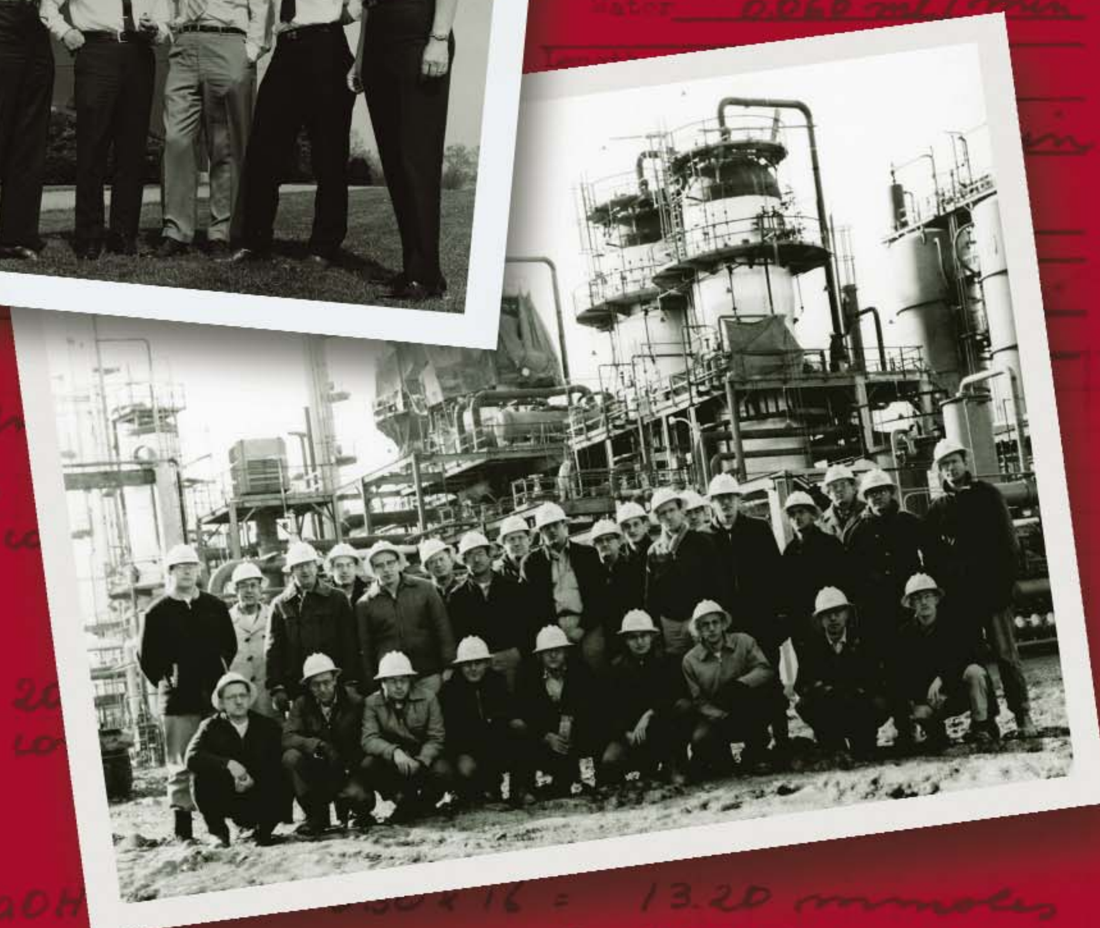
The Sohio Acrylonitrile Process

November 14, 2007

A National Historic Chemical Landmark



American Chemical Society
SCIENCE THAT MATTERS

acrylonitrile

“In many ways, [the Sohio Acrylonitrile Process] was considered one of the most important achievements of its time.” Peter H. Spitz, *Petrochemicals: The Rise of an Industry.* John Wiley and Sons, 1988, p. 297

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 thermoplastic 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. These plastics are ideal for shatterproof bottles that hold chemicals and cosmetics and for clear “blister packs” that keep meats fresh and medical supplies sterile. Acrylonitrile 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. The acrylonitrile manufacturing and catalyst and licensing businesses are now part of INEOS. 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 INEOS or made under its license.

Early History

Acrylonitrile, first synthesized in 1893 by Charles Moureu, did not become important commercially 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 and work began in 1953.

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.

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 he 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 four 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 the INEOS (Sohio) Acrylonitrile Process is utililzed in over 90% of the world's acrylonitrile production, representing plants in sixteen countries worldwide. Annual worldwide production of acrylonitrile has grown from 260 million pounds in 1960 to more than 11.4 billion pounds in 2005.

Since 1960 several improved catalyst formulations have been developed, most of them based on the original bismuth phosphomolybdate catalyst. INEOS's current research focuses on further improvements to the Sohio Acrylonitrile Process.

National Historic Chemical Landmark

The American Chemical Society designated the Sohio Acrylonitrile process as a National Historic Chemical Landmark in a ceremony in Warrensville Heights, Ohio, on September 13, 1996. A second designation ceremony took place on November 14, 2007 at the headquarters of INEOS, in League City, Texas. The commemorative plaque reads:

In Cleveland, Ohio, 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, over ninety percent of the world's acrylonitrile is produced by the Sohio process. The Sohio acrylonitrile manufacturing and catalyst and licensing businesses, formerly owned by Sohio and subsequently BP Chemicals, are now part of INEOS. Catalysts developed by INEOS scientists and engineers are used in acrylonitrile plants around the world.

About the National Historic Chemical Landmarks Program

The American Chemical Society, the world's largest scientific society with more than 160,000 members, has designated landmarks in the history of chemistry for more than a decade. The process begins at the local level. Members identify milestones in their cities or regions, document their importance, and nominate them for landmark designation. An international committee of chemists, chemical engineers, museum curators, and historians evaluates each nomination. For more information, please call the Office of Communications at 202-872-6274 or 800-227-5558, e-mail us at nhclp@acs.org, or visit our web site: www.chemistry.org/landmarks.

A nonprofit organization, the American Chemical Society publishes scientific journals and databases, convenes major research conferences, and provides educational, science policy, and career programs in chemistry. Its main offices are in Washington, DC, and Columbus, Ohio.

Acknowledgments:

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The American Chemical Society thanks Jeff D. Denson, Logistics SHE Consultant, INEOS Nitriles and Mark C. Cesa, Senior Research Associate, INEOS Nitriles for their contributions to the duplicate plaque text and the revised brochure. Thanks also to Kris Garza of INEOS Nitriles for all her help.

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