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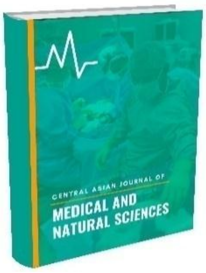

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Recent Innovation in Chemical Sciences

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Abstract: Recently, IUPAC introduced the "Top Ten Emerging Technologies in Chemistry" . This initiative commemorated both IUPAC's 100th anniversary and the International Year of the Periodic Table, a worldwide event that celebrated 150 years since the first publication of Mendeleev's most famous chemistry icon. Now, IUPAC wants to transform this project into yet another landmark. Every year, the "Top Ten Emerging Technologies in Chemistry" will identify innovations with tremendous potential to change the current chemical and industrial landscape. Throughout the past year, chemists around the globe have suggested remarkable technologies and innovations in their respective fields. A team of experts recruited by IUPAC curated the proposals and selected the most disruptive and forward-thinking—promising ideas with excellent chances for achievement. Some of them have already started weaving a network of spin-offs and attracting the interest of the chemical enterprise. The "Top Ten Emerging Technologies in Chemistry" are also aligned with the United Nations' Sustainable Development Goals (SDG).* The selected technologies will change our world for the better, making a more thoughtful use of our resources, favouring more efficient transformations, and providing more sustainable solutions in applications ranging from new materials and more efficient batteries to extremely precise sensors and personalised medicine. Furthermore, this year the world is facing an unprecedented challenge—fighting one of the worst pandemics since the Hong Kong flu in 1968.* COVID-19 has affected our society across many levels, and will most likely transform our lives in ways we are yet unable to anticipate.

Key words: IUPAC, COVID-19, Chemistry, technology, recent, innovations, sciences, chemical.

In this global fight against coronavirus, chemists will play a key role.* From soap and clean water to tests and new drugs, chemistry will be paramount to defeat this new threat.* Thus, two of the technologies focus on solutions that will be crucial—rapid tests and RNA vaccines.

Introduction

Start-ups have indeed become important vehicles for innovation in chemistry. But they aren't the only means. The R&D departments at traditional chemical and engineering companies are still inventing, developing, and commercializing new chemical processes and materials. Chemistry news pages are filled with items about corporate investment in new products, new plants, and new technologies. But the short format of many stories doesn't permit us to detail how the technologies work or what problems they are meant to solve. With this feature, we go deep into five new technologies from established companies. In each of these case studies, big companies tackle important problems. And in each case, given their large scale and resources, the companies stand a good chance of making a consequential impact on the market and, often, the environment.[1,2]

The EPA recently emphasized the need to supplement those efforts with surfaces and surface treatments that provide long-lasting activity against viruses and other microbes. In October, the agency issued guidance on how companies can prove a product's efficacy against SARS-CoV-2 before making such claims, a move EPA administrator Andrew Wheeler says in a news release would provide "an expedited path for our nation's manufacturers and innovators to get cutting-edge, long-lasting disinfecting products into the marketplace as safely and quickly as possible."Elemental copper provides permanent antimicrobial activity, but large surfaces clad in copper are expensive and not the right look for most places. To bring the disinfecting power of copper to a broader range of walls, handrails, and other surfaces around the home and workplace, Corning developed a copper-containing biphasic glass-ceramic material it calls Guardiant and worked with PPG Industries to incorporate it into a line of latex paints called Copper Armor.

The overall idea here was to create a material that maintains the antimicrobial potency of copper while getting rid of its metallic character and metallic look so that it could be incorporated into a wide variety of materials and surfaces," says Joydeep Lahiri, vice president of Corning's specialty surfaces division. Though the pure Guardiant material is a pale blue-green powder, PPG was able to flex its formulation experience to make the paint in all the normal shades and sheens.Cu^{+1} is the active antimicrobial form of the element. The challenge that Corning's technology solved, Lahiri says, was keeping the copper in that oxidation state while also letting it get to the microbes. In April 2019, the firms published a paper in Nature Communications on their innovation, which they describe as an "alkali copper aluminoborophosphosilicate glass ceramic material that acts as a sustainable delivery system for Cu^{+1} ions". As the publication date testifies, the firms were working together on the technology before the pandemic hit. But the novel coronavirus accelerated the formulation and commercialization work, says Eric Stevenson, director of product management for architectural coatings at PPG. "The COVID pandemic has heightened everyone's awareness of viruses and bacteria and how quickly they spread," he says. The R&D team found literature describing the use of glass to keep copper in the +1 state, Lahiri explains. But in the team's tests, paint incorporating a copper-glass phase wasn't effective against pathogens, probably because the copper couldn't escape the glass to do any microbe killing. Replacing some of the aluminum oxide in the glass with boron, phosphorus, and potassium oxides created a second phase in the material that is more water labile. Paint made with the biphasic ceramic-glass copper material reduced counts of SARS-CoV-2 as well as Staphylococcus aureus, Pseudomonas aeruginosa, Klebsiella aerogenes, and Escherichia coli on the surface by more than 99.9%, matching an efficacy previously achieved by metallic copper using EPA test standards. In fact, Lahiri says, the firms went beyond the industry standard tests, which analyze the kill rate under warm, wet conditions. The paint also got a kill rate of 99.9% while dry at room temperature, much more like what it would see in a real-world setting.[3,4]

Though it may seem like the water-labile phase would wash away during cleaning before long, Stevenson says PPG's wear-simulation tests suggest that the antimicrobial action will stand up to more than 5 years of scrubbing and still meet that 99.9% kill standard. The firms are awaiting EPA approval and expect the paint to hit the market in the next few months.

The first licensee for a new rhodium-catalyzed process for making isononyl alcohol. Zibo Qixiang Tengda Chemical will build a plant in Zibo, China, that can make 200,000 metric tons per year of the alcohol, a precursor to plasticizers for polyvinyl chloride (PVC).Hydroformylation, or oxo synthesis, is the process of converting alkenes to aldehydes by adding a CHO group and a hydrogen across the double bond. A subsequent hydrogenation step turns the aldehydes into alcohols. The process was discovered in 1938 by the German chemist Otto Roelen. But Roelen's cobalt-catalyzed method required high pressures and temperatures, making manufacturing plants expensive to build and prone to generate lots of by-products. The goal of those 1960s researchers was to find new catalysts that would do the reaction at low pressures and temperatures. Together, the cross-Atlantic team succeeded. The companies commercialized the rhodium-based technology in the 1970s, applying it mainly in plants that convert propylene to butyraldehyde and then to n-butyl alcohol, isobutyl alcohol, and 2-ethylhexyl alcohol. 2-Ethylhexyl alcohol is a raw material for the PVC plasticizer di(2-ethylhexyl) phthalate, which helped turn PVC into a major commodity used in all manner of flexible vinyl goods. These days, though, di(2-ethylhexyl) phthalate is associated with reproductive effects and is prohibited in consumer products sold in the European Union. Fraser Archibald, licensing manager at JM, says users in Europe and elsewhere are shifting to higher-molecular-weight plasticizers, including diisononyl phthalate and diisononyl adipate, both based on isononyl alcohol.

Early efforts to convert longer-chain alcohol production from cobalt to rhodium catalysts were unfruitful. Attempts to operate at lower pressures resulted in catalyst instability, and lower temperatures sapped catalyst activity. Dow and JM have been working to overcome these obstacles since the 1980s, Tang says, but "the effort definitely stepped up in recent years," including the start of isononyl alcohol technology development .[5,6]

Discussion

A key advance was new rhodium ligands, a strategy the teams used before. One of their earlier improvements to the propylene-based process was to replace the triphenyl phosphine ligand on which it was founded with polyorganophosphite-based ligands. This and other catalyst advances boosted the ratio of desirable n-butyl alcohol to less-desirable isobutyl alcohol from 10:1 in the 1980s to more than 30:1 today, Archibald says. Ligand improvement also helped cut the concentration of rhodium in the catalyst to about 25% of what it was in the 1980s.To pioneer a new rhodium-based isononyl alcohol process, Dow and JM considered multiple new ligands. Many worked in the laboratory, Archibald says, but finding ones that could stand up to commercial conditions—during testing at pilot plants run by Dow in Texas and JM in England—was another matter. Only a few proved to be both stable and easily separable from the aldehyde at the end of the reaction. "That was one of our major breakthroughs—finding a way of doing the separation while maintaining the stability of the rhodium-ligand complex," Archibald says.

Dow and JM claim the new technology will allow customers to build isononyl alcohol plants for much less than is needed for incumbent cobalt-catalyzed plants. And while Qixiang Tengda is building a brand-new plant, the partners say they can also retrofit the technology on existing plants that make butanol and 2-ethylhexyl alcohol. Although the new technology is soon to be commercial, Archibald and Tang say their work isn't done. Just as they did for the older process, the two firms will continue to tweak the new technology. “This is isononyl alcohol 1.0,” Archibald says. “In the next iteration, the performance is only going to improve.”

The nature of polyurethanes—custom blends of molecules bound tightly and often irreversibly with cross-links—makes recycling them a challenge compared with thermoplastics like polyethylene terephthalate (PET) or polypropylene, which can be melted down again. Plastics producers have attempted to boost the sustainability of polyurethanes with greener inputs, such as polyols derived from soybean oil. Huntsman is taking a similar strategy, except in its case it is making polyurethanes more sustainable in a way that helps address the broader plastic waste problem: by using polyols derived from recycled plastics.The company just opened a plant in Taiwan that makes its Terol aromatic polyester polyols from postconsumer PET bottles. The 22,000-metric-ton-per-year plant is its second to use the technology. Huntsman started operating the first in Houston in 2013, where it says it has since consumed the equivalent of 5 billion PET bottles.At these plants, Huntsman starts with a glycolysis-like process that breaks down the PET into shorter-chain oligomers. This is in contrast to companies such as Loop Industries and Eastman Chemical that depolymerize PET all the way down to the building-block chemicals dimethyl terephthalate and ethylene glycol for condensation back into PET or other polyesters.

Huntsman reengineers the oligomers to build up desirable molecular weights, functionalizes the polymer backbones, and combines the resulting aromatic polyester polyols with other polyols to get desired properties for various applications. Pavneet Mumick, Huntsman’s global vice president of polyurethane technology and innovation, says the final polyols the firm is making now have 30–40% recycled content. Huntsman can boost the total postconsumer content number to 60%, he says.Huntsman doesn’t pick up the bottles curbside and process them itself. Rather, it buys flaked PET made from bottles that recycling companies have already collected, sorted, and cleaned. That final part is important. According to Mumick, tight quality control of incoming recycled PET is critical to maintain the high quality standards of the polyol products. Aromatic polyester polyols impart rigidity, insulation properties, and fire performance to polyurethane foams, Mumick says, making them a good fit for insulation board and spray foam insulation for construction applications. This is in contrast to polyether polyols, which are more flexible and find themselves in applications like memory-foam mattresses.A chronic problem in plastics recycling is downcycling, in which plastics are turned into objects less valuable than what they were originally used for. Mumick calls Terol an example of upcycling because the recycled polymers are used in applications like insulation that help conserve energy for many years.“When all of those things start to add up, they become a very good sustainability story,” Mumick says.[7,8]

The recycled content appeals to industrial customers, many of which aim to include 15–20% recycled content in their own products. “That gives us a competitive edge,” Mumick says.Huntsman isn’t alone in seeing the potential of recycling polymers in specialty chemicals. Resinate Materials Group, headquartered in Plymouth, Michigan, has also been developing a glycolysis process to convert PET into polyester polyols. Menlo Park, California–based BioCellection is developing a thermal oxidative decomposition process to convert polyethylene into chemicals that can be made into polyurethanes. And the Canadian firm GreenMantra is using a thermocatalytic process to make polymer additives from mixed polyolefins. Now that Huntsman has established the plant in Taiwan, its next steps include potentially building a facility in Europe. The market, Mumick says, will gobble it all up. “We can grow this thing at 10% a year if we need to for the next 10 years, if the market continues to demand the product,” he says.

Results

Essential-oil producers steam-distill the fragrance ingredient—which has a rich herbal scent reminiscent of hops, eucalyptus, and Angostura bitters—from shredded sandalwood trees. The trees become richer in oil as they grow older and are harvested when they are between 15 and 30 years old.But demand has grown faster than the trees themselves, leading to unsustainable cultivation practices and even illegal harvesting of trees from protected woodlands in Australia, India, and Hawaii. The supply of sandalwood oil is volatile because of weather and labor issues, and difficult to scale up because of the long wait for mature trees. In fact, the global population of Santalum album, Indian sandalwood, is on the decline, according to the International Union for Conservation of Nature and Natural Resources. "Naturals are very expensive. Think of how much water, how much land usage, how much shipping" that route requires, says Kate Prigge, manager of applied research at the flavor and fragrance maker Symrise. Quality and chemical proportions can also vary widely from year to year, she says, which are big downsides for an industry in which a predictable balance of flavor or aroma is crucial to a brand's product identity.

By making your ingredients in the lab, using either hard synthesis or fermentation, Prigge says, "you can have a much more steady, reliable, economically priced, controlled source and get that same impression."

To meet the demand for natural sandalwood oil without dependence on a vulnerable supply chain, BASF is turning to fermentation. In 2019, the big chemical maker acquired Isobionics, a Dutch biotech firm focused on flavors and fragrances. In July of this year, the firms launched a microbially derived sandalwood oil replacement they call Isobionics Santalol. Isobionics also ferments several other aromatic compounds, mostly related to citrus. Traditional sandalwood oil gets its scent primarily from two compounds, α-santalol and β-santalol. The α form of the aromatic alcohol generally dominates at around 55% of the mix, with the β version at around 25% and other related compounds making up the balance. BASF says its fermentation process yields α- and β-santalol in a ratio similar to what's in sandalwood oil. Isobionics Santalol "represents the heart note of sandalwood oil and makes it a close alternative to sandalwood oil," the firm says.[9,10]

Instead of relying on stressed and seasonal sandalwood trees, BASF ferments its product from cornstarch-derived sugars using Rhodobacter sphaeroides, Isobionics founder Toine Janssen says. Currently, the firm gets its raw material from European corn. Fermenting with sugar from other sources could make new facilities near target markets straightforward to build, staff, and supply. India, for example, has a customer base in Ayurvedic medical practitioners that use sandalwood oil for skin care, anxiety, and muscle spasms. Janssen says the ability to produce ingredients year-round without worrying about weather or other cultivation woes gives BASF's sandalwood oil replacement a key advantage for fragrance and flavor customers: consistency. "The reliable availability of fermentation-based ingredients reassures our customers and simplifies delivery processes," he says.

BASF is already a player in synthetic flavors and fragrances, and adding Isobionics' biotech route allows the firm to serve a growing part of that market. Crucially, regulations in most areas allow ingredients produced via fermentation to carry "natural" labeling. Indeed, although a well-engineered synthesis can yield a precise chemical product with minimal waste and cost, Symrise's Prigge says fermentation is growing in popularity as a way to produce flavor and fragrance molecules in part because of the marketing advantage it has over chemical synthesis. "What consumers want pushes the market," she says.

Conclusions

The cellulose acetate maker Celanese traces its roots back to 1918, when Camille Dreyfus established the American Cellulose & Chemical Manufacturing Co. to produce an alternative to the highly flammable material celluloid.

Cellulose acetate came to be used in fibers, film, and molded parts. But by the 1960s, it was getting displaced by new petrochemical thermoplastics like polyethylene and polypropylene.

In recent years, the public has become increasingly alarmed about the mounting waste created by these petrochemical plastics, which can linger in the environment for centuries.

And so Celanese detects an opportunity for cellulose acetate to mount a comeback. Last month, the company launched BlueRidge, a cellulose acetate product line that it says can be used to make objects like straws that are backyard compostable or broadly biodegradable.[11]

Cellulose acetate is made by acetylating cellulose, normally derived from wood pulp, with acetic anhydride to give it plastic properties such as durability and flexibility. Esterase enzymes in nature act on cellulose acetate to deacetylate it into bare cellulose, which further biodegrades. The more substituted with acetate groups the cellulose backbone is, the less readily it degrades.

Because of the acetylation, cellulose acetate doesn't biodegrade as quickly as paper. But it does break down in months or years, unlike petrochemical plastics that take decades or centuries.

Kevin Norfleet, senior program manager for sustainability and emerging markets at Celanese, rates the biodegradability of the BlueRidge products somewhere above polylactic acid, which biodegrades readily only in an industrial composting facility, and below polyhydroxyalkanoates, which break down quickly in the ambient environment.

The BlueRidge products, up to a certain thickness, have achieved certifications such as TÜV Austria's home composting standard. They have also attained ASTM International's D6400 standard for industrial composting.

With the products, Celanese might be targeting a viable niche. The global market for biobased and biodegradable polymers is expected to grow quickly—16.1% annually through 2027 from a base of $8.3 billion in 2019, according to a report from Grand View Research.

Celanese isn't making major modifications to the conventional acetylation process. The biggest difference between BlueRidge and other cellulose acetate products, Norfleet says, is that Celanese compounds the polymer with biobased plasticizers so it can be melted or softened with heat and processed in standard thermoplastic injection molding, extrusion, and thermoforming machinery. Conventional cellulose acetate today, used in applications such as fiber tow for cigarette filters, is normally processed using solvents. Norfleet says the plasticizers also enhance biodegradability.

The products, Norfleet says, have the "look and feel of plastics but have more of the biodegradability and compostability benefits."

Norfleet says BlueRidge products are a good fit for some of the single-use plastic products that are under fire and facing bans, such as injection-molded flatware, extruded straws, and thermoformed drink lids and takeout containers.

The mechanical properties of the polymers are similar to those of the engineering plastic acrylonitrile-butadiene-styrene, Norfleet says: strong and stiff. These are unusual attributes for single-use plastics, and he notes that these properties might allow for thinner plastic objects, which would assist biodegradability.

Norfleet acknowledges that cellulose acetate doesn't provide enough of a vapor barrier for many packaging applications. However, the permeability can be an advantage. For instance, cellulose acetate is used for the windows of doughnut boxes because it allows vapor to pass through without fogging. This might also be a good attribute for takeout food containers, Norfleet says.

For now, Celanese is establishing a beachhead in the packaging market with BlueRidge. In the future, Norfleet says, the company might make changes to the plastics by, for instance, tweaking the amount of acetyl saturation in their backbones to boost biodegradability.

Being deft at both engineering polymer compounding and acetyl chemistry is an advantage for Celanese, Norfleet says. “There are a lot of knobs that we can turn.”[12]

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