SUPERCRITICAL FLUID SPRAY APPLICATION TECHNOLOGY: A POLLUTION PREVENTION TECHNOLOGY FOR THE FUTURE

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ABSTRACT

Supercritical carbon dioxide can be used in the spra application of coatings to replace the volatile organic solvent fraction that is used to obtain atomization viscosity. This enables applicators to reduce volatile organic compound (VOC) emissions by 30 to 70 percent whil continuing to use higher-molecular-weight polymer systems that give superior coating performance. Only a much smal amount of medium-to-slow evaporating solvents are used fo film coalescence, leveling, and reflow. Supercritical carbon dioxide can produce vigorous atomization that remedies the deficiencies of the airless spray process so that high quality coatings can be applied. It can produc fine droplet size and a "feathered" spray that resembles air spray system but without the high air volume. The technology is applicable to most spray applied coatings a has been demonstrated using acrylics, polyesters, cellulosics, alkyds, and commercial paints and lacquers i clear, pigmented, and metallic systems. The technology c be retrofitted into existing coating operations to utiliz existing investment.

INTRODUCTION

Emission of organic solvents during spray application of coatings is a significant source of air pollution by volatile organic compounds (VOC). Therefore, coating formulators and applicators are under increasing governmental pressure to reduce emissions and achieve the VOC standards established by the Clean Air Act and state and local regulations.

A primary function of the solvent blend in coatings is to reduce viscosity so the coating can be atomized into a spray of fine droplets, which is necessary to deposit a high quality coating film. However, the viscosity needed for atomization is much lower than the viscosity needed for film coalescence and leveling. Therefore, coatings are presently formulated so that much if not most of the solvent evaporates in the spray or very soon after deposition, so the coating does not run or sag. Often this excess atomization solvent must be allowed to flash off between coats as film thickness is built up.

Union Carbide's UNICARB^{TM} System enables volatile organic compound (VOC) emissions to be reduced 30 to 70 percent, in applying high quality coatings, by using environmentally acceptable supercritical fluids to replace the volatile organic solvent fraction that is used to obtain atomization viscosity. Only the smaller amount of solvent needed for film coalescence and leveling is used. Therefore, the reformulated coating has a high solids level, but it can utilize higher-molecular-weight polymers that give superior coating performance.

SUPERCRITICAL FLUIDS AS SOLVENTS

Supercritical fluids are interesting and useful because they have properties that are intermediate to those of normal liquids and gases. The supercritical fluid region on a phase diagram corresponds to temperatures and pressures near or above the critical point of the fluid, where the properties of the liquid and gas are similar or identical, so that in effect only one fluid phase exists, which is simultaneously liquid-like and gas-like.

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Because normal liquids become supercritical at high temperatures, the most widely used supercritical fluids are compressed gases such as carbon dioxide, ammonia, nitrous oxide, ethane, ethylene, and propane (Table 1), which become supercritical at mild temperatures.

During the last decade, supercritical fluids have been useful solvents in a variety of industrial and analytical separation processes, such as extraction, polymer fractionation, chromatography, and catalyst regeneration. They are also used as a reaction medium. Supercritical fluid applications and properties are reviewed by Johnston (1) and McHugh and Krukonis (2).

Supercritical fluids have been used in separations because of their important properties. Perhaps the most important is that density, and hence solubility, is a strong function of pressure, not just temperature. Supercritical fluids are highly compressible, that is, large changes in density can occur from relatively small changes in pressure. This causes large changes in solubility. Furthermore, solvation states can occur that are not found in normal solvents, because supercritical fluid densities, typically 0.2 to 0.8 grams per milliliter, are lower than normal liquid densities.

Supercritical fluids have been used in separations because they also have much higher diffusivity, much lower viscosity, and better penetration ability than normal liquid solvents. Typically, diffusivity is a hundred times greater (.001 square centimeters per second) and viscosity is ten times smaller (.1 centipoise). Therefore, supercritical fluids mix and equilibrate faster than normal solvents. Because they are usually smaller molecules, they can penetrate polymer configurations and solids better.

SUPERCRITICAL CARBON DIOXIDE AS A COATING SOLVENT

Supercritical carbon dioxide is an attractive supercritical fluid for the spray application of coatings because it has many useful attributes besides the properties it shares with other supercritical fluids. Supercritical nitrous oxide has similar properties and might be more environmentally acceptable, because it dissociates to nitrogen and oxygen, but it does not have the low cost and wide availability of carbon dioxide.

Environmental Compatibility

Carbon dioxide is environmentally compatible because it is not a volatile organic compound and it is on the Environmental Protection Agency's list of permissible emissions. Furthermore, it replaces organic solvents that contribute to air pollution.

Using carbon dioxide as a coating solvent also reduces the amount of "green house" carbon dioxide gas that is emitted from coating operations.

1) The process uses byproduct carbon dioxide that is produced by natural gas wells, fermentation plants, and ammonia plants, which would be released to the atmosphere anyway. Therefore, no new carbon dioxide is generated.

2) One pound of organic solvent emitted to the air eventually produces 2.3 to 3.3 pounds of new carbon dioxide as it is oxidized in the environment (Table 2). This is replaced by just 0.7 to 1.0 pounds of byproduct carbon dioxide.

3) Incineration to abate solvent emissions burns a lot of fuel because the solvent concentration is so low in the spray booth air. In one paint operation that we have studied, incineration produces 18 pounds of new carbon dioxide per pound of organic solvent.

The amount of carbon dioxide used to apply coatings would certainly be dwarfed by carbon dioxide emissions from power plants, home heating, transportation, and the food industry.

Carbon Dioxide Advantages

In addition to being environmentally compatible, carbon dioxide has other advantages that make it ideal for coating applications (Figure 1).

1) The critical temperature of carbon dioxide, 31 degrees Celsius (88 degrees Fahrenheit), is just above room temperature, so supercritical temperatures are mild and easily obtained.

2) The critical pressure of carbon dioxide, 1070 pounds per square inch (73 atmospheres), is well within the design parameters of airless spray equipment.

3) The health effects of carbon dioxide are exceedingly slight and it is much less toxic than organic solvents. The threshold limit value (TLV) for exposure is 5000 parts per million (0.5%). A concentration above 5% by volume can cause suffocation by suppressing breathing, but the concentrations anticipated in the spray process are well below the TLV level and therefore are relatively innocuous.

4) Carbon dioxide is nonflammable and mostly inert.

5) Carbon dioxide is an low cost commodity chemical that is readily available throughout the developed world. In the United States, four billion pounds are marketed yearly at a bulk price of about five cents per pound.

6) Supercritical carbon dioxide has high solubility in most coating formulations and it is a good viscosity reducer for polymer solutions.

Pure carbon dioxide is available in any amount. Small amounts are supplied in compressed gas cylinders as a liquid at room temperature and a vapor pressure of 850 pounds per square inch, which is just below critical conditions. Commercial amounts are supplied in cryogenic cylinders or refrigerated tanks at a temperature of -18 degrees Celsius (zero degree Fahrenheit) and a vapor pressure of 300 pounds per square inch. Tanks are available with up to 50 ton capacity. Bulk deliveries are by tank truck.

PHASE CHEMISTRY

Coating formulations can be exceedingly complex, so for the purpose of comparing phase relationships, conventional formulations will be considered to have three major components: film forming polymer, active solvents, and diluent solvents. The phase relationships between the relative amounts of these components can be shown on a triangular diagram (Figure 2).

Phase Diagram With Diluent Solvents

The active solvents are good solvents for dissolving the polymer system, giving a single phase in all proportions. They are usually oxygenated solvents such as ketones, alcohols, esters, and glycol ethers (some hydrocarbon solvents might be active solvents for some polymer systems). They not only dissolve the polymer and reduce viscosity, but provide proper film coalescence, leveling, and reflow during application and curing.

The diluent solvents are poor solvents for the polymer system, being essentially unable to dissolve the polymer by themselves. They are usually hydrocarbon solvents such as toluene, xylene, naphtha, and mineral spirits. They are used in coating formulations because they have lower cost than the active solvents. Generally as much diluent solvent as possible is used without exceeding the solubility limit and entering the two-phase region, which would give a poor coating. The main function of the diluent solvent is to economically lower the viscosity of the coating formulation so that it can be easily spray applied.

The relative evaporation rates of the active and diluent solvents must be carefully balanced to avoid phase separation during application and film formation. Generally the diluent solvents must evaporate faster than the active solvents. The film forming pathway is usually parallel to the two-phase boundary on the phase diagram (Figure 2).

Phase Diagram With Supercritical Fluids

From the perspective of a coating formulator, supercritical carbon dioxide has solvent properties like a diluent solvent (Figure 3). It is sometimes considered to be a solvent like heptane, but this is an inadequate analogy, because in some polymer systems it is several times more soluble than heptane. Furthermore, its solvency is a function of pressure, so the phase diagram has another degree of freedom. Solubility increases with higher pressure, but unlike liquid solvents, it decreases with higher temperature.

Although supercritical carbon dioxide behaves like a diluent solvent, it replaces most of the highly volatile solvents in a coating formulation, diluent and active solvents alike. These solvents evaporate in the spray or shortly after application, so they do not contribute much to film coalescence and leveling like the less volatile solvents that are kept in the reformulated coating. Ideally, the solvent composition of coatings sprayed conventionally and with supercritical fluids are the same once the coating is deposited onto the substrate.

The reformulated coating is sometimes called a coating concentrate because it contains less solvent. Its composition lies along the right-hand side of the phase diagram (Figure 3). The composition of the mixture of coating concentrate and supercritical carbon dioxide lies along the dashed line shown connecting the concentrate composition and the opposite corner (pure carbon dioxide). The volatile organic compound (VOC) content of the mixture is the same as the coating concentrate.

It is important to realize that the supercritical carbon dioxide and coating concentrate dissolve to form a liquid spray solution that is not supercritical; it contains a supercritical component.

Carbon dioxide solubilities as high as fifty percent have been measured. Generally solubility is not a limiting factor for spray application. Excess carbon dioxide above the solubility limit causes a two-phase system to form, but usually no harm results if a small excess is present.

The film forming path is quite different from conventional formulations because the carbon dioxide escapes from the spray solution extremely fast. The spray reverts to the coating concentrate before the solvent evaporates, so the pathway is always away from the two-phase region (Figure 3).

VISCOSITY REDUCTION

An important function of the supercritical carbon dioxide is to reduce the viscosity of the coating concentrate in order to form a spray solution that can be readily atomized into a spray of fine droplets.

The type of viscosity reduction that can be expected from a medium molecular weight commercial acrylic vehicle is illustrated in Figure 4. Viscosity reduction curves are shown for concentrates with 65% and 75% polymer levels. The viscosities are 300 and 2000 centipoise, respectively, when the concentrates are heated to a temperature of 50 degrees Celsius. Forming a spray solution with 28% supercritical carbon dioxide reduces the viscosity of both concentrates to less than 40 centipoise. The solubility limit is about 32%.

For this polymer system, the viscosity reduction with supercritical carbon dioxide is similar that obtained by diluting the concentrate with methyl amyl ketone, at the same temperature. Roughly one pound of carbon dioxide gives the same viscosity reduction as one pound of the diluent solvent. In other systems, often less carbon dioxide than an equal weight replacement is needed to obtain the proper spray viscosity.

SPRAY GENERATION

The supercritical fluid spray process uses equipment that is compatible with coating materials and the properties of supercritical fluids:

1) Because carbon dioxide is a gas at ordinary conditions, it is usually proportioned and mixed with the coating concentrate as the coating is sprayed (Figure 5).

2) The supercritical pressures are typical of airless spraying, so airless spray guns and nozzles are used. However, supercritical fluids can remedy the deficiencies of the airless spray process.

3) The supercritical temperatures are typical of conventional heated paint systems.

Union Carbide has developed a fluid delivery system for the spray application of coatings with compressible supercritical fluids. The coating concentrate and carbon dioxide are accurately metered and mixed, pressurized, and heated to the spray conditions. Carbon dioxide is supplied from gas cylinders or cryogenic cylinders and tanks. No refrigeration is used to suppress compressibility or pump cavitation. Coating concentrate is supplied from pressure pots, drums, or tanks. Spray solution is supplied to the spray guns on demand. The system is automated and can operate continuously or intermittently. Conventional plural-component coating proportioning systems are unable to handle the properties of supercritical fluids.

The coating concentrate, because it contains less solvent, is more viscous than conventional formulations. The viscosity is usually 500 to 3000 centipoise at room temperature, although much higher viscosities have been sprayed. It is a function of the solids level, the molecular weight distribution and type of polymer, and the solvent blend.

SPRAY CONDITIONS

The spray solution usually contains 10 to 50 weight percent supercritical carbon dioxide. The amount used in any given application depends upon the solubility, the viscosity reduction curve, the solids level, the pigment loading of the coating formulation, and the spray temperature and pressure. Usually a single-phase solution is sprayed (carbon dioxide totally dissolved).

The spray solution is usually heated to a spray temperature of 40 to 70 degrees Celsius (100 to 160 degrees Fahrenheit). It is heated to make the carbon dioxide supercritical and to offset cooling that occurs as the carbon dioxide is released from solution and expands as a free gas in the spray. Higher temperature lowers viscosity but it also decreases carbon dioxide solubility, so an optimum temperature can exist.

The spray pressure is usually 1200 to 1600 pounds per square inch, although higher pressures can also be used.

The spray viscosity is usually less than 50 centipoise. It is a function of the concentrate viscosity, the carbon dioxide concentration, and temperature.

The spray solution and coating concentrate have a much higher flash point than conventional coating formulations. They contain much less solvent and the highly volatile solvents have been eliminated and replaced by nonflammable carbon dioxide.

SPRAY CHARACTERISTICS

Supercritical carbon dioxide not only functions as a viscosity reducer, more importantly, it produces vigorous atomization that can remedy the defects of airless spraying and can produce high quality coatings.

Conventional Airless Sprays

Airless spray uses a high pressure drop across the spray orifice to propel the coating formulation through the orifice at high velocity. In normal sprays, the coating exits the orifice as a liquid film that becomes unstable from shear induced by its high velocity relative to the surrounding air. Waves grow in the liquid film, become unstable, and break up into liquid filaments that likewise become unstable and break up into droplets. This mechanism is well known for the atomization of normal incompressible liquids. Atomization occurs because the surface tension and cohesion forces, which hold the liquid together, are overcome by shear and fluid inertia forces, which break it apart. However, surface tension is not entirely overcome and it profoundly affects the spray.

Conventional airless spray techniques are known to produce coarse atomization and defective spray fans that limit their usefulness to applying low quality coating films. The spray characteristically forms what is known as a "tailing" or "fishtail" spray pattern. An example is shown in the photograph in Figure 6. Surface tension gathers more liquid at the edges of the fan than in the center, and this produces coarsely atomized jets of coating. Sometimes the jets separate from the spray and deposit separate bands of coating. At other times they thicken the edges so that more coating is deposited at the top and bottom than in the center of the spray. These deficiencies make it difficult to apply a uniform coating.

Supercritical Fluid Sprays

Supercritical carbon dioxide can change the atomization mechanism and produce an airless spray that has the good characteristics of an air spray, but without the large air volume. The vigorous decompressive atomization can produce the fine droplet size needed for high quality coatings and a "feathered" spray that gives uniform coating thickness. The coarse droplet size and fishtail spray of conventional airless sprays are eliminated. The carbon dioxide escapes from the spray droplets as free gas, but the volume is small.

The vigorous decompressive atomization is believed to be produced by the dissolved supercritical carbon dioxide in the spray solution suddenly becoming exceedingly supersaturated as the spray leaves the nozzle and experiences sudden and large drop in pressure. This creates a very large driving force for gasification of the dissolved carbon dioxide, which overwhelms the surface tension forces that oppose atomization and bind the fluid flow together into a "fishtail" type of spray.

A different atomization mechanism is evident because atomization begins right at the spray orifice instead of downstream from it. Atomization is apparently no longer due to break up of a liquid film from shear with the surrounding air. Instead it is due to the expansive forces of the compressible fluid. Therefore, no liquid film is visible coming out of the nozzle. Furthermore, because the spray is no longer bound by surface tension, it leaves the nozzle at a much wider angle than normal airless sprays and produces a "feathered" spray that has tapered edges like an air spray. This produces a rounded parabolic shaped spray fan instead of the sharp angular fans typical of conventional airless sprays. Spray photographs are shown in Figures 7 and 8.

The spray pattern deposits coating uniformly in a wide central portion and then progressively less coating at the edges of the spray. This is particularly desirable to enable adjacent layers of sprayed coating to be overlapped to produce a coating film of uniform thickness. This is one of the principle reasons why air sprays are used instead of airless sprays to provide coatings with high quality finishes.

Although the spray leaves the nozzle at a much wider angle and it produces a wider fan width than normal airless sprays, the fan width can be indexed to give any fan width from narrow to very wide by changing the fan width rating of the airless spray tip, as is currently done.

Laser light scattering measurements and comparative spray tests show that the vigorous atomization can produce fine droplets that are in the same size range as air spray systems (20 to 50 microns) instead of the coarse droplets produced by normal airless sprays (70 to 150 microns). The droplet size range and distribution for a properly formulated coating are ideal for minimizing orange peel and other surface defects commonly associated with spray application.

This fine particle size provides ample surface area for the dissolved carbon dioxide to very rapidly diffuse from the droplets within a relatively short distance from the spray nozzle. Because it is a dissolved supercritical gas and has high diffusivity, it behaves like an extremely fast evaporating solvent. This produces a very fast but smooth venting of the carbon dioxide from the spray droplets. Therefore the coating is essentially free of carbon dioxide before it is deposited onto the substrate.

The rapid release of carbon dioxide from solution is evident in the very rapid cooling of the heated spray that occurs within a very short distance of the spray nozzle. Figure 9 compares temperature profiles for conventional heated airless sprays and a supercritical fluid spray that is heated to a temperature that compensates for expansive cooling. The conventional spray cools to ambient temperature within six inches from the nozzle because the solvent evaporates and ambient air is entrained into the spray. Therefore the coating is deposited at ambient temperature. The supercritical fluid spray typically cools to ambient temperature within about one inch of the nozzle. In some cases the spray might briefly subcool, but the entrainment of ambient air ensures that the coating is also deposited at ambient temperature. The cooling depends upon the concentration of supercritical carbon dioxide.

The rapid cooling is beneficial because it reduces solvent evaporation in the spray, so little solvent is lost from a properly formulated coating. Therefore solvent is used efficiently. Worker exposure to solvent vapors in the spray booth is also reduced to a lower level. Measurements for one coating system showed that the solids content of the deposited coating was only about 2% higher than the solids content of the coating concentrate. Therefore, the viscosities of the coating concentrate and the deposited coating should be similar.

The released carbon dioxide gas forms a shroud that tends to displace moisture, oxygen, and dust from the spray. This lowers the local dew point so that moisture absorption is less likely in humid environments. The lower oxygen level reduces spray flammability.

The supercritical carbon dioxide has been found to be an insulating solvent that can give the spray solution the proper electrical resistivity for good electrostatic wrap. The displacement of moisture from the spray also helps droplets retain their electric charge.

Spray Gun Requirements

The supercritical fluid spray process has been demonstrated using conventional, manual and automatic, electrostatic and non-electrostatic, airless spray guns and tips manufactured by a number of spray equipment suppliers. However, the spray solution has unique properties, namely, it is a heated compressible fluid that contains a high concentration of dissolved supercritical carbon dioxide. Therefore, the process has unique spray gun requirements for best performance:

1) Good temperature control; the spray gun should not cool off when it is idle.

2) Clean shut off of the spray; the valve and tip should not cause spits.

3) No excessive pressure drop in the spray nozzle; the turbulence promoters that are often used with conventional airless spray tips are not needed.

The spray gun must be pressure rated for the spray pressure being used. Airless spray guns and tips are being designed by spray gun suppliers for commercial application of supercritical fluid spraying.

COATING FORMULATIONS

The supercritical fluid spray process has been used to apply a variety of high-quality clear, pigmented, and metallic coatings using thermosetting, thermoplastic, and air-dry polymers. The polymer systems used include low, medium, and high molecular weight acrylics; polyesters; alkyds; cellulose acetate butyrate; melamine formaldehydes; nitrocellulose; and commercial paints and lacquers. The pigments tested include titanium dioxide, carbon black, aluminum flake, organic blue, calcium carbonate, silica, and clay. All polymers and pigments tested were found to be compatible with carbon dioxide. Most polymeric materials used in conventional solvent borne coatings are believed to be applicable to supercritical fluid spraying. For many applications, we expect that little or no adjustment will be needed in the polymer system, only the solvent blend will need reformulation.

In conventional spray coatings, the solvent blend consists of a mixture of fast, medium, and slow evaporating solvents that are formulated to provide the properties needed to form a smooth coating. The fast solvents provide better atomization but are quickly lost by evaporation in the spray, which increases the coating viscosity and allows it to remain in place on the substrate without running or sagging. The medium solvents provide for a modicum of flow, which aids leveling of the coating. They are lost during the flash off period before final bake or forced air drying. The slow or "tail" solvents keep the film "open" during final cure and are responsible for reflow in baked systems.

The formulation strategy for supercritical fluid spray coatings is quite different from that for conventional spray coatings. Because the supercritical carbon dioxide replaces nearly all of the fast solvent and some of the medium solvent, which are lost in the spray or soon afterward, the solvents of choice are the medium-to-slow evaporating active solvents (moderate-to-higher boiling solvents). These solvents are chosen for their coalescence, leveling, and reflow properties for the polymer system employed, the application, and the drying or curing conditions.

The reformulated coating concentrate will typically have a viscosity between 500 and 3000 centipoise, depending upon the solids level, molecular weight of the polymer system, and the requirements of the application. The highest viscosity consistent with good performance should be used to minimize the volatile organic compound (VOC) content.

Calculations show that the higher viscosity of the concentrate presents no problem in circulating the coatings over long piping runs from the coating feed tanks to the spray booths. The pressure drops for circulating a coating concentrate with a viscosity of 1000 centipoise are shown below. Very viscous concentrates can be pumped more easily by heating them to lower their viscosity.

Pipe Size	Flow Rate	Pressure Drop
1.5 inch NPT pipe	1 gallon/minute	4.5 psi/100-feet
1.5 inch NPT pipe	2 gallon/minute	6.0 psi/100-feet
2.0 inch NPT pipe	1 gallon/minute	1.5 psi/100-feet
2.0 inch NPT pipe	2 gallon/minute	2.3 psi/100-feet

VOLATILE ORGANIC COMPOUND EMISSIONS

The volatile organic compounds (VOC) emitted from supercritical fluid spray applied coatings can be 30 to 70 percent less than the emissions arising from conventional solvent borne coatings, based on the same polymeric compositions. Although the technology has not been fully evaluated by the regulatory agencies at this time, they have indicated that carbon dioxide will not be included in the VOC calculation. Therefore, the VOC of the coating concentrate and the spray will be the same.

There is another factor that further favors supercritical fluid spraying. The technology uses mostly the higher boiling, slower evaporating solvents and deliberately avoids the lower boiling, faster solvents. Therefore, only a small portion of the solvent evaporates in the spray booth, where large volumes of air are required. VOC emissions are largely confined to the dry line or oven space, where air flows are more moderate and incineration equipment and solvent recovery procedures are less costly. In typical thermosetting coatings, 70 to 80 percent of the solvent used in the new process will be collected in the oven exhaust and only 20 to 30 percent in the spray booth. Therefore, supercritical fluid spray technology can be a key component in a systems approach to very low VOC emissions.

CONCLUSIONS

The supercritical fluid spray process for the application of coatings is an effective and economical pollution avoidance technology that allows applicators to reduce VOC emissions by 30 to 70 percent while continuing to use existing high-performance polymer systems.

Supercritical carbon dioxide has proven to be a very effective solvent for spraying coatings. It is an effective viscosity reducer and it remedies the deficiencies of the airless spray process so that high quality coatings can be applied.

Union Carbide believes the technology will be broadly applicable to most spray applied systems and that it can be easily retrofitted into existing spray operations. In most cases, little or no change in the polymer system will be required and only the solvent blend will need reformulation. Some of the anticipated end uses are automotive topcoats and component finishing, automotive refinish, wood and metal furniture, appliances, pails and drums, aerospace, machinery and equipment, trucks and buses, and structural steel.

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2. McHugh, M. A. and Krukonis, V. Supercritical Fluid Extraction. Butterworths, Boston. 1986.

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We especially acknowledge the valuable contribution of Professor Marc D. Donohue of Johns Hopkins University.

TABLE 1

EXAMPLES OF SUPERCRITICAL FLUIDS

Compound	Boiling Point (C)	Critical Temperature (C)	Critical Pressure (atm)	Critical Density (g/ml)
Ethylene	-103.7	9.2	49.7	0.22
Xenon	-108.2	16.6	57.6	0.12
Chlorotrifluoroethane	-31.2	28.0	38.7	0.58
Carbon Dioxide	-78.5	31.3	72.9	0.45
Ethane	-88.6	32.3	48.1	0.20
Nitrous Oxide	-88.6	36.5	71.7	0.45
Monofluoromethane	-78.4	44.6	58.0	0.3
Propane	-42.1	96.7	41.9	0.22
Ammonia	-33.4	132.4	112.5	0.24

FIGURE 8

WIDER SPRAY WITH SUPERCRITICAL CARBON DIOXIDE

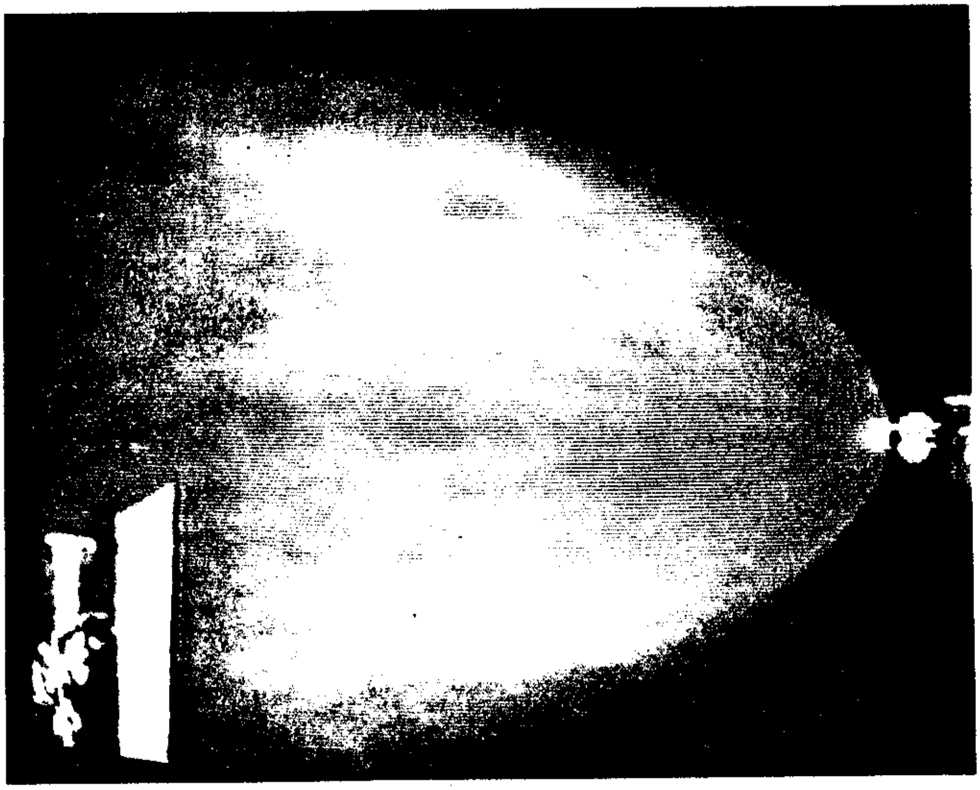


FIGURE 9

TEMPERATURE PROFILE OF SPRAY

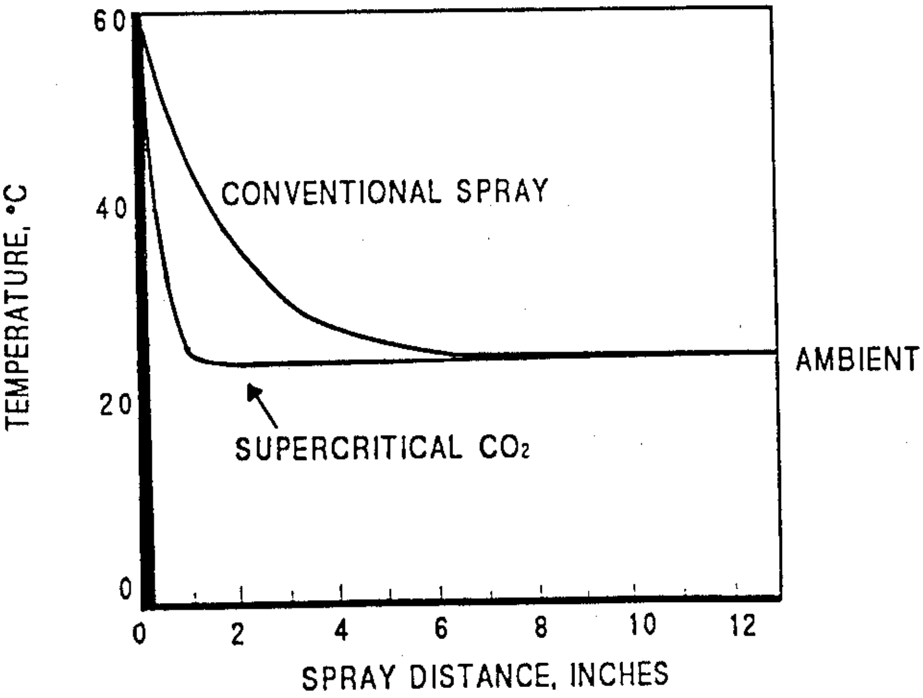


FIGURE 6

CONVENTIONAL AIRLESS "FISHTAIL" SPRAY

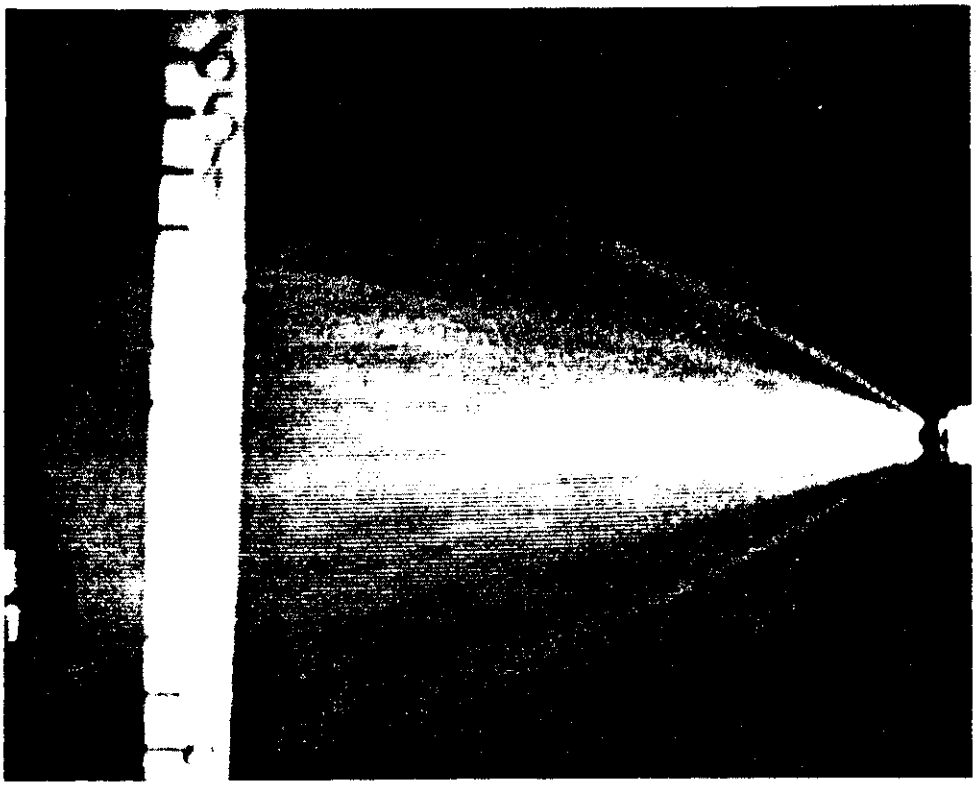


FIGURE 7

"FEATHERED" SPRAY WITH SUPERCRITICAL CARBON DIOXIDE

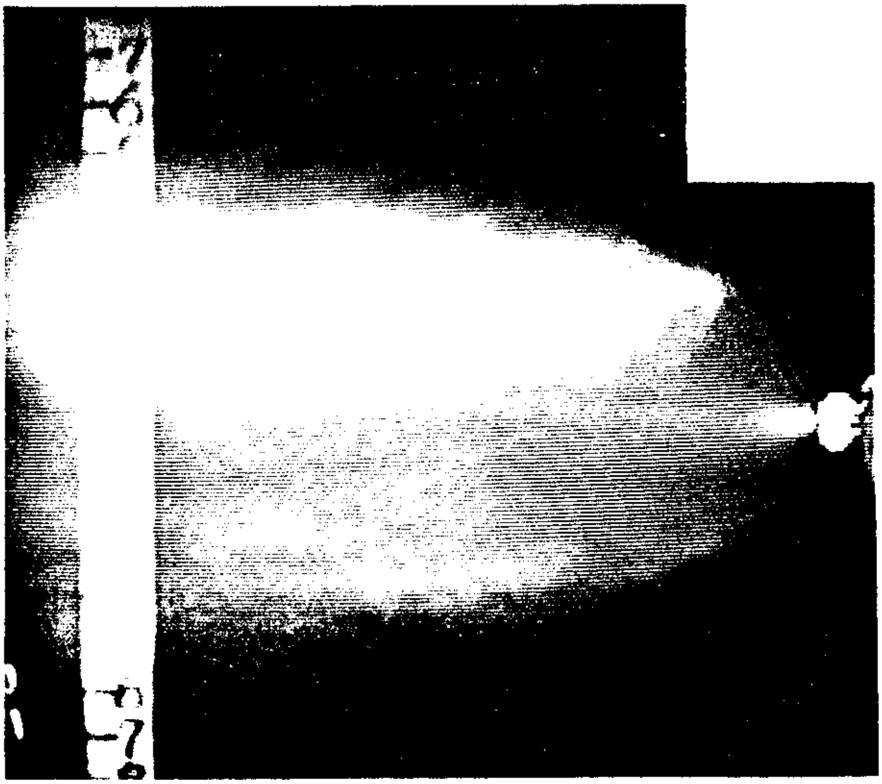


FIGURE 4

VISCOSITY REDUCTION BY CARBON DIOXIDE

TEMPERATURE = 50°C

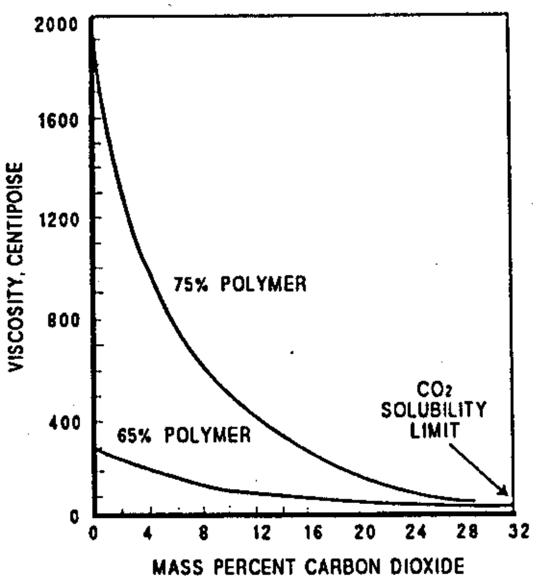


FIGURE 5

SPRAY CONCEPT

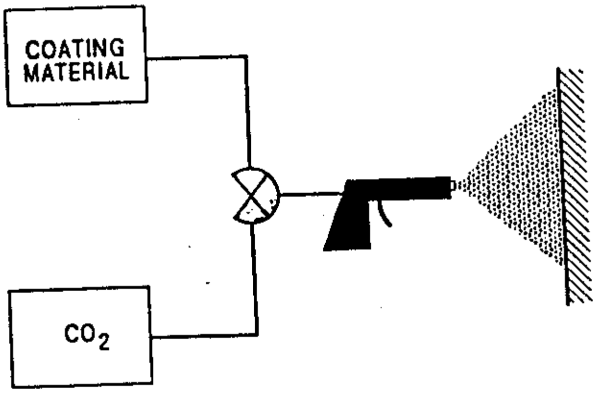


TABLE 2

POUNDS CARBON DIOXIDE PRODUCED PER POUND OF ORGANIC SOLVENT THROUGH INCINERATION OR NATURAL OXIDATION

Acetone	2.3 pound/pound
Butyl Acetate	2.3
Butyl CARBITOL^{TM} Acetate	3.0
n-Butanol	2.4
Diisobutyl Ketone	2.8
Methyl Amyl Ketone	2.7
Methyl Ethyl Ketone	2.4
Toluene	3.3
Xylene	3.3

FIGURE 1

PHASE DIAGRAM FOR CARBON DIOXIDE

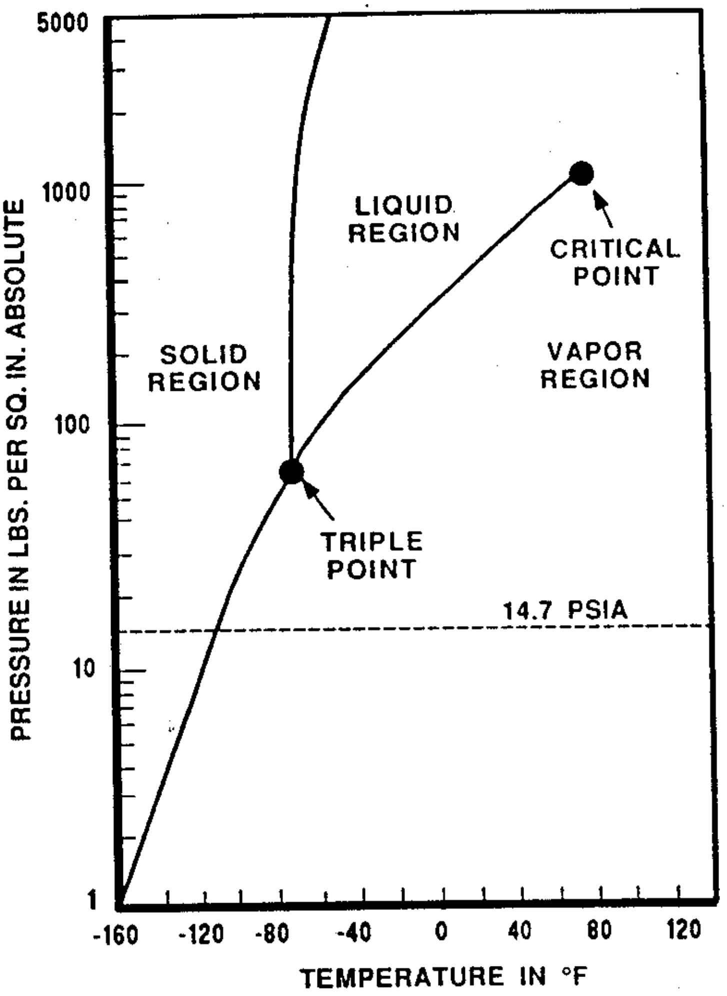


FIGURE 2

PHASE DIAGRAM FOR HYDROCARBONS

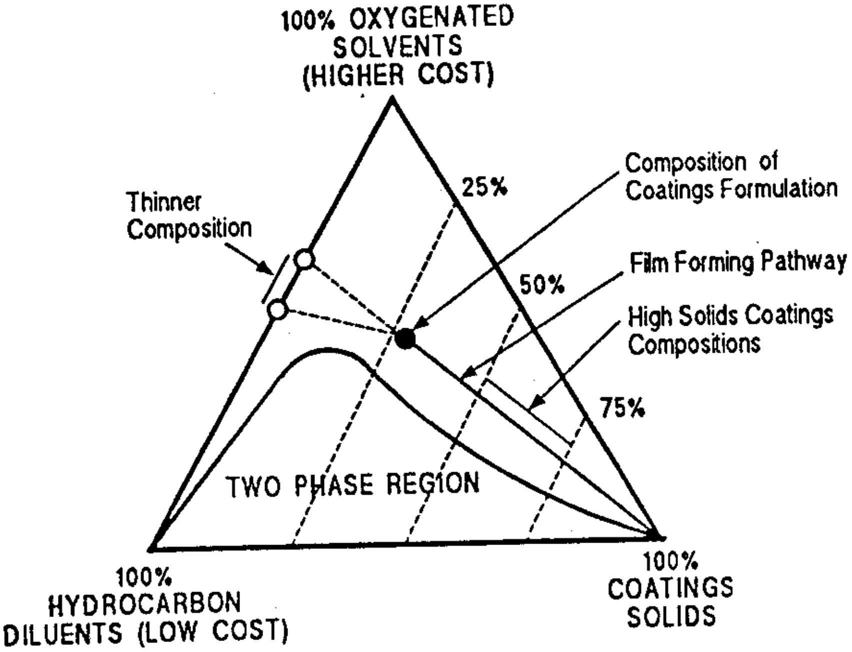
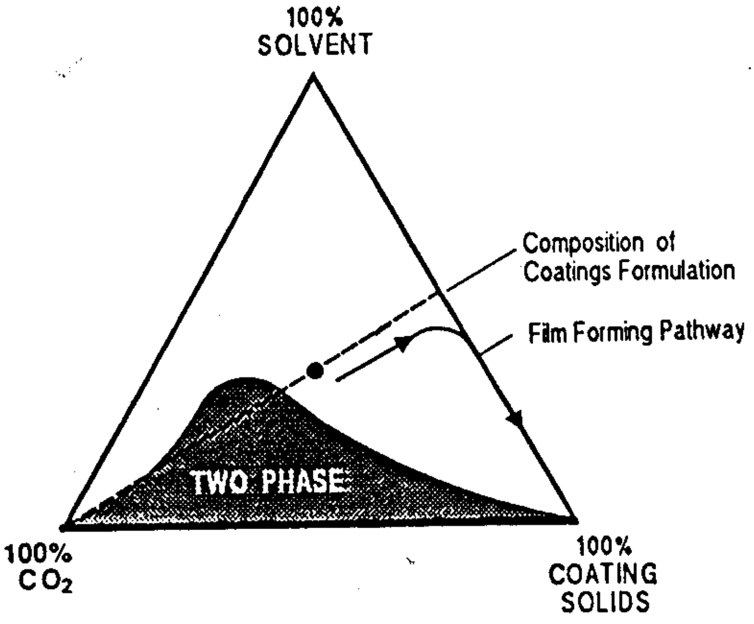


FIGURE 3

PHASE DIAGRAM OF SUPERCRITICAL CO_2 SPRAY APPLIED COATING



UNICARB® System Fits the "Bill"

Lawmakers hailed it, the President signed it, and American industry breathed deep and swallowed hard. Of all the legislation emanating out of Washington in recent months, none is of more concern to domestic coaters—and the manufacturing and chemical companies that supply them—than the Clean Air Act Amendments of 1990.

Capping some 13 years of legislative give-and-take, the 700-page clean air bill sets forth a series of rules, regulations, and a must-meet timetable to rid the environment of smog-causing chemicals, toxic compounds, and the effects of acid rain on sensitive ecosystems. For coaters, and the rest of U.S. industry, the ramifications are far reaching. Estimates indicate it will cost businesses at least $25 billion annually to make the bill's mandates an environmental reality.

Closer to home, the anticipated impact is equally dramatic. "In the overall context, the Clean Air Act Amendments of 1990 represent both an enormous challenge and an important opportunity for Union Carbide," says Peter Molinaro, Washington Representative for the Corporation's Federal Government Relations Department.

The challenge? "Complying with the provisions of the overhaul as they relate to our own facilities," the government relations expert notes. The opportunity? "Developing products and technology that will enhance our customer's ability to comply with the law," Molinaro says. "And that's where the UNICARB® System fits in."

Although a variety of options are available, the unique capability of the UNICARB System to reduce volatile organic compounds (VOCs) makes it a valuable offensive weapon for finishers facing an avalanche of new regulatory requirements. By substituting carbon dioxide for a substantial portion of the solvent normally required for many spray coatings application systems, the UNICARB System can reduce VOCs by up to 70 percent.

For spray coaters, that reduction can mean the difference between meeting or falling short, and eventually prey, to the provisions of the recently revised clean air bill, particularly two of the law's eight sections or titles. These include Title One, which focuses on reducing ozone and smog formation from stationary or typically industrial/commercial sources and Title Three, which addresses toxic air pollutants.

Zeroing-In on Ozone

Before the recent revision, the nation's anti-smog law essentially required areas to meet health standards for half-a-dozen pollutants including ground-level ozone, which is a primary ingredient of urban smog. To burn through and clear up hazy definitions, the new provisions establish five categories of ozone non-attainment areas—marginal, moderate, serious, severe, extreme—and sets deadlines of 3, 6, 9, 15, and 20 years respectively for attaining standards. Currently, Los Angeles, is the only city in the "extreme" category.

Responsibility for actually determining what areas belong in what category falls to the federal Environmental Protection Agency (EPA) and the states. "There are over 100 urban areas that are in non-attainment," Molinaro notes. "The EPA and the states will work together to designate which areas are which based upon a system of design values indicating how many parts per million of ozone are permitted in a certain area."

According to the government affairs executive, all areas except those categorized as "marginal" must achieve 15 percent reductions in their baseline emissions of VOCs within six years of the legislation's enactment. "After that," he says, "most other areas will have to achieve three percent reductions per year."

Depending on the severity of the ozone problem in a given area, manufacturers will be required to implement one of three different levels of control technology, either Reasonably Available Control Technology, Best Available Control Technology, or Lowest Achievable Emissions Rate. The permitting authorities will decide what level of control is required as well as the respective level of

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competing abatement technologies.

Although Molinaro doesn't expect the government to dictate the use of a specific technology, he is convinced the UNICARB System will play an important role as coaters mount their drive toward compliance. "EPA will make a determination regarding which level of control the UNICARB System provides," he says. "To the extent that the UNICARB System is a low emission technology, it may wind up being deemed Reasonably Available or even Lowest Achievable control technology.

"If we have an approach that will give people up to 70 percent reduction in VOCs," Molinaro predicts confidently, "we are going to be one of the technologies of choice in areas where ozone pollution is a problem.

The UNICARB® System is being viewed as an important stepping stone to future growth and expansion

The UNICARB System is being viewed as an important stepping stone to future growth and expansion for spray coaters around the country. As part of the recently revised clean air bill, finishers eyeing the expansion of an existing plant or addition of a new one must meet certain "offset" requirements.

"Essentially, new or modified sources of VOCs will have to be issued permits and undergo review," Molinaro explains. "And, they must meet certain offset requirements which vary according to the severity of the ozone problem in a given area.

"The worse the ozone pollution, the higher the offset requirements," he emphasizes, citing a sliding scale of offset ratios ranging from 1.1 to 1.0, to 1.5 to 1.0. "In extreme areas, that means if you want to expand facilities, you have to reduce your existing emissions by a pound-and-a-half for every pound of emissions you add, Molinaro elaborates. And that situation is almost tailor-made for the VOC-reducing capabilities of UNICARB."

Slaying Toxics

The technology's solvents-reducing talents are also expected to help coaters comply with Title Three of the new Clean Air bill, which zeroes in on toxic air pollutants. Prior to the recent overhaul, the EPA was required to protect public health from toxic chemicals in the air with "an ample margin of safety." Seven chemicals were regulated since 1970.

Considerably more comprehensive and stringent, the new provisions list 189 toxic pollutants and require the EPA to establish a list of source categories of hazardous pollutants for the purpose of promulgating standards. The regulations are intended to reduce the emissions of toxic air pollutants by as much as 90 percent by the year 2003.

"Essentially, Title Three requires the installation of something called 'maximum achievable control technology' on sources emitting more than ten tons annually of any one of the 189 individual pollutants which includes numerous solvents, or 25 tons in aggregate," says Molinaro. "Wherever possible, the EPA is required to set a numerical limit—such as an emissions rate—rather than specify a certain type of control device.

"As a result, the manufacturer will enjoy some flexibility in choosing which technology will be implemented to achieve the required reduction," he points out. "And I think the UNICARB System will be among the top choices."

A further incentive, Molinaro notes, is a wrinkle written into the law that provides for companies to stretch out their compliance date if they reduce emissions by 90 percent earlier than scheduled. "The UNICARB System can't get them to 90 percent on its own," Molinaro comments. "But, we can give coaters a big lift toward getting a six year extension of the compliance date.

"One way or another, the UNICARB System will play an important role," he predicts. "It gives finishers a way to reduce VOCs, meet the ozone non-attainment provisions, and maybe even get a jump on reducing other emissions so they can buy some time to comply with toxic air provisions mandating the installation of maximum achievable control technology."