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LLNL-TR-747187

# Development and Implementaton of Advanced Materials for Aircraft Engine Applications Development and Implementation of Nanostructure Laminates Final Report CRADA No. TC-0497-93-B

T. W. Barbee, W. Yee

March 2, 2018

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# Development and Implementation of AdvancedMaterials for Aircraft Engine Applications
# Development and Implementation of Nanostructure Laminates

## Final Report

CRADA No. TC-0497-93-B

Date: May 15, 1998 Revision: 1

A. Parties

The project was a relationship between the Lawrence Livermore National Laboratory (LLNL) and United Technologies, Pratt & Whitney.

University of California
Lawrence Livermore National Laboratory
7000 East Avenue, L-795
Livermore, CA 94550

United Technologies, Pratt & Whitney
P.O. Box 109600
West Palm Beach, FL 33410-9600

B. Project Scope

The objective of this project was to develop engineered nanostructure laminate materials for applications in gas turbine engines. Although the focus of this effort was on developing improved thermal barrier coatings, the data and experience gained through such project tasks as basic theoretical work and modeling of composition/structure property relationships can be applied to the development of microstructure laminates for other applications.

C. Technical

During this project LLNL was responsible for experimentally developing a database of ceramic/ceramic nanostructure-laminate fabrication processes to enable the selection of a material and structure that provides significantly enhanced thermal barrier coating performance. This included the development of a ceramic/ceramic nanostructure microlaminate database for thermal barrier coatings and the development of fabrication processes, structure and composition characterization methods, and determination of performance under application-specific conditions.

After the database was developed LLNL selected candidate coating material systems and fabrication techniques, using as a basis for selection the expected thermal barrier performance and functionally graded structures. In addition, LLNL and Pratt & Whitney jointly fabricated thermal barrier coating structures and characterized the composition and structural, thermal, mechanical, and environmental properties of the fabricated structures.

Next, LLNL and Pratt & Whitney developed several candidate application-defined ceramic/metal nanostructure microlaminates for thermal barrier turbine blade coatings. This involved fabricating the microlaminate materials, characterizing of the composition and the structural, thermal, mechanical, and environmental properties of the microlaminates, and correlating the microlaminate properties with process variables and optimizing fabrication processes. At the conclusion of this development effort a down-select was made to choose the best candidates for advanced characterization and deposition on candidate engine parts.

The next stage of the project required LLNL personnel to train Pratt & Whitney personnel in advanced laboratory techniques such as transmission electron microscopy (TEM) and grazing-angle x-ray scattering for microlaminate characterization. Next, these characterization capabilities were applied to in situ studies of interfaces and failure mechanisms for thermal barrier coatings currently used by Pratt & Whitney.

In the final project stage LLNL and Pratt & Whitney deposited several selected microlaminates on prototype components supplied by Pratt & Whitney, and Pratt & Whitney conducted laboratory tests of thermal, mechanical, and environmental properties of the microlaminate-coated prototypes. Pratt & Whitney then down-selected candidate coating systems based on its desired application-specific properties and initiated full-scale engine testing of final candidate coating systems.

## D. Partner Contribution

The responsibilities of Pratt &Whitney were to define application-specific performance requirements, to provide access to their extensive database for gas turbine engine coatings, to perform testing of the nanostructure laminates in application simulation environments, and to provide base materials for sample preparation, in addition to their in-house development of fabrication technologies and preparation of experimental samples.

## E. Documents/Reference List

a) Subject Inventions disclosed by LLNL:

A subject invention was disclosed by LLNL in the quarterly report for the reporting period 7/1/94 - 9/30/94. The Regents elected title and patented that invention. The following patents were issued:

1. U.S. Patent No. 5,538,795 (IL-9509A) Ignitable Heterogeneous Stratified Structure for the Propagation of an Internal Exothermic Chemical Reaction Along an Expanding Wavefront and Method of Making Same. Inventors Troy W. Barbee, Jr., Timothy Weihs. Issue Date: 7/23/96

2. U.S. Patent No. 5,547,715 (IL-9509B) Method for Fabricating an Ignitable Heterogeneous Stratified Metal Structure. Inventors Troy W. Barbee, Jr., Timothy Weihs. Issue Date: 8/20/96

Subject Inventions disclosed by Participant: None.

b) Licensing status:

Article XIV of the CRADA provides that each Party shall have first option to elect title to any invention made by its employees under the CRADA. If an invention is made solely by personnel of a Party, that invention shall be the property of that Party (the Inventing Party). The Inventing Party shall provide to the other Party a license option in accordance with the terms of Appendix C, Intellectual Property Agreement.

For project Intellectual Property (including Subject Inventions) first arising or produced under this CRADA, the Regents shall negotiate in good faith with Participant for a license to rights in such project Intellectual Property. The period of time reserved for Participant to negotiate a license shall be the term of the CRADA plus six months after the completion or termination of the CRADA, unless extended by The Regents. Licenses to be granted to the Participant shall be considered for aerospace applications of advanced materials for aircraft engines. Pratt & Whitney did not approach LLNL for a license in any CRADA Subject Invention or Background Intellectual Property.

## F. Acknowledgment

Participant's signature of the final report indicates the following:

1) The Participant has reviewed the final report and concurs with the statements made therein.
2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project.
3) The Participant certifies that:
   a) all reports either completed or in process are listed;
   b) all subject inventions attributable to the project have been disclosed or are included on a list attached to this report; and
   c) appropriate measures have been taken to protect intellectual property attributable to this project.
4) The Participant certifies that if tangible personal property was exchanged during the agreement, all has either been returned to the initial custodian or transferred permanently.
5) The Participant certifies that proprietary information has been returned or destroyed by LLNL.

| | | | |
|---|---|---|---|
| 12/21/98 | | 01/12/98 | |
| William Yee | Date | Troy Barbee, Jr. | Date |
| Pratt & Whitney | | Lawrence Livermore National Laboratory | |

Attachment I – Final Abstract
Attachment II – Project Accomplishments Summary
Attachment III – Final Quarterly Report

# Development and Implementation of Advanced Materials for Aircraft Engine Applications

**Final Abstract**
**Attachment I**
CRADA No. TC-0497-93-B

The objective of this project was to develop engineered nanostructure laminate materials for applications in gas turbine engines. Although the focus of this effort was on developing improved thermal barrier coatings, the data and experience gained through such project tasks as basic theoretical work and modeling of composition/structure property relationships can be applied to the development of microstructure laminates for other applications.

# Development And Implementation Of Advanced Materials For Aircraft Engine Applications:
# Development And Implementation Of Nanostructure Laminates

**Project Accomplishments Summary (Attachment II)**
**CRADA No. TC-0497-93-B**

Date: May 15, 1998 Revision: 2

## A. Parties

The project was a relationship between the Lawrence Livermore National Laboratory (LLNL) and United Technologies, Pratt & Whitney.


University of California
Lawrence Livermore National Laboratory
7000 East Avenue, L-795
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United Technologies, Pratt & Whitney Division
P.O. Box 10960
West Palm Beach, FL 33410-9600


## B. Background

Nanostructure materials represent the cutting edge of materials engineering technology. Because they can be built essentially atom by atom and molecule by molecule, the resulting materials can be designed to have new or enhanced mechanical, thermal, and other physical properties. During the 1970's multilayer films, a type of nanostructure material, became essential to the semiconductor industry for making everything from computer chips to hard disk drives. Researchers now at LLNL pioneered significant advances in multilayer fabrication technology, and developed multilayers for a wide variety of applications in the x-ray, soft x-ray, and extreme ultraviolet regions of the spectrum. Advances such as those led to the development of high-reflectivity multilayer mirrors for a new class of telescopes now being used in solar physics and astronomical research. Multilayer optics also have found applications in electron microprobes, scanning electron microscopes, x-ray lasers (especially in laser-fusion diagnostic systems) and particle beamlines in accelerators.

There are also potential applications for nanostructure materials in other types of products and components. Products incorporating nanostructure materials can potentially be produced to have such desirable properties as higher strength-to-weight ratios, lower friction surfaces, higher temperature operation, and greater corrosion resistance and fracture toughness. Multilayer nanostructure materials can also have a profound impact on manufacturing processes by decreasing the amount of machining necessary between raw material and finished product.

This project was part of a collaboration among several national laboratories and industrial participants to improve the manufacture of aircraft engines. The integrated proposal, which was

approved by the Department of Energy (DOE) as part of the 1993 TII "call for proposals," stemmed from a DOE/P&W Materials and Processing Workshop held by Pratt & Whitney in West Palm Beach, Florida, in April of 1992.

The discussions at that meeting concluded that nanostructured materials and coatings have the potential to significantly increase the performance, improve the durability, and reduce the weight of both commercial and military aircraft engines through the development of high-temperature coating materials that could allow the engines to safely be operated at higher temperatures, thereby permitting the engines to develop greater thrust. This would significantly reduce the direct operating cost (DOC) and life cycle cost (LCC) of such engines and would provide the U.S. with a technological and competitive advantage against the rising foreign aerospace industry and decrease the U.S. dependence on foreign oil, as well as increase exports by US manufacturers, which already accounted for more than $25B in annual export sales.

The development of engineered nanostructure laminate materials for such applications requires a complementary array of competencies. Pratt & Whitney is a major US supplier of aircraft engines and components, with experience in commercial and military aircraft engine materials research, development, engineering, and production. LLNL is a world leader in multilayer science, primarily because of its expertise in the design, modeling, characterization and fabrication of nanostructure materials. LLNL scientists have developed deposition processes to allow nanoengineering of materials with highly controlled structure and composition.

## C. Description

The objective of this project was to develop engineered nanostructure laminate materials for applications in gas turbine engines. Although the focus of this effort was on developing improved thermal barrier coatings, the data and experience gained through such project tasks as basic theoretical work and modeling of composition/structure property relationships can be applied to the development of microstructure laminates for other applications.

During this project LLNL was responsible for experimentally developing a database of ceramic/ceramic nanostructure-laminate fabrication processes to enable the selection of a material and structure that provides significantly enhanced thermal barrier coating performance. This included the development of a ceramic/ceramic nanostructure microlaminate database for thermal barrier coatings and the development of fabrication processes, structure and composition characterization methods, and determination of performance under application-specific conditions.

After the database was developed LLNL selected candidate coating material systems and fabrication techniques, using as a basis for selection the expected thermal barrier performance and functionally graded structures. In addition, LLNL and Pratt & Whitney jointly fabricated thermal barrier coating structures and characterized the composition and structural, thermal, mechanical, and environmental properties of the fabricated structures.

Next, LLNL and Pratt & Whitney developed several candidate application-defined ceramic/metal nanostructure microlaminates for thermal barrier turbine blade coatings. This involved fabricating

the microlaminate materials, characterization of the composition and the structural, thermal, mechanical, and environmental properties of the microlaminates, and correlating the microlaminate properties with process variables and optimizing fabrication processes. At the conclusion of this development effort a down-select was made to choose the best candidates for advanced characterization and deposition on candidate engine parts.

The next stage of the project required LLNL personnel to train Pratt & Whitney personnel in advanced laboratory techniques such as transmission electron microscopy (TEM) and grazing-angle x-ray scattering for microlaminate characterization. Next, these characterization capabilities were applied to in situ studies of interfaces and failure mechanisms for thermal barrier coatings currently used by Pratt & Whitney.

In the final project stage LLNL and Pratt & Whitney deposited several selected microlaminates on prototype components supplied by Pratt & Whitney, and Pratt & Whitney conducted laboratory tests of thermal, mechanical, and environmental properties of the microlaminate-coated prototypes. Pratt & Whitney then down-selected candidate coating systems based on its desired application-specific properties and initiated full-scale engine testing of final candidate coating systems.

D. Expected Economic Impact

The microstructure laminates developed under this project to be applied as coatings for gas turbine engine parts will enhance the physical properties of those components, reducing their DOC and LCC. The microlaminate coatings developed under this project were developed for a specific application, and Pratt & Whitney expects them to contribute to enhanced performance and characteristics of selected engine components. While it is difficult to quantify the economic impact of the specific materials developed here, the technology development conducted by the parties here has applications for the development of other microlaminate materials for other specific applications. The cumulative impact of microlaminate materials is projected to be significant, as discussed in the "Background" section of this report.

Pratt & Whitney, now that it has the TEM and x-ray characterization technology transferred under this project, can continue the assessment and characterization of additional materials for other specific applications.

E. Benefits to DOE

(1) Multilayer deposition techniques are used to produce mechanically tough, free-standing foils for various inertial confinement fusion (ICF) experiments. These support dynamic testing and pulsed power technologies, enhancing the capabilities of above-ground experiment (AGEX) programs. These AGEX capabilities may become absolutely crucial in the future as support for a total test ban grows.

In 1997, for example, the LLNL research team, led by Dr. Troy Barbee, produced more than 250 multilayer optics for laser applications, particularly for laser fusion research. Multilayer optics make possible x-ray interferometry for characterizing plasmas created by high-power lasers. These types

of optics are the only workable diagnostic tool to directly look at extremely hot, high-electron-density plasmas of matter produced in inertial confinement fusion experiments. Dr. Barbee, along with other members of the research team, has also published numerous technical articles in the field, such as "Probing High-Energy Plasmas with X-ray Lasers," "Diagnostics for High Density Implosions at Nova and the National Ignition Facility," and "Preparation of Multilayered Materials in Cross-Section for In Situ TEM Tensile Deformation Studies."

(2) Additionally, the DOE Defense Critical Technologies can benefit directly from this program. The Drell Panel recommended that positive steps be taken to eliminate the potential for accidental detonation or dispersal of weapons material present in current armaments or new weapons. Nanostructure multilayer materials are now under development for this application and show technical promise in tests to date in the fire-resistant portion of the program. Nanostructure laminate technology also has the potential to impact pulse-power technology by enabling fabrication of robust, high-energy-density capacitor devices important in many weapons and weapon simulation systems.

(3) Nanolaminate technology is also being developed to produce energy storage structures for pulsed power and electric-vehicle-load balancing applications. This CRADA will provide technical capability enhancing LLNL's efforts in these other areas. The LLNL research team involved in this project is actively conducting research into applications for nanostructure multilayer materials in energy-storage technology. Descriptions of this work can be found in such publications as "Nanostructure Multilayer Technology Fabrication of High Energy Density Capacitors for the Power Electronic Building Block" by Barbee, Johnson and Wagner.

## F. Industry Area

Aircraft

## G. Project Status

This project is completed.

## H. LLNL Point of Contact for Project Information

Troy W. Barbee, Jr.
L-350
Ph. 925.423.7796
Fax: 925.422.6892
email: barbee2@llnl.gov

## I. Company Size and Point(s) of Contact

Company Information:

United Technologies, Pratt & Whitney Division
Annual sales of Pratt & Whitney Division is $6B
Pratt & Whitney Division has 31,000 employees
Ph: 203.565.4321
Fax: 203.565.8896

Company contact at Government Engines and Space Propulsion:

William Yee
United Technologies/Pratt & Whitney
MS706-06
P.O. Box 109600
West Palm Beach, FL 33410-9600

## J. Project Examples

The purpose of this project was to conduct research into new materials for application in areas of interest to Pratt & Whitney. There are not yet product examples specifically in the area of aircraft engines.

However, several inventions made under this project have been patented by LLNL and in which there is commercial interest. Nanostructure technology was used to develop a multilayer foil with an interesting property: a match or spark from a 9 volt battery can ignite a self-propagating exothermic reaction in the foil. Such foils can be placed between two surfaces and ignited to bond the surfaces together. Such "welding foils" are a significant improvement over current bonding materials because the multilayer deposition technique produces foils that can be engineered to produce the precise heat-release rate and final temperature needed for a specific application. The foils are too expensive at present to use in general manufacturing, but there has been significant commercial interest in specific applications where cost is not such a factor.

**K. Release of Information**

I certify that all information contained in this report is accurate and releasable to the best of my knowledge.

Norma E Dunifice 2/10/99

for Karena McKinley, Director
Industrial Partnerships
and Commercialization

Date

Troy Barbee Jr. 01/12/99

Troy Barbee, Jr.
LLNL Principal Investigator

Date

RELEASE OF INFORMATION

I have reviewed the attached Project Accomplishment Summary prepared by Lawrence Livermore National Laboratory and agree that the information about our CRADA may be released for external distribution.

Bill Yee 12/21/98

William Yee
United Technologies/
Pratt & Whitney

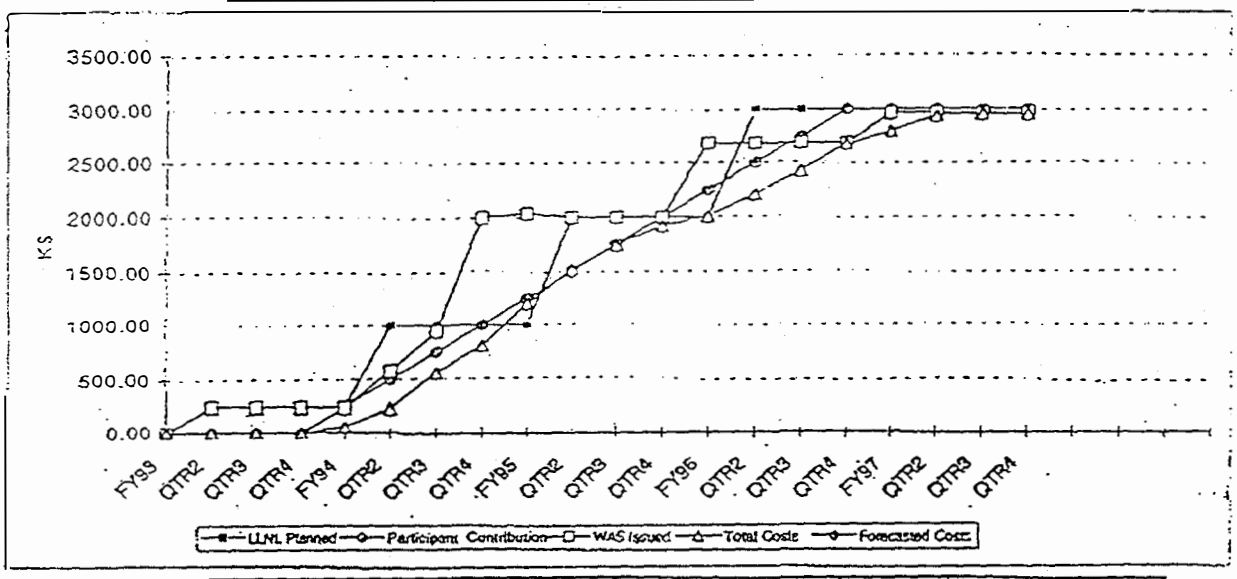
Date

## Lawrence Livermore National Laboratory

| | | | |
|---|---|---|---|
| Title: | Develop. & Implementation of Adv. Materials.. | Reporting Period: | 09/30/96 - 09/30/97 |
| Participant: | United Technologies Pratt & Whitney | Date CRADA Executed: | 10/26/93 |
| DOE TTI No.: | 93-MULT-021-D1 | DOE Approval Date: | 10/15/93 |
| CRADA No.: | TC-0497-93-B | Scheduled Ending Date: | 10/26/96 |
| Account No's.: | 4796-12 to 16, 7608-78 | Completion Date: | |
| Accounts Closed: | N/A | B & R Code (S): | DP0301, 35DP03 |

Approved Funding Profile ($K)

| | FY93 | FY94 | FY95 | FY96 | FY97 | Total |
|---|---|---|---|---|---|---|
| LLNL Planned | 246 | 754 | 1000 | 1000 | 0 | 3000 |
| Participant In-Kind | 0 | 1000 | 1000 | 1000 | 0 | 3000 |
| Participant Funds-In | 0 | 0 | 0 | 0 | 0 | 0 |
| WAS DP0301 | 246 | 1654 | -40 | 710 | 242 | 2822 |
| WAS 35DP03 | 0 | 90 | 40 | -14 | 30 | 146 |
| Total Costs | 0 | 806 | 1116 | 763 | 269 | 2952 |




| DP0301 | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | Jun | July | Aug | Sep | FYTD | 2836 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FY93 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| FY94 | 0 | 23 | 28 | 53 | 54 | 67 | 85 | 126 | 99 | 78 | 101 | 71 | 799 | |
| FY95 | 135 | 139 | 102 | 109 | 102 | 95 | 103 | 64 | 55 | 60 | 62 | 27 | 1054 | |
| FY96 | 22 | 16 | 41 | 54 | 76 | 70 | 73 | 73 | 57 | 32 | 42 | 182 | 745 | |
| FY97 | 36 | 45 | 38 | 53 | 43 | 14 | 13 | 1 | 6 | -1 | 0 | -9 | 239 | |

| 35DP03 | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | Jun | July | Aug | Sep | FYTD | 116 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FY93 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| FY94 | 0 | 0 | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | |
| FY95 | 2 | 0 | 15 | 9 | 7 | 0 | 0 | 2 | 0 | 21 | 7 | 0 | 62 | |
| FY96 | 0 | 0 | 7 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 3 | 12 | |
| FY97 | 0 | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 30 | |

STAFF w/phone:

Lab Pt: Troy Barbee Jr. (510) 423-7796 — Participant: John Appleby (407) 796-6518

Resource Manager: Al Moser (510) 423-0326

DOE OAK: Jerry Scheinberg (510) 637-1653 — DOE HQ: R. Peavy (202) 586-7907

Lawrence Livermore National Laboratory

Reporting Period: 09/30/96 - 09/30/97
DOE TTI No.: 93-MULT-021-D1
CRADA No.: TC-0497-93-B



Milestones and Deliverables:

List the complete set of milestones for all phases of the CRADA. Continue on a separate page if necessary.
Report any changes from the original CRADA or previous quarterly report on the CRADA Change Form.

| | Completion Date: Scheduled | Actual |
|---|---|---|
| 1. Fabrication and characterization of ceramic/ceramic thermal barrier coatings synthesized on P&W supplied substrates. First down selection of candidate materials. Transfer of characterization procedures to P&W. | 10/31/94 | 10/1/94 |
| 2. Fabrication and characterization of metal/ceramic and metal/metal for enhanced erosion, corrosion and oxidation resistance. Down selection of materials and engine components to be coated for prototype evaluation, and conceptual design of prototype manufacturing equipment. | 10/31/95 | 12/15/95 |
| 3. Prototype manufacturing system constructed and performance evaluated. ENL coatings deposited onto prototype parts and performance evaluated under simulated service conditions. | 10/31/96 | 6/30/97 |

Verification of participants' in-kind contribution was made in accordance with LLNL policy. Explain basis of verification:

Please initial: YES X NO

The industrial partner, Pratt & Whitney, has performed in kind work in accordance with the CRADA statement of work and has fulfilled contractual obligations, completing the majority of the milestones at this time.
Rainbow Engine tests to evaluate multilayer TBC materials and prototype manufacturing facility design and operation have been completed.

List any subject inventions by either party (include IL# for LLNL inventions), additional background intellectual property, patents applied for, software copyrights, publications, awards, licenses granted or reportable economic impacts

LLNL Patent # 5,547,715 – Method for Fabricating an Ignitable Heterogeneous Stratified I
LLNL Patent # 5,538,795 – Ignitable Heterogeneous Stratified Structure for the Propagation of an Internal Exothermic Chemical Reaction Along an Expanding Wavefront and Method of Making Same

Accomplishments

Describe Technical/Non-Technical lessons learned (address and be specific about milestones, participant contributions)
Summarize causes/justification of deviations from original scope of work. Continue on a separate page if necessary.

See attached

Reviewed by CRADA project Program Manager: Lloyd L. Chase Date:

Reviewed by Karena McKinley, Director, LLNL/IP&C: Norma E Dungee Date: 2/10/99

Direct questions regarding this Report to IP&C Resource Manager, Carol Asher, at (510) 422-7618