'Self-cleaning' pollution-control technology could do more harm than good, study suggests

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Research by Indiana University environmental scientists shows that air-pollution-removal technology used in "self-cleaning" paints and building surfaces may actually cause more problems than they solve.

The study finds that titanium dioxide coatings, seen as promising for their role in breaking down airborne pollutants on contact, are likely in real-world conditions to convert abundant ammonia to nitrogen oxide, the key precursor of harmful ozone pollution.

"As air quality standards become more stringent, people are going to be thinking about other technologies that can reduce pollution," said Jonathan D. Raff, assistant professor in the School of Public and Environmental Affairs at IU Bloomington and an author of the study. "Our research suggests that this may not be one of them."

"Photooxidation of Ammonia on TiO2 as a Source of NO and NO2 under Atmospheric Conditions" is being published by the *Journal of the American Chemical Society* and is available online. Other authors include SPEA doctoral students Mulu Kebede and Nicole Scharko, Mychel Varner of the University of California-Irvine and R. Benny Gerber of UC-Irvine and the Hebrew University in Jerusalem.

The researchers calculate that, in areas where the titanium dioxide technology is used, ammonia degradation could account for up to 13 percent of the nitrogen oxides in the immediate vicinity. This suggests that widespread use of the technology could contribute significantly to ozone formation.

The findings are timely because the Environmental Protection Agency is developing stricter regulations for ground-level ozone, a primary component in photochemical smog. The pollution is linked to serious health problems, including breathing difficulties and heart and lung disease.

Ozone is produced by reactions involving nitrogen oxides (NOx), which come primarily from motor vehicle emissions, and volatile organic compounds resulting from industrial processes. Equipping cars with catalytic converters has been effective at reducing ozone in urban areas. But different technologies may be needed to meet tighter air-quality standards of the future.

The need has sparked interest in titanium dioxide, a common mineral that is used as a whitening agent in paints and surface coatings. The compound acts as a photocatalyst, breaking down nitrogen oxides, ammonia and other pollutants in the presence of sunlight. "Self-cleaning" surfaces coated with titanium dioxide can break down chemical grime that will otherwise adhere to urban buildings. News stories have celebrated "smog-eating" tiles and concrete surfaces coated with the compound.

But Raff and his colleagues show that, in normal environmental conditions, titanium dioxide also catalyzes the incomplete breakdown of ammonia into nitrogen oxides. Ammonia is an abundant constituent in motor vehicle emissions, and its conversion to nitrogen oxides could result in increases in harmful ozone concentrations.

"We show that uptake of atmospheric NH3 (ammonia) onto surfaces containing TiO_2 (titanium dioxide) is not a permanent removal process, as previously thought, but rather a photochemical route for generating reactive oxides of nitrogen that play a role in air pollution and are associated with significant health effects," the authors write.

Raff, who is also an adjunct professor of chemistry in the IU College of Arts and Sciences, said other studies missed the effect on ammonia because they investigated reactions that occur with high levels of emissions under industrial conditions, not the low levels and actual humidity levels typically present in urban environments.

The findings also call into question other suggestions for using titanium dioxide for environmental remediation—for example, to remove odor-causing organic compounds from emissions produced by confined livestock feeding operations. Titanium dioxide has also been suggested as a geo-engineering substance that could be injected into the upper atmosphere to reflect sunlight away from the Earth and combat global warming.

Further studies in Raff's lab are aimed at producing better understanding of the molecular processes involved when titanium dioxide catalyzes the breakdown of ammonia. The results could suggest approaches for developing more effective pollution-control equipment as well as improvements in industrial processes involving ammonia.

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