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EVALUATION OF SUPERCRITICAL CO_2 SPRAY TECHNOLOGY AS A COST EFFECTIVE APPROACH TO REDUCTION OF SOLVENTS IN WOOD FINISHING

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ABSTRACT

Product quality, waste reduction, and economic issues were evaluated for a spray paint application technology using supercritical carbon dioxide to replace some of the solvent in a conventional solvent-borne coatings formulation. Product quality was evaluated by comparing product finishes for a nitrocellulose coating applied by conventional spray with that of a similar coating applied by supercritical carbon dioxide (CO_2) technology. Waste reduction and economics were documented from company records and interviews with key company personnel. The technology was found to have good potential to reduce waste without affecting product quality.

INTRODUCTION

This program was conducted by Battelle for the Pollution Prevention Research Branch (PPRB) of the U.S. Environmental Protection Agency with the cooperation of Union Carbide Corporation, Nordson Corporation, and Pennsylvania House Furniture Company. The PPRB is evaluating and demonstrating new technologies for pollution prevention through the Pollution Prevention Clean Technology Demonstration (CTD) Program.[1]

This report reviews the use of supercritical CO_2 technology for paint spray application. Pennsylvania House Furniture Company has used supercritical CO_2 coating technology for more than a year to apply a nitrocellulose lacquer finish to oak and cherry furniture on a chair-finishing line. At current Pennsylvania House production rates, more than 250 furniture units per day are coated with nitrocellulose lacquer by this process.

During the subject technology evaluation, three aspects of this technology were examined:

- Product Quality: To show that coating applied by this spray technology meets company standards for a quality finish

- Pollution Prevention Potential: To demonstrate that use of this spray application technology for solvent replacement in coatings reduces volatile organic compounds (VOCs) released during finishing operations

- Economic Ramifications: To document the cost to install and operate this pollution prevention technology on an existing spray coating finish line.

PROCESS DESCRIPTION

In the supercritical CO_2 spray process, the solvent-like properties of supercritical CO_2 are exploited to replace a portion of the solvent in the conventional solvent-borne coating formulation. Supercritical CO_2 acts as a diluent solvent to thin the viscous coating just before application, allowing the coating to be atomized and applied with a modified spray gun. Typically, most of the volatile, fast-drying solvents and some of the medium-drying solvents are eliminated. Enough medium- and slow-evaporating solvents are retained to obtain proper leveling and film coalescence. The remaining solvent blend is adjusted to optimize performance without changing the resin chemistry or pigment-loading levels. The actual amount of solvent-content reduction that can be achieved is affected by the type of coating, the desired film thickness, the desired properties of the applied coating, and the environment in which the coating is being applied. Union Carbide Corporation developed the use of supercritical CO_2 for spray coating applications, introducing this technology commercially in 1988 under the UNICARB™ tradename.[2,3] Thermosetting, thermoplastic, air-dry, and two-component formulations, in clear, pigmented, and metallic coating systems, have been developed successfully for use with the UNICARB™ process.

Supercritical fluids are gases that exist at temperatures and pressures near or above the critical point of the fluid as depicted on a phase diagram (Figure 1). At the critical point, the properties of the liquid and the gas are similar or identical. The resulting single-phase fluid exhibits solvent-like properties that can be altered by adjusting temperature and pressure. A number of gases have been examined for use as supercritical fluids in applications such as industrial and analytical separation processes, cleaning, chromatography, and coating. The UNICARB™ process for coating uses nontoxic, nonflammable carbon dioxide as the supercritical fluid for coating dilution. Carbon dioxide, readily available as a by-product of a variety of industrial processes, has a critical temperature of 31°C (88°F) and a critical pressure of 73 atm (1070 psi), falling within the ranges already used for heated paint systems and airless spray equipment.

Special equipment is needed to introduce the CO_2 into the reduced-solvent formulations and to heat and pressurize the resultant mixture before spraying. Typically 10% to 50% by weight CO_2 may be introduced. Usually, the coating is heated to 40° to 70°C and applied with spray pressures of 82 to 109 atm (1200 to 1600 psi). Coatings used at Pennsylvania House are applied with spray guns similar to those used for airless applications. However, the spray-gun nozzle design was slightly modified to optimize the spray pattern because the decompression of supercritical CO_2 results in finer atomization of the sprayed coating and smaller particles than are common with the use of airless spray equipment.

Pennsylvania House uses supercritical CO_2 spray technology on the chair-finishing line to apply nitrocellulose lacquer finishes while reducing the VOC emissions from their finishing operation. To bring this technology to production-line use, Pennsylvania House worked closely with manufacturers and suppliers to optimize supercritical CO_2 technology including process, equipment, and coatings formulations. In the conventional finishing process, two coats of nitrocellulose lacquer (21 to 23% solids) are applied manually with airless spray equipment. The supercritical CO_2 finishing process uses only one coat of nitrocellulose lacquer to achieve the desired film build and finish quality. The nitrocellulose lacquer formulation, optimized for the supercritical CO_2 spray system, has approximately a 41% solids content.

PRODUCT QUALITY EVALUATION

The specific objective of the product quality evaluation was to determine whether nitrocellulose lacquer, applied by the supercritical CO_2 spray process, provided a wood finish of equal or better quality than that applied by the conventional nitrocellulose formulation and spray technique previously used by Pennsylvania House. At Pennsylvania House, the appearance and quality of the final finish are judged through visual examination by inspectors on the coating line. Special attention is given to gloss, smoothness, and the lack of surface defects such as blisters or pinholes.

Product quality was evaluated through subjective evaluations performed by Pennsylvania House staff members and a panel of Battelle coatings personnel. Test substrates were finished on the production lines during an on-site visit. A set of samples was finished using the one-coat UNICARB™ process, and two other sets were finished using one and two coats of the "standard" nitrocellulose formulation and the airless spray equipment still in place on the chair-finishing line. All panels were finished by the same production methods that typically are used on the chair line at Pennsylvania House.

The subjective product quality evaluations demonstrated that a coating applied by the supercritical CO_2 spray process yielded a product with a finish quality equal to or better than the finish quality obtained by conventional materials and methods. Samples finished by the supercritical CO_2 process and by the two-coat conventional process were rated as "acceptable" (Table 1). Samples sprayed with one coat of the nitrocellulose by the conventional process were not acceptable.

In addition to the subjective visual inspections of the test samples, Battelle staff made measurements of gloss (Table 2) using ASTM D529. These measurements provide some quantitative insight into the physical attributes of the finish of each of the coating processes.

The test procedure outlined in ASTM D529 recommends averaging six gloss measurements for a 3-inch x 6-inch sample area, which correlates to 49 measurements on the 7-inch x 21-inch test substance used here. The mean and standard deviation of the 49 data points represent the overall gloss appearance of each sample, alleviating subjective biases of the person performing the measurements while still incorporating the assessment of any nonuniformity in the gloss across the sample surface. The breadth in standard deviation of the data can be used as a gauge of the uniformity of the sample finish across the complex geometry of the test panels. Gloss test results for each of the nine panels are reported as the mean of 49 determinations and then averaged for each of the sample sets for easy comparison among each of the finishing processes in Table 2. The averaged gloss data for the UNICARB™ samples are statistically the same as those for the conventional two-coat process. The gloss data of both of these sets show that they are substantially glossier than the one-coat conventional finish sample set.

These results are supported by Pennsylvania House records for consumer acceptance. Internal quality control audits on chair-line products show a decrease in finish defects using the supercritical CO_2 system. Based on the number of furniture units requiring rework because of finish defects, production efficiency has improved since the UNICARB™ process was implemented.

POLLUTION PREVENTION POTENTIAL

The pollution prevention potential of this technology is based on reducing the emissions of organic solvents without adding to other wastestreams. The nitrocellulose lacquer finishing process used on the chair line can contribute to pollution in two ways: VOC emissions from the coating formulation during the finishing operation, and spray-booth wastes, including solvent-laden filters and nitrocellulose "dust". A blend of fast-evaporating solvents, medium-evaporating solvents, and slow-evaporating solvents is used in conventional spray coatings. In the supercritical CO_2 spray process, most of the fast- and medium-drying solvents are replaced by supercritical CO_2 and the slow-drying solvents are adjusted slightly for better film formation. Although reducing VOC emissions is important, it is equally important to demonstrate that the supercritical CO_2 process does not add pollutants to other wastestreams.

Pennsylvania House has been able to reduce the number of coats of nitrocellulose lacquer from two to one. The volume of nitrocellulose lacquer used in each finishing operation was determined during the initial phases of implementing the supercritical CO_2 process at Pennsylvania House. Metering devices were placed in-line on the airless spray guns used to apply the conventional nitrocellulose formulation, and on the coating inlet line to the supercritical fluid supply unit used to feed the coating mixture concentrate and the supercritical CO_2 to the modified spray guns used with the UNICARB™ process.

Pennsylvania House records indicate that it takes approximately 473 ml of the conventional formulation to apply the two coats needed to achieve the desired quality in the finished product. The UNICARB™ process required about 207 ml of the reduced-solvent formulation per furniture unit to achieve the same quality.

Table 3 compares the volatile solvent content (% by weight) of the two formulations used by Pennsylvania House. The UNICARB™ coating is formulated using 17.5% less solvents (on an absolute basis) than the conventional formulation. Only 9.67% of the UNICARB™ formulation is comprised of Hazardous Air Pollutant (HAP) materials, compared to 35.78% for the conventional formulation. On a per-gallon-of-coating-sprayed basis, this difference would result in a relative decrease in VOC emissions of 22.81%, with a 72.97% decrease in HAPs using the

UNICARB™ formulation. VOC contents are reported as 563 gms/ℓ for the UNICARB™ formulation and 707 gms/ℓ for the conventional system.

Assuming an average yearly production of 50,000 units and the use of 207 ml for the one-coat UNICARB™ process and 474 ml for the two-coat conventional formulation, the UNICARB™ formulation uses 10,220 ℓ and the conventional formulation uses 24,604 ℓ to finish the units. Based on the reported VOC contents, this system change corresponds to an annual reduction in VOC emissions of 67.5% when the newer process is used.

Supercritical CO_2 is used in the UNICARB™ process to decrease VOC emissions. Carbon dioxide is not being produced through use of the UNICARB™ process. The CO_2 used in this technology is supplied by various distributors of CO_2 which obtain CO_2 as a by-product of other chemical processes. Thus, the supercritical CO_2 method of applying coatings does not actually contribute to the emission of additional CO_2 into the atmosphere.

Coating overspray at Pennsylvania House is collected on dry filters that are compressed and stored in 208-ℓ (55-gal) drums for disposal by landfill. Waste products include dry and solvent-laden filters and nitrocellulose "dust", both loose and trapped in the filters. The solid waste was not increased or decreased by implementing the supercritical CO_2 technology.

ECONOMIC ANALYSIS

The objective of the economic analysis was to determine the payback period for the switch to the supercritical CO_2 process from the previously used conventional system. The initial investment in capital equipment and installation costs were considered along with operating costs (materials, waste disposal, labor, and utilities). A return-on-investment (ROI) was calculated, based on the costs associated with capital expenditures, including equipment and installation, and the return generated through lower personnel, operating, and materials costs. Details on this ROI calculated using worksheets provided in the Waste Minimization Opportunity Manual (U.S. EPA, 1988) are included in the full report.[1]

Implementing the UNICARB™ finishing process on the chair line at Pennsylvania House resulted in substantial annual savings in both utilities and labor as shown in Table 4. The annual operating costs were based on the production of 50,000 chairs per year. The UNICARB™ process costs of $46,000 include $37,000 for the coatings formulation and CO_2 concentrate and $9,000 for the CO_2 equipment rental. The conventional formulation costs for the same number of furniture units would be $47,000. By converting from a two-coat process to the one-coat process, Pennsylvania House was able to decrease its utility costs by $11,000 because there was one less booth to operate. Labor costs were reduced by $46,000 because one less finisher and one less sander were needed. Waste handling and disposal costs and finishing line maintenance remained the same for both processes.

Cost savings, realized from a decrease in raw materials costs, were offset by the leasing fees for the CO_2 tank and pump at Pennsylvania House. Additional savings could be realized by decreasing the size of the existing ovens to reflect the change to a one-coat system. Pennsylvania House has not downsized the production ovens to gain gas utility savings.

The annual operating cost of the supercritical CO_2 finish line is approximately $58,000 less per year than that of the conventional line. The initial capital investment for the UNICARB™

process was \$58,000, of which \$46,000 was for equipment purchase and \$12,000 for installation of the equipment.

The more detailed economic evaluation found in the full report demonstrates a positive return on investment after the first year, with a total payback period within three years if gas utility savings are included, and five years if gas utilities are not included.

CONCLUSIONS

This technology evaluation shows that supercritical CO_2 spray technology has potential as a pollution prevention option in the application of solvent-borne coatings. This supercritical CO_2 technology is not limited to one coating type, but could be used to reduce the solvent level required to spray apply a variety of solvent-borne coatings. The wood furniture facility, where this evaluation was conducted, maintained product quality with a nitrocellulose lacquer finish and reduced VOC emissions from the coating process. No additional wastes entered the waste-stream. Immediate operating savings of \$58,000/year were realized. A 100% ROI should be achieved within five years after implementation.

LITERATURE CITED

1. Heater, K. J., Parsons, A. B., Olfenbuttel, R. F., Randall, P., "Evaluation of Supercritical Carbon Dioxide Technology to Reduce Solvent in Spray Coating Applications," U.S. Environmental Protection Agency report in press.

2. "Carbide Licenses Coatings Technology". *Chem. Engr. News*, July 30, p. 9 (1990).

3. Hoy, K., "Unicarb System for Spray Coatings — A Contribution to Pollution Prevention." *Eur. Polym. Paint Colour J.* 181: 438, 440-2 (1991).

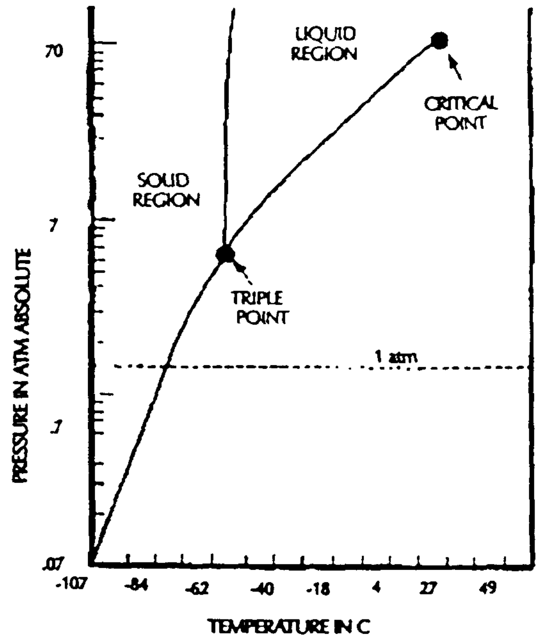

Figure 1. Phase diagram for carbon dioxide.*

*** Nielsen, K.A., Busby, D.C., Glancy, C.W., Hoy, K.L., Kuo, A.C., and Lee, C., "Supercritical Fluid Spray Application Technology: A Pollution Prevention Technology for the Future," Union Carbide Chemicals and Plastics Company, Inc. Presented at the 17th Water-Borne & Higher-Solids Coatings Symposium, February 21-23, 1990, New Orleans, LA.**

Table 1. Sample Panel Finish Quality Results for Subjection Gloss

Process	Acceptable Gloss (% panels)	Unacceptable Gloss (% Panels)
Conventional One-Coat Process	33[a] (33)[b]	67 (67)
Conventional Two-Coat Process	100 (100)	0 (0)
Supercritical CO_2 One-Coat Process	100 (100)	0 (0)

[a] Evaluations by furniture company staff are stated first.
[b] Evaluations by Battelle Coating staff are enclosed with parentheses.

Table 2. Gloss Data on Sample Panels

Finishing Process	Sample Number	Average Gloss Data/Panel	Average Gloss Data/Set
Conventional One Coat	46482-9-1	20.3 ± 4.3	20.3
	46482-9-2	20.4 ± 3.1	
	46482-9-3	20.3 ± 3.1	
Conventional Two Coat	46482-10-1	33.2 ± 1.6	32.3
	46482-10-2	35.0 ± 2.2	
	46482-10-3	28.7 ± 2.8	
UNICARB™	46482-11-1	35.3 ± 3.2	31.5
	46482-11-2	30.5 ± 3.1	
	46482-11-3	28.7 ± 2.9	

Table 3. Comparison of Volatile Solvent Content of Conventional and UNICARB™ Coating Formulations as Percent Weight

Materials Description	HAP (Y/N)	Conventional (% by weight)	UNICARB™ (% by weight)
MEK-heptanone	No		37.25
methoxypropylacetate	No	7.36	
xylene	Yes	16.80	
isopropanol	No	11.20	6.55
toluene	Yes	10.39	
N-butyl acetate	No	11.83	
isobutyl acetate	No	6.89	
2-butoxyethanol	Yes	3.27	9.67
MIBK	Yes	5.32	
isopropyl acetate	No	1.46	
Other		2.37	5.87
Total VOC (% by weight)		76.88	59.34

Table 4. Summary of Annual Operating Cost Comparing Conventional Finish Line with Supercritical CO_2 Finish Line

Item	Conventional ($/year)	Supercritical CO_2 ($/year)
Coating Materials	47,000	37,000
CO_2 Storage Equipment	—	9,000
Spray Booth #2		
Finish Labor	23,000	—
Sanding Labor	23,000	—
Electricity	11,000	—
TOTAL	104,000	46,000
SAVINGS	= 58,000	