Titanium Dioxide: Environmental White Knight?

Titanium dioxide (TiO_2) is a multifaceted compound. It's the stuff that makes toothpaste white and paint opaque. TiO_2 is also a potent photocatalyst that can break down almost any organic compound, and a number of companies are seeking to capitalize on TiO_2's reactivity by developing a wide range of environmentally beneficial products.

Tile Tales

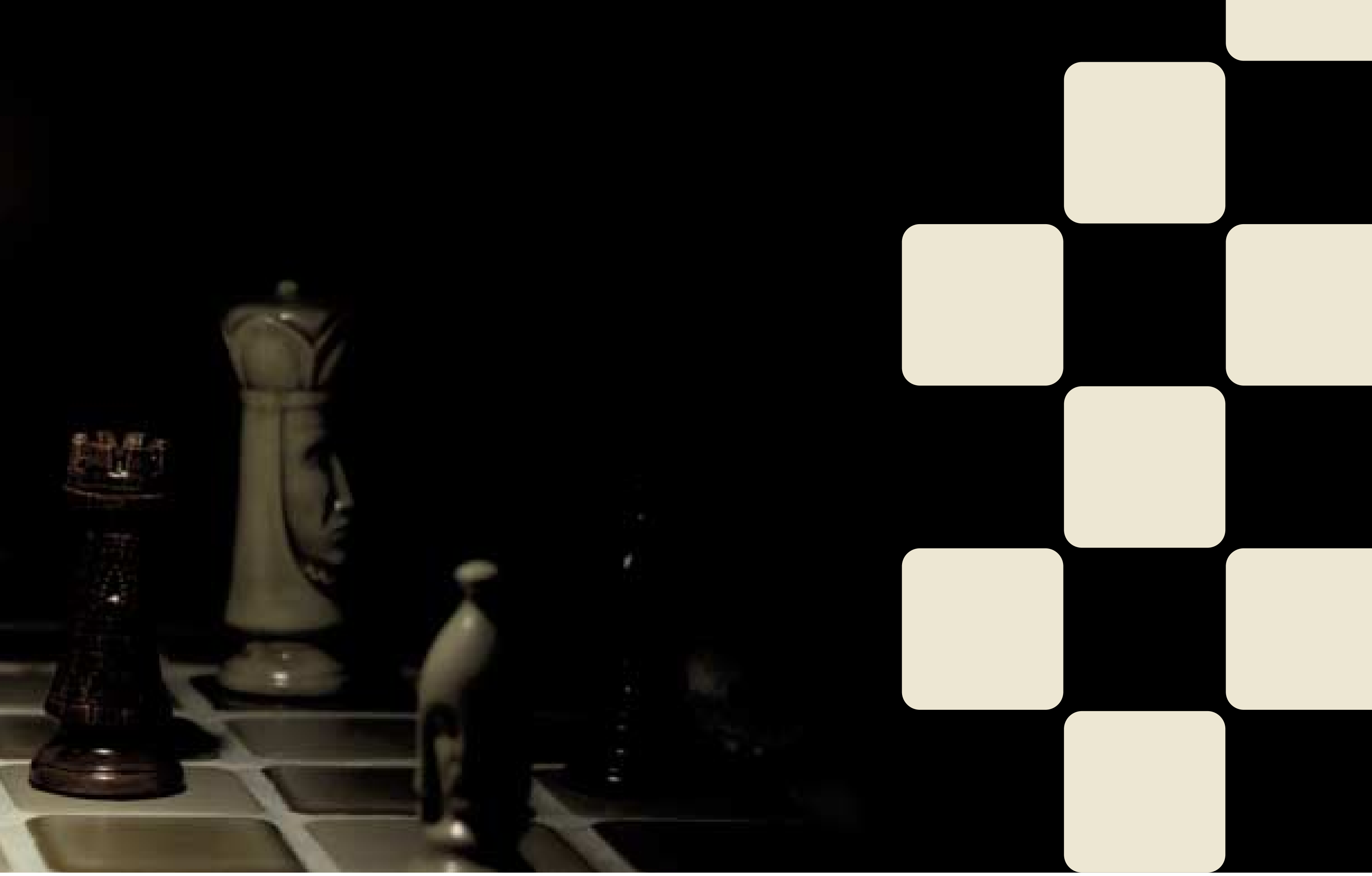
During the late 1970s, scientists began to realize that the propensity of TiO_2 to absorb energy from the UV end of the solar spectrum and then react with water vapor to produce oxygen could be used to create surfaces that were, for all practical purposes, self-cleaning. According to Daniel Blake, principal scientist at the Department of Energy's National Renewable Energy Laboratory in Golden, Colorado, when TiO_2 is exposed to UV light of a wavelength below 385 nanometers in the presence of water vapor, two highly reactive substances are formed: hydroxyl radicals [OH] and a superoxide ion [O_2^{-1}]. Says Blake, "These are highly reactive chemical species. Hydroxyl radicals are very strong oxidizers and will attack all kinds of organic materials, including those that make up living cells."

Toto Frontier USA, based in Long Beach, California, is using TiO_2 to make self-cleaning ceramic tiles for use in hospitals, public restrooms, and other settings where cleanliness is vitally important, as well as on hard-to-reach rooftops, where simple sunlight and rainwater can help prolong the life of the roof. The tiles are made by applying a one-micron layer of TiO_2 to ceramic blanks immediately as they exit the kiln. (Toto has filed a patent for their specially developed "short fire" kiln, which makes the process more economically competitive, although Harvey Malloy, director of sales and marketing for the company, admits that the tiles still cost 10–20% more than regular ceramic tiles.) The result is a photocatalytic coating that bonds with the tile and remains in place for the normal life of the tile itself. This coating has several intriguing properties.

First, it can break down organic matter into carbon dioxide (CO_2) and water. When organic matter lands on a TiO_2-coated tile and water is applied, the hydroxyl radicals break down the cell wall and outer membrane, allowing cell contents to leak out and TiO_2 particles to enter, thereby causing cell damage and death. Hydroxyl radicals are highly reactive and thus short-lived. Superoxide ions, while longer-lived, cannot penetrate the cell membrane because of their negative charge. Therefore, both must interact immediately with the outer surface of an organism unless the TiO_2 particle has already penetrated the cell. Research at the National Renewable Energy Laboratory shows that the process works equally well on bacterial and fungal spores. Tests performed by Toto and presented at a July 2000 Air and Waste Management Association symposium indicate that the TiO_2-treated tiles achieve a 99.9% bacterial kill rate within one hour for such strains as penicillin-resistant *Staphylococcus aureus* and *Escherichia coli*.

Another useful property of TiO_2 is that it is superhydrophilic—the surface of a tile treated with it attracts water rather than repelling it. In the September 1999 issue of *Ceramic Industry*, Malloy explained the importance of this property: "Generally, water droplets form on the surface of a

Reuther/EHP, Greenwell/EHP



ceramic tile at a contact angle of 43 degrees. These tiles are considered hydrophobic. Over time, contaminants collect on the surface of the tile in droplets and remain on the surface after the water evaporates. Water dropped on the surface of a photocatalytic superhydrophilic tile has been shown to spread and form at a contact angle of only 7 degrees in exterior applications and 25 degrees in interior applications." This means surface wetting and rinsing is more uniform; water slides under and floats away organic surface contaminants. These tiles are significantly easier to maintain in interior applications because they don't require the use of bleaches and detergents, wrote Malloy, and they allow for the creation of exterior ceramic facades and roofs that are self-cleaning with rainwater.

These surfaces are in fairly wide use throughout Japan and are being marketed in Europe as well, but they have not yet reached the U.S. market. Malloy says Toto is working on two products for the U.S. market including a self-cleaning exterior facade and interior tile surfaces. However, he says, there are regulatory roadblocks to cross first, especially for interior tile applications. "If we make the claim that the tile is antibacterial, we could be going outside of what is allowable under current Environmental Protection Agency standards," he says. Current standards require a specific kill level within a certain amount of time. TiO_2 achieves the kill level but in a longer period of time. However, while slower than an agent like alcohol or bleach, TiO_2 is also less harmful to the environment, so it would be useful where a high kill rate needs to be maintained over a long period of time.

Road Warrior

Some of the 400 miles of pavement in the Westminster borough of London may soon have a role that goes far beyond smoothing footpaths and roadways. Japan's Mitsubishi Materials Corporation has developed a paving stone it calls "Noxer" that uses the catalytic properties of TiO_2 to remove nitrogen oxide (NO_x) from the air, breaking it down into more environmentally benign substances that can then be washed away by rainwater. NO_x is produced in abundance through vehicle emissions.

The initial Noxer block design involved a 200 millimeter (mm) by 100 mm block with a 5–7 mm thick surface layer containing TiO_2 mounted on a cement mortar base to a total thickness of 60 mm. In tests by Mitsubishi, the block was set in a reaction vessel and exposed to a mixture of air and 1 part per million (ppm) NO_x to simulate vehicle emissions. A hole in the box allowed for the addition of UV light, and a variety of humidities were tested. According to Mitsubishi, when the surface of the Noxer slab is irradiated, oxygen is created, which oxidizes NO_x in the air into nitric acid ions. These ions can then be washed away by rainfall or neutralized by the alkaline composition of the concrete.

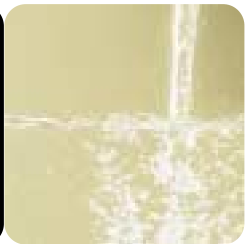
Results of these tests showed an 80% NO_x removal rate based on an intensity of UV light of 1–12 watts per square meter (W/m^2) (the UV intensity of direct sunlight in summer is 20–30 W/m^2, compared to 1 W/m^2 on a cloudy winter day). The blocks functioned best under humidity conditions of 10–80%, with an inverse relationship between NO_x removal and humidity. According to Mitsubishi spokesperson

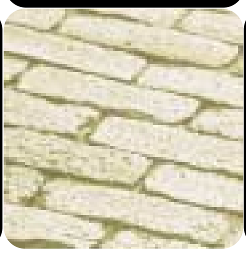
Yoshihiko Murata, in use outdoors the NO_x removal rate varies depending on the concentration of NO_x in the air. The company is currently conducting tests using computer simulations of pollution and actual street measurements.

The Noxer blocks will be manufactured for testing by Marshalls (the United Kingdom's largest manufacturer of landscape, building, and drainage materials for the construction industry and domestic home improvement markets) as a concrete base topped by a one-centimeter layer of a mixture of TiO_2, zeolite, and sand, crushed quartz, or ground glass. Marshalls will use the same manufacturing processes and machinery as for their traditional products, but company PR manager Rachel Brown says, "In principle, there's no reason why the Noxer technology could not be adapted for walling, tunnels, curbs, and so on to reduce the effects of vehicular emissions in the environment." In addition to the proposed Westminster trials, Noxer blocks are also being tested in Osaka and Chiba, Japan.

"NO_x removal using TiO_2 coatings and additions to paving materials and large-scale panels on road sides and the like is a very practical approach," says Blake. "It's passive, in the sense that it relies on natural sunlight and air movement, and no lamps or fans are required; thus, it's simple to implement. Adverse effects of the system seem unlikely because the quantity of the NO_x is very low to begin with, and it's distributed over large areas."

Reynaldo Barreto, a chemistry professor at Purdue University in West Lafayette, Indiana, agrees it is an interesting idea, but, he says, "I think we'd be better off dealing with NO_x as it comes out of the exhaust. NO_x is a product of high-temperature combustion, and it's something we have to deal with one way or another. If you tried to do it in a tunnel with the proper lighting spectrum it might work, but on the pavement? Seems like a hard way to make your point."





A Fresh Application

In addition to cleansing the air outside, TiO_2 is being used to treat the air in fruit, vegetable, and cut flower storage areas to prevent spoilage and increase the products' shelf life. The Kennesaw, Georgia–based KES Science & Technology has commercialized the work of Marc Anderson, a professor of environmental engineering and materials science at the University of Wisconsin at Madison to create an enclosed system that uses the photocatalytic properties of TiO_2 to remove ethylene from the air. Ethylene is a naturally occurring gaseous growth hormone produced by plant tissue that in concentrations as low as 1 ppm triggers the ripening of fruits and vegetables. Ethylene is also produced from other sources including internal combustion engines, certain fungi, and cigarette smoke.

Originally developed for use aboard the space shuttle, the Bio-KES system breaks down ethylene into CO_2 and water. According to Anderson, the University of Wisconsin was active in producing plant growth chambers for shuttle experiments. He says, "We had to develop a way to remove the ethylene from the air because otherwise it would retard growth and spoil the plants. Conventional filtration would just remove particulates from the air, but we needed a way to break down this gaseous substance in an efficient manner while producing no hazardous by-products." The Bio-KES system has been used successfully on six shuttle missions since 1993.

The system draws air through small borosilicate tubes (4 mm in diameter by 12 mm long) that have been lined with a TiO_2 coating. Each system can handle volumes up to 10,000 cubic feet and contains 48 eight-watt UVA bulbs and six eight-watt UVC bulbs. According to KES Science & Technology, the combined action of UV light and TiO_2 oxidizes ethylene into CO_2 and water vapor at a rate of more than 32 milliliters of ethylene gas per hour. University of Wisconsin researchers are working on a treatment for the TiO_2 crystals that would accelerate the reaction by four to six times. The Bio-KES system is currently being used primarily by commercial florists. KES Science & Technology is also developing models for use in sea/land cargo containers and in truck and train transportation.

Diverse Decontaminator

Still other researchers are working on ways to use TiO_2's properties to benefit the environment. Barreto has developed an experimental method of removing the gasoline additive methyl-*tert*-butyl ether (MTBE, used as an octane enhancer) from water by bubbling oxygen into the contaminated water and adding TiO_2, a process that converts both MTBE and another additive, *tert*-butyl alcohol, to CO_2 with a 90% efficiency rate in as little as four hours. MTBE is a potential human carcinogen, and concerns have been raised about its potential for acute effects from exposures by inhalation and long-term exposures from drinking water. Barreto's technology is still under study and has not yet been commercially developed.

Researchers at Robert Gordon University in Aberdeen, Scotland, have experimented with degrading microcystins (toxins produced by cyanobacteria that are linked with liver cancer and can cause death in immunosuppressed people) by simply stirring in TiO_2 and exposing the water to UV light. Results show a complete degradation of the toxin microcystin-LR in less than 20 minutes. Says Blake, "[This application] is quite interesting because the TiO_2 will work under ambient sunlight. This has the potential for applications where one could use solar ponds [artificially created, enclosed bodies of water that use ambient light as part of a treatment process] or other means to treat large areas or quantities of water where the processing rate didn't have to be on the order of millions of gallons a day."

Research suggests that TiO_2 may be useful in other applications to remove organic contaminants from water. In experiments at Sandia National Laboratories in which contaminated water was flowed through glass pipes lined with TiO_2 while being exposed to UV light, researchers were able to reduce concentrations of trichloroethylene (TCE) from 1.2 ppm to less than 50 parts per billion in only 5 minutes. (The project never reached commercialization, however.) Michael Prairie, a principal investigator at Sandia, was lead investigator on a number of TiO_2 research projects at Sandia in the early 1990s, including using TiO_2 to remove explosives residue from water, work that he says was eventually

Reuther/EHP (photos clockwise from top: Greenwell/EHP; Taglia e Incolla; PhotoDisc; PhotoDisc) dropped because the kinetics were too slow or the reaction didn't reach completion. "We tried piggybacking photocatalysis with biodegradation in a two-step process and had some success there," he says, "but it just doesn't seem to work well enough on large groups of compounds. . . . And we've done some work on metals reduction using TiO_2—which seems to work best with mercury—where you could use it as a treatment or for metals recovery."

A Chink in the Armor?

One concern raised about the use of TiO_2 is the formation of potentially harmful intermediate products during the breakdown of organic substances. The 1979 report *Bioassay of Titanium Dioxide for Possible Carcinogenicity NTIS# PB288780/AS (CAS No. 13463-67-7)* states that TiO_2 itself shows no evidence of carcinogenicity. But Carl Koval, a chemist at the University of Colorado in Boulder, and others have raised the concern that the reactions produced by TiO_2 may create substances more dangerous than the original pollutant.

Says Koval, "When illuminated TiO_2 is used to decompose organic compounds, a large number of intermediate compounds are usually formed. In some cases, these intermediate compounds can be more hazardous than the compound being decomposed." For example, he says, the breakdown of TCE yields trichloroacetic acid (a substance almost as toxic as TCE) and, in the gaseous phase, phosgene (a chemical warfare agent). However, he says, this doesn't mean that all applications using TiO_2 would be dangerous. "In situations where this type of process was being proposed for outdoor use, I see no problems with it, because similar things occur naturally in the atmosphere, and it would be unlikely that concentrations of the hazardous chemical would reach toxic levels. . . . However, [in an indoor setting] who knows what would be formed if TiO_2 photocatalysis were used to decompose plasticizers, bacteria, and so on, and what the health effects might be from inhaling such compounds?"

Certainly there is cause for caution, agrees Anderson. "But given time and control over the process," he adds, "these daughter products do break down into environmentally benign substances, a process which can be monitored using a gas chromatograph." And, says Blake, "All oxidization processes have the potential to produce partial oxidization products. It comes down to a question of the fraction of the target compounds that are converted to the intermediate products and how much of those produced are released into the air or water. The amount released will be a function of the efficiency of the photocatalytic device and the way it is constructed and operated."

All that being said, in the realm of environmental cleanup technology is TiO_2 indeed the white knight riding to the rescue or something less? Says Blake, "There is no single technology that can address the very wide range of contamination problems in the environment. Most workers in the field recognize that the photocatalytic chemistry of TiO_2 has pluses and minuses that make it attractive for some applications and not for others. The photocatalytic chemistry of TiO_2 is very intriguing. It works in water or air, it uses light instead of heat, and it is such a simple concept. Engineering it with the right balance of economics and performance is the challenge."

Lance Frazer

Tart/EHP

The Road to Greener Blacktop

What's black and white and green all over? Asphalt pavement! Covering 94% of paved U.S. roads, asphalt pavement is completely recyclable, and research in recent years has yielded many ways to enhance asphalt mixes and save landfill space by incorporating both the pavement itself and waste materials that otherwise would be landfill-bound. About 18 million tons of asphalt pavement occupying some 10 million cubic yards of space is sent to landfills each year. Without the recycling already being done today, that volume would climb to nearly 52 million cubic yards.

Asphalt pavement is composed of 95% crushed rock aggregate and 5% asphalt cement, a sticky petroleum refining by-product that holds it all together. According to the National Asphalt Pavement Association, about 80% of the asphalt pavement taken up each year—some 73 million tons—is recycled and reused in highway applications. Asphalt pavement can be stockpiled and recycled later by milling into gravel-size chunks, heating, and adding more liquid asphalt cement and aggregate as needed. Or it can be recycled on the spot using techniques known as hot in-place and cold in-place recycling, which basically involve digging up and crushing the pavement, mixing it with fresh asphalt emulsion, and laying it back down, all in one pass.

Among the many recyclables that can be added to asphalt pavements are rubber tires and waste toner. According to the Rubber Pavements Association, asphalt pavement supplemented with ground rubber tires provides a quieter ride and a strong surface with less material. Rubber-modified asphalt pavement currently eats up about 10 million scrap tires per year, says Doug Carlson, director of government relations for the association. Industry figures indicate that 273 million scrap tires were being generated annually as of 2000. Carlson says that if 25% of total lane miles of urban U.S. roads were surfaced with rubber asphalt pavement annually, nearly all the nation's discarded tires could be removed from the waste stream.

Studies at the Center for Transportation Research at the University at Texas at Austin show that toner from spent cartridges and manufacturing waste can fortify asphalt pavements, making a "stiffer" mix that holds up well in hot areas. Toner, made of styrene polymers and carbon, is considered environmentally benign. In September 2000 the Texas Department of Transportation, which sponsored the studies, patented preferred methods for creating toner-modified asphalt.

The 1998 Transportation Equity Act for the 21st Century promotes recycling in U.S. road construction. Under the act, the Recycled Materials Resource Center was established at the University of New Hampshire in Durham. Director T. Taylor Eighmy says the center is developing standards and procedures for optimizing various recycling techniques. For more guidance, the United States is turning to several European countries that already have experience with sustainable road building. In 1999 a delegate of U.S. engineers, scientists, and paving specialists met with representatives from Sweden, Denmark, Germany, The Netherlands, and France to learn more about the policies, programs, and techniques being used successfully in those countries. **–Susan M. Booker**

Suggested Reading

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