New Developments in Fluorocarbon Finishing of Textiles

Hans Götz, Wolfgang Knaup
Clariant Produkte (Deutschland) GmbH

Introduction

Fluorocarbons represent the state of the art in „repellent finishes“. They impart washfast water-, oil- and soil repellent properties. Although more expensive than repellents on the basis of silicones or paraffin waxes, their price is compensated by the small amounts necessary to achieve the wished repellent properties.

Clariant manufactures Nuva® water-, oil- and soil repellents based upon fluorotelomers:

- Nuva® fluoro emulsions are waterborne
- Nuva® fluoro emulsions are based on high molecular weight (meth)acrylic copolymers
- Nuva® fluoro emulsions contain perfluoroalkylated and non-fluorinated alkyl groups
- Nuva® fluoro emulsions are either anionic, cationic or non-ionic stabilized
- Nuva® fluoro emulsions are used as water-, oil-, soil repellent and/or soil release finishes

Nuva® provides a durable fluorochemical finish which acts as an invisible shield around each fibre. The fluorocarbon side chains pack closely together to create a low energy surface. While many stain resistant products are merely a surface coating for fabrics, Nuva® works on the nano scale – that is on the molecular level – to protect each fibre.

Clariant relies on the so-called telomerization process of tetrafluoroethylene to prepare the fluorocarbon compounds. Several reaction steps are necessary to obtain the Nuva® dispersions from the fluorotelomer raw materials.

Application on Textile

For optimum performance a wide range of factors have to be considered. The length of the fluorocarbon chain itself has an influence on the repellence. The choice of monomers contributes to achieve different properties, such as improved water repellence, wash permanence, soil release etc. Further additives are used to facilitate proper emulsification and polymerization, leading to the Nuva® dispersion.

The customer then applies the dispersion on the textile, where suitable conditions have to be chosen for homogeneous material deposition and film formation. If all factors coincide perfectly, the fluorinated material phase separates to the top of the coating to exert the repellent effects.
Preparation of Nuva® Dispersions

\[ C_2F_8I + n \text{CF}_2=\text{CF}_2 \rightarrow \text{Telomerization} \]

\[ R_fI \rightarrow \text{Fluowet}^\circ \text{I Iodide} \]

\[ \text{CH}_2=\text{CH}_2 \rightarrow \text{Fluowet}^\circ \text{El Ethyliodide} \]

\[ R_fC_2H_4I \rightarrow \text{NMP/H}_2\text{O} \rightarrow \text{Fluowet}^\circ \text{EA Ethylalcohol} \]

\[ R_fC_2H_4OH \rightarrow \text{CH}_3C\text{R(OH)COOH} \rightarrow \text{Fluowet}^\circ \text{AC MA (Meth)acrylate} \]

\[ R_fC_2H_4OCOCH=\text{CH}_2 \rightarrow \text{Poly(meth)acrylates} \rightarrow \text{NUVA}^\circ \text{ Dispersion} \]

**Important Steps for efficient Nuva® performance**

- RF-chain + monomer structure
- Create specific polymer structure
- Textile application
- Adsorption to surface
- Phase separation (fluoro- and non-fluoro part)
- Film formation

Nuva dispersion

Important Steps for efficient Nuva® performance
Environmental Issues

With the occurrence of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in the environment, the origin and consequences of these chemicals is widely discussed. 3M initiated a voluntary phase-out of PFOS (perfluorooctyl sulfonate) based fluorochemicals (Scotchgard™) beginning in 2000 because data indicated that PFOS is persistent in the environment, accumulates in biological systems and is toxic in tests with laboratory animals. Several years later, 3M opted to introduce perfluorobutane sulfonic acid (PFBS) as an analogue with a shorter fluorocarbon chain length.

Whereas the source of PFOS is the industrial scale production of its derivatives by electrochemical fluorination in the so-called Simons process, the situation is more complicated for PFOA, which has been manufactured by both industrial processes - electrochemical fluorination and telomerization.

PFOA and its salts has been used as surfactant in different industry sectors such as electroplating, fire-fighting foams and was required for the production of fluoroelastomers, e.g. polytetrafluoroethylene (PTFE). PFOA and potential precursors are of increasing scientific and regulating interest because they are persistent in the environment and have been found globally in wildlife and humans. In the last years some manufacturers have made significant progress and an increasing number of fluoropolymer manufacturers avoid the use of PFOA by utilizing alternative surfactants. Apart from its possible origin in the fluoroelastomer industry, PFOA is also found in traces as an unintended by-product in the telomerization process. Importantly, in contrast to common reports, PFOA and PFOS are not actively used to finish textiles. Commenting on PFOA, the U.S. Environmental Protection Agency (EPA) has said it “does not believe there is any reason for consumers to stop using any consumer or industrial related products.”

Clariant, like other major fluorotelomer producers, participates in the voluntary PFOA and residual emission reduction stewardship program of the Environmental Protection Agency (EPA), USA. As part of this program Clariant is committed to reduce PFOA emissions by 95% until 2010.

Within an extensive testing program, Clariant has shown that Nuva® polymers are considered to be safe for the environment and consumers:

- Nuva® polymers are high molecular weight polymeric fluorocompounds which show no toxicity even at the highest applied doses
- Nuva® polymers show no bioavailability and non-degradation to bioavailable fluorine containing products
- Nuva® polymers are not inherently biodegradable
- Nuva® polymers (applied on fabrics) show no hydrolysis
**Nuva N Series**

Classical fluorocarbon finishes mainly consist of C8 fluorotelomer chemistry, which is due to their higher effectiveness as water-, oil- and soil repellent. The classical Nuva® products from Clariant are state of the art and are based on purified C8 chemistry with reduced levels of PFOA and reduced amounts of fluorotelomer by-products.

The new so-called *Nuva® N* series goes a step further and is based on C6 fluorotelomer chemistry which offers unique finishing effects at the highest performance level in addition to several other important advantages:

- it does not bioaccumulate
- it does not result in PFOA or C8 residues
- it is of higher overall purity
- it exhibits a level of PFOA which is below the limit of detection with current analytical methods.

Clariant has introduced several *Nuva® N* products to cover different application profiles. *Nuva® N 2114* offers active protection and acts as a classical oil- and water-repellent. Representative for passive protection, *Nuva® N 4118* allows soils to penetrate the fabric, yet releases them from the fabric to the washing liquor during the washing procedure (stain release).

Both effects are combined in the developmental Dual Action product *Nuva RP 2145*. *Nuva® N 5117* is optimized for carpet application and offers stain repellency for all types of carpet.
The following example shows the water and oil repellence performance of Nuva® N 2114 which is equal or even better when compared to classic C8 based fluorotelomer chemistry. In comparison to a competition product based on C6 chemistry the effect level is much higher.

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<th>Active Protection</th>
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Performance Profile of Nuva® N 2114

The presentation discusses the technology behind the Nuva® N series; compares C6 with C8 based repellent materials and shows results of effects achievable with Nuva® N material in repellent as well as in release textile finishing applications.