



Effective Sol-Gel and Related Smart and Functional Coatings

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Introduction

Sol-gel materials include a wide range of inorganic and hybrid organic/inorganic compounds which are prepared by a common synthesis method described by sol-gel-technology. They are made from metal alkoxide precursors that undergo transformation from singular molecules through sols, which progress to gels and then to strong solid materials. Since the precursors are liquid in nature, sol-gels are ideal materials to be used in coatings for standard, and especially complex shapes. An essential element of the sol-gel process is the hydrolysis and consequent polymerization of the metal-oxide backbone, which is of key importance to form coatings. In fact, due to the large versatility in choice of precursors, sol-gel-technology may be utilized to formulate coatings with specific functionalities such as easy-to-clean, superhydrophobic, superhydrophilic or self-cleaning; either as stand-alone attributes, or as combinations.

Easy-to-clean coatings mechanism and performance

Although there is no exact definition of easy-to-clean coatings, the function of easy to clean, often abbreviated as E2C may be indicated as such, by several tests:

- Contact Angle (water and hexadecane), ISO 19403-2
- Anti-graffiti, NF 31-112
- Dirt pickup

These tests all rely on the repulsion of the coated surface to liquids and soil, prompted by the hydrophobicity and oleophobicity of the surface chemistry. In fact, the hydrophobicity and oleophobicity of the surface can be precisely determined by measuring the contact angle. It is generally accepted that a hydrophobic surface has a contact angle to water of $>90^\circ$, a very hydrophobic surface of greater than 110° , and with a superhydrophobic surface the contact angle exceeds 140° . The first two situations may be achieved by chemistry, but in the latter case, the surface morphology plays an important role which will be discussed later.

The Young's state determines the surface energy and maximum contact angle that can be achieved for very hydrophobic flat surfaces. Typically, in practice maximum contact angles of $115-120^\circ$ are reached (Figure 1).

Being fully dependent on the chemistry, such surfaces typically are built from silicone and fluorocarbon groups. As surface energy decreases with the order: $-\text{CH}_3 > \text{SiO}_2 > -\text{CF}_3$, the hydrophobicity of a coating built upon these groups increases inversely proportional to the decrease in surface energy.

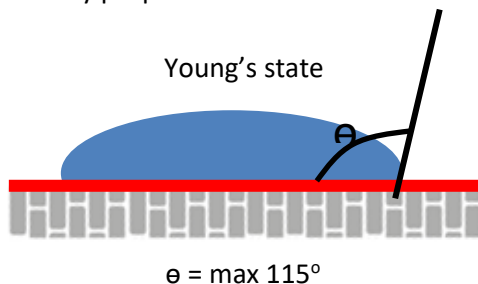


Figure 1. Max contact angle flat surfaces



Since graffiti sprays are often solvent based, oleophobicity is also important to such coatings. Compounds showing both hydrophobic and oleophobic behaviour are called omniphobic. A standard surface or coating typically possesses little oleophobicity, which is determined using hexadecane (HD) instead of water while measuring the contact angle. Contact angles to HD are normally zero for metal, plastics and concrete, as well as for polyurethane, acrylic, alkyd and epoxy coatings. Well-known chemical groups to increase oleophobicity are fluorine-based compounds. PTFE (Polytetrafluoroethylene) for example shows contact angles to HD of around 40° while perfluorinated compounds may reach 65° which is about the maximum to be achieved with flat non-structured coatings. The values are reciprocal to the surface energy which may decrease below 18 dynes per cm for perfluorinated compounds.

The chemical moiety responsible for lowering surface energies is the C-F bond and the surface energy decreases with the saturation of the alkyl chain with C-F bonds; for example: $-\text{CH}_2-\text{CH}_2\text{F}$ $-\text{CH}_2-\text{CF}_3$ $-\text{CF}_2-\text{CF}_3$. As soon as all the hydrogens are replaced by fluorine it is called a perfluorinated moiety.

While being excellent omniphobic non-stick compounds, fluorine compounds adhere poorly to substrates, regardless of type (metal, plastics, glass). This we experience for example, while trying to adhere PTFE (fluorine-based polymer) to metal valve fittings to create water taps that are water tight. This behaviour in fact continues to worsen, when the fluorine content in the system increases. In coatings this is seen by delamination failures as shown Figure 2.



Figure 2. Example delamination fluorine based coating on metal

A method to prevent the adhesion failure is to build a coating system comprised of a surface adhering side and an omniphobic-repellent air interface side (topside). Organometallic systems based on metal alkoxides and omniphobic repellent moieties as depicted in Figure 3 demonstrate such behaviour.

The metal alkoxides serve in fact 4 functions:

- Bonding element between omniphobic groups
- Adhesion of coating to substrate with covalent bonds
- Increase the hardness of a coating while being preceramic in nature
- Act as crosslinkers

An example of the preparation of such a hybrid system is shown in below reaction scheme.

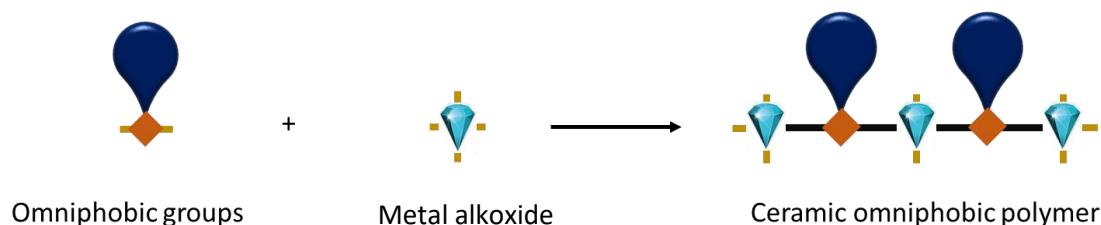


Figure 3. Scheme of omniphobic polymer

The ceramic omniphobic polymer crosslinks to a high density planar thin coating in the presence of water vapour from the air (Figure 4). Moreover, during the curing process covalent bonds with the substrate are formed.

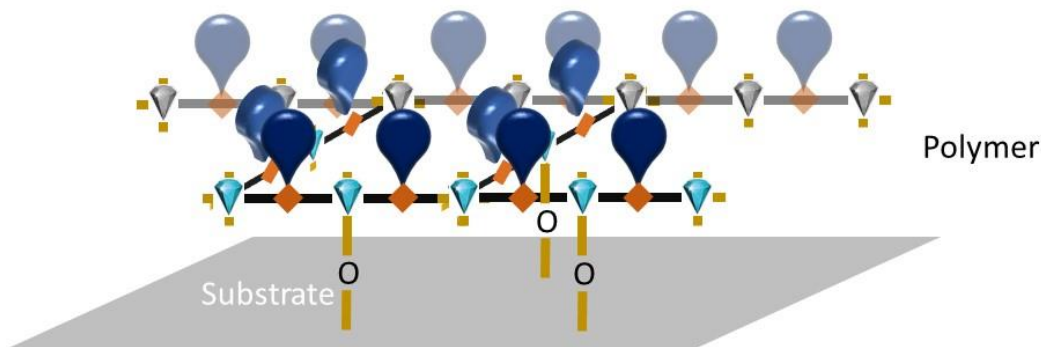


Figure 4. Formation of highly crosslinked coating network with covalent bonding to the substrate

Contact angles

In the experiment of measuring the contact angle to water, a droplet of water is placed on the coated surface (Figure 5) and subsequently the angle the droplet makes with surface is measured (Figure 6). The measurement is obtained using visual data from a camera and the contact angle is obtained by computer analysis.



Figure 5.

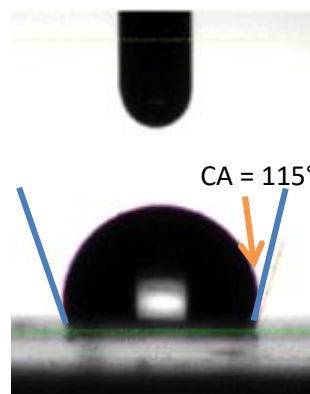


Figure 6.

For 2 ceramic omniphobic polymers we were able to measure a contact angle higher than 100°.

	E. 143	E. AG-2
Contact Angle °(water)	115	110
Contact Angle °(HD)	57	50

Dirt pickup Test

In the dirt pickup test, a 1% carbon black dispersion is poured onto the coated substrate and allowed to dry for 24hrs under ambient conditions. After drying, the surface is rinsed with a water hose. To quantify this cleanability, the total colour change ΔE (ASTM D2244-16) before exposure to carbon black and after cleaning was determined. The colour change ΔE can be classified as follows:

$\Delta E < 5 \rightarrow$ no significant visual change.

$\Delta E > 5 \rightarrow$ visual appearance is modified.

Two tests on aluminum plates were run with a result of $\Delta E < 5$. It means that the coatings are not substantially affected by spraying a carbon black dispersion and are considered easy to clean.



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	Test 1	Test 2
ΔE (E. AG-2 coated Alu)	3.6	3.2

Anti-Graffiti

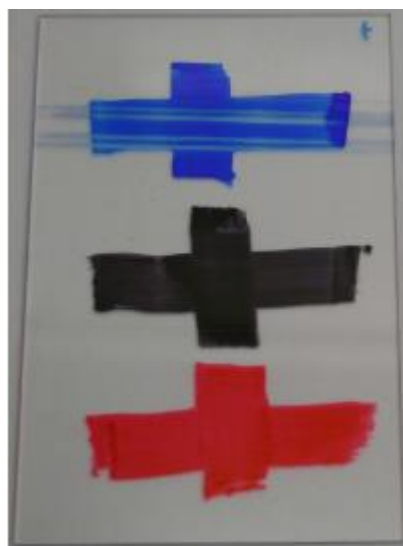
The anti-graffiti test is determined while following the normative test NF F31-112. It consists of the application of (a) a cross mark with Edding 850 markers on the substrates and (b) examination to determine if the graffiti is cleanable. Three colours (black, red, blue) are applied on substrates coated and dried during 48h before being tested.

To test the cleanability, 20 wiping cycles with a cotton cloth, using an Erichsen 494 MC machine, are completed. After 20 cycles, the samples are examined. The classification of the results is recorded following the cleaning conditions:

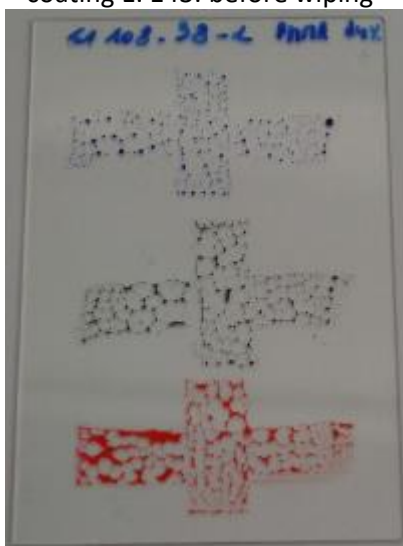
- G0 Cleanable with water or dry cloth
- G1 Cleanable with a product without safety labelling
- G2 Cleanable with a product labelled Xi and/or easily flammable
- G3 Cleanable with a product labelled Xn and/or easily corrosive

The result with E. 143 coated PMMA was G0 and thus considered easy to clean. In Figure 7 the test and result are shown.

PMMA no coating (after wiping)



PMMA coated with anti-graffiti coating E. 143: before wiping



PMMA coated with anti-graffiti coating E. 143: after G0 wipe



Figure 7. NF 31-112 Anti-graffiti test

A real-world test with graffiti spray paint has been evaluated on a metal plate. Before the pink coating was sprayed (Figure 8) the right side of the plate was pre-coated with a hybrid organic/inorganic (E.143) anti-graffiti paint. It can be seen from the picture that the graffiti wets out fully on the uncoated left side but is not able to sufficiently wet the surface on the right side. The precoated surface has a surface energy which is too low for the graffiti to properly wet out.



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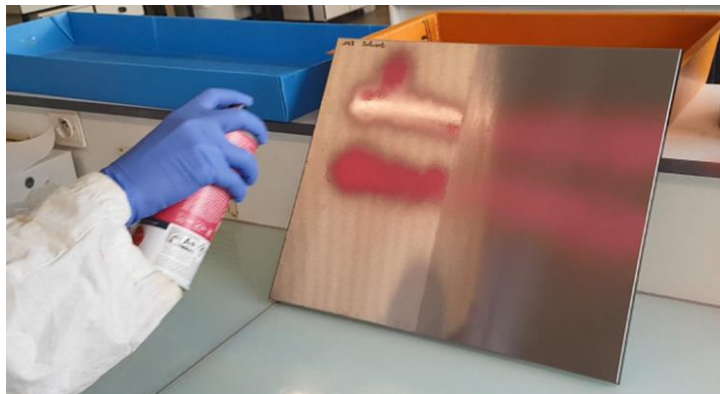


Figure 8. Graffiti test: left bare metal, right anti-graffiti pre-coated plate (E. 143)

The graffiti was dried for 24 hours to determine if the graffiti could be scrubbed off with a cloth according to the G0 classification from NF 31-112 anti-graffiti test. The result is shown in Figure 9 in which it is shown that the anti-graffiti pre-coated part, on the right is easily cleaned whereas the graffiti strongly adhered to the non pre-coated left side which was consequently uncleanable.

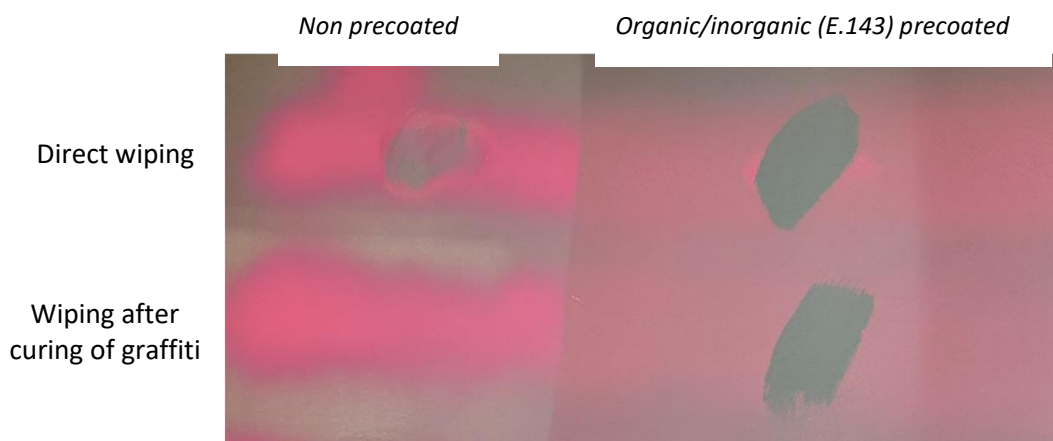


Figure 9. Wiping down of graffiti paint.

Such behaviour is of extreme importance to create anti-graffiti walls, trains, bridges and architectural structures in the public domain. First, taggers are discouraged by the difficult wetting of the graffiti on the coated surface; second, the graffiti is easily removed afterwards without the requirement of harsh cleaners or abrasives.

Superhydrophobic coatings

In the second paragraph we noted the limitations of flat coatings to create superhydrophobicity. With the aid of low surface energy groups flat surfaces are limited to a contact angle to water of 115-120°. A method to impart superhydrophobicity to flat surfaces is by introducing surface roughness in a very controlled way. Already in 1944, A. Cassie and S. Baxterⁱⁱ introduced the explanation and equation why roughened surfaces amplify a surface’s hydrophobicity with the following equation:

$$\cos \theta(\text{new}) = r \cos \theta(\text{old})$$

In which θ represents the contact angle of the surface in flat conditions and r the surface roughness.



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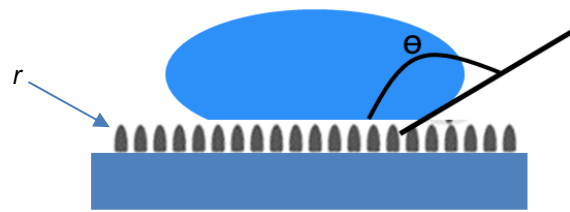


Figure 10. Nano structure of superhydrophobic coating and contact angle

In Figure 10 such a roughened surface with nanomorphology is depicted. If the chemistry results in a flat surface with $\theta=115^\circ$ ($=\theta(\text{old})$), the described factor r should be beyond 1.8 to reach a superhydrophobic surface generally described as a contact angle to water of 140° ($\theta(\text{new})$), as: $\theta(\text{new}) = \text{acos}(\theta(\text{old}) * 1.8)$.

To create a roughened surface, we need a sophisticated and controlled process in which we build the morphology from bottom up. Such process control can be provided by sol-gel chemistry.

Figure 11 explains the process of sol-gel-technology to create superhydrophobicity. From metal oxide precursors with valence states of 3 to 6, it is possible to create 3-dimensional sphere-shaped particles with hydrophobic shells. When such particle lands on a surface it is capable to organise itself to create a defined roughened surface with nanomorphology. One can prove this by capturing a SEM (scanning electron microscopic) picture of the coating, with the spheres clearly visible (right picture in Figure 11). Such surface morphology will give water contact angles of greater the 140° called super hydrophobicity in jargon as already shown in Figure 10.

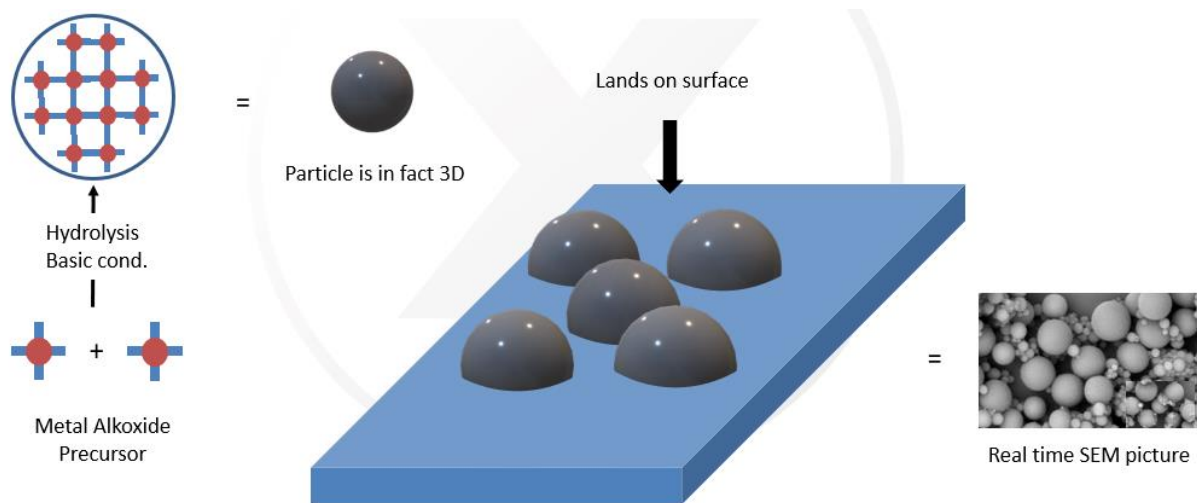


Figure 11. Animation of development of superhydrophobic coating

Various industries are looking for innovative superhydrophobic coatings to create extremely water repellent, stain free, icephobic, self-cleaning surfaces or to produce water tight electronics and equipment.

Nanostructured coatings for glass

With Axcentive's EXOCOAT technology it is possible to eliminate rain from windscreens and to create a clear view, improving drivers' comfort and safety in wet weather conditions. This approach is also proposed for glass used on solar panels and skyscrapers.



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In Figure 12 and Figure 13 the effect of such nanostructure is shown on glass. Due to the creation of the nanostructured coating: E. Clearview, the surface energy of the surface drops dramatically and water is repelled completely leaving no traces.

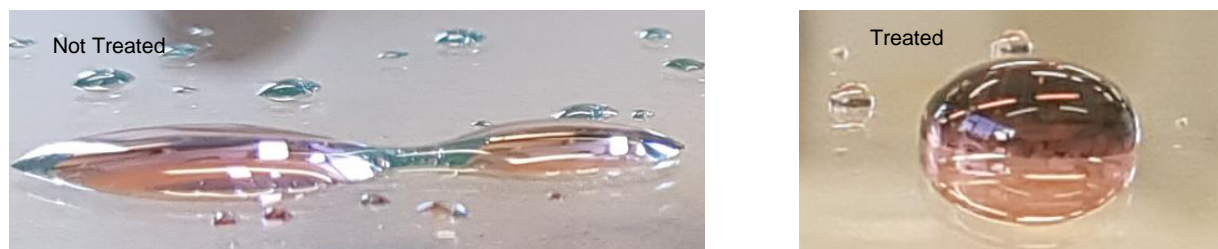


Figure 12. Non-treated vs E. CV treated glass; low vs high contact angle due to nanostructure



Figure 13. Effect on car windscreen of high contact angle coating (E. CV), full water repellence. Tilt angle of windscreen 25°.

Superhydrophobic mineral substrates

Superhydrophobic coatings may be used on walls to generate liquid spill-resistant walls. Application of self-organizing nanospheres turns a mineral substrate into a superhydrophobic surface. In Figure 14 a gypsum panel is shown for which the right side is not treated and hence is very hydrophilic absorbing quickly any soil, dirt or water. On the left side the same gypsum was treated with superhydrophobic spheres (E. SH) to generate a nanostructured coating to which the liquid dirt does not adhere. It immediately runs down the plate.



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Figure 14. Superhydrophobic gypsum, left side treated with E. SH, right side not treated

Self-cleaning effect by superhydrophobic coatings

Superhydrophobic layers can turn substrates into self-cleaning surfaces. In Figure 15 the concept of self-cleaning is shown on the top side showing the animation. Dirt typically does not ingress into these nanosphere based coatings and as soon as water impacts the surface it incorporates or dissolves the dirt and the slurried dirt rolls down as a snowball progressing down a hill. The minimal inclination of surfaces in order to show the self-cleaning effect is typically 10°. This test method is also known as the “roll-off test”, the minimum angle that a droplet of clean or dirty water rolls off down the surface.

On the lower side of Figure 15, a gypsum panel coated with the superhydrophobic nanospheres was smeared with solid dirt (on the left), then rinsed with water (middle 2 pictures). It is shown that when smearing the plate with dirt, simple rinsing with a bucket of water leaves the gypsum completely clean (right pictures).

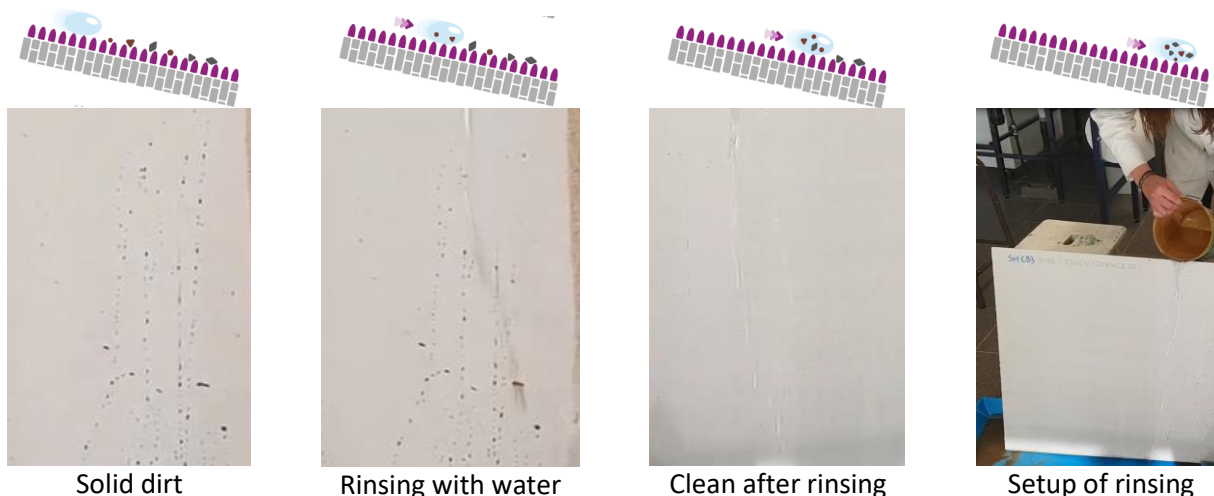


Figure 15. Concept of self-cleaning through a superhydrophobic coating

Printed circuit board protection

An excellent case for superhydrophobic nanospheres is their use as conformal coatings for printed circuit boards (PCB). According to market studiesⁱⁱⁱ waterproofing of electronics is one of the main concerns of (consumer) electronics manufacturers, since in connected buildings and houses there is more and more equipment placed in harsh wet conditions prone to corrode and oxidize.



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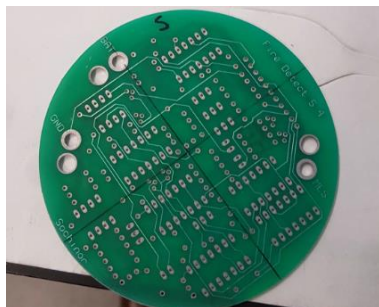


Figure 16. Superhydrophobic E. AQ Seal coated PCB

Moreover, printed circuit boards as for example used in phones and wearables (heart rate monitors, watches) are prone to spilled liquids and water as well as salt from sweat which may create short circuits.

Most major handheld electronics manufacturers have made their devices water resistant in the last few years. One method to achieve this is by making devices physically impenetrable for liquids.

However, superhydrophobic nanospheres can perform the same function for a fraction of the cost.

In the case of the technology used in E. AQ Seal, complex plasma or vapor disposition techniques can be avoided, as this can be done by simple spray and drying with hot air or even at room temperature. A summary of the technology is described in below table.

Product designation	E. AQ SEAL
Type	Sol-gel based nanospheres to create superhydrophobic coatings
Application	Spray
DFT	Monolayer
Curing conditions	Hot air, 15 min or room temperature for 1 hour
Benefits	Superhydrophobic, $CA_{H_2O} = 140$ Oleophobic, $CA_{HD} = 120$

ⁱ Young, T.; *Philosophical Transactions of the Royal Society of London*, 95, 1805, 65–87

ⁱⁱ Cassie, A. B. D.; Baxter, S.; *Transactions of the Faraday Society*, 40, 1944, 546–551

ⁱⁱⁱ *Future markets inc.* 2018



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