ADMINISTRATIVE INFORMATION

1. **Project Name:** Development Of Process Optimization Strategies, Models, And Chemical Databases For On-Line Coating Of Float Glass

2. **Lead Organization:** PPG Industries, Inc.
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5. **Date Project Initiated:** February 14, 2001

6. **Expected Completion Date:** June 30, 2004

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:**

The objectives of this project are as follows:

1. Identify modifications to existing APCVD coater designs and/or new coater designs that will double the efficiency of reactant utilization, thereby substantially reducing waste emissions and purchases of raw materials.
2. Develop validated computational models to predict defects due to thickness nonuniformity and haze; use these to reduce defect frequency and improve the overall energy efficiency of the process by reducing the amount of rejected glass that must be remelted.
3. Generate a database of fundamental thermodynamic and kinetic information for APCVD.
4. Provide enhanced understanding of the underlying chemical reactions that control APCVD, which will enable the development of improved process models and control strategies for float-glass coating and other types of glass, such as containers, that use APCVD coatings.

8. **Technical Barrier(s) Being Addressed:**

This project addresses the need to improve the efficiency of on-line atmospheric pressure chemical vapor deposition (APCVD) processes used primarily to deposit coatings on float glass, but also on glass containers. APCVD processes in the flat-glass industry at present can be as little as 10% efficient (i.e., only 10% of the incoming precursor chemicals are converted to coating), resulting in annual production and waste-treatment disposal costs to the industry of nearly \$23 million. In addition, remelting of glass due to defects in the coatings results in over 1.1×10^{11} Btu/year of unproductive energy usage.

9. **Project Pathway:**

The approach used in this project to overcome the barriers cited above is to develop models capable of predicting coating growth rates as a function of process parameters, test and validate them using experimental data obtained in laboratory reactors, and then apply the models to identify strategies for optimizing coating precursor utilization and minimizing defects. On-line testing of these strategies occurs through pilot- and full-scale tests conducted at the facilities of the industrial partner. By necessity, a substantial amount of fundamental data concerning reaction thermodynamics, gas-phase kinetics, and growth rates was generated as part of this project. Thus, to provide benefit to the entire segment of the glass industry interested in on-line coating, these data are being made available through a combination of publications, technical presentations, reports, and web releases. Certain results are expected to have potential for patenting and these will be pursued at the appropriate time. If successful, these technologies will be licensed to interested parties.

10. **Critical Technical Metrics:**

Double the efficiency of tin oxide precursor utilization relative to the present rate employed by PPG in their on-line coating operations.

Development of a comprehensive database of fundamental information relevant to APCVD of tin oxide, including gas-phase thermochemical data, kinetic data describing precursor reactions, and mechanisms predicting tin oxide growth rates. No such data existed for the widely used industrial precursor MBTC at the start of this project.

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:**

This project is complete except for the writing of a final report. The following key milestones were met:

Two strategies for increasing precursor utilization in on-line APCVD were identified and tested in full-scale plant trials at a PPG coating facility. Both strategies proved to be effective and are now undergoing further testing to determine the optimal conditions for operation. It is expected that both will be implemented in PPG's APCVD process. The combination of these two strategies is capable of meeting the project's objective of doubling the baseline usage rate of the tin oxide precursor. (Objective 1 above)

Experimentally validated models of tin oxide CVD were developed that predict all trends observed in a laboratory reactor, including the effects of temperature, pressure, reactant concentration and flow rate. The models were transferred to PPG for further use in modeling their APCVD process and will be made available to the glass industry through one or more reviewed technical papers. (Objective 2 above)

A database of fundamental information pertinent to modeling APCVD tin oxide processes was generated. Multiple technical presentations that describe these data are being prepared, including articles in publications focused on the glass industry. (Objectives 3 and 4 above)

12. **Future Plans:**

Sept. 30, 2004	Completion of project final report
Dec. 31, 2004	Complete publication of fundamental data generated by the project.

13. **Project Changes:**

No changes in scope, approach, or schedule occurred in the final year of the project.

14. **Commercialization Potential, Plans, and Activities:**

On-line atmospheric pressure chemical vapor deposition (APCVD) techniques used to manufacture coatings on glass are a critical technology in the flat-glass industry, responsible for the production of approximately 110 million ft^2/year of highly value-added products. These consist primarily of low-emissivity ("low-E") and solar-control glasses for architectural applications, but also coatings for solar cells, computer screens, automotive applications, and xerography. The markets for these products are strong and growing. Coated glass for energy-conserving windows constitutes a roughly $600 million market for the raw glass alone; the total value of the final manufactured product (primarily dual-pane glass units) is in the billions of dollars. To maximize production rates, on-line methods are a virtual necessity; other methods, such as vapor deposition (sputtering), either cannot be performed at atmospheric pressure or cannot deposit material at rates fast enough to be compatible with glass ribbons speeds on typical float lines (about 1 ft/s). APCVD is thus an economically attractive, but technologically very challenging, manufacturing process. The highest-volume material manufactured by on-line deposition is tin oxide (SnO_2) and is produced by all major flat-glass manufacturers in both the U.S. and worldwide.

Technology transfer to the marketplace is being accomplished by several means. First, optimization strategies developed in the project have been successfully demonstrated and are expected to be implemented by PPG. Since PPG is the largest manufacturer of coated glass in U.S., this represents a major commercialization activity. Second, certain technologies developed as a result of this project appear to hold potential for commercialization and the CRADA with PPG has been extended for one year to allow time to develop these technologies, pending receipt of a modest amount of additional funding from DOE/ITP. A patent investigation by Sandia demonstrated the potential for developing additional intellectual property in this area. If successful, we will pursue licensing arrangements. Third, non-proprietary results of this project (which are extensive) are being published in the open literature, as discussed above.

15. **Patents, Publications, Presentations:**

A.M.B. van Mol, Y. Chae, A. H. McDaniel, and M.D. Allendorf "Chemical Vapour deposition of Tin Oxide: Fundamentals and Applications," submitted to *Thin Sol. Films*, April 2004.

Yongkee Chae, William G. Houf, Anthony H. McDaniel, and Mark D. Allendorf "Analysis of Reaction Mechanisms for Tin Oxide Chemical Vapor Deposition from Monobutyltintrichloride," submitted to *J. Electrochem. Soc.*, 2004.

M. D. Allendorf, C. F. Melius "BAC-MP4 Predictions of Thermochemistry for Gas-Phase Tin Compounds in the Sn-H-C-Cl System," submitted to *J. Phys. Chem. A*, 2004.

Yongkee Chae, William G. Houf, Anthony H. McDaniel, Jill Troup, Mark D. Allendorf "Stagnation Flow Reactor Investigation of Tin Oxide CVD from Monobutyltintrichloride," accepted for publication in *J. Electrochem. Soc.*, 2004.

M. D. Allendorf, A. M. B. van Mol "Gas-Phase Thermochemistry and Mechanism of Organometallic Tin Oxide Precursors," accepted for publication in *Topics in Organometallic Chemistry*, 2004.

Y. Chae, A. H. McDaniel, M. D. Allendorf "Kinetics of Tin Oxide CVD by Oxidation and Hydrolysis of Monobutyltintrichloride," presented at the fall meeting of the AIChE, San Francisco, Nov. 2003.