# FOILING FINGERPRINTS

*New coating helps keep appliances clean.*

by steven block, peter hupfield, yasuo itami, eiji kitaura, don kleyer, tetsuya masutani, and yasuhiro nakai

***Steven Block*** *is commercial manager, and* ***Don Kleyer*** *is associate research scientist, Dow Corning Corp., Midland, Mich.*

***Peter Hupfield*** *is senior development specialist, Dow Corning Ltd., U.K.*

***Eiji Kitaura*** *is application engineer, Dow Corning Toray Ltd., Japan.*

***Yasuo Itami*** *is chief researcher,* ***Tetsuya Masutani*** *is business development manager, and* ***Yasuhiro Nakai*** *is research chemist, Daikin Industries Ltd., Japan.*

Keeping surfaces on residential and commercial appliances free of contamination from fingerprints and dirt, as well as making them easier to clean, is an active field of research and technology development. Recent development in the hybridization of perfluoropolyether polymers modified with organofunctional silanes has created stay-clean and easy-to-clean surface properties. Creating an anti-fouling surface on appliances has many advantages, including a reduced need for cleaning, easier cleaning, and all-around improved aesthetics.

Hydrophobic and oleophobic properties obtained with polymeric coatings containing fluorine and silicon result in very high water and oil contact angles and good roll off properties. Resistance to rubbing and long term durability is achieved by the inclusion of alkoxy silane reactive components to the patented polymer composition. This coating technology can also be used on glass, metal, and plastics such as acrylic, PMMA, and polycarbonate. Cost effectiveness in the intended applications is achieved to ensure sustainability of this high performing material.

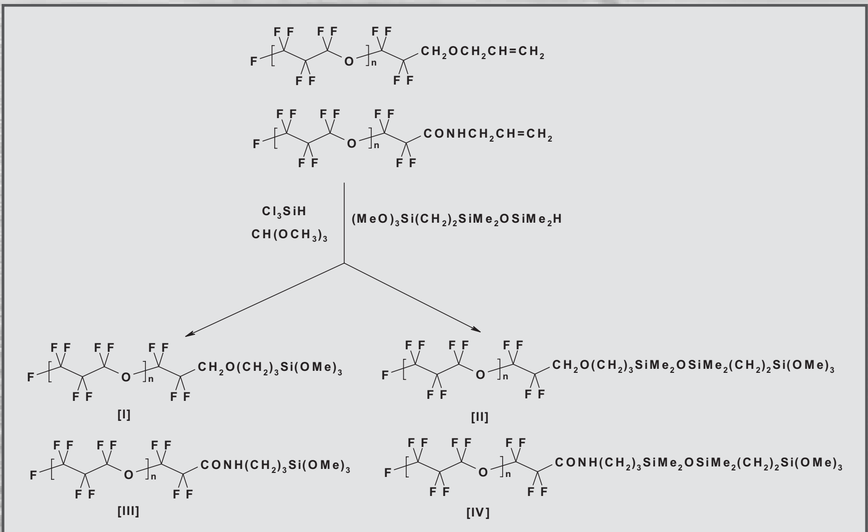


**Fig. 1.** Synthesis of alkoxysilyl perfluoropolyether adducts.

| Structure | I | II | III | IV |
|---|---|---|---|---|
| Contact angle for Water (deg) | 113.0 | 110.6 | 110.9 | 108.7 |
| Contact angle for n-Hexadecane (deg) | 67.1 | 64.6 | 69.9 | 67.0 |
| Sliding angle for Water (deg) | 3.2 | 4.7 | 5.2 | 8.8 |
| Sliding angle for n-Hexadecane (deg) | 3.1 | 4.3 | 3.8 | 6.0 |

**Table 1.** Contact angle data for treated glass surfaces.

Achieving oil and water repellency on surfaces is easily obtained with the use of fluoroalkyl modified silanes. While perfluoroalkyl modified silanes exhibit high static and advancing water and oil contact angles, their low receding contact angles mean the oil and water will not readily slide over the treated surface. The resulting effect of these characteristics yields a surface that is both easy to clean and stays clean longer. These modified perfluoropolyether silanes give the unique combination of high static and water contact angles along with low receding angles. The effects is long term surface modification that stays clean and is easy to clean. The influence of structure modification and impact on performance by application method is also important.

The goal of these improvements is twofold: to modify the surface of various substrates by applying a low surface tension layer or a dirt preventive layer and to establish a method for applying the coating material. A wide range of applications will benefit from these surface improvements including touch screen displays, glass surfaces, optical displays, reflecting mirrors, and ceramic fixtures. The surfaces of such products are routinely subjected to touch and are frequently stained with fingerprints, skin oil, sweat, and cosmetics. Once the surface is contaminated, the stains are not easily removed, or cleaning materials are needed. Obtaining a surface that is resistant to fouling and exhibits long term durability is challenging in applications such as kitchen appliances, handheld electronic devices, and automobile windows — all of which experience regular skin contact.

To solve such problems relating to oil and water repellency, various stain-proofing agents and coatings have been previously proposed. However, these coatings have insufficient stain resistance properties, especially on the most important stains such as fingerprints, skin oil, sweat, and cosmetics. Obtaining the desired performance of high water and oil contact angles and low sliding angles required chemical modification of a linear perfluoropolyether. Four alkoxysilyl perfluoropolyether adducts were synthesized as shown in ***Fig. 1.***

After synthesis of the material, a series of performance tests were done to assess its anti-staining performance. These silyl modified perfluoropolyethers [I] to [IV] were applied on glass test pieces. The anti-staining coatings were applied both by chemical vapor deposition (CVD) and dip coating in a dilute solution as described in ***Fig. 2.*** The impact of the alkoxysilyl structure of the modified perfluoropolyether was evaluated while keeping the polyether chain length constant (n=20) when using the dip coating application method. The surface properties of the treated glass substrates were compared using static contact angle and sliding angles of water and n-hexadecane. ***(See Table 1.)***

As the table shows, high water and oil (n-hexadecane) contact angles were observed in all cases. The simpler alkoxysilyl group in [I] and [III] gave slightly higher static contact angles and slightly lower sliding angles for both water and n-hexadecane when compared with [II] and [IV]. The organic linking group between the Si and the perfluoropolyether backbone also had a slight impact on the results with

## Application Methods

1. **Dip Coating Method**
   a. Clean surface with suitable solvent such as perfluorohexane or hexafluoroethane.
   b. Dip glass test piece in a 0.1 percent solution of the PFPE-silane chemical for 30 seconds.
   c. Dry at room temperature and 50 percent relative humidity for 8 hours (alternatively dry at 50 DegC and 50 percent relative humidity for 1 hour).
   d. Rinse substrates in a sonication bath with a suitable solvent.
   e. Dry for 1 hour at room temperature.

2. **Chemical Vapor Deposition (CVD) Method**
   a. Evaporate diluted PFPE-silane on a porous pellet and place in CVD chamber.
   b. Place substrate in CVD chamber.
   c. Evacuate chamber to a pressure of 1 x $10^{-5}$ Torr.
   d. Apply current, or mild temperature, to pellet.

**Fig. 2.** Summary of application methods for glass test pieces.

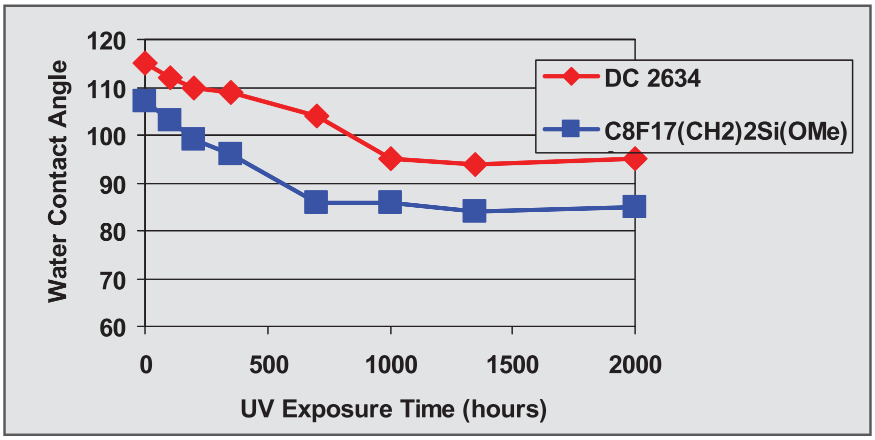


**Fig. 3.** Impact of UV irradiation on water contact angles.

| Structure | N – number of PFPE units | Application Method | Water Contact Angle (deg) | Water Sliding Angle (deg) |
|---|---|---|---|---|
| [I] | 10 | Dip Coating | 113.0 | 2.4 |
| [I] | 10 | CVD | 113.0 | 5.0 |
| [I] | 20 | Dip Coating | 113.0 | 3.2 |
| [I] | 20 | CVD | 109.0 | 15.0 |

**Table 2.** Impact of the application method on water contact angle.

| Structure | Dow Corning 2634 Coating | Common Material | Untreated Control |
|---|---|---|---|
| Contact angle for Water (deg) | 113.0 | 110.0 | <10 |
| Contact angle for n-Hexadecane (deg) | 67.1 | 48.0 | n/a |
| Sliding angle for Water (deg) | 3.2 | 38.0 | n/a |
| Sliding angle for n-Hexadecane (deg) | 3.1 | 24.0 | n/a |

**Table 3.** Comparative water and n-hexadecane contact and sliding angles.

the amide containing group [III/IV] giving lower water contact angles and high n-hexadecane contact angles. The results suggest that highly organized molecular arrangement of the alkoxysilyl perfluoropolyethers can be achieved on this surface. In all cases the degree of surface hysteresis is small, as shown by the very low sliding angles.

Interestingly, the application method was found to have the most significant impact on the contact angle. While the contact angle data was similar for the two application methods, the CVD application method gave significantly higher sliding angle for water, regardless of the molecular weight. ***(See Table 2.)*** This behavior would seem to suggest that components present in the products that can be deposited on the glass surface by dip coating are not deposited by the CVD method due to their higher boiling point. However, the n-hexadecane sliding angle is not affected by application method.

The product, called Dow Corning® 2634 Coating, was developed as a result of the alkoxysilyl perfluoropolyether synthesis. It was compared on a glass substrate to a common anti-staining material ($C8F_{17}(CH_2)_2Si(OMe)_3$) and a control sample with no surface treatment. Measurements of water and n-hexadecane contact angle and sliding angle gave the results shown in ***Table 3***.

Water and n-hexadecane contact and sliding angles are important after aging to ensure that the surface is resistant in the proposed application and will provide anti-stain performance over time. UV exposure and rubbing durability of the treated surface are methods commonly used to predict the effective life of the surface modification. The impact of UV exposure on water contact angle was determined using a Sunshine Weather-O-Meter and compared to the commercially known surface treatment known as $C_8F_{17}(CH_2)_2Si(OMe)_3$. ***(See Fig. 3)***. There was a significant improvement of UV exposure resistance of the alkoxysilyl perfluoropolyether, as measured by water contact angle over the test period.

The effect of rubbing durability is also a key parameter when considering the use of the akoxylsilyl perfluoropolyether coating on surfaces that are subjected to physical wear. Applications such as display screens, eyeglass lenses, camera lenses, portable electronic devices, and auto interiors require resistance to rubbing to ensure long term hydrophobic and oleophobic properties. Durability testing is typically carried out using a device that applies a constant pressure on a uniform surface area that cycles from side to side across the surface. The glass test pieces were subjected to a 500 g force applied by a cotton cloth fixed to an aluminum block. Water contact angle is measured after various intervals to obtain the relationship with rubbing cycles. A comparative method is typically needed to assess durability, as there are no absolute pass/fail values. ***(See Fig. 4.)***

As ***Fig. 4*** shows, there is a significant difference in the resistance to rubbing, as measured by water contact angle. After 5,000 cycles the commercial $C_8F_{17}(CH_2)_2Si(OMe)_3$ material has an 8 degree reduction in water contact angle, while the alkoxysilyl perfluoropolyether shows only a 1 degree change.

Ease of cleaning can also be improved by the new alkoxysilyl perfluoropolyether technology. A comparison of sliding and

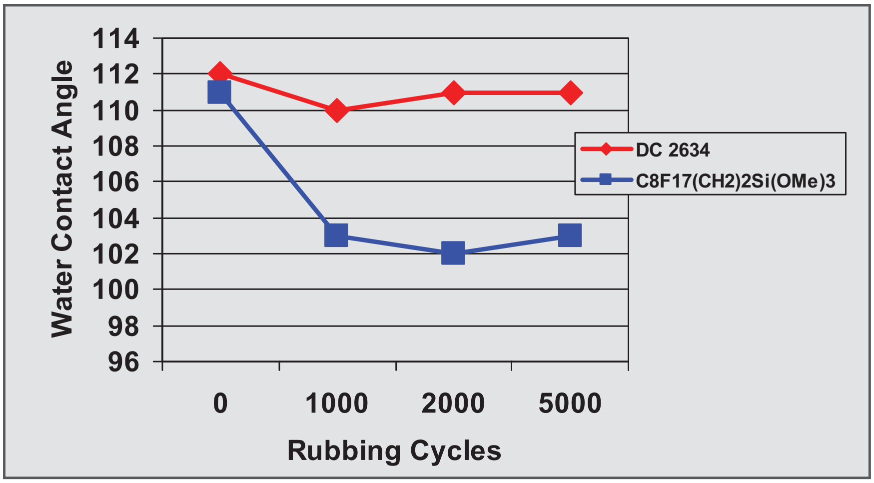


**Fig. 4.** Impact of rubbing durability on water contact angles.

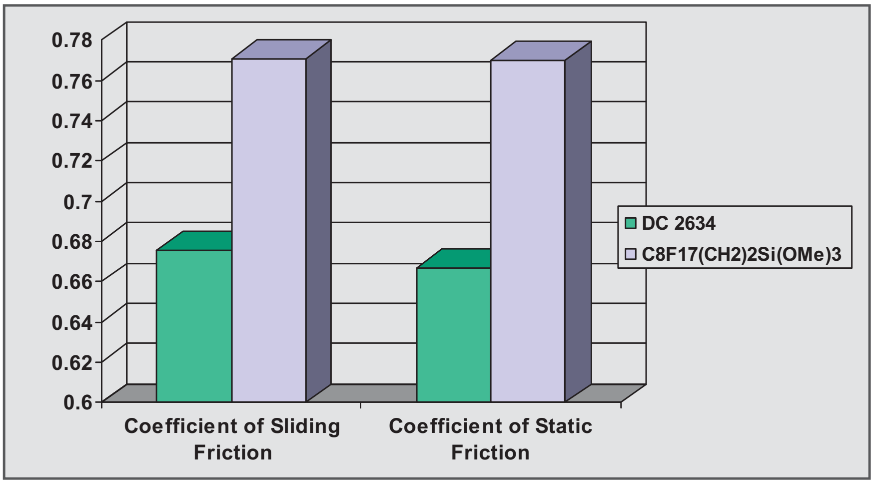


**Fig. 5.** Coefficient of sliding and static friction.

static coefficients of friction provides a comparative insight into the easy cleaning property. ***(See Fig. 5.)*** The lower sliding and static coefficients of friction predict that the alkoxysilyl perfluoropolyether will have both better stay clean and easy clean characteristics.

To summarize, a series of alkoxysilyl perfluoropolyethers have been synthesized, and the impact of perfluoropolyether molecular weight, application method, and coating durability (by UV exposure and rubbing) were evaluated. The impact of application method on performance shows a significant effect with the components studied. In all cases large static contact angles were observed in combination with very low sliding angles. The stay clean and easy clean performance characteristics are predicted to be superior for the alkoxysilyl perfluoropolythers as compared to the current $C_8F_{17}(CH_2)_2Si(OMe)_3$ coatings. The antistaining properties and durability performance of this new technology make it particularly useful in applications where touch by skin regularly occurs. Specific interest lies in applications such as kitchen appliances, automotive interiors, optical lenses and electronic displays. ■

For more information, email: *steve.block@dowcorning.com*