U.S. Navy - Office of Naval Research - AASERT Program
----- Final Project Report -----

Surface Layer Dynamics for Compliant Foul-Release Coatings

A. Project Number: N00014-94-10760 [01JUL94 - 30SEP97]
Parent Grant: N00014-89-J3101 [01JUN89 - 31JUL98]
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Name	Affiliation
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Carol Rabke, Ph.D.	Burleigh Instruments, Fishers, NY
Nissim Garti, Ph.D.	Cassali School of Applied Chemistry Tel Aviv University, Israel
Colin Rosslee	Decora/Wearlon Industries
Claes Lundgren, M.D., Ph.D.	Center for Research and Education in Special Environments, SUNYat Buffalo
William Rae, Ph.D.	Department of Mechanical and Aerospace Engineering, SUNY at Buffalo

D. Project Results

During a 3-year cooperative program, with government and industry partners specializing in nonstick coatings, the project team identified superior nontoxic, nonpolluting coating formulations for use as easy-release paints to minimize biofouling in freshwater systems. As an unexpected result, a preferred range of coating surface texture+chemistry combinations was identified that also imparted the highly desired feature of drag reduction to such foul-release systems. At the fundamental level, magnetic resonance spectroscopic data were developed that indicate how differential structuring of water clusters near hydrophobic vs hydrophilic boundaries can account for these findings. Abstracts of the two resulting M.S. theses are appended.

IUCB
INDUSTRY/UNIVERSITY
COOPERATIVE RESEARCH CENTER
FOR BIOSURFACES

DATE: 27 July 1998

RE: Submission of Final Report
Grant Number: N00014-94-1-0760
[AASERT Project]

Enclosed are copies of our final project report to ONR, as required by the grant referenced above. Also enclosed are copies of the AASERT Report (A2-2), to parties designated by the grant.

Distribution - Final Report		Distribution AASERT A2-2
3 copies	Scientific Officer Harold Guard, Ph.D. - Code 335 Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5660	1 copy for each of 3 years
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n/a	ONR Code 11SP Attn: AASERT/94 800 North Quincy Street Arlington, VA 22217-5660	1 copy for each of 3 years

Please contact me if you have any questions. Thank you.

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27 JUL 98

D.1. Meeting the Objectives

A well-trained, cross-disciplinary engineer has received his MS in Mechanical and Aerospace Engineering, based on the successfully defended thesis "Investigation of Possible Mechanisms for Inherent Drag Reduction by Biofouling-Release Coatings", and is currently employed in New York State as bioengineer in a manufacturing firm. Selected coating compositions and associated surface textures (roughness features) were identified in laboratory bench-scale trials, pilot-scale tunnel tests, and full field applications as superior performing paints for both biofouling control and energy efficiency (minimal drag). This work received additional support from the New York Sea Grant Program and from Decora/Wearlon Division, during the first year. Another student, receiving an M.S. in Biophysics for her thesis on "Use of Nuclear Magnetic Resonance to Characterize Liquids Structured From Various Liquid-Solid Interfaces", is applying for Ph.D. programs elsewhere.

D.2. Technical Poblems Overcome

Two main technical problems were encountered: (1) need for a bench scale screening test of potential drag-reducing formulations, and (2) development of an appropriate pilot-scale test of hydrodynamic performance at the extreme low-drag limit.

Prior work by the project team, utilized by industry (both national and international), and by the U.S.Navy, had already identified unique generic-level surface properties obtainable in methylsilicone-based polymeric coatings that would allow easy-release (less than 20 psi cleaning stress required) of all biofouling deposits. In question was the issue of superficial drag, the extra friction of water moving past these coatings of varying detailed surface chemical combinations and textures, and how to measure it at practical scales for coatings that were already near the hydrodynamic, theoretical minimum-drag limit. This technical problem was overcome at two levels: (a) at the bench-scale, by development, proof-testing, and application of a novel drag-flow-cell apparatus allowing determination of drag coefficients at Reynolds Numbers orders of magnitude lower than those required for pipe flow or flat plate flow; and (b) at the pilot scale, by employing aerodynamically/hydrodynamically, ideally-shaped helicopter tail rotor blades as the test objects to be coated and driven through the waters of a 60-foot-diameter, 9-foot-wide by 9-foot-deep annular channel while recording the drag forces from strain gages on the above-water-mounted helicopter blade mounting post, at velocities up to 13 knots.

D.3. New Research Directions

This project has opened up three significant new research directions: (1) optimization of the surface microarchitectures of various materials/coatings, to minimize hydrodynamic drag penalties in many circumstances of ship flow through water as well as water flow through pipes, flumes, and valves; (2) correlation of microscopic properties of materials with their macroscopic performance as foul-release coatings in challenging, biologically sensitive environments; and (3) control of exotic species transfers from ballast water compartments by nontoxic, nonpolluting coatings allowing improved flushing at available energy levels.

D.4. Ancillary Research Topics

Two important ancillary research topics were addressed, the first dealing with the "structuring" of water at the interfaces of successful foul-release, drag-reducing coatings, and the second addressing issues of potential bioremediation techniques that might be required for appropriate treatment before disposal of sand-blast-cleaning wastes from silicone-based ship coatings in dock/repair facilities.

The first topic was investigated, with support of this Navy AASERT funding, at the graduate level, resulting in the Master of Science (Biophysics) thesis " Use of Nuclear Magnetic Resonance to Characterize Liquids Structured from Various Solid-Liquid Interfaces" successfully defended by Ms.Vittoria Fruci under the supervision of project P.I., Dr. Robert Baier.

The second topic was investigated with the help of a series of undergraduate research assistants supported by the National Science Foundation's Minority, Women, and Handicapped Undergraduate Research Fellows program. Early results were presented to the 1998 Annual Meeting of the International Association for Great Lakes Research, in a paper titled "Remediation of Hydrocarbon- and Silicone-Contaminated Sand Beds by Sequential Surface-Active Displacement and Bacterial Infusion" .

D.5. Technology and Information Transfer

The project team, led by an industry partner (Mr.Colin Rosslee, Vice President, Decora Manufacturing), engaged in a significant effort for technology and information transfer to the potable water and energy generation/management sectors, submitting a winning proposal for related projects to the NYS Energy Research and Development Authority in response to PON No. 316-95, on May 30, 1995.

Beginning in July 1995, the project team worked with New York Sea Grant (NYSG) to bring this project's goals to the public's attention, culminating in a short piece titled "Release Coatings Show Promise against Fouling Organisms", published in Coastlines, Volume 25, Number 2, a publication of the New York Sea Grant Institute in Summer 1995. This was followed in August 1995 by information transfer to NYSG representative Julie Zeidner resulting in a brief for the Zebra Mussel Update Newsletter.

Important and productive technology transfer efforts were made in 1995 to provide the developing technology to Niagara Mohawk Power Corporation for testing in difficult trash-rack-coating applications. A test rack coating was deployed at Niagara Mohawk's Medina/Glenwood Lake-Oak Orchard Creek hydroelectric plant with the engineering consultation of Gibert Commonwealth Engineers and Consultants (now Parsons Power). The University at Buffalo project team worked together with the Gilbert Commonwealth Engineers through the end of 1996 in providing inspections/testing of the Decora/Wearlon release coating and formulations from competing coatings manufacturers, as well as primer-coat-only and cast black-polyethylene trash rack controls. The Wearlon coating still was performing best against raking-induced damage, while also showing easy-release properties, in June 1998.

In November 1995, the project team again worked closely with NYSG representative, Ms.Judy Hogan, obtaining press release material on the Fellowship program from Wearlon Coatings: Division of Decora Manufacturing: " We are extremely pleased.......We expect to be able to accelerate the development and full commercialization of our zebra mussel foul release coating systems and as a result be able to provide an economical, low environmental impact method to help water users in their efforts to palliate the effects of the zebra mussel plague."

Also in November 1995, the project team worked with Melissa Ratherdale, Media Assistant of the National Sea Grant College Program, to produce a broadcast release on "The Secrets of Surfaces".

In March 1996, the project team presented emerging technical results to the Sixth International Zebra Mussel and other Aquatic Nuisance Species Conference, hosted by the Michigan Sea Grant College Program in Dearborn, Michigan, and popularized a general public understanding of these results by promulgating this "20/20 rule" : The quantitative mechanical requirement for nontoxic coatings to be designated as "foul-relase" or easy-release" is that they can be cleaned of all visible biofouling at pressures less than 20 psi without losing their initial chemical/energetic qualities for at least 20 cleaning cycles. In short, 20/20 "perfect" coatings are those that can be easily cleaned at least 20 times with a hose or damp rag and still be as good as new!

In May 1996, the detailed project results were shared with other investigators and research managers at the U.S.Naval Research Laboratory, the U.S. Navy Office of Naval Research, the New York State Museum Biological Survey, the New York State College of Ceramics, Bioceramics Institute, and the Niagara Mohawk Power Corporation, in addition to investigators and managers at the University at Buffalo and Decora Manufacturing/Wearlon Division.

In July 1996, the Office of Naval Research was given advance notice of a planned international presentation of Mark Ricotta's exciting research results on drag-reducing properties of the foul-release coatings, and also of the additional industry support contribution to be made of training/access for Atomic Force Microscopy of the project's test coatings by Burleigh Instruments Corporation of Fishers, NY.

In March 1997, significant technical findings of the project were presented to a U.S. Office of Naval Research-sponsored U.S.-Pacific Rim Workshop on Emerging Nonmetallic Materials for the Marine Environment, under the title "Intrinsic Drag Reduction of Biofouling-Resistant Coatings" by Robert E. Baier, Anne E. Meyer, Robert L. Forsberg, and Mark S. Ricotta.

In May/June 1997, the project team was contacted by and responded to the University of Wisconsin Sea Grant Institute, adding information to their builiding national Sea Grant worldwide web site to provide access to all Sea Grant research and outreach on zebra mussels and other aquatic nuisance species.

In July 1997, the project team publicly demonstrated the actual pilot-scale testing of successful drag-reducing coatings on helicopter tail rotor blades, forced at increasing velocities up to 13 knots through the annular water channel of the Center for Research and Education in Special Environments, under the direction of Claes Lundgren, MD, PhD. Present for the demonstrations were Ms. Jody Wood, Branch Head of the Non-Acoustics Branch, U.S. Navy Coastal Systems Station, Panama City, FL, and Mr. Bruce Johnson, Engineer, Underwater Projects, NAVEODTECHDIV, Indian Head, MD. A video tape of the testing procedure/data acquisition steps has been made and shared with technical colleagues; a short sequence is scheduled to appear with other project-related footage in a nationally distributed video tape being prepared by the University of California at Berkeley for the U.S. National Science Foundation's Industry/University Cooperative Research Centers Program.

Also in preparation is an "Applications Note" to be published by Burleigh Instruments Corporation in their industrial series, demonstrating the impressive capabilities of Atomic Force Microscopy to discern microstructural surface details of the drag-reducing coatings.

An invention disclosure also is in preparation, at the University at Buffalo, teaching uniquely suitable combinations of surface chemistry and surface texture that maximize drag-reduction performance of foul-release coatings.

The project results on both successful and unsuccessful coatings are reviewed, graphed and tabulated in Volume Four/1997 of Naval Research Reviews, under the title "Certification of Properties of Nontoxic Fouling-Release Coatings Exposed to Abrasion and Long-Term Immersion". Anticipating future broad use of the coatings developed from this work, public notice also been given of the need to be concerned about the entire product life-cycle--especially including possible generation of silicone-coated paint-blasting wastes, sands, and sludges that may require special considerations for remediation. A technical paper presented by the project team at the 41st conference of the International Association for Great Lakes Research, May 1998, addressed this issue under the title "Remediation of Hydrocarbon- and Silicone-Contaminated Sand Beds by Sequential Surface-Active Displacement and Bacterial Infusion".

E. Accomplishments

This project has met its main goals of providing graduate educational opportunities to two Masters Degree candidates, while demonstrating that practical, abrasion-resistant paints can serve as nontoxic, nonpolluting coatings that provide easy-release of attached biofouling debris. Beyond those goals, the project has opened the way to unanticipated cost and energy savings by minimizing the surface drag associated not only with fouled toxic, prior-art paints but also with the clean surfaces of easy-release, nontoxic paints freshly applied. A reward for the original investment in good environmental stewardship --replacing poison paints with biocompatible coatings-- has been discovery of an entirely new path to energy efficiency.

Details of this advancement in scientific knowledge, and its reduction to engineering practice, are published in the Master of Science thesis "Investigation of Possible Mechanisms for Inherent Drag Reduction by Biofouling-Release Coatings", produced by Graduate Fellow Mark Ricotta. Western New York industry has gained a uniquely trained and exceptionally well-qualified bioengineer, employing Mark Ricotta now as a research engineer with Harmac Medical Products, a leading local manufacturer of flow-sensitive medical devices, including blood tubing sets and catheters.

E.1. Students Supported

Mark S. Ricotta
Master of Science in Mechanical and Aerospace Engineering
February, 1998
Thesis title: "Investigation of Possible Mechanisms for Inherent Drag Reduction of Biofouling-Release Coatings"
State University of New York at Buffalo - Buffalo, NY 14260
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Vittoria Fruci
Master of Science in Biophysics
February, 1997
Thesis title: "Use of Nuclear Magnetic Resonance to Characterize Liquids Structured from Various Liquid-Solid Interfaces"
State University of New York at Buffalo - Buffalo, NY 14260
Currently applying to Ph.D. programs nationally

E.2. Publications

Baier RE, Meyer AE, Forsberg RL, and Ricotta MS (1997) Intrinsic Drag Reduction of Biofouling-Resistant Coatings. Proceedings, Emerging Nonmetallic Materials for the Marine Environment, March 18-20, 1997, Honolulu, HI, sponsored by U.S. Office of Naval Research, pp 1/35-1/40.

Matousek JA, Meyer AE, Wells AW, and Baier RE (1997) Evaluation of Nontoxic Fouling-Release Coatings as a Means of Reducing the Attachment of Zebra Mussels (*Dreissena polymorpha*) at Great Lakes Generating Stations. Final Project Report, prepared for Niagara Mohawk Power Corporation, Syracuse, NY.

Meyer AE, Baier RE, Kohl J, Singer IL, Griffith J, Haslbeck E, Montemarano JA, Ross A, Schultz M, and Swain G (1997) Duplex Foul-Release Coatings; Environmental Security Technology Certification Program: Advanced Nontoxic Antifouling Coatings Technology Demonstration. Naval Surface Warfare Center, Carderock Division, Report NSWCCD-TR-64-96/15.

Meyer AE and Baier RE (1997) Examination of Silicone Release from Biofouling-Control Coatings. Abstract Volume, IAGLR '97, International Association of Great Lakes Research, June 1-5, 1997, Buffalo, NY, page 31.

Wells AW, Meyer AE, Matousek JA, Baier RE, and Neuhauser EF (1997) Nontoxic Foul-Release Coatings for Zebra Mussel Control. Waterpower '97:Proceedings of the International Conference on Hydropower, American Society of Civil Engineers, August 1997, Vol. I, pp 451-460.

Baier RE, Meyer AE, and Forsberg RL (1997) Certification of Properties of Nontoxic Fouling-Release Coatings Exposed to Abrasion and Long-Term Immersion. Naval Research Reviews, XLIX(4):60-65.

Baier RE, Gollus SM, Patel J, Miller SM, and Forsberg RL (1998) Remediation of Hydrocarbon- and Silicone-Contaminated Sand Beds by Sequential Surface-Active Displacement and Bacterial Infusion. Abstracts Volume, IAGLR '98, International Association of Great Lakes Research, May 18-22, 1998, Hamilton, Ontario, page 44.

E.3. Patents

An invention disclosure is in preparation, describing uniquely suitable combinations of surface texture and surface composition for minimizing surface drag of environmental coatings, and methods for the production/control of such coating features.

F. Benefits

Benefits from the project have been, first and foremost, the successful education and training of 2 Master of Science students--culminating in award of the M.S. in Biophysics, in 1997, and M.S. degree in engineering, in 1998, based on immediate and continuous experience in the connection of basic research with applied problem solving. Further, a working network has been formed among national and international leaders in the fields of surface science and coating technology, as exemplified in the joint publications referenced herein, showing the way to development of graduate programs customized to emphasize interdisciplinary approaches leading to broad employment opportunities as well as doctoral study options after completion of the Masters Degree program. Project P.I., Dr. Robert Baier, has been appointed as of January,1998 to the academic position of Director of the Interdisciplinary Graduate Program in Biomaterials at the State University of New York, and will extend these successful activities to many more deserving candidates through a distance-learning network now in the curriculum design phase.

Benefits to government and industry partners have been intensive study of and data development for numerous coating formulations, with identification of a key, basic formulation as the best performer in the context of both easy-release of biofouling and in drag minimization. Basic research ranging from the atomic level, gaging water structural details by magnetic resonance spectroscopy and surface textural details by Atomic Force Microscopy, to the macroscopic level, correlating formulation chemistry with actual drag reduction performance on large hydrofoil blades, has provided the Navy and industry with guidance for future optimization of formulations and application procedures. The initial working relationship between one industry partner and the university was strengthened because of the availablity of federal funding. This opportunity to form relationships with and among many industries is a hallmark of the industry/university cooperative research program headquartered at SUNY Buffalo, engaging 4 universities (Memphis, Alfred, and Miami, in addition to Buffalo), 15 industry sponsors, and 3 federal agency sponsors in addition to the U. S. Office of Naval Research.

Benefits to the university and its faculty have included (a) provision of fellowship support to two deserving graduate students, (b) provision of critical financial support for basic research on the role of surface chemistry and physics in biological adhesion, and (c) development of working relationships with industry, strengthening the mutual commitments of the industry-university partners to assure that common objectives are met.

Benefits to the U.S. Navy and the nation have been (a) the transformation of two young Bachelor's level engineers to the Master of Science level, skilled in the application of analytical and surface science principles to coating design and control of hydrodynamic performance, (b) demonstration of both successful and unsuccessful aspects of industry/university mechanisms for jointly performing and cost-sharing collaborative scientific research, and (c) advances in nontoxic coating technology for controlling, with increased efficiency and economy, the effects of biological fouling on industry and commerce (e.g. power generation, potable water handling), recreation (e.g. boating), and ecosystem health (e.g exotic species flushing during ballast water exchange).

G. *Desiderata*

Slides and video tapes showing the accomplishments of this project are available. The University at Buffalo investigators are working actively with members of the investment community to acquire commercial rights to the advanced technology/formulations demonstrated, leading to economic development and improved environmental and public health --at lower cost--in New York State and nationally. Although the emphasis in this project has been on nontoxic, nonpolluting coatings to control biofouling in flowing water, the project team has become convinced that these same types of coatings hold exceptional promise as hardy, easy-clean, infection-resistant paints for clinical facilities, operating rooms, and food handling establishments.

USE OF NUCLEAR MAGNETIC RESONANCE TO CHARACTERIZE LIQUIDS STRUCTURED FROM VARIOUS LIQUID-SOLID INTERFACES

by Vittoria Fruci

January, 1997

A thesis submitted

to the Department of Biophysics

Faculty of the Roswell Park Division

of the State University of New York at Buffalo,

in partial fulfillment of the requirements for the degree of

Master of Science

Acknowledgments

I would like to thank the Office of Naval Research for funding this work, Grant N00014-94-1-0760, and Dr. R. Baier, Principal Investigator of this research and my major advisor.

This work could not have been accomplished without the enormous contribution of my committee members, Dr. R. Mazurchuk, and Dr. J. Alderfer. Dr. Mazurchuk's unending guidance and help throughout my student status, and critical evaluation of my thesis were immensely appreciated. Dr. Alderfer's help and guidance with the MR Spectroscopy experiments were also greatly appreciated, along with support from the Roswell Park Cancer Institute Core, Grant CA16056, to the Nuclear Magnetic Resonance Facility.

Dr. H. Box was wonderfully supportive throughout my student status and with the use of his labs. I am grateful for having had the pleasure of learning from Ed Budzinski and Harold Freund in the labs and shop. Special thanks to Patty Pohl for her helpful suggestions to my numerous questions.

Dr. R. Wollman was invaluable in teaching me the MR Spectroscopy technique, as was Matt Budzinski with the MR Imaging techniques and I am grateful for all their help. Walt Tabaczynski also provided instruction with the MR Spectroscopy technique. Donation of L-DOPA-Lys from Dr. M. Olivieri was appreciated.

Thanks to Dr. Meyer, Bob Forsberg, Lee Webber, and the entire IUCB staff for their help.

Special thanks to my family, for their support and patience throughout this trial.

ABSTRACT

Biofouling debris is more easily detached from hydrophobic methylated surfaces than from higher-surface-energy, hydrophilic materials contacting biological systems. For methylsilicone polymers, hydrodynamic drag reduction may accompany easy-release of biological slimes in turbulent flow conditions. This study explored the use of magnetic resonance spectroscopy (MRS) and magnetic resonance imaging (MRI), to detect liquid structure differences induced by contact at hydrophobic versus hydrophilic boundaries.

Examinations of tubes by MRS showed that methylated walls induced apparently more stable, organized liquid structures than hydrophilic specimens, suggesting a mechanism for drag reduction by the boundary layer stabilization adjacent to methylsilicone coatings. Specifically, this research found significant differences in T2 relaxation times as measured by full width at half maximum (fwhm), between hydrophilic and hydrophobic tubes filled with water/acetone solutions and acetone alone.

Higher T2 for the hydrophilic tubes correlate with liquids free to rotate in solution. Shorter T2 for the methylated surfaces correlate with protons less mobile in solution and represent a more structured or ordered liquid phase. The differential mobility of liquids adjacent to hydrophilic versus hydrophobic surfaces, as measured by T2 and fwhm is illustrated with schematics of possible organized structures.

Three experimental standards containing control and treated glass tubes were constructed and examined by spin-echo and short-time inversion recovery MRI techniques. Each standard included methylated (hydrophobic) glass tubes and otherwise identical gas-plasma-treated (hydrophilic) glass tubes filled with various combinations of

water, deuterium oxide, acetone, adhesive dipeptide solution, hydrophilic fumed silica, or hydrophobic fumed silica. Three different experimental standards were constructed in order to increase the number of specimens that could be imaged at one time. Single static MRI images of adjacent liquid-filled tubes resulted in heterogeneous signal intensities as a function of tube treatment, water dilution, and instrument operating conditions. Preliminary MRI flow experiments yielded changes in magnetic resonance signal intensity as a function of flow velocity using rectangular flow channels and controlled conditions.

INVESTIGATION OF POSSIBLE MECHANISMS FOR INHERENT DRAG REDUCTION BY BIOFOULING-RELEASE COATINGS

by

Mark S. Ricotta

January, 1998

A thesis submitted to the Faculty of the Mechanical and Aerospace Engineering Department of the State University of New York at Buffalo in partial fulfillment of the requirements for the degree of

Master of Science

ABSTRACT

Biofouling has become an area of major concern for hydroelectric power plants, marine industries, and other aquatic operations. Zebra mussel fouling, for instance, decreases water flow through intakes and trash racks, decreases speed of boats, and increases power expended by ships due to high surface drag forces. Nontoxic biofouling-release coatings have been developed to decrease this problem. In addition to having nonstick, easy-release properties, low-adhesion surfaces have exhibited modest drag reduction, although the exact mechanism is not known.

The objective of this research was to investigate the possible mechanisms for this inherent drag reduction, using both macroscale and microscale experiments. A Stagnation Point Flow Cell was employed to measure the flow properties of microscope-slide-sized samples, while a larger scale Water Tunnel Drag Study tested the drag on coated helicopter tail rotor blades. Surface analytical techniques of MAIR Infrared Spectroscopy, Contact Angle Analysis, Atomic Force Microscopy, and Stylus Profilometry were used to characterize each surface.

Results suggest that low-adhesion surfaces best reduce drag by the combination of at least three different mechanisms: (1) low- to very-low surface energies, as a result of methyl siliconization, partial fluorination, or outermost surfaces dominated by closely packed methyl groups that shed accumulated biomass deposits at very low shear stresses; (2) surface-layer turbulence suppression by coating compliance; and (3) microroughness, at a scale that supports nucleation, entrapment and release of microbubbles into the boundary layer and free stream flow.

Section 6 CONCLUSIONS AND FUTURE CONSIDERATIONS

The research performed spanned two main areas: (1) fluid mechanics, by way of drag measurements, and (2) surface science, by means of surface analytical techniques. The latter provided the means by which the flow phenomena could be explained. It is now clear that a combination of factors is necessary to initiate and enhance the empirically observed inherent drag reduction of some low-adhesion surfaces. Low-surface-energy (low critical surface tension) coatings with biofouling-release, low-adhesion surfaces dominated by closely packed methyl groups, have been shown earlier to yield reductions in drag in a stagnation point flow cell. This research now shows that the presence of a particular range of surface microroughnesses, as determined by atomic force microscopy and stylus profilometry, improves said drag reductions, by the probable mechanism of recurrent microbubble nucleation, growth and release into the boundary layer of the flow. The maximum amount of drag reduction was achieved by coatings combining these surface modifications. In a practical, large-scale experiment, testing the drag on coated helicopter tail rotor blades, these coatings performed well in reducing drag under controlled conditions. Limits of arithmetic average roughness and peak roughness height were noted, at which increases in drag were measured when the values were exceeded.

On an economic and industrial level, some of these coatings are already commercially available and no drag increases are associated with them when there is correct coating application. The new ability of controlled surfaces to resist biofouling, while at the same time to hold fuel, power, and other economic costs to a minimum or reduce them, may seem revolutionary. Yet, the results reported here suggest reasonable mechanisms by which such surfaces do reduce drag. By no means is the investigation into this problem final. Theoretical and experimental background has been given to substantiate a new theory explaining the observed drag reductions. Extensive research beyond the scope of this project will be required for a complete answer, but may begin with the following suggestions.

The blade mounting and data recording system may perform better with some improvements. As this was a first design, it is probable that there were a few errors present. The ability to coat the blades to manufacturers' exact specifications will surely enhance the ability to make direct correlations between the data and the best coating qualities. That does not imply, however, that the coating procedure used here tainted the results; it actually allowed for a deeper look into the mechanism of drag due to surface irregularities, and revealed that these formulations can be extremely application-sensitive. Another suggestion is to reposition the blade, as a slight pitch in the blade may have increased contribution of form drag. While great care was taken to maximize the skin friction while reducing the form drag, there is the chance that it still could be improved upon.

Further investigation should address the theory of microbubble-associated drag reduction. Perhaps a method should be tried to visualize what is occurring at the surface, such as Doppler Imaging, or high speed filming. Doppler may be the better technique, however, as it is currently used to detect bubbles in high pressure blood flow experiments at the University at Buffalo's Physiology Department and the Center for Research and

Education in Special Environments. If possible, this may present a means by which the numbers or sizes of bubbles present, could be determined, supporting this proposed breakthrough in fouling-control coating technology.

ACKNOWLEDGMENTS

Work of this caliber cannot be performed wholly by one person, and requires the input, experience, and help of others. I would like to thank the following people for their time and patience in helping with this project:

Dr. R. E. Baier, my major advisor, for providing guidance when I needed it and the enthusiasm for work that inspired me; Dr. A. E. Meyer, outside reader and advisor, for laboratory training and the reminders to get motivated; Dr. W. J. Rae, committee member, for help with questions; and Dr. R. E. Mates, committee member, who led me to Dr. Baier at the start of my Graduate School career.

Dr. C. Lundgren, for patience, and use of the centrifuge and water tank for drag studies; David Suggs and Bruce Laraway, for help with the water tunnel drag study; Robert L. Forsberg, for the much appreciated help in the lab; Lucas Latini, for obtaining the helicopter tail rotor blades and help with the blade mounting; Fred D. Archer III, for help in the laboratory, and the comic relief; Zair Fishkin, for help with the strain gage apparatus; Jim Zobel and Carol Rabke at Burleigh Instruments (Fishers, NY), for the opportunity to use Atomic Force Microscopy; and John Smith and others at Wearlon (Fort Edwards, NY), for materials used.

I would also like to thank my family, for their support and encouragement throughout this endeavor, and all my friends, both from home, and from the Industry/University Center for Biosurfaces at the University at Buffalo, for their support.

REPORT DOCUMENTATION PAGE			*Form Approved* *OMB No. 0704-0188*
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.			
1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE 24JUL98	3. REPORT TYPE AND DATES COVERED Final [01JUL94 - 30SEP97	
4. TITLE AND SUBTITLE Surface Layer Dynamics for Compliant Foul-Release Coatings			5. FUNDING NUMBERS N00014-94-1-0760 [AASERT grant] [parent grant is N00014-89-J-3101]
6. AUTHORS Robert E. Baier, Ph.D., P.E.			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) State University of New York at Buffalo Industry/University Center for Biosurfaces 110 Parker Hall Buffalo, NY 14214-3007			8. PERFORMING ORGANIZATION REPORT NUMBER 150-4938A-Final
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5660			10. SPONSORING / MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES [parent grant performance period is 01JUN89 - 31JUN98; final report submitted separately]			
12a. DISTRIBUTION / AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This project experimentally validated prior observations and theoretical justifications of the Zisman "critical surface tension"(CST) zone between 20 and 30 mN/m as the least retentive of deposited biomass, thus defining a useful "window" for selection of nontoxic,nonpolluting easy-release coatings for control of biofouling. Two Masters Degree thesis projects, one dealing with correlation of surface properties and hydrodynamic drag reduction, the other with magnetic resonance spectroscopy/imaging studies of structured water adjacent to controlled surfaces, extended these findings to circumstances where true drag reduction, from about 2% to over 20%, was obtained with biofouling-release coatings having distinct combinations of hydrophobicity and surface texture while also meeting the Zisman CST criterion.

14. SUBJECT TERMS coatings , surface energy, surface texture, critical surface tension, biofouling, drag reduction			15. NUMBER OF PAGES 18
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT unlimited