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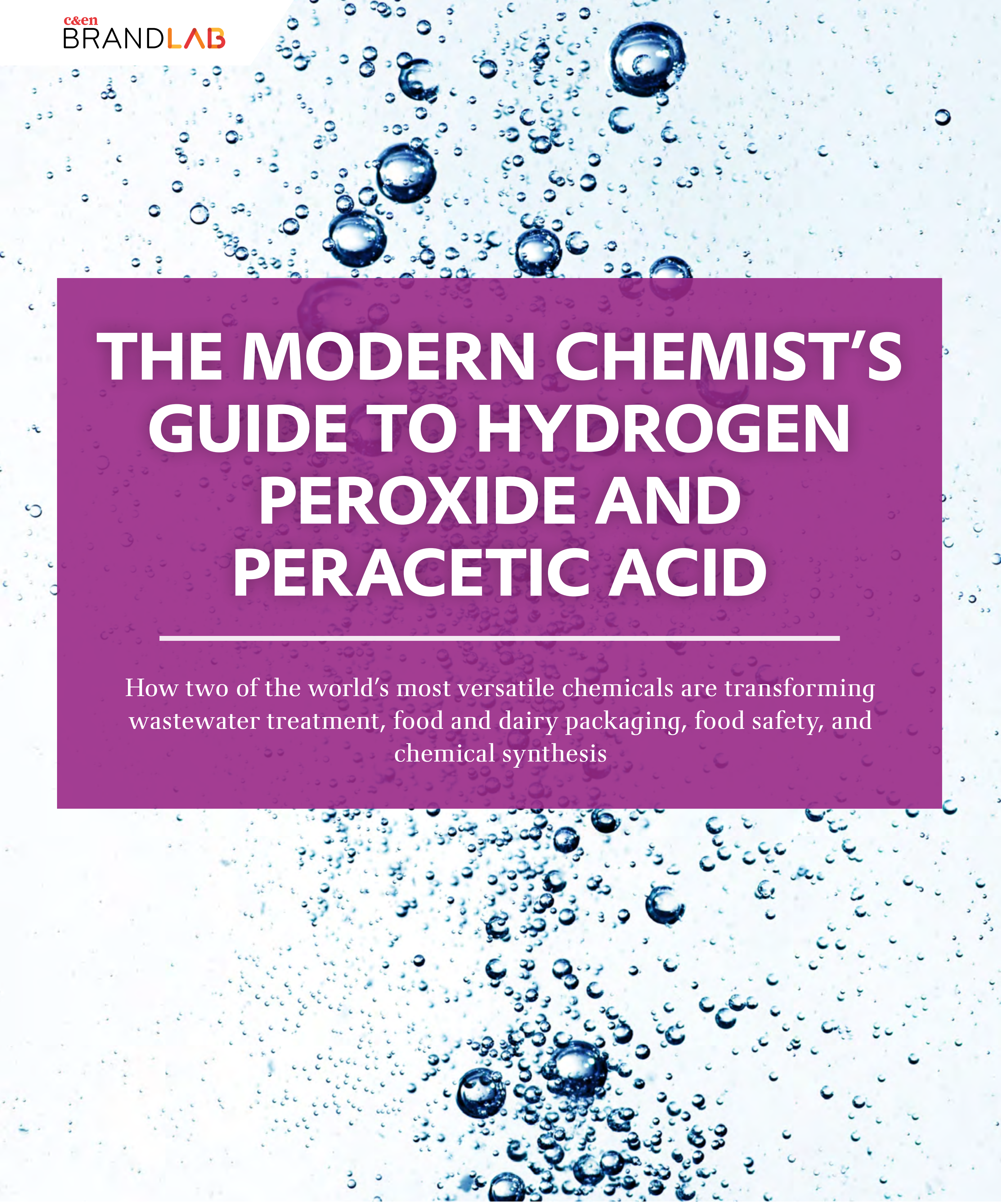

THE MODERN CHEMIST'S GUIDE TO HYDROGEN PEROXIDE AND PERACETIC ACID

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

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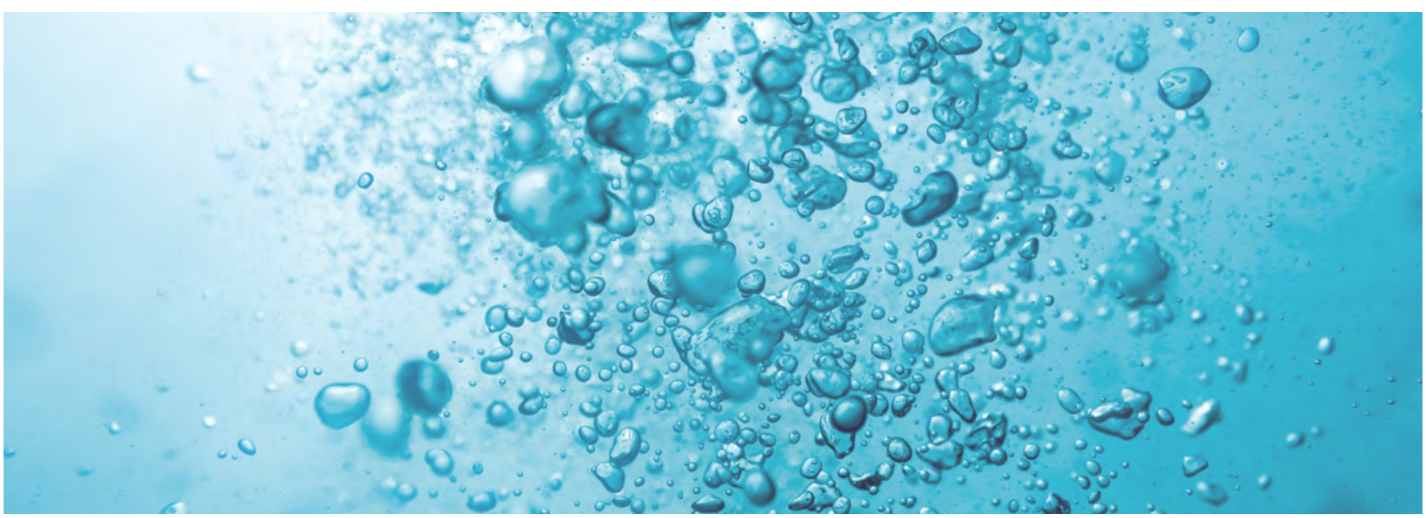

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Introduction

It is difficult to think of two more versatile chemicals than hydrogen peroxide and peracetic acid.

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. As early as 1818, hydrogen peroxide was recognized for its capacity to reduce odors and serve as a disinfectant. It can kill the harmful pathogenic bacteria that could otherwise contaminate packaged food and beverages and supply essential oxygen to the beneficial bacteria that are a key component of municipal wastewater treatment. Of course, hydrogen peroxide is also a staple of the drugstore and first aid kit, serving as an antiseptic for open wounds, among other uses.[1]

Peracetic acid, an analog of hydrogen peroxide in which one of the hydrogen units is replaced with an acetyl group, is also an important industrial chemical. First synthesized in the early 1900s, peracetic acid is used in chemical synthesis, the epoxidation of fatty oils, pharmaceutical manufacturing, and water clarification, and as a disinfectant and sterilant. Its strength as a biocide has made it a sterilant for stethoscopes and dental instrumentation, a sanitizer for hard surfaces, an eliminator of human pathogenic organisms in the food industry, and, more recently, a wastewater disinfectant.

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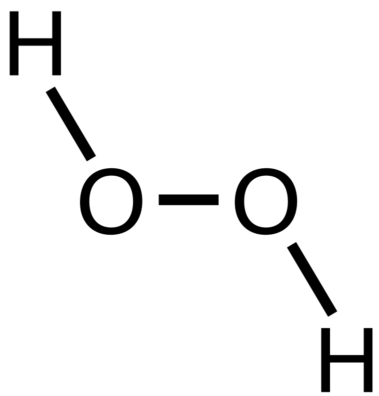
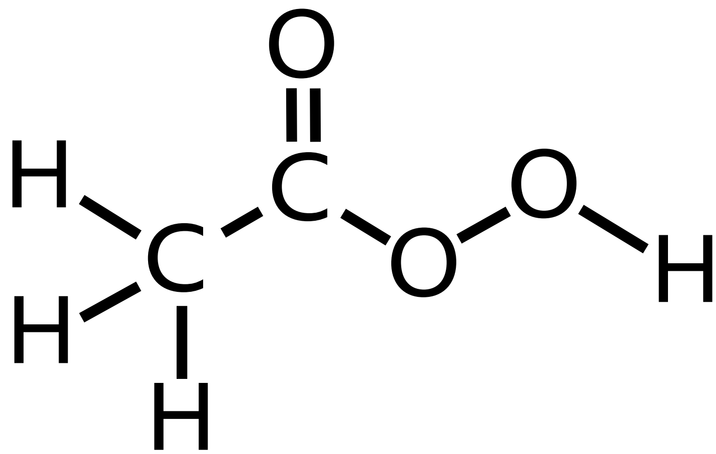
HYDROGEN PEROXIDE



PERACETIC ACID



FUNDAMENTAL CHEMISTRY AND PROPERTIES

Hydrogen peroxide is a molecule consisting 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.

It acts as a relatively weak—and therefore selective—oxidizing agent, specializing in the delivery of single oxygen atoms. It excels at oxidizing sulfur compounds, for instance, a reaction with 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.

However, the O–O 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 is an analog to hydrogen peroxide and exists as an equilibrium mixture of peracetic acid, hydrogen peroxide, acetic acid, and water. Typical commercial peracetic acid compositions range in peracetic acid concentrations from 5 to 40% weight. This strong oxidant is used in chemical synthesis and is a particularly efficient biocide, with applications including wastewater treatment and aseptic food packaging.

Hydrogen peroxide and peracetic acid are stable substances that, if handled correctly, can be stored for up to a year with little degradation or safety risk. Leading hydrogen peroxide and peracetic acid suppliers can advise customers on safe handling, as well as on planning for and building hydrogen peroxide and peracetic acid storage tanks.

1. Rosaria Ciriminna et al., "Hydrogen Peroxide: A Key Chemical for Today's Sustainable Development," ChemSusChem 9, no. 24 (Dec. 20, 2016): 3374–81, https://doi.org/10.1002/cssc.201600895.

HYDROGEN PEROXIDE, PERACETIC ACID, AND SUSTAINABILITY

The unique chemical properties of hydrogen peroxide and peracetic acid make them a great choice for antimicrobial applications, and even more so when sustainability is involved. As the subsequent chapters will show, there are numerous examples where hydrogen peroxide and peracetic acid can prevent or reduce the environmental consequences associated with other methods of microbial reduction, such as chlorination in wastewater treatment or the use of antibiotics in agriculture. In contrast to many other antimicrobial agents, hydrogen peroxide and peracetic acid do not create potentially toxic byproducts, and they degrade after use to water, oxygen, and acetic acid (in the case of peracetic acid), none of which are toxic to aquatic life in particular.

CHAPTER 1

Environmental Applications

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

INTRODUCTION

Thanks to increased emphasis 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 clearer than in wastewater treatment.

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

Increasingly, however, cleaning wastewater for safe discharge into the environment is only part of the equation. Treated municipal wastewater is becoming recognized as an important source of fresh water. For instance, reclaimed water supplies 40% of demand on the water-scarce island state of Singapore.[3] Orange County, California, is another pioneer in wastewater reuse. 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. The default option for water-scarce regions has often been to look to the ocean and build desalination plants to turn seawater into drinking water. "Seawater desalination is quite energy intensive and not that environmentally friendly," Fan says. Wastewater recycling could be a greener, more sustainable option.

Hydrogen peroxide, with its natural disinfectant and oxidant properties, is an attractive choice for cleaning wastewater and gas streams. It's also used to clean the soil as well as groundwater contaminated with organic pollutants. But performance and versatility are just two of the environmental credentials of hydrogen peroxide and its derivatives. The reagent also breaks down to give only oxygen and water. Hydrogen peroxide–based processes have twice received the US Environmental Protection Agency's Presidential Green Chemistry Challenge Award for their environmental friendliness.[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—the acidic component of table vinegar—which is readily biodegradable. In the environmental sector, peracetic acid is typically used for its powerful disinfectant properties, as it kills 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.

MUNICIPAL WASTEWATER TREATMENT

The strong oxidative properties and low aquatic toxicity and environmental impact of hydrogen peroxide and peracetic acid make these chemicals ideally suited for treating municipal wastewater and drinking water. Their biocidal capabilities and versatility in breaking down all manner of pollutants enable their use as components of highly effective water treatment systems.

SUSTAINABLE WASTEWATER TREATMENT WITH PERACETIC ACID

Before treated wastewater is discharged into the environment, it undergoes a disinfection process to remove pathogenic bacteria, such as Escherichia coli, fecal coliforms, and *Enteroccoci*. This step prevents the bacteria from reaching natural waterways used for recreation or fishing.

Wastewater disinfection was mandated in the US in 1972, when chlorine-based disinfection was the method of choice. Though chlorine and hypochlorite are effective, inexpensive disinfectants, both chemicals have since been proved to have significant environmental downsides.

Residual chlorine is toxic to aquatic organisms in the rivers, streams, and lakes into which the treated wastewater is discharged; it also reacts with organic molecules in wastewater to produce disinfection by-products. Some of these, 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 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 common drinking-water disinfectant, but it generates high levels of NDMA in the wastewater so is not suitable for this application.[5] Peracetic acid is a sustainable option, as it decomposes into water and vinegar, does not generate chlorinated disinfection by-products, and has a low aquatic toxicity.

This fast-acting, broad-spectrum biocide does not leave harmful by-products. Peracetic acid's biocidal mode of action is essentially the same as that of chlorine and chlorine dioxide.[6] 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 its inner workings.

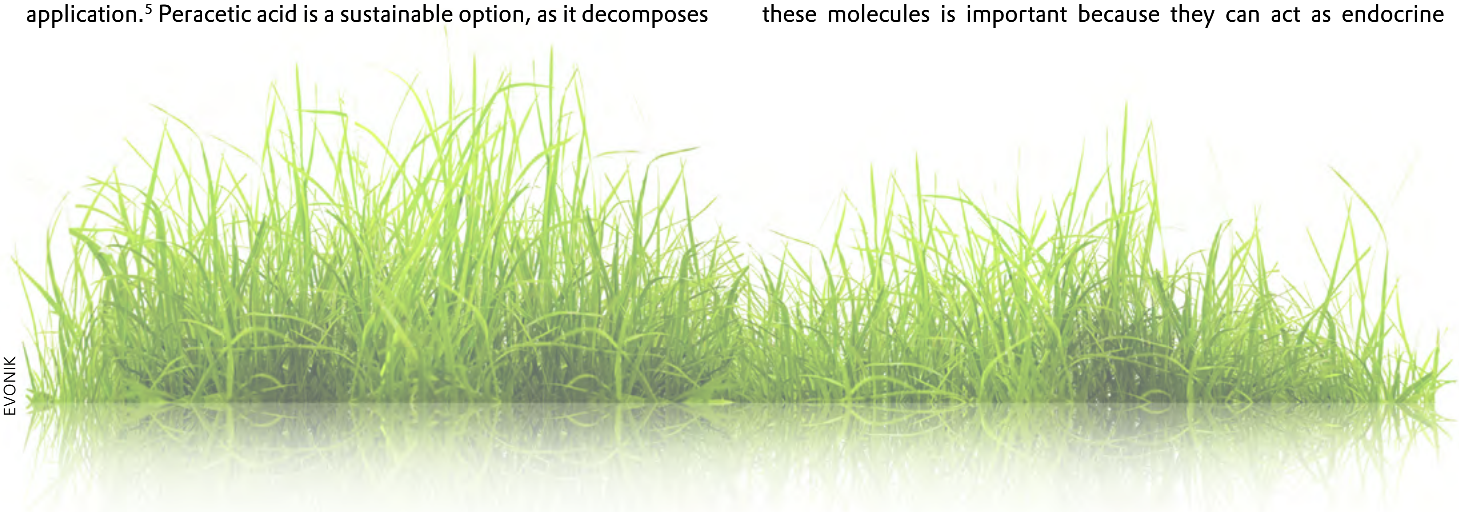
Existing chlorine treatment infrastructure can be converted to peracetic acid with little capital expenditure by retrofitting with the necessary equipment. Peracetic acid disinfection has been successfully deployed permanently at many municipal wastewater treatment plants in the US, including plants in Memphis, the world's largest peracetic application for wastewater disinfection, and Denver. It is also in use in Milan.

A recent market analysis confirms that in a world increasingly focused on the environment, the use of peracetic acid is only set to grow. It is unique among potential biocides in combining a high score for environmental friendliness with a high rating for its effectiveness as a biocide for fluids and for surfaces, according to a recent market report.[7]

"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 strong growth for peracetic acid is projected for sustainable and cost-effective wastewater treatment, the report notes.

ADVANCED OXIDATION PROCESSES WITH UV, FENTONS' REAGENT, OR OZONE

Advanced oxidation processes (AOPs) are powerful oxidant systems that 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



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disrupters in waterways. AOPs can also eliminate disinfection by-products.

The key oxidant species typically generated by an AOP is the hydroxyl radical, which is 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 (UV) 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, which oxidatively attack the micropollutants 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 directly broken down by the UV light, he says.

"A major advantage of peracetic acid over chlorine-based disinfectants is that it reacts and decomposes quickly. It is believed to produce little to no toxic by-products upon reaction with wastewater or natural organic matter."

—Juan Pavissich, University of Notre Dame

Fan agrees. "The 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. The sweet spot for these AOPs is often industrial wastewater treatment.

COMBINED SEWER OVERFLOW SYSTEMS DISINFECTION

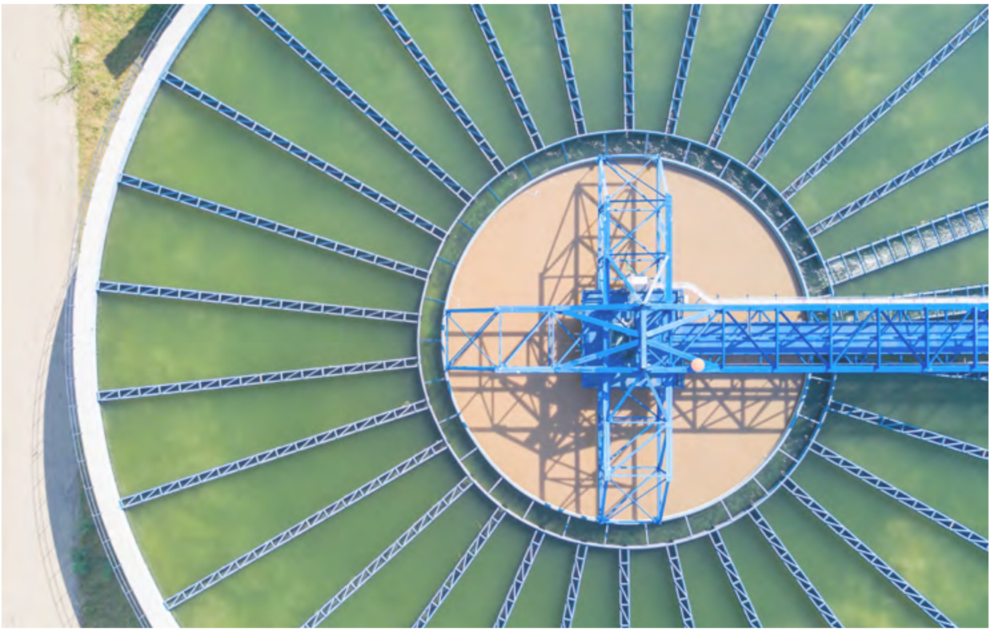
Modern wastewater collection systems are typically constructed to handle two separate flows: one set of pipes collects sewage from houses and other buildings and transports it to a wastewater treatment plant, while a second set handles stormwater runoff. Older sewage systems collect both water flows 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; in fact, many of the world's older cities still have combined sewers. According to the EPA, about 860 municipalities in the US alone still use them.[8]

The problem with combined sewer systems arises with heavy rainfall or snowmelt. The volume of water flowing through the 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 goes 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 body of water poses a health risk.[9] The European Union has recently issued directives limiting the amount of these bacteria in water used for bathing or swimming and other recreational uses.[10]

Climate change is predicted to increase the frequency of heavy-rainfall events, and combined sewer overflow will become a growing problem. Tightening environmental regulations have put greater focus on disinfecting combined sewer outflow before it enters the environment.[11]

Chlorine-based treatments were traditionally used to disinfect combined sewer outflow, but they carry the same environmental concerns as chlorine disinfection of treated wastewater noted above. The intermittent and highly variable nature of this water flow makes it 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.

Recent research has shown that peracetic acid is an effective alternative to chlorine for combined sewer outflow disinfection. "A major advantage of peracetic acid over chlorine-based disinfectants is that it reacts and decomposes quickly," Juan Pavissich, a researcher at the University of Notre Dame, wrote in a 2017 article in Science of the Total Environment.[12] "It is believed to produce little to no toxic by-products upon reaction with wastewater or natural organic matter." Pavissich's study showed that particulates in the water had no effect on peracetic acid's antimicrobial performance.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The combination of hydrogen peroxide and UV light breaks 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.[3] 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.

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.[13]

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 that 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[14] and 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 to let only water molecules pass through it, but it doesn't always work that way.

"Some harmful chemicals can pass through the reverse osmosis membrane and get into the filtrate," Fan says. Micropollutants that can slip through the membrane include pharmaceutical compounds and chlorine disinfection by-products. "They can be very harmful compounds, such as NDMA, [per- and polyfluoroalkyl substances], and trihalomethanes," Fan says. "Our research is to treat the reverse osmosis–treated water to make sure everything has been removed."

OXYGEN SUPPLY AND 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. These biological partners in wastewater cleanup sometimes need a little help from hydrogen peroxide to carry out their role.

One way to help 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. Oxygen demand sometimes can exceed supply—for example, because of seasonal weather patterns of a particularly high quantity of organic matter entering the wastewater stream.

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MUNICIPALITIES IN THE UNITED STATES ALONE STILL USE COMBINED SEWERS

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. "The growth of filamentous bacteria can create headaches for management of wastewater treatment ponds," says Jacobo Villagran, the marketing manager for aseptic packaging and environmental at Evonik Active Oxygens. "You can use hydrogen peroxide to remove the filamentous and to add oxygen."

Hydrogen peroxide naturally breaks down to produce water and oxygen, but aerobic bacteria contain peroxidase enzymes. These enzymes rapidly break down the peroxide 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 earlier 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.[7] "Strict pollution control has increased the usage of hydrogen peroxide and can be a growth driver in the upcoming years."

ODOR CONTROL AND REMOVAL OF SULFITE AND SULFIDE

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. "They just stink," says Greg Melenkevitz, the director of applied technology at Evonik Active Oxygens. "Imagine having one of those in your neighborhood." The way to control the smell is to dose with hydrogen peroxide.

There are other reasons beyond 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 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 controlling hydrogen sulfide. 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, for several reasons, increasingly replacing chlorine as the standard pretreatment to prevent hydrogen sulfide from entering wastewater treatment facilities.[15] Using hydrogen peroxide solution avoids the need to store compressed, toxic chlorine gas and comply with the relevant occupational health and safety requirements. In addition, 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. Finally, there is little to no cost penalty to using hydrogen peroxide in place of chlorine.

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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. Reusing process water can significantly reduce manufacturing industries' water footprint and associated costs and can avoid negative environmental impacts.

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, Evonik's head of environmental technology. "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 that is relatively simple to install and operate, Blesgen says. The downside is that UV lamps consume a great deal 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. In addition, UV is not suitable for turbid wastewater streams that the light cannot penetrate. In those cases, Fenton's reagent might be a better AOP option.

The reaction combines hydrogen peroxide and 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.[16] 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 of. But the precipitation can be a distinct advantage, says Jochen Schumacher, who worked at the water treatment system provider Eisenmann and is now the global head of sales at BHU Umwelttechnik. 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 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 when organic precipitation takes place, Schumacher adds.

In addition, Evonik can offer HYPROX® OHP in-house environmental and process engineering for wastewater treatment technologies, enabled by its purchase of PeroxyChem in 2020. HYPROX® OHP is an environmentally safe grade of hydrogen peroxide, specially developed for its use in HYPROX® OHP wastewater treatment plants or in general Fenton chemical oxidation treatment processes for the sustainable reduction of high chemical oxygen demand (COD) and total organic carbon (TOC) levels in wastewater.

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."

"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."

—Andree Blesgen, head of environmental technology, process technology, and engineering at Evonik

Plant managers who do not want to deal with the sludge Fenton's reagent always generates should consider ozone-peroxide. "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. The sweet spot for ozone is wastewater with a relatively low COD, mainly because there is a limit to how much of it, as a gas, can be transferred into the water.

EISENMANN

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

When trying to decide which AOP to use as the most sustainable and economical treatment solution, the answer requires 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 to use 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 straightforward to use in 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 and peracetic acid have 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 warm environment, creating a biofilm that gradually clogs the system. "When that biofilm becomes too thick, it needs to be removed, and that can be quite difficult to accomplish," Villagran says.

Regular, small injections of hydrogen peroxide or peracetic acid into the cooling water, a process known as shock treatment, is one option for controlling biofilm formation. This method can also be effective for controlling the strain of Legionella bacteria that cause Legionnaires' disease. Contaminated cooling towers are a well-known source of the bacterium.[17] In addition to ongoing treatments, concentrated hydrogen peroxide can be used for longer-term cleaning and maintenance cycles. "A hydrogen peroxide flushing can remove the biofilm," Villagran says.

Flushing the system involves pumping a 50% hydrogen peroxide solution into the cooling system and recirculating it for 6 hours, by which time 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."

INDUSTRIAL FLUE GAS SCRUBBERS

Sulfur dioxide is a gaseous by-product generated by a number of industrial sites, including fossil fuel power plants and pharmaceutical production facilities. Sulfur dioxide reacts in the atmosphere to produce sulfuric acid, which contributes 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 effectively capture sulfur dioxide emissions, whether the gas is present in high or low concentration. Sulfur dioxide reacts 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.[18]

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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.

Nitrous oxide compounds in flue gas emissions can lead to haze and smog. Addition of hydrogen peroxide by itself or in combination with urea can convert these compounds to water-soluble nitrogen compounds. These in turn can be eliminated from the effluent gas stream via common scrubbing techniques.

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 bleaching. Half of all hydrogen peroxide is used this way,[19] but the chemical is also increasingly being used to help treat the high volume 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.[20] Given the large volumes of wastewater from paper mills, the most economical option is generally to use advanced oxidation to break down these recalcitrant compounds into biodegradable molecules that can then be fully removed in a subsequent biological treatment step.

Paper-mill waste streams typically handled by other means can require hydrogen peroxide intervention, Melenkevitz says. Paper produced by the Kraft process—which uses hot water, sodium hydroxide, and sodium sulfite to turn wood chips into pulp—generates a dark, toxic waste liquid full of 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. "All of the sudden, the water oxygen levels plummet and the pond's whole ecosystem is at risk," says Melenkevitz. To avoid killing the beneficial aerobic bacteria in the pond, the fastest and simplest thing to do is to add peroxide. "You can try to force oxygen into solution with aeration spargers," Melenkevitz says. "Or you just drop in some peroxide and problem solved."

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

"You can try to force oxygen into solution with aeration spargers. Or you just drop in some peroxide and problem solved."

— Greg Melenkevitz, director of applied technology at Evonik Active Oxygens

CONTROLLING HARMFUL ALGAL BLOOMS

Large blooms of blue-green algae are becoming a more common occurrence within natural waterways. The 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 growing prevalence of algal blooms. Hydrogen peroxide is proving to be an effective treatment for the blooms, selectively killing the algae with minimal effects on the rest of the ecosystem.[21]

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 also comes out. This water can contain sulfides that, as with municipal wastewater, can pose an odor problem and can form corrosive sulfuric acid. The water might also contain microbes and algae that cause biological fouling of the production well, says Robert Gec, technical product manager, North America, for Evonik Active Oxygens.

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, though now it's more typically used as a liquid for hydraulic fracturing. Other sources of water for fracking can also be pretreated with peracetic acid to prevent biological fouling of the equipment.

SHUTTERSTOCK

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.

SOIL REMEDIATION

As populations grow and cities expand, land once part of an 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 are gargantuan tasks because of 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.

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 modified for use in soil. A more concentrated hydrogen peroxide solution, combined with an iron(III) catalyst, is typically employed.

Calling this process in situ chemical oxidation, as it is known, is somewhat inaccurate, as more than oxidation is going on under typical conditions. A better term is catalyzed hydrogen peroxide propagations, or HPP.[22] Under these conditions, the hydroxyl radical is not the only active species formed; the perhydroxyl radical ($HO2^{\bullet}$), superoxide radical anion ($O2^{\bullet-}$), and hydroperoxide anion ($HO2^{-}$) 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 aids the process. In water, superoxide ions have low activity because they become surrounded by water molecules. But 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 from protective soil particles and into solution, where they can then be broken down.[23] Recent research has shown that even contaminants resistant to oxidative remediation, such as carbon tetrachlorine and the persistent, bioaccumulative perfluorinated compounds such as perfluorooctanoic acid, can be treated this way.[24]

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, aldehydes, sodium hypochlorite, and others," a recent market report says.[7] It concludes, however, that none of the alternatives can match hydrogen peroxide and peracetic acid's combination of performance and environmental benefits.

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CHAPTER 2

Chemical Synthesis

INTRODUCTION

The oxidation reaction is one of the most common reactions organic chemists use 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 at Urbana-Champaign.[2] "Compared with oxidizers based on chlorine, hydrogen peroxide produces mainly water as a by-product."

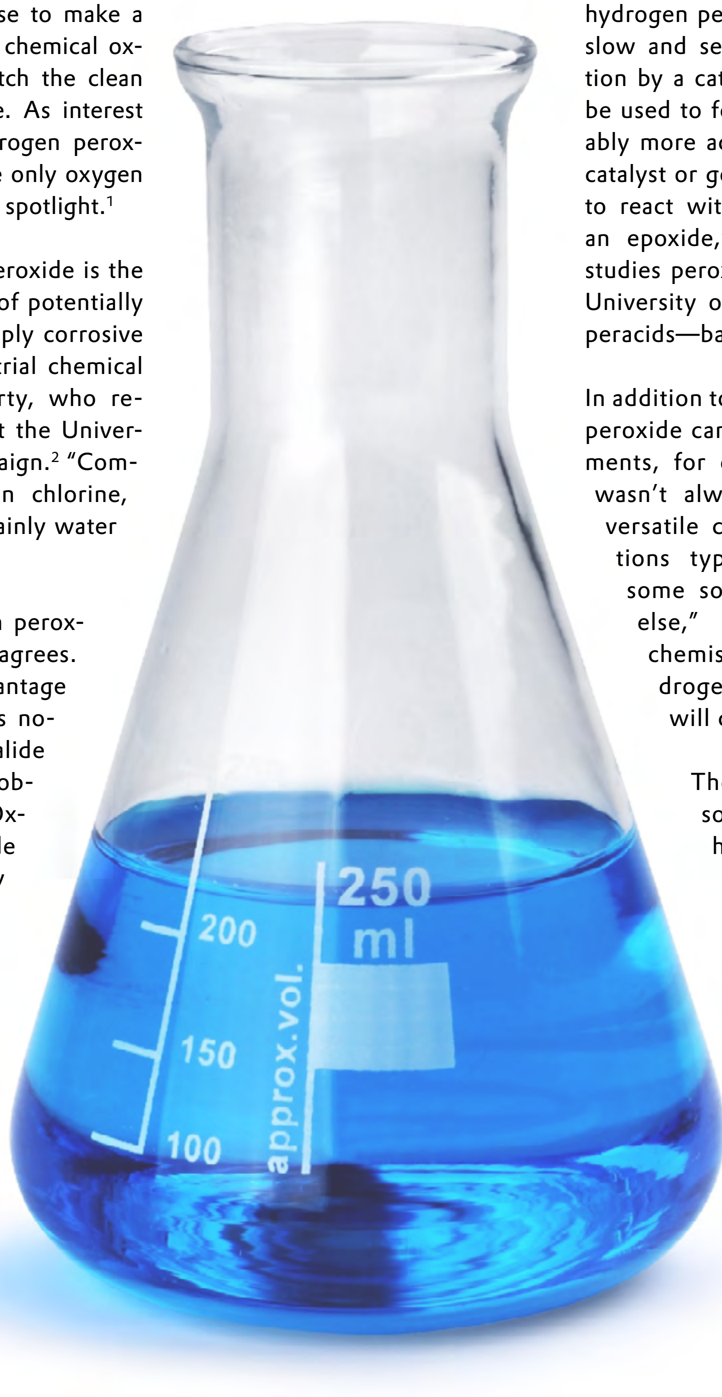
Jürgen Glenneberg, a hydrogen peroxide process chemist at Evonik, agrees. "Hydrogen peroxide's main advantage is safety," he says. "Chlorine is notorious for producing toxic halide by-products, which aren't a problem for hydrogen peroxide." Oxidation with hydrogen peroxide also doesn't produce briny, 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 at Evonik Active Oxygens. "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 it 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. "Hydrogen peroxide wasn't always considered a particularly versatile chemical. In the past, applications typically involved bleaching of some sort: hair, paper, or something else," says Leininger. "Nowadays, chemists are getting creative with hydrogen peroxide, a trend I anticipate will continue."

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 proved chemical transformations. It is hoped that this review of hydrogen peroxide chemistry will inspire yet more uses of this green, versatile reagent.



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HETEROGENEOUS CATALYSIS: HYDROGEN PEROXIDE TO PROPYLENE OXIDE AND CAPROLACTAM

Propylene oxide is a chemical in high demand. This epoxide is used to make polyurethane foams, which have applications in items including car bumpers, sofas, and thermal insulation for refrigerators. Demand for propylene oxide is rising at a projected 3.7% per year; in 2018, global production exceeded 10 million metric tons (t).[4] A new and efficient green process called hydrogen peroxide to propylene oxide (HPPO) is increasingly meeting this demand.

The key to the HPPO process was the 1983 discovery by Italian chemical company EniChem (now named Versalis) 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, vice president 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, according to Marc Brendel, Evonik's head of HPPO technology. Every metric ton of propylene oxide produces 2.1 t 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 US, cleaning up the wastewater produced in order to comply with environmental regulations is a major downside to the process. "I doubt there will be any new chlorohydrin plants," Bode says.

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.

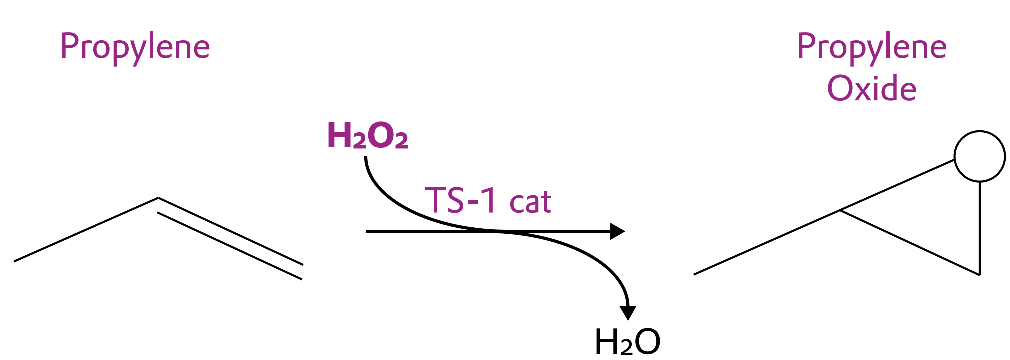
DEMAND FOR PROPYLENE OXIDE IS RISING AT A YEARLY RATE OF

3.7%

The issue with this reaction was not environmental but economic. When you produce 1 ton of propylene oxide, you get 2.3 t of styrene or 2.8 t 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 has no such disadvantages. Propylene oxide is the sole product, and the only significant reaction by-product is water. The key to the HPPO process was the discovery by Italian company EniChem (now 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. The reaction between titanium and hydrogen peroxide to create titanium peroxide is well established, Brendel 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. Hydrogen peroxide and propylene enter the TS-1 zeolite's channels, and the hydrogen peroxide reacts with the zeolite to form titanium peroxo species that oxidize the propylene to propylene oxide.

For Evonik, a major producer of hydrogen peroxide as well as a maker of zeolite catalysts, the reaction was a clear fit. Teaming up with Thyssenkrupp Industrial Solutions, Evonik developed the HPPO process, which it now licenses to interested companies.[7, 8] The first global-scale HPPO production plant, built by SK picglobal (formerly SKC) in Ulsan, South Korea, uses this technology. Evonik supplies the catalyst and hydrogen peroxide as part of the deal. There are three more HPPO plants using Evonik-Thyssenkrupp technology that have been brought on line or are under construction.

Dow and BASF also worked together to develop their own HPPO process.[9] The companies use the propylene oxide to make downstream products. The key knowledge Evonik and BASF have independently developed relates to the zeolite catalyst, according to Glenneberg, who adds that the catalyst is initially formed as a fine powder, which is not ideal for industrial use. "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," he says.

> **"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

The uses of zeolite catalysts 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," says Flaherty at Urbana-Champaign. "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, as it might do on a surface-catalyzed process, further boosting selectivity and yield.

For example, the same TS-1 catalyst used in the HPPO process is 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 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. 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 more 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 that 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]

Investment 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."

EVONIK

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.

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'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.

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

Glenneberg agrees "It's pretty clear that we are going to see more applications where hydrogen peroxide and titanium zeolites are brought together," he says.

"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

Over half of the Airbus A350 XWB aircraft, one of the newest and most profitable commercial jets, is built from composite materials. Far lighter than corresponding aluminum parts, composites are key to the construction of such a quiet, efficient giant. Many composite components—including the including the outer and center wing box (covers, stringers, spars), fuselage (skin, frame, keel beam, and rear fuselage) and the empennage (horizontal and vertical tailplanes)—consist of carbon fiber wrapped in an epoxy resin. 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]

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.

Evonik has successfully tested the reaction to pilot scale, according to Wiederhold, and Bode says the company is seeking partners to transfer this technology to a commercial scale. They list the advantages of the reaction:

- Zero salt waste
- Reduction in chlorinated hydrocarbon by-products
- Small volume of wastewater
- Lower consumption of steam
- Better yields
- Increased reaction selectivity

One of the largest homogeneously catalyzed hydrogen peroxide reactions already employed in industry is used in the production of alkyl peroxides such as di-tert-butyl peroxide and methyl ethyl ketone peroxide.[15] These products are made 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.

SHUTTERSTOCK

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.

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."

SHUTTERSTOCK

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.

Epoxidations can be highly exothermic reactions, but for homogeneous processes that excess heat can be shed using a simple, inexpensive heat exchanger. "And the reaction selectivity and activity is usually very high," Wiederhold says, "because you have one well-defined active site and mild reaction conditions."

The Evonik epichlorohydrin process has been designed as a "feed and forget" catalyst, he adds. "Catalyst and hydrogen peroxide costs can add up, so the team strived to minimize the amounts necessary without compromising the reaction."

"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.

One of the chemical industry's biggest uses of peracids formed in situ is for producing epoxidized vegetable oils and epoxidized fatty acid methyl ester, Wiederhold says. These substances, produced at the scale of about 500,000 t per year, are used primarily 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, according to Glenneberg. "Formic acid is a strong organic acid and reacts quickly 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 UK by the specialty chemical company Ingevity, 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 mimic how 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 a common 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 transformation is the combination of ammonia and hydrogen peroxide to form hydrazine, 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 broad, but the reactions are typically reported at the scale of just a few grams. There are many reactions that use hydrogen peroxide, but the question is always how much can you scale up, 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."

"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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CHAPTER 3

Aseptic Packaging

INTRODUCTION: PACKAGING TRENDS IN THE FOOD AND BEVERAGE INDUSTRY

With today's hectic lifestyles, consumers want packaged foods and beverages they can grab and consume on the go. At the same time, consumers are becoming increasingly health conscious, seeking products that taste good and stay fresh longer yet contain fewer preservatives, says Jacobo Villagran, marketing manager of aseptic packaging and environmental at Evonik Active Oxygens.

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 conflicting consumer demands for long shelf life, freshness, and convenience. The key appeal of aseptic packaging is that it extends shelf life by months without the use of chemical preservatives and without harsh physical preserving treatments to the food product itself.

Food-packaging company Tetra Pak developed its plastic-coated paperboard cartons in the 1960s and filled supermarket shelves with them. Since then, aseptic packaging has enabled food and beverage companies to satisfy evolving 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 entered the aseptic packaging market later have also adopted hydrogen peroxide sterilization. Hydrogen peroxide remains the most important chemical for aseptic sterilization treatments from a technical, economical, and sustainability point of view.

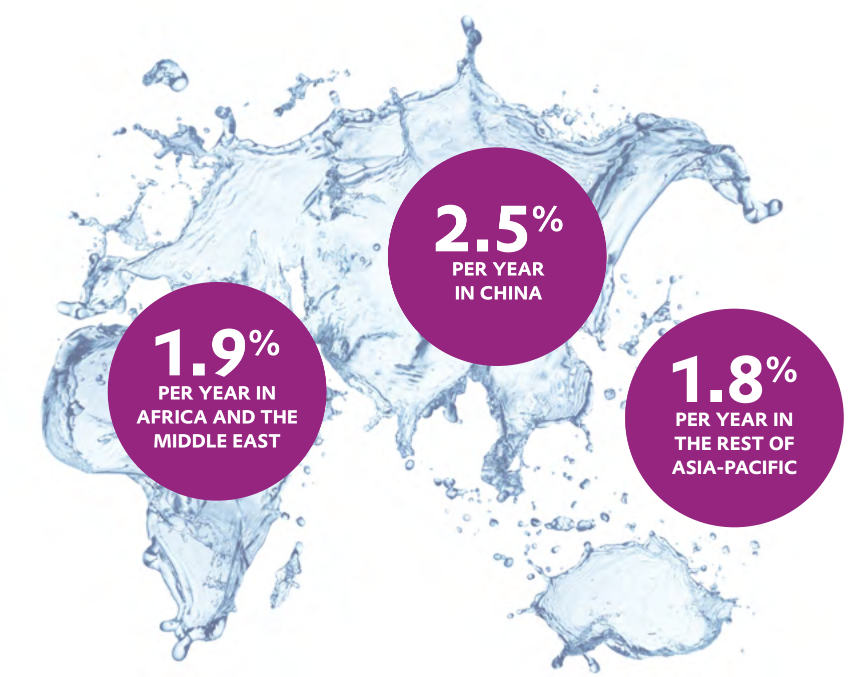
Traditionally, aseptically packaged products meant cartons filled with fruit juices and dairy products. These products have been joined by sports drinks, health-oriented nutraceuticals, protein-enriched milk shakes, plant-based milk products, ready-made coffees and iced teas, and on-the-go items that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

In addition, aseptic packaging is expanding into new regional markets. Economic growth and a growing middle class in many parts of Asia, as well as areas of Africa and the Middle East, are providing large new outlets for aseptically packaged goods, according to 2020 data from the food-packaging company Krones.[5] Between 2020 and 2023, consumption of packaged beverages in China is expected to grow almost 2.5% per year, and the rest of Asia-Pacific has been predicted to grow almost 1.8% annually over the same period. Growth in Africa and the Middle East is forecast to be 1.9% per year.

APPLICATION AREAS FOR ASEPTIC PACKAGING

Liquid or semiliquid food and beverages, naturally at risk of microbiological spoilage, are the primary products that benefit from aseptic packaging. A product's pH 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. Those such as milk, fruit juice, sports drinks, and noncarbonated soft drinks are at a pH above 4.5; they also contain the water

Between 2020 and 2023, consumption of packaged beverages is expected to grow ...



and nutrients that microbes need to grow. Such products require some kind of chemical or heat treatment to extend their shelf life.

Aseptically packaged, low-acid foods such as dairy products are briefly subjected to a ultra-high-temperature, or pasteurization, treatment: the product is rapidly heated, then cooled, to kill microbes with minimal impact on food quality. A separate chemical treatment sterilizes the food packaging just before the product is poured into it and the package 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 and Packaging. Patrick Engelhard, head of process technology at Krones, agrees: "Aseptic is a sign of a high-quality product."

Aseptic packaging 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.

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

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's a challenge to attach the top of the can to seal the product under aseptic conditions. 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 product inside.

Paperboard and plastic aseptic packages are cheaper than glass and metal. They require less material and are much lighter, which reduces the energy demands of shipping.[6,7]

Once an aseptic pack is sealed, it can be stored for extended periods without spoiling, even in 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 Combibloc. "The shelf life is up to 20 months, depending on the product and the packaging material— and this is all because of hydrogen peroxide."

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

TECHNOLOGY

TECHNOLOGY OVERVIEW

Aseptic food-packaging machines are large, complex devices. They 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. Some of the high-speed aseptic machines can fill 50,000 PET bottles or beverage cartons per hour. "There is a great deal that can go wrong with packaging machines," says Sandro Bergmann, manager of applied technology at Evonik Active Oxygens EMEA.

Their powerful oxidizing effect makes hydrogen peroxide and peracetic acid noted sterilants. Chlorine-based compounds are also effective sterilants 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 membrane of the cell as well as the enzymes within it that are crucial to the cell's functioning. "Hydrogen peroxide acts a bit like a hammer," says Sebastian Imm, head of applied technology at Evonik Active Oxygens. "It just destroys the whole cell, very simple."

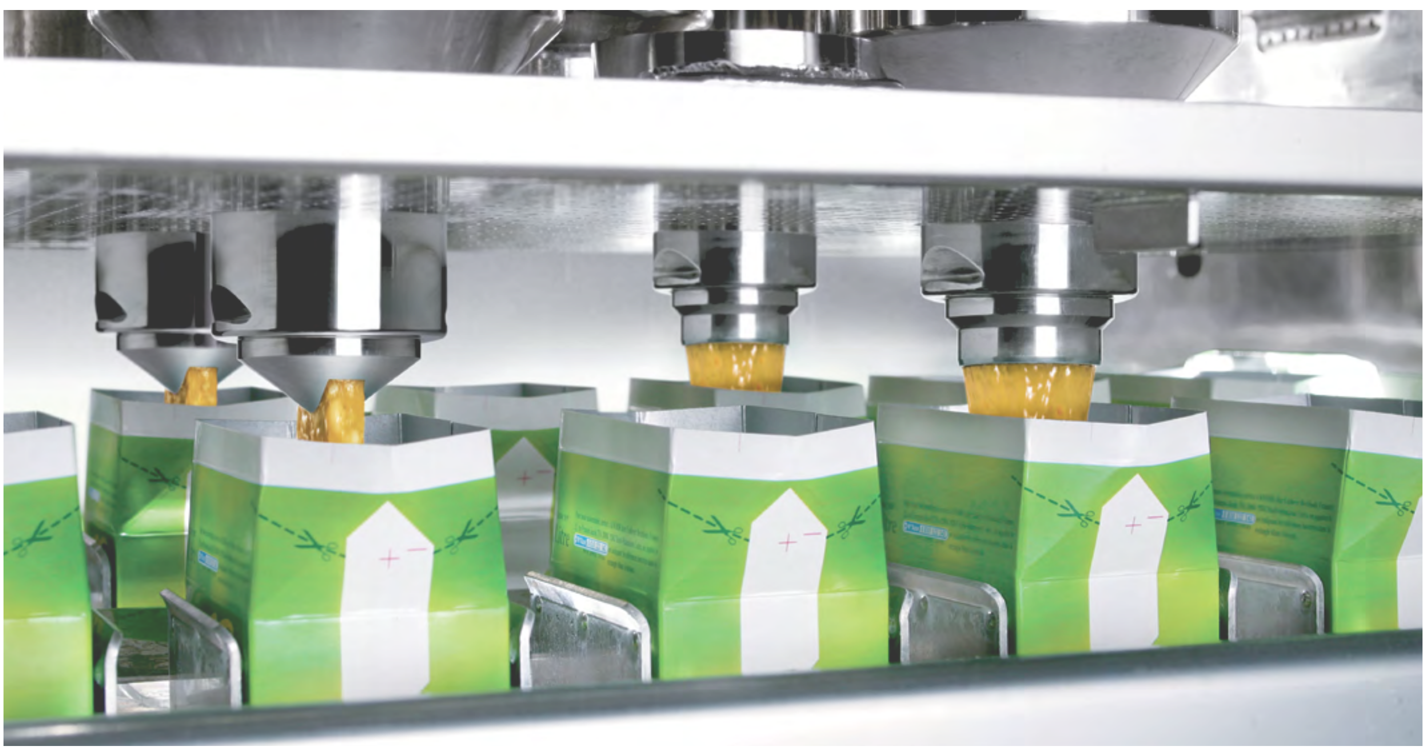
Peracetic acid is a stronger oxidizing agent than hydrogen peroxide. In being slightly more lipophilic than hydrogen peroxide, it is more readily able to penetrate the microbial cell membrane and attack it from the inside. Peracetic acid has the added features of avoiding decomposition by peroxidases, unlike hydrogen peroxide, and remaining active in the presence of organic loads.[8] These contribute to peracetic acid's being a more effective sterilant than hydrogen peroxide under comparable operating conditions. Peracetic acid concentration depends on the target microorganism, the desired kill rate, and operating conditions, such as contact time and temperature.

Various technologies have been developed to apply the sterilant 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 widely used, passes the flat carton material through a hydrogen peroxide bath to kill microbes. Once sterilized, the cartons are formed, filled, and sealed—all under aseptic conditions inside the packaging machine.

To achieve the necessary level of decontamination while maintaining an acceptable machine throughput, a 35% solution of hydrogen peroxide is used, and the bath is heated to between



SIG

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

70 °C and 86 °C. Under these conditions, a contact time of a few seconds achieves the desired level of microbial reduction.[9]

Once the packaging has passed through the bath, a pair of squeegee rollers squeezes off most of the residual hydrogen peroxide before a hot-air knife 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 grade specifically developed for this application. A high-purity hydrogen peroxide with a certain stability is needed in this aseptic filling process, Imm says.

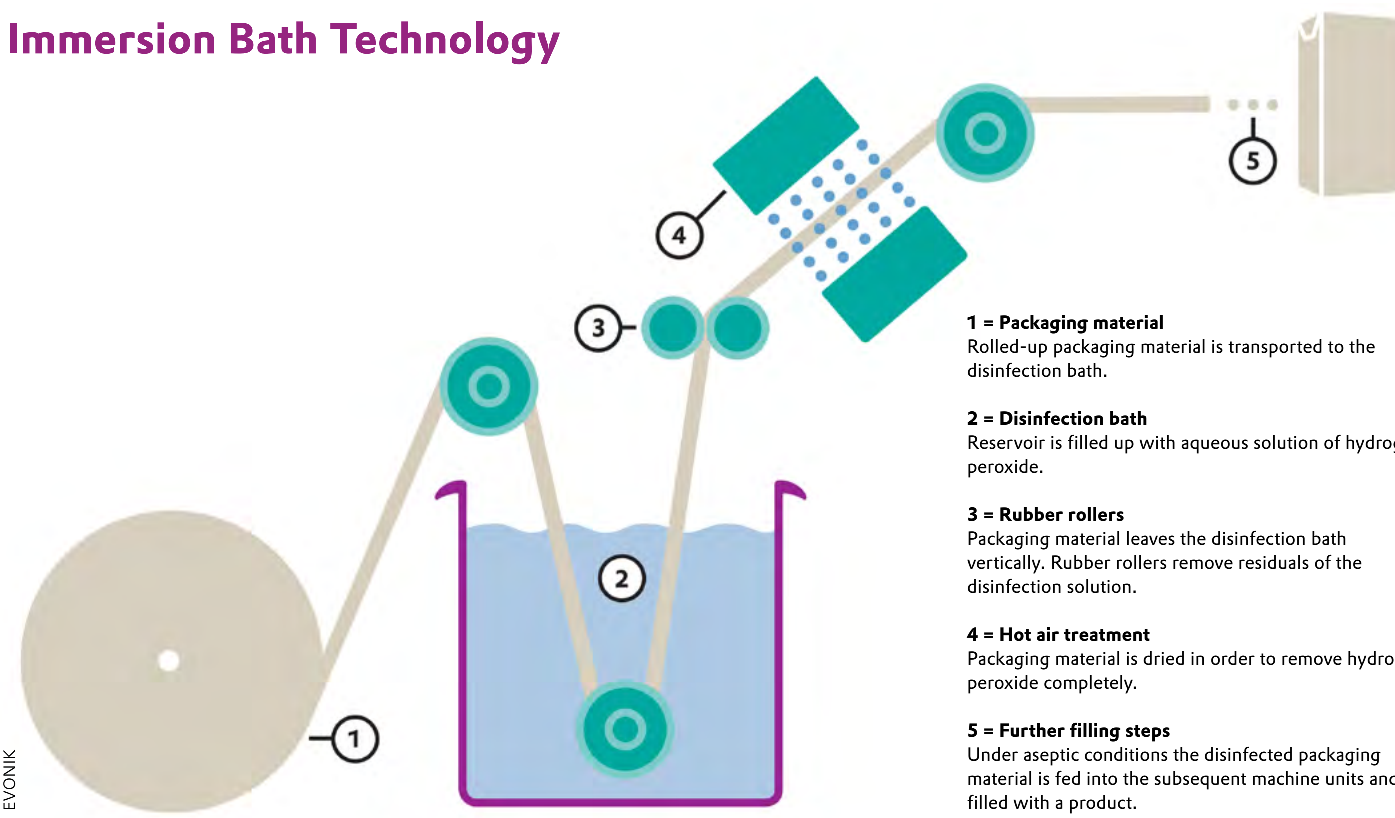
Although hydrogen peroxide is stable for long periods if stored and handled correctly, the compound can be decomposed rapidly into oxygen and water by four key factors: UV light, high pH, high temperature, and traces of metal.

In the immersion sterilization process, the paper foil travels through the bath of hydrogen peroxide in a stainless steel container. "A hydrogen peroxide that remains stable for at least a week is key," Bergmann says, otherwise the bath may need to be emptied and refilled, causing unnecessary downtime. The special grade of hydrogen peroxide sold for immersion bath aseptic packaging is formulated for high stability to minimize decomposition. Evonik has been producing this application-specific formulation for over 50 years, Bergmann says.

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

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.

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VAPORIZED HYDROGEN PEROXIDE TECHNOLOGY IN ASEPTIC PACKAGING AND HYDROGEN PEROXIDE REQUIREMENTS

Vaporized hydrogen peroxide (VHP) aseptic packaging machines preform the carton and then sterilize it with vaporized hydrogen peroxide. Once dried, the aseptic carton is filled and sealed.

A typical example of aseptic filling machines using VHP sterilization is Sig Combibloc technology, in which a mixture of air and 35% hydrogen peroxide passes through a pair of heated tubes that bring the mixture to 270 °C—well above hydrogen peroxide's boiling point of 150 °C. The packaging itself is also heated to about 60 °C, which ensures that 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.

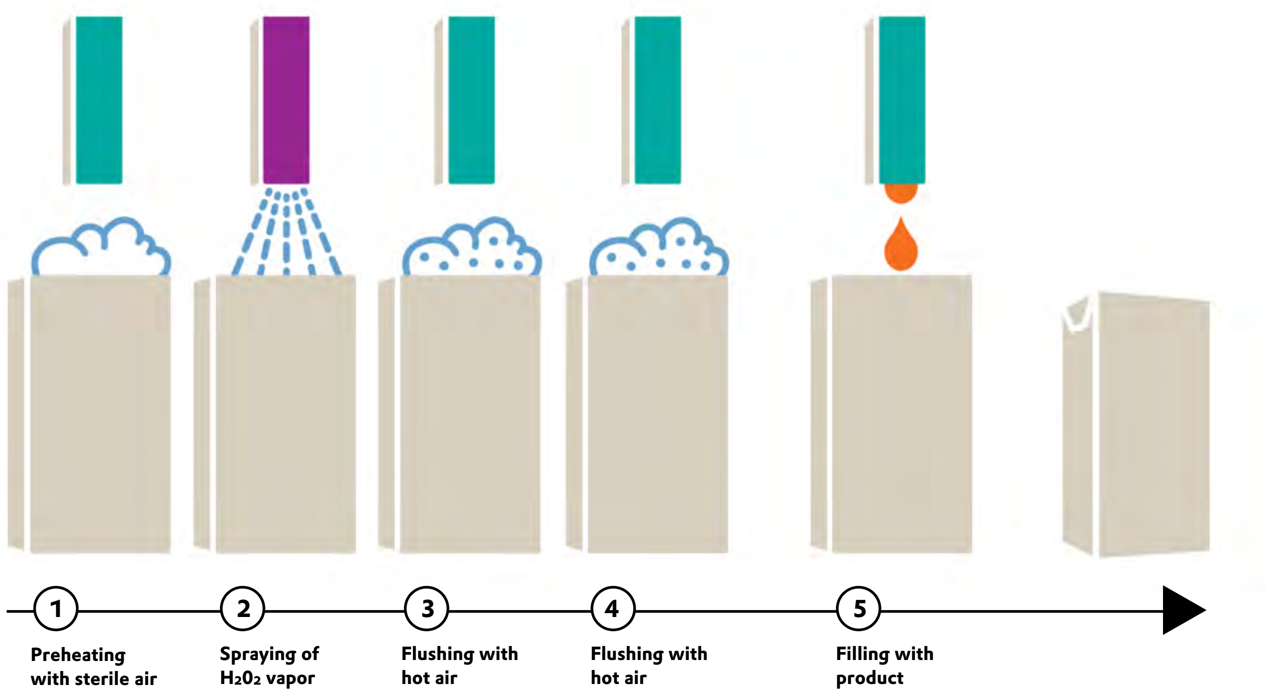
Avoiding condensation makes it much easier to remove the hydrogen peroxide before carton filling, Geissler says. "We reduced the number of preheating and drying steps from seven to five." As a result, the aseptic spray cycle time fell below 2 s. For naturally acidic products, with a pH too low for bacterial 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 VHP aseptic packaging machines, but the formulation is almost the complete opposite. Whereas the hydrogen peroxide in a bath technology must be stable for a week, in the VHP machine it is consumed almost the moment it enters the system. Hydrogen peroxide grades developed for VHP machines contain the minimum amount of stabilizer possible to avoid stabilizer residue accumulating 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 use special grades of high-quality purified hydrogen peroxide to make the vapor grades suitable for VHP sterilization," says Pavel Korzinek, business aseptic manager at Evonik Active Oxygens Americas. "The high purity of the feedstock allows us to use a minimum amount of stabilizer. The result is a VHP grade that is stable enough to ship to the customer but with very low residue buildup on the vaporizer."

Aseptic filling machines vary, and each type requires the selection of an appropriate subgrade of hydrogen peroxide. Even varieties of spray-type filling machines benefit from selecting a particular grade of peroxide. Customers often compare different peroxide products by running them side by side, Korzinek says. "An outstanding performance is the best advertisement because

Spraying Technology



EVONIK

it can increase productivity, lower maintenance cost, and improve product quality."

"Technical support is as important as product quality," says Kevin Huang, principal chemist at Evonik Active Oxygens USA. "Educating customers will help them avoid mistakes in using our products and explore the full advantages."

PERACETIC ACID IN ASEPTIC PACKAGING

PET is an increasingly sought-after aseptic packaging material. For one thing, it has good oxygen barrier properties,[10] which prevents 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 that have high consumer appeal. PET bottles are also recyclable and fit well in a circular economy focused on sustainability.

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."

There are a few distinctive technologies used in the aseptic PET container decontamination:

1. **Wet peracetic rinse sterilization technology.** This technology is based on spraying liquid peracetic acid at high pressure and subsequently rinsing with sterile water to remove residuals of the sterilizing solution from the container.[11] This sterilization process is typically used in GEA Procomac aseptic systems.

2. **Peracetic acid and steam sterilization.** In Krones's aseptic PET packaging machines, peracetic acid and steam are blown into the bottle through a mixing nozzle, creating a mist on the inner surface. After two such treatments, the bottles are rinsed twice with sterilized water to ensure that all traces of peracetic acid are flushed out. Both the wet peracetic acid rinse and peracetic acid steam technologies are robust thanks to the additional mechanical action of the peracetic acid jet inside the bottle. The major disadvantage is relatively high usage of the rinse water and the peracetic acid sterilant. For this reason, these sterilization technologies have been on a decline and newly developed VHP sterilizations have seen a rapid increase in market share over the past 5 years.

3. **VHP sterilization of the bottle.** Similar to the beverage-carton sterilization, this technique involves injecting a mixture of hydrogen peroxide vapor and hot air inside the bottle. Depending on the aseptic system, efficacy targets, the type of bottle, and other factors, the sterilizing mixture can condense into microdroplets or can remain in vapor phase. After a certain amount of contact time, the condensate or vapor is removed with hot air. The advantage of the VHP bottle-sterilization system is that there is no need for rinse water; the system's challenges include the management of sterilant residuals in the container and the narrow operating window between the contact time (machine speed), contact temperature, and residuals. In particular, the contact temperature required for some sensitive, low-acid products may cause shrinkage and deformation, given that blow-molded PET bottles start to shrink above 70 °C.

4. **VHP sterilization of PET preforms.** Instead of decontaminating the entire blow-molded bottle, this latest technology uses VHP to decontaminate the preform before the blow-molding process under aseptic conditions. Since the preform is smaller and thicker than the bottle, the risk of shrinkage is minimized and the operating window wider. The aseptic blow molder can be conveniently connected directly to the aseptic filler. There are proprietary technologies for the preform sterilization before, in, or after the oven depending on the system manufacturer.

OUTLOOK

Some aseptic sterilization technologies have been commercialized and proved over the course of 50-plus years and will continue. There's a reason Tetra Pak still uses the same hydrogen peroxide bath technology for aseptic cartons, Engelhard says. When a process works so well, why change it? "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.

"On the other hand, the latest developments in VHP preform sterilization show a shift in aseptic technology from a peracetic acid rinse to vaporized hydrogen peroxide, demonstrating the ongoing potential for improvement," Korzinek says. The aseptic beverage and dairy industry's focus is on sustainability and a circular economy. All major beverage and dairy processors and aseptic equipment manufacturers have ongoing research and development efforts and investments in aseptic packaging that is recyclable and better for the earth.

ABOUT FRAUNHOFER

The Fraunhofer Institute for Process Engineering and Packaging IVV 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 COMBIBLOC

Sig Combibloc 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.

ABOUT KRONES

Krones plans, develops, and manufactures and installs machines and complete lines for the fields of process, filling, and packaging technology. Its experience and innovative vigor, underpinned by optimal synergizing 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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CHAPTER 4

Food Safety

The U.S. Agriculture Department's National Organic Program permits the use of peracetic acid with few restrictions as a disinfectant in organic livestock production and as a sterilant on food contact surfaces and processing equipment.

INTRODUCTION

Healthy eating means more than managing calories or choosing a balanced diet of nutrient-rich foods. It also means consuming food that is safe to eat, without microbial contamination that can cause foodborne illness and spoilage. While consumers play an important role in food safety, the food industry works hard to ensure that the items purchased are free of microbial contamination. Consumers need to feel confident in their food for a market to grow; peracetic acid may be key to building that confidence by making food safe to eat and increasing shelf life.

MICROBIAL REDUCTION IN BEEF, POULTRY, AND SEAFOOD

Acetic acid and hydrogen peroxide mixed together as a cleaning agent have a long history of use in commercial livestock production, particularly for sterilizing equipment, processing sheds, and barns. Though some smaller farms continue to use this time-tested method to keep their animals healthy and limit the use of antibiotics, peracetic acid has gained a major foothold as a sterilant in animal-based agriculture.

"Treating animal protein products with peracetic acid is a proven method of effectively reducing naturally present microbial loads and food pathogens," says Andrea Johnson, vice president of food safety for Evonik Active Oxygens.

Unlike other sterilants such as chlorine, hypochlorite, iodine, and chlorohexidine, peracetic acid is considered acceptable for use in organic and sustainable agriculture— an important point with health-conscious consumers. In fact, the US Department of Agriculture's National Organic Program permits with few restrictions the use of peracetic acid as a disinfectant in organic livestock production and as a sterilant on food-contact surfaces and processing equipment.

Chicken and beef treated with peracetic acid are also accepted by many export markets. Russia for example, has banned imports of US chickens treated with chlorine or hypochlorite but allows chicken products treated with peracetic acid. While the European Food Safety Authority has deemed peracetic acid safe as a microbial reducing agent and has approved it for cleaning processing equipment, the European Union has not yet lifted its prohibition on US-produced chicken, even though few are still treated with chlorine or hypochlorite. Increased food safety requirements in many countries favor animal proteins treated with peracetic acid because it can provide the needed microbial reductions to meet export requirements, Johnson says.

"Not allowing chemical treated carcasses into Europe is not due to a safety issue, since the use of peracetic acid has been evaluated by the European Food Safety Agency as safe," says María José Rodríguez Dopazo, the European application law and marketing manager for agriculture at Evonik Active Oxygens. She notes that while the US Food and Drug Administration has given blanket approval for peracetic acid's use as a food sterilant, EU regulations require approval for each specific disinfectant used in food of animal origin.

Current methods for processing freshly slaughtered beef or poultry rely on using water for various functions, including cleaning the inside and outside of the carcass as well as chilling the carcass to preserve meat quality and retard microbial growth. To control the microorganisms that can cause foodborne illness or cause meat to spoil, processors commonly add peracetic acid to the wash and rinse water at levels in the 50–800 ppm range, depending on the length of exposure. With only a short treatment time, bacterial loads are reduced by at least 100-fold.[1,2,3] Any residual peracetic acid degrades within 30 min on poultry and 5 min on beef.[4] Processors also recycle much of the water and rely on peracetic acid to prevent microbial buildup and cross contamination in the recycled water.

Dana Dittoe, a research associate in the meat science and animal biologics discovery program at the University of Wisconsin–Madison, says peracetic acid washing is well accepted by poultry and beef processors, in large part because of its broad activity spectrum and ability to work in conditions in which there is a high level of organic matter in the wash waters. It also finds extensive use in sterilizing processing equipment.[5,6]


SHUTTERSTOCK

Dittoe notes that another point for peracetic acid over other antimicrobials is that discharged water is free of microbial and chemical contamination, reducing post-use treatment costs.

Achieving optimal results in both antimicrobial activity and processing costs requires carefully tailoring the application of peracetic acid to the specific product and processing operation, says Leah Kramkowski, a product manager at Evonik Active Oxygens. "Peracetic acid is a simple chemistry but requires expertise to produce it correctly and use it in food applications," Kramkowski says. Evonik not only produces peracetic acid but provides start-to-finish expertise from engineers, microbiologists, and chemists.

Keeping recirculating aquaculture systems free from microbial contamination is a relatively new but growing application for peracetic acid and hydrogen peroxide, particularly in Asia, where land-based aquaculture systems are springing up for fin fish and shrimp production. "We assume that by 2030, at least a third of all Atlantic salmon will be produced on land," says Stephan Neumayer, senior manager of global business development at Evonik Active Oxygens. He notes that major shrimp-producing countries, including Vietnam, are transitioning their shrimp farms to land to increase productivity and reduce environmental impact for more sustainable growth.

Aquaculture is an ideal application for Evonik's end-to-end approach to deploying peracetic acid as a sterilant in food production.[7] "These are increasingly super-intensive farms that require very intense process control to reduce the risk of losing any fraction of the production," Neumayer says. Evonik has pilot-phase demonstrations in progress in Asia and the US.

FRUIT, VEGETABLE, AND CROP PROCESSING

To reduce pathogens, most fresh vegetables are washed in an antimicrobial solution. The traditional choice has been chlorine (aqueous hypochlorite solution), and recent years have seen a growing move to peracetic acid washes.[8,9]

There are three uses of peracetic acid in fresh and fresh-cut fruit and vegetable processing: wash-water disinfection, product sanitation, and equipment sanitation. Wash-water disinfection prevents cross contamination of produce by the recycled water that large-scale washing equipment uses.

In the field as well as after harvesting, peracetic acid has been used as a spray or in dip tanks to reduce fruit and vegetable spoilage from bacteria and fungi, a use that was first patented in 1950.[9] Peracetic acid in the concentration range of 80–250 mg/L kills a variety of pathogenic organisms, including viruses, found on fresh produce.[9,11] In doing so, peracetic acid treatment improves the postharvest lifetime of fruits and vegetables without affecting their taste. As it does in meat processing, peracetic acid effectively decontaminates recycled wash water used in fresh fruit and vegetable processing to prevent cross contamination.[12]

Peracetic acid can control harmful microorganisms that target plants, thereby increasing crop yields and postharvest product quality. For example, peracetic acid on sugar cane can decrease Leuconostoc bacteria, which enter the cane and consume the sugar as their energy source. Applying peracetic acid during harvesting can increase the crop yield and bring a higher value to the market place. Another such application is protecting barley and other grains from Fusarium head blight. These filamentous fungi can impact grain germination and form mycotoxins, such as deoxynivalenol. Washing barley grains with pH-adjusted peracetic acid before malting can lessen the impact of Fusarium and the potential toxic impact from a high concentration of Fusarium-generated deoxynivalenol. This treatment also helps to prevent gushing, the industry term for the overflow that can occur when a beer is cracked open. Fusarium blight on malting barley is a worsening issue for beer producers. Evonik recently developed a peracetic acid-based biocide in their VigorOx® Ceres line for beer producers that the industry received with great interest, says John Wallace, the director of business development at Evonik Active Oxygens Americas.

PERACETIC ACID AND SUSTAINABILITY IN AGRICULTURE

One attribute of sustainable agriculture is its emphasis on reducing farmers' use of antibiotics and other chemicals that can harm the environment. Peracetic acid can play an important role in meeting that goal. To start, because its breakdown products are water, oxygen, and acetic acid, it leaves no lasting trace in the environment or food products. As a result, while broad-spectrum antimicrobial agents are generally considered incompatible with sustainable agriculture, peracetic acid is an exception whose use enables proper sanitation, both on farms and in processing plants.

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About Evonik

Evonik is one of the world's largest producers of hydrogen peroxide and peracetic acid, with a worldwide capacity of more than 1 million t of hydrogen peroxide per year. It is also one of the world's most experienced hydrogen peroxide producers, with 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 employed today, in the 1960s; and starting the world's first HPPO plant. 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 19 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 to specific applications, including fine chemical production, municipal and industrial wastewater treatment, food processing and safety, aseptic packaging, active pharmaceutical ingredients, and cosmetics made to good manufacturing practice guidelines. For more information on hydrogen peroxide and peracetic acid, please visit us at www.evonik.com/active-oxygens.

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