispersion stabilised by a diblock copolymer



Powder coatings

The most recent developments in powder coatings include:

- fine particles of controlled shape for thin film coating
- UV curing ability, where significant opportunities have been proposed both for natural wood and wood composites[33]
- low temperature cure for use on wood and plastic substrates
- novel curing mechanisms

Wood presents certain difficulties for powder coating because of its variable nature and moisture content. The University of St Andrews has expertise and quite large scale supercritical fluid equipment for de-watering ancient wood such as timber from the ship, the Mary Rose. This is achieved using methanol to displace water followed by $scCO_2$ to displace the methanol. However it is unlikely that this technology could be applied to large scale applications.

Though powder coating of wood presents some problems and orange peeling is difficult to avoid, serious work is underway on coating medium density fibreboard (MDF) for window frames.

Supercritical fluids can be used to create powders by rapid expansion spraying into air[34] or precipitation in a supercritical anti-solvent[1a] and the Ferro VAMP process[35] has received much publicity and is becoming a commercial reality. It is claimed that this process can provide control over particle size/distribution and shape, coupled with lower production temperatures to allow access with improved economics to a wide selection of low temperature crosslinking systems.

The Unicarb process has been described as a liquid powder coating technique since the incipient coating system can act as a modified powder coating. Therefore this process can be considered as an alternative to normal powder coating and can offer formulation advantages over powder coatings.

Inverse microemulsions

$scCO_2$ can act as the oil phase in inverse microemulsions. The CO_2 phase can encapsulate a low concentration of tiny droplets of water which can be used to extract or impregnate water-soluble, but $scCO_2$ insoluble, materials such as ionics or even enzymes and peptides.

Microporosity

The development of wood coating systems that prevent the ingress of liquids but allow the passage of vapours is desirable but difficult to achieve. Fluorocarbons, some of which are liquids used as gas-transporting blood plasma substitutes and breathable fabric coatings, have high gas transport capacity coupled with very low surface energy which yields high liquid repellancy. These might aid development of microporous systems.

Future developments

At the beginning of this article, the authors listed what appeared to be an impossible combination of attributes required for an ideal biocidal system, but which could apply equally well to improved coatings for exterior timber. The above discussion has demonstrated hopefully that supercritical fluid technologies have the potential to assist in meeting many, if not all, of these requirements. There are still problems to be solved, particularly:

1. The possibility of designing semi-continuous batch systems to treat large sections of timber for window, door and exterior furniture production.
2. Coping on a production scale with the rate of decompressive gas evolution from chamber impregnation.
3. Employing minimum pressures, down to liquid CO_2, in order to minimise the expense of safe equipment as pressures and scale-up increase.

4. Recycling of the carbon dioxide.
5. Material selection and development.

The final item on this list is one aspect of supercritical coatings science which will be studied within a new centre for supercritical coating technologies (Surrey Coating & Related Technologies Centre; S-COAT) which is being set up in the UK, at the University of Surrey, in conjunction with partners such as Chemical & Polymer, the University of Nottingham and Union Carbide. The presence of this Centre, funded by the UK Engineering and Physical Sciences Research Council (EPSRC) and by industrial subscriptions, should help to raise the level of understanding of the potential benefits of supercritical coating technology. It is the intention to provide a forum in which interested parties may work in concert to create, amongst other things, viable wood treatment systems which are designed with safety, health and environment in mind, but which can still provide opportunities for improved timber products. Interested parties may include the following:

- timber suppliers
- biocide producers
- timber product manufacturers
- pressure equipment producers
- computer control designers
- resin suppliers
- coating producers
- gas suppliers
- trade associations
- universities
- legislators

The authors believe that the aims can be achieved, but support is needed from experts in wood technologies. Supercritical fluid technology may offer potential for simultaneous solutions to many of the problems today facing the timber product industry, particularly for exterior use. The ideal combination of material properties needs to be met as far as possible to ensure a viable future for the industry, which is faced with increasing competition from alternative materials.

References

1 (a). McHugh MA and Krukonis VJ, *Supercritical Fluid Extraction: Principles & Practice*, Butterworth, 1994.

1 (b). Phelps CL, Smart NG and Wai CM, *J. Chem. Ed.*, **73**, 1163, 1996.

2. Howdle SM, Ramsay JM and Cooper AI, *J. Polym. Sci. B: Polym. Phys.*, **32**, 541, 1994.

3. DeSimone JM, Guan Z and Elsbernd CS, *Science*, **257**, 945, 1992.

4. Rindfleisch F, DiNoia TP and McHugh MA, *J. Phys. Chem.*, **100**, 15581, 1996.

5. Shaffer KS and DeSimone JM, *Trends Polym. Sci.*, **3**, 146, 1995.

6. Sahle-Demessie E, Levien KL and Morrell JJ, *Chemtech*, 12, March, 1998.

7. Kiran E, *ACS Symp. Ser. (Innovations in Supercritical Fluids Science and Technology)*, **608**, 380, 1995.

8. Kiran E and Balkan H, *J. Supercrit. Fluids*, **7**, 75, 1994.

9. Imsgard F, Henriksen O and Schonemann H, *4th Conference on Supercritical Fluids and Environment*, Lyon, 20–21 January 1997.

10. Sahle-Demessie E, Levien KL and Morrell JJ, *ACS Symp. Ser. (Innovations in Supercritical Fluids Science and Technology)*, **608**, 415, 1995.

11. Iida I, Ikeuchi A and Imamura Y, *Mokuzai Gakkaishi*, **41**, 811, 1995 (*CA*, **124**(4), 138, 1996).

12. Van Oost H, Gastiger M, Eymard P and Masson D, private communication to K Johns.

13. Kayihan F, *USP 5,094,892*, 10/3/92.

14. Hassan A, Levien KL and Morrell JJ, *ACS Symp. Ser. (Innovations in Supercritical Fluids Science and Technology)*, **608**, 402, 1995.

15. Acda MN, Morrell JJ and Levien KL, *Wood Fiber Sci.*, **29**, 121, 1997.

16. Smith SM, Sahle-Demessie E, Morrell JJ, Levien KL and Ng H, *Wood Fiber Sci.*, **25**, 119, 1993.

17. Jones TG, Walker JCF and Langrish TAG, *Wood Sci. Technol.*, **29**, 171, 1995.

18. Sahle-Demessie E, Yi JS, Levien KL and Morrell JJ, *Sep. Sci. Technol.*, **32**, 1067, 1997.

19. Suzuki T, Doi S, Yamakawa M, Yamamoto K, Watanabe T and Funaki M, *Holzforschung*, **51**, 214, 1997.

20. Pape PG and Romenesko DJ, *J. Vinyl Addit. Technol.*, **3**, 225, 1997.

21. Myoshi T, Sato T and Inoe Y, *JP 08,217,977*, 27/8/96.

22. Coventry P, *Proceedings of Seminar on Clean Coatings Technology*, Telford, PRA, Paper 9, 1995.

23. Anon, *Coatings COMET*, 51, October, 1995.

24. Maty J, *Amer. Paint Coat. J.*, 11, 28 August 1995.

25. Grasso J, *Coatings World*, 53, March 1998.

26. Manjarekar SB, *Finish*, 7, July-September 1995.

27. Moudden B in *Proceeding of Fluorine in Coatings II*, PRA, Munich, 24–26 February 1997.

28. DeSimone JM, Maury EE, Menceloglu YZ, McClain JB, Romack TJ and Combes JR, *Science*, **265**, 356, 1994.

29. Cooper AI and DeSimone JM, *Curr. Opinion Solid State Mater. Sci.*, **1**, 761, 1996.

30. Canelas DA and DeSimone JM, *Adv. Polym. Sci.*, **133**, 103, 1997.

31. Canelas DA and DeSimone JM, *Chem. Brit.*, 38, August 1998.

32. Hay JN, *European Coatings Journal*, 542, 1998.

33. Blatter K, MacFadden B, Strid M and Niggemann F, *Coatings World*, 26, March 1998.

34. Eckert CA, Knutson BL and Debenedetti PG, *Nature*, **383**, 313, 1996.

35. Mandel F in *Proceedings of Fluorine in Coatings II*, PRA, Munich, 24–26 February 1997.

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