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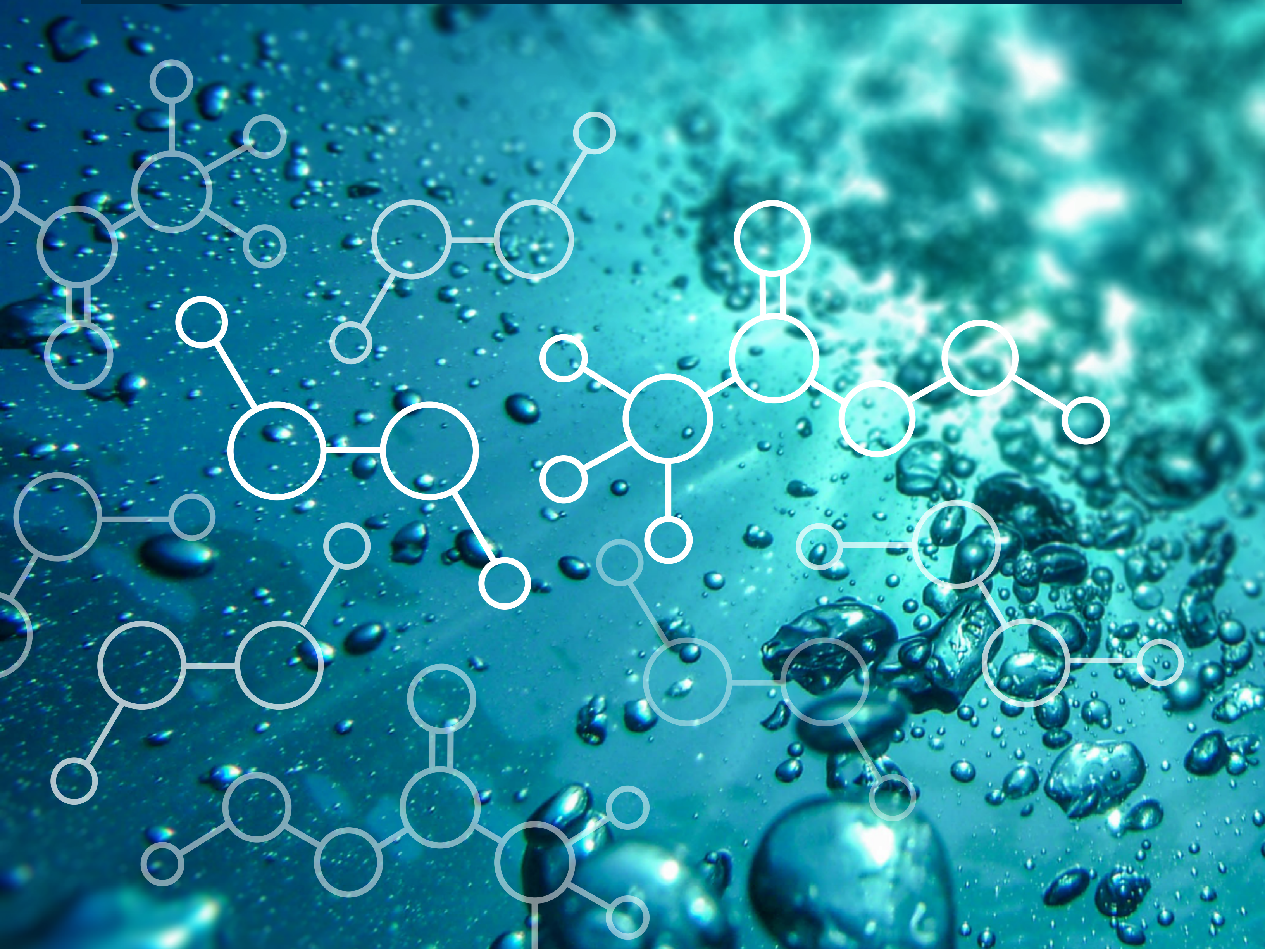
The Modern Chemist's Guide to Hydrogen Peroxide and Peracetic Acid

How two of the world's most versatile chemicals are transforming wastewater treatment, food and dairy packaging, and chemical synthesis



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Introduction

It is difficult to think of a more versatile chemical than hydrogen peroxide.

As of early 2015, the global capacity for uses for hydrogen peroxide had reached 5.5 million metric tons per year. Three decades ago, global utilization of the chemical was 0.5 million metric tons per year. As capacity has grown, "hydrogen peroxide turned from being an expensive specialty chemical into a large-scale commodity, plentiful and affordable, opening up the route to several new uses of this valued substance, which are highly beneficial to the environment," Mario Pagliaro and his colleagues from the Italian National Research Council recently reported in a green chemistry journal.[1]

Hydrogen peroxide can be used to build up high-value organic molecules such as pharmaceuticals, or to break down the most stubborn industrial by-products. It can kill the harmful pathogenic bacteria that could otherwise contaminate packaged food and beverages, or it can supply essential oxygen to the beneficial bacteria that are a key component of municipal wastewater treatment. Factor in the additional potential uses of hydrogen peroxide's close chemical cousin, peracetic acid, and the number of applications expands again.

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Fundamental Chemistry and Properties

Hydrogen peroxide is a simple molecule that consists of two hydrogen atoms and two oxygen atoms paired together. At the heart of the pairing lies a relatively weak oxygen-oxygen chemical bond. That weak bond is central to much of hydrogen peroxide's chemistry.

Hydrogen peroxide is a colorless liquid that is soluble in water and various organic solvents. It is available as an aqueous solution in a range of concentrations. A common industrial concentration of 35% hydrogen peroxide in solution remains liquid between −33 and 108 °C.

Hydrogen peroxide acts as a relatively weak—and therefore, selective—oxidizing agent, specializing in the delivery of single oxygen atoms. Hydrogen peroxide excels at oxidizing sulfur compounds, for example—a reaction that has applications within chemical synthesis as well as to eliminate harmful and malodorous hydrogen sulfide from municipal wastewater.

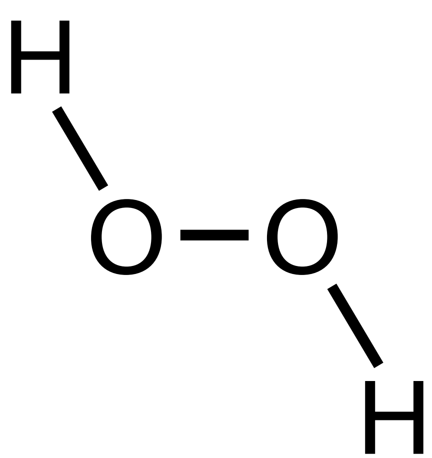
For other oxidation applications, hydrogen peroxide is combined with activating agents such as a catalyst, as in the hydrogen peroxide to propylene oxide (HPPO) process.

But the oxygen-oxygen bond can also be broken in a homolytic fashion to form two hydroxyl radicals. These powerful oxidants can be used to break down many organic compounds found in industrial effluent or to clean up contaminated soils.

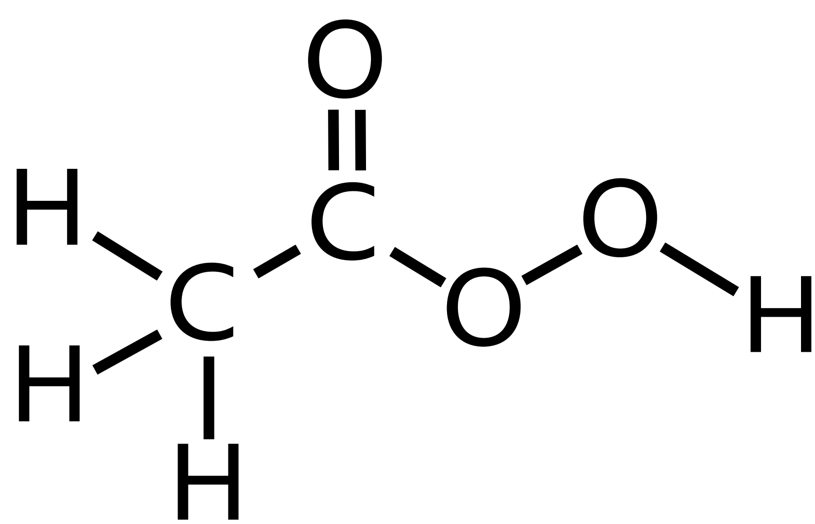
Peracetic acid exists as an equilibrium mixture of peracetic acid, hydrogen peroxide, acetic acid, and water. This strong oxidant is used in chemical synthesis and is a particularly efficient biocide, with uses ranging from wastewater treatment to aseptic food packaging.

Hydrogen peroxide and peracetic acid are stable substances that, if handled correctly, can be stored for years with little degradation and no safety risk. Leading hydrogen peroxide suppliers can advise customers on safe handling as well as the planning and construction of hydrogen peroxide and peracetic acid storage tanks.

HYDROGEN PEROXIDE



PERACETIC ACID



About Evonik

Evonik is one of the world's largest producers of hydrogen peroxide and peracetic acid, with a worldwide capacity of more than 950,000 metric tons per year. It is also one of the world's most experienced hydrogen peroxide producers, having over 100 years of history with the product. Some of the company's notable milestones include opening the first industrial-scale electrolytic hydrogen peroxide production plant in 1910; opening the first modern hydrogen peroxide plant, which used the anthraquinone-based process still used today, in the 1960s; and starting the world's first HPPO plant last decade. The company's activity is characterized by industry-leading innovation, justifying its vision to "futurize peroxide."

Evonik has hydrogen peroxide and peracetic acid production facilities at 13 locations around the world (see map). Its hydrogen peroxide plants can be found in Europe, North America, South America, Africa, Asia, and Oceania, ensuring ready availability of hydrogen peroxide no matter where a customer is located. Its peracetic acid production facilities also span the globe.

The company offers a wide variety of hydrogen peroxide and peracetic acid products tailored toward specific applications, including fine chemical production, to municipal and industrial wastewater treatment, food processing, aseptic packaging, active pharmaceutical ingredients, and cosmetics made to GMP guidelines.

REFERENCE

1. 1 Ciriminna, R., L. Albanese, F. Meneguzzo, and M. Pagliaro, "Hydrogen Peroxide: A Key Chemical for Today's Sustainable Development," ChemSusChem 9, no. 24 (2016): 3374–81.

Environmental Applications

Introduction

Thanks to the increased focus on the health of the environment, regulatory requirements on the discharge of waste have become more stringent around the globe. Nowhere is this environmental awareness more clear than the treatment of wastewater.

Modern municipal sewage treatment facilities typically use a three-step process to clean wastewater. But Switzerland is among the first jurisdictions to mandate a fourth step to remove traces of "micropollutants," such as pharmaceuticals, which can pass intact through conventional municipal sewage works and can remain bioactive even in minute concentrations.[1] Meanwhile, countries in the developing world are catching up with developed nations. China now has the second-largest sewage treatment capacity in the world after the United States.[2]

But cleaning up wastewater for safe discharge into the environment is, increasingly, only part of the equation. Treated municipal wastewater is becoming recognized as an important source of fresh water. On the water-scarce island state of Singapore, reclaimed water already supplies 40% of the country's water needs.[3] Orange County, California, is another wastewater reuse pioneer. Many other regions are set to follow.

"As populations grow, and climates change, we have less freshwater supply, so you have to consider these other water sources," says Linhua Fan, a water reuse researcher at RMIT University in Melbourne, Australia. The default option for water-scarce regions has often been to look to the ocean, building desalination plants to turn seawater into drinking water. "Seawater desalination is quite energy-intensive and not that environmentally friendly," says Fan. Wastewater recycling could be a greener, more sustainable option.

Hydrogen peroxide, with its natural disinfectant and oxidant properties, is a very attractive option for cleaning wastewater and gas streams. It's also used to clean land or groundwater contaminated with organic pollutants. But performance and versatility are only part of the environmental credentials of hydrogen peroxide and its derivatives. The reagent's great advantage is that it breaks down to give only oxygen and water. Hydrogen-peroxide-based processes have twice received the U.S. Environmental Protection Agency's Presidential Green Chemistry Challenge award for their environmentally friendly performance.[4]

Peracetic acid, which is produced from hydrogen peroxide and is an even stronger oxidant and biocide, is similarly environmentally benign, degrading to give water, oxygen, and acetic acid. Acetic acid—the acidic component of table vinegar—is readily biodegradable. In the environmental sector, peracetic acid is typically used for its powerful disinfectant properties, to kill harmful microbes in municipal and other wastewater streams to prevent them from entering waterways.

Evonik produces hydrogen peroxide and peracetic acid grades specifically designed for environmental use.

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Main Application Areas

MUNICIPAL WASTEWATER TREATMENT

Hydrogen peroxide's uses for cleaning up municipal wastewater at multiple points of the treatment process showcase the compound's versatility for breaking down all manner of pollutants while itself remaining entirely benign. The compound can even help clean municipal wastewater to the point that it can be returned to the drinking water supply.

ODOR CONTROL AND SULFITE/SULFIDE REMOVAL

In the oxygen-free conditions that often develop within municipal wastewater collection systems, anaerobic bacteria become active. They reduce sulfates invariably found in the wastewater and produce hydrogen sulfide. This unpleasant gas is best known for its powerful "rotten egg" smell, which can be particularly problematic at lift stations, explains Rex D. Stutchman III, Evonik Active Oxygens sales manager for the southeastern United States. "The sewage from several neighborhoods will all run downhill toward a lift station, which pumps it up to a main sewer line," he says. "Those lift stations can smell horrible and they're located right in the neighborhood." The solution is to dose with hydrogen peroxide to control the smell.

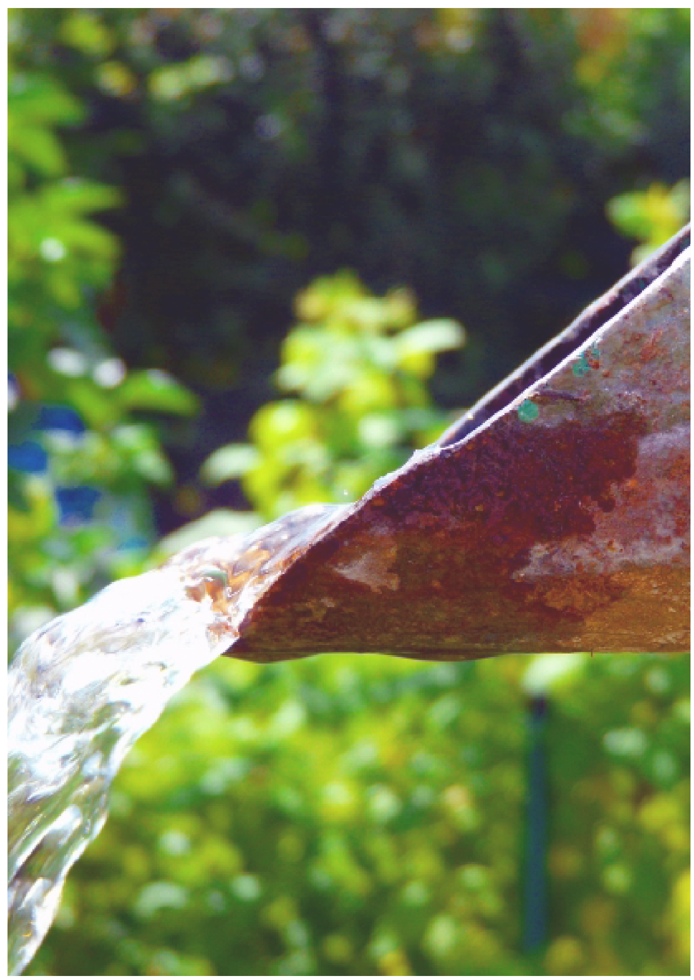
But there are more reasons than simple odor pollution control for removing hydrogen sulfide from wastewater. Aerobic bacteria can convert hydrogen sulfide into sulfuric acid, which causes expensive corrosion damage to pump station equipment and concrete sewer pipes.

Hydrogen sulfide itself can also be dangerous. If concentrations of the gas reach 100 ppm, it becomes harmful to workers' health; it can be lethal if concentrations reach 300 ppm within an enclosed space.

Hydrogen peroxide offers dual modes of action for keeping hydrogen sulfide under control. First, it adds oxygen to the water and prevents the conditions under which the hydrogen-sulfide-forming anaerobic bacteria thrive. Second, it specifically oxidizes sulfides and related sulfur species. The final product of this oxidation process depends on the wastewater stream's pH. Under alkaline conditions, the problematic compounds are converted to harmless sulfates. At neutral pH (the typical pH of municipal wastewater) and below, elemental sulfur is formed. This biologically inert material adsorbs to sludge particles and is disposed of with the sludge.

Hydrogen peroxide is increasingly replacing chlorine as the standard pretreatment to prevent hydrogen sulfide from entering wastewater treatment facilities.[5] Using hydrogen peroxide solution avoids the need to store compressed toxic gas and comply with the relevant occupational health and safety requirements. Also, excess chlorine can react with organic components in the wastewater to produce harmful by-products; excess hydrogen peroxide simply breaks down to water and oxygen, improving the water's dissolved oxygen content.

Last, there is little to no cost penalty in using hydrogen peroxide in place of chlorine.



Hydrogen peroxide and peracetic acid are used at several steps of the water treatment process to clean wastewater for discharge into the environment.
EVONIK

OXYGEN SUPPLY/PEAK LOAD SMOOTHING

Once municipal wastewater reaches the water treatment plant, a primary treatment step separates out debris and larger solids. The remaining liquid passes to the secondary treatment, a biological process in which aerobic bacteria break down the organic matter in the wastewater.

Sometimes, these biological partners in wastewater cleanup need a little help from hydrogen peroxide to carry out their role.

The first scenario is to simply boost the dissolved oxygen content of the wastewater. The biological oxygen demand (BOD) of a water sample is the amount of dissolved oxygen the aerobic bacteria need to break down all the organic material in a sample over a certain time. Sometimes, oxygen demand can exceed supply—for example, because a particularly high quantity of organic matter enters the wastewater stream or due to seasonal weather patterns. The higher the temperature, the lower the amount of oxygen that can dissolve into water.

As oxygen levels fall, filamentous bacteria can begin to dominate the treatment pond. These species form floating bacterial mats that capture sediment particles—or sludge—and stop it from settling out. "If filamentou [bacteria] start to dominate, you get bulking of your sludge, which makes it float, and you'll carry solids over your weir and into your outflow," says Greg Melenkevitz, applications manager, Active Oxygens, at Evonik. "You can use hydrogen peroxide to remove the filamentous and to add oxygen."

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Hydrogen peroxide naturally breaks down to give water and oxygen, but aerobic bacteria contain peroxidase enzymes. These enzymes rapidly break the peroxide down and release oxygen. Therefore, hydrogen peroxide treatment is a near-instant way to boost dissolved oxygen content.

At the same time, hydrogen peroxide can reduce the wastewater's BOD by directly oxidizing some of the organic molecules present. Sulfur-containing compounds can be oxidized by hydrogen peroxide alone; if necessary, less readily oxidized compounds can be oxidized by combining the hydrogen peroxide with an activating agent such as Fenton's reagent (see Advanced Oxidation Processes later in the chapter).

"Oxidizing compounds such as chlorine have increasingly been replaced by hydrogen peroxide in almost every application area," a recent market report concluded.6 "Strict pollution control … increased the usage of hydrogen peroxide and can be a growth driver in the upcoming years."

WASTEWATER DISINFECTION WITH PERACETIC ACID

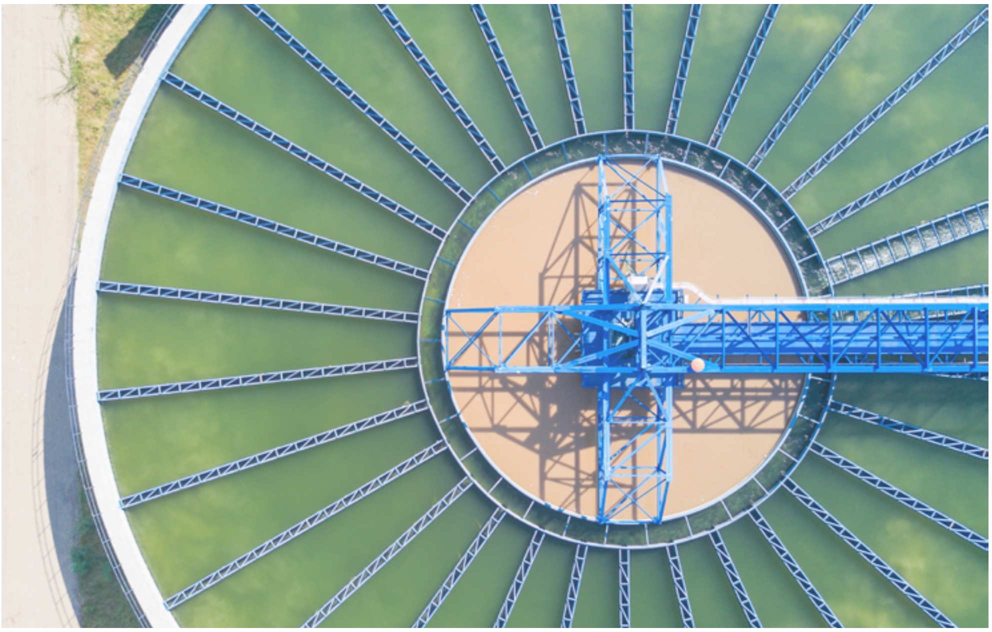
Before treated wastewater is discharged into the environment, it undergoes a third step: a disinfection process to remove pathogenic bacteria. This step prevents the bacteria from reaching natural waterways people use for recreation or fishing.

When wastewater disinfection was first introduced—in the United States, it was mandated in 1972—chlorine-based disinfection was the method of choice. Chlorine and hypochlorite are effective, inexpensive disinfectants. However, both chemicals have since proved to have significant environmental downsides. Residual chlorine is toxic to aquatic organisms in the receiving water. The chlorine also reacts with organic molecules in the wastewater to produce disinfection by-products. Some of these by-products, especially N-nitrosodimethylamine (NDMA) and trihalomethanes, are carcinogens harmful to human health.

Many wastewater treatment plants have added a dechlorination process to remove the residual chlorine and meet their permitted limits. (Hydrogen peroxide is an excellent, environmentally friendly dechlorination chemical.) But dechlorination does not remove the disinfection by-products.

The alternative approach is to use a different chemical disinfectant. Ozone is a commonly used water disinfectant, but ozone also generates high levels of NDMA in the wastewater so is not suitable for this application.[7] Peracetic acid is an attractive option. This fast-acting, broad-spectrum biocide doesn't leave harmful by-products.

Peracetic acid's biocidal mode of action is essentially the same as that of chlorine and chlorine dioxide.[8] A strong oxidant, peracetic acid causes fatal chemical damage to microbes' cell walls. It can also slip through the cell wall and directly



oxidize the amino acids and proteins inside the cell, destroying the cell's inner workings.

Existing chlorine treatment infrastructure can be converted to peracetic acid by retrofitting with the necessary equipment, with little capital expenditure required. Peracetic acid disinfection has been successfully deployed at full-scale municipal wastewater treatment plants, for example, at Northwest Langley in metro Vancouver, Canada.[9]

A recent market analysis confirms that in an increasingly environment-focused world, peracetic acid's use is only set to grow. Peracetic acid is unique among potential biocides in combining a "high" environmental friendliness score with a "high" rating for its effectiveness as a biocide for fluids and for surfaces, says a recent market report.[10]

"The global disinfectant market will grow at a high rate that is expected to drive the overall peracetic acid market consumption," the report says. Particularly high growth for peracetic acid is projected for wastewater treatment, the report notes.

COMBINED SEWER OVERFLOW SYSTEMS DISINFECTION

Modern wastewater collection systems are typically constructed to handle two separate flows: one set of pipes collects sewage from houses and other buildings and transports it to a wastewater treatment plant; a second set of pipes handles stormwater runoff.
But older sewage systems collect both water flows in a combined sewer system. These networks were built before the development of sewage treatment plants, when there was no need to keep the two streams separate. Many of the world's older cities still have combined sewers. According to the EPA, approximately 860 municipalities still use them in the United States alone.[11]

The problem with combined sewer systems comes up during heavy rainfall or snowmelt. The volume of water flowing through the sewer system can far exceed the capacity of the wastewater treatment plant receiving it. Combined sewer mains typically incorporate a dam or weir within the pipework; at periods of heavy flow, the excess water flows over the dam and into a holding area, or discharges directly into a river. Untreated sewage and industrial wastewater are discharged into the environment. This inflow of pathogenic microbes into the receiving water body poses a health risk.[12] The European Union has recently issued a series of directives limiting the amount of these bacteria in water used for bathing, swimming, and other recreational use.[13]

Climate change is predicted to increase the frequency of high rainfall events. Combined sewer overflow will become a growing problem.

Tightening environmental regulations have placed an increased focus on disinfecting combined sewer outflow before it enters the environment.[14] Chlorine-based treatments were traditionally used to disinfect combined sewer outflow, but they carry the same environmental concerns as chlorine disinfection of treated wastewater. The intermittent and highly variable nature of this water flow makes it very difficult to dose combined sewer outflow without leaving toxic residual chlorine in the outflowing water. Dosing combined sewer outflow with chlorine also generates carcinogenic disinfection by-products. The high proportion of suspended solids in combined sewer outflow water can also shelter pathogens from chlorine disinfection.

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MUNICIPALITIES IN THE UNITED STATES ALONE STILL USE COMBINED SEWERS

Peracetic acid is an effective alternative to chlorine for combined sewer outflow disinfection, recent research has shown. "A major advantage of peracetic acid over chlorine-based disinfectants is that it reacts and decomposes quickly," Juan Pavissich from the University of Notre Dame wrote in an article in *Science of the Total Environment* in 2017.[15] "It is believed to produce little to no toxic by-products upon reaction with wastewater or natural organic matter." Pavissich's study showed particulates in the water had no effect on peracetic acid's antimicrobial performance. Disinfection with peracetic acid was recently found to be particularly applicable in combined sewer outflow systems that allow a peracetic acid contact time of several hours before water discharge.[16]

DRINKING WATER PREPARATION (REUSE)

Once wastewater has passed through the third treatment step of disinfection, the water generally is considered clean enough for discharge into the environment. But with further treatment, it can be made so clean it can be reused as drinking water. This unconventional water source can be significantly more sustainable than other sources, such as seawater desalination. Water-scarce jurisdictions such as Orange County, California, already recycle wastewater this way.[17] And they use hydrogen peroxide to do it.

The first step in wastewater reuse is to pass the treated water through a reverse osmosis process, explains RMIT's Fan, who studies the process for Australia's largest water reuse scheme in southern Queensland. Reverse osmosis uses high pressures to drive water through a membrane designed only to let water molecules pass through it. However, the process is not perfect. "Some harmful chemicals can pass through the reverse osmosis membrane and get into the filtrate," Fan says. Micropollutants that can slip through the reverse osmosis membrane include pharmaceutical compounds and chlorine disinfection by-products. "They can be very harmful compounds, such as NDMA and trihalomethanes," Fan says. "Our research is to treat the reverse-osmosis-treated water to make sure everything has been removed."

A combination of hydrogen peroxide and UV light (see next section) is used to break down any remaining organic contaminants in the reverse osmosis filtrate, Fan says. This treated water is cleaner than typical tap water and can be sold to industries that require highly pure water.[18] It can also be returned to the drinking water system. The water is transferred to a reservoir where it mixes with natural water. This water passes through the regular drinking water treatment plant and into the water supply.

ADVANCED OXIDATION PROCESSES WITH UV, FENTON'S REAGENT, OR OZONE

Advanced oxidation processes (AOP) are powerful oxidant systems that can be used to remove problematic organic molecules from wastewater streams. AOPs can eliminate organic molecules, such as pharmaceuticals, that are resistant to biological breakdown. Eliminating these molecules is important because they can act as endocrine disrupters in receiving waterways. AOPs can also eliminate disinfection by-products.

The key oxidant species typically generated by AOP is the hydroxyl radical, a very powerful oxidant second only to fluorine in its oxidation potential. Because hydroxyl radicals are so reactive, they must be continually generated in situ. Hydrogen peroxide is an excellent potential source of hydroxyl radicals for wastewater treatment. The hydroxyl radicals can be generated in several different ways.

"Certain AOPs have sweet spots for certain applications," says Jens Scheideler, an AOP expert at Xylem, a multinational company offering several AOP water treatment technologies. For potable reuse, the combination of hydrogen peroxide and ultraviolet light is ideal, he says. Light at UVC wavelengths is absorbed by the hydrogen peroxide molecule and homolytically splits its weak oxygen-oxygen bond to generate a pair of hydroxyl radicals. These radicals oxidatively attack the micro pollutants in the reverse osmosis filtrate.

"For potable water reuse, UV-based AOPs are superior because reverse osmosis permeate has a very high UV light transmittance," Scheideler says. An added benefit is that NDMA is a photoactive molecule that is directly broken down by the UV light, he adds. Fan agrees. "UV-peroxide process is considered very, very effective at removing the compounds that may be in the RO [reverse osmosis] filtrate," she says.

Other AOPs for water treatment include combining hydrogen peroxide with ozone gas or with iron (II) salts to form the oxidant known as Fenton's reagent. For these AOPs, the sweet spot is often industrial wastewater treatment.

INDUSTRIAL PROCESSES AND PROCESS WATER REUSE APPLICATIONS

The same attributes that make hydrogen peroxide and peracetic acid effective, environmentally benign municipal wastewater cleaning agents also make them well suited to industrial wastewater streams.

INDUSTRIAL AOPs

AOPs are typically deployed late in municipal wastewater treatment to remove pollutants not broken down by biological treatment. In industry, AOPs are generally used at the start of the process. "Industrially, usually we use AOPs as a pretreatment step, either to increase the biodegradability of complex molecules or to handle toxic constituents which would be biodegradable if the toxicity could be removed," says Andree Blesgen, head of environmental technology, process technology, and engineering, at Evonik. "So we pretreat a waste stream with AOP then send it to a central wastewater treatment plant in a chemical plant, for example."

UV-peroxide can be a nice process, Blesgen says, that is relatively simple to install and operate. The downside is that UV lamps consume a lot of electricity and have a relatively short lifetime. "You have to swap your lamps maybe three or four times a year, which is a big cost factor," he says. And, of course, UV isn't suitable for turbid wastewater streams that the light can't penetrate.

In those cases, Fenton's reagent might be a better AOP option. The reaction combines hydrogen peroxide with iron (II), which, under acidic conditions, react to generate hydroxyl radicals. Formaldehyde, a common industrial wastewater constituent, is readily oxidized by Fenton's reagent. Phenols, toxic compounds that could harm the aerobic bacteria used in the biological treatment step, can be oxidized as well.[19] Oxidation by Fenton's reagent opens the phenol ring and can ultimately break the molecule all the way down to carbon dioxide and water.

From the process technology point of view, Fenton's reagent is a bit more complex to implement than UV, Blesgen says. The solution must have acid added to lower the pH for the reaction, then be neutralized again afterward. "But the advantage is a very robust process once it is calibrated," he says. A broad range of constituents can be treated, and the process handles fluctuations in wastewater contents relatively well. Reaction parameters such as temperature, residence time, and peroxide dosing can also be easily adjusted. "That gives you quite a few handles to play with to optimize your process."

One perceived downside of Fenton's reagent is that when the pH is raised after the oxidation treatment is finished, iron (III) hydroxide precipitates to form a solid sludge that must be disposed. But the precipitation can be a distinct advantage, says Jochen Schumacher, who works for the water treatment system provider Eisenmann. The company has developed a proprietary, two-reactor Fenton's reagent–based process called Fentox.

For example, in a waste steam containing bisphenol S, a sulfonyl compound incorporating two phenol rings, the Fentox treatment induced not an oxidation, but a polymerization, Schumacher says. Upon neutralization, the polymerized organic matter precipitated out of solution along with the iron. The organic material can then be skimmed off the water. "We see for many

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applications that with Fenton's reagent, you have not only the oxidation but a high removal of organic compounds with the sludge," he says. "Fifty to sixty percent of the organic layer can be removed with the sludge, which is sent for incineration or disposal." The dual action of the iron can make the Fenton process very cost-effective in those cases where organic precipitation takes place, he adds.

It is also possible to add UV light in a photo-Fenton process. When iron (II) reacts with peroxide to generate hydroxyl radicals, it is converted to iron (III). But a second reaction slowly converts iron (III) back into iron (II), Schumacher says. "Applying the UV lamps tremendously accelerates the back reaction, so you need less iron."

A wastewater treatment plant that uses Eisenmann's proprietary, two-reactor Fenton's reagent–based process called Fentox. EISENMANN

For plant managers who don't want to deal with the sludge Fenton's reagent always generates, there's ozone-peroxide to consider. "Ozone AOP is a waste-free process, capable of improving organic biodegradability of compounds," Xylem's Scheideler says. The treated water can be fed to a microbial water treatment facility.

Ozone's sweet spot is for wastewaters with a relatively low chemical oxygen demand—mainly because there is a limit to how much of it, as a gas, can be transferred into the water.

How to decide which AOP to use? Testing. "Every wastewater is different, and every customer's needs are different from site to site," Schumacher says. Blesgen agrees. "In wastewater treatment, often it is very difficult to foresee which technology works or not, depending on the different constituents you have in your wastewater," he says. "Every time you have a different wastewater, you should run a lab experiment at least, if not a pilot scale test. Different constituents react differently on different oxidation methods."

The first test Blesgen usually runs is a simple dose of hydrogen peroxide. "Of course, we are a producer of it, but that's not the main reason," he says. The compound is versatile, relatively easy to handle, and easy to use over a broad range of applications. "A dose of peroxide is the simplest thing you can do, and if that is already effective, then it is a very economical process," Blesgen says. "You don't need a fancy plant or a fancy treatment process."

COOLING TOWER WATER TREATMENT

Hydrogen peroxide has many environmental applications beyond wastewater treatment. One example is in cleaning biofilms from cooling towers.

The microorganisms present in cooling and process water like to set up home in this nice warm environment, creating a biofilm that gradually clogs the system. "That film creates a barrier on the heat transfer system, and when it becomes too thick, it has to be removed," says Maria Alejandra Aldon, Evonik's applications specialist for Active Oxygens based in New Jersey.

Regular small injections of hydrogen peroxide into the cooling water, a process known as shock treatment, is one option for keeping biofilm formation under control. This method can also be effective for controlling the *Legionella* bacterium that causes outbreaks of Legionnaire's disease. Contaminated cooling towers are a well-known source of the bacterium.[20]

In addition to ongoing treatments, concentrated hydrogen peroxide can be used for longer-term cleaning and maintenance cycles. "We can flush the system with hydrogen peroxide to remove the biofilm," Aldon says.

Flushing the system involves pumping a 50% hydrogen peroxide solution into the cooling system and recirculating it for six hours until the biofilm is removed. "As soon as the peroxide hits, you start to see it all falling from the cooling tower into the reservoir at the bottom."

The microorganisms present in cooling and process water like to set up home in cooling towers, creating a biofilm that gradually clogs the system. Concentrated hydrogen peroxide can be used for longer-term cleaning and maintenance cycles in cooling tower systems.

The chemical's main effect is that it effervesces when it hits the organic matter. "You generate scrubbing bubbles that help the biofilm break up and fall off," Aldon says. The bubbles mechanically lift the biofilm as the solution is pumped around the cooling tower. Within a single day, the cooling tower is cleaned and ready for business again.[21]

PULP AND PAPER PROCESS AND WASTEWATER APPLICATIONS

The pulp and paper industry is the biggest single consumer of hydrogen peroxide, which the industry uses for its bleaching purposes. Half of all hydrogen peroxide is used this way.[22]

But the chemical is also increasingly being used to help treat the high volumes of wastewater the pulp and paper industry generates.

Many of the components in paper-mill effluent originate in the wood itself. The wastewater can be rich in suspended solids and chemical components such as tannins, resin acids, and lignin and its derivatives. Because many of these compounds are resistant to biological breakdown, chemical treatment by advanced oxidation processes is used.[23] Given the large volumes of wastewater paper mills generate, the most economical option is generally to use advanced oxidation to break down these recalcitrant compounds into biodegradable molecules that can then be fully broken down in a subsequent biological treatment step.

Other paper-mill waste streams usually handled by other means can sometimes require hydrogen peroxide intervention, Stutchman says. Paper produced by the Kraft process—which uses hot water, sodium hydroxide, and sodium sulfide to break wood chips into pulp—generates a dark, toxic waste liquid rich in lignin and cellulose, plus various sodium salts. This "black liquor" is usually treated in a recovery boiler that burns or gasifies the toxic organics to extract energy while recovering the inorganic chemicals. But sometimes a problem with the process means the mill has to discharge the black liquor into its wastewater pond. "When that happens it causes a huge oxygen demand on the pond," Stutchman says. To avoid killing the beneficial aerobic bacteria in the pond, the fastest and simplest thing to do is to add peroxide. "Most ponds have aeration spargers, but there you're trying to force oxygen into the solution," Stutchman says. "With peroxide, it's already there; you just put it in and you get your oxygen, so the bugs stay alive and everything keeps working."

Hydrogen peroxide can also be used to oxidize odiferous sulfur molecules that can be released while regenerating the Kraft process reagents.

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— Rex D. Stutchman III, Evonik Active Oxygens sales manager for the southeastern United States

CONTROLLING HARMFUL ALGAL BLOOMS

Large blooms of blue-green algae are becoming an increasingly common occurrence within natural waterways. The algal outbreaks can have a highly damaging effect on aquatic ecosystems, triggering large-scale fish kills. Water thick with algae can damage fish gills; the algae release toxins; and when the algae die, the bacteria that decompose them consume so much of the dissolved oxygen in the water that fish and other species cannot survive.

Warmer water temperatures due to global warming, and the runoff of excess nitrogen and phosphorus into rivers, are some of the factors believed to be behind the increasing prevalence of algal blooms. Hydrogen peroxide is proving to be an effective treatment for algal blooms, selectively killing the algae with minimal effects on the rest of the ecosystem.[24]

OIL AND GAS MARKET

Subterranean reservoirs of oil and gas often contain significant quantities of water in the same underground formation. When the hydrocarbons are tapped by oil and gas extraction companies, the water comes out too. This water can contain sulfides that, as with municipal wastewater, can pose an odor problem and can form corrosive sulfuric acid. The water can also contain microbes and algae that can cause biological fouling of the production well, adds Robert Gec, Evonik's product technical manager, Active Oxygens, for North America.

A one-two treatment system of hydrogen peroxide and peracetic acid makes a cost-effective, environmentally benign treatment system to solve both problems, Gec says. "In the first stage you treat the produced water with hydrogen peroxide to oxidize the sulfides. Then you do a biocide treatment with peracetic acid."

This pretreated wastewater can be sent for further cleanup and disposal. Or, more typically these days, it can be used as a liquid for hydraulic fracturing.

Other sources of water used for fracking can also be pretreated with peracetic acid to prevent biological fouling of the equipment.

SOIL REMEDIATION

As populations grow and cities expand, land once part of the industrial zone on the urban fringe often becomes prime real estate for housing and commercial use. In this common scenario, land earmarked for redevelopment is frequently found to be contaminated with chemicals related to its former industrial use.

Physically removing the contaminated soil, or pumping away contaminated groundwater, for off-site treatment is a gargantuan task due to the sheer volume of soil or water involved. A simpler, equally effective approach can be to treat the soil in situ using a chemical oxidation process.

Cyanobacteria, or "blue-green" algae, which develop at the surface of slow-flow freshwater rivers and lakes in the summer, can be harmful to people and animals.

As a strong yet environmentally benign oxidant, hydrogen peroxide is the chemical oxidant of choice for cleaning up contaminated soil. The general approach is to use a version of Fenton's reagent, but modified for use in soil. A more concentrated hydrogen peroxide solution, combined with an iron (III) catalyst, is typically used.

Despite being known as in situ chemical oxidation, the name is something of a misnomer; under the typical conditions used, there is more than oxidation going on. A better term is catalyzed hydrogen peroxide propagations, or HPP.[25] Under these conditions, the hydroxyl radical is not the only active species formed; the perhydroxyl radical ($HO_2\bullet$), superoxide radical anion ($O_2\bullet^-$), and hydroperoxide anion (HO_2^-) are all also generated in a series of "propagation" reactions. The superoxide radical anion is a nucleophile and reducing agent; the hydroperoxide anion is also a powerful nucleophile.

Contaminants susceptible to oxidative attack, nucleophilic attack, and reductive attack can all be broken down by this versatile mixture. This makes hydrogen peroxide an excellent choice for most chemical cleanup scenarios.

The presence of hydrogen peroxide itself in the mixture also helps the process. In water, superoxide ions have low activity because they become surrounded by water molecules. But the presence of hydrogen peroxide seems to alter the solvation around the superoxide and boosts its reactivity significantly. This potent, versatile mixture is also able to strip contaminants away from protective soil particles and into solution, where they can then be broken down.[26]

Recent research has shown that even contaminants resistant to oxidative remediation, such as carbon tetrachlorine and the persistent, bioacumulative perfluorinated compounds such as perfluorooctanoic acid, can be treated this way.[27]

INDUSTRIAL FLUE GAS SCRUBBERS

Sulfur dioxide is a gaseous by-product generated by many industrial facilities, from fossil fuel power plants to pharmaceutical production. Sulfur dioxide reacts in the atmosphere to produce sulfuric acid and contribute to acid rain. Modern discharge limits strictly control sulfur dioxide release.

Flue gas scrubbers containing a small amount of hydrogen peroxide in a dilute sulfuric acid can very effectively capture sulfur dioxide emissions, whether the gas is present in high or low concentration. Sulfur dioxide reacts very quickly and exothermally with hydrogen peroxide to produce sulfuric acid. As the scrubber liquor gradually becomes more concentrated in sulfuric acid, the liquor can be extracted and the valuable acid reused.[28]

OUTLOOK

Hydrogen peroxide and peracetic acid possess a unique combination of versatility, efficacy and environmental friendliness that no rival chemical can match in the environmental space.

"There are many biocides available in the market, such as ozone, chlorine dioxide, hydrogen peroxide, aldehydes, sodium hypochlorite, and others," says a recent market report.[10] As the report concludes, however, none of the alternatives can match hydrogen peroxide and peracetic acid's combination of performance and environmental benefits.

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Chemical Synthesis

Introduction

The oxidation reaction is one of the most common reactions used by organic chemists to make a product. Although many chemical oxidants are known, few can match the clean simplicity of hydrogen peroxide. As interest grows in green chemistry, hydrogen peroxide—which breaks down to give only oxygen and water—is increasingly in the spotlight.[1]

"What drew me to hydrogen peroxide is the idea it could replace a number of potentially hazardous, carcinogenic, or simply corrosive oxidants, used widely in industrial chemical production," says David Flaherty, who researches sustainable catalysis at the University of Illinois, Urbana-Champaign.[2] "Compared with oxidizers based on chlorine, hydrogen peroxide produces mainly water as a by-product."

Matthias Pascaly, director of research and development at Evonik, agrees. "Hydrogen peroxide's appeal is its simplicity and nontoxicity," he says. "With chlorine, which is the main competitor, you produce lots of toxic organic halides. We might have trace by-products with hydrogen peroxide, but nothing close to the toxicity of the halides." Oxidation with hydrogen peroxide also doesn't produce briny, salty wastewater that chlorine-based oxidations typically generate.

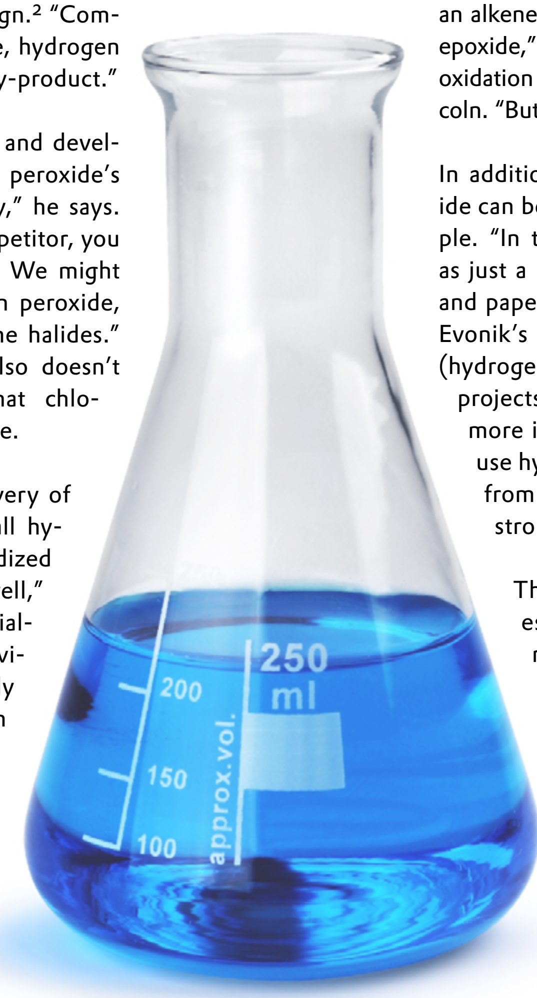
Hydrogen peroxide excels in the delivery of single oxygen atoms. "The French call hydrogen peroxide l'eau oxygénée—oxidized water—which I think describes it well," says Stefan Leininger, director of specialty products in the Active Oxygens division of Evonik. "You have a very weakly bound oxygen. Hydrogen peroxide can do a lot of different reaction pathways depending on the activation of the hydrogen peroxide." Using a catalyst can direct the reaction along the desired pathway, he adds.

Combined with the right catalyst, hydrogen peroxide will react with an alkene—a molecule containing a carbon-carbon double bond—and donate an oxygen atom to that double bond to form a three-membered oxygen-containing ring called an epoxide. This class of compound is highly valued because of the large range of ring-opening reactions, with various reaction partners, that they can subsequently undergo.[3]

As an oxidant, hydrogen peroxide has the benefit of being slow and selective, often requiring activation by a catalyst. But the reagent can also be used to form peracids that are considerably more active oxidants. "It takes a good catalyst or good conditions to get an alkene to react with hydrogen peroxide to make an epoxide," says Patrick Dussault, who studies peroxide oxidation chemistry at the University of Nebraska, Lincoln. "But with peracids—bang, that's what they do."

In addition to oxidation reactions, hydrogen peroxide can be used to trigger rearrangements, for example. "In the past, hydrogen peroxide was regarded as just a kind of bleaching agent—from hair to pulp and paper," says Bernd Jaeger, formerly in charge of Evonik's R&D in this space and now head of HPPO (hydrogen peroxide to propylene oxide) licensing projects. "In the past decade you can see more and more interesting applications are popping up that use hydrogen peroxide as a chemical reagent, and from my point of view, that will become even stronger."

The following sections cover some of the latest applications of hydrogen peroxide and related peracids in the field of chemical synthesis. The emphasis is on industrially proven chemical transformations that have been performed on the hundreds of kilogram or multiton scale. It is hoped that this review of hydrogen peroxide chemistry will inspire yet more uses of this green, versatile reagent.



EVONIK

Heterogeneous Catalysis: HPPO and Caprolactam

Propylene oxide is a chemical in high demand. This epoxide is used to make polyurethane foams, which have uses ranging from car bumpers to sofas to thermal insulation for refrigerators. Demand for propylene oxide is rising at a steady 3.5% per year; in 2018, global production is expected to hit 10 million metric tons for the year.[4] A short, efficient, green new process called hydrogen peroxide to propylene oxide is increasingly meeting this demand.

In the HPPO process, propylene oxide is the sole product, and the only reaction by-product is water. The key to the HPPO process was the discovery by Italian chemical company EniChem (now named Versalis) in 1983 of a catalyst that would activate hydrogen peroxide to directly and selectively epoxidize propylene to give propylene oxide.

Until HPPO came along, the methods for making propylene oxide had some serious limitations. "Chlorohydrin technology is the oldest and is still the dominant technology for producing propylene oxide," says Thomas Bode, head of performance oxidants at Evonik. First introduced in the 1950s, the process combines propylene, chlorine, and water to produce propylene chlorohydrin. In the presence of calcium hydroxide, the chlorohydrin converts to the desired epoxide.[5]

The problem with this process is its environmental footprint, Pascaly explains. Every metric ton of propylene oxide produces 2.1 metric tons of calcium chloride salt. The salty effluent from the reaction also contains traces of chlorinated by-products, making the effluent difficult to treat.

As a result, the chlorohydrin process has fallen out of favor. "In China, there is a ban on building new chlorohydrin production plants," Bode says. "They are trying to motivate the [propylene oxide] producers to use HPPO." Although there is no outright ban in Europe or the U.S., cleaning up the wastewater that the chlorohydrin process produces to meet modern environmental regulations is a major disadvantage. "I doubt there will be any new chlorohydrin plants," Bode says.

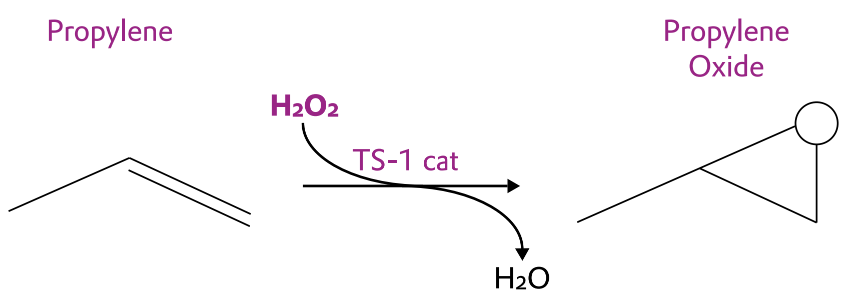
DEMAND FOR PROPYLENE OXIDE IS RISING AT A YEARLY RATE OF

3.5%

The traditional alternative to chlorohydrin for propylene oxide production was the hydroperoxide process. An organic molecule was oxidized to form a hydroperoxide (R-OOH), which would react with propylene in situ to form propylene oxide. The organic reaction partner forms the reaction coproduct, which must also be sold. Depending on the organic used, styrene or methyl tert-butyl ether are the coproducts.

The issue with this reaction was not environmental but economic. When you produce 1 ton of propylene oxide, you get 2.3 tons of styrene or 2.8 tons of methyl tert-butyl ether. "So that means propylene oxide is more the coproduct than the main product," Bode says. "The economics depend very much on the sales price you can get for the coproduct."

The HPPO process suffers no such drawbacks. Propylene oxide is the sole product, and the only reaction by-product is water. The key to the HPPO process was the discovery by Italian chemical company EniChem (now named Versalis) in 1983 of a catalyst that would activate hydrogen peroxide to directly and selectively epoxidize propylene to give propylene oxide.[6]



The titanium silicalite catalyst, TS-1, incorporates titanium atoms into a porous solid material known as a zeolite. Titanium was known to react with hydrogen peroxide, Pascaly says. "The activity of titanium to produce titanium peroxide species was well-known for decades," he says. The challenge was to find a way to control the reactivity of the titanium peroxide so that it would selectively oxidize an alkene to form a desired epoxide. Zeolites turned out to be ideal for the job.

"Zeolites have these channels that are the proper size to allow hydrogen peroxide to enter and form these titania species," Pascaly says. Hydrogen peroxide and propylene enter the TS-1 zeolite's channels; the hydrogen peroxide reacts with the zeolite to form titanium peroxo species that oxidize the propylene to propylene oxide.

As a major producer of hydrogen peroxide and as a company that also makes zeolite catalysts the reaction was a clear fit for Evonik. Teaming up with thyssenkrupp Industrial Solutions, the company developed the HPPO process, which it now licenses out to interested companies.[7, 8] The first global-scale HPPO production plant, built by SKC in Ulsan, South Korea, uses this technology. Evonik supplies the catalyst and hydrogen peroxide as part of the deal.

"For epoxidation reactions, transition-metal-substituted zeolites are pretty effective. You get the chemistry inherent to the metal you substitute into the framework, and you can manipulate the porous environment surrounding the metal to provide some shape selectivity to the oxidations you perform."

— David Flaherty, sustainable-catalysis researcher at the University of Illinois, Urbana-Champaign

Dow and BASF also worked together to develop their own HPPO process.[9] The companies use the propylene oxide in-house to make downstream products. The key knowledge Evonik and BASF have independently developed relates to the zeolite catalyst, says Jürgen Glenneberg, hydrogen peroxide process chemist at Evonik. The catalyst is initially formed as a fine powder, which is not ideal for industrial use, Glenneberg says. "You need to know how to make the active catalyst and then how to make that into bigger pieces for a fixed-bed reactor—that's the trick."

Zeolite catalysts' uses go far beyond HPPO. "For industrial use, TS-1 is the major catalyst of interest for hydrogen peroxide oxidation reactions," Glenneberg says. "For epoxidation reactions, transition-metal-substituted zeolites are pretty effective," Illinois's Flaherty agrees. "You get the chemistry inherent to the metal you substitute into the framework, and you can manipulate the porous environment surrounding the metal to provide some shape selectivity to the oxidations you perform."

The zeolite environment can also serve to increase reaction rates by solvating the appropriate transition state, Flaherty adds. It also prevents the transition state from leaching away into the solvent like it might do on a surface-catalyzed process, which further boosts selectivity and yield.

For example, the same TS-1 catalyst used in the HPPO process is also used to produce caprolactam, a feedstock for making nylon 6.[10] Caprolactam synthesis starts from cyclohexanone. In the traditional method for making caprolactam, adding hydroxylamine and sulfuric acid to cyclohexanone generated the cycloheximine, which was then reacted with more sulfuric acid and ammonia to trigger a Beckmann rearrangement to caprolactam, a seven-membered ring. "This rearrangement needed a lot of sulfuric acid, so you had a lot of ammonium sulfate as by-product," Glenneberg says. Like the chlorohydrin process, a salty effluent was generated that had to be cleaned up.

EniChem researchers discovered that the TS-1 catalyst offered a major advantage for the first step. Rather than add sulfuric acid and hydroxylamine, scientists could simply mix cyclohexanone, ammonia, and hydrogen peroxide in the presence of TS-1.[11]

The small pores of the TS-1 catalyst allow only small molecules into the zeolite to react. Molecules of six carbons or larger can't get into the pores, Glenneberg says. The ammonia and hydrogen peroxide enter the catalyst and are converted into hydroxylamine, which reacts with cyclohexanone when it comes out of the zeolite to form the cycloheximine.

The Japanese chemical company Sumitomo subsequently discovered a second zeolite catalyst could then convert the cycloheximine to the desired caprolactam, so no sulfuric acid is required for this step either. By using ammonia, hydrogen peroxide, and TS-1, scientists could avoid the salt wastewater.[12]

HPPO plants are typically built right next door to a hydrogen peroxide plant, so that the oxidant can be piped directly 'over the fence' for the clean, green production of propylene oxide. EVONIK

"We're trying to understand how changing three or four aspects of a zeolite catalyst will impact the rates and selectivities for alkene epoxidations," Flaherty says. "We want to develop quantitative structure-function relationships that would allow us to look at an alkene and decide what material would be optimal for getting the greatest yield of a valuable epoxide while minimizing the amount of hydrogen peroxide that decomposes nonselectively." The team is systematically testing different transition metals substituted into the framework and different zeolite pore diameters around that active site. It is also testing whether hydroxyl groups within the pore space might assist the reaction by facilitating hydrogen bonding with transition states and reactive intermediates.

"Overall, investment costs are lower and production costs are lower because the hydroxylamine is made in situ from inexpensive starting materials in the first step," Glenneberg says. "The environmental credentials of the process are also far better because the problematic salt by-products are avoided in each step."

The TS-1 catalyst and hydrogen peroxide make a powerful pair that is likely to find uses beyond the HPPO and caprolactam processes. EniChem also used it as a phenol oxidation catalyst, for example, Glenneberg says. Flaherty is exploring many more potential applications.

"We've tried to independently vary each parameter to see how they affect the rates of reaction," Flaherty says. Tuning each of these parameters can significantly change reaction selectivity, he adds.

Flaherty knows that the right combination of parameters will have a notable impact on industrial-scale applications. "A significant fraction of this work is inspired by the success of the HPPO process," Flaherty says. "It's a shining example of what you can achieve."

"I'm very certain there will be more processes developed that combine hydrogen peroxide with a titanium zeolite," Pascaly agrees.

"A significant fraction of this work is inspired by the success of the HPPO process. It's a shining example of what you can achieve."

— David Flaherty, sustainable-catalysis researcher at the University of Illinois, Urbana-Champaign

Homogeneous Catalysis: Epichlorohydrin Production and Related Reactions

The Airbus A380 aircraft, the largest and most spacious civil aircraft ever made, is built from about 40% composite materials. Far lighter than corresponding aluminum parts, composites are key to the construction of such a large aircraft. Many composite components—including the leading edge of the tail, the aileron flaps on the wings, the floor panels, and the landing gear doors—consist of carbon fiber wrapped in an epoxy resin.[13] The epoxy resin is made from epichlorohydrin, a three-carbon molecule bearing an epoxide and a chlorine group.[14]

The Airbus A380 aircraft is made up of about 40% composite materials. Many of these consist of carbon fiber wrapped in an epoxy resin made from epichlorohydrin, a three-carbon molecule bearing an epoxide and a chlorine group. The manufacturing process for epichlorohydrin produces an environmentally harmful by-product, but Evonik researchers have pioneered an approach to epichlorohydrin that does not generate salt wastewater and minimizes harmful by-products.

Current manufacturing techniques for epichlorohydrin require a two-step process and produce an environmentally harmful by-product that must be cleaned up. One route starts with allyl chloride and reacts it with hydrochlorous acid to generate dichloropropanol. The other route reacts glycerol with hydrochloric acid to generate the same intermediate. Adding sodium or potassium hydroxide to dichloropropanol induces an intramolecular elimination of a chloride ion to give the desired epoxide. "This reaction results in epichlorohydrin, but you will have wastewater with a high content of sodium or potassium chloride," says Holger Wiederhold, a chemist at Evonik responsible for developing new processes that use hydrogen peroxide as an oxidant. "That is the drawback to this technology."

Evonik researchers have pioneered a one-step approach to epichlorohydrin without the generation of waste salt. They used a homogenous manganese catalyst that will drive the direct epoxidation of allyl chloride with hydrogen peroxide.

So far, the reaction has been successfully tested to pilot scale at Evonik, says Wiederhold, and David Bolz, senior project manager of licensing projects, adds that Evonik is seeking partners to transfer this technology to a commercial scale. Both list the advantages of the reaction: "We have no salt waste. We have reduced the chlorinated hydrocarbon by-products to a very small amount. We have a small amount of wastewater, lower steam consumption, and better yields. It is a higher-selective reaction."

One of the largest homogeneously catalyzed hydrogen peroxide reactions already used in industry is in the production of alkyl peroxides, such as di-tert-butyl peroxide and methyl ethyl ketone peroxide.[15] These products are produced from tert-butyl alcohol and methyl ethyl ketone, respectively, using sulfuric acid as the catalyst. The compounds are used as radical initiators in organic synthesis and for polymerization reactions, especially as curing reagents for unsaturated polyester resins.

There is a rich history of combining hydrogen peroxide with a homogeneous catalyst to epoxidize a target alkene, Glenneberg says. "Tungsten is quite often used as a catalyst in reactions with hydrogen peroxide in academic labs," he says. "But it has also had industrial applications. It is a reaction that can be used not just to make a few kilograms but to make multiton quantities."

One product that has been made this way is glycidol, the epoxide of allyl alcohol. The tungsten and hydrogen peroxide form a metal-peroxo complex that will selectively epoxidize activated double bonds, Glenneberg says. In the case of glycidol, the tungsten peroxo species complexes to the allyl alcohol's hydroxyl group, which directs it to react with the double bond to form the epoxide. Molybdenum, selenium, and boron compounds can also form metal hydroperoxides or peroxo species that react in a similar way.[16]

These catalysts have many potential uses beyond glycidol production. One thing to note is that, as the tungsten catalyst is water soluble, it forms in the aqueous layer of the reaction mixture. But water-insoluble alkenes can be epoxidized by this method simply by adding a phase-transfer catalyst, Glenneberg says. "There are a lot of possible modifications."

The only downside of this type of reaction is trying to get the tungsten back at the end of the reaction. "If you have a high-priced chemical to make, the tungsten price may be negligible," Glenneberg says. "Tungsten is not a poisonous metal, so maybe for precursors for pharmaceuticals, this chemistry may be applicable."

"In general, the homogeneous reaction has several advantages, except one, which is the recovery of the catalyst," Wiederhold agrees. Epoxidations can be highly exothermic reactions, but for homogeneous processes, that excess heat can be shed using a simple, inexpensive heat exchanger, he says. "And the reaction selectivity and activity is usually very high because you have one well-defined active site and mild reaction conditions."

The Evonik epichlorohydrin process has been designed so that the catalyst is "feed and forget," Bolz adds. "We have optimized this reaction for minimum use of catalyst and hydrogen peroxide, resulting in an economically favorable situation."

"A lot of the attention from academics is on developing better catalysts that will enable the use of 'green' reagents like hydrogen peroxide," the University of Nebraska's Dussault says. "People are still interested in metal complexes of things like tungsten, molybdenum, chromium—metals that are high oxidation state, that have been known to activate hydrogen peroxide for a long time," he says. The aim now is to develop processes that will run with parts-per-million concentrations of catalyst.

Peracids

Whereas hydrogen peroxide is a gentle epoxidation reagent typically requiring a catalyst, peroxy acids are far more reactive. "The peracids are very good reagents to make epoxides, diols, and so on," Glenneberg says.

Today, one of the chemical industry's biggest use of peracids formed in situ is for the production of epoxidized vegetable oils and epoxidized fatty acid methyl ester, Wiederhold says. These substances, produced at the scale of about 500,000 metric tons per year, are mainly used as green, low-volatile-organic-compound plasticizers and stabilizers for polyvinyl chloride and polyurethane foam production.

Although a wide variety of peroxy acids can be formed, peracetic acid and performic acid are the two simplest and most commonly used. The reagents are made by mixing hydrogen peroxide with acetic acid or formic acid, respectively.

Performic acid is easy to make in situ and is an efficient reactant, Glenneberg says. "Formic acid is a strong organic acid and reacts fast to form performic acid. The disadvantage is in certain circumstances it is sensitive to explosion." For industrial processes, careful observation of safety guidelines is essential to avoid the potential of forming a shock-sensitive explosive mixture.

Peracetic acid is safer to handle but not quite so easily formed in situ. Hydrogen peroxide and acetic acid form an equilibrium mixture of peracetic acid. "When you mix acetic acid and hydrogen peroxide, the equilibrium takes some time to establish," Glenneberg says. Adding sulfuric acid can accelerate the process, but care must be taken if the epoxide is acid sensitive because the formed epoxide can be ring opened to form the corresponding diol. "If you want the epoxide, you have to be careful with the reaction conditions," Glenneberg says. But if the diol is the desired product, these conditions can be ideal.

Alternatively, the sulfuric acid issue can be avoided by purchasing preformed equilibrium peracetic acid from suppliers such as Evonik. Several fine chemicals are produced by the use of equilibrium peracetic acid. "Higher-concentration equilibrium peracetic acid is mainly used in advanced pharmaceutical synthesis," Evonik's Leininger says. "Peracetic acid prefers electrophilic oxidations."

That preference means it will selectively oxidize nitrogen or sulfur heteroatoms, for example. "Penicillin synthesis uses peracetic acid to do the selective sulfur oxidation," Leininger adds.

Even sterically hindered, relatively unreactive alkenes can be epoxidized this way. An important product in the flavor and fragrance industry, α-pinene is epoxidized using this method. Because the product is acid labile and prone to ring opening, the reaction mixture is buffered using a mixture of sodium acetate and sodium carbonate.[17]

In addition to epoxidation reactions and heteroatom oxidations, peracetic acid is used industrially to make caprolactone, a seven-membered lactone ring.[18] The reaction, carried out in the U.K. by the Swedish specialty chemical company Perstorp, is a Baeyer-Villiger reaction. The transformation combines an oxidation with a rearrangement to convert cyclohexanone to the caprolactone.

Reactions of peracetic acid or hydrogen peroxide with ketones are akin to the way nature uses peroxides, Dussault says. "The original is the Baeyer-Villiger process, and there are all sorts of modern versions of it." It's a convenient way to insert an oxygen atom into the carbon skeleton of a molecule, which might be hard to achieve in other ways.

Miscellaneous Uses

Epoxidations are the major current industrial-scale reactions involving hydrogen peroxide and peracetic acid. But countless other useful conversions using the reagents have been proved to work effectively at industrial scale.

Heteroatom oxidations are one significant area of application. Tertiary amines oxidized to the corresponding amine oxide are important surfactants produced in thousands of tons for products such as shampoos and detergents.[19] The reaction typically proceeds simply by mixing the amine and hydrogen peroxide together.

A more complex process is the combination of ammonia and hydrogen peroxide to form hydrazine, a transformation also known as the Pechiney-Ugine-Kuhlmann process.[20, 21] The reaction requires a ketone such as methyl ethyl ketone; in the presence of ammonia and hydrogen peroxide, two ketone molecules become joined by a pair of nitrogen atoms in a structure called a ketazine. A subsequent hydrolysis reaction produces hydrazine and simultaneously regenerates the original ketone, which can be recycled.[22] "Today, some 10,000 tons are still produced by this process," Glenneberg says.

Sulfur heteroatom oxidations can also be carried out at industrial scale. Thiourea is converted to thiourea dioxide by the simple addition of hydrogen peroxide. The compound is a reducing agent that is used in the textile industry for making felt. In a related industrial-scale sulfur oxidation, hydrogen peroxide is used to make methyl isothiocyanate, a bioactive compound that can be used as a wood preservative.

In the chemical literature, the uses of hydrogen peroxide at academic lab scale is very broad—but the reactions are typically reported at the scale of just a few grams. "There are many reactions which use hydrogen peroxide, but the question is always whether you can use it in hundred-kilogram or [multi]-ton amounts," Glenneberg says. In many cases, an industrial-scale precedent for a reaction of interest can be found. "We want to make people aware that hydrogen peroxide can be used not only for gram quantities but for bigger applications."

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"We want to make people aware that hydrogen peroxide can be used not only for gram quantities but for bigger applications."

— Jürgen Glenneberg, hydrogen peroxide process chemist at Evonik

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Aseptic Packaging

Introduction

PACKAGING TRENDS IN THE FOOD AND BEVERAGE INDUSTRY

In balancing hectic lifestyles, consumers today want packaged foods and beverages they can grab and consume on the go. But they are also becoming increasingly health conscious, seeking fresher products that taste good and contain fewer preservatives.[1]

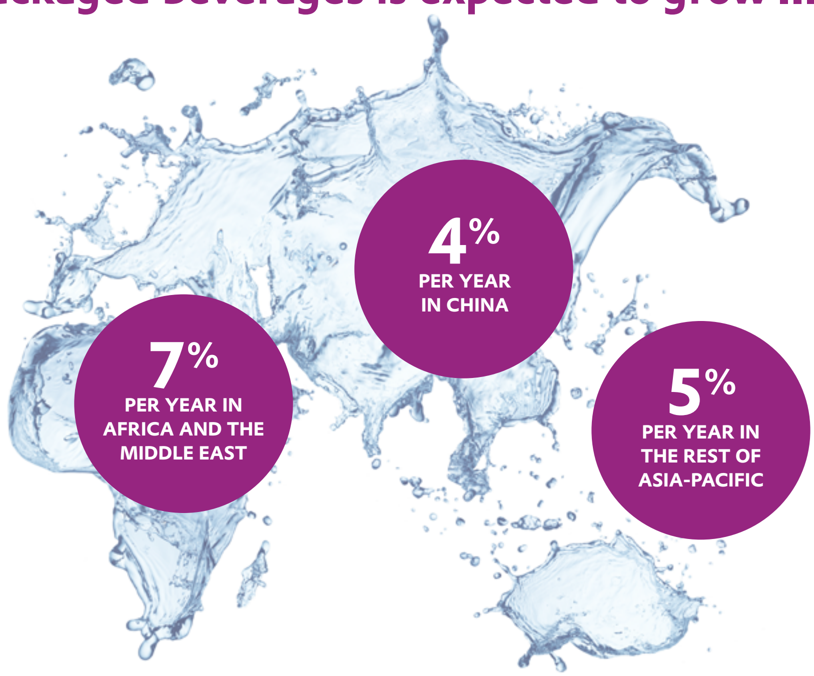
Aseptically packaged food—in which the packaging is sterilized, filled with a heat-treated product, and sealed under aseptic conditions—can be the ideal technology to satisfy the conflicting consumer demands for long shelf life, freshness, and convenience. The key appeal of aseptic packaging is that it extends the shelf life of a product by months without the use of chemical preservatives and without very harsh physical preserving treatments to the food product itself.

Food packaging company Tetra Pak developed its iconic plastic-coated paperboard cartons in the 1960s and filled the shelves of newly formed supermarkets with the cartons. Since then, aseptic packaging has enabled food and beverage companies to satisfy evolving consumer needs.[2,3] Tetra Pak sterilized its cartons using hydrogen peroxide. Applied under correct process conditions, the chemical is a powerful biocide that breaks down to form harmless oxygen and water. Many companies that have since entered the aseptic packaging market have also adopted hydrogen peroxide sterilization. Hydrogen peroxide remains the most important chemical for aseptic sterilization treatments today.

Traditionally, aseptically packaged products mainly meant cartons filled with fruit juices and dairy products. Today, these products have been joined by sports drinks, health-oriented nutraceuticals, ready-made coffees and iced teas, and on-the-go breakfast products that incorporate breakfast cereal into the beverage.[4] These newer products are often aseptically packaged in polyethylene terephthalate (PET) bottles.

In addition to new product types, aseptic packaging is also expanding into new regional markets. Economic growth and a growing middle class in many parts of Asia, as well as in parts of Africa and the Middle East, are providing large new markets for aseptically packaged goods, according to 2016 data from market research firm Euromonitor International and food packaging company Krones. The market for packaged beverages in China is expected to grow almost 4% per year to the end of the decade, and the rest of Asia-Pacific has been predicted to grow almost 5% annually over the same period. Growth in Africa and the Middle East is forecast to be even higher, at more than 7% per year.[5]

By the end of the decade, the market for packaged beverages is expected to grow ...



APPLICATION AREAS FOR ASEPTIC PACKAGING

Liquid or semiliquid foods and beverages naturally at risk of microbiological spoilage are the primary products that benefit from aseptic packaging. The pH of the product is a key factor in spoilage risk. Products below pH 4.5, such as carbonated soft drinks, are too acidic for microbial spores to grow in, so they naturally have a long shelf life. Products such as milk, fruit juice, sports drinks, and noncarbonated soft drinks are at a pH above 4.5; they also contain the water and nutrients that microbes need to grow. Such products require some kind of chemical or heat treatment to extend their shelf life.

Aseptically packaged food is subjected to a brief ultra-high-temperature (UHT) treatment, rapidly heating then cooling the product to kill microbes with minimal impact on the quality of the food product itself. A separate chemical treatment sterilizes the food packaging just before the product is poured into it and the packaging is sealed.

"This is the advantage of aseptic—you can treat the food in an optimal manner," says Joachim Wunderlich from the Fraunhofer Institute for Process Engineering & Packaging. Patrick Engelhard, head of process technology at Krones, agrees: "Aseptic is a sign of a high-quality product."

Aseptic packaging typically involves paperboard cartons. Paperboard that incorporates an aluminum layer is particularly good for long-shelf-life products, Wunderlich says, because it provides an excellent barrier to light and to oxygen, which can degrade the taste and nutritional contents of the product inside. PET bottles with enhanced oxygen and light barrier properties are also being developed for the aseptic market, Wunderlich adds.

Traditional food packaging materials, such as glass bottles or aluminum cans, can be sterilized with a blast of steam. But these materials have several drawbacks. Aluminum is expensive, and it is difficult to attach the top of the can to seal the product under aseptic conditions. Glass bottles are heavy and brittle, which makes them difficult and expensive to transport. Glass is also highly transparent to light, which leads to photochemical degradation of the food.

Paperboard and plastic aseptic packaging are cheaper than glass and metal cans. They require less material to make and are also much lighter, reducing the energy demands of shipping.[6,7]

Once an aseptic pack is sealed, it can be stored for extended periods without spoiling, even in hot, tropical locations. "Our customers deliver milk rice for the Red Cross for disaster relief, and the sterility of the product is all done by the aseptic processing," says food chemist Hanno Geissler, head of technology services at aseptic packaging company SIG. "The shelf life is up to 20 months, depending on the product and the packaging material—and this is all because of hydrogen peroxide."

Aseptic packaging typically involves paperboard cartons. Paperboard that incorporates an aluminum layer is particularly good for long-shelf-life products, because it provides an excellent barrier to light and to oxygen, which can degrade the taste and nutritional contents of the product inside.

Paperboard aseptic packaging requires less material to make and is also much lighter, reducing the energy demands of shipping. EVONIK

Technology

TECHNOLOGY OVERVIEW

Aseptic food packaging machines are large, complex devices. The machines sterilize, form, fill, and seal the package under aseptic conditions. The exact order of steps depends on the food product and the packaging technology being used. The fastest aseptic machines can fill up to 50,000 PET bottles per hour. "Packaging machines are very complex; there is a lot that can go wrong," says Friedhelm Brandner, manager of applied technology in Evonik Active Oxygens.

The machines can be the size of a small house, notes Sebastian Imm, head of applied technology in Evonik Active Oxygens. "One part of that is the peroxide bath. It is a very small part, but a very important part."

Hydrogen peroxide and peracetic acid are noted disinfectants, thanks to their powerful oxidant effect. Chlorine-based compounds are also effective disinfectants but can generate toxic by-products and would corrode the machine. Hydrogen peroxide and peracetic acid are selected for their efficacy and lack of harmful by-products. Both attack the cell's membrane as well as the essential enzymes within the cell that are crucial to the cell's functioning. "Hydrogen peroxide acts a bit like a hammer," Imm says. "It just destroys the whole cell, very simple."

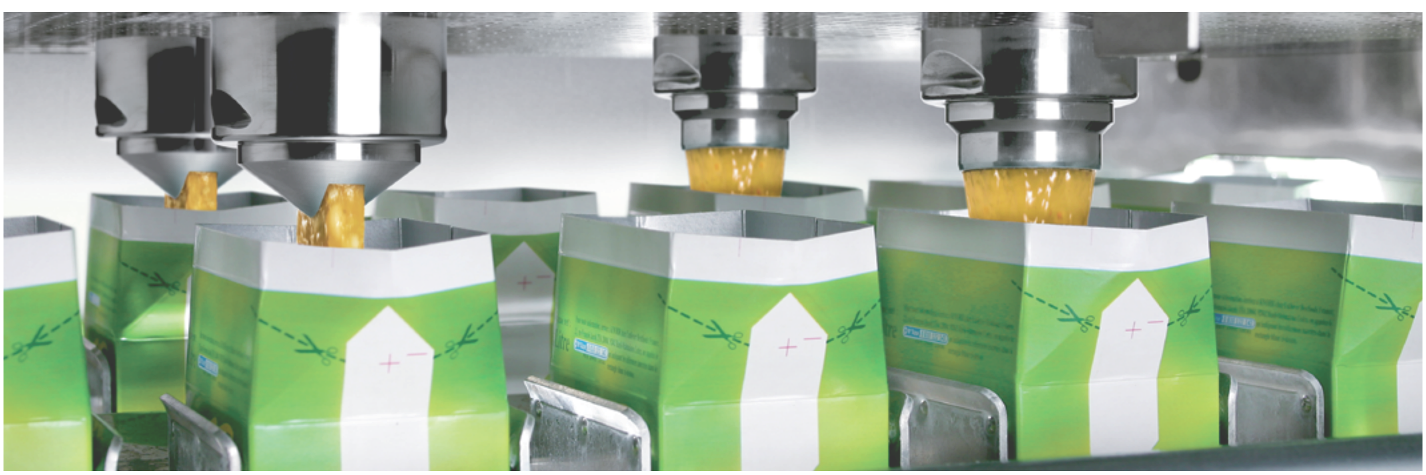
Peracetic acid is a slightly stronger oxidizing agent than hydrogen peroxide. In being slightly more lipophilic than hydrogen peroxide, it is more readily able to penetrate the microbial cell membrane and attack it from the inside. These factors contribute to peracetic acid being a more effective disinfectant than hydrogen peroxide. As a result, peracetic acid grades with a concentration of typically 5–15% are applied, whereas a 35% hydrogen peroxide solution is used.[8] Concentrations depend on the machine type and parameters. Achieving the required level of sterilization is a balance of biocide concentration, temperature, and reaction time.

Various technologies, including baths and sprays, have been developed to apply hydrogen peroxide to the packaging's inner surface. The following sections discuss the details of these technologies.

BATH TECHNOLOGY IN ASEPTIC PACKAGING AND HYDROGEN PEROXIDE REQUIREMENTS

The original aseptic packaging technology, pioneered by Tetra Pak in the 1960s and still used widely today, passes the flat carton material through a hydrogen peroxide bath to kill microbes on the packaging. Once disinfected, the cartons are formed, filled, and sealed—all under aseptic conditions inside the packaging machine.

To achieve the necessary level of disinfection while maintaining an acceptable machine throughput, a 35% solution of hydrogen peroxide is used, and the bath is heated to between 70 and 85 °C. A contact time of a few seconds under these conditions achieves the desired level of microbial reduction.[9]



Aseptic food packaging machines sterilize, form, fill, and seal the package under aseptic conditions. SIG

Once the packaging has passed through the bath, a pair of rubber rollers squeezes off most of the residual hydrogen peroxide before a hot-air treatment dries off any remaining traces of the disinfecting liquid before the package is formed and filled.

The hydrogen peroxide used for aseptic bath technology is a special grade specifically developed for this application. "You need a very high purity hydrogen peroxide because the packaging material will be in contact with food," Imm says. "You also need a certain stability of hydrogen peroxide in the aseptic filling process."

Although hydrogen peroxide is stable for long periods if stored and handled correctly, the compound can be decomposed rapidly into oxygen and water by four key factors: ultraviolet light, high pH, high temperature, and traces of metal.

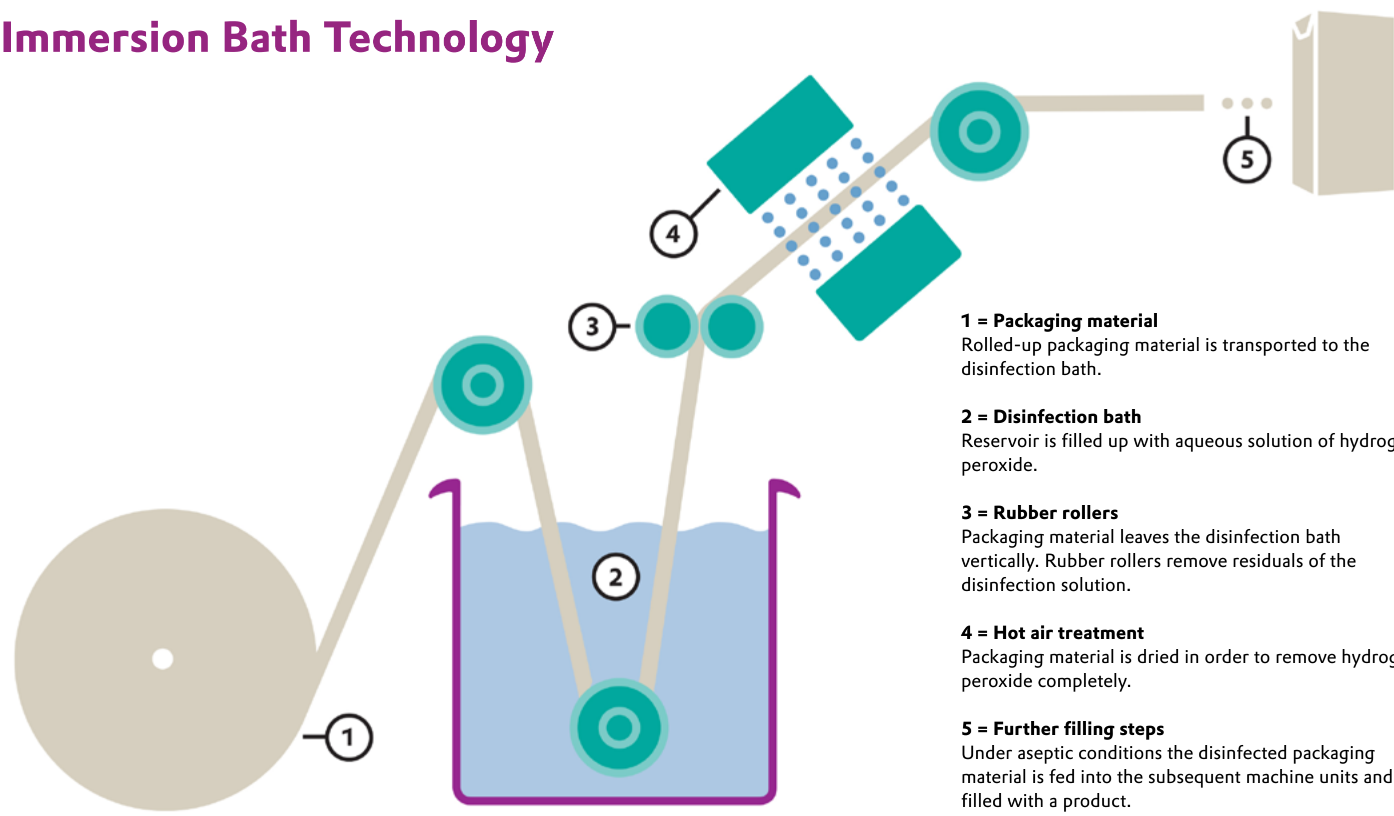
In the case of aseptic packaging machines, the hydrogen peroxide is continually heated in a metal bath. To avoid unnecessary downtime while the bath is emptied and refilled, the hydrogen peroxide in the bath must remain stable for at least a week, Brandner says. The special grade of hydrogen peroxide sold for immersion bath aseptic packaging contains strong stabilizers to minimize decomposition. "In 1970, Evonik started to produce special peroxide for this use," Brandner says.

The stabilizer does not directly affect the hydrogen peroxide, Imm explains. "It protects the hydrogen peroxide against metal traces." The stabilizer captures any traces of metal that enter the bath, either leached from the surface of the metal bath or carried in on the packaging.

Every hydrogen peroxide producer has a proprietary recipe for the stabilizer. "The stabilizer is the key knowledge," Imm says. The difference between hydrogen peroxide suppliers is the stabilizer blend. Evonik recently released a new stabilizer, which was five years in development from idea through initial testing, on-site testing, and finally product release.

A low-quality peroxide with a poor-quality stabilizer leaves a white, chalky residue buildup on the inside of the glass window of the immersion bath section of the packaging machine. "You can easily see if the hydrogen peroxide is a good quality or not," Brandner says.

Immersion Bath Technology



1 = Packaging material
Rolled-up packaging material is transported to the disinfection bath.

2 = Disinfection bath
Reservoir is filled up with aqueous solution of hydrogen peroxide.

3 = Rubber rollers
Packaging material leaves the disinfection bath vertically. Rubber rollers remove residuals of the disinfection solution.

4 = Hot air treatment
Packaging material is dried in order to remove hydrogen peroxide completely.

5 = Further filling steps
Under aseptic conditions the disinfected packaging material is fed into the subsequent machine units and filled with a product.

EVONIK

SPRAY TECHNOLOGY IN ASEPTIC PACKAGING AND HYDROGEN PEROXIDE REQUIREMENTS

Spray-based aseptic packaging machines preform the carton and then sterilize it with a jet of hot hydrogen peroxide. Once dried, the aseptic carton is filled and sealed.

For modern aseptic packaging machines, "spray" is something of a misnomer. A gas-phase vapor is used, not a liquid spray of hydrogen peroxide droplets.

Today's spray machines use a vapor to sterilize the entire carton's surface. The machine passes a mixture of air and 35% hydrogen peroxide through a pair of heated tubes that brings the mixture to 270 °C, well above hydrogen peroxide's 150 °C boiling point. The packaging itself is also heated to around 60 °C, which ensures the puff of hydrogen peroxide vapor does not cool enough to condense into droplets on the carton's surface. Flushing with hot air blows away the hydrogen peroxide from the now-sterile carton.

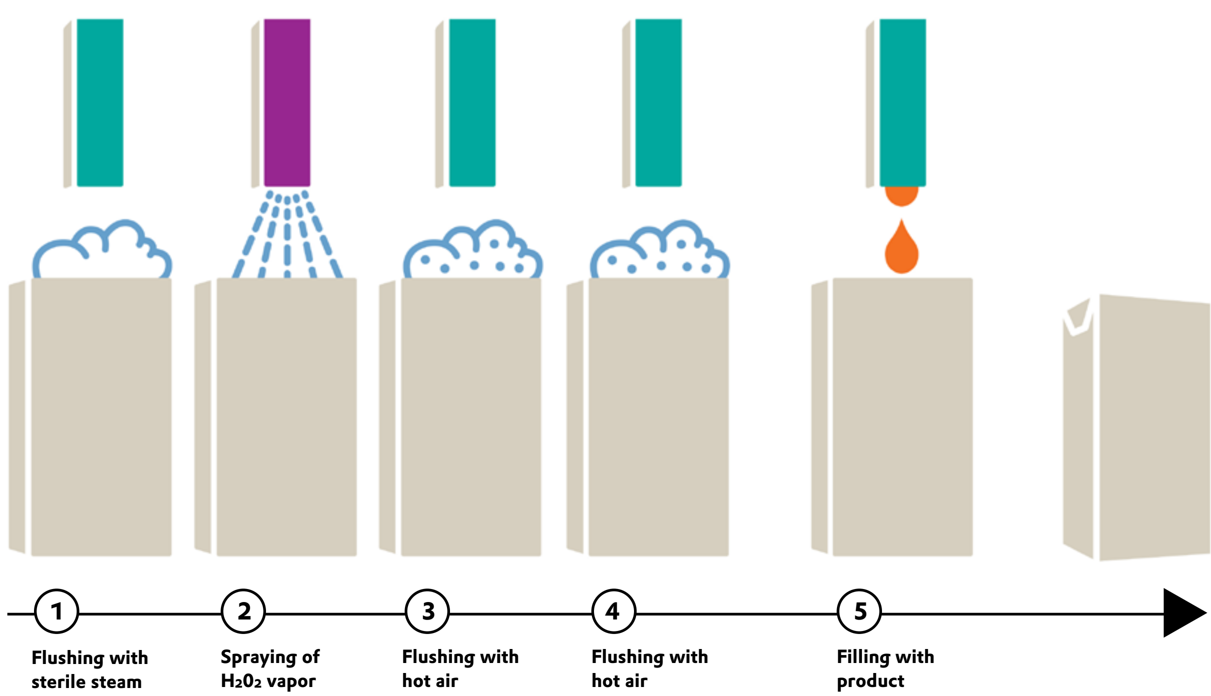
Avoiding condensation makes it much easier to remove the hydrogen peroxide before carton filling, Geissler says. "We reduced the number of preheating and drying steps from seven to five." As a result, the aseptic spray cycle time fell below two seconds, he adds.

For naturally acidic products, with a pH too low for bacterial spores to germinate and grow, vapor that's 2% hydrogen peroxide by volume is used. For less-acidic substances for which the spores must be deactivated, less air is mixed in and a vapor up to 7% hydrogen peroxide by volume is used.

As with the bath technology, specialized grades of hydrogen peroxide are used for spray-based aseptic packaging machines, but the formulation is almost the complete opposite of that used for the baths. Whereas the hydrogen peroxide in a bath technology must be stable for a week, in the spray machine the hydrogen peroxide is consumed almost the moment it enters the machine.[10] Hydrogen peroxide grades developed for spray machines contain the minimum amount of stabilizer possible to avoid stabilizer residue building up and clogging the vapor nozzles. "The importance of using the right grade is as important as not putting petrol in a diesel car—the machine stops working after a very short time," Geissler says.

"We have to ship the spray-grade hydrogen peroxide to the customer, so it still has to be stabilized, but we reduce the stabilizer to a minimum," Imm says. The imperative then is that spray-grade hydrogen peroxide is handled correctly, to avoid any potential contaminants that would quickly decompose the stabilized product, he adds. "You need well-trained people who are aware of that."

Spraying Technology



EVONIK

Peracetic Acid in Aseptic Packaging

PET is an increasingly sought-after aseptic packaging material. For one thing, it has good oxygen barrier properties,[11] preventing oxidative degradation of the product, says Krones's Engelhard. Perhaps more significantly, PET plastic is suitable for blow molding. "You are totally free with the bottle design," Engelhard says. "Marketing people really like PET because you can create your own shape of bottle, which is really hard to do with carton." Premium products can be packaged into novel or bespoke shapes with high consumer appeal.

However, PET has special demands when used for aseptic packaging. If heated to above 70 °C, the formed bottle starts to shrink. "We used peracetic acid because that has a really high efficacy at moderate temperatures," Engelhard says. "Between 40 and 65 °C, peracetic acid has a really high efficiency against microorganisms, especially against bacterial spores."

In Krones's aseptic PET packaging machines, peracetic acid and steam are blown into the bottle through a mixing nozzle, creating a mist that coats the bottles' inside surfaces. After two such treatments, the bottles are rinsed twice with sterilized water to ensure all traces of peracetic acid are flushed out before the bottle is filled.

The added benefit of all that flushing with liquid is that it rinses away traces of dust or dirt that may have found their way onto the packaging material. Overall, it's a straightforward and robust process, particularly suited to developing-world countries, where the food handling of the product through the process chain may not meet developed-world standards, Engelhard says.

DRY DISINFECTION

The major disadvantage with peracetic acid sterilization is the water it consumes during the rinsing step. To address this issue, methods for the dry disinfection of aseptic PET packaging have been developed in the past 10 years.

In a technique similar to the vapor technology used for cartons, a hydrogen peroxide vapor is applied to the inside of the bottle at elevated temperatures that prevent hydrogen peroxide from condensing on the bottles' inner walls.

Because formed, blow-molded PET bottles start to shrink above 70 °C, one option is to sterilize the PET before blow molding it, sidestepping the shrinkage issue. Alternatively, hydrogen peroxide heated to 100–130 °C and mixed with hot, dry air can be used on the formed bottle. Because heat transfer from air to the bottle is slow, the formed bottle will not get hot enough to shrink if the treatment is brief. The window for achieving a sterile surface without shrinking the bottle is not wide, Engelhard says, but it can be done.

Whether rinsing with peracetic acid or using a dry disinfection technique is the best method for aseptic PET packaging varies region by region, Imm says. In places with plenty of water available, peracetic acid sterilization is attractive because it is easier to operate, compared to the precise timing and temperature control required for dry disinfection. "In regions where clean, fresh water is scarce, dry disinfection is more appealing," Imm says.

OUTLOOK

There's a reason Tetra Pak still uses the same hydrogen peroxide bath technology for aseptic cartons that it first introduced over 40 years ago, Engelhard says. When a process works so well, why change it?

Consumer demands might have significantly changed since the 1960s, when aseptic packaging first appeared, but the latest implementations of the technology still satisfy consumer trends today.

"We have used hydrogen peroxide in our machines from the very start, and we plan to continue using it long into the future," Geissler says.

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— Hanno Geissler, head of technology services, SIG

ABOUT FRAUNHOFER

The Fraunhofer Institute for Process Engineering and Packaging IVV, located in Freising, Germany, stands for high-quality food products and safe, effective, and convenient packaging systems. Efficient use of raw materials and minimal environmental impact are priorities in the organization's development work.

ABOUT SIG

SIG is one of the world's leading solution providers for the food and beverage industry within the field of carton packs and filling technology. SIG has more than 5,000 employees worldwide and a 2017 sales of €1.66 billion.

ABOUT KRONES

Krones AG plans, develops and manufactures and installs machines and complete lines for the fields of process, filling and packaging technology. Its experience and its innovative vigour, underpinned by optimal synergising of mechanical engineering, line expertise, process technology, microbiology and information technology, have made the company into the world's leading vendor of holistic systems engineering.

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