Zeolites Catalyze Patent Dispute

Patent infringement suits involving corporate giants could hinge on esoteric points of analytic data; much is at stake

A high-stakes patent dispute whose outcome could affect hundreds of millions of dollars worth of business has been taking place in the chemical industry over the past few years. It involves several corporate giants, including Mobil Oil, Union Carbide, and Standard Oil of Indiana, which are battling over rights to catalysts called zeolites. The contest is likely to be decided in part on some fine points of analytical chemistry.

Until the early 1960's, the study of the cage-like zeolite molecules was a sleepy business, and their main use was as ion-exchange resins in water softeners. That picture has changed radically, however. Hundreds of synthetic zeolites have now been produced, and they have found broad commercial use as catalysts in processes ranging from petroleum refining to the preparation of specialty chemicals. U.S. oil refineries must replenish more than 2000 tons of catalyst per day, according to an industry source.

Mobil pioneered much of the technology and currently dominates the field. It has been using zeolites extensively to produce high-octane unleaded gasoline, an application that is likely to expand outside the United States as the use of lead additives to boost octane ratings is phased out in Europe.

More recently, Union Carbide and Amoco Chemicals, a subsidiary of Standard Oil of Indiana, have entered the field with zeolites of their own. Union Carbide has concentrated on the manufacture and sale of the materials to other firms that use them in production processes. However, during the past few years, Union Carbide has invested in firms that are developing catalytic processes, suggesting a deepening corporate interest in the technology. Amoco has been using xeolites in a variety of processes, including the production of xylene.

As the applications of zeolites expanded and the commercial stakes increased—some industry analysts predict that potential uses of the materials will involve hundreds of millions of dollars—it was perhaps inevitable that the major competitors would come into legal conflict over rights to the technology. The first move was made by Union Carbide. In 1982, it filed suit against Mobil, contending that claims in several of Mobil's basic zeolite catalyst patents are invalid and asking the court to enjoin Mobil from threatening Union Carbide with a patent infringement suit.

A few months later, Mobil filed a suit of its own against Amoco. It alleges that Amoco infringed Mobil's basic zeolite catalyst patents, and also broke a licensing agreement between the two corporations governing Amoco's commercial production of xylene. Mobil says the royalties that were owed when the suit was filed exceeded $1 million. The company is seeking an injunction against Amoco and recovery of all costs and triple payment of damages.

Amoco subsequently lodged a countersuit that, like Union Carbide's, asks the court to agree that Amoco is not infringing on Mobil's key patents but also to declare those patents invalid. Amoco says that it has observed the licensing agreements between the two companies and that it has paid "substantial royalties . . . and lease fees to Mobil." Amoco also asserts that Mobil is "unlawfully suppressing and controlling competition" for the use and sale of zeolite catalysts in the United States.

"Mobil has tried to lock this field up," asserts one industry scientist. But many other companies are now developing zeolite catalysts, and "nobody has a lock on intelligence."

These legal actions are currently bogged down in the pretrial "discovery" phase during which the companies' scientists and lawyers pore over the documents that will either make or break their respective cases. Negotiations to find an out-of-court settlement are also taking place, according to sources who asked not to be identified. Although the outcome of the two closely related contests is by no means clear yet, it could determine whether Mobil will continue to dominate this growing but already lucrative field and it will have implications for other companies in the petrochemical industry, some of which have partnership development agreements with the parties to the lawsuit. "Mobil has tried to lock this field up," asserts one industry scientist. But many other companies are now developing zeolite catalysts, and "nobody has a lock on intelligence."

Just what is so special about zeolites that has catapulted them into such widespread use and made them a focus of controversy? Their key feature is their characteristic structures. They typically consist of metallosilicate units linked in ordered arrays that form pores, or windows, opening into cavities in which ions, water molecules, and other chemicals can fit. Zeolites were first discovered in natural minerals, including clays, but hundreds, perhaps thousands of different zeolites have now been made, and the natural versions have become outdated prototypes.

The materials are often called molecular sieves because the shape of both the pores and the internal spaces permits only certain molecules to enter into the cavities, based on their peculiar shapes and sizes. Catalysis itself is believed to depend on the ions associated with a particular zeolite. This controversial, albeit oversimplified, explanation for the mechanism of zeolite catalysis could figure prominently in deciding some of the issues pending before the court.

The details of the two cases differ considerably because Union Carbide and Amoco have developed zeolites that are alleged to infringe on Mobil's materials in distinct ways. Union Carbide's zeolites are known as silicalites; Amoco's as borosilicates; and Mobil's as crystalline aluminosilicates. Mobil's products frequently are referred to as the "ZSM" series, and this series includes by now an extensive variety of zeolites. Mobil scientists have obtained scores of patents covering these materials and how to make them—dominating by far other contenders with the sheer number of U.S. patents for this technology.

Union Carbide's lawsuit against Mobil was prompted, in part, by discussions between the two companies over whether Union Carbide was infringing on the oil company's ZSM-5 patent, which was awarded in 1972 and is probably Mobil's key patent in this area. "ZSM-5 sat on the shelf for 5 years" until uses were found for it, says one industry source.

"Then the whole industry got interested."

At issue is whether Mobil's ZSM-5 and Union Carbide's silicalite are different or essentially the same material. Both are synthetic zeolites. Mobil's ZSM-5 is defined as an aluminosilicate, whereas Union Carbide's silicalite is made with silicates but without aluminum. Mobil's assertion that its patents are being infringed rests on the allegation that Union Carbide's silicalite contains aluminum and thus is indistinguishable from ZSM-5. Union Carbide vigorously denies this allegation. Silicalite is "essentially a silica polymorph, with no aluminum in it," asserts Union Carbide attorney H. M. Humphreys.

Union Carbide scientists have maintained that silicalite is free of aluminum, except for trace contamination. This contention is based partly on x-ray diffraction pattern analysis, which traditionally has been the standard technique for analyzing zeolite structure and composition.

However, in 1982 a team of chemists from the University of Guelph in Canada and the University of Cambridge in England published their analysis of several zeolites based on the technique of magic-angle-spinning nuclear magnetic resonance (NMR). They found that, contrary to Union Carbide's claims, silicalite contains more than trace amounts of aluminum. Moreover, even when present in slight amounts, the aluminum forms an integral part of the zeolite's structure. This finding has since been repeated and published in several papers.

"We have recently developed techniques to remove aluminum very efficiently from zeolites," Colin Fyfe, one of the University of Guelph chemists, told *Science*. Fyfe, who has been asked by Mobil to serve as a witness when the Union Carbide lawsuit comes to trial, says that this refined technique makes the NMR data "more meaningful." Removing most of the aluminum from a sample of ZSM-5 "transforms" it into silicalite, he asserts. "The aluminum [NMR spectral] signal stays in the same position, which suggests it [the aluminum] is in the structure. My belief is the structures [of the Mobil and Union Carbide products] are the same."

Some scientists assert that the presence of aluminum or similar metallic elements is, besides being integral to the structure, also essential for catalytic activity of the zeolites. "Aluminum is present everywhere as an impurity," points out one industry scientist whose company is not directly involved in the current lawsuits. He says that Union Carbide scientists have argued that avoiding aluminum in silicalite is practically impossible because it is present "in all reactants." But winning this argument may not win the lawsuit for Union Carbide, he says. "I personally think that catalytic activity is proportional to the aluminum in the structure." Adds a university researcher recalling conversations with industry colleagues who have firsthand experience, "I think the [aluminum-free] zeolite is a dud as a catalyst."

In spite of this assertion, Mobil has been trying to extend its aluminosilicate line of zeolites toward the aluminum-free end of the product spectrum. Company scientists have patented an extensive series of zeolite compounds having very low levels of aluminum. The company also has had the patent office reissue an earlier document claiming, for Mobil, metal organosilicates "essentially free of group IIIA metals," such as aluminum. Although Union Carbide scientists hold several patents for zeolites, a company attorney says there is "no enforceable U.S. patent" for silicalite. But that fact "has no bearing . . . Union Carbide wants the court to look at the [Mobil] patents and our silicalite product and see that our sieve does not infringe on any valid claims of the patents."

The dispute between Mobil and Amoco sounds similar but is built around another chemical element—boron. Amoco's Marvin Klotz has obtained several U.S. patents during the past few years covering boron-containing zeolites. He and his associate Stephen Ely carefully distinguished their "crystalline borosilicate" from particular Mobil zeolites, which they describe as "synthetic crystalline aluminosilicates containing a minor amount of boria. . . ." Mobil claims that its chemists hold earlier patents than Amoco's, and thus it, rather than Amoco, is entitled to the exclusive use of boron-containing zeolites.

Amoco insists that its borosilicate molecular sieve material contains boron in its molecular framework and is thus distinct from Mobil's catalysts. Industry observers say that the presence of boron in particular formulations of zeolites is "important for catalytic activity" and that it gives "advantages when it comes to selectivity." Thus Amoco seems to be on solid scientific footing in claiming that its scientists "discovered an original, proprietary xylene isomerization catalyst." However, the company's crucial assertion that use of this catalyst "does not use any Mobil technical information or fall within any Mobil patent rights" has become a matter for the court to decide.—**JEFFREY L. FOX**

Two Chilean Professors Released

Word has come from Chile that two of the three mathematics professors seized by the government in November have been released unharmed (*Science*, 21 December 1984, p. 1405). The third, Douglas Fuente, is being held in a detention center.

The seizures were among thousands of arrests and detentions that have been occurring in the wake of nationwide antigovernment demonstrations in September.

The sources in Chile reportedly attribute the release of the two professors at least in part to the surge of telegrams sent to Chile's military-run government by professional societies in the United States, Canada, France, Argentina, and Brazil.

—**CONSTANCE HOLDEN**

Scientific Boycott Proposed to Aid Refusenik

Four American and British microbiologists have called on their colleagues to stop sending bacterial strains to Soviet scientists as a protest over the stalled emigration plans of molecular geneticist David Goldfarb.

Goldfarb was planning to leave Moscow last April when the KGB stepped in, confiscated his strains, and blocked his visa (*Science*, 11 May 1984, p. 582).

Now Max Gottesman of the National Cancer Institute and Charles Yanofsky of Stanford University have sent letters to American biologists through the Committee of Concerned Scientists in which they propose a moratorium on sending strains to the Soviet Union until Goldfarb is allowed to leave. A similar initiative has been taken by Michael Yudkin of the University of Oxford and Simon Baumberg of the University of Leeds.

Goldfarb is being detained for "security" reasons although he says he never worked with secret material. Formerly the director of the Laboratory of Molecular Genetics of Bacteria and Bacteriophages in Moscow, he obtained some of his original strains from the United States, including