Grime prevention

It can be difficult to formulate coatings which are able to retain easy-clean or stay-clean properties after abrasion or other damage. Three different approaches to creating coatings of this type are described. All make use of the synergy between the oleophobicity of fluoropolymers and the resistance to wear provided by silicone-based materials.

Hybrid coatings facilitate easy removal of contamination
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Recent developments in the field of fluorosilicone hybrid coatings and additives have successfully bridged the gap between demanding environmental and end-use requirements.

Fluorosilane anti-fingerprint coatings, hydroxilation-cure tetrafluoroethylene easy-to-clean coatings and fluorosilicone UV-cure resin coatings are some examples of these new anti-fouling surface technologies.

The synergistic effect of combining fluorine and silicone chemistry results in protective coatings with excellent chemical resistance, weatherability, abrasion resistance and thermal stability.

Many differing technical approaches can be taken to achieve an anti-fouling surface. Three technologies that have the capability to achieve this important property will be discussed and compared below.

Contact angles indicate resistance to dirt pick-up

Easy-to-clean or stay-clean properties can be measured indirectly by looking at the contact angle of a fluid on a rigid surface in both static and dynamic states. Consider a drop of liquid on a flat surface.

If the droplet is highly attracted to the surface it will tend to spread out and try to completely wet the surface. In this case there is a very small contact angle and the surface is defined as being hydrophilic or oleophilic. Hydrophilic or oleophilic surfaces have a contact angle of less than 30 degrees. Conversely, a hydrophobic or oleophobic surface causes the liquid drop to bead up, giving a contact angle of greater than 90 degrees. The higher the contact angle the more the surface seeks to repel the liquid.

Stay-clean surfaces have higher liquid contact angles, and the higher the contact angle the better the stay-clean performance. The contact angle provides information directly on the interaction energy between the surface and the liquid and therefore on the surface aesthetics. Since all of the surfaces under consideration will be subjected to some type of rubbing or abrasion, a critical aspect of a hydrophobic coating is retaining the initial performance over a long period of time in actual service. Obtaining a very high initial contact angle and/or a low sliding angle is much less difficult than achieving the targeted contact angle after durability testing.

Hysteresis values are correlated with cleanability

Hysteresis is the difference between the advancing and receding contact angles. Measuring the hysteresis of a liquid drop gives an indirect prediction of easy-to-clean performance. This test is performed by placing a fixed volume of liquid on a solid surface. Once this drop is resting on the surface, the receding angle is obtained when liquid is removed from the drop without changing the surface-to-liquid contact area. At the point in time when the surface-to-liquid interface area changes, the receding angle is determined.

When the liquid is added to the drop on a rigid surface the advancing angle is obtained at the moment just as the interfacial area increases. The difference between the advancing and receding angles is the contact angle hysteresis (Table 1). The lower the hysteresis, the easier the surface is to clean.

Consider a real application. For example, take a glass surface on the front of a kitchen oven. When dirt or oil contaminates the chemically treated surface, which is meant to give a pleasant look to the kitchen, a low hysteresis means the contaminant can be wiped off very easily without leaving a smudge or haze behind.

Oleophobicity and hydrophobicity are assessed by a relative comparison of contact angle with the higher contact angle giving a better stay-clean surface. Today there are no standard tests (ASTM, DIN, JIS, etc.) for anti-fingerprint performance so it is common and accepted practice to use these predictive measures to suggest the level of anti-fouling obtained.

UV-curing hardcoat combines advanced technologies

The protection of surfaces that are prone to abrasion and staining represents a significant technical challenge. Developing a hardcoat technology that provides excellent abrasion resistance, UV stability, weatherability, dirt resistance and anti-fouling is possible by combining a silicone hardcoat with a functional perfluoropolyether (PFPE) polymer.

PFPE surface modification lowers the surface energy of a treated substrate but it does not substantially improve the abrasion resistance. Conversely, silicone hardcoat technologies significantly improve the abrasion resistance but do not positively affect anti-fouling properties. A hybrid approach is possible, in order to obtain a synergistic combination of silicone and fluorine. The net result is a technology that is capable of finding a route to the combined strengths of each type of chemistry. UV cure has been incorporated as the cure mechanism to support the industry’s needs for improved production and energy conservation.

Environmental sustainability is also evaluated alongside product performance to ensure that the best long-term solution results. UV cure technology is now a well known method of both improving productivity via its fast cure and
Four alkoxysilyl perfluoropolyether adducts were synthesised as shown in Figure 1. After synthesis, performance tests were carried out to assess stay-clean and easy-to-clean performance. These silyl-modified perfluoropolyethers [I] to [IV] were applied on glass test pieces and evaluated for contact and sliding angle for water and n-hexadecane (Table 3).

These new hybrid polymers exhibit the oleophobicity of fluorine and the hydrophobicity and durability of silicone. Improved durability over current chemical treatments is obtained by the use of a monofunctional terminal alkoxy silane modification to the linear PFPE polymer. The alkoxy silane reactive end will covalently bond to the surface via hydrolysis and condensation reactions to either hydroxyl- or silanol-containing compounds. This covalent bond gives the durability needed in touch-screen display applications and eyewear.

Meanwhile the long flexible perfluoropolyether tails cover the surface in what can be imagined as a hair-like structure. These "hairs" will naturally reach an equilibrium condition relative to each other resulting in the lowest surface energy. The resistance to wear by rubbing makes the surface stay cleaner for a longer period of time, which is a major improvement of this new technology. The easy-to-clean surface comes from this very low surface energy of the alkoxy silane functional PFPE polymer. That means the need for cleaning chemicals to remove oil, water and dirt is minimised, and the aesthetics are improved. A comparison of effects on surface cleanliness is shown in Figure 2.

Anti-stain and anti-graffiti surfaces

Although a wide range of fluoropolymer coatings exists today that provides substantial performance benefits to the end user, many of these coatings are limited by the processing conditions required to form a film on a substrate. The introduction of reactive functional groups in tetrafluoroethylene (TFE) derived copolymers enables the fluoropolymer to crosslink once deposited as a film on the surface of a substrate.

As can be seen from Table 4, the TFE-cured coating provides excellent stain resistance and easy-clean properties across a range of common staining agents, with improved performance in some areas when compared with the acrylic-urethane reference coating. The idea of developing a fluorine- and silicone-containing hybrid coating was investigated for a number of reasons. Silicones provide excellent release due to the flexible nature of the CH3(CH3)2SiO)xCH3 siloxane polymer backbone (low Tg). The poor compatibility and solubility of silicone polymers with fluoropolymers may provide a mechanism for surface segregation and enrichment.

The main area of focus was the use of organofunctional siloxanes as reactive surface modification agents to yield the hybrid polymers. The effect of having no reactive functionality on the siloxane was also determined. Figure 3 illustrates the concept behind the siloxane and fluoropolymer hybrid.

Energy reduction is environmentally significant

Among the most obvious, and measurable, benefits to the balance of business and the environment are ways to reduce energy usage. Most coating technologies need energy to cure. Heat cure is a common curing method for urethanes, acrylic, fluorine and silicones. Finding ways to reduce the curing temperature or the time to cure will save energy. For example, in a coil coating operation, heat is required to cure these coatings; however, the coil itself heats up, absorbing more energy and therefore costing more to operate the coating line.

To understand the effect on the overall heat requirements, a simple example will highlight the potential impact. In 2006 approximately 6.7 million tons of steel was coated globally in coil coating processes. If 8 % of the coil is coated with the new UV-cure hybrid technology it will reduce the energy demand by 4.74 x 1016 Joules/year, or 4.5 x 1013 MCF of natural gas.

This means the reduction in natural gas combustion would yield a corresponding reduction of 2.2 million metric tonnes of CO2 and eventually result in 2.9 million fewer trees needed to convert this CO2 back to oxygen. The energy savings from using the UV-cure coating technology in this example would heat approximately 180,000 houses in the U.S.A. each year.

Chemical strategies for reducing fingerprinting

Various fingerprint-reducing agents have been previously proposed to solve problems relating to oil and water repellency. 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 di-silane 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 an alkoxysilane 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 requires chemical modification of a linear perfluoropolyether (PFPE).

Hybrid polymer has excellent adhesion and durability

Reducing energy costs by the elimination of curing and post curing ovens, which often operate at 230 °C. The new UV-cure fluorosilicone hybrid hardcoat technology gives the benefits of cost savings from lower energy demands as well as improved hydrophobic, oleophobic and easy-to-clean properties (see Table 2). While the initial contact angle data is very useful and makes a very good initial comparison, the performance of the coating surface over time is really the critical, and often differentiating, factor.

A variety of tests are used to measure the effect of abrasion on the ability to maintain the early stay-clean and easy-to-clean properties. In the case of this technology, a "Taber Abraser" and abrasion by steel wool have been used to measure the impact on water and oil repellency.
full removal on dry wiping using the same cure conditions and evaluation conditions as previously described. Surprisingly, the non-reactive organofunctional siloxane (NROS) did not provide the same performance benefit although some visual improvement was observed over the standard TFE coating. There was also an observed increase in water and oil repellency with the hybrid material, indicating some synergistic effect as seen by the contact angles to water and hexadecane (Table 5).

Combined strength keeps dirt at bay
Protective coatings using hybrid materials derived from fluoropolymers and reactive siloxanes and silanes provide excellent stain resistance and easy-clean properties. Three new generations of hydrophobic and oleophobic fluorosilicone hybrid surface modifiers have been developed to meet emerging unmet needs. By combining fluorine and silicone chemistries, highly effective solutions are now possible in a wide range of applications.

Results at a glance
While it is not difficult to produce an extremely hydrophobic coating that will resist dirt pickup, it is harder to retain these properties after abrasion or other damage. Three different approaches to solving this problem are described. A UV curable fluorosilicone hardcoat was produced which was shown to retain its easy-clean properties very effectively after abrasion testing. The use of UV curing significantly reduces energy consumption and thus enhances sustainability. A series of four hybrid alkoxysilyl/perfluoropolyether adducts was prepared, and this combination was able to provide very high contact angles to both water and n-hexadecane. A tetrafluoroethylene/isocyanate copolymer was prepared and tested in combination with either a reactive organofunctional siloxane or a non-reactive one. Only the reactive type was found to provide a substantial improvement in staining resistance.

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Figure 1: Synthesis of alkoxy silyl perfluoropolyether adducts
Figure 2: Visual comparison of the degree of finger marking on different surfaces

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<th>Fingerprint before wiping</th>
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<td>C₈F₁₇ silane</td>
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<td>Untreated</td>
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Figure 3: Concept behind the siloxane and fluoropolymer hybrid