E-book

FUNCTIONAL SURFACES:

Added value with textures & coatings

sirris
driving industry by technology

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Application domains of FUNCTIONAL SURFACES

New methods, including smarter, digital and connected production processes are needed today to cash in on the activities of manufacturing companies. It is important to manufacture products with high added value that are attractive on the international market.

Products such as sports equipment, medical equipment, car parts or kitchen utensils, derive much of their functional properties from how their surfaces interact with their surroundings. A bicycle helmet has more value if it is more aerodynamic or if it repels dirt better. A plastic container that is water repellent and therefore easy to clean is more hygienic by preventing biofilm formation over time. Creating a specific surface functionality from the intrinsic material properties of a >

component is limited as the choice of material is often dominated by the mechanical requirements of the piece.

To maximise the value of a product, it is therefore necessary to give it the necessary surface functionality. There are two commonly used options for this purpose:

- The application of another material in a thin surface layer (Coatings)
- Structuring the surface (Texturing)

Coatings are a tried and tested method to give components extra functionality. Just think of hard, ceramic coatings that make the operation of tools more durable or easy-to-clean coatings that make surfaces water-repellent. However, in addition to a wide range of commercially available products, there are still new innovations in this field that can add functionality and, therefore value, in sometimes unexpected places. Moreover, it is not always obvious to switch from 'need for a coating' to 'use of a specific coating in a certain way and with a certain process'. This is a complex decision-making process requiring strong knowledge of all steps.

Textures, or structured surfaces, are a less well-known and therefore less frequent way of applying functionalities. Yet this method exists in nature for a long time. The lotus leaf, for example, is extremely water repellent because it is covered with upright 'stubbles' (papilae) that minimise the contact surface with water. This keeps the leaves free of water and contamination, allowing them to always receive optimal light and not sink under water after a rainstorm. A shark's skin has a specific texture that both repels bacteria and improves its >

hydrodynamic properties. However, applying such functionalities via textures to technical components involves more than just copying the textures from nature. The texture geometry and the technology to apply them both play an important role in this.

In this case book we want to give innovative (manufacturing) companies like yours, a few examples of functionalities and functional surfaces that provide added value. With this we want to inspire you to use these technologies on your own products, in order to raise your products to a higher level.

Sirris, with more than 150 technological experts, has two teams specialised in functional surfaces: the first group of experts focuses on multifunctional coatings, the second on the structuring of surfaces through texturing. Both have a high-tech infrastructure for this and can boast extensive experience, built up in the industry through numerous cases.

1. Durability in manufacturing industry

The first examples we showed in this publication are not accidentally in the domain of the manufacturing industry, the sector in which most of the Sirris members operate. These companies produce components, ranging from consumer goods to machinery and car.

1. Textures to achieve a customised friction coefficient
2. Coatings to minimise friction and wear

We will discuss both in detail.

1. Customised friction coefficients

The wear of components has a large impact on the lifecycle and efficiency of machines. The wear is largely caused by the friction between moving components. This can be reduced by applying a structure on the friction surface. Certain applications may benefit more from another option, i.e. controlled friction.

Components in a wide range of applications, including cars, agricultural vehicles, airplanes and machines, are often affected by wear. This wear is one of the main factors in determining the lifespan and efficiency of these machines, and eventually, also their cost. A decisive factor is the friction coefficient of a surface: the higher the coefficient, the more friction is caused between the two surfaces and, therefore, more wear as time goes by.

It is therefore very important that we reduce the friction coefficients for components which move against each other. Gears are an excellent example, as well as bearing seats of axes and guide rails. A special technical application, for which we want to be able to control the friction coefficient and achieve a certain dynamic behaviour instead of reducing it, are CVTs. These transmissions work by means of friction between two discs, and this friction in turn determines the behaviour of the car.

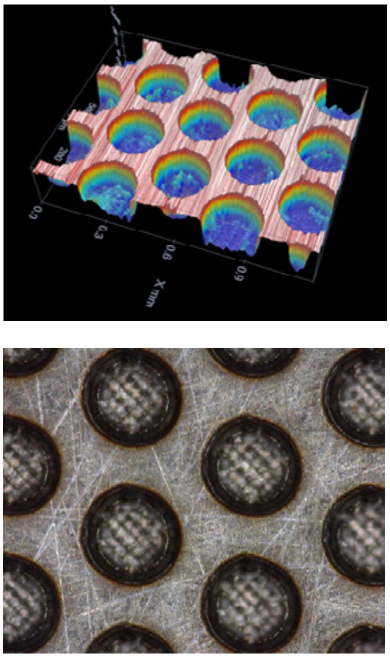


Figure 1: *3D measurement of low-friction texture (above) and top view of this texture (below)*

The use of textures makes it possible both to reduce friction coefficients and to control them. Ultra-fast pulsed lasers (fs, 10^{-15}s) are very interesting to apply because they perform ‘cold’ laser processing: no heat is introduced into the piece, and no fusion zones with fractures are formed. This property is extremely important in components that are frequently subjected to cyclic loading. It is also perfectly possible to use femtosecond lasers in hard materials (hardened steels, cemented carbides or ceramics) and even to work in or through coatings, regardless of the nature of these coatings.

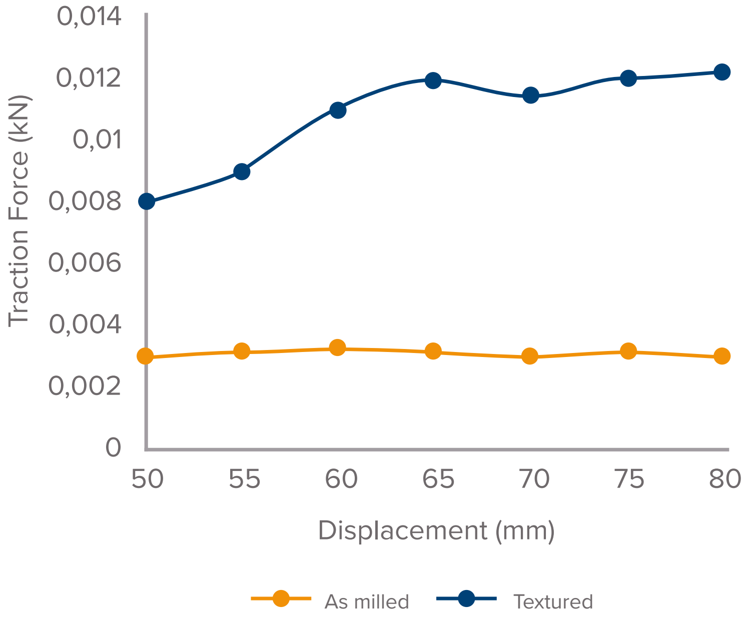


Figure 2: *friction force for a milled and textured surface*

Initial tests at Sirris indicate that a cavity structure with holes spaced apart at 200 µm and 150 µm and with a depth of 20 µm in an oil bath (such as, for example, gears in a gearbox or CVTs) results in a 75 per cent reduction in friction coefficient. The size of the holes, the distance between the holes and the depth play a role in this, making it possible to adjust the coefficient of friction to a particular application. In particular, it is even possible to create stick-slip effects, which means that overcoming a high static friction coefficient does not automatically result in a lower dynamic friction coefficient.

2. Low friction with coatings

Besides texturing, coatings are a proven method to create low friction in applications in the manufacturing industry and to prevent rapid wear and tear. In addition, the process conditions can also be improved or it is possible to work without or with less liquid lubricants. This leads directly to savings in lubricants and environmental costs. In other applications, the use of liquid lubricants is not even possible. Think of production machines developed for the medical or food industry. Another application would be a closed design which makes it impossible to provide regular lubrication.

Because of the wide applicability, different types of coatings were developed, the best-known ones undoubtedly being molybdenum disulfide (MoS_2), diamond-like carbon (DLC), fluoropolymers and Nickel-PTFE. DLC and fluoropolymers are both collective names for a whole range of different coatings which were developed for specific applications ***(Figure 3)***.

a)

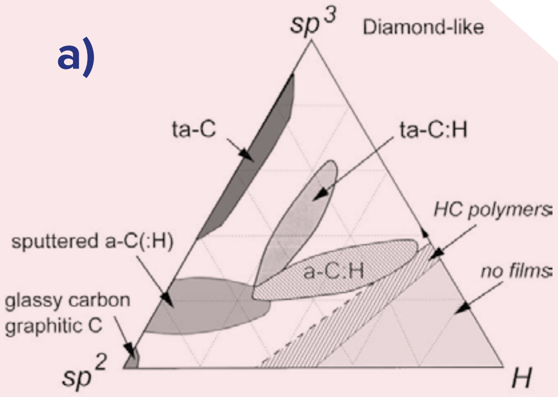


Figure 3: ***a)*** *overview of all different types of DLC, depending on the composition*[1]*;* ***b)*** *overview of mechanical properties and friction coefficient for different fluoropolymers*[2]

b)

	ASTM Standard	Unit	PTFE	FEP	PFA	FEP
Specific Gravity	D792	--	2.15	2.15	2.15	1.76
Tensile Strength	D1457 D1708 D638	MPa (psi)	21-34 (3,000-5,000)	23 (3,400)	25 (3,600)	40-46 (5,800-6,700)
Elongation	D1457 D1708 D638	%	300-500	325	300	150-300
Flexural Modulus	D790	MPa (psi)	496 (72,000)	586 (85,000)	586 (85,000)	1,172 (170,000)
Folding Modulus	D2176	(MIT) cycles	$>10^6$	5-80 x 10^3	10-500 x 10^3	10-27 x 10^3
Impact Strength	D256	J/m (ft•lb/in)	189 (3.5)	No break	No break	No break
Hardness	D2240	Shore D pencil	50-65 HB	56 HB	60	72
Coefficient of Friction, Dynamic	D1894	--	0.05-0.10	0.08-0.3	--	0.3-0.4

The operating environment (e.g. temperature, humidity), the type of wear (e.g. abrasive, adhesive, erosive), the process parameters (e.g. load, speed, frequency) and substrate material properties (e.g. hardness, yield strength) determine to a large extent which coating will provide the highest added value to the product or process.

PTFE coatings have a very low friction coefficient, but are less durable than the other types. Especially when the temperature in the contact rises, PTFE coatings soon lose their applicability, due to the inadequate heat dissipation.

If the combination of low friction and high wear resistance is important in an application, the DLC coatings are an excellent choice compared to other types of coatings. However, most DLC coatings do have a temperature limit. In temperatures above 250-300 °C the properties of these coatings diminish resulting in a significant rise of the friction ***(Figure 4a).***

An alternative way to combine wear resistance with low friction is by adding, for example, PTFE particles to nickel coatings. Nickel, applicable through an electrochemical process, is wear-resistant and offers protection against corrosion. By adding PTFE particles to it, these layers also achieve a low friction coefficient, down to 0.05. In addition, these coatings also have hydrophobic properties, which makes them more dirt-repellent.

Another example is the influence of moisture on MoS_2 and hydrogen-free DLC coatings. MoS_2 coatings have a low friction coefficient in a vacuum or in low humidity, but in a humid atmosphere the friction is significantly worse. For hydrogen-free DLC coatings the opposite is true. The higher the humidity, the lower the friction coefficient ***(Figure 4b).***

These examples show that it is important to adequately analyse what the working conditions will be before applying a low-friction coating. That is the only way to make a right choice and obtain the desired result. >

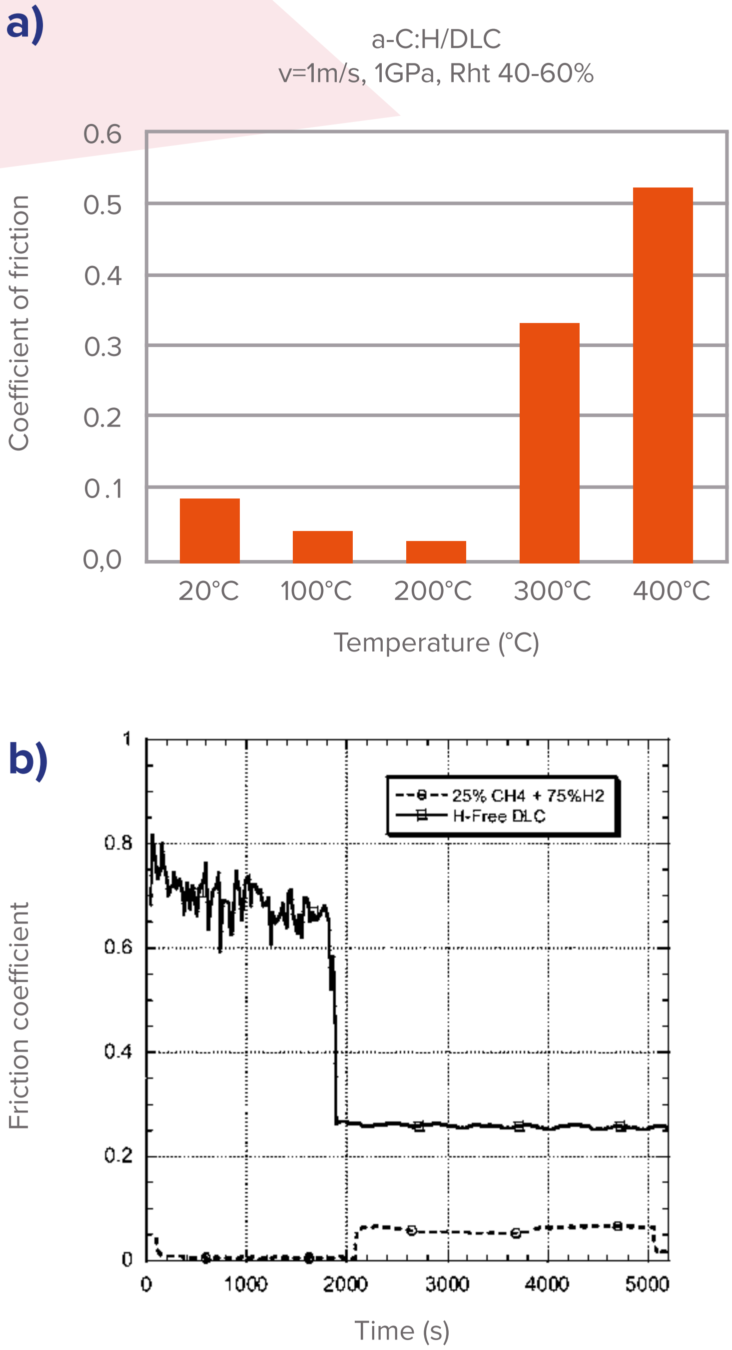


***Figure 4**: **a)** Influence of process temperature on the friction coefficient of DLC coatings.*[3]*; **b)** Influence of humidity on friction coefficient for DLC coatings (transition from inert to humid atmosphere after 2,000 sec)*[4]

The automotive industry makes plenty of use of DLC coatings for e.g. pistons, roller followers, tappets, camshaft accelerators and piston rings. MoS_2 coatings are perfect for applications in vacuum (like in the aerospace industry) or in low humidity applications. PTFE is interesting in applications that are not heavily loaded, but require very low friction, such as funnels, screw nuts or conductors.

3. Combination of texturing and coatings

Finally, the newest developments, which combine laser texturing with coatings, are also interesting to obtain excellent results by combining low friction and wear resistance. One example is the test in which the cutting face of cutting tools were first textured with a femtosecond laser and then coated with wolfram disulfide coating (WS_2) with characteristics similar to an MoS_2 coating ***(see Figure 5)***. During chipping tests the temperature and the friction coefficient were monitored at different cutting speeds. ***Figure 6*** clearly shows that both the texture alone, and the texture with coating, has a positive effect on both friction and temperature of the tool. >

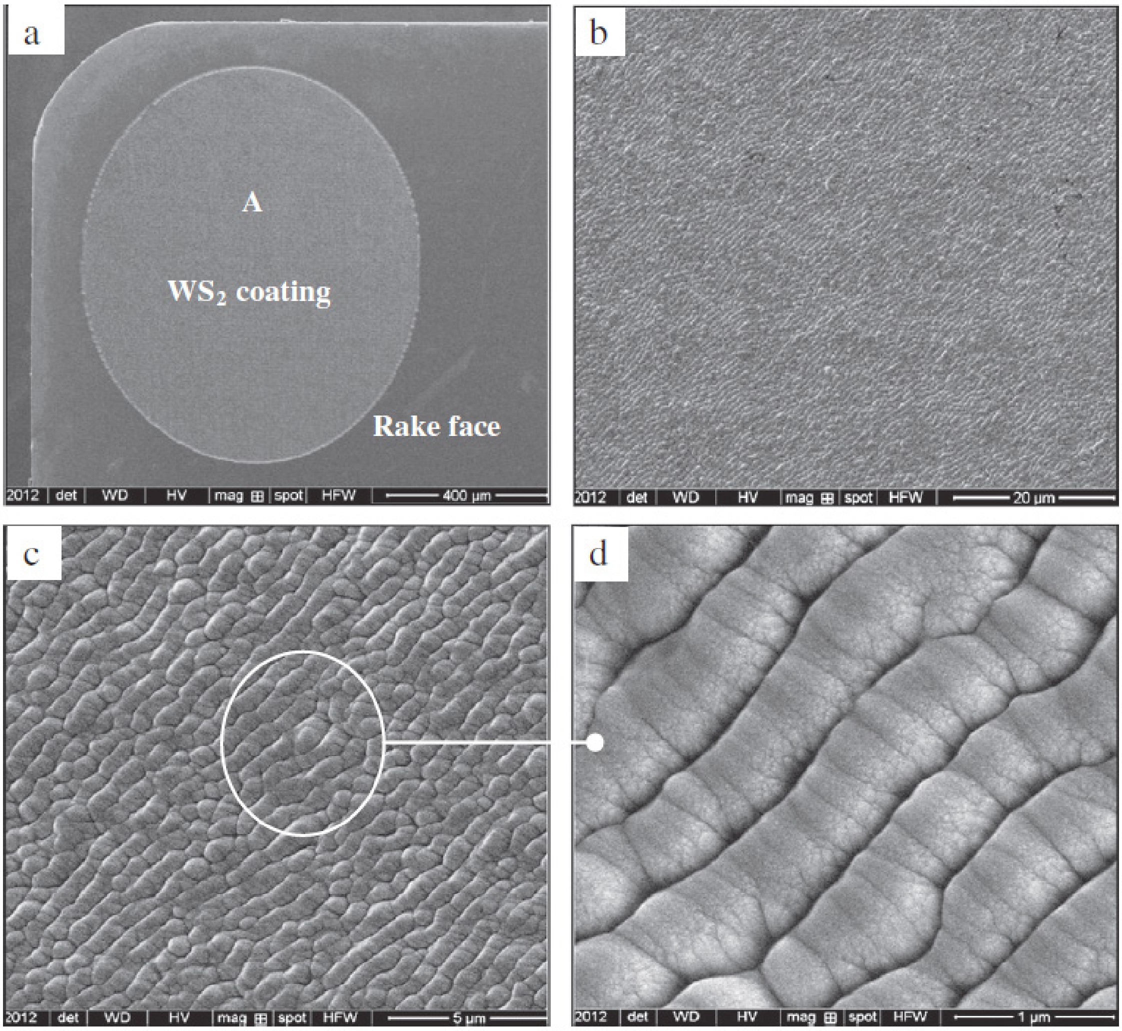


Figure 5: *SEM photos of the laser-textured cutting face with WS2 low-friction coating*[5]

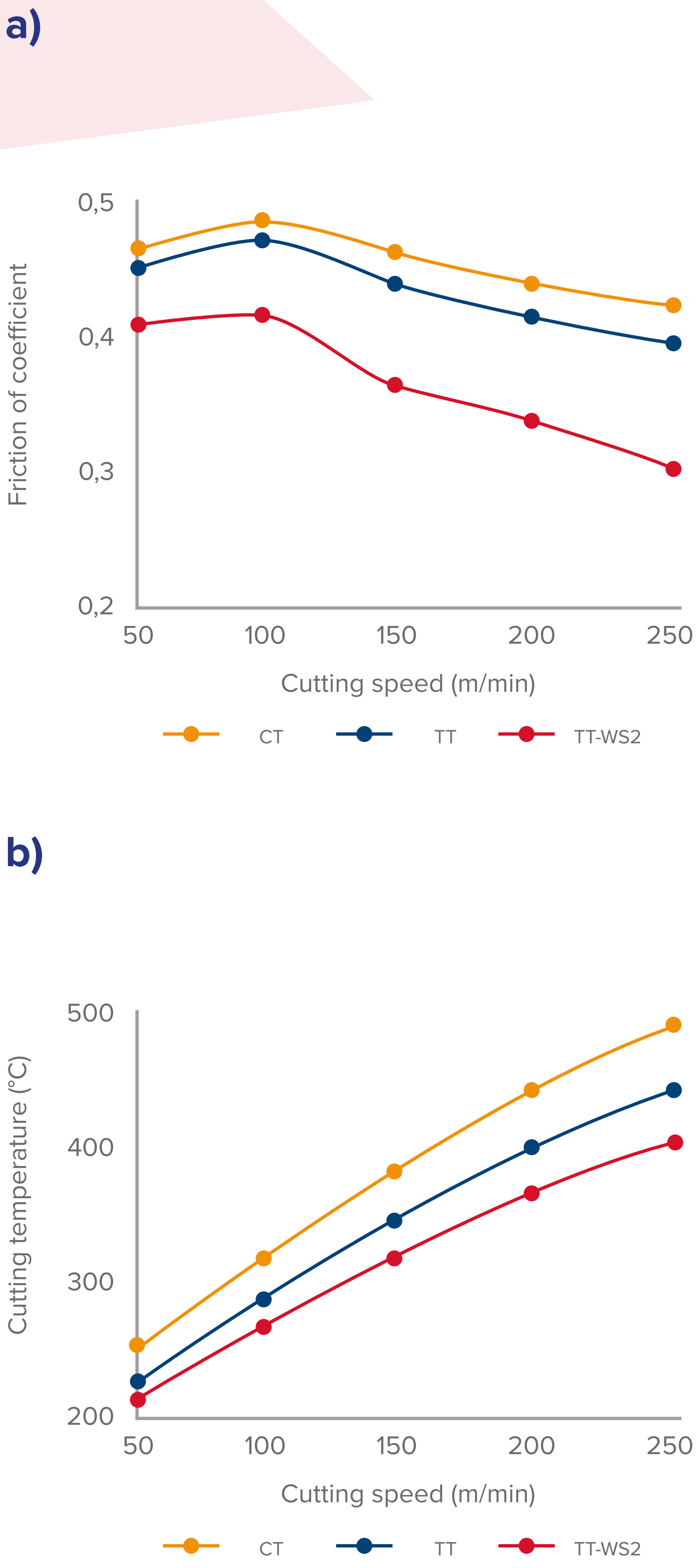


Figure 6: *Impact of texture (TT) and texture+coating (TT-WS2) compared to standard tool (CT) on* **a)** *the friction coefficient and* **b)** *the temperature of the tool*[5]

2. Cleanability in the food industry

In addition to the manufacturing industry, another particularly large sector also benefits greatly from the use of advanced surface functionalities: the food processing industry and producers of packaging for this sector. Easy-to-clean surfaces are of primary importance in the food processing industry. Keeping equipment clean during the production process is a constant challenge. In addition, the provision of sustainable packaging is becoming increasingly important.

Control of all sources of contamination requires a major effort to ensure food quality and safety. Mineral products such as $CaCO_3$, organic soils (e.g. lipids, proteins and sugars) and microbiological contaminants (bacteria, viruses, fungi and yeasts) are harmful to equipment and can often only be removed when the production is interrupted. Cleaning by removing contaminants accounts for up to 15% of total production time in the dairy.[6] Coatings or surface treatments that facilitate cleanability can be a valuable part of a hygiene plan in a food factory.

A second major challenge facing these sectors is the need to make packaging more sustainable. One of the aspects that plays a role is the avoidance of food wastage because of food remaining in the packaging. Think of soups, sauces and ready-made meals. To ensure that no food is left behind, the surface of the packaging should be made as hydrophobic as possible, so that liquids can easily slide off the packaging. Another aspect that plays a role is that packaging needs to be more reusable and that more quality and functionality is expected from these reusable packagings. Just like in the production process, the possibility to clean easily is essential here.

1. Hydrophobic surfaces

These two requirements mean that hydrophobic functionality must be achieved on plastics: water and aqueous solutions must be able to flow smoothly out of the packaging and also be wiped off smoothly. In this way, dirt, such as dust and food residues, is easily transported.

There are two possible solutions:

- Creating textures during injection moulding of packaging materials
- Applying easy-to-clean coatings

Both will be explained in greater detail below.

2. Packaging

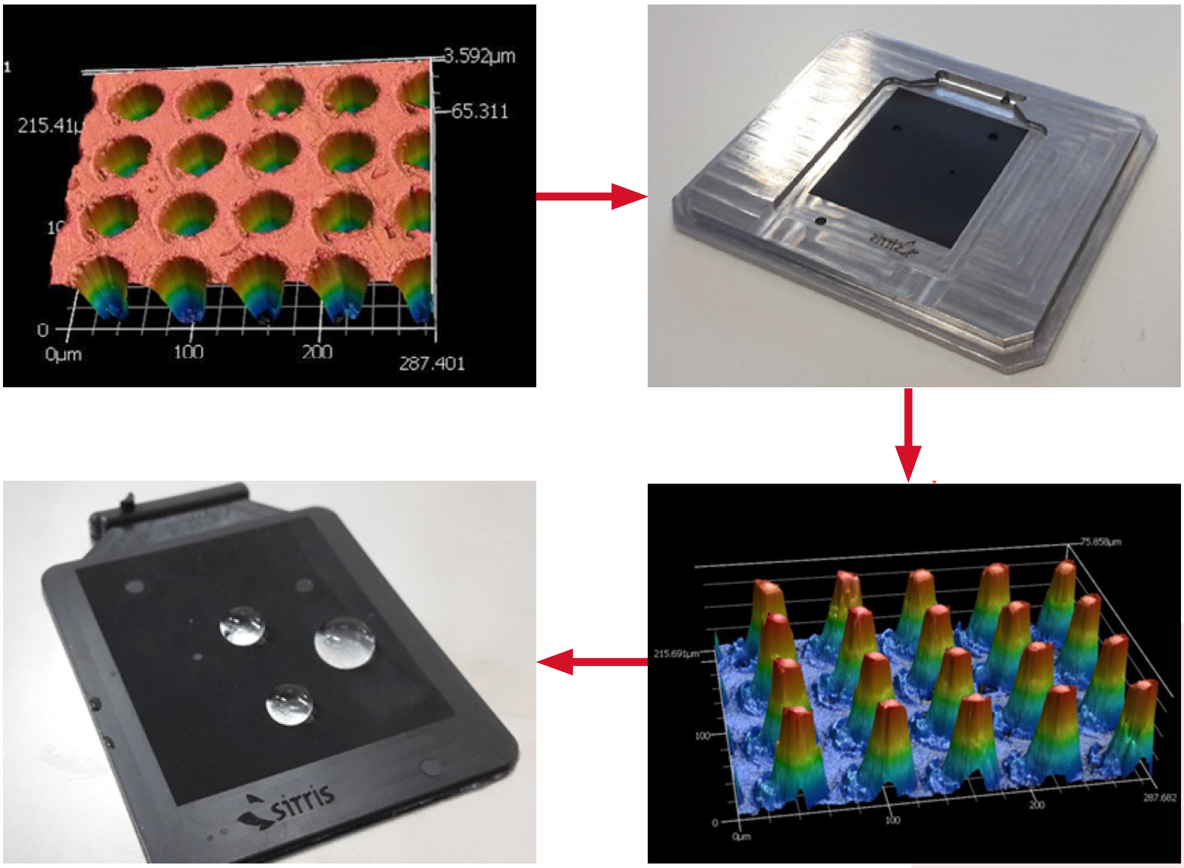
Textures for water-repellent injection moulding products

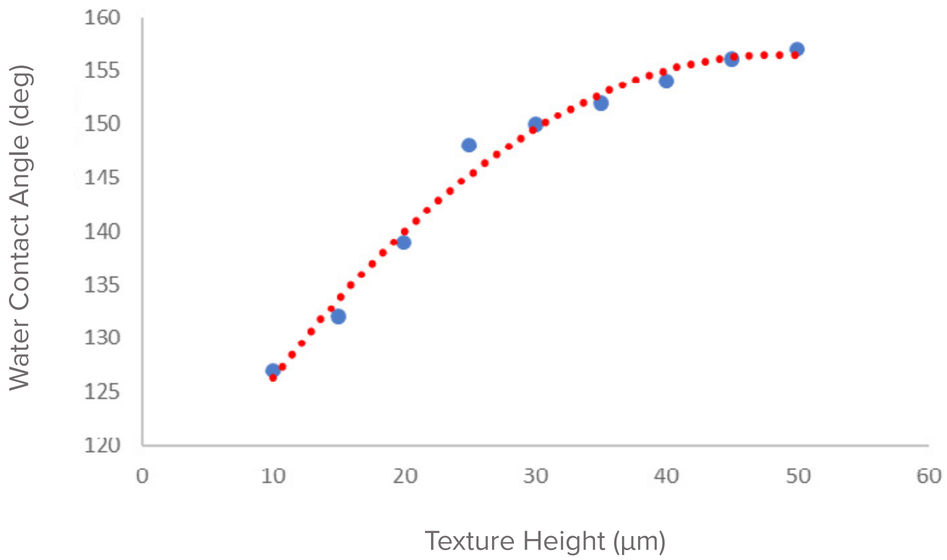
Millions of packagings are made each year for the food industry, ranging from disposable single use packaging to high-quality food containers that last for years. Both types are manufactured by injection moulding. During injection moulding, hot plastic is pressed into a mould and thus takes on its shape as it solidifies. It is also a cost-effective method of transferring complex surface structures to a mass-produced component, with the ultimate aim of adding additional functionality to the piece. This can be achieved by structuring the mould with a negative geometry of the desired surface structure.

In particular, water resistance (i.e. the wetting behaviour of the plastic surface with water) is important. The larger contact angle and low roll-off angle with water make it easy for drops to roll off the surface and carry dust with them. This creates a self-cleaning effect, which has many interesting applications in several sectors, such as shoes, sports equipment, mirror caps and spoilers. It also makes the administration of medication by means of syringes much easier and more accurate. It is particularly interesting for food packaging because it makes it easier to clean and easier to use the entire contents. >

The water repellent effect is achieved by creating small upright pillars that lock air between the water and the material. It is this air, which can no longer escape, that causes the contact angle to increase significantly and the desired functionality to be achieved.

To create this effect, we textured a mould with small holes (Ø 40 µm, depth 60 µm) at a distance of 60 µm from each other. This mould is injected with hot PP, so that the cavities are filled and the resulting texture is (negatively) copied on the plastic part. This texture is very similar to that of a lotus leaf and also has the same properties: contact angles of up to 160° are achieved, combined with very small roll-off angles. The plastic piece has therefore become water repellent.





The height of the upright columns is the most important factor that determines the contact angle. By varying these, by adjusting the injection moulding process, different texture heights can be achieved. The water contact angle is shown in the graph above.

Combination of texture and coating

However, the best results can be achieved when texture is combined with a coating. This results in super-hydrophobic surfaces with excellent water resistance.

Two recently developed technologies are, for example, SLIPS® and Liquid Pattern surfaces (LiquiGlide™), in which a textured surface is finished with a coating by means of impregnation. They ensure that liquids can run over structured surfaces while these remain smooth and clean. Depending on the product in the packaging, the composition of the coating must be adjusted to ensure optimal action. However, substances approved for food packaging will always be used.

3. Food Industry Production Process

In the food processing industry, the surfaces are mainly made of stainless steel. A typical finish of the surfaces is the staining and passivation or wet blasting of those surfaces. Surface treatments such as electropolishing or amorphising can already make surfaces more resistant to dirt and easier to clean without the need to apply a coating. What actually happens here is that the surface is very smooth, so dirt and bacteria cannot easily adhere to form a biofilm. In addition to a smooth surface, coatings could also play an important role here in achieving an easy to clean effect so that production downtime is kept to a minimum.

There are basically three main groups of coatings that can be considered. Which type of coating is used depends on many different factors, including abrasion resistance, chemical resistance, dimensions and complexity of the component and process temperature.

There's the **ceramic PVD coatings** that are highly abrasion-resistant and can be used at high temperatures. These can be used, for example, for process components where food has to be ground or processed. A disadvantage is that this cannot be applied to very large parts.

A second group are the **inorganic (silicon-based)** coatings that can be applied by spray coating and also have a high thermal application.

A third group are the more well-known **fluoropolymer coatings**, such as the well-known Teflon®, applied to frying pans, for example. This group of coatings consists of many variants of fluoropolymers and has very good anti-stick properties. A well-known disadvantage, however, is the lower temperature resistance of this type of coating and the lower wear resistance than the previous one.

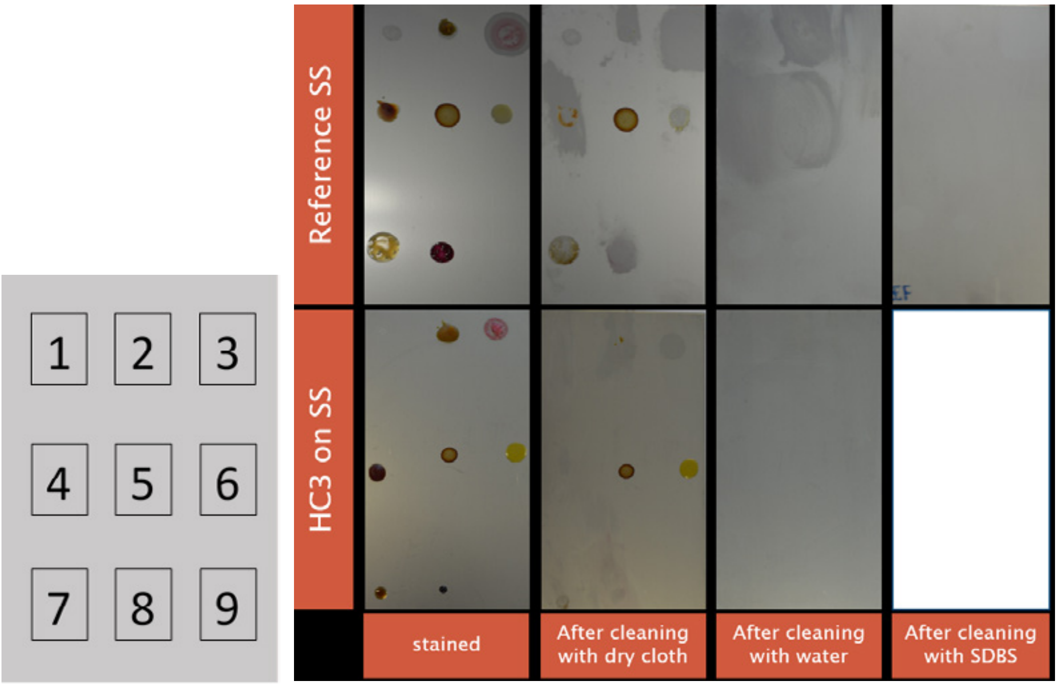
4. Challenges and research

Although there are many easy-to-clean coatings on the market, they are not yet widely used in the food industry. One of the most important reasons is that the coatings must, of course, be Food Approved before they can be applied. On the other hand, it must also be possible to apply the coating to existing installations and the cost price and life span also play a role in the consideration of using coatings in the production process.

Chemical resistance is also an important issue, as thorough cleaning will continue to take place in the food industry.

Two years ago Sirris carried out a **benchmark study** on the applicability[7] of easy-to-clean coatings for food applications. Ten different commercial easy-to-clean coatings were examined. Five could be classified as hydrophobic and five as superhydrophobic coatings, as indicated by the supplier. The figure below shows some results of cleanability after several products were applied to one of the coated surfaces and could act on it for 24 hours.

***1** vinegar, **2** mustard, **3** acid detergent, **4** ketchup, **5** coffee, **6** orange juice, **7** Coca-Cola, **8** wine, **9** MEK (i.e. the solvent methyl ethyl ketone)*



The results showed that in addition to the contact angle and the roll-off angle, coatings play an important role in achieving an easy to clean effect, depending on the type of contamination. They can therefore be of particular interest to the food industry.

The most important conclusion is that finding the optimal surface treatment is a complex task, because there are so many additional factors involved and there is currently not a single coating that can provide a solution for all applications. Depending on the type of dirt, adhesion of the dirt to the substrate, surface parameters and geometries and chemical influences, a suitable coating or surface treatment must always be selected.

Sirris, together with Flanders' Food, KULeuven, Ilvo and UGent is also currently conducting an extensive **feasibility study** - CLEANSURFACE - on the application of coatings and surface treatment in the food industry and their effect on the biofilm formation and cleanability of these surfaces.[8] Only coatings and surface treatments that already bear the ‘Food Approved’ label and that can be applied immediately in the industry if the results are favourable are studied.

By subjecting coated stainless steel plates to contamination in a biofilm reactor, where they are exposed to milk, meat, and egg proteins or starch, the formation of biofilm and fouling can be evaluated.

The anti-adhesion behaviour of treated stainless steel is evaluated via three parameters: the degree of fouling, the removal of fouling by a rinsing process and the removal by cleaning with cleaning agents.

3. Reflectivity in optical applications

Surfaces can be adapted to provide different optical effects. This has a variety of applications, the most interesting of which are scientific applications in which light has to be diffracted or a single colour (wavelength) has to be isolated from the light bundle. Think of spectroscopy, where diffracted light is spread over a detector in order to determine the chemical composition of the light source, such as a star or a flame. Surface optical behaviour can be achieved with both texture or coating, both of which will be explained further in depth in the two following sections.

1. Textures

The application of textures to create optical effects, such as scattering, diffraction and light entrapment (optical black) is not uncommon. Femtosecond lasers offer unique opportunities to create such textures by virtue of LIPSS (laser-induced periodic surface structures). These ripples, as shown in ***Figure 7***, are the result of the interference between surface plasmon polaritons (SPPs) and the laser light, resulting in LIPSS. Given that this process creates nanostructures with dimensions that are identical to the wavelength of the laser light, it is possible to use this to create, for example, diffraction gratings and light entrapment structures (optical black).

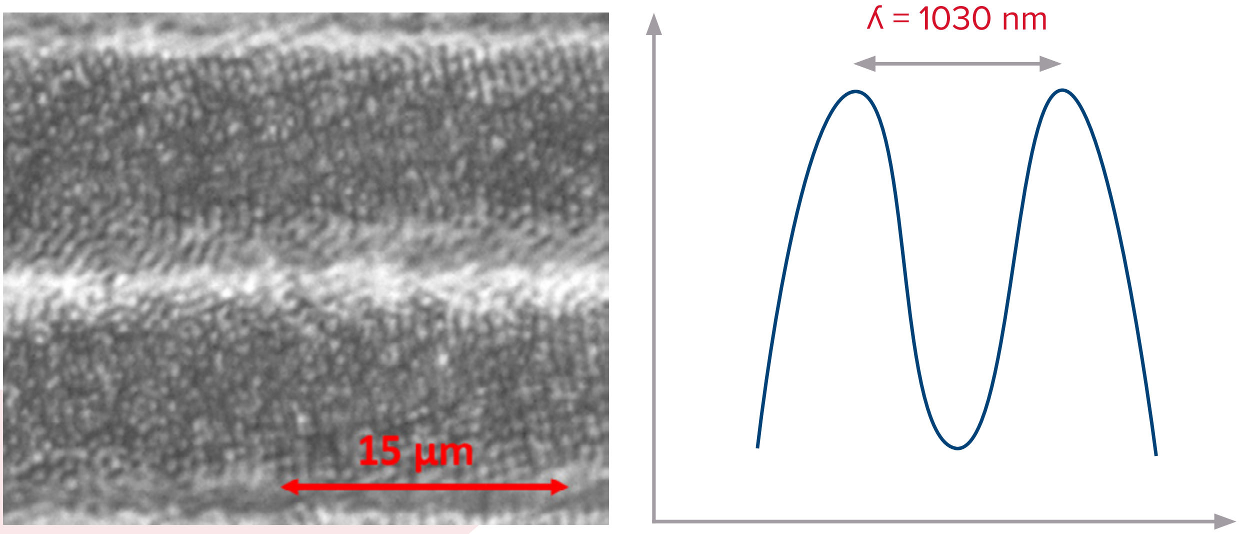


Figure 7: *Ripple surface structure*

In this research, a 250 fs 10 W laser (1,030 nm) is used to create a diffraction pattern in polished 316L stainless steel. Light polarisation was kept constant throughout the operation. Depending on the laser fluence (J/cm^2), different microstructures are observed on the surface, ranging from soft ablation in which only the edges of the craters are visible (0.315 J/cm^2), line structures (1,17 J/cm^2) to random upstanding pillars (2,52 J/cm^2) ***(Figure 8)***.

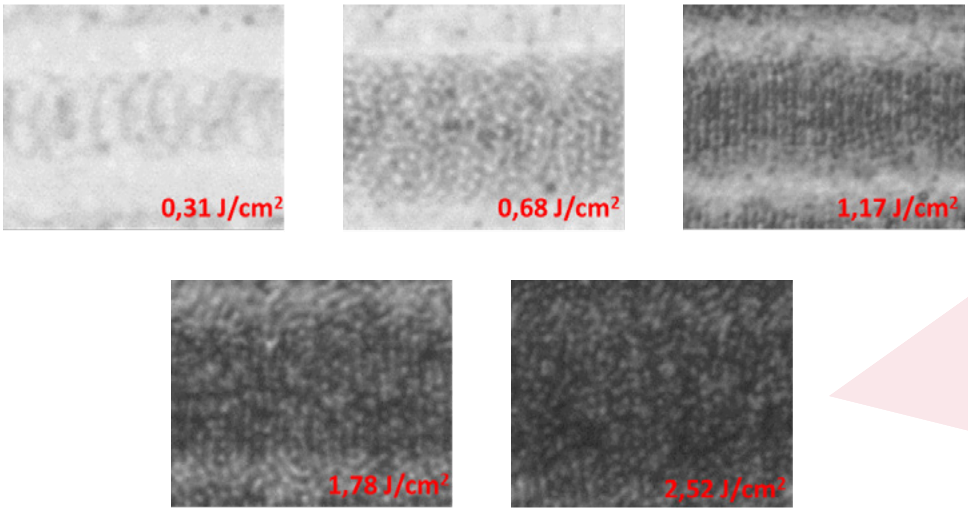


Figure 8: *Different LIPSS structures created depending on Laser Fluence*

As can be seen, the structures obtained with a laser fluence of 1.17 J/cm^2 resemble a grating structure: lines (ripples) placed at 1 µm intervals. The behaviour of light interacting with this surface is governed by the grating equation:

With n = order, λ wavelength, d = diffraction spacing and ϴ = zero order angle and ϴ’ first order angle. It can be seen from this equation that, by changing the diffraction spacing d, the behaviour of the grating can be tuned to diffract differently. The angle is also determined by the light wavelength, with red resulting in larger angles than green and blue; ***see Figure 9*** in which a spacing d = 1 µm is used.

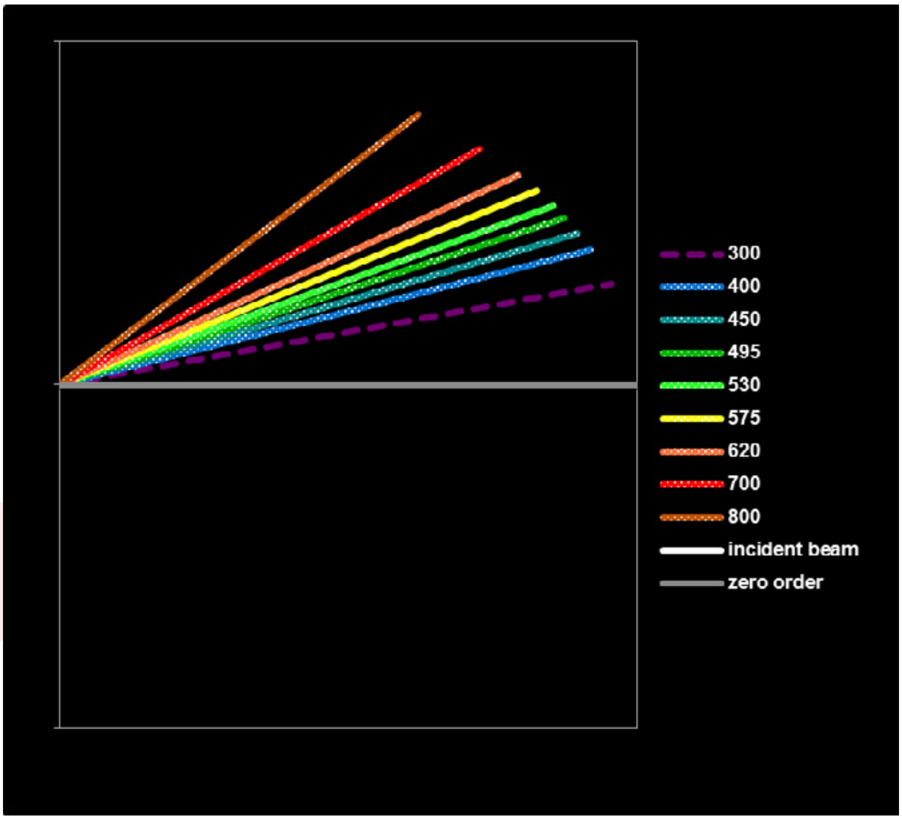


Figure 9: *Visualisation of the grating equation*

The other laser fluence settings resulted in nearly invisible ablation (0.31 J/cm^2) or matte surface quality with no diffractive properties (2.52 J/cm^2). 1.17 J/cm^2 resulted in the diffractive grating shown in ***Figure 10.*** This diffraction pattern is suitable for spectroscopic applications, while much cheaper and faster to produce than classical gratings.

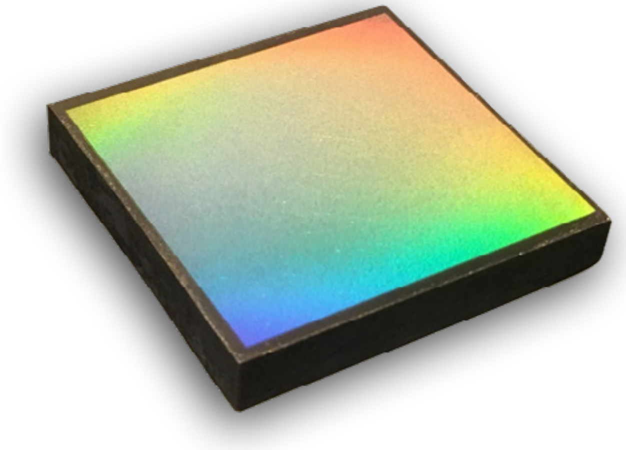


Figure 10: *LIPSS Diffraction grating*

Optical coatings

Optical coatings are frequently used to enhance the optical properties of optical components such as windows, mirrors or lenses. One way of realising such a coating is by using a thin layer of a material with the required properties. A typical example is the metallic reflection layer of a mirror. In practice the metals aluminium, silver and gold are most frequently used for this purpose. ***Figure 11*** shows the reflectance of the three metals from the ultraviolet (UV) to the infrared (IR) region. Aluminium has an average reflectivity in the visible range and is often used, especially when reflection in the UV region is important. Silver has the highest reflection over the visible range and gold is preferred when the highest reflection in the IR and near-IR range is required. The yellow colour of gold is a consequence of absorption below around 550 nm. Only a thin layer, in the region of 100 nm, of metal is required to obtain the maximum reflective properties. By decreasing the thickness below this value, reflection decreases and transmission increases based on the thickness of the coating layer. This effect is used in beam splitters and neutral density filters or semi-transparent windows. Because the thin metallic layer is easily damaged by scratches or corrosion (aluminium and silver) a protective coating such as a silica layer or varnish is often applied and the mirror is called “a protected metal mirror”. The protective layer slightly reduces the reflective properties.

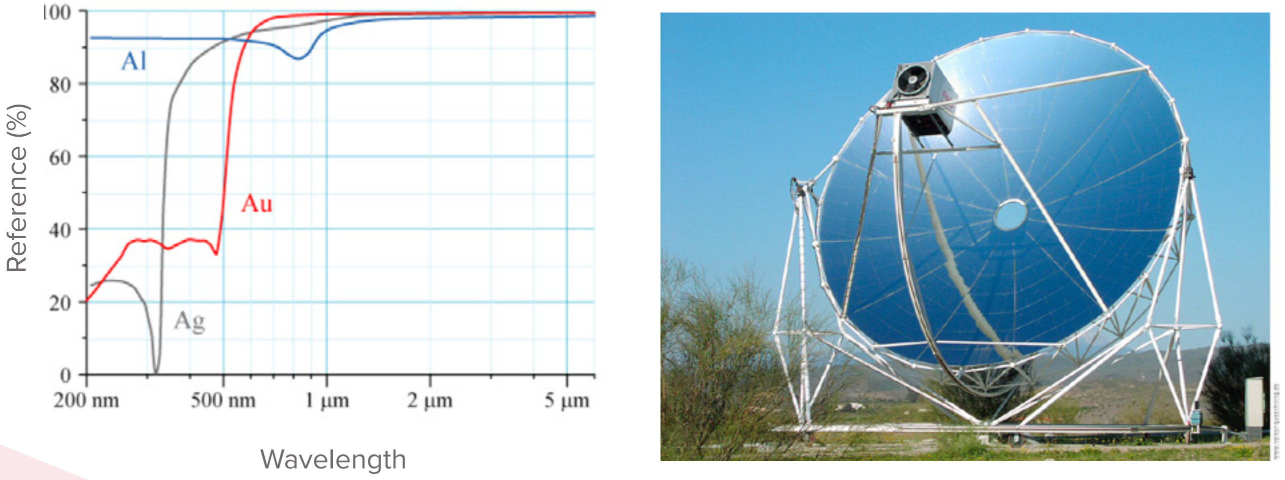


Figure 11: *The reflective properties of aluminium, silver and gold from UV to IR (left) and an example of the application of a metal mirror coating in a large parabolic heat collector.*

2. Optical interference coatings

Light consists of electromagnetic waves and it is well known that, depending on the phase difference between two waves, these waves can amplify or weaken when added up. ***Figure 12*** illustrates how this interference effect can be used to influence the optical properties of a surface by applying a thin coating to that surface. The coating creates a double interface, air-coating and coating-substrate; hence, there will be two reflected light rays. When the reflected waves are out of phase, they partially or totally cancel, a phenomenon which is called destructive interference and the coating behaves as an anti-reflection coating. The reflection will be minimal (180° phase difference) for the following conditions: (a) the refractive index of the coating must be smaller than that of the substrate, and (b) the optical thickness of the coating must be equal to one fourth of the wavelength of the incident light. Mathematically this is expressed as:

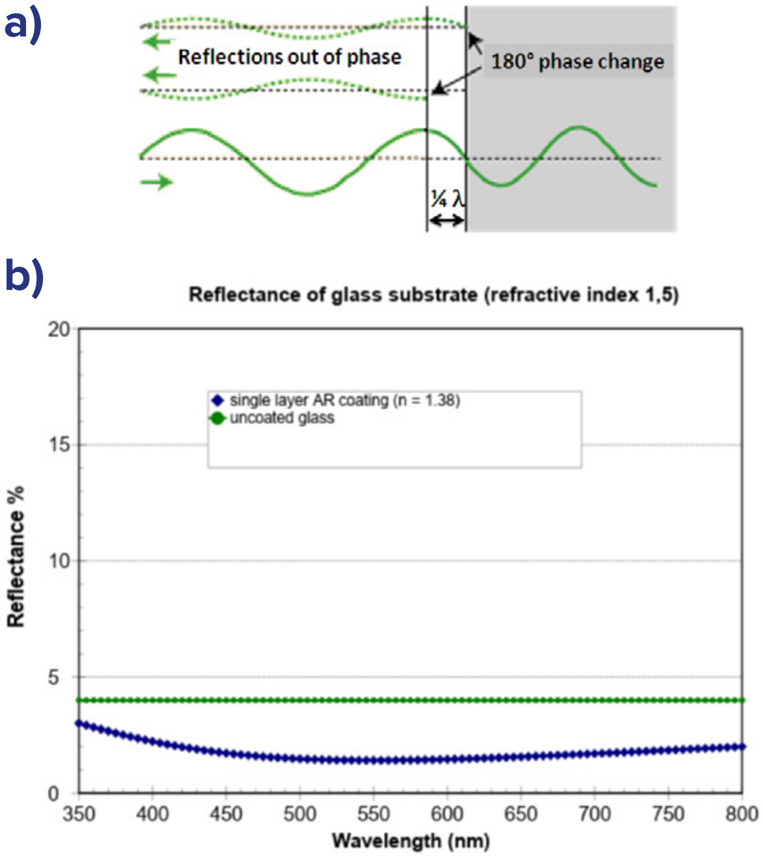


Figure 12: *Principle of a quarter wavelength anti-reflection coating and calculated reflectance spectrum of such coating on glass for MgF (n = 1.38; thickness = 99.6 nm).*

$$n\,d = \lambda / 4$$

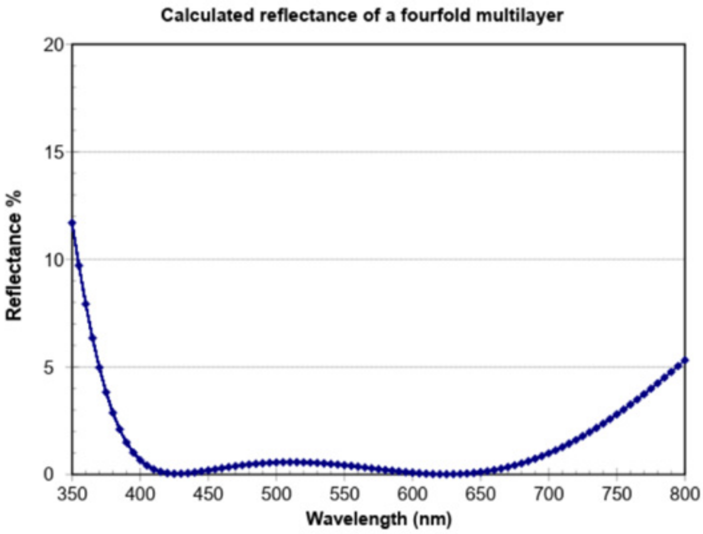
with n the refractive index of the coating, d its thickness and λ the light wavelength. The product $n\,d$ is referred to as the optical thickness of the coating.

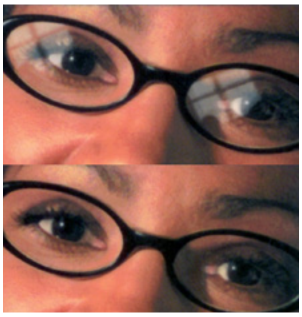
An anti-reflection coating consisting of a single layer is only optimal for one wavelength. Usually the middle of the visible range (around 550 nm) is taken. This wavelength is referred to as the design wavelength. So, at the design wavelength the reflection spectrum shows a minimum. This minimum is theoretically zero when the refractive index of the coating n equals the square root of the refractive index of the substrate n_s:

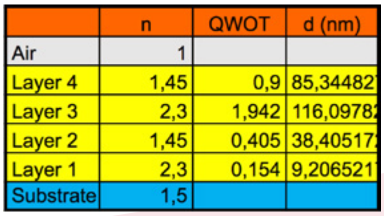
$$n = (ns)1/2$$

but in practice the refractive index cannot be chosen freely and one is limited by the use of a low index material such as magnesium fluoride (n = 1.38).

Instead of using a single layer, anti-reflection coatings can be made more effective by using multiple thin layers which have an alternately low and high refractive index. Such a multilayer structure, also referred to as an optical stack, has the advantage of potentially minimising the reflection over a broad wavelength range, typically the whole visible region. In addition, use of materials with a lower refractive index than that of the substrate is not required. The design and calculation of the properties of a multilayer structure are quite complicated; however, several mathematical techniques have been developed. In ***Figure 13***, the properties of a typical anti-reflection multilayer coating, such as used on ophthalmic lenses, are shown. Similar multilayer anti-reflection coatings are used on camera lenses, electronic device screens and windows.







	n	QWOT	d (nm)
Air	1		
Layer 4	1,45	0,9	85,34482
Layer 3	2,3	1,942	116,0978
Layer 2	1,45	0,405	38,40517
Layer 1	2,3	0,154	9,206521
Substrate	1,5		

Figure 13: *Reflectance spectrum of a multilayer AR structure consisting of layers of* SiO_2 *(n=1.45) and* TiO_2 *(n=2.3).*

Besides anti-reflection, multilayer optical coatings have many other applications such as:

- Enhanced metal reflectors on which a multilayer structure is deposited on top of the metal layer, enabling reflectivity values of more than 99% in the visible range,
- Bandpass filters which only transmit light in a specified wavelength range,
- Edge filters blocking the light below (or above) a specified wavelength. An example of an edge filter is a hot mirror coating, which is designed to reflect infrared radiation and transmit visible light.

A special case of such a hot mirror coating is the low-emission coating nowadays used on insulating window glass. As illustrated in ***Figure 14***, visible light can pass through the coated window, while infrared radiation is highly reflected. High reflectivity for infrared is linked to low emissivity, which explains the name low-e glass. These coatings are multilayer structures which contain one or more very thin silver layers of a few nanometres to obtain the required properties. The advantage of low-e glass is clear both in cold or warm weather conditions. When it is cold outside, IR radiation from inside is reflected back, keeping the warmth inside. When it is hot outside, heat radiation from the sun is blocked, keeping the interior cooler.

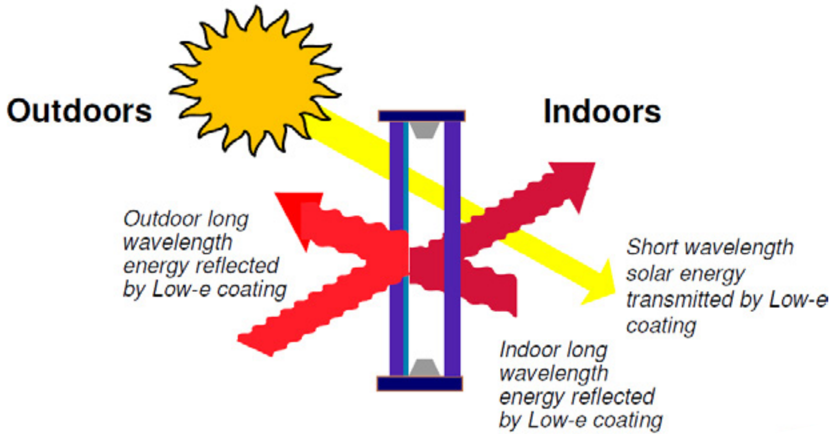


Figure 14: *Working principle of a low-e coating on insulating window glass.*

4. Biocompatible and anti-microbial surfaces

Surface functionality is of extreme importance for the healthcare industry. For a large part, because of a similar reason as for the food and packaging industries: medication packaging and application devices, such as syringes, are more easily emptied, because of hydrophobicity and/or lower friction coefficients. However, other important applications are possible in this industry, namely influencing the behaviour of biological matter on a surface. In general, application can be divided into two main topics:

- Anti-biofouling/anti-microbial surfaces
- Improving cellular adhesion

In the next paragraphs some examples of both coatings and textures are elaborated.

1. Textures and biological matter

When a surface is submerged into for example seawater or any other liquid which contains biological matter, **biofouling** can occur. In maritime industry this is very visible by the formation of first green algae, then other organisms which hinder ship operations and can cause significant increase in fuel consumption due to degraded hydrodynamic behaviour. In the healthcare industry, the adhesion of biological matter such as bacteria and spores to a surface can cause significant health hazards. A good example of where this problem plays a role are temporary implants such as biosensors, catheters, drug-delivery devices, bone plates, fasteners, ventilation tubes, needleless connectors and ventilator tubes. Urinary catheter calcification due to bacterial colonisation can cause infections and bladder stones. It is therefore important to use for these applications parts with surfaces that are less prone to such biofouling and bacterial colonisation.

Nature has already found a solution for this problem. Sharks have developed a skin which helps them to swim by reducing hydrodynamic drag, but it can also contribute to avoiding formation of algae and bacteria. The specific skin texture is the cause for this phenomenon. Recent work by academics and Sharklet Technologies have shown that using a shark skin inspired texture in plastics can significantly lower the biofouling behaviour of a surface.

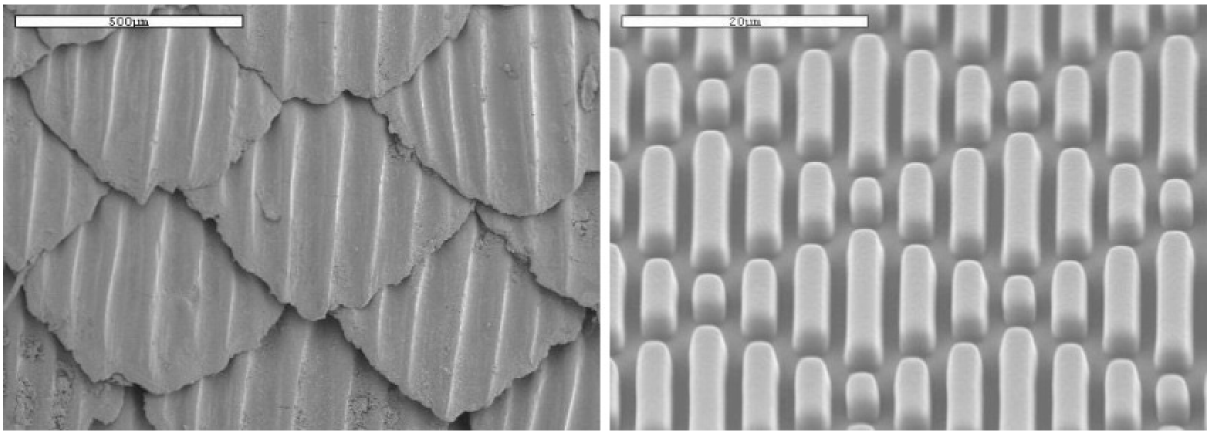


Figure 15: *Shark skin left, Skarklet texture right*[9]

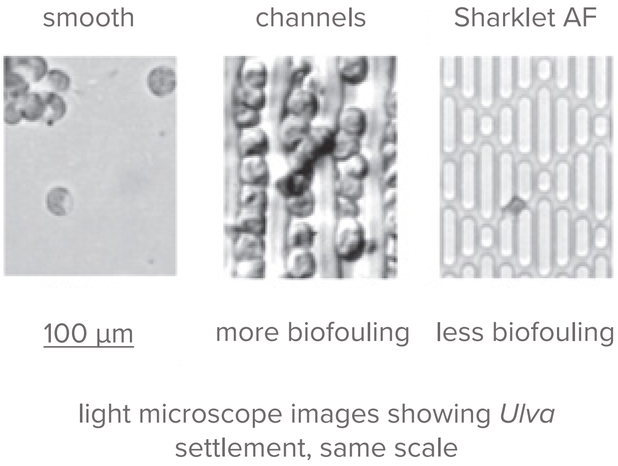


Figure 16: *Ulva biofouling tests, results*[10]

Because it is mostly used on plastic parts, the sharklet texture can be easily used by means of injection moulding or roll-to-roll processes, allowing the creation of a foil which can be applied to any surface and easily replaced.

Another application which is exactly the reverse of anti-biofouling is using textures to improve the **adhesion of cells to a surface**. This is interesting when talking about implants (knee, hip and dental for example). Improved cellular adhesion to a titanium or zirconia surface can speed up bone regrowth around the implant and consequently, speed up patient recovery. Recent work has shown that using LIPSS (laser-induced periodic surface structures), which are created by femtosecond lasers and have characteristic dimensions equal to the wavelength of the laser light, can significantly alter the adhesion of cells om a metallic surface. It is possible to guide cellular adhesion and increase the adhesion by means of LIPSS ***(Figure 18)***.

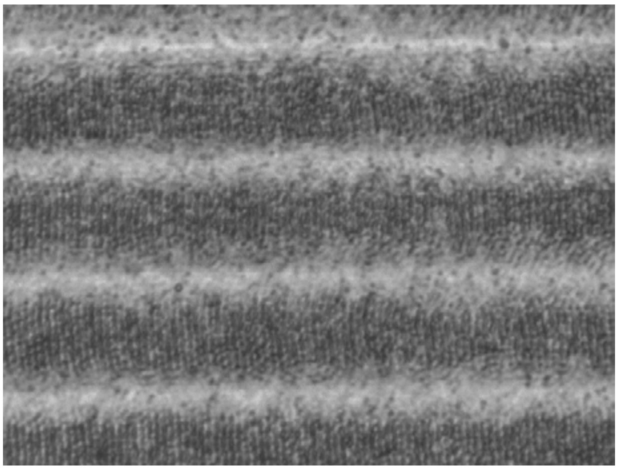


Figure 17: *LIPSS ripples (pitch = 1µm)*

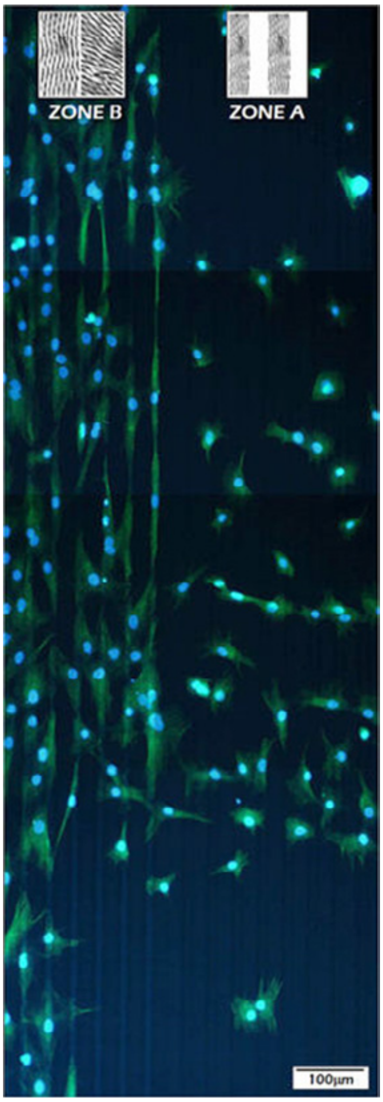


Figure 18: *Human stem cells on LIPSS (left) and polished (right) surfaces*[11]

Orientation and size of these LIPSS structures are defined by the laser parameters and, more specifically, the wavelength and polarisation. Each ripple is perpendicular to the polarisation of the light. Guiding cellular adhesion, and specifically of human stem cells, without the use of etching (which is currently used to create the commonly used SLA surface grade in implants) and with femtosecond lasers allows the creation of implants with improved integration properties. In addition, when considering the manufacturing standpoint, using lasers to functionalise the surface of a implant fits well with other short lead time technologies such as 3D printing, lowering the waiting time of patients and providing them with customised solutions.

2. Coatings

Coatings are widespread in healthcare and medical applications. The purpose for applying a coating can be manifold both for implantable and non-implantable medical device applications. There are low friction coatings to minimise irritation and inflammation when bringing medical devices into the body. Antimicrobial coatings are developed to reduce the chance of infection and are one of the strategies in the battle against hospital-acquired infections, which are a major health-challenge in healthcare centres worldwide. There are coatings that enhance the growth of tissue on medical implants to help the healing process and coatings to prevent corrosion and wear to make implants long lasting for the patients. Further in this article, we will go deeper into the antimicrobial coatings and coatings to enhance tissue growth.

Antimicrobial coatings

Whilst the spread of infections, and specifically hospital-acquired infections, becomes a persistent and growing problem in healthcare facilities, there is a huge drive to find solutions to fight them.[12] [13] As shown in the previous paragraph, one of the strategies is to design surfaces with a specific structure to make the surface **non-adhesive** to microbes. This can also be done by applying superhydrophobic coatings like siloxanes or fluorosiloxanes or combine these with a nanotexture. Another successful approach is described in literature

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using zwitterionic polymer brushes. A second approach is **contact-active** surfaces. These coatings are killing bacteria on contact without releasing biocides. A well-known type of these coatings are based on quaternary ammonium compounds (QACs). **Biocide releasing** coatings are broadly used and well-known examples are silver- and copper-based coatings. These coatings work very well but have as a disadvantage that they are toxic to all bacteria and have a limited lifetime, with a gradual decrease in activity as the active ingredient is leached out, creating the possibility for the bacteria to form a resistance against the biocide. An interesting alternative for this are photo-catalytical active coatings, which need UV radiation and moisture to become active, but can be regenerated time upon time throughout their lifetime. A known example are the TiO2-coatings which also find application in easy-to-clean windows nowadays. As there is no natural UV light in hospitals and regular healthcare settings, research in this type of coatings is focused on shifting the photo-catalytical activity towards the visible light, so the coatings can be activated indoors.

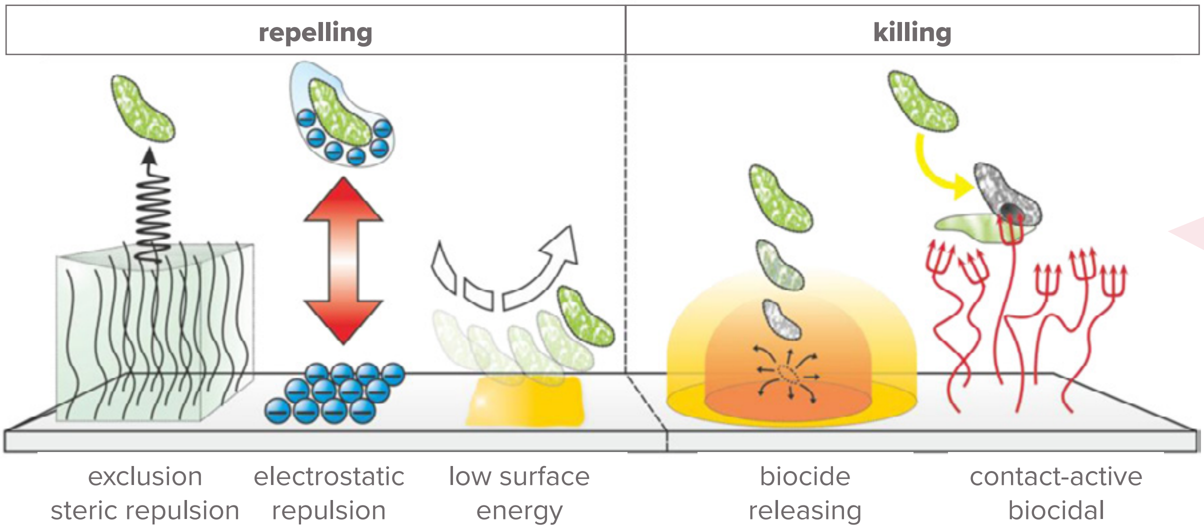

Figure 19: *General principles of antimicrobial surfaces.*[14]

Although durability is a critical property for this type of coatings to be useful in clinical settings, it is often overlooked as the focus is mainly on the antimicrobial effect and not so much on mechanical stability or even adhesion to the substrate. Research efforts focusing on long term stability turn to plasma-deposited coatings such as diamond-like carbon (DLC) coatings or the whole range of physical vapour deposited (PVD) ceramic coatings, which do not possess antimicrobial properties,

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but can be used as a mechanically and chemically stable and highly durable carrier matrix for antibacterial components.

In order to streamline the European efforts in research and development on this type of coatings, several European networks have been created. Sirris is an active member in the European COST-action network AMiCI, whose main goal is to evaluate the impact of (introducing) anti-microbial coatings in healthcare on the spread of infections and on the efficacy in fighting healthcare associated infections and bacterial resistance to current antibiotics.[15]

While the AMICI action network will focus on innovative AMC on non-invasive materials and surfaces, such as operating tables, walls, the interior of ambulances, door handles, textiles etc., a complementary COST-action network iPROMEDAI focuses on timed presentation and local delivery of antimicrobial active compounds from medical devices, such as catheters, to reduce the incidence of device-associated infections that originate from bacteria developing in biofilms.[16]

Coatings to enhance tissue growth

Coatings are an important aspect when placing implants. Studies show that the coating is even more important than the quality of the bone structure itself in the success rate of a good implantation.[17]

Apart from surface modifications such as roughening the surface by blasting, chemical processes, plasma pre-treatments or structuring, a whole range of coatings have been studied to investigate an enhanced biocompatibility and adhesion of tissue to all sorts of implants. In some cases, a combination of biocompatibility, anti-corrosion and anti-microbial effects are targeted.[18]

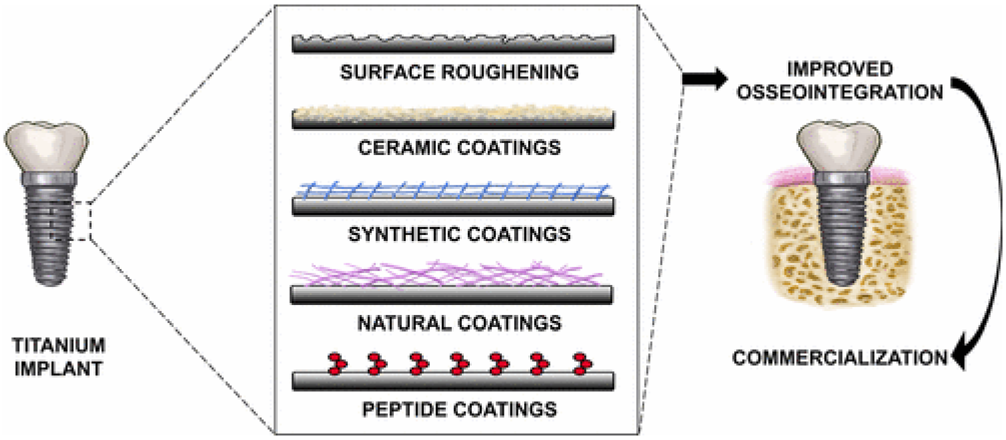

Figure 20: *Overview of possible surface modifications for improved osseointegration of Ti-dental implants.*[19]

Among the most studied coating materials are the calcium phosphate (CaP) based alloys, including the well-known hydroxyapatite coating, which can be deposited by a whole range of technologies such as magnetron sputtering, plasma spray, sol-gel or pulsed laser deposition. Another type of coating is TiO_2, sometimes in combination with the incorporation of silver nanoparticles for anti-bacterial purposes. Nitride coatings, such as TiN, AlN or TaN coatings, have been studied as a suitable coating combining biocompatibility, durability and anti-corrosion.[20]

5. Aesthetic applications

An interesting domain of application for textures and/or coatings is aesthetics, such as on jewellery or watches.

Currently, textures are already used for a variety of aesthetic applications in watches. Because of the characteristics of a femtosecond laser, very fine engravings and textures can be made without any melt zones and/or cracks and/or oxidation. However, next to these more classically “milled” surfaces, several unique aesthetic surface functionalities can be achieved with femtosecond laser texturing.

Figure 21: *Optical black*[21]

A first example is the capability to create black without any paint, by means of reducing the reflectivity of a surface.

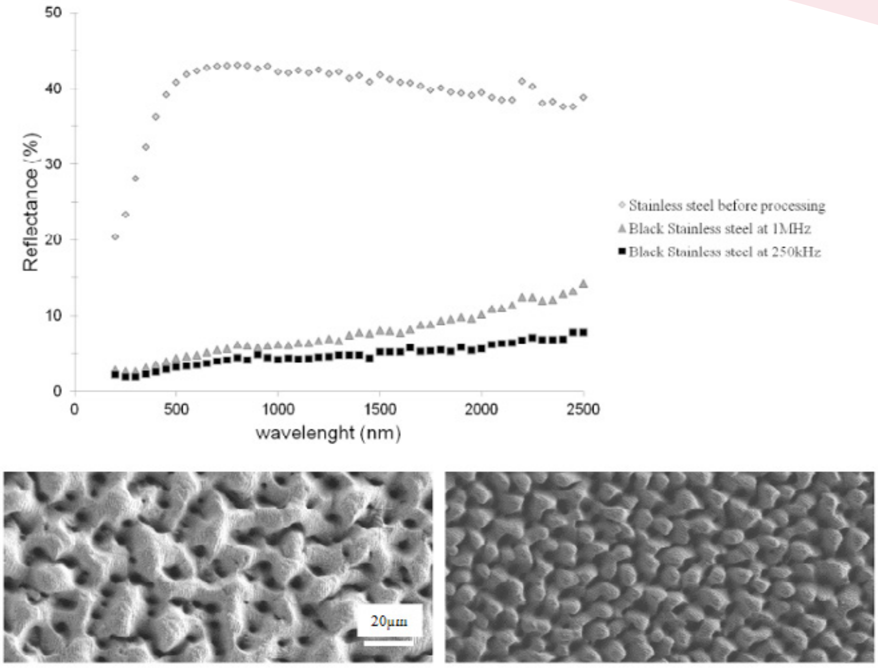

Figure 22: *Reflectivity of stainless steel after laser texturing (250 kHz right, 1 MHz left)*[22]

Using the correct laser parameters, laser induced periodic surface structures (LIPSS) can be created ***(Figure 22)***, which consist of upstanding pillars, with cavities between them. Incoming light is entrapped between these pillars and cannot be reflected, which results in “optical black”. The reason for this is that the cavities and pillar have dimensions in the same range of the wave length of the incoming light, effectively trapping it instead of reflecting it. The same effect can be achieved in aluminium, titanium, and copper.

Decorative Coatings

Decorative coatings are well known and all around you on products and consumer goods. In order to enhance the aesthetical aspects of products, it is not just about colour but can also include for example a specific metallic look, a matt or gloss finish, an antique look or a soft touch. Additionally, it is very important that this look and feel remains on the product for the total lifetime. This means that apart from the aesthetical aspect, an additional protective (functional) coating is applied as a top coat. Examples are a UV-blocking coating to prevent fading of the colour of a product in time ***(See Figure 23)*** or a scratch-resistant coating to protect the surface from damage.

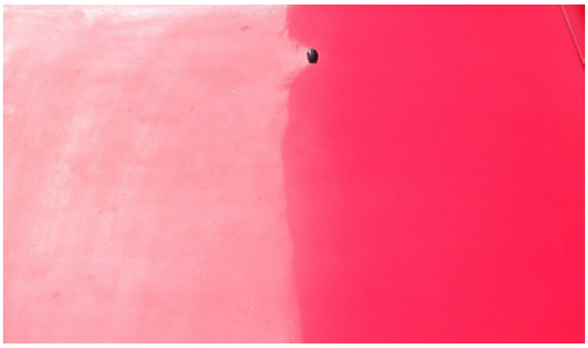

Figure 23: *colour fading due to UV-radiation*

When using ceramic PVD coatings, no protective topcoat is necessary as the coating is wear-resistant enough to protect the surface against damage. An example[23] are the casings of high-end smartphones which are coated with a PVD coating.

As the ceramic PVD coatings are metal based, the range of colours is limited in comparison to wet-chemical coatings where all kinds of colour pigments can be added to the coating. However, when limiting the thickness of a PVD TiO_2 or SiN_2-coating, it is possible to get alternative colours. This is an effect of optical interference as shown in ***Figure 24***. As the different colours are within very narrow thickness bands, it is crucial to have the deposition rate of the coating under control. ***Figure 25*** shows the result of an art-object on which a specific blue colour coating was applied using this technique.

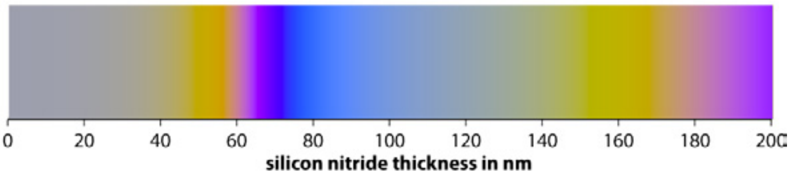

Figure 24: *optical interference colours for* SiN_2

Figure 25: *art-object designed by Maxime Christiaensen*[24]

Combination of coatings and textures

Another method of creating contrast and aesthetic effects in (metallic) parts is to combine coatings and textures. In particular femtosecond lasers are highly effective to machine coatings, since the absence of heat input means there is no risk of delamination, cracks, melt zones and debris fields, which would otherwise damage the coating. In addition, the small spot size allows for machining inside a coating with only a few micrometres of thickness. Sirris created a functional demo piece to show this: a watch.

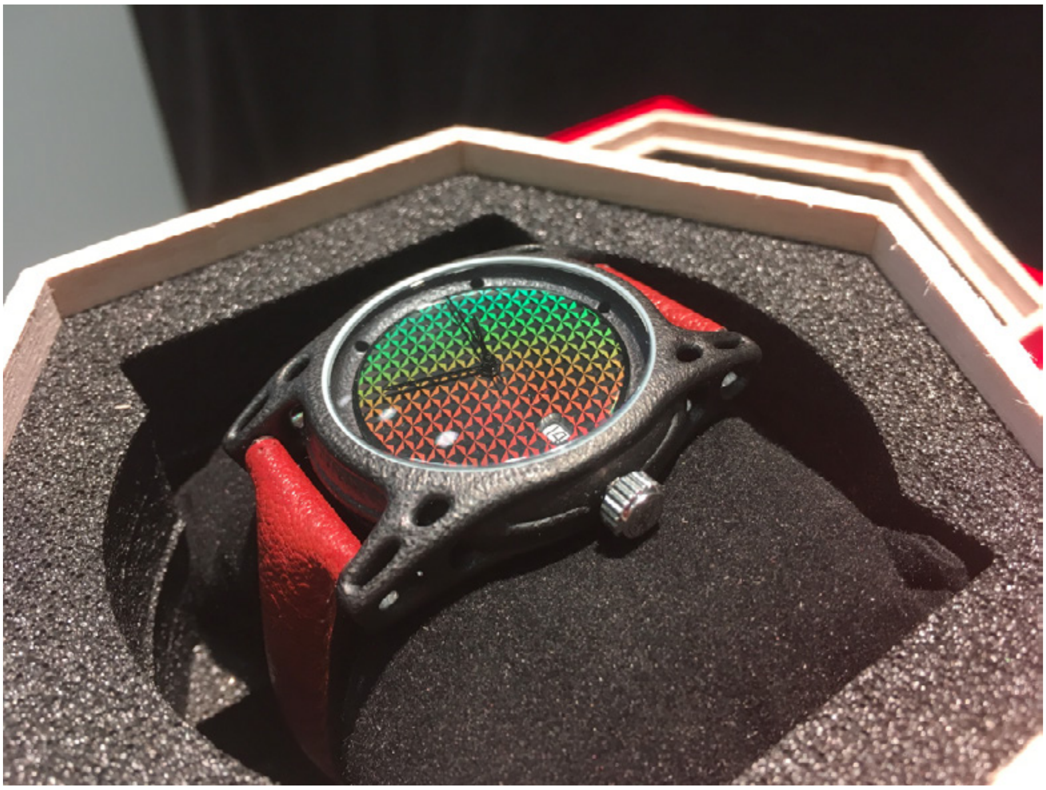

Figure 26: *Sirris watch with diffraction effect in CrCN coating*

This watch was 3D printed out of maraging steel, then finished using high-precision milling, to achieve tight tolerances for all the watch parts: the front glass, the backplate, the inner works and the dial. In order to protect the surface from wear and corrosion, a CrCN coating was applied. A Cr layer was applied first, to insure the proper adhesion of the ceramic and hard coating on the maraging steel.

To make the watch plate more appealing, a surface texture was required. However, this needed to be done in such a way that at least the Cr coating remained intact, in order to provide sufficient corrosion resistance over time: the watch plate cannot rust or show colouring over time. Using different laser parameters, a LIPSS structure was created halfway the coating, which created a diffraction effect ***(See Figure 26)***.

This project is supported, within the ERDF framework "Integration of 3D-metal printing", by the European Union, the Flemish Government, Flanders Innovation & Entrepreneurship (VLAIO) and the Province of Limburg.

	Gesteund bedrag
Europees Fonds voor Regionale Ontwikkeling	**€ 222.276,68**
Cofinanciering Vlaamse Minister Economie - Hermes	**€ 55.569,17**
Cofinanciering Provincie Limburg	**€ 111.138,34**
Totale kost	**€ 555.691,71**

6. Future outlook

In this casebook several novel surface functionalities have been shown and it is made clear that a wide range of potential applications and markets can benefit from the increasing value functional surfaces offer. The choice for either textures or coatings depends greatly on the desired function, application and production process requirements (batch vs in-line). A general outlook is that more and more advanced functionalities due to either coatings, textures or a combination of both will be developed, and this in such a way that application will be economically feasible.

A great example of these advanced functionalities can be for example anti-icing surfaces. Currently, there are textures which inhibit the formation of ice due to rain drops, however, ice formed by means of rime/condensation cannot be avoided by this. Novel nanotextures on the slopes of microtextures or a hydrophobic nanocoating will be needed to create a true icephobic surface. The potential application area of these surfaces is enormous, from wind turbine blades to aircraft wings, antennas, power lines and even rockets which are filled with LOX (Liquid Oxygen) can benefit from icephobic behaviour.

To achieve this a continuing research effort in research institutes, universities and end users is required. What is noticeable is that the quality of the functionalities is greatly depending on the technologies associated with either the coating or the texturing process. Therefore, the main trends in these fields will dominate the development of novel surface functionalities in the near future.

1. Trends in laser texturing

1. Increasing production speed

Laser texturing as a method to apply surface functionality, while inherently capable of delivering precise textures which offer enhanced functionalities, is currently limited from a process point of view. Recent advances in laser technology have already pushed the average power and frequency for ultrashort pulsed lasers from less than a single watt and a few kilohertz (early 2000s) up to more than 400 W and 100-200 MHz, which greatly increases the speed at which surfaces can be textured. However, even with these higher powered lasers, surface texturing is still limited to smaller components and smaller series. Markets such as that of the automotive need very short processing times to be competitive, while aerospace and wind energy sectors require the capability to texture very large areas (wings, nacelles, wind turbine blades, …). This required a multi-kW femtosecond laser, very high repetition rates and suitable optics to match these. It is expected that in the coming years the average power of ultrashort pulsed lasers will continue to increased due to an increased research and development effort.

In particular, multi-beam systems equipped with spatial light modulators (SLM's) can take advantage of these more highly powered lasers by covering lager areas more efficiently and therefore increase production speeds exponentially. Extremely fast galvometer scanning systems and polygon scanners are becoming available commercially. It is expected that within 5 to 10 years ultrafast laser beam sources of > 10 kW coupled with suitable optics are available, making direct mass production of functionalised parts economically competitive.

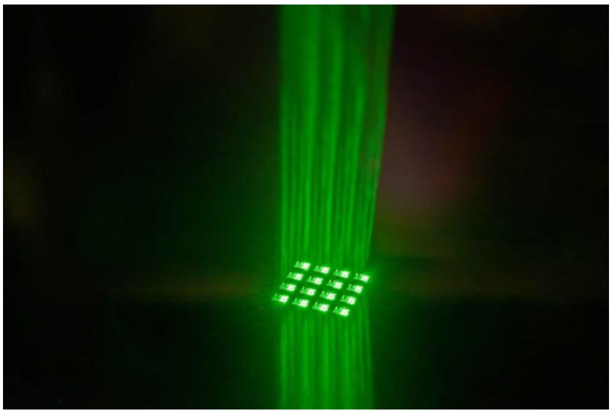

Figure 27: *Multi-beam ultra fast laser machining*[25]

In addition to these multi-beam technologies, hybrid laser processes can also greatly improve production speeds. A hybrid process uses nanosecond lasers to “roughly” machine a surface, which in general is a lot faster dan pico- or femto-second laser machining. In order to achieve sufficient quality levels, only the last steps are finished with pico- or femto-second lasers.

Lasers can also be used to texture rolls or dies, which on their turn apply the texture to millions of parts due to the roll-to-roll process or die-stamping process. These indirect methods, which also include injection moulding, are a cost effective method to mass-produce parts with laser textured functionality.

2. Increased integration

Ultrashort pulsed-laser texturing as a means of surface functionalisation is increasingly finding its place in modern production units. In particular, laser texturing can play an important role in the creation of so-called “superfunctional products”: products that combine multi-enhanced functionalities or properties given to it by means of the use of a series of production technologies and/or specific materials. Among them are:

- Surface functionality
- Geometric functionality
- Material functionality
- Smart functionality

Geometric functionality can be achieved by means of for example metal 3D printing. The possibility to create intricate geometries allows for enhanced component functionality. Think about adding cooling channels, weight saving due to topological optimisation, scaffolding that allows for increasing bone regrowth and so on. Material functionality refers to the basic material properties such as E-modulus, strength, damping, thermal and electrical conductivity and hardness, amongst others. Choosing the correct material for an application can result in added functionality. Last but not least, adding integrated sensory capability to components can make true smart products. Monitoring and control allows for example increased life expectancy of components by actively monitoring the strain levels and adapting the load accordingly.

Sirris has built a pilot plant in which all these technologies and knowledge has been combined to allow for the integrated production of additive parts, in combination with high precision milling, digital part tracking and data logging, femtosecond laser texturing, advanced coatings, polishing and thermal treatment, which allows the cost-effective fabrication of these superfunctional parts, which are particularly interesting for producers of producers of a lot of different high value parts with a lot of customisation and in which added value by functionalisation can provide a competitive advantage.

3. Digitisation in photonic manufacturing

Light is an extremely flexible "tool" when one considers making parts. Key parameters can be kept completely under control and verified digitally, there is no need for tools and in principle it does not matter if the lot size is small or large. Clamping of parts is often not required since no forces are applied to components during machining. The entire process can also be simulated, providing a digital shadow allowing quick and easy adaptations to the process.

This makes laser-based manufacturing, and in this case laser texturing, a very attractive fabrication method to be used in an Industry 4.0 context. Currently, when considering fabricating a part using ultrashort pulsed-laser manufacturing, a lot depends on the knowledge of the operator: which laser parameters, which speeds and which strategy does he need to apply to reach a texture geometry and consequently a functionality.

One of the trends we expect to see emerging in the coming years is the advent of self-learning laser-texturing machines which can, based upon a simple set of operations, learn correct laser parameters in order to create a certain surface texture. This surface texture can then on its turn be linked to a functionality determined in the CAD drawings supplied by the customer to program the laser pathways. The integration of measurement capability in the laser texturing machine, artificial intelligence or machine learning algorithms and a method to store large amounts of data are essential in this. This opens up ultrafast laser texturing as an affordable, easy to use way to functionalise parts to small SMEs who in general do not have a laser specialist at hand and allows easy optimisation of the part performance and quality in time.

4. Superior and novel functionalities

Academic literature, some of which is mentioned in this casebook, has proven to us that ultrashort pulsed-laser texturing allows for a broad range of surface functionalities. In particular, progressing beyond the use of lasers as a means of simply "milling" a surface to achieve novel functionalities. Some have already been shown in this casebook: LIPSS structures allow for grating effects or improved cellular adhesion It is expected that together with advances in laser technology and more fundamental research, more functionalities like these will be available.

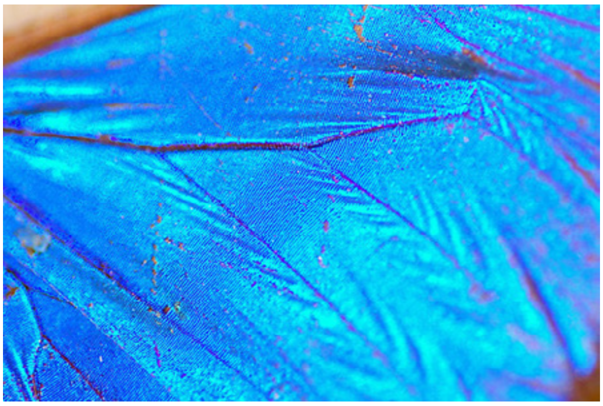

Figure 28: *Nano textured butterfly wing*

5. Trends in Coatings

1. Sustainable and eco-friendly coatings

Sustainability and eco-friendly are topics that come forward in a lot of sectors and industries and that is not any different with coatings. This comes forward in different aspects of coating development and application for which three important aspects are given below.

The majority of wet-chemical coatings today consist of a significant amount of **volatile organic compounds (VOCs)** but there is an ongoing effort to limit these products in coatings because they are polluting and not healthy when used indoor. However, limiting the VOCs results in a shorter drying time of the coatings which can have a negative effect on the flow and final look of the coating. New formulations have >

to be made to compensate for the low VOC content and alternative application techniques have to be found to deposit these coatings with the same results as the high VOC coatings used today.

Another issue is the REACH legislation which encompasses the registration of all chemicals used and sold in the European Union. Depending on the classification of the chemicals with regard to health and safety issues, some chemicals or additives will no longer be usable in future products and alternative sustainable and eco-friendly products or formulations have to be found in time to serve as an alternative for the withdrawn products. Research shows that is very challenging to develop eco-friendly products with the same functionality and properties when some substances can not be used anymore but there is no way back.

A third transition happening today is change towards the use of bio-based materials to develop coatings without going into competition with food production. Therefore, the focus is on bio-based scrap and waste material and the development of completely new bio-based raw materials. Important aspect is that these materials will be more expensive than traditional products so the quality that it brings should be at least as good as the product from today or it will be very difficult to get these products into the market.

2. Durability of protective coatings

Offshore applications such as wind turbines are growing fast and adequate coatings are necessary to protect these structures against environmental impact (corrosion, erosion, UV radiation, ice-formation). Improving the durability of coatings used in these applications is an important aspect as repair of coatings on off-shore structures is extremely expensive with a cost that is typically 100 times higher than a similar repair on land. New coating systems are expected to last more than 25 years before first maintenance should be necessary. Additionally, there is a demand for faster drying, lower thickness, fewer coats and ease of application.

Nowadays, the coatings which are used in applications requiring high durability are mostly epoxy and polyurethane based. We expect that in the near future coatings based on hybrid silicone technology and on fluoropolymers will further gain importance and will be more and more used for the most demanding applications. Both types of coatings have denser polymer networks and stronger molecular bonds, which increase their resistance against moisture and diverse chemical substances and make the coatings more resistant to UV radiation, high temperatures and severe weather conditions in general.

3. New functional and multifunctional coating properties

In addition to traditional protective and decorative coating properties, we have seen an enormous evolution in new functionalities and combinations of properties. This evolution is partially supported by developments in chemical nanotechnology allowing the development of coatings with an organic-inorganic hybrid structure in which molecular groups with new functionalities can be incorporated. This evolution will continue and is driven by particular needs in high-tech applications. We give three examples:

- Wind energy: a coating is needed to protect the blade edges from impacts of rain droplets and insects. Also suitable droplets and insects but also icephobicity is needed to prevent ice build-up on the blade, because of the danger of detached ice that is swept away over a large distance.
- For many small electronic equipments a continuous power source is desired. Energy harvesting coatings, based on thermo-electric or photovoltaic conversion offer here a solution.
- The development of smart products requires smart surfaces as well: coatings with built-in pressure or temperature sensors are developed and research is being done to integrate these coatings on the surface of products.

4. New coating technology

In the coating industry, there is an evolution towards more sustainable, more efficient and faster technologies. Especially in curing there is a trend from conventional curing by heating towards radiation curing techniques such as ultraviolet (UV and UV-LED) curing and electron beam (EB) curing. The radiation of specially developed (‘UV-curable’ or ‘EB-curable’) coatings results in a chemical reaction and instant curing. Compared to coatings that cure by solvent evaporation, these are energy-friendly techniques with almost no emissions of VOCs, a short curing time with reduced space requirement and an excellent quality finish. Where both techniques are mainly used for flat surfaces, the development of UV-LED techniques will in time broaden the range of applications towards 3D objects and energy efficiency becomes even better.

The development of dual cure coatings, which can cure with through exposure to UV light as well as to air, makes it possible to have a very efficient coating system with a high throughput of products in the production process. The high throughput is possible by curing the outer product surfaces with UV so they can be handled immediately in further processing steps, while the inner surfaces of the product can cure in time without risking defects through handling or other process steps.

In the future, more and more processes will be combined in hybrid techniques. Today for example, the decorative metallic parts in a car are plastic substrates coated with a metallic PVD (physical vapour deposition) coating which is in between a levelling primer coating and a protective transparent topcoat. As discussed before, the combination of coatings and textures can become very beneficial in creating functionalities such as easy-to-clean, ice-phobic surfaces, decorative aspects or smart electronic functionalities.

New coating technologies or renewed interest in existing technologies are also the consequence of legislation. For instance the phasing out of processes that use Cr^{6+} cause that the alternative coating techniques to increase the wear resistance of metal tools and components gain in importance or are further developed. Hard chrome layers can be deposited by newly developed Cr^{3+} processes or can be replaced >

by thermal sprayed coatings using the high velocity oxygen fuel process. Diffusive heat treatments to harden steel surfaces such as nitriding and nitrocarburising can be a valuable alternative, but also new, thin ceramic layers obtained by physical vapour deposition, sometimes in combination with plasmanitriding, are being developed to replace hard chrome. For local treatments or repair of eroded zones, the laser cladding technique is available and resulting layers are being improved.

5. Automation

Just as is the case in other industrial areas, the automation of processes is also an important aspect in the coating industry. Recent advancements have made the use and the affordability of robots also possible for small companies or job coaters. User friendly techniques have been developed to make programming and controlling the robots easily. The automation makes it possible to deliver constant quality on the product and over time, reduce overspray in spraying jobs and increase throughput.

Sirris has a state-of-the-art spray coating installation with a teach-by-demonstration robot which can easily be programmed to show you the possibilities what automation can mean for your products.

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