LAYING THE FOUNDATION

for New Technologies

3M creates a new building block for its fluorosurfactants.

Fluorosurfactants have been an integral part of the coatings industry's technology advance. These products appear in virtually all media — water- or solventborne — and function well at reducing surface tension levels more effectively than competing technologies. Reducing the surface tension of coating formulations helps eliminate surface defects by improving flow, wetting and leveling.

Two years ago, 3M voluntarily phased out substances that contained perfluorooctanyl groups, a chemical component of previously commercialized fluorosurfactants. The company immediately began developing alternative chemistries that could meet or exceed customer needs. The company's researchers worked toward solutions that had both the performance factors customers expect, as well as an improved environmental profile. Two alternative products — 3M™ Fluorad™ fluorosurfactants FC-4430 and FC-4432 — were sampled to the coatings industry.

Two New Solutions

Fluorad FC-4430 and FC-4432 are polymeric, non-ionic fluorosurfactants for use in a range of coatings, including waterborne, solventborne, UV-curable, water-reducible and high-solids. They are compatible with a variety of resins, including urethanes, epoxies, polyesters and acrylics. Furthermore, they can be used with reactive monomers such as isocyanates. These new fluorosurfactants are very effective at reducing surface tension. Internal and independent testing has indicated that FC-4430 and FC-4432 provide surface tensions superior or comparable to hydrocarbons, silicone and other commercialized non-ionic fluorocarbon surfactants.

"These two new fluorosurfactants have exceeded our performance expectations and are gaining customer acceptance in a variety of applications," said Dr. Michael Terrazas, research specialist, 3M Performance Materials Division. "Originally intended to be an FC-430

By Dr. Darlene Brezinski / Editor

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replacement, data is showing the versatility of these fluorosurfactants in applications that formerly used other nonionic fluorosurfactants, and have even found some success in aqueous applications that previously had used anionic fluorosurfactants."

Based on an entirely new fluorochemical building block, FC-4430 and FC-4432 are high-molecular-weight polymers that show the same performance benefits that have long differentiated fluorochemicals from competing surfactant technologies, such as silicones and hydrocarbons. The company believes this stems from the physical properties of the fluorochemical component of these materials. Very little product is necessary to afford a significant surface tension reduction of a formulation, which for customers means low use levels. Hydrocarbons, in contrast, often require an order of magnitude more product to significantly reduce surface tensions, and the surface tension levels reached do not approach those possible with FC-4430 or FC-4432.

Second-coat adhesion can often be adversely affected when using silicone or conventional fluorochemical surfactants. However, this has not been observed when using FC-4430 or FC-4432, even at higher loading levels. This is due to the shorter fluoroalkyl chain length incorporated into these new materials.

Overall, the performance of the fluorosurfactants has been exceptional. Customers report excellent leveling/wetting and improved flow even in harsh conditions; good smoothing of high-gloss coatings in the automotive and aerospace industries; and superior coatings in industrial-maintenance products for use on wood, metals and plastics.

Getting to this point has been a story of perseverance.

A Century of Innovation

3M has a century of innovation under its belt. Invention, innovation and discovery have been standard operating procedures since the 1920s. Technical employees have the liberty to use 15% of their time working on projects of their own choosing. Opportunities have paid off on numerous occasions.

When the company decided to reformulate its Fluorad fluorosurfactant line, numerous ideas were already forming in the minds of 3M scientists. The final choice of molecules, however, would depend upon three factors.

1. *Sustainable technology that stands the test of time.* Long-term sustainability is key to developing viable products and applications. Researchers turned to technology platforms that had a proven track record — electrochemical fluorination (ECF).

Although both fluorosurfactants and hydrocarbon surfactants can lower surface tension, fluorosurfactants are able to drastically lower surface tension in both aqueous and oily-phase systems — to levels well beyond the reach of hydrocarbons.

Resin	Control	HC Surfactant 1.00%	FC-4430 0.3%	FC-4432 0.3%	Competitive FC Surfactant 0.3%	Silicone Surfactant 0.5%
NeoCryl® A-550	36.7	27.2	29.6	22.3	26.8	24.6
NeoCryl A-6099	39.1	29	24.3	20.1	26.1	27.3
NeoRez® R-941	43.1	29.8	21.2	19.9	24.4	23.8
NeoRez R-9621	47.4	33.1	21.2	20.4	24.2	22.8
Joncryl® 537	37.4	31.8	19.7	21.0	25.6	27.6
Joncryl 1532	38.4	32.9	21.2	23.4	26.9	28.9
Joncryl 1925	41	31.2	19.7	20.2	25.4	27.1
Joncryl 1972	38.9	27.6	22.4	21.9	26.3	27.6

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2. *The new building block had to be versatile enough to provide good performance in a variety of applications.* "Because we were looking to replace an entire family of materials, the base chemistry had to provide good performance across a range of industries and in a number of different applications," said Dr. Larry Wendling, vice president, 3M Performance Materials Division.
3. *It must have a good* EHS&R *profile.* The environmental landscape and regulations continue to change.

Using ECF, a number of shorter chain length prototype molecules were created. After experimentations and testing were completed, the perfluorobutyl (PFB) chemical component was chosen as the building block molecule for the surfactants (a four-carbon perfluorinated group). "We investigated the use of even shorter chained fluorochemicals such as perfluoromethyl and perfluoroethyl," said Terrazas, "but found they could not provide the performance the industry demanded. Perfluorobutyl moieties simply struck the best balance between high performance, low toxicity and environmental acceptability."

Environmental, Health, Safety & Regulatory (EHS&R)

Environmental aspects of this technology were a crucial part of this decision. "3M has always been on the forefront of reducing the environmental impact at every stage of a product, from design to manufacturing, to use and disposal," Wendling said. "Our aim was to introduce a new technology that adhered to the company's environmental principles."

Before the company would release any product for sampling or sale, environmental fate and effects testing was conducted on the ultimate degradation product of

The PFBS environmental and safety summary shows the substance has a very low order of toxicity as determined by a range of toxicity studies.

the residuals present in the product — perfluorobutane sulfonate (PFBS). The toxicological profiles of the compound were assessed, including mammalian toxicity, chronic mammalian toxicity, bioconcentration factor and persistence. The PFBS environmental and safety summary shows the substance has a very low order of toxicity as determined by a range of toxicity studies. These test findings indicate the substance would not be considered bioaccumulative or toxic (BT) under the U.S. EPA's PBT chemical policy.

The new PFB formulation behaved largely as predicted, demonstrating an excellent environmental profile.

- Every toxicity test conducted determined that PFBS fell within the smallest hazard classification for both the U.S. National Institute of Occupational Safety and Health (NIOSH) and the European Union. This also carried into the multi-generational reproduction study where once again PFBS received the smallest hazard classification available from NIOSH and the European Union.
- PFBS is persistent, but persistence in and of itself is not a concern, if a material has very low toxicity and does not bioconcentrate. Nevertheless, to minimize the exposure to the environment, 3M currently limits sales of PFBS-based surfactants to non-dispersive applications or applications with low emissions to the environment. Prior to commercialization, the company performs a Life Cycle Management Screen of each new product and application paying particular attention to worker and environmental exposure.

The U.S. EPA has since reviewed both of the Fluorad fluorosurfactants and placed them on the TSCA inventory. FC-4430 and FC-4432 have been commercialized in the United States and in Europe, and commercialization is being pursued in additional countries.

The Path Forward

Now that the building block has been found and the first two products rolled out, the question must be asked: what's next?

For 3M, the answer is inevitable: new products. For a century, the company has invented, discovered and pioneered, and this culture will continue.

"In the past, the Fluorad product line consisted of anionic, cationic, and nonionic materials targeted to specific applications, specific substrates and specific base materials," Terrazas said. "We want to get back to that. We're working hard to develop new materials to fill out and develop this product line, so that it is every bit as comprehensive as it once was."

To get there, the company is investing heavily in Six Sigma methodologies, and is working with formulators and end-users to meet industry needs. Just as FC-4430 and FC-4432 are not a direct drop-in replacement for FC-430, Terrazas emphasizes that the products in development are completely new. "This is an entirely new platform for 3M," he said. "There will be work that needs to be done by both 3M and our customers, but in the end, we are confident these materials will do the job and do the job well."

For more information on fluorosurfactants, contact 3M, Performance Materials Division, 3M Center, Building 223-6S-04, St. Paul, MN 55144-1000; phone 800/541.6752; e-mail mster-razas@mmm.com; or visit www.3m.com/paintsandcoatings.