PEROXIDE POWER

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Cosmetics, cleaning agents, microelectronics—hydrogen peroxide has been inspiring innovative applications in chemistry for two centuries. As a supplementary propellant for rockets, this compound of hydrogen and oxygen is now playing a major role in ensuring greener propulsion in space

Good to go: A Soyuz rocket in Kourou is being prepared for launch. On board is a supply of H_2O_2.

It's three hours after sunset, and it's now pitch-black in the jungle. The night ends at a barbed-wire fence that stretches across the tropical landscape. Behind it is a space rocket that towers more than 46 meters into the air and is brilliantly illuminated by floodlights. Over a loudspeaker we can hear the voice of the Directeur des Opérations announcing the rocket's imminent takeoff: *"À tous de DDO: Attention pour moins d'une minute."*

We're at the European spaceport in Kourou, French Guiana, and the local time is 9:46 p.m. on November 6, 2018. We're witnessing the countdown for the launch of a Soyuz rocket that will transport the Metop-C weather satellite to its orbit high above the earth. On board is a supply of hydrogen peroxide (H_2O_2) from Evonik. The spectacular launch can be followed on a live video stream offered by the aerospace company Arianespace.

It's 20 seconds before takeoff. A flash of light signals the ignition of the powerful engines that will propel the gigantic 300-ton rocket into space. The roaring and hissing of the engines grow louder and louder. The engines' power is increased step by step until finally the booster jets and the main engine are burning more than 450 kilograms of kerosene and 1,100 kilograms of liquid oxygen per second. The control center makes another announcement: *"Attention pour le décompte final."* The final seconds are counted down: *"…trois, deux, unité."* The entire launchpad is enveloped in an orange glow. *"Top, décollage…"* The rocket rises majestically into the sky. It flies ever higher in a sweeping curve. About an hour after the launch, a spokeswoman of the European weather satellite organization Eumetsat announces that the first signals sent out by the Metop-C have been received. The mission is a success.

Evonik has played a major role in this success. "Today every Soyuz rocket has about ten metric tons of ultrapure, highly concentrated H_2O_2 on board. It's used for driving the turbopumps, which force the actual propellants into the combustion chamber at high pressure," says Dr. Stefan Leininger, who is in charge of business operations for special applications of H_2O_2 at Evonik's Resource Efficiency Segment. Ten metric tons are still a manageable amount. Evonik is one of the world's leading producers of hydrogen peroxide. The Group can produce more than 950,000 metric tons of it annually at 13 locations on six continents.

This liquid compound of hydrogen and oxygen has been known for two centuries (see the timeline on page 18), but it's still conquering new markets. Today H_2O_2 and other peroxides are used in a wide variety of areas such as semiconductor production, paper manufacturing, and food technology. "That's largely due to this material's excellent environmental compatibility and its efficiency," says Leininger. →

Paper production in Eilenburg/Saxony: In the bleaching process, hydrogen peroxide replaces chlorine-based agents that harm the environment

“The fact that H_2O_2 keeps conquering new markets is due to its excellent environmental compatibility and its efficiency”

DR. STEFAN LEININGER,
BUSINESS DIRECTOR SPECIALTY CHEMICALS

These properties are also becoming increasingly important in the aerospace industry. The aerospace market is in a state of transition. Private suppliers such as SpaceX, the company founded by the Tesla inventor Elon Musk; its competitor Blue Origin, which was founded by Amazon CEO Jeff Bezos; and other companies such as OneWeb and Rocketlab are moving to the forefront. A total of 114 rockets—more than ever before—were launched in 2018. Meanwhile, the average size of the satellites these rockets are propelling into space is shrinking. Nanosatellites (with a mass of 10 kilograms or less) and microsatellites (up to a mass of 100 kilograms) are being launched more and more often. As many as 2,600 of these small artificial satellites may be launched in the next five years, according to a forecast of the consulting company Spaceworks Inc. There's also a trend toward using smaller rockets.

“At the moment, the entire market is experiencing the next evolutionary step,” says Leininger. “During this phase, H_2O_2 is playing an important role as a propellant because of its excellent handling properties.” Previously, other compounds such as hydrazine and its derivatives were used for this purpose. However, hydrazine is suspected of being carcinogenic, and its use may be banned in the EU in the future. H_2O_2 would be a clean alternative. When it's used as a rocket propellant and comes into contact with a suitable catalyst, it develops tremendous heat and decomposes to form water vapor and oxygen.

GREEN ROCKETRY

Thus H_2O_2 is driving a global trend. Under the banner of “green rocketry,” numerous companies and organizations are now attempting to make space travel more sustainable and more environmentally friendly. In addition to the economic aspects, these are also the goals of the Future Launchers Preparatory Programme (FLPP), in which the European Space Agency (ESA) is researching technologies for the next-but-one generation of rockets. “From our perspective, environmentally friendly propellants are important,” says Johann-Dietrich Wörner, the Director General of the European Space Agency (see the interview starting on page 22). Wörner explains that the ESA has been promoting sustainable development on earth for many years and will continue to do so in the future.

One step in this direction was made possible by the Hyprogeo project, which was funded by the European Commission as part of the Horizon 2020 framework program for research (funding code: 634534 HYPROGEO). The goal of Hyprogeo was to construct a hybrid rocket engine that burns polyethylene as the solid propellant, using hydrogen peroxide as an oxidant. “Our task as a project partner was to produce H_2O_2 that was as highly concentrated as possible,” Leininger explains. For this purpose, Evonik developed a dedicated process that produces H_2O_2 in concentrations of up to 98 percent—a peak value for industrial production. “The actual manufacturing process of H_2O_2 produces a 40 or 50 percent solution, but the subsequent distillation and crystallization processes enable us to reach the desired final concentration,” says Leininger.

SPICK AND SPAN

Hydrogen peroxide also develops its innovative power in environmental applications such as soil remediation and wastewater purification. In the USA, sewage treatment plants often chlorinate wastewater before channeling it into rivers or lakes. For the past few years, the US Environmental Protection Agency (EPA) has been promoting the use of alternative methods of water purification. One of them is the treatment of wastewater with H_2O_2 or peracetic acid (PAA). This is an environmentally friendly solution, because the only byproducts of these two peroxides are water and acetic acid, which is readily biodegradable.

The peroxides, which are strong oxidizing agents, combat the pathogenic organisms in the wastewater. Viruses, bacteria, and other microbes are killed via non-specific mechanisms of action. “The peroxides penetrate the cell envelope of microorganisms and change it so that it loses its barrier function,” says Leininger, the expert from Evonik. In addition, the enzymes in the cell's interior are oxidized and thus irreversibly damaged. Both of these processes cause a breakdown of the cell's metabolism. PAA has proved to be an especially potent disinfectant. It requires only a hundredth of the corresponding dose of H_2O_2 to achieve a comparable effect. “PAA can penetrate the cell →

Green processes, thanks to H_2O_2

Hydrogen peroxide and electric current have had a close relationship for a long time. The Weißenstein process for producing H_2O_2 on an industrial scale, which was invented more than 100 years ago, is based on electrolysis. Nowadays industrial companies almost exclusively use the anthraquinone process (see the box on page 20), in which hydrogen peroxide is produced with the help of a reaction carrier. The Danish company HPNow, a startup based in Copenhagen, is now developing a process that harks back to the origins of H_2O_2 production. It has developed a technology that uses a fully automatic system to transform water, air, and electricity into hydrogen peroxide. This technology looks so promising that Evonik's venture capital arm acquired a minority share in the young company as part of its Series A financing round at the end of 2017. “HPNow can help the electrochemical production of H_2O_2 to achieve a breakthrough,” says Bernhard Mohr, the Head of Venture Capital at Evonik.

The core of the system is a modular generator that can produce hydrogen peroxide. In a catalytic cell, water and oxygen are converted into H_2O_2 in a single electrochemical step. Thanks to this distributed approach, the peroxide could be used in the future even in places where its use has been limited because of the costs of transportation and storage—for example, in greenhouses for vegetables or flowers. To make sure that the hoses for drip irrigation don't get clogged, they have to be rinsed regularly. In the past, many growers used fairly aggressive cleaning agents or chlorine-based products instead of environmentally friendly hydrogen peroxide. The use of H_2O_2, whose only byproduct is water, used to be too expensive for growers. “The technology developed by HPNow is making it possible for the first time to produce hydrogen peroxide when it's needed and to use it directly on site,” says Mohr.

The new system has already passed the first set of practical tests with great success.

Far from the factory: Distributed H_2O_2 production in a greenhouse in Denmark

HYDROGEN PEROXIDE: 201 YEARS OF INNOVATIONS

1818

Hydrogen peroxide is produced for the first time by the French chemist **Louis Jacques Thénard** by means of a reaction between barium peroxide and nitric acid

1857

The English hygiene expert Benjamin Ward Richardson discovers that hydrogen peroxide can be used in the **treatment of wounds.** Today it is still used for disinfecting medical equipment

1873

The first plant for the **industrial production** of 3 percent hydrogen peroxide from barium peroxide is built by the Schering company in Berlin. This solution gradually becomes popular in German households as a hair bleach and an antibacterial cleaning agent

1894

Pure hydrogen peroxide is produced for the first time by the German chemist Richard Wolffenstein through a **vacuum distillation** method

1906

Otto Margulies, the founder of the Österreichische Chemische Werke (ÖCW), acquires a patent for an electrochemical method for manufacturing hydrogen peroxide. The factory that will use this method is built in the town of **Weißenstein** in the Austrian state of Carinthia

1907

Degussa delivers its first order of sodium perborate to the Henkel company for producing the laundry detergent **Persil.** This active ingredient is now made from hydrogen peroxide

1910

Degussa acquire shares in the ÖCW company. The Weißenstein factory goes into operation in January. The production of **highly concentrated hydrogen peroxide** (30 percent) is now possible for the first time

1935

Hellmuth Walter is the first German inventor to use hydrogen peroxide as an **engine fuel.** Hydrogen peroxide is subsequently also used as a propellant in rocket technology

1953

The first industrial-scale production plant to use the **anthraquinone autoxidation process** is opened by the DuPont company in Memphis, Tennessee

1989

The first patent application is submitted for a **teeth-whitening gel** based on hydrogen peroxide

1995

Degussa is the first company to transport hydrogen peroxide **by ship,** from Alabama to Lemont, a suburb of Chicago

2018

Evonik Industries signs a contract with One Equity Partners for the takeover of **Peroxy-Chem,** a US manufacturer of hydrogen peroxide and peracetic acid

membrane especially easily because of the lipophilic properties of the acetyl part of the molecule," Leininger explains. In addition, PAA—unlike H_2O_2—cannot be decomposed by a special enzyme called microbial catalase. As a result, no resistance mechanisms against PAA have been discovered to date.

More and more municipalities in the USA are starting to appreciate these benefits. For example, a few years ago the city government of Memphis, which has a population of 650,000, decided to begin using PAA for its wastewater treatment. It concluded a "take or pay" contract with the US company Peroxychem to secure a long-term supply of PAA. As a result, two years ago Peroxychem began to plan the construction of a new PAA factory in the region. At the beginning of November 2018, Evonik announced its intention to acquire Peroxychem.

Peroxides such as H_2O_2 and PAA do more than just reducing the germ load. They also eliminate the persistent organic trace substances that can cause problems when sewage treatment plants channel purified water into surface water. In addition, hydrogen peroxide is used to decontaminate wastewater containing cyanide, which comes from electroplating works, hardening plants, blast furnace gas, and mines. H_2O_2 oxidizes cyanide to form cyanate, which is then hydrolyzed to form ammonia and carbonic acid. Hydrogen peroxide is also used in electroplating works to oxidize nitrogen oxides, which have been generated from nitric acid in the etching process, back into nitric acid.

However, some contaminants cannot be eliminated by H_2O_2 alone. For example, if benzenes and phenolic compounds have to be eliminated from wastewater, chemists use a certain trick. Hydrogen peroxide molecules can be split by either bivalent iron ions (Fe^{2+}), UV radiation or ozone to form hydroxyl radicals (•OH). This radical is one of the strongest oxidizing agents in existence, and it reacts with almost all organic compounds.

AN ENVIRONMENTALLY FRIENDLY ALTERNATIVE

Demand for H_2O_2 is booming, especially in Asia. Semiconductor manufacturers there use ultrapure hydrogen peroxide, either alone or in combination with sulfuric acid, to remove photoresists from silicon wafers and coat them with an oxidation layer that is only a few nanometers thick. The combination of hydrogen peroxide and sulfuric acid is also used as an etching agent in the production of circuit boards. According to Dr. Jürgen Glenneberg, Head of Process Engineering at the Active Oxygens Business Line, "Hydrogen peroxide/sulfuric acid etching agents are used often on account of their low cost, high degree of effectiveness, and relatively low disposal problems." H_2O_2 is also being increasingly used in the production of liquid crystal displays (LCDs). Here, hydrogen peroxide solutions are used to etch out the copper circuits that supply the LCDs with electricity.

H_2O_2 is also used in a series of industrial-scale syntheses—for example, in the production of epoxidized soybean oil, which is an important plasticizer for PVC plastisols and is also being increasingly used in other plastics. In this process, a mixture of hydrogen peroxide and formic acid oxidizes the carbon-carbon double bonds in the fatty acid chains while forming the corresponding epoxides. In recent years a process based on hydrogen peroxide has become widely used for the synthesis of caprolactam, which is used to manufacture nylon fibers and other products. In this process, ammonia is oxidized selectively with H_2O_2 to form hydroxylamine, which reacts in situ with cyclohexanone to form caprolactam. In contrast to traditional procedures, this process makes it possible to avoid the formation of thousands of metric tons of sulfate-containing waste products. →

Germ-free: Peroxides combat microorganisms in wastewater

How H_2O_2 is produced: The anthraquinone process

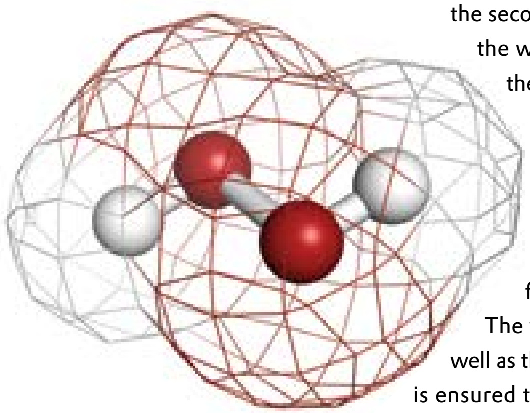
The industrial production of hydrogen peroxide began in the town of Weißenstein in the Austrian state of Carinthia. This is where the Österreichische Chemische Werke company operated the world's first hydrogen peroxide factory using electrolysis. Today this production plant is part of Evonik. The Weißenstein process made it possible to produce hydrogen peroxide on an industrial scale for the first time. Today this plant uses the autoxidation process, as do almost all the other hydrogen peroxide factories in the world. This process was developed by Georg Pfleiderer and Hans-Joachim Riedl at IG Farben in Ludwigshafen between 1935 and 1945, and since then it has been continuously refined. The process is based on the cyclical reduction and oxidation of an alkylated anthraquinone.

The first step, hydrogenation, takes place in a reactor full of a solution of the anthraquinone (the "working solution"). "In the reactor, in the presence of a palladium catalyst hydrogen combines with the reaction carrier, a quinone derivative, to form a hydroquinone," explains Dr. Jürgen Glenneberg, Head of Process Engineering at the Active Oxygens Business Line. The catalyst is then completely filtered out of the working solution. In the second step, the oxidation stage, huge compressors pump air into a bubble reactor that is full of the working solution. When the hydroquinone in the organic phase comes into contact with the oxygen in the air, it oxidizes spontaneously back into quinone, forming hydrogen peroxide in the process. Because this reaction takes place without the presence of a catalyst, it is called an autoxidation process.

In the third step, extraction, the working solution is poured into a separation column. The H_2O_2 in the working solution is extracted by adding water to the solution in a countercurrent process. The result is a 35 to 50 percent aqueous solution that can be processed further by means of vacuum distillation or additional purification steps, for example.

The working solution in itself poses a special technical challenge to the process. The quinone as well as the hydroquinone must remain dissolved in the solution without flocculation. Their solubility is ensured through the choice of a suitable alkyl substituent and the composition of the solvent mix. "Typical alkylated anthraquinone derivatives such as 2-ethyl-, 2-tert-butyl-, and 2-amylanthraquinone are used for this purpose," says Glenneberg. In order to keep the quinone in solution, nonpolar substances such as C9/C10-alkylbenzenes are often used as part of the working solution. Polar substances such as tris(2-ethylhexyl) phosphate, diisobutyl carbinol or methyl cyclohexyl acetate take over this function for the hydroquinone.

To make sure the process unfolds successfully, it's important to regularly purify the working solution in the facility. Theoretically, the working solution can be used indefinitely. However, if only 0.1% of the quinone were to be irreversibly damaged in each cycle, the entire process would break down within two months. The oldest working solution at Evonik is being used at the plant in Antwerp. It was originally mixed in 1969.



Oxygen (red) and hydrogen (white) form an energy-rich compound: a molecule of hydrogen peroxide

In addition to hydrogen peroxide itself, a number of derivatives are also used. When H_2O_2 reacts with sodium carbonate (soda), the solid adduct sodium percarbonate is formed. On account of its outstanding properties, this adduct is used as a bleaching agent in heavy-duty laundry detergents and as a bleaching and disinfectant in dishwashing detergents. Another "solid hydrogen peroxide" is percarbamide, a compound of H_2O_2 and urea, which is used for bleaching hair and teeth. An especially important H_2O_2 derivative is peracetic acid, which is actually an equilibrium mixture of acetic acid, hydrogen peroxide, and peracetic acid. Because of their strong germicidal effect, various formulations are primarily used for disinfection processes in the food industry and for animal hygiene, laundry disinfection, and environmental applications.

Today the broadest single application of hydrogen peroxide is in the synthesis of propylene oxide, an important starting material for the production of plastics based on polyurethanes. These plastics are used in the upholstery of car seats and furniture and as insulation material for cooling appliances, for example. In the HPPO process, H_2O_2 is used as an oxidizing agent to epoxidize propylene into propylene oxide, with water as the only joint product.

Thanks to the catalyst titanium silicate (TS-1), which was developed especially for the HPPO process, this reaction can take place in relatively mild environmental conditions. "This process is very cost-effective, because it utilizes the raw materials with extreme efficiency, the catalyst is especially powerful, and the investment costs are relatively low," explains Dr. Florian Lode, who is a Vice President Strategic Projects at the Active Oxygens Business Line.

Healthy and durable: In the food industry, PET bottles are sterilized with hydrogen peroxide before being filled

> "Hydrogen peroxide makes multifaceted chemistry possible—and decomposes into water and oxygen when done"
>
> DR. FLORIAN LODE, VICE PRESIDENT STRATEGIC PROJECTS, PERFORMANCE OXIDANTS

A PARTNERSHIP FOR PLASTICS

The process was developed by Evonik and ThyssenKrupp Industrial Solutions, and the two companies are now also issuing joint licenses for it. ThyssenKrupp Industrial Solutions is primarily responsible for building the production plants, and Evonik is supplying the licensees with hydrogen peroxide and the catalyst, TS-1. "The HPPO process is enabling our customers to minimize their environmental impact and also to manufacture their products sustainably and cost-effectively," says Lode. "It's a perfect example of resource efficiency in the chemical industry."

One of the places where this can be seen in practice is Tiszaújváros, a town of 17,000 inhabitants in northern Hungary. Here the Hungarian MOL Group is currently building a gigantic HPPO plant that is expected to go into operation in the first half of 2021. The plant is part of an investment program worth a total of almost US$2 billion, through which MOL aims to become the leading chemical company in Central Eastern Europe as well as the only integrated polyol producer in the region. The HPPO process has been used successfully in Asia for several years. The first two commercial facilities were established in Ulsan (South Korea) and Jilin (China).

The aerospace industry, microtechnology, environmental applications, chemical syntheses—H_2O_2 is a powerhouse that has become an essential part of our world today. But according to the Evonik expert Lode, the power of hydrogen peroxide has still not been fully exploited. "Hydrogen peroxide makes multifaceted chemistry possible—through processes whose only byproduct is water. In this era of heightened awareness of the environment, that makes it very exciting to search for new applications of this product."