New Anti-Fingerprint Coatings

By
Mr. Steven Block,
Commercial Manager,
Dow Corning Corporation, U.S.A.

Dr. Peter Hupfield,
Senior Development Specialist,
Dow Corning Ltd., United Kingdom

Dr. Yasuo Itami,
Chief Researcher,
Daikin Industries Ltd., Japan

Mr. Eiji Kitaura,
Application Engineer,
Dow Corning Toray Ltd., Japan

Dr. Don Kleyer,
Associate Research Scientist,
Dow Corning Corporation, U.S.A

Dr. Tetsuya Masutani,
Business Development Manager,
Daikin Industries Ltd., Japan

Dr. Yasuhiro Nakai,
Research Chemist,
Daikin Industries Ltd., Japan

DOW CORNING

Dow Corning Silicone Solutions

As the pioneer of silicon-based technology, Dow Corning has been improving customers' products and profitability for more than 60 years. With a full range of product and application solutions, reliable supply, world-class manufacturing, and global reach, Dow Corning can meet virtually any silicone-related need through our total solution offering and technology leadership. For more information, call +1 989 496 6000. Dow Corning (www.dowcorning.com) provides performance-enhancing solutions to serve the diverse needs of more than 25,000 customers worldwide. A global leader in technology and innovation, offering more than 7,000 products and services, Dow Corning is equally owned by The Dow Chemical Company and Corning Incorporated. More than half of Dow Corning's annual sales are outside the United States.

Abstract

Keeping surfaces 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 advances in the hybridization of perfluoropolyether polymers modified with organofunctional silanes have led to unique stay-clean and easy-to-clean surface properties. Creating an anti-fouling surface on plastics has many advantages from a reduced need for cleaning to improved safety. 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. Weather resistance and durability are achieved by the inclusion of alkoxy silane-reactive components to the patented polymer composition. This coating technology can also be used on glass and metal in addition to many common plastics like acrylic, PMMA, and polycarbonate. Cost effectiveness in the intended applications is achieved to ensure sustainability of this high-performing material.

New Anti-Fingerprint Coatings

Mr. Steven Block*, Dow Corning Corporation, U.S.A.;
Dr. Peter Hupfield, Dow Corning Ltd., United Kingdom; Dr. Yasuo Itami, Daikin Industries Ltd., Japan;
Mr. Eiji Kitaura, Dow Corning Toray Ltd., Japan; Dr. Don Kleyer, Dow Corning Corporation, U.S.A;
Dr. Tetsuya Masutani, Daikin Industries Ltd., Japan; Dr. Yasuhiro Nakai, Daikin Industries Ltd., Japan

Introduction

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. Ultimately, modified perfluoropolyether silanes give high static and advancing water and oil contact angles as well as high receding contact angles resulting in a very low sliding angle. The influence of structure modification of the silane and the perfluoropolyether component is examined. Their impact on performance by application method is also discussed.

Results and Discussion

The goal of these improvements is a surface modified for use in forming a low-surface-tension layer or a dirt-preventive layer on the surface of various substrates and a method for applying the coating material. A wide range of uses will benefit from these surface improvements including applications such as optical members (e.g., anti-reflective films, optical filters, ophthalmic lenses, mirrors), electronic display screens (e.g., liquid crystal displays, CRT displays, plasma displays, projection TVs), consumer appliances, treated glass, and earthenware. Surfaces that are routinely subjected to touch are commonly stained with fingerprints, skin oil, sweat, and cosmetics when used. Once the surface is contaminated, the stains are not easily removed, or cleaning materials are needed. Dirt and fingerprints on surfaces that have an anti-reflective coating are very sensitive to surface contamination and cause not just an unpleasant aesthetic appearance but can also result in safety issues.

Obtaining a surface that is resistant to fouling and has long-term surface performance durability becomes another hurdle in challenging applications like automobile windows, handheld electronic devices, and kitchen appliances, which all have frequent skin contact.

To solve such problems relating to oil and water repellency, various stain-proofing agents have been previously proposed. One proposal was a stain-resistant anti-reflective coating obtained by surface treating a substrate with a perfluoroalkyl group containing compound. Another approach was a stain-resistant low-reflection plastic that has a polyfluoroalkyl group containing mono and disilane compounds and halogen, alkyl, or alkoxysilane compounds as a surface-modification coating. A third option that has been proposed is forming a copolymer of perfluoroalkyl (meth)acrylate and alkoxy silane group containing monomer on an optical thin film mainly consisting of silicon dioxide. 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 Figure 1.

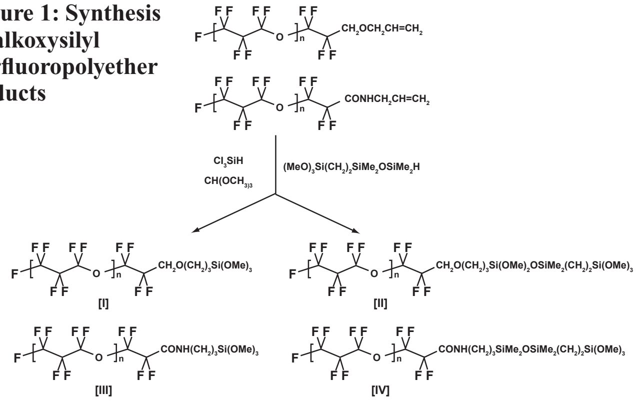


Figure 1: Synthesis of alkoxysilyl perfluoropolyether adducts

After synthesis, a series of performance tests was done to assess anti-staining performance. These silyl-modified perfluoropolyethers [I] to [IV] were applied on glass test pieces. The anti-staining coatings were applied both by CVD (chemical vapor deposition) and dip coating in a dilute solution, as described in Figure 2.

Figure 2: Summary of application methods for glass test pieces

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% solution of the PFPE-silane chemical for 30 seconds
    c. Dry at room temperature and 50% relative humidity for 8 hours (alternatively dry at 50ºC and 50% relative humidity for 1 hour)
    d. Rinse substrates in a perfluorohexane sonication bath
    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 glass test piece in CVD chamber
    c. Evacuate chamber to a pressure of E-5 Torr
    d. Apply current to pellet

* Corresponding author

The impact of the alkoxysilyl structure on the modified perfluoropolyether was evaluated while keeping the polyether chain length constant (n = 20) 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 (Table 1).

As can be seen in Table 1, 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 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.

The effect of perfluoropolyether molecular weight was evaluated by adjusting the degree of polymerization of the polyether backbone (n) of structure [I]. Water and n-hexadecane contact and sliding angles are summarized in Table 2 using the dip coating application method.

No clear trend was seen for the water and n-hexadecane contact angles although the data did suggest that as the perfluoropolyether molecular weight increased, the sliding angle for water also increased. For the n-hexadecane sliding angle there was no observable relationship with polymer molecular weight.

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, as shown in Table 3. 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 recently developed as a result of the alkoxysilyl perfluoropolyether synthesis, *Dow Corning*® 2604 Coating, was compared on a glass substrate to a common anti-staining material ($C_8F_{17}(CH_2)_2Si(OMe)_3$) and a control sample with no surface treatment. Measurements of water and n-hexadecane contact angle and sliding angle gave the results in Table 4.

Water and n-hexadecane contact and sliding angles are important after aging to ensure the surface is resistant to the elements of a given application and will provide anti-stain performance over time.

Table 1: Contact Angle Data for Treated Glass Surfaces

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 2: The Impact of Perfluoropolyether Molecular Weight

	I (n = 10)	I (n = 20)	I (n = 30)
Contact Angle for Water (deg)	113.0	113.0	111.7
Contact Angle for n-Hexadecane (deg)	68.6	67.1	67.4
Sliding Angle for Water (deg)	2.4	3.2	6.4
Sliding Angle for n-Hexadecane (deg)	5.0	3.1	6.7

Table 3: Impact of the Application Method on Water Contact Angle

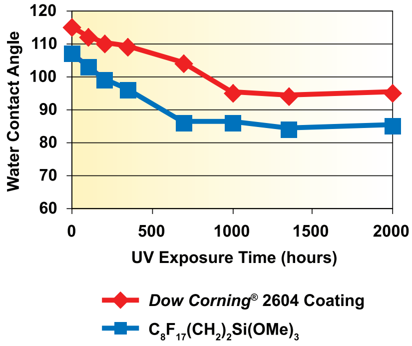
Structure	N – Number of PFPE units	Application Method	Water Contact Angle (deg)	Water Sliding Angle (deg)
[I]	10	Dip Coating	113.0	2.4
[I]	10	CVD	113.0	5.0
[I]	20	Dip Coating	113.0	3.2
[I]	20	CVD	109.0	15.0

Table 4: Comparative Water and n-Hexadecane Contact and Sliding Angles

	Dow Corning 2604 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

Using 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 $C_8F_{17}(CH_2)_2Si(OMe)_3$ (Figure 3).

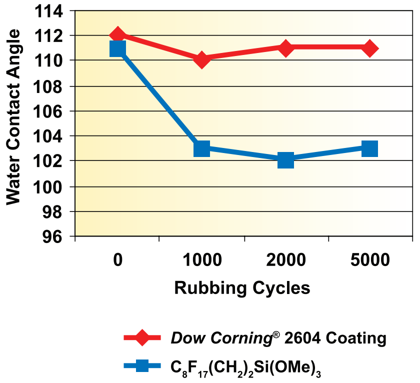
Figure 3: Impact of UV Irradiation on Water Contact Angles



There was a significant improvement of UV irradiation 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 subjected to physical wear. Applications such as ophthalmic 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-gram 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 (Figure 4).

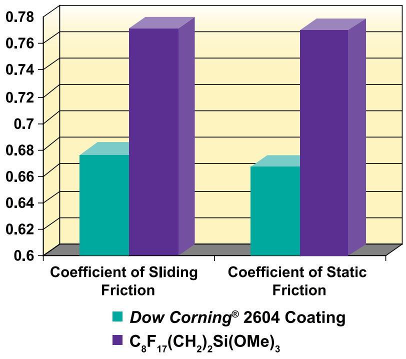
Figure 4: Impact of Rubbing Durability on Water Contact Angles



As can be seen from Figure 4, there is a significant difference in the resistance to rubbing as measured by water contact angle. After 5000 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. The decrease in contact angle of the $C_8F_{17}(CH_2)_2Si(OMe)_3$ material takes effect before 1000 rubbing cycles, and is then constant at 103 degrees for the balance of the test period.

Ease of cleaning can also be improved by the new alkoxysilyl perfluoropolyether technology. A comparison of sliding and static coefficients of friction provides a comparative insight into the easy-to-clean property (Figure 5). The lower sliding and static coefficients of friction predict that the alkoxysilyl perfluoropolyether will have both better stay-clean and easy-to-clean characteristics.

Figure 5: Coefficient of Sliding and Static Friction



Conclusion

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

How to Contact Us

Dow Corning has sales offices, manufacturing sites, and science and technology laboratories around the globe. Telephone numbers of locations near you are available on the World Wide Web at **www.dowcorning.com**, or by calling one of our primary locations listed below.

Your Global Connection

Asia
Dow Corning Toray Co. Ltd. – Japan
Tel: +81 3 3287 8300

Dow Corning Korea Ltd.
Tel: +82 2 551 7600

Dow Corning (Shanghai) Co. Ltd.
Tel: +86 21 6288 2626

Dow Corning Singapore Pte. Ltd.
Tel: +65 6253 6611

Australia & New Zealand
Dow Corning Australia Pty. Ltd.
Tel: +61 1300 360 732

Europe
Dow Corning Europe – Belgium
Tel: +32 64 88 80 00

Dow Corning Ltd. – UK
Tel: +44 1676 528 000

North America
Dow Corning Corporation – USA
World Headquarters
Tel: +1 989 496 7881 (Customer Service)
Tel: +1 989 496 4000 (Corporate Center)

South America
Dow Corning do Brasil Ltda.
Tel: +55 19 3887 9797

Dow Corning Technical Information Centers

The Americas
+1 989 496 6000, or
+1 800 248 2481 (Toll-Free from the USA)

Asia
+86 21 3774 7110

Europe
English +49 (0)611 237 778
French +49 (0)611 237 773
German +49 (0)611 237 779

We help you invent the future.™

www.dowcorning.com

Printed in USA AGP9317 Form No. 26-1625-01