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TRIAD CHEMICAL TIMES

Central North Carolina Section American Chemical Society

Upcoming Events

September 13, 2023: Local Section Meeting: "Vinyl Chloride, Cancer and Technology: How Science Saved a Business"
Dr. William F. Carroll, former ACS President; JSNN Auditorium, Greensboro
Social: 6:00, Meeting: 7 pm

October 7, 2023: **Stream Cleanup** (details to follow)

October 13, 2023: Local Section Meeting: "Minerals in meteorites: the elemental encyclopedia of early solar system history " Mr. Anthony Love, Department of Geological and Environmental Sciences, Appalachian State University GTCC Cline Observatory, Jamestown campus (details to follow)

October 15-21, 2023 : National Chemistry Week Theme: The Healing Power of Chemistry (details to follow)

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Highlights in this issue:

ACS Chemistry for Life®

September Section Meeting

Dr. William F. Carroll, Jr. holds a B.A. in chemistry and physics from DePauw University (1973), an MS from Tulane University in Organic Chemistry (1975) and a PhD in Organic Chemistry from Indiana University, Bloomington (1978). He retired from Occidental Chemical Corporation in 2015 after 37 years and now heads his own company, Carroll Applied Science, LLC.

His career has involved management of technology, commercial development, political advocacy and environmental issues management. He has been a member of numerous panels for the United Nations Environment Programme, including those writing and implementing the Stockholm Convention on Persistent Organic Pollutants, a treaty ratified by over 170 countries. He currently is Chief Technical Officer for a United Nations Industrial Development Organization project in China under the Minamata Convention, whose aim is elimination of the industrial use of mercury.

Bill has been an Adjunct Professor of Chemistry at Indiana for almost 25 years, with activities ranging from teaching courses to department career counselor, his current assignment.

He served as President (2005) and later as Chair of the Board of Directors (2012-14) of the American Chemical Society (ACS). As such, he is one of three living members to hold both offices. He is a Fellow of ACS as well as the American Association for the Advancement of Science and the Royal Society of Chemistry. In 2009 he was chair of the Council of Scientific Society Presidents.

Bill has received Distinguished Alumni Awards from both Indiana and DePauw, and numerous ACS division and local section awards. He has received an honorary Doctor of Science from DePauw and is the 2023 recipient of the ACS Charles Lathrop Parsons award.

He is active in the ACS Committee on Committees, the ACS Insurance Trust Board of Trustees, the ACS Careers area, and is a Certified Retirement Coach. He holds two patents, has published five books and has nearly one hundred publications in the fields of organic electrochemistry, polymer chemistry, combustion chemistry, incineration, plastics recycling, sustainability and…popular music history and analytics.

Vinyl Chloride, Cancer and Technology: How Science Saved a Business

William F. Carroll, Jr. Ph.D.
ACS President, 2005; Board Chair 2012-14

On February 3, 2023 a train derailed in the little town of East Palestine, Ohio. Some of the cars contained liquid chemicals which spilled and ignited. However, the main concern centered around five cars of vinyl chloride which had not breached but were in the wreckage and fire zone. Eventually, the decision was made to vent the cars and burn off the vinyl chloride, a huge fire.

Vinyl chloride is used to make Poly(vinyl chloride) or “vinyl, ” one of the four main commodity polymers manufactured in the US. Billions of pounds are made in the US every year; however, there was a time in the 1970s when many doubted that the industry would exist at all in 1980, let alone 2023. It was in those days that the raw material, vinyl chloride, was found to cause cancer in laboratory animals, then in humans--specifically, four workers in polymerization operations.

This presentation reviews the East Palestine situation, the history of vinyl chloride toxicology, the events of 1974 and 1975 when cancer cases in workers were confirmed and how this situation became one of the landmark events in the history of industrial hygiene. Most important is what was done by chemists and engineers in the US and abroad to modify technology and reinvent the product and the industry along the way. Over 100 billion pounds a year of material is now produced safely using a known human carcinogen.

As a bonus, we’ll talk about the way vinyl chloride is made in China—and only in China—by a process eliminated in most of the rest of the world 50 years ago. It depends on mercury as a catalyst and must be phased out in the next few years under a new international treaty: The Minamata Convention. The history of the so-called “carbide process” is a fascinating study in industrial evolution.

Joint School of Nanoscience and Nanoengineering

Street address of the JSNN is 2907 E. Gate City Blvd, Greensboro, NC 27401

The front of the building, which faces a parking lot, has plenty of free parking space available

Cliff Bell passed away on June 15, 2023. Cliff was the Chair of the local section in 2013 and an active member of the section. Cliff was hred in 1990 as a Laboratory Manager in the Department of Chemistry at Winston Salem State University. He was instrumental in recruiting students to attend WSSU and helped initiate the Department of Chemistry Alumni Advisory Board. As a member of the advisory board, he worked to create the Herrell-Bell Scholarship. Mr. Bell retired from WSSU in 2014.

OBITUARY

Clifton Earl Bell Jr. was born to the late Clifton Sr. and Clara Kearns Bell on July 24, 1952, at St. Joseph's Hospital in Southern Pines, NC. He departed this life on June 15, 2023, in Greensboro, NC.

His parents and sister, Jacqueline Bell Verbal preceded him in death.

After graduating from Pinecrest High School in 1971, Clifton joined the US Navy. Following his Honorable Discharge, he continued his education to earn a BS and MS Degree in Biology and Chemistry at North Carolina A&T State University.
For 29 years, Cliff taught Chemistry at Winston-Salem State University. Two of the highlights of his time there were assisting with establishing a Math/Science scholarship, with the first recipient being the daughter of a childhood friend, who is now a veterinarian. He also established an endowment of the Harrell/Bell

Endowment at WSSU. Believing in the importance of education for young people, he sought ways to help students succeed. In many ways, their successes were his as well. He was an Alpha Phi Alpha Fraternity, Incorporated member and enjoyed the brotherhood tremendously. He grew up hunting and fishing, which remained his source of relaxation throughout his life. Just let him get a space on the boat to cast his line, and he was a happy kid.

Clifton also had a strong belief in Christ that was nurtured at First Missionary Baptist Church in Southern Pines, until he became an adult and went on to other places. He served thirty years under the leadership of his older brother, Reverend Joseph F. Kearns, at Marston First Baptist, then at Greater St. John Missionary Baptist Church in Asheboro, NC, where he taught Sunday School, sang with the choir, and worked with the youth. He was a member of the General Baptist State Convention Laymen's League. And, for more years than we can count, he was a proud member of the American Legion Department of North Carolina, through which he served as the Revitalization Commander of Rufus McLaughlin Post 177, Southern Pines, NC, and District 16 Commander, Department of North Carolina. He has received several recognitions from local, State, and National Departments for his excellence in service, always diligently working to meet goals. His heart was in working on behalf of Veterans, assuring that they could access all available services. His latest venture was joining forces with a local organization, Teamwork, which serves the needs of the homeless. This partnership was to better provide housing and other services by working together to maximize resources to serve all. Clifton lived his adult life serving others, often through physical challenges that never kept him from meeting an obligation. His last call to service was June 9th, when, from a wheelchair, he completed his assignment with the NC American Legion Convention. The only thing to say is, *"sun has set, shadows have come, time has fled; scouts must go to their beds, always true to the promise they made."*

Clifton leaves, with awesome memories of great times together, his brothers, Pinkney E. Kearns (Shirley) of Marston, NC, Reverend Joseph F. Kearns (Shirley) of Fayetteville, NC, and Timothy Bell, also of Fayetteville; his sisters, Tessie Taylor of Southern Pines, NC, and Dana Love (Jeffrey), of Riverview, FL.; his uncle, Halbert Kearns (Jeanette) of Southern Pines; his aunt, Lillian Kearns of the Eastwood, Community in West End, NC; a god-brother, Tyler Reece Jr. (Carlean); his god-sisters, Shemise Adkins, Maria Lee, Sheila, Pam, and Pat Farmer; cousins, too many to name; a real village of the family and friends nationwide who will really miss our "Babs."

A recent article in C&E News with some local connections . . .

ENVIRONMENT

Asphalt that's safer for humans and the environment

Asphalt surfaces emit harmful gases throughout their life. Researchers want to change that

PAYAL DHAR, SPECIAL TO C&EN

Elham Fini holds a sample of her lab's biochar-enhanced asphalt.

Asphalt is used for millions of kilometers of roads globally, as well as sidewalks, roofs, parking lots, and other outdoor areas. It's used for waterproofing and soundproofing, and in construction and manufacturing. On top of that, it's cheap, easy to repair, and 100% recyclable.

But if you've ever smelled fresh asphalt on a newly laid road and imagined your life being shortened by a couple of days, that may not be too far from the truth. Recent explorations into the volatile emissions from asphalt are beginning to show that roads release chemicals that can be harmful not just to the environment, but also to human health directly.

Asphalt is not a single substance. It is a mixture of many chemicals, and there are thousands of different asphalt mixes designed for different budgets, levels of traffic, environments, climates, and existing surface structures. As a fossil fuel product whose manufacture requires temperatures of up to 350 °C, the material has a not-insignificant carbon footprint. According to the trade group National Asphalt Pavement Association, between 2009 and 2019, US greenhouse gas emissions from the manufacture of asphalt mix hovered at around 20 million metric tons of carbon dioxide equivalent annually—which in 2019 would have amounted to about 0.3% of the US total of such emissions. (For comparison, the US Environmental Protection Agency estimated that commercial air transportation contributed about 2.1% of US emissions in the same year.) This estimate does not account for other stages of asphalt's lifecycle such as transport, installation, and disposal.

Asphalt's impact on human health is a relatively new field of study. Recent research suggests that asphalt surfaces can emit particulate air pollution and other volatile compounds that are hazardous to humans. Because asphalt consists of a complex combination of tens of thousands of chemicals, correlations between exposure and health effects are difficult to measure.

Strategies to minimize the negative impacts of roads and other asphalt surfaces have traditionally focused only on the environmental aspect. But having defined links to human health, some researchers now believe that making the next generation of asphalt will be a balancing act between mitigating carbon footprint, enhancing durability, and limiting adverse health outcomes for people paving and living near the roads. They are exploring asphalt additives such as non-fossil-derived components and devising mixes that better withstand what traffic and nature throw at them—all to keep volatile pollutants from entering the air we breathe.

Traditionally, asphalt binder is made from sticky, viscous asphaltenes—bottom-of-the-barrel residues left when gasoline, diesel, jet fuel, and other compounds are removed from crude oil during the refining process—and lighter maltenes. While we usually refer to paving material as "asphalt," only about 5% of the jet-black mixture dumped on roads is true asphalt. It binds the other 95%, which is made up of gravel and other aggregates.

After this chemical blend is laid on roads, it is barraged by heat, sun, and other weather conditions, as well as the weight of traffic, until it breaks down into smaller, lighter molecules. The heat

"I can use something that has a lower carbon footprint, but it could degrade and release toxic compounds to the air that we breathe."

—**Elham Fini,** engineer, Arizona State University can coax these molecules to vaporize and float off, producing that pungent smell we all know.

The emissions comprise potentially hazardous volatile organic compounds (VOCs) such as oxygen- or sulfur-carrying aromatics, including benzofuran, benzoic acid, dibenzothiophene, hexanethiol, and polycyclic aromatic hydrocarbons (PAHs). Some VOCs can irritate the eyes, nose, and throat, damage nerves and other organs, and possibly cause cancer, according to the American Lung Association. PAHs have also been linked to blood and liver problems.

"There are emissions from asphalt products over a range of temperatures," even "pretty modest" ones, says Albert Presto, a chemical engineer at Carnegie Mellon University. His team, along with Drew Gentner's group at Yale University, evaluated asphalt emissions as an unaccounted-for source of pollution in urban air quality calculations (*Sci. Adv.* 2020, DOI: 10.1126/sciadv.abb9785).

The researchers heated fresh asphalt to different temperatures, exposed it to simulated sunlight, and found that the material was emitting a mélange of PAHs, alkanes, and aromatic compounds. They saw a 300% jump in VOC emissions when they exposed the asphalt to moderate solar radiation and a 70% increase in those emissions for every 20 °C that they cranked up the ambient temperature.

Occupational exposure is the most obvious threat as VOCs waft out of newly laid pavement and crews are regularly subjected to high-concentration emissions. But "more broadly, across a whole city, you have lots of [asphalt] surfaces emitting at a low level for a long time," Presto says. "That's ultimately contributing to secondary aerosols"—organic chemicals that undergo further oxidation once they're airborne and agglomerate into particulate matter.

Even if these surfaces' contributions to the total aerosol load is small, they should be monitored because they continue for a long time and can potentially affect a lot of people. Measuring human exposure to asphalt is only half the problem. Researchers and regulators also don't know all the potential health impacts of the material's myriad components, individually or in combination, says Arizona State University's Judith Klein-Seetharaman, who studies computational protein biochemistry.

As things stand, determining unhealthy exposure to many of the compounds found in asphalt depends on a list of reference compounds and their accepted

"Even though I notice a lot of resistance and delays, as long as you continue sharing knowledge, I have hope that we can push our industry . . . in a more sustainable direction."

—Shenghua Wu, civil engineer, University of South Alabama

exposure limits. But those limits were calculated according to what could be practically detected using spectrographic and chromatographic analysis and surface-sampling methods at the time, which in some cases was in the early 1990s. These approaches don't provide enough information to draw conclusions about how these chemicals might react in combination, according to Klein-Seetharaman.

"It's an oversimplification," she says, because analysis has shown that asphalt emissions comprise several thousand compounds, including some whose health outcomes haven't even been measured.

Klein-Seetharaman would also like studies to account for the long-term accumulation of these chemicals in the human body. She notes the possibility of secondary systemic effects, in which VOCs can initially enter a person's system via inhalation, for example, and be transported through the bloodstream to other organs. Some of these pollutants can linger, hidden inside lipid droplets, and emerge into the bloodstream when the lipids are metabolized years later, causing long-term effects.

To get a better sense of the web of interactions, Klein-Seetharaman and her colleagues reviewed literature documenting the effects of known compounds in asphalt and their cellular biomarkers. They mapped interconnections between these pollutants, the various genes affected by those pollutants, and the potential health effects, including cardiovascular disease, liver damage, asthma, chronic obstructive pulmonary disease, and skin conditions.

Many researchers believe that most asphalt emissions occur during the road construction phase, but Elham Fini, one of Klein-Seetharaman's collaborators at Arizona State, points out that she smells asphalt fumes in the desert summer year after year. This indicates that paved surfaces are continuing to degrade.

Fini's lab is working toward a solution by making an asphalt binder that emits fewer harmful chemicals. In doing so, her team also wants to keep asphalt's carbon footprint in check. The researchers are investigating biomass-derived additives as a low-carbon option. These are inherently carbon sinks and can grab VOCs before they float off into the air.

One of these materials is iron-rich biochar, which comes from the thermochemical conversion of waste biomass like algae and manure. Biochar is a carbonaceous material that has been used for CO_2 capture and environmental cleanup because its highly porous structure can trap gas and heavy-metal molecules. Fini and her colleagues found that introducing an iron-rich version of biochar to asphalt resulted in a 76% reduction in VOC emissions, versus 59% with regular biochar. In computer simulations, the team saw that functional groups containing iron-nitrogen bonds could efficiently adsorb and catalytically degrade VOCs (*ACS Sustainable Chem. Eng.* 2023, DOI: 10.1021/acssuschemeng.2c06292).

The team is working on using a material derived from liquefied algae biomass and adding it to asphalt to snatch organic compounds that are precursors to VOCs and secondary aerosol pollutants before they become airborne. The researchers have dubbed the biomass production process AirDuo because they do it in two steps: they employ carbon capture technology to harvest CO_2 from air and then feed that CO_2 to the algae or some other biological material. When mixed into asphalt, the resulting binder selectively adsorbs and retains various reactive pollutants and their precursors. In other words, the asphalt cleans up after itself (*ACS Sustainable Chem. Eng.* 2021, DOI: 10.1021/acssuschemeng.1c03827).

AirDuo can be tailored to remove volatiles not just from asphalt but from other sources, such as refineries or car exhaust. "Wherever you get to sequester carbon and prevent it from going back to the air, it's good," Fini says. Her team is working on scaling up the technology.

Lab experiments show that, apart from controlling air quality, Fini's additives increase the durability of roads. This is yet another force to balance when designing new asphalt mixes: if roads are more resilient, their breakdown can be slowed, and they don't have to get repaved as often. That leads to lower asphalt consumption and the potential reduction of VOC and PAH releases.

Andrew Barron, a chemical engineer at Swansea University, is applying nanotechnology to this fundamental issue. As it weathers, asphalt breaks down chemically, but it also breaks down physically. That fragmentation leads to more exposed surfaces, which causes additional degradation into VOCs. Water exacerbates this process as it flows into cracks and further breaks up the asphalt.

A study from Barron's lab reported that adding engineered clay or silica nanoparticles to asphalt binders helps alleviate degradation and extends a road's lifetime. The nanoparticles coat the asphalt, creating a composite material that acts as a shield against oxidation, heat, and water. The heat resistivity prevents the decomposition of chemical bonds in the asphalt, Barron says, thus reducing cracking and the consequent emissions normally coming off roads. Under high-temperature, -pressure, and -ultraviolet-light conditions, asphalt mixtures with 0.2–0.3% of the nanoparticles by weight kept 1.5–2 times as much viscosity, a proxy for aging, as normal asphalt. (*Nanotechnol. Rev.* 2022, DOI: 10.1515/ntrev-2022-0062).

Barron is optimistic about commercializing the technology. The materials his team needs to make its nanoparticles are already being manufactured at large scale, he says. And because the nanoparticles can be mixed into asphalt on-site, the additive wouldn't require any changes in the road-laying process.

Shenghua Wu, a civil engineer at the University of South Alabama, notes that what works great in the lab may not be practical on the ground. "We can have a design idea, but the people who are going to make that happen have to feel comfortable about making the change."

Richard Willis, vice president of engineering, research, and technology at the National Asphalt Pavement Association, admits that the industry is not necessarily the quickest to adapt to new technologies, mostly because of issues related to economies of scale—it takes a long time to swap out every kilometer of asphalt.

Wu says that collaboration between labs, companies, and government agencies is key. Achieving carbon-neutral goals will require a lot of work, he says. "Even though I notice a lot of resistance and delays, as long as you continue sharing knowledge, I have hope that we can push our industry . . . in a more sustainable direction."

Fini says that sustainability is about more than carbon emissions, though, and factoring in health is essential: "I can use something that has a lower carbon footprint, but it could degrade and release toxic compounds to the air that we breathe." Breathing in CO_2 from asphalt might give you a headache, but breathing in the same amount of benzothiophene could be much, much worse, she adds.

ACS central science

Payal Dhar is a freelance writer based in Bangalore, India. A version of this story first appeared in *ACS Central Science*: cenm.ag/healthyroads.

Elections coming at the November Meeting

The local section will vote for Executive Level positions at the November local section meeting. There are also non elected sub-committee positions that are still open. If you are willing to volunteer for any of the positions, please contact Kent Kabler (kent.kabler@syngenta.com).

Please give thought to giving back to your profession.

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