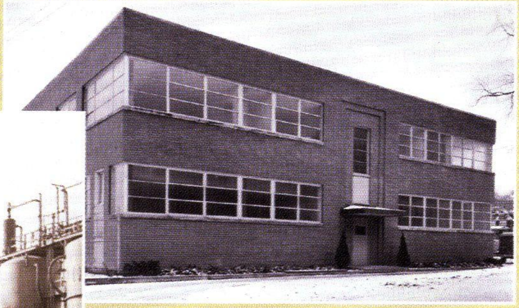
# A NATIONAL HISTORIC CHEMICAL LANDMARK

# THE SOHIO ACRYLONITRILE PROCESS

BP CHEMICALS INC.
WARRENSVILLE HEIGHTS, OHIO

SEPTEMBER 13, 1996




AMERICAN CHEMICAL SOCIETY
Division of the History of Chemistry and
The Office of Public Outreach

This booklet commemorates the designation of the Sohio Acrylonitrile Process as a National Historic Chemical Landmark. The honor was conferred by the American Chemical Society, a non-profit scientific and educational organization of 150,000 chemists and chemical engineers. A plaque marking the designation was presented to BP Chemicals Inc. at the company's headquarters and research and development center in Warrensville Heights, Ohio, on September 13, 1996. The inscription reads:

At this site, Sohio researchers developed the "Sohio Acrylonitrile Process," an innovative single-step method of production that made acrylonitrile available as a key raw material for chemical manufacturing worldwide. Sohio's groundbreaking experimentation and bold engineering brought plentiful, inexpensive, high-purity acrylonitrile to the market, a principal factor in the evolution and dramatic growth of the acrylic plastics and fibers industries. Today, nearly all acrylonitrile is produced by the Sohio process, and catalysts developed at the Warrensville Laboratory are used in acrylonitrile plants around the world. Sohio became part of The British Petroleum Company p.l.c. in 1987.

***On the Cover:*** **(Clockwise) Sohio's Cornell Road research laboratory, about 1942; the acrylonitrile R&D team; workers in front of Sohio's first acrylonitrile plant, Lima, Ohio.**

***Acknowledgments:***

**The American Chemical Society gratefully acknowledges the assistance of those who helped prepare this booklet, including Mark C. Cesa, James F. Brazdil, Lynn M. Moravcik, Frederick A. Pesa, Wilfrid G. Shaw, and Anthony A. Kozlowski, all of BP Chemicals Inc.; Jim Marino of By Jim Marino; and Paul R. Jones, University of Michigan, the NHCLP Advisory Committee liaison.**

**This booklet was produced by the ACS Office of Public Outreach. Layout: Dahlman/Middour Design. Photographs courtesy of BP Chemicals Inc.**

# ACRYLONITRILE

Chances are that acrylonitrile touches everyone in some way every day. Acrylonitrile is the key ingredient in the acrylic fiber used to make clothing and carpeting; in acrylonitrile-butadiene-styrene (ABS), a durable material used in automobile components, telephone and computer casings, and sports equipment; and in nitrile rubber, which is used in the manufacture of hoses for pumping fuel.

Acrylonitrile is used to produce plastics that are impermeable to gases and are ideal for shatter-proof bottles that hold chemicals and cosmetics, clear "blister packs" that keep meats fresh and medical supplies sterile, and packaging for many other products. It is also a component in plastic resins, paints, adhesives, and coatings.

The acrylonitrile in those products was made by a process discovered and developed in the 1950s by scientists and engineers at The Standard Oil Company, or Sohio, which became part of British Petroleum (BP) in 1987. The process is a single-step direct method for manufacturing acrylonitrile from propylene, ammonia, and air over a fluidized bed catalyst.

The discovery and commercialization of this process were the result of the talent, imagination, teamwork, and risk-taking by Sohio's employees. Sohio's discovery led to the production of plentiful and inexpensive acrylonitrile of high purity as a raw material and to dramatic growth in the thermoplastics, synthetic fiber, and food packaging industries. Today more than 95% of the world's acrylonitrile is produced by BP or made under its license.

## Early History

Acrylonitrile, first synthesized in 1893 by Charles Moureu, did not become important until the 1930s, when industry began using it in new applications such as acrylic fibers for textiles and synthetic rubber.

Although by the late 1940s the utility of acrylonitrile was unquestioned, existing manufacturing methods were expensive, multistep processes. They seemed reserved for the world's largest and wealthiest principal manufacturers: American Cyanamid, Union Carbide, DuPont, and Monsanto. At such high production costs, acrylonitrile could well have remained little more than an interesting, low-volume specialty chemical with limited applications.

In the late 1950s, however, Sohio's research into selective catalytic oxidation led to a breakthrough in acrylonitrile manufacture. The people who invented, developed, and commercialized the process showed as much skill in marketing as in chemistry. The result was such a dramatic lowering of process costs that all other methods of producing acrylonitrile, predominantly through acetylene, soon became obsolete.

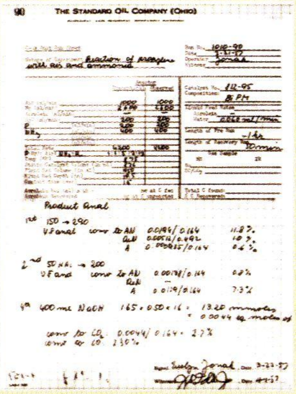
# THE SOHIO PROCESS

Founded by John D. Rockefeller, Sohio was a petroleum company known for efficient refining and skilled marketing. Before 1953, it had done no research on chemicals or petrochemicals—research was limited to the development of petroleum products and processes. No one among the 80 researchers working at Sohio's laboratory, then located on Cornell Road in Cleveland, was thinking about a shortcut to world-class acrylonitrile production.

The picture changed when Franklin Veatch, a research supervisor reporting to E.C. Hughes, director of research, proposed that converting light refinery gases such as the aliphatic hydrocarbon propane to oxygenates—compounds containing oxygen—could be profitable. At the time, oxidation of aliphatic hydrocarbons was primitive and expensive. Veatch's idea was to use metal oxides to convert hydrocarbons to oxygenates. Funding was approved for this effort beginning in 1953.


***Left to right:*** **Jim Callahan, Ernie Milberger, Jim Idol, Frank Veatch, and Gordon Cross, 1971.**

In addition to starting new research, Sohio ventured into the petrochemical business by building ammonia and nitrogen plants in Lima, Ohio, and near Joplin, Missouri, to use by-products from its petroleum refinery. It was a conservative move, but it encouraged Sohio to view chemicals as a commercial enterprise—a venture that would lead to remarkable success.




**A page of Evelyn Jonak's March 22, 1957, laboratory notes from the first single-step synthesis of acrylonitrile. The experiment worked on the first try.**

Early experiments in Veatch's research yielded no major developments, and he was given a six-week deadline. The resulting crash program succeeded when a test run was made on propylene over a modified vanadium pentoxide oxidant, and the resultant odor was instantly recognizable as acrolein. Veatch knew that one more oxidation step would take acrolein to acrylic acid—an important, expensive, fast-growing monomer. For the next two years, several researchers, including Ernest C. Milberger, James L. Callahan, Robert W. Foreman, James D. Idol, Jr., Evelyn Jonak, and Emily A. Ross, were involved in this development effort.

In 1955 the team began testing oxidants as direct oxidation catalysts. In an experiment designed by Jim Callahan and performed by Emily Ross, bismuth phosphomolybdate produced acrolein in yields of 40 percent or more. This was a first-magnitude discovery: propylene to acrolein in a single catalytic reaction step. Acrylic acid could be made in a subsequent step. Callahan, Foreman, and Veatch secured key patents on the bismuth phosphomolybdate catalyst, and from then on, things were destined to happen fast.

Jim Idol suggested acrylonitrile as a derivative of acrylic acid and successfully carried out catalytic conversion of the ammonium salt of acrylic acid. Next, acrylonitrile was made by feeding acrolein, ammonia, and air over the catalyst that produced acrylic acid from acrolein. This success suggested that acrylonitrile might be made directly from propylene by carrying out the entire reaction in a single step with bismuth phosphomolybdate. The experiment, designed by Idol and performed by Evelyn Jonak in March 1957, resulted in ammoxidation, a process that produced acrylonitrile in about 50 percent yield with acetonitrile and hydrogen cyanide as co-products.

With the capacity to make acrolein, acrylic acid, and acrylonitrile by efficient, revolutionary new processes, Veatch pressed for a strong development and commercialization effort. The Patents and Licensing department went to work on securing an iron-clad patent position. Because manufacturing both acrylic acid and acrylonitrile proved to be too ambitious, acrylonitrile production became the priority.

Sohio's process economics for acrylonitrile were so positive that the decision was made to proceed with commercialization even though early market development efforts were discouraging. Major users were unsure that Sohio acrylonitrile would satisfy their needs. One major chemical company declined an opportunity for a joint venture. Another company announced plans for a new 100-million-pound-per-year acrylonitrile plant based on the old acetylene technology, at a cost of $100 million.

Still, Sohio commissioned the design of a detailed acrylonitrile plant. A pilot plant was constructed under the direction of Gordon G. Cross at Sohio's new laboratory in Warrensville Heights, a Cleveland suburb, where Ernie Milberger was instrumental in designing large laboratory-scale reactors and obtaining process design and development data from them.

In a bold move, it was decided to design the commercial plant on the basis of bench-scale laboratory development data rather than wait for pilot plant results. The time gained by eliminating this stage of development offset the added risk. Milberger's bench-scale unit, which required about 4 pounds of catalyst, generated the key data for the design of commercial reactors holding 40 tons.

By early 1958, the commercial design was going forward under the direction of Edward F. Morrill; a pilot plant was in operation; the catalyst was in final development by Callahan and his team with provisions for large-scale manufacture; and advancement work on reactor operation, product purification, and waste disposal was being coordinated. A key innovation was the successful development of a fluidized bed catalyst to allow for removal of the heat produced by the ammoxidation reaction.

By mid-winter 1959–60, the Lima, Ohio, plant, which cost $10 million to build, was complete. In less than four years since the discovery of bismuth phosphomolybdate as the direct propylene oxidation catalyst and the discovery of propylene ammoxidation, a full-scale commercial plant designed to produce 47.5 million pounds of acrylonitrile per year was ready to go.

There was but one challenge left—an economic one. Soon after Sohio's entry, a major manufacturer cut its price in half. Sohio met the lower price and still managed to make a profit. The competitor scrapped its own expansion plans and took a license from Sohio. Other acrylonitrile producers soon became licensees of the Sohio process, and within a few years, acetylene-based acrylonitrile production had been replaced by the Sohio process.

To gain a larger share of the overall market, Sohio decided to promote the licensing of the process rather than keep the manufacturing to itself. Sohio's license to The People's Republic of China in 1973 was the first transaction by an American company after China opened its doors to U.S. investment. Today, following Sohio's lead, BP has licensed 42 companies to produce acrylonitrile in 77 plants in 21 countries. Annual worldwide production of acrylonitrile has grown from 260 million pounds in 1960 to more than 9 billion pounds in 1995.

Since 1960 BP Chemicals has developed and commercialized seven improved catalyst formulations, most of them based on the original bismuth phosphomolybdate catalyst. BP's current research focuses on further improvements to the Sohio Acrylonitrile Process and on new technology using the less expensive propane as feedstock.

**Sohio's Warrensville Research Center in 1984.**

# THE PEOPLE

Six individuals played the most prominent roles in Sohio's acrylonitrile project.

**Franklin Veatch** was research supervisor for petro-chemicals, polymers, and new petroleum processes. He possessed a technical, creative genius, and he inspired co-workers to achieve a goal, however impossible it might seem. Veatch received his B.S. and M.S. degrees from the University of Arizona and his Ph.D. from Stanford University in 1947. He held 61 U.S. patents by the time of his retirement in 1978. He died in 1980.

**James L. Callahan,** a research associate, coordinated catalyst research and development, including the discovery of improved methods of catalyst manufacture. He was renowned for converting hydrocarbon materials to petrochemicals. Callahan received his B.S. degree from Baldwin-Wallace College and his M.S. degree and, in 1957, his Ph.D. from Case Western Reserve University. Retired since 1985, he is credited with more than 200 patents and publications.

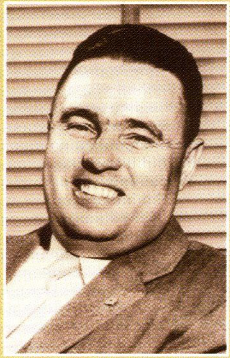
**Edward F. Morrill,** as president of Vistron Corp., was the product–process champion on the business side. Vistron was the chemical division of Sohio from 1966 to 1982. Morrill received his bachelor's degree in civil engineering from Case Institute of Technology in 1929. His ability to "see" a revolutionary and economically dominating chemical process was crucial to the project's success. Morrill took the necessary risks that led to successful commercialization.

**James D. Idol, Jr.,** a research associate who supervised and carried out research and feasibility testing, holds the basic patent for the process. He received his B.A. degree in chemistry from William Jewell College and, in 1955, his Ph.D. in chemistry from Purdue University.

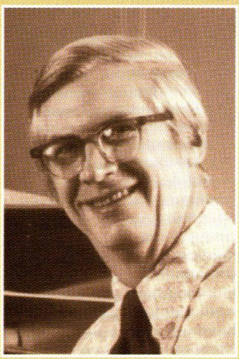
**Ernest C. Milberger,** a research associate, carried out the advancement of the Sohio process from small-scale research to pilot plant. He received his A.B. and M.A. degrees in chemistry from the University of Missouri and his Ph.D. from Case Western Reserve University in 1957. He holds 80 patents, mostly in the catalytic process area.

**Gordon G. Cross,** a development supervisor, was responsible for pilot plant development of the Sohio process, as well as for preliminary engineering and precommercial economic evaluation of the overall process concept. He received his B.S. degree in chemical engineering from Ohio State University and, in 1960, his M.S. degree in engineering administration from Case Institute of Technology.

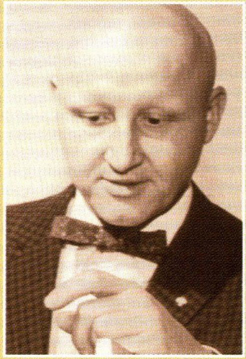
Other significant contributors to the invention, development, and commercialization of the Sohio process include **Arthur F. Miller**, a research associate who developed the commercial method for manufacturing improved catalysts; **Robert K. Grasselli**, a catalyst research associate who was involved in the early oxidation research, the development of subsequent generations of Sohio catalysts, and the detailed mechanisms of ammoxidation reactions; and **Robert W. Foreman**, a group leader during the early research phase and a co-inventor of the bismuth phosphomolybdate propylene-to-acrolein catalyst.



Ed Morrill



Art Miller



Bob Foreman

Bob Grasselli

# FURTHER READING


B. D. Berber and K. E. Anderson. "Petrochemicals," *Modern Petroleum—A Basic Primer of the Industry*. Tulsa, OK: Petroleum Publishing Co., 1978.

J. F. Brazdil. "Acrylonitrile," *Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 1*. New York: Wiley-Interscience, 1991.

J. L. Callahan, R. W. Foreman, and F. Veatch. "Process for the Oxidation of Olefins," *U.S. Patent No. 2,941,007*, June 14, 1960.

J. L. Callahan, R. K. Grasselli, E. C. Milberger, and H. A. Strecker. "Oxidation and Ammoxidation of Propylene Over Bismuth Molybdate Catalyst," *Industrial and Engineering Chemistry Product Research and Development*, 9 (1970): 134–42.

J. F. Henahan, senior editor. "The Chemical Innovators 14. James D. Idol, Jr.—Setting the World of Nitrile Chemistry Afire," *Chemical & Engineering News*, 49(27) 1971: 16–18.

J. D. Idol, Jr. "Process for the Manufacture of Acrylonitrile," *U.S. Patent No. 2,904,580*, Sept. 15, 1959.

"Pace Setter in New Acrylonitrile Process," *Chemical Week*, 88(3) (1961): 39–40.

"Profitable Process Patent," *Forbes*, 95(5) (1965).

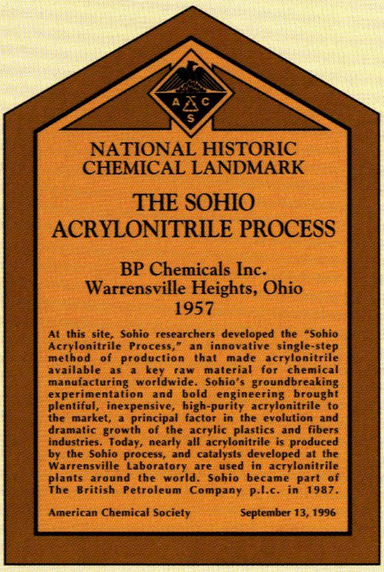
"Sohio Has Shortcut to Acrylonitrile," *The Oil and Gas Journal*, June 22, 1959, 80–81.

P. H. Spitz. *Petrochemicals—The Rise of an Industry*. New York: Wiley and Sons, 1988.

F. Veatch, J. L. Callahan, J. D. Idol, Jr., and E. C. Milberger. "New Route to Acrylonitrile," *Chemical Engineering Progress*, 56(10) (1960): 65–67.

K. Weissermel and H-J. Arpe. "Acrylonitrile," *Industrial Organic Chemistry, Second Edition*. New York: VCH, 1993.


# THE NATIONAL HISTORIC CHEMICAL LANDMARKS PROGRAM OF THE AMERICAN CHEMICAL SOCIETY




The ACS National Historic Chemical Landmarks Program recognizes our scientific and technical heritage and encourages the preservation of historically important achievements and artifacts in chemistry, chemical engineering, and the chemical process industries. It provides an annotated roster to remind chemists, chemical engineers, students, educators, historians, and travelers of an inspiring heritage that illuminates both where we have been and where we might go when traveling the diverse paths to discovery.

The BP Chemicals - Sohio Acrylonitrile Process is the 11th National Historic Chemical Landmark to be designated under this program.

An ACS Historic Chemical Milestone designation marks a landmark step in the evolution of the chemical sciences and technologies. A Site designation marks the location of an artifact, event, or other development of clear historical importance to chemists and chemical engineers. An Historic Collection designation marks the contributions of a number of objects with special significance to the historical development of chemistry and chemical engineering.

This program began in 1992, when the Division of the History of Chemistry of the ACS formed an international Advisory Committee. The Committee, composed of chemists, chemical engineers, and historians of science and technology, works with the ACS Office of Public Outreach and is assisted by the Chemical Heritage Foundation. Together, these organizations provide a public service by examining, noting, recording, and acknowledging particularly significant achievements in chemistry and chemical engineering. For further information, please contact the ACS Office of Public Outreach, 1155 Sixteenth Street, N.W., Washington, DC 20036; 1-800-ACS-5558, ext. 6274.

**The American Chemical Society**
Ronald Breslow, President
Paul S. Anderson, President-Elect
Joan E. Shields, Board Chairman
John K Crum, Executive Director
Ann B. Messmore, Director, Public Outreach

**ACS Division of the History of Chemistry**
Joseph B. Lambert, Chairman
Harold Goldwhite, Chairman-Elect
Vera V. Mainz, Secretary-Treasurer

**ACS Cleveland Section**
James Murtagh, Chairman
James D. Burrington, Chairman-Elect
Mark C. Cesa, Immediate Past Chairman
Anthony J. Pearson, Acting Secretary
David W. Ball, Treasurer
Charles K. Beck, Chairman, Archives Committee

**BP Chemicals Inc.**
Bryan Sanderson, Chief Executive Officer
Chris Gibson-Smith, Deputy Chief Executive Officer
Robert Mesel, Chief Executive, Nitriles Division

**ACS Advisory Committee on National Historic Chemical Landmarks**

*Chairman:*
Ned D. Heindel, Lehigh University
James J. Bohning, American Chemical Society
Jon B. Eklund, National Museum of American History
Yasu Furukawa, Tokyo Denki University
Leon Gortler, Brooklyn College
Paul R. Jones, University of Michigan
James W. Long, University of Oregon
Peter J. T. Morris, Science Museum, London
Mary Jo Nye, Oregon State University
Stanley I. Proctor, Jr., Proctor Consulting Service
David J. Rhees, Bakken Library and Museum
Jeffrey L. Sturchio, Merck & Co., Inc.
Frankie K. Wood-Black, Phillips Petroleum
Ann C. Higgins, ACS Staff Liaison

**American Chemical Society**
1155 Sixteenth Street, N.W.
Washington, D.C. 20036