4th Quarter PROGRESS and FINAL REPORT
NONPROPRIETARY VERSION

Project Title: "Multi-Partner Demonstration Of Energy Efficient And Environmentally Improved Methods For The Production Of Polyurethane Foam"

Covering Period: March 1, 2002 through August 28, 2005

Date of Report: November 30, 2005

Recipient: Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195

Award Number: DE-FC36-02ID14321

Subcontractors: None

Contact(s): Mark Listemann, 610-481-8590, listemml@airproducts.com

Project Team: Technical Project Officer: Fran Geurink – fran.geurink@go.doe.gov
OIT chemical lead – Brian Valentine – brian.valentine@ee.doe.gov
Golden Field Office Internet Based Reporting System –
<https://gowba.go.doe.gov/uploadreports/login.asp>

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their awardees, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.

Project Objective:

The work carried out during this project has sought to commercialize new energy-efficient, enabling technology (silicone surfactants) that will allow the flexible foam industry to utilize environmentally benign liquid CO₂ as a blowing agent. These new products provide the means for more cost-effective and energy-efficient production of foam in an industry that is under increasing threat from foreign competition and environmental regulation. The annual U.S. production of flexible slab stock foam is valued at \$2 billion, and the consumer goods manufactured from this foam are valued at \$269 billion. At least half this value is amenable to liquid CO₂ production technology.

Foam production is a complex chemical process. New technology was needed in order to provide the proper balance between (1) reactant and blowing agent (CO₂) emulsification and (2) foam processability. To accomplish these goals, the project team:

- Produced drum-scale quantities of the new surfactant technology and demonstrated them at partners' production facilities using commercial-scale equipment to produce critical flexible foam grades.
- Down-selected the most favorable surfactants to produce a wide spectrum of foam grades using the liquid CO₂ process based on results from demonstrations on partners' foam production lines.
- Scaled up and commercialized optimum surfactant products at an accelerated rate to realize the goals of improved energy and raw materials use, greater environmental protection and resource sustainability, and improved U.S. economic competitiveness.

Background:

Air Products has developed enabling liquid CO₂ surfactant technology based on laboratory data and pilot testing. This technology was thoroughly demonstrated on full-scale production lines in order to prove its performance and benefit to flexible foam manufacturers. Three companies teamed with Air Products in order to conduct full-scale production trials in their facilities to produce flexible foam based on liquid CO₂ technology. This was a critical step in order to provide validation of the technology's performance. Dow Corning has produced laboratory- and commercial-scale quantities of the necessary surfactants for these demonstrations, including any engineering process development required to demonstrate the manufacture of new products on a commercial-demonstration scale. During this process they have defined manufacturing processing parameters to achieve the most favorable and economic scaleup methodology for a high-quality end product. The project team has conducted all foam evaluations, as well as the generation and analysis of foam performance data.

Dow Corning has manufactured the newly developed surfactants for the project. The demonstration team has evaluated 55-gal-drum quantities of surfactants on production-scale equipment in the partners' plants in order to generate adequate validation data. Performance was rated on the basis of both foam processing and foam properties. Processing can be defined as the ability to produce a grade of foam in a consistent manner over a wide range of chemical and mechanical variations. This is a critical hurdle to overcome based on the negative economic impact that would result if excess scrap foam were produced or if line operators would have to constantly change formulations and processing conditions during the foam production process. Chemical variations include changes in catalyst types and levels.

Mechanical variations include such variables as volume throughput and system pressures on the processing equipment. Foam physical properties include not only the standard foam properties such as density, hardness, and foam porosity, but also foam appearance, or more

specifically, cell size and distribution and patterns in the foam. Foam appearance is especially critical in CO₂-produced foams; because of their appearance, CO₂-produced foams are often considered to be of inferior quality compared to foam produced with solvents such as MeCl₂. The proper surfactant would make the CO₂-produced foams as marketable as solvent-blown foam.

The most promising candidates were evaluated in a number of formulations that represent the diversity of foam grades that must be produced by manufacturers using CO₂ to blow their foam. The variations in foam grades included low- to high-density, soft to hard foams, as well as flame-retardant and non-flame-retardant foams. The surfactant that performed best in these extensive evaluations was scaled up to production status and is being made available to the CO₂-blown flexible foam industry. Therefore, in partnership with the DOE, the overall project goal to accelerate the successful demonstration of a technology that will provide energy and environmental benefits to a risk-averse sector of the chemical industry has been achieved.

4th Quarter Status:

Task 1: Laboratory Prescreening of Surfactants

Complete.

Task 2: Initial Evaluation of Surfactants

Complete. Learnings from Q3 were subsequently utilized in Task 3.

Task 3: Second Level Evaluation

Evaluations of the commercial prototype surfactant at a trial partner in a broader spectrum of formulations that included higher density, non-fire-retardant (FR), filled foam, and alternative blowing agents such as acetone and all-water, demonstrated performance superior to the control (current product) with regard to processability, emulsification, stabilization and foam cell structure. Overall processing on 90+% of the equipment types used in the industry was better than that of the control.

Task 4: Commercialization

This product was formally introduced and is commercially available to the industry as DABCO[®] DC5986. Further dissemination of the technology through the industry occurred by presentation of a technical paper and slide presentation at the Polyurethane Foam Association industry conference October 6, 2005. In addition to the foam production team members, three customers have expressed significant interest by placing orders for trial quantities of material. Due to the global nature of many companies in the slab stock industry, trials in Europe, Central America and Brazil have been scheduled for January 2006, which is earlier than anticipated. All material will be manufactured in the U.S. The first commercial batch has already been sold for trials, and the second batch is scheduled for November 2005.

Task 5: Management and Reporting

This is the fourth quarterly report for FY2005, covering the period from July 1, 2005 through September 30, 2005. This is also the final project report, covering the entire project from March 1, 2002 to September 30, 2005.

Plans for Next Quarter:

The project was completed on schedule; no further work is planned.

Patents:

None

Publications/Presentations:

A project review was presented to DOE on April 27, 2005. The introduction of DABCO® DC5986 included a technical paper entitled "Formulating Efficiencies for Flexible Slabstock Polyurethane Foam" and a slide presentation at the Polyurethane Foam Association industry conference on October 6, 2005.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
Task 1	<i>Laboratory Prescreening of Surfactants</i>	2QFY02	2QFY02	
Task 2	<i>Initial Evaluation of Surfactants</i>	3QFY02	3-4QFY02	Due to positive results from early trials, had increased number of trial surfactants.
Task 3	<i>Second-Level Evaluation</i>	1QFY05	4QFY05	Completed broad formulation range
Task 4	<i>Commercialization</i>	4QFY05	1QFY06	Second-generation product commercialized October 25, 2005.
Task 5	<i>Management and Reporting</i>	4QFY05	4QFY05	

Final Project Summary and Major Accomplishments:

Year 1 (review for DOE, February 2003) – completed laboratory evaluations and initiated work with team members. Eleven surfactant candidates were evaluated in the laboratory; three were down-selected for second-level evaluations. Comparisons were made against existing technology. Two second-level candidates demonstrated superior performance/quality in terms of finer cell structure (better appearance), higher bun heights (better yield), better top-to-bottom physical property gradient (product consistency) and better compatibility with flame retardants.

Year 2 (review for DOE, June 2004) – second- and third-level evaluations were completed. Fourteen candidates were evaluated, with three candidates qualifying for second-level evaluation. Comparisons were again made against existing technology. One material was determined to be superior to the commercial controls. However, commercialization was deferred due to poor economic conditions in the industry. The decision was made to pursue experimental molecules outside the DOE project to improve efficiency and foam stabilization and develop a third-generation surfactant.

From July 1, 2003 through December 31, 2003, laboratory-scale experimental designs for higher efficiency molecules were completed, and two new experimental molecules were scaled up. From January 1, 2004 through June 30, 2004, field evaluations of the two experimental

samples were conducted. The results were sufficiently encouraging to support additional confirming trials. At this point, work under DOE funding resumed, and a six-month extension to August 2005 was approved.

Year 3 (review for DOE, April 27, 2005) – commercial batch of third-generation experimental molecule was completed, and field evaluations resumed. Commercial product DABCO® DC5986 launched October 2005.

The goal of the third-generation surfactant work was to enable foam producers to maintain production efficiency, which was restricted by the mandated change from MeCl₂ to liquid CO₂. First-generation liquid CO₂ surfactants did not permit production of as large a range of foam grades as was possible with MeCl₂, thus placing U.S. industry at a competitive disadvantage to regions in which MeCl₂ use is still allowed. Benefits of the new surfactant include using higher CO₂ levels for softer, lower density foams, which formerly required high MeCl₂ levels; and lower FR levels for improved economics and improved surfactant efficiency and stabilization. The commercial batch was produced in August 2004, and field trials, including multi-drum quantities, were conducted from September 2004 through August 2005. DOE made a site visit to one of the three team companies for validation and verification on March 17, 2005.

Evaluations of the commercial prototype surfactant at the team company in a broader spectrum of formulations that included higher density, non-fire-retardant (FR), filled foam, and alternative blowing agents such as acetone and all-water, demonstrated performance superior to the control (current product) with regard to processability, emulsification, stabilization and foam cell structure. Processing on both round and flat lines, representing 90+% of the equipment types used in the industry, was better than that of the control. The commercial product DABCO® DC5986 was launched in October 2005.

Energy and Environmental Make Good

The impact table from the original proposal is included below.

Updated Assumptions:

Overall Assumptions for the Market and Production of Flexible Foam

1. The FY 2006 flexible foam market size has grown to 1.8 billion lbs of foam.
2. The market share of foams produced with auxiliary blowing agents has increased from 40% in 2000 (MeCl₂) to 50% in 2006, equivalent to 900 million lbs of flexible foam now being produced with liquid CO₂ as the blowing agent.
3. Originally number 6 below. FY2004 estimated distribution of blowing agents in slab stock foam is 18.3% acetone blown, 65% CO₂ blown, VPF 6.7% and water 10%. FY2006 actual is <10% acetone blown, 50% CO₂ blown, and water 40%.

Energy Impact

The current 2006 market share for liquid CO₂ blown foam (900 million pounds) is 10 percentage points higher than the methylene chloride share in 2000, demonstrating broader adoption of this energy-efficient technology. The transition away from methylene chloride was essentially complete in 2003, requiring utilization of first-generation liquid CO₂ surfactant technology. This technology initially produced foam of inferior quality relative to methylene chloride blowing, and prevented roughly 20% of foam grades (primarily low-density, soft grades) from being produced

at all, placing U.S. manufacturers at a competitive disadvantage globally. With the amenable market for the state-of-the-art Dabco DC5986 technology of 900 million pounds of foam, ultimate energy savings utilizing this technology can reach 5.66×10^{11} BTUs, up from the original prediction of 4.27×10^{11} BTUs (energy assumptions, number 4 below). In addition to the immediate benefits from improved foam quality, U.S. competitiveness will be further improved by resuming the manufacture of the low-density, soft-foam grades over the next few years.

Environmental Impact

The environmental benefit of methylene chloride elimination was achieved independently by the entire industry in 2003.

Impact Table

	New Technology (Liquid CO ₂)	Current Technology (MeCl ₂)	Difference (Current- New)	Comment
Energy Use (BTU's per lb. of product(s))				
Electricity	6 BTU/lb foam	313 BTU/lb foam	307 BTU/lb foam	
Natural Gas				
Petroleum				
Coal				
Biomass				
Other	0	322 BTU/lb foam	322 BTU/lb foam	Steam
Total	6 BTU/lb foam	635 BTU/lb foam	629 BTU/lb foam	
Feedstock Use (per lb. of product(s))				
Petroleum (lbs)				
Other (lbs)				
Environmental Impact : Non-Combustion Related Emissions (per lb. of product(s))				
Carbon Dioxide (lbs)	0.073 lb/lb foam	0.073 lb/lb foam	0	
SOx (lbs)				
NOx (lbs)				
Particulates (lbs)				
VOC's (lbs)				
Other (lbs) Methylene Chloride (HAP)	0	0.059 lb/lb foam	0.059 lb/lb foam	

Overall Assumptions for the Market and Production of Flexible Foam

1. The FY 2000 flexible foam market size is 1.7 billion lbs of foam.
2. Approximately 40% or 680 million lbs of flexible foam are produced using methylene chloride as the blowing agent.
3. Methylene chloride is 5.9 weight % of the foam formulation or raw material used to make 1 lb of foam.
4. When foam is produced using liquid CO₂ technology, the amount of CO₂ used is 2.0 weight % of the foam formulation or raw material used to make 1 lb of foam.
5. Total lbs of MeCl₂ used in FY00 foam production = 40.1 million lbs per year (Calculation: 1.7 billion lbs foam market x 5.9 wt % MeCl₂ of foam formulation x 40% of foam blown using MeCl₂ technology = 40.1 million lb/yr).
6. FY2004 estimated distribution of blowing agents in slab stock foam is 18.3% acetone blown, 65% CO₂ blown, VPF 6.7% and water 10%.

Energy Assumptions

1. The primary energy savings from the new liquid CO₂ technology result from the elimination of MeCl₂. The **total electricity consumption for the production of MeCl₂ is 5.30×10^3 BTUs per pound of MeCl₂**. Due to the energy intensity of chlorine production, which, in turn, is used to produce MeCl₂, the energy consumed in the production of chlorine is included in these calculations. The calculations are based on the energy information taken from the Process Economics Program reports, SRI, Menlo Park, CA. Chlorine (Cl₂) production requires 1.4kwh/lb (diaphragm process, Table 5.32, page 118, Report No. 61B). Methanol production requires 0.026 kwh/lb (methanol from natural gas by the Lurgi process, Table 5.18, page 100, Report No. 43B). MeCl₂ production requires 0.19 kwh/lb (MeCl₂ from methanol and chlorine, Table 5.8, Page 139, Report No. 126). 0.96 lbs of Cl₂ and 0.358 lbs of methanol are used per lb of MeCl₂ produced. The total kwh/lb to produce MeCl₂ is therefore 1.41kwh/lb chlorine (0.96 lb Cl₂/lb MeCl₂) + 0.026kwh/lb methanol (0.358 lb methanol/lb MeCl₂) + 0.19 kwh/lb MeCl₂. Total = 1.55 kwh/lb or 5.30×10^3 BTU/lb MeCl₂.

Using overall assumptions 1 - 5 above, the total electricity consumption required to produce the MeCl₂ used to produce 1 lb of foam is (0.059 lb MeCl₂/lb foam) (5.30×10^3 BTU/lb MeCl₂) = 313 BTU/lb foam.

2. The **electricity consumed to generate and liquefy CO₂ is 0.092 kwh/lb, or 314 BTU/lb**. As noted in overall assumption 4, the volume of CO₂ is 1/3 that of MeCl₂ used in foam production. The electricity consumed is (0.020 lb CO₂/lb foam) (314 BTU/lb CO₂) = 6.26 BTU/lb foam. The amount of energy required to liquefy CO₂ is deducted from the MeCl₂ electricity cost, yielding a net savings for flexible foam production of 313 – 6 = **307 BTU/lb foam**.
3. **Total steam consumption is 5.46×10^3 BTU/lb for MeCl₂**, assuming 85% efficiency in steam utilization. The calculations are based on the energy information taken from the Process Economics Program reports, SRI, Menlo Park, CA. Chlorine (Cl₂) production requires 2.42 lb steam/lb (diaphragm process, Table 5.32, page 118, Report No. 61B). Methanol production requires -0.045 lb steam/lb (methanol from natural gas by the Lurgi process; note that the Lurgi process is exothermic, so it produces a small amount of energy; Table 5.18, page 100, Report No. 43B). MeCl₂ production requires 2.33 lb steam/lb (MeCl₂ from methanol and chlorine, Table 5.8, Page 139, Report No. 126).

0.96 lbs of Cl_2 and 0.358 lb of methanol are used per lb of MeCl_2 produced. The total lb steam to produce MeCl_2 is therefore $[2.42 \text{ lb steam/lb chlorine } (0.96 \text{ lb } \text{Cl}_2/\text{lb } \text{MeCl}_2) + (-0.045 \text{ lb steam/lb methanol}) (0.358 \text{ lb methanol/lb } \text{MeCl}_2) + 2.33 \text{ lb steam/lb } \text{MeCl}_2]/0.85$. Total = 5.46 lb steam/lb MeCl_2 or $5.46 \times 10^3 \text{ BTU/lb } \text{MeCl}_2$, assuming 1 lb steam = 1000 BTU under average industrial conditions and 85 % steam efficiency. No steam is required to produce CO_2 .

Using overall assumptions 1 - 5 above, the total steam consumption required to produce the MeCl_2 used to produce 1 lb of foam is $(0.059 \text{ lb } \text{MeCl}_2/\text{lb foam}) (5.46 \times 10^3 \text{ BTU/lb } \text{MeCl}_2) = 322 \text{ BTU/lb foam}$.

4. **Total net energy savings from electricity and steam (2) + (3) equals 629 BTU/lb foam. Overall and conservatively this results in an annual savings of 4.27×10^{11} BTUs by implementing this technology.**

Environmental Assumptions

Methylene Chloride (MeCl_2)

1. Using current technology, **0.059 lb MeCl_2 /lb foam** is released as a hazardous air pollutant (HAP).

Carbon Dioxide (CO_2)

1. Assuming the total electricity and steam energy savings above eliminate the need for fossil fuel combustion, the CO_2 formation associated with that energy production will also be eliminated.
2. Total energy savings of 4.27×10^{11} BTUs corresponds to 1.25×10^8 kwh.
3. Given: 0.00061 metric ton of CO_2 /kwh is produced from fossil fuel combustion.
4. Tons CO_2 per year = $0.00061 \text{ ton } \text{CO}_2/\text{kwh} \times 1.25 \times 10^8 \text{ kwh/yr} = 76,250 \text{ tons/yr}$.
5. Per lb of foam: $76,250 \text{ tons/yr} \div 680 \text{ million lb of foam/year} = 1.12 \times 10^{-4} \text{ tons/ lb foam}$.
6. Per lb of foam: $= 1.12 \times 10^{-4} \text{ tons/lb foam} \times 2200 \text{ lb/metric ton} = 0.25 \text{ lb/lb foam}$
7. Assume on average 3 weight % water is used in both current MeCl_2 and liquid CO_2 technologies. This water reacts with isocyanate to produce CO_2 gas, which is also used to expand the foam. This results in the release of 0.073 lb of CO_2 /lb foam.

*

Final Summary Budget Data:

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	March 2002	September 2002	\$43,441	\$43,442	\$86,883	\$43,441	\$43,442	\$86,863
Year 2	October 2002	September 2003	\$66,497	\$66,497	\$132,994	\$66,497	\$66,497	\$132,994
Year 3	October 2003	September 2004	\$45,038	\$45,037	\$90,075	\$5,661	\$5,662	\$11,323
Year 4	October 2004	August 2005	\$179,186	\$179,186	\$358,372	\$37,889	\$37,890	\$75,779
Year 5								
Totals			\$334,162	\$334,162	\$668,324	\$153,489	\$153,491	\$306,959