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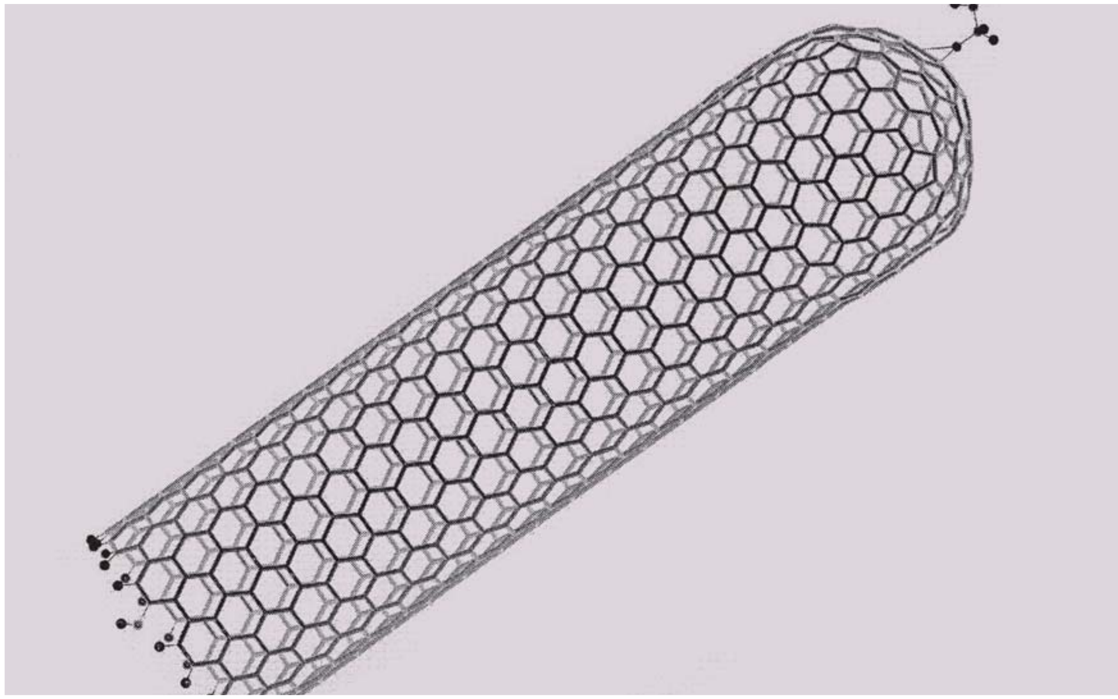
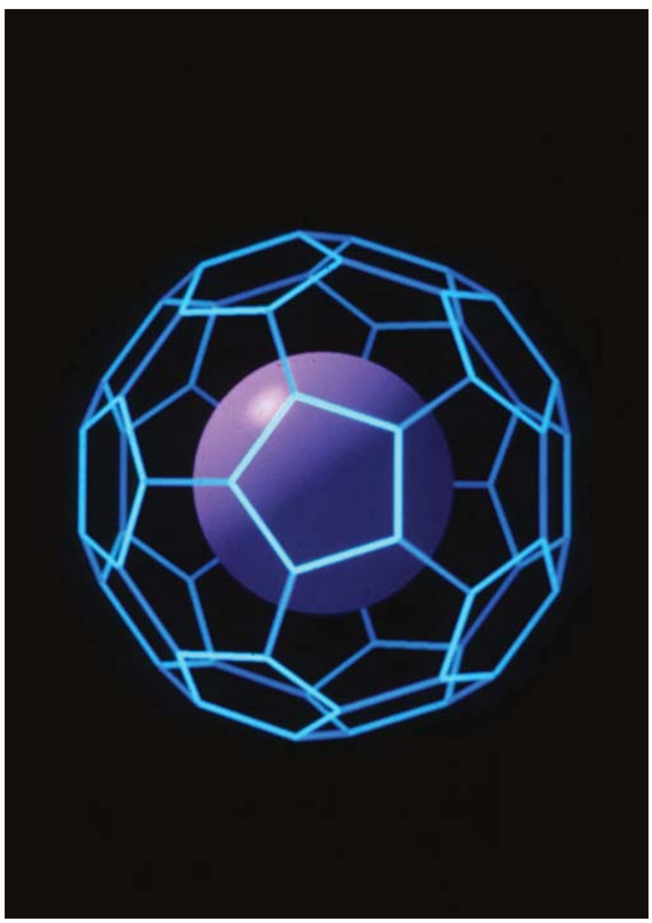
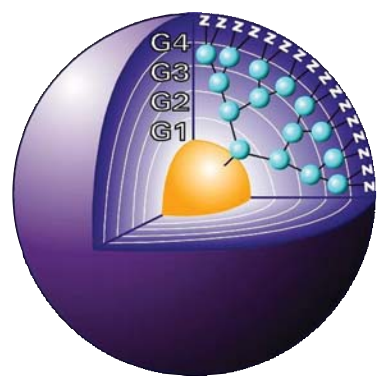
Studies in Materials Innovation

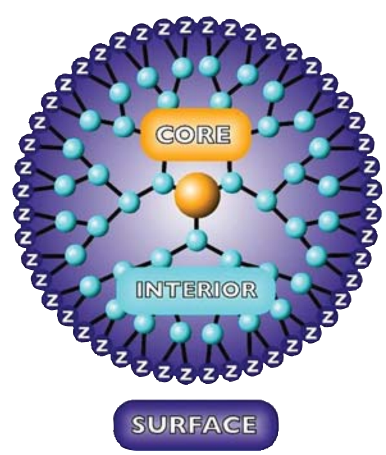
Innovation and Regulation on the Open Seas: The Development of Sea-Nine Marine Antifouling Paint

Jody A. Roberts









Chemical Heritage Foundation

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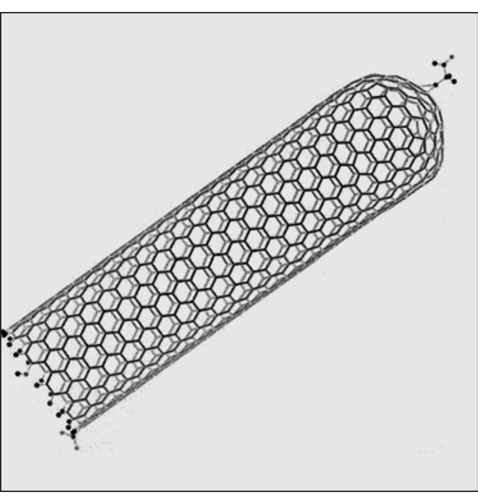

Printed in the United States of America.

For information about the Chemical Heritage Foundation, its Center for Contemporary History and Policy, and its publications write:

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Design by Willie•Fetchko Graphic Design

Cover: Buckytube and buckyball images, gift of Richard E. Smalley, Chemical Heritage Foundation Collections.
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I. EXECUTIVE SUMMARY

The development of Sea-Nine marine antifouling paint linked agricultural biocides, coatings research, and federal and international regulation. The introduction of the marine coating in the 1990s was heralded as a “green” alternative to the toxic tin-based coatings widely used up to that point. Arriving at the final product, however, required the team at Rohm and Haas to negotiate a tricky technical and legal terrain. Drawing on internal expertise as well as outside help, the company was able to develop and deliver its new product in a timely manner. Meanwhile, work with and through the regulatory systems helped open new market possibilities for the company and place Sea-Nine at the forefront of a previously unexplored marketing niche. The case offers a number of important lessons for current molecular research, emphasizing the role of collaboration for expertise and the ways in which regulation (real and pending) can spur the innovation process.

II. INTRODUCTION: TECHNOLOGICAL CHANGE AND AN OPEN MARKET

The need to protect surfaces exposed to marine environments from "fouling" by both organic and inorganic matter has been and continues to be a prominent concern among those operating in these environments. Fouling, or the buildup of unwanted matter on the surface of, for example, a ship hull, presents a host of problems. Damage to the material surface is first among these. However, innovations in materials used in marine environments coupled with rising energy costs have shifted concerns away from damage toward the problems associated with drag, which causes increased energy consumption and therefore a loss of energy efficiency.[1]

Fouling can be addressed by two primary means: either preventing the initial attachment and therefore the buildup of the fouling material or using a toxic substance to kill any biological fouling materials. In the past, antifouling methods emphasized coatings that could be applied to surfaces to prevent the attachment of fouling matter. More recently, coatings research has merged with chemical-pesticide technologies to create coatings that both inhibit attachment and provide a toxic environment for any organic matter that does latch on. In the later twentieth century this method has been used to a great extent.

Increasing concerns over the toxicity of the leaching biocides, however, have created another shift in marine antifouling technology. Early coatings employed a multitude of heavy metals—arsenic and mercury, for example—as their key biocides. But as evidence of the persistence and toxicity of these elements grew in other arenas, these metals were replaced, primarily by the use of tributyltin, known more generically (especially in the legal literature) as organotin. This organic metal matrix slowly leached from the surface coating to kill any organic matter that had attached to the surface of the submerged material.[2]

By the early 1980s evidence demonstrating the toxicity of organotin compounds in salt and fresh water began to emerge, and the United States passed the "Organotin Antifouling Paint Control Act of 1988." While the legislation was a significant development, it only applied to vessels less than 25 meters long. The more important developments were international in scope, encouraged in large part by research conducted in

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[1] For some history on marine fouling, or biofouling, see E. Almeida, T. C. Diamantino, and O. de Sousa, "Marine Paints: The Particular Case of Antifouling Paints," *Progress in Organic Coatings* 59:1 (2007), 2–20.

[2] For rising concerns related to the use of biocides and specifically to tributyltin, see I. J. Boyer, "Toxicity of Dibutyltin, Tributyltin and Other Organotin Compounds to Humans and to Experimental-Animals," *Toxicology* 55:3 (1989), 253–298; G. W. Bryan and W. J. Langston, "Bioavailability, Accumulation and Effects of Heavy-Metals in Sediments with Special Reference to United-Kingdom Estuaries—a Review," *Environmental Pollution* 76:2 (1992), 89–131; and J. P. Meador, "Predicting the Fate and Effects of Tributyltin in Marine Systems," in *Reviews of Environmental Contamination and Toxicology,* ed. George W. Ware, vol. 166, 1–48 (New York: Springer-Verlag, 2000).

Japan, which helped lead to efforts by the International Maritime Organization to push for an outright ban on the use of organotin-based antifouling coatings. Despite attempts on the part of the organotin manufacturers to prevent the adoption of a ban, the race was already on to find the next generation of marine antifouling agents.

ORIGINS OF A MOLECULE

In 1970 researchers at Rohm and Haas submitted a patent application for a new class of compounds that they grouped under the title 3-isothiazolones. They listed eighty-one examples of these chemicals. In the patent the authors highlighted the promise these chemicals offered in terms of their broad-based biocidal properties, with specific attention to their role in the control of the growth of microorganisms. By the end of the 1970s Rohm and Haas was actively cataloging the biocidal properties of many of these molecules.[3]

It should come as no surprise then that the 3-isothiazolones found their way to market through the agricultural division of the company. The general molecular structure was adapted through the years for various applications, including polymer latex, cosmetics, metal cutting, and cooling towers. Biocide business opportunities are niche markets, however, and so finding new applications for the 3-isothiazolones was an ongoing activity.[4]

Research results from the agricultural and biocides division made their way to the coatings division at Rohm and Haas through the attempt to create a paint moldicide to be used in coatings applications. The experience of placing active biocides in a coatings medium opened the door to the pursuit of what eventually became Sea-Nine.

ORIGINS OF THE PROJECT

Rohm and Haas began setting up the platform on which Sea-Nine would be built in the early 1980s, just as research on the lingering effects of organotin compounds was first emerging in the scientific literature. The project began slowly, but by 1988 the company decided to begin the necessary background data collection for final Environmental Protection Agency (EPA) approval.

Getting Sea-Nine ready for regulatory approval required Rohm and Haas to mobilize forces. Experts on testing, ecotoxicity, and biotoxicity were brought into the project. But while managers worked to navigate a changing regulatory environment, standards for testing this new product in aquatic environments still needed to be constructed. Researchers at the company needed to engage with new customers. The logistics of producing a new product and distributing it to new users required coordination. Technical aspects of working in a new medium needed to be explored. And an entire industry needed to be convinced that this new, more expensive alternative should be adopted.

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[3] See the following patents: Sheldon N. Lewis, George A. Miller, and Andrew B. Law, 1970, Certain Z-Carbamoyl-J-isothiazolones, U.S. patent 3,523,121, filed Oct. 3, 1967, and issued August 4, 1970; idem., 1973, 3-Isothiazolones, U.S. patent 3,761,488, filed Jun. 25, 1969, and issued Sept. 25, 1973; and idem., 1978, 3-Isothiazolones as biocides, U.S. patent 4,105,431, filed Jun. 8, 1973, and issued Aug. 8, 1978. For a more general discussion of biocide activity at Rohm and Haas during this period see Sheldon Hochheiser, *Rohm and Haas: History of a Chemical Company* (Philadelphia: University of Pennsylvania Press, 1986), 33–40, 186–194.

[4] Hochheiser, *Rohm and Haas,* 186–194.

III. USERS

The development of Sea-Nine required the personnel at Rohm and Haas to partner with a fresh user base. The users, in this case the firms responsible for the creation of coatings for use in marine environments, were a circumscribed group composed of between six and ten major businesses, mostly northern European. But since the global ban on organotin antifoulants was expected to extend beyond the 25-meter rule developed in the 1988 U.S. law to an outright ban on all vessels, the U.S. Navy also became an important partner.

Users had two main reasons to cooperate closely with the team at Rohm and Haas. First, the looming tin ban threatened to leave them without a viable product. And while some companies chose to wait for more obvious signs that the ban was coming, others actively sought out partners for the development of next-generation antifouling coatings. Second, the coatings manufacturers knew that careful consideration needed to be paid to the incorporation of any antifouling agent into their coatings.

DEVELOPING RELATIONSHIPS IN ANTICIPATION OF THE BAN

Major manufacturers of marine coatings found themselves in a difficult position in the later 1980s. Evidence against organotin antifoulants was accumulating, and a ban seemed inevitable. But there was no clear timeline to anticipate when the ban would go into effect. To avoid the prospect of finding themselves with no product to offer legally, many companies began to seek partnerships with specialty-chemical manufacturers to pursue the next generation of marine antifoulants.

BORROWING EXPERTISE

These early partnerships were beneficial to both the chemical manufacturers and the paint producers because it allowed them the time to ensure that 1) the new product would clear regulatory hurdles, 2) the product would be functional, and 3) the antifouling components would be successfully worked into the coatings formulations. For those working in coatings research this last point was clearly the most important. Coatings formulations require a delicate balancing act since every time an ingredient is added or adjusted, testing must be done to ensure that the properties of the individual components as well as of the overall product have not been affected.

Antifouling works at two different levels. "Hard" antifouling works to prevent such events as barnacle growth. "Soft" antifouling works on smaller organisms. In the case of Sea-Nine, researchers wanted to incorporate both aspects into the coatings. The 3-isothiazolones, as biocides for microorganisms, aimed at the soft-fouling targets. The coating still needed to incorporate a metal to contribute the hard-fouling protection needed for large oceangoing vessels. Of course, this metal could not be a number of previously used elements (mercury, arsenic, and now tin) but had to be toxic to a specific range of organisms. Thus, Sea-Nine is actually a two-part toxic formulation: it uses isothiazolones to eliminate microorganisms and copper to prevent barnacle growth.

In designing and formulating the active ingredients in the final product two concerns must be addressed: the active ingredient has to be released slowly to ensure the product has a long lifetime but remains effective, and the ingredient must not present any major problems for formulation. Researchers working at Rohm and Haas encountered both problems while working with end users. First, the active ingredients, more precisely the isothiazolones, needed to be placed into a medium—some sort of molecular "cage"—that would allow for a controlled release. Further, the structure of these molecular cages needed to be compatible with the other ingredients found in the coating. While Rohm and Haas eventually found a way to stabilize the molecule, this area of research is ongoing. The second problem, making the ingredient compatible with the coatings formulation, also emerged during early collaborations. The active ingredient in its stabilized form polymerized the coating in an unanticipated and undesired way. The team at this point needed to share polymer expertise between Rohm and Haas and user groups. The partnership helped the team overcome the unanticipated consequences of product development.

IV. REGULATIONS

Regulation served as an important motivator in the development of Sea-Nine antifouling paint—if not the most important. While the 1988 U.S. legislation left a large portion of the marine-coatings business unaffected, it signaled the validity of the growing concerns over the continued use of organotins. The focus also shifted away from the United States to an international context dominated in large part by research and pressure coming from Japan and northern European countries. The emerging regulations offered a number of opportunities for the researchers working on Sea-Nine. The search for alternative antifouling agents allowed Rohm and Haas to enter into a relatively closed market and to participate in establishing new techniques for testing leaching of agents into marine environments.

WORKING WITH AND FOR REGULATION

Rohm and Haas had already begun the development of Sea-Nine when the United States passed their restrictions on organotin compounds in 1988. The passing of the legislation and the impending international regulation, however, encouraged researchers and managers at Rohm and Haas to increase the pace at which they were exploring the possibility of placing their biocide into a marine coating. The company was in a good position. As an outsider to the marine-coatings industry they had little to lose initially if the ban did not happen but plenty to gain if it did. The company took a two-pronged approach. From a technical perspective the Sea-Nine team began the long (in this case exceedingly long) EPA approval process. At the same time the company actively supported the ban. Supporting the ban was made easier because the company was able to demonstrate that alternatives to the tin-based compounds could be made and that these alternatives were equal or superior to the materials they were designed to replace.[5]

WHAT COUNTS AS AN ADEQUATE TEST?

The registration process, however, highlighted another problem: what would count as an adequate test for the environmental impact of these new compounds? Since the isothiazolones under development were relatively new to the marine environment (although having been thoroughly tested in other environments), there was little base knowledge to draw on for testing for their sloughing rate, biopersistence, and biotoxicity. Since the

[5] See, for example, G. L. Willingham and A. H. Jacobson, "Efficacy and Environmental Fate of a New Isothiazolone Antifoulant," in *The Proceedings of the Third Asia-Pacific Conference of the Paint Research Assocation,* 14.1–14.13 (Brussels: International Centre for Coatings Technology, 1993); and G. L. Willingham and A. H. Jacobson, "Designing an Environmentally Safe Marine Antifoulant," in *Designing Safer Chemicals,* edited by S. C. DeVito and R. L. Garrett (Washington, DC: American Chemical Society, 1996), 224–233.

experts on these matters were already housed within Rohm and Haas, the company was able to participate in the establishment of the new standards.

THE SHIFTING OF MARKETS

But it was not just the EPA that needed to be convinced. Users of the intermediate product (coatings manufacturers) and users of the final product (those requiring marine coatings) had to be convinced that the ban was indeed coming and that this new product delivered performance that warranted its adoption. While Sea-Nine entered the market in 1995 to much fanfare, sales were sluggish until the end of the decade when experience by Japanese firms (who had been using the product the longest) combined with a deadline for the international tin ban in 2003. The early release of Sea-Nine (and a few competitors) helped make the transition from the pre- to post-tin era relatively uneventful in the marine world.[6]

Early introduction of Sea-Nine has also allowed for its ongoing development. While many of the team members have moved back or moved on to other projects, a new team continues to work on tweaking the many variables at play. Controlling the release of the active ingredient with new molecular structures continues to be an area of intense interest. And researchers have also had to grapple with the ongoing evolution of the toxicological fate of Sea-Nine. Finally, research in the area of antifouling coatings continues with new tools that use nanotechnology and obviate the need for toxic components through the creation of surfaces that prevent the adherence of fouling agents.[7]

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[6] For examples of the news surrounding the release of Sea-Nine see Elizabeth S. Kiesche and David Hunter, "Regulations Create a Hairy Environment for Biocides; EPA Reregistration Drives Up Costs," *Chemical Week* 151 (1992), 24; Associated Press, "Rohm and Haas Receives EPA Registration for Marine Paint Biocide," LexisNexis, 5 April 1994; Allison Lucas, "Rohm and Haas Enters U.S. Marine Biocides Market," *Chemical Week* 154 (1994), 12.

[7] As with most new chemicals, it was hard to truly understand what the fate of Sea-Nine would be once it was in commercial use. However, as new tributyltin alternatives have gone into use, testing for the presence and toxicity of these antifoulants has steadily increased, which has offered a slightly different picture of these molecules. See, for example, A. H. Jacobson and G. L. Willingham, "Sea-Nine Antifoulant: An Environmentally Acceptable Alternative to Organotin Antifoulants," *Science of the Total Environment* 258 (2000), 103–110; Naomasa Kobayashi and Hideo Okamura, "Effects of New Antifouling Compounds on the Development of Sea Urchin," *Marine Pollution Bulletin* 44 (2002), 748–751; Dorthe K. Larsen, Inge Wagner, Kim Gustavson, Valery E. Forbes, and Torben Lund, "Long-Term Effect of Sea-Nine on Natural Coastal Phytoplankton Communities Assessed by Pollution Induced Community Tolerance, *Aquatic Toxicology* 62 (2003), 35–44; and I. K. Konstantinou and T. A. Albanis, "Worldwide Occurrence and Effects of Antifouling Paint Booster Biocides in the Aquatic Environment: A Review," *Environment International* 30 (2004), 235–248.

V. FINDINGS

The case of the development of Sea-Nine marine antifouling paint offers three lessons that can be applied to current innovations in the molecular sciences.

1. Unanticipated consequences that inevitably emerge during material innovation can be more easily managed through the networks between researchers and users.

   The early establishment of networks between research, development, and use was not only advantageous from a marketing perspective but also from a technical perspective. It gave the Rohm and Haas team the ability to work through hidden problems (like the polymerizing properties of isothiazolones) before the product hit the market. It also provided the opportunity to tailor research to fit the intended uses.

2. Collaborations between users and researchers can last beyond the life of the project, both literally and conceptually through the codevelopment of new expertise.

   Many of those involved with the development of Sea-Nine saw the most important outcome as the connections made between those working within the company and experts on the outside. Sharing expertise on a project that benefits multiple parties had two distinct benefits. First, it allowed Rohm and Haas to expand its knowledge base quickly through collaboration rather than taking the time to develop its own expertise internally, a long-term investment. Second, it provided a platform to test future collaborative possibilities with little to no commitment.

3. Regulation and the anticipation of regulation can provide strong incentive to innovate within old markets.

   Perhaps the most relevant finding of this case is the role that perceived future regulation played in the development of Sea-Nine. While researchers at Rohm and Haas had begun investigations into the potential use of 3-isothiazolones in such alternative mediums as aquatic coatings, it was the forecasted ban on organotins that encouraged the development of the product. The pending ban created new market opportunities, the opportunity to collaborate with new external partners, and the ability to help shape the standards later adopted for aquatic testing. Further, the progress made at Rohm and Haas (and by its competitors) added security to a market that felt threatened by what paint manufacturers feared would be a transition period after the tin ban went into effect. Ultimately, the research and development of Sea-Nine made the global ban possible, just as Sea-Nine was made possible by the prospect of the regulation.

VI. APPENDIXES

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2. ACKNOWLEDGMENTS AND AUTHOR'S NOTE

The author wishes to thank the Chemical Heritage Foundation's Gore Innovation Project for initial support in the research involved in the construction of this case. Thanks to the interviewees, Wendy Bingman, Lou Graziano, Andy Jacobson, Rich Nichols, and Mike Sheehan. Special thanks to Betsy Taube of Rohm and Haas for coordinating the interviews and my trips to Spring House.

3. ABOUT THE ROBERT W. GORE MATERIALS INNOVATION PROJECT

Begun in 2006, the Robert W. Gore Materials Innovation Project, conducted by the Chemical Heritage Foundation's Center for Contemporary History and Policy, aims to illuminate the diverse contributions of materials innovation within the broader process of technological development in the contemporary age. Conceived as a three-year project, it documents, analyzes, and makes known the immense benefits of materials innovation through its white paper series, Studies in Materials Innovation, and public symposia.

The Gore Innovation Project is made possible by the generous financial contribution of Robert W. Gore, chairman of W. L. Gore & Associates.

Many staff members within the Chemical Heritage Foundation made the project possible. In particular, Arthur Daemmrich and Arnold Thackray were instrumental in conceptualizing the project. Thanks to Ron Reynolds and Jody Roberts, for providing intellectual support, and to Chi Chan, for the excellent and much-needed administrative skills that sustained the project. Special thanks are accorded to the scholars who contributed research and writing expertise for the case studies in the series.

Finally, we were fortunate to establish a partnership with the Center for Nanotechnology in Society, University of California, Santa Barbara (CNS-UCSB), which is supported by the National Science Foundation cooperative agreement #SES-0531184. Barbara Herr Harthorn, director of CNS-UCSB, generously offered to provide assistance in distributing the completed case studies through the CNS network. The Chemical Heritage Foundation is grateful for this unique opportunity that allows us to spread the results of our project more broadly.

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About the author

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