Supercritical Carbon Dioxide and Paints: The UNICARB® Process

Volatile organic compounds (VOCs) represent a hazard to both the environment and workers who are exposed to them. In American industries alone, more than 1.5 billion liters of coatings and paints are sprayed every year, which release an average of 550 grams of VOCs for each liter sprayed. To put this into perspective, the VOC emissions from painting an automobile are greater than those from the engine's exhaust over its lifetime. When released into the atmosphere, VOCs facilitate the production of ground level ozone; short term exposure can contribute to eye, nose and throat irritation, while long term exposure has been linked to emphysema, fibrosis, bronchopneumonia, and congenital birth defects[1]. VOCs migrate from the atmosphere into water systems, taint seafood, contaminate drinking water, and are toxic to aquatic life[2]. Environmental regulations, including the clean air act, impact nearly every type of industrial coating application. To aid in reducing VOC emissions, a new spraying process, UNICARB®, was developed.

Paint mixtures that are applied by spraying usually consist of polymer, pigment, and two different types of solvent, a fast-evaporating diluent and a slow-evaporating solvent. The main purpose of the fast solvent is to reduce the viscosity of the mixture to be sprayed. The fast solvent allows the atomization of the polymeric material for an even coating and evaporates while the spray droplets are in flight. The slow-evaporating solvent, on the other hand, is necessary to dissolve the polymer and promote proper film formation. The goal of this work is to replace the fast-evaporating solvent with supercritical carbon dioxide. This new system, called the supercritical fluid spray process, has been shown to reduce harmful VOC emissions by up to 80%, and improves the quality of the finished product due to improved atomization and spray characteristics[3,4]. It has been patented and commercialized under the name UNICARB®. For this system to work, it is important to understand the phase behavior of ternary mixtures of polymers, solvent, and carbon dioxide.

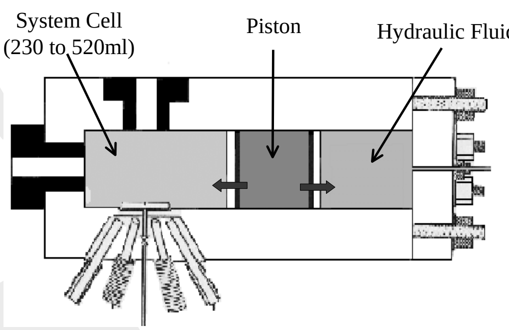

Figure 1: A schematic of the high pressure cell used to measure polymer phase behavior.

The phase behavior of these systems is mapped out in an experimental high pressure cell, which is schematically illustrated in Figure 1. It is based on an improvement of a design originally proposed by McHugh[5]. The cell has a chamber for the sample that is embedded with electric heating elements. A hydraulic pump and piston are used to control the pressure. A magnetic stirrer keeps the sample well mixed, and a view port, light source, and camera have been included for visual observation. Although phase behavior is sometimes determined visually, we have developed a method by which the various phase transitions can be identified from cusps in pressure-volume measurements.

The results of this project show that ideal spraying results from following the line drawn in Figure 2. The spraying apparatus is shown in Figure 3. The mixture initially starts at high

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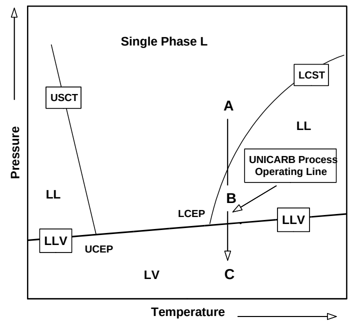

Figure 2: A typical phase diagram of a polymer-solvent-carbon dioxide mixture. The UNICARB® operating line, which runs from point A to B to C, is labelled.

pressure, typically about 100 bar, in the one phase region. Immediately after passing through the nozzle, the pressure decreases, and the mixture passes into a two-phase liquid-liquid region. Here, the mixture begins to form small droplets of the second phase. Upon further reduction of the pressure, the fluid passes through the three phase liquid-liquid-vapor line and into a two-phase liquid-vapor region. Bubbles of vapor, composed of more than 90% carbon dioxide, form and leave the mixture. This contributes to the atomization process and increases the viscosity of the mixture. This entire process takes place very quickly after leaving the nozzle.

Future research in this area focuses on extending current understanding to new coatings systems, especially high performance, metallic, and chemical resistance. Current projects include the reduction in size of the spraying equipment to enable portability and cost reduction.

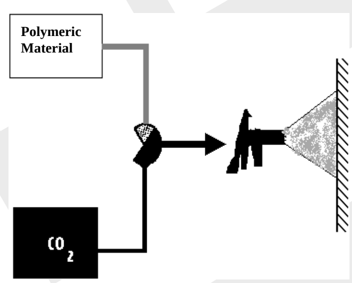

Figure 3: A simplified diagram of the spraying apparatus used in the UNICARB® process.

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[2] National Research Council, Division of Medical Sciences, Assembly of Life Sciences. In *Vapor-Phase Organic Pollutants*; National Academy of Sciences: Washington, D.C., 1976, pp 236-270.

[3] Lee, C.; Hoy, K. L.; Donohue, M. D. Supercritical Fluids as Diluents in Liquid Spray Applications of Coatings. U. S. Patent 4 923 720, 1990; U. S. Patent 5 027 742, 1991.

[4] Hoy, K. L.; Nielsen, K. A.; Lee, C. Liquid Spray Applications of Coatings with Supercritical Fluids as Diluents and Spraying from an Orifice. U. S. Patent 5 108 799, 1992; U. S. Patent 5 203 843, 1993.

[5] McHugh, M. A.; Guckes, T. L. *Marcomolecules* **1985**, 18, 674.

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