Firefighters put out a tank fire using fire-suppressing foam.

CREDIT: LARGE ATMOSPHERIC STORAGE TANK FIRES PROJECT

SPECIALTY CHEMICAL

The price of fire safety

Firefighting-foam makers ponder the environmental cost of fluorosurfactants

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Straight out of college, Ted Schaefer's first assignment at 3M Canada was to provide technical support and formulate firefighting foams. It was 1980, and 3M was the dominant producer of fluorosurfactant-containing foams used to quell hydrocarbon fires after aircraft crash landings and to put out fires at oil refineries, chemical plants, and storage-tank facilities.

From the 1970s through the 1990s, 3M's Light Water fire suppressant—and other fluorosurfactant-based firefighting foams like it—were the "highest performing" foams available, recalls Schaefer, who earned a degree in chemistry from the University of Waterloo. The foams seemed to have few, if any, drawbacks.

A concentrated formula, diluted with water, forms a heat-resistant foam blanket that rapidly cools and smothers most hydrocarbon-fueled fires. The fluorine content helps create a low-surface-tension film that rapidly spreads across the surface of a flammable liquid. A foam's quick action in a fire can mean the difference between life and death.

Fluorosurfactants are a class of fluorine-based chemicals also used in fabric-protection sprays sold under names such as Scotchgard and Teflon and, previously, as processing aids in the manufacture of nonstick pots and pans. But because firefighting foams are applied in the outdoor environment, they are a major vector for the release of fluorochemicals into drinking water, where their presence is associated with diseases including cancer.

Schaefer recalls asking fellow 3M scientists how fluorosurfactants degrade in the environment. "I was told that fluorosurfactants are nonreactive, inert materials," he says. "They should be thought of as 'chemical rocks.'" His colleagues assured him that the surfactants would do no harm when they got into the environment.

The 3M scientists were wrong. In 2000 the company admitted that surfactants based on perfluorooctane sulfonic acid (PFOS), which were used in Light Water, were accumulating in the environment and showing up in humans and animals at levels that raised health questions. Similar fluorosurfactants based on perfluorooctanoic acid (PFOA), another eight-carbon fluorochemical, have been linked to human health concerns as well.

However, many firefighting experts, including US military scientists, consider fluorosurfactant-containing foams essential to preserving life and property because they suppress fires more quickly than alternatives, such as old-style protein foams containing hydrocarbon surfactants and ground animal hooves.

Layered on top of the safety debate are lawsuits from firefighters and people claiming illness from drinking water contaminated with PFOA- and PFOS-based fluorosurfactants and their six-carbon replacements—compounds that together are known as per- and polyfluoroalkyl substances (PFAS). States and municipalities have also filed lawsuits seeking to recoup costs for water filtration systems.

A 2016 Harvard T.H. Chan School of Public Health study using US Environmental Protection Agency data found PFAS in drinking water at 664 military training facilities and 533 civilian airports. A Department of Defense report to Congress in late 2017 acknowledged 393 active and closed military installations where the department knows or suspects it contaminated drinking water with PFOA or PFOS compounds.

Last year, the state of Washington passed legislation to ban PFAS-containing firefighting foams beginning in 2020. Fire trucks will no longer be able to use them on fuel spills and car fires, though use will continue at airports, military bases, petroleum refineries, and chemical plants.

In October, President Donald J. Trump signed the Federal Aviation Administration

Reauthorization Act of 2018 requiring the FAA to allow civilian airports to use fluorine-free foams by 2021. Rules now require US airports to use military-grade foams that contain PFAS. Public-interest groups such as the Environmental Working Group and the International Persistent Organic Pollutants Elimination Network (IPEN) want an end to the use of PFAS in all firefighting foams.

For their part, fluorochemical suppliers such as Chemours, Dynax, and AGC Chemicals and foam makers such as Perimeter Solutions and Solberg are calling for a more measured approach. With few exceptions, all have turned to C_6 fluorosurfactants, which they consider safer and less likely to bioaccumulate than surfactants based on PFOA and PFOS.

To limit environmental exposure, foam makers have also called on all users to stop training exercises using fluorosurfactant-containing foam. Others champion fluorine-free foams that they consider just as good as the fluorosurfactant types. Though not everyone agrees that fluorine-free foams are up to the task, pressure is mounting to severely restrict fluorosurfactants or remove them completely from firefighting foam.

A high standard

"I feel badly if I did something that led to people being hurt," says Schaefer, the former 3M fluorochemical foam formulator. In 2003, while still working for 3M, he developed and patented the first modern fluorine-free foams. 3M later decided it no longer wanted to be involved in firefighting foams, and in 2007 it sold the patents to Solberg.

Shortly after the sale, Schaefer joined Solberg. Until his retirement in 2015, he led the formulation and sale of fluorine-free foams in Australia, where he had worked for 3M since the late 1980s. "The technology of fluorine-free foam that I developed utilized a lot of organic chemicals, including complex sugars and starches," Schaefer says. "These add heat resistance and stability to the foam."

Schaefer's work garnered Solberg a Presidential Green Chemistry Challenge Award in 2014 for its fluorine-free foams. The EPA presents the award to recognize technologies that prevent pollution and match or improve the performance of existing products.

Eduard Kleiner, president of Dynax, a C_6 fluorosurfactant maker, disagrees that fluorine-free foams are up to the task. A former director of corporate research at Ciba-Geigy, a onetime fluorosurfactant producer, he refers to himself as "the old man in the field." Kleiner founded Dynax in 1991.

"The fluorine haters are looking for any possible deficiency" to remove fluorosurfactants from foams, Kleiner says. "They ignore the fact that fluorine-free foam can't meet the most stringent performance specifications" demanded by the US military.

The haters, Kleiner says, lump all fluorosurfactant chemistries together, but the C_6 compounds have a much better toxicological profile than PFOS- and PFOA-related materials, he claims.

Many foam formulations containing C_6 fluorosurfactants now meet US military specifications, Kleiner says. None of the fluorine-free foams can do that, he notes. "If 200 passengers burn up in a crash landing because firefighters use fluorine-free foam, I'm willing to testify this could have been foreseen and likely avoided by the use of C_6 fluorosurfactant-based foams."

Kleiner acknowledges that fluorosurfactants, including C_6 types, persist in the environment. But he says the C_6-based surfactants do not bioaccumulate. He supports the use of alternatives for small hydrocarbon fires and says firefighters should not use fluorine-containing foams in training exercises. "I personally think it is good" that military scientists "are searching for fluorine-free foam meeting military specifications," he says.

Researchers at the US Naval Research Laboratory (NRL) who write the specifications for firefighting foams are actively looking at fluorine-free alternatives, but they say they haven't found any that meet performance standards that include extinguishing a 2.6 m^2 test fire in as little as 30 s.

John Farley, director of fire test operations at NRL, says the lab has qualified 16 firefighting foams containing C_6 chemistry. They are mostly updated recipes for PFOA-based materials. "We need to come up with fluorine-free foam. But what's available now can't meet specification," he says.

Katherine M. Hinnant, a chemical engineer who leads NRL research on firefighting foams, says fluorinated foams "outperform fluorine-free foams by a factor of four to five," by containing a fire and suppressing vapors that can reignite. Fluorine-free foams are stable for 3 min, she says, while the fluorosurfactant kind can last 30 min.

In the search for more effective fluorine-free foams, Hinnant says she is evaluating hydrocarbon surfactants, silicones, and sulfonated surfactants. "Fluorine is really amazing," she says, but "we are focusing on eliminating fluorine."

Safety versus the environment

Hinnant and other government researchers are well aware that ineffective firefighting foams contributed to the deaths of 134 sailors on board the navy's USS *Forrestal* in 1967. It was in an effort to avoid similar catastrophes that the navy developed a fluorosurfactant-containing foam with 3M.

However, some who use firefighting foams in critical situations claim that fluorine-free foams already perform as well as fluorine-containing ones. London's Heathrow Airport switched to fluorine-free foams in 2013 after a 15-month evaluation project, says airport fire regulation and oversight manager Graeme Day. He has no qualms about performance. "It's been absolutely excellent," he says.

Two incidents at the airport, both in 2013, convinced Day that he had made the right choice. In the first, an Airbus 319 en route to Oslo, Norway, from London had to make an emergency landing at Heathrow after covers blew off both engines, knocking out one and setting the other on fire. The pilot landed the plane with the one good engine "fully involved" in fire, Day says.

Firefighters spray fluorine-free foam on a hydrocarbon test fire at Dallas Fort Worth Airport.

CREDIT: LARGE ATMOSPHERIC STORAGE TANK FIRES PROJECT

Firefighters were able to quell the fire with the fluorine-free foam in less than 3 min after the plane touched down. They also safely evacuated all 80 people. "That incident boosted our confidence" in fluorine-free foams, Day says.

Afterward, maintenance crews washed the runoff into drains feeding the airport's water treatment plant, Day says. A 2008 incident using a fluorosurfactant-containing foam required collection and disposal of the effluent to prevent release of the persistent ingredient into the environment, he says.

In the second, less serious incident, firefighters quickly put out a fuselage fire in a parked Boeing 787 Dreamliner using a fluorine-free foam.

Day acknowledges that putting out large fuel-tank fires isn't part of his job. Firms such as BP, ExxonMobil, and Shell that do deal with such fires have banded together in a group called the Large Atmospheric Storage Tank Fires project to reduce the risk of tank fires and to test foam performance.

"Fluorinated foams are a major issue," says project coordinator Niall Ramsden. "Our priority is to get an end-user picture of what can and what cannot be done with various foams. We see the way the world is going. Our current testing focus is on foams that do not contain fluorosurfactants."

So far, tests show fluorine-free foams perform as well as the fluorine-containing kind for smaller tank fires, Ramsden says. But for large tanks (those with a diameter of 100 m or larger), he indicates that fluorochemical-containing foams still perform best.

Despite growing skepticism over fluorosurfactant foams, Perimeter Solutions, a leading foam maker, has yet to see a drop in US demand for C_6 foams. Still, many customers in northern Europe and Australia are shifting to fluorine-free foams, CEO Edward Goldberg says. Goldberg expects an eventual shift in the US as well, given recent legislation in Washington State and at the federal level.

The firm started in the fire-retardant business as a maker of phosphate-based retardants used on forest fires. It acquired the Spanish C_6 foam maker Auxquimia in 2014. And Perimeter is now offering fluorine-free foams. Earlier this month, it completed the acquisition of Solberg, the firm that bought Schaefer's patents on fluorine-free foams.

The move from C_6 fluorochemical foams to fluorine-free versions "is a natural evolution of the market," Goldberg says. However, the shift will involve a trade-off, he says. "Fluorine-free foam can't match the performance of C_6 foams. When life and property are at risk, you want to put the fire out as quickly as possible," and that currently requires fluorosurfactant chemistry in many cases, he says.

In fact it was a Solberg representative that made the case for C_6 fluorochemical foams at the Washington State foam legislation hearings in February 2018. "The fluorine-free foams are very effective on spill fires," Mitch Hubert, Solberg's global product development vice president, told the legislators. But when those foams are used on fuel-tank fires, the foam plunges below the surface, picks up fuel, and contributes to the fire, he said.

"You don't want a situation like they had in Buncefield, England," he said, "where one tank caught on fire and then another one caught on fire... and you had a huge ecological disaster from their inability to extinguish the first fire."

News reports described the 2005 Buncefield fuel-depot fire, which involved 20 big fuel tanks, as the largest of its kind in Europe since World War II. A delay in spraying fluorochemical-containing foams on the flames, in part because of ecological concerns, allowed the fire to grow. The local water utility closed a nearby pumping station after PFOS contamination was found in groundwater nearby.

Firefighters weigh in

Users of fluorochemical-containing foams are worried about what exposure to the foams means for their health. Testifying to Congress in September 2018 before it passed the legislation allowing civilian airports to use fluorine-free foams, Timothy Putnam, a 24-year civilian firefighter for the navy, said he recalled using fluorine-containing foam—in the days before scientists raised safety flags—"as a substitute for vehicle soap to wash fire department vehicles. We also used [it] to clean the fire station floors."

Now, Putnam said, he is worried about "human impacts" of the exposure. And he didn't accept the argument that C_6 fluorosurfactants are safer than PFOA- and PFOS-containing foams. Though the C_6 formulas "are generally less toxic and less persistent in the environment compared to the longer-chain PFOA... they are likely to contain trace amounts of PFOA as a by-product," he said.

CREDIT: SHUTTERSTOCK (AIRPLANE); WIKIMEDIA COMMONS (USS *FORRESTAL*); 3M (LOGO)

A firefighting foam legacy

Fluorosurfactant-containing foams were developed in the 1960s. But new knowledge about the persistence of fluorosurfactants and worries over their impact on human health have led to reformulations and lawsuits.

1967: A catastrophic event
A fire on board the USS *Forrestal* kills 134 sailors and prompts calls to use fluorine-containing foams at military installations.

2007: 3M sells patents
3M sells fluorine-free foam patents to Solberg Foam.

1961–66: Research on new foams
3M and the US Naval Research Lab develop fluorosurfactant-containing foams to quickly put out hydrocarbon fires.

1969: Military specifications published
The US Naval Research Lab outlines military specifications for fluorosurfactant-containing foams.

1999: Fluorosurfactant persistence documented
Jennifer Field and Cheryl Moody publish a paper in *Environmental Science and Technology* (DOI: 10.1021/es981355) showing the presence of fluorochemicals in groundwater at two US military bases 7–10 years after they were closed.

2000–02: 3M bows out
3M agrees with the Environmental Protection Agency to phase out the manufacture of PFOS. 3M discontinues its Light Water foam.

Other firefighters are worried as well. In October, lawyers filed a class-action suit in the US District Court for the Southern District of Ohio against fluorosurfactant makers, including 3M and Chemours, seeking unspecified relief for health-related injuries. The case, which names firefighter Kevin D. Hardwick as the lead plaintiff, doesn't restrict plaintiffs to firefighters. All individuals residing in the US who "have a detectable level of PFAS materials in their blood serum" are named as members of the class.

One feature of the case is a request that the presiding judge appoint a panel of scientific experts to evaluate evidence and determine probable links between PFAS exposure, including C_6 fluorosurfactants, and health problems. A panel appointed as part of a similar 2004 class-action case against DuPont, Chemours's former parent, found probable connections between PFOA and health problems, including thyroid disease, testicular and kidney cancers, pregnancy-induced hypertension, and ulcerative colitis.

The panel's findings ultimately led DuPont and Chemours to pay $670 million to settle 3,550 lawsuits by residents living near a PFOA plant in West Virginia. Claimants said that drinking PFOA-contaminated water made them ill.

The Hardwick case is one of more than 70 firefighting-foam-related cases that a panel of federal judges is reviewing for consolidation. Cases include claims against 3M, Tyco Fire Products, Chemguard, and other firms that have made PFOA- and PFOS-containing firefighting foams.

Whether the fluorosurfactants used in foam are based on PFOA, PFOS, or C_6 chemistry, "these are tough chemicals," says Stephen Korzeniowski, a consultant who earlier worked as a fluorotechnology expert for Chemours and DuPont. The molecules' carbon-fluorine bonds "are one of the toughest bonds known. That can be both a blessing and a curse," he says.

Those tough bonds mean the fluorosurfactants are chemical and heat resistant—and also environmentally persistent, Korzeniowski says. But in work for the FluoroCouncil, which represents fluorochemical users and makers, researchers found that C_6 fluorosurfactants are not bioaccumulative (*Regul. Toxicol. Pharmacol.* 2019, DOI: 10.1016/j.yrtph.2019.01.019) and have a "significantly better" toxicological profile than PFOA- and PFOS-based surfactants, he says.

Environmental groups say they are concerned about the use of any fluorosurfactant foams.

The C_6 products appear to be less bioaccumulative than those containing PFOS and PFOA, acknowledges David Andrews, a senior scientist at the Environmental Working Group. But the C_6 surfactants are still environmentally persistent and have toxicity end points similar to those of PFOS and PFOA types, Andrews says. EWG estimates that up to 110 million Americans could have PFAS in their drinking water. "Fluorine free is the much better option," he says.

When the United Nations Stockholm Convention on Persistent Organic Pollutants banned PFOS in 2015, it made an exception for use in firefighting foam. Governments are now considering lifting the exception for PFOS foams and adding a ban on PFOA foams.

IPEN, a Sweden-based public-interest group, released a report recommending that governments ban all PFAS surfactants, including the C_6 chemistries, in firefighting foam. IPEN science adviser Sara Brosché, a chemist, says PFAS are "too dangerous to deal with one at a time, and countries should take action to address them as a class and remove all of them."

If governments vote in favor of such a ban, that would mean the end to PFAS in firefighting foams. However, such a ban is unlikely. IPEN points out that China still produces large quantities of PFOA, and industry experts say PFOA is still widely used to make firefighting foams in Asia.

Schaefer, the father of fluorine-free foams, says he is confident that continued research and testing will yield fluorine-free foams that can meet the most demanding requirements. "I expect the pressure will continue and even US defense forces will get away from fluorosurfactants," he predicts. If that happens, fluorine-based firefighting foams could become a thing of the past. ■

CREDIT: SHUTTERSTOCK

2008: PFOA linked to disease
A science panel finds a probable link between PFOA exposure and diseases such as testicular and kidney cancer and medical conditions such as high cholesterol.

2009: PFOS deemed a pollutant
The Stockholm convention classifies PFOS as a persistent organic pollutant. Countries impose use restrictions.

2010–15: PFOA slated for elimination
Under an EPA stewardship program, eight fluorochemical makers agree to eliminate PFOA by 2015. Makers shift to six-carbon replacements.

2016: EPA limits PFOA and PFOS in water
The EPA establishes a drinking-water exposure limit for PFOA and PFOS combined of 70 parts per trillion.

2017: Military accounts for contamination
A US Department of Defense survey finds fluorochemical contamination in drinking water linked to firefighting foam use at 393 active and closed military bases.

2017: Settlement reached
DuPont and its spin-off Chemours pay $670 million to settle claims of PFOA-related illness by residents living near a plant in Parkersburg, West Virginia.

2018: Firefighters sue
Firefighters file a class-action lawsuit against 3M and others. They seek compensation for exposure to per- and polyfluoroalkyl substances, including PFOA, PFOS, and short-chain substitutes. The suit seeks creation of a science panel to determine probable links between exposure and human health.

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