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Development of Superhydrophobic Coatings for Textile and Glass Surfaces

MASTER DISSERTATION

Maria Raquel de Vasconcelos Barros Jardim

MASTER IN NANOCHEMISTRY AND NANOMATERIALS

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Development of superhydrophobic coatings for textile and glass surfaces

Dissertation submitted to the University of Madeira in fulfillment of the requirements for the degree of Master in Nanochemistry and Nanomaterials

by Maria Raquel de Vasconcelos Barros Jardim

Work developed under the supervision of
Professor Doutor João Manuel Cunha Rodrigues
in cooperation with the company

Extermínio - Higiene Control, Lda

Faculdade de Ciências Exatas e de Engenharia,

Centro de Química da Madeira,

Campus Universitário da Penteada,

Funchal–Portugal
February 2018

In partnership with:

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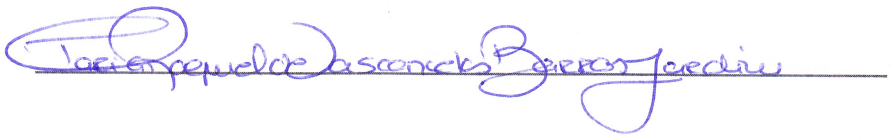

Dedication

In memory of Sr. António Sales Caldeira.

Thank you for believing and taking chances.

You will always be remembered.

ACKNOWLEDGEMENTS

This thesis was only possible with the help and support of many people to whom I am entirely grateful:

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- To my father, mother, sisters, and brothers-in-law. They know why;
- To husband André and my son Manuel for all the patience and encouragement and because without you nothing would make sense.

My deepest gratitude to you all.

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ABSTRACT

Superhydrophobic surfaces have been widely explored by the scientific community and commercial market due to their remarkable properties as these surfaces are expected to repel water and show self-cleaning properties. These surfaces induce the beading of water drops, repelling them and dragging the accumulated dirt on the surface with them. This kind of surfaces has a wide range of applications.

The present study is the result of a partnership between a private company, Extermínio, and the R&D centre, CQM (a National Research Laboratory). The goal of this partnership was the development of a superhydrophobic coating that could be applied to already existing surfaces, namely textiles and commercial glass, in order to turn them into superhydrophobic surfaces with the aim of making them easier to clean and increasing their durability, consequently decreasing the chemical products consumption used in those processes. For textiles, the selected samples were table linen, namely 100% cotton samples, both white and coloured and 50%/50% polyester/cotton coloured samples, and for commercial glass samples, flat glass was chosen.

Different variables were considered when developing the coating solutions: pre-treated (chemically etched) and non-treated surfaces; different formulations but all silica-based (SiO_2 10nm, SiO_2 20nm and SiO_2-PDMS); diverse solvents system; different concentrations; coating methods (dip coating and spray coating); number of coating layers; durability of the coatings (1hour, 24hours and 2 months) and contact angle measurements (24hours and 2 months).

The different variables tested showed distinct results on both type of samples, but regarding the nanoparticles used, the SiO_2-PDMS nanoparticles were the ones that revealed the best results.

Lasting hydrophobic results were achieved for both type of samples ($\theta \geq 126°$) which is an indicator that these coatings will ease the cleaning process and increase the durability the surfaces. No superhydrophobicity was attained ($\theta = 180°$), and therefore no self-cleaning property is expected from these coatings.

The accomplished results are promising. More tests should be performed to understand the relationsip between the surface and the applied coatings.

The first part of this dissertation is the presentation of the project framework and motivation that lead to its development as well as the intended goals. The work methodology and its structure are also briefly explained.

The second part is dedicated to the theoretical introduction, in order to facilitate the concepts perception of this subject, starting with the historical perspective of superhydrophobic surfaces and its applications, as well as theoretical concepts as wettability and contact angle, surface roughness, contact angle hysteresis and measurements, as well as the creation of superhydrophobic surfaces.

On the third part, the materials and methods applied to the development of the laboratory activities are described.

The forth part is dedicated to explaining the choices of approach and also the presentation of the obtained results and its interpretation.

Lastly, the fifth part is about the conclusions of the present work, as well as the learning's and main difficulties found and some suggestion about future work that could be done to follow up the study carried out in this essay.

Keywords: Superhydrophobicity, Hydrophobicity, SiO_2-PDMS, Textiles, Glass, Contact angle

RESUMO

As superfícies superhidrofóbicas têm sido amplamente exploradas pela comunidade cientifica e pelo mercado devido às suas notáveis propriedades, nomeadamente por estas superfícies repelirem a água e apresentarem propriedades de autolimpeza. Superfícies deste tipo induzem a contração das gotas de água repelindo-as e arrastando consigo a sujidade acumulada nas superfícies.

O presente estudo é o resultado de uma parceria entre uma empresa privada, a Extermínio, e o Centro de I&D, CQM (Laboratório de Investigação Nacional), com o objetivo de desenvolver um revestimento superhidrofóbico que possa ser aplicado em superfícies já existentes, nomeadamente têxteis e vidro comercial, de modo a transformá-las em superfícies superhidrofóbicas e torná-las mais fáceis de limpar. Aumentando por isso a sua durabilidade e, consequentemente, diminuindo o consumo de produtos químicos utilizados nestes processos. Para os têxteis, as amostras selecionadas foram toalhas de mesa, nomeadamente amostras de 100% algodão, tanto brancas como coloridas, e de 50%/50% poliéster/algodão coloridas, e para as amostras de vidro comercial foi escolhido o vidro plano.

Foram testadas diferentes variáveis aquando do desenvolvimento das soluções de revestimento: superfícies pré-tratadas (quimicamente cauterizadas) e não tratadas; diferentes formulações porém todas à base de sílica (SiO_2 10nm, SiO_2 20nm e SiO_2-PDMS) diferentes sistemas de solventes; diferentes concentrações; diferentes métodos de revestimento (por imersão e por pulverização); número de camadas de revestimento; durabilidade dos revestimentos (1 hora, 24 horas e 2 meses) e medição de ângulos de contacto (24 horas e 2 meses).

As diferentes variáveis testadas mostraram resultados distintos em ambos os tipos de amostras. No que toca às nanopartículas utilizadas, as nanopartículas de SiO2-PDMS foram as que revelaram os melhores resultados.

Foram obtidos resultados hidrofóbicos duradouros para ambos os tipos de amostras ($\theta \geq 126°$), o que é um indicador de que estes revestimentos irão facilitar o processo de limpeza e aumentar a durabilidade das superfícies. Não foi alcançada superhidrofobicidade ($\theta = 180°$) e, portanto, não foi esperada nenhuma propriedade autolimpeza destes revestimentos.

Apesar dos resultados alcançados terem sido promissores para uma aplicação comercial deverão ser realizados mais testes para compreender a relação entre a superfície e os revestimentos aplicados e melhorar a formulação e o tratamento das superfícies.

A primeira parte desta dissertação é constituída pela apresentação da estrutura do projeto e da motivação que levou ao seu desenvolvimento, bem como os objetivos definidos. A metodologia do trabalho e o seu enquadramento são também brevemente explicados.

A segunda parte é dedicada à introdução teórica, de forma a facilitar a compreensão dos conceitos apresentados, partindo de uma perspetiva histórica das superfícies superhidrofóbicas e as suas aplicações, bem como os conceitos teóricos como molhabilidade e angulo de contacto, rugosidade da superfície, histerese do angulo de contacto e medições, bem como a criação de superfícies superhidrofóbicas.

Na terceira parte, estão descritos os materiais e métodos aplicados no desenvolvimento das atividades laboratoriais descritas.

A quarta parte é dedicada a explicar as abordagens escolhidas, assim como a apresentação dos resultados obtidos e sua interpretação.

Finalmente, na quinta parte são apresentadas as conclusões do trabalho, bem como as aprendizagens e principais dificuldades encontradas e algumas sugestões para futuros trabalhos a desenvolver neste estudo.

Palavras-chave: Superhidrofobicidade, Hidrofobicidade, SiO2-PDMS, Têxteis, Vidros, Ângulos de contacto.

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LIST OF ACRONYMS, ABBREVIATURES AND SYMBOLS

µL – Micro litre

BHT – Butylated Hydroxytoluene

Brenntsolv – 60/40% ethanol/2-propanol

CaO – Calcium oxide

CC – Cotton light pink coloured

CH_3 – Methyl group

cm – Centimeter

cm^3 – Cubic Centimeter

CQM – Madeira Chemistry Research Centre

CW – Cotton white

d – Droplet's diameter

DSA – Drop shadow analysis

f – Surface fraction

f_s – Solid area fractions

FTIR – Fourier-transform infrared spectroscopy

f_v – vapor area fractions

g – grams

g – gravitational acceleration

H_2Op – Production water

L – Liquid

l – liter

Lda. – *Limitada*

m – Mass

m^2 - square meter

n – the number of repetitions

nm – nanometer

Nº - number

°C – degree Celsius

PCW – polyester/cotton white

PDMS – Polydimethylsiloxane

R&D – Research & Development

Ref. – Reference

r– roughness factor

s – Solid

SEM – Scanning Electron Microscopy

SME- Small and Medium Enterprise

THF – Tetrahydrofuran

UV/vis – Ultraviolet-visible spectroscopy

v – vapor

v/v – volume per volume

w/v – weight per volume

α – sliding angle

θ – contact angle

θ_{app}– apparent angle

θ_r– receding angle

θ_{rough} - apparent static angle

θ_s– liquid/solid contact angles

θ_v– liquid/vapor contact angles

θ_a– advancing angle

γ_{LS}– solid/vapor surface tension

γ_{LV}– liquid/vapor surface tension

γ_{SV}– liquid/vapor surface tension

1. INTRODUCTION

1.1. FRAMEWORK AND GOALS

The dissertation herein presented is the result of a partnership between the Madeira Chemistry Research Centre (CQM) and the company “Extermínio - Higiene Control, Lda” (Extermínio).

Extermínio is a well-established and distinguished SME leader based in Madeira Island operating since 1990. The scope of Extermínio’s works and services is client-oriented pest control services and development of cleaning solutions made specifically to meet their client’s demands and needs. Among a wide range of clients, tourism linked activities are an important segment of Extermínio activity. This sector is a very demanding one being cleaning a crucial factor and, therefore, the company is always seeking for new approaches and solutions to meet the client’s needs.

From their client’s point of view, the fact of operating on an island where the sea breeze and air humidity are a constant, associated with the fact of seasoning peaks of tourist’s affluence through the year, increases the difficulties on maintaining the cleaning standards required as the cleaning process should always be fast, effective, efficient and safe. The biggest hindrances pointed by the clients are the maintenance of cleaning processes for textiles, namely table linen, for sanitary ware, such as showers cabinets and mirrors, and for window glasses because of the stains, limescale and salt depositions which can be hard and time-consuming to remove.

Hence, new viable alternatives are continuously being sought to accelerate the cleaning process without compromising the quality standards. In this quest, superhydrophobic and hydrophobic surfaces are an ideal solution as their cleaning process is easier and faster without compromising the standards and, also makes the process safer and environmentally friendly as it decreases the number of chemicals used in this process.

Many superhydrophobic solutions can be found on the market nowadays. However, most of them require special equipment and techniques for their application or are towards the manufacturing of the surfaces with superhydrophobic or hydrophobic characteristics instead of coating existing ones. Also, the importing costs of these products in large scale to the island make its application unviable due to its high costs.

Because of the market analysis, Extermínio decided to start its quest to develop a superhydrophobic coating solution. Therefore, partners with the capacity of innovation and research were sought, and CQM stood out.

CQM is a research and development (R&D) centre from University of Madeira, supported by the Fundação para a Ciência e a Tecnologia (FCT) with a stated, solid and peer-recognized reputation due to its researches and scientific contributions throughout the years.

This partnership's desired outcome was the research of new cleaning solutions involving superhydrophobic coatings by trying to use as many of the available resources at Extermínio, namely raw materials, techniques, equipment and final products. The goal was to develop a superhydrophobic coating for targeted surfaces that when applied should retard or prevent the soaking and staining (on textiles) and dirt, salt, and limescale deposition (on sanitary ware and windows) which would translate on easy-to-clean and more durable surfaces.

Due to unforeseen reasons, the project had to be divided into two phases and conducted by different researchers. The first phase was focused on textiles (table linen) and the second phase continued the tests on textiles, but glass surfaces were also targeted. This second phase of the project was the base for the present dissertation.

1.2. WORK METHODOLOGY

To develop a coating product as requested, a work plan was made, which started by researching commercial products that already exist in the market, its application methods and features. The theoretical research was done to know which techniques were accessible for hydrophobic coating on existing surfaces and what kind of available materials could be used. After the selection of materials and techniques according to the settled parameters defined by the partners, non-systematic and systematic tests were performed, using as samples, 100% cotton (both white and coloured textile samples) and 50/50% polyester/cotton textile samples and commercial glass.

Then, assays were performed to evaluate the influence of working with pre-treated and non-treated surfaces, the influence of the number of coating layers, the influence of solution’s concentration, treated samples contact angles, the durability of the coating throughout time and if the results are preserved after washing.

1.3. DISSERTATION STRUCTURE

The first part of this dissertation is the presentation of the project framework and motivation that lead to its development as well as the intended goals. The work methodology and its structure are also briefly explained.

The second part is dedicated to the theoretical introduction, in order to facilitate the concepts perception of this subject, starting with the historical perspective of superhydrophobic surfaces and its applications, as well as theoretical concepts as wettability and contact angle, surface roughness, contact angle hysteresis and measurements, as well as the creation of superhydrophobic surfaces.

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2. THEORETICAL

2.1. HISTORICAL PERSPECTIVE ON HYDROPHOBIC SURFACES

The terms hydrophobicity and hydrophilicity come from the combination of Greek words *hydro* that means water and *phobicity* meaning absence of affinity or *philicity* meaning affinity.[1]

Many examples of natural occurring hydrophobic surfaces can be found, such as plant leaves, bird feathers, insect wings, among others. These surfaces have been very appealing to the scientific community due to their unique properties as they show not only great water repellency but also self-cleaning properties. When a water droplet is placed in contact with those surfaces, it will be highly beaded taking the dirt particles with it and leaving the surface clean and dry.[1–5] The most well-known and studied example is the Lotus leaf that shows great water repellency and self-cleaning properties which are associated to the superficial roughness of the leaf's surface.[3,4]

The first and more important studies about the increased hydrophobicity of surfaces were developed in the first half of XX century by Wenzel, Cassie, and Baxter who purposed different theoretical models to explain the superhydrophobic phenomenon.[2,6]

In 1997, Barthlott and Neinhuis reported the existence of fractal structures on natural surfaces and made the association of this existence with the hydrophobicity behaviour of some natural structures namely the Lotus leaf. Their studies stated that the capacity of the Lotus leaf to repel water drops, even dew and fog also lead to the complete removal of particle contamination that would exist on the leaf surface, being this occurrence called the "Lotus effect".[3–5]

Figure 1. Lotus Leaf and Lotus Effect (adapted from Ref. 7)

These statements lead to an increase of the investigations on the superhydrophobic phenomenon in the past two decades. It has sparked interest in both the scientific community and the

commercial market because of its many applications. Research on this subject can be divided into three main categories, being one of them dedicated to the theoretical modelling of superhydrophobic surfaces; a second one devoted to the description of natural superhydrophobic surfaces; and a third one that has its focus in developing artificial superhydrophobic surfaces with plenty of study on biomimetic materials.[8] The markets invest mostly on this third category with the purpose of developing products and materials with superhydrophobic properties[8]. In the last decade, there has been a great increase of different solutions being commercially offered and patents filled on this subject.[9]

2.2. APPLICATIONS

Inspired on the Lotus effect, many researchers have been developing hydrophobic and superhydrophobic surfaces due to their potential in many different applications, such as self-cleaning, anti-corrosion, anti-fogging, oil repellency, anti-icing, drag reduction and anti-dust properties, among others.[10,11] Its applications are vast.

For textiles, hydrophobic and superhydrophobic surfaces have been developed to produce waterproof materials with enhanced performances going from waterproofing shoes, clothing, table linen and others with self-cleaning and long-lasting antibacterial properties.[12,13]

In the metal industry, granting hydrophobic properties to metals is a highly sought achievement because it can increase the metal corrosion resistance and this increment allows the metals to be exposed to environmental conditions for longer periods without sustaining damage.[13–16]

Making electronic devices such as mobile phones, watches, sensors, controllers, transistors, solar panels and other hardware devices superhydrophobic is the desired accomplishment as it would prevent damage to these devices when exposed to water.[13,17–19]

Many coatings like paints, polishes and others coating materials include hydrophobic materials to grant them self-cleaning and anti-corrosion properties.[20]

Many other applications can be applied to this kind of materials in different fields such as health, medical appliances, solar energy, etc.[13,21]

2.3. WETTABILITY AND CONTACT ANGLE

One of the properties that is often evaluated on solid surfaces is their wettability. The wettability of a surface is the ability of liquids to spread out, or not, onto a surface. The term hydrophilic refers to a surface that easily wets by a liquid, and the term hydrophobic is used for surfaces where the water is repelled. This property is a consequence of the intermolecular interactions between the liquid and the surface and can also be related to the surface energy and roughness.[22]

A drop is formed by the superficial tension of a liquid. Considering a pure liquid, each molecule present is pulled with equal forces in every direction by the surrounding molecules resulting in a net force equal to zero. When a liquid is in contact with a surface, the molecules that are exposed at the surface are not surrounded in every way by identical molecules and are pulled into the interior, as it can be observed in Figure 2, creating internal pressure and forcing contraction of the liquid surface in order to keep the minimum surface energy. This intermolecular force is known as surface tension.[22–24]

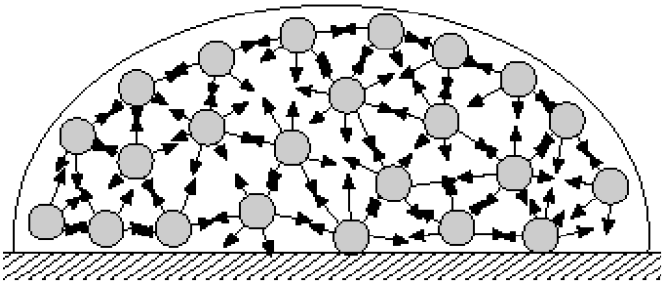

Figure 2. The Superficial tension of a liquid in contact with a surface. (adapted from Ref. 23)

When in contact with an ideally solid surface (flat, rigid, smooth and chemically homogeneous) a static liquid drop forms a triple interface between the liquid (L), the solid (S) and the surrounding vapor (V). The contact angle (θ) is the angle formed between the solid surface and the drop of the liquid and can be determined by a balance between the three interfacial surface energy vectors: the liquid/vapor surface tension (γ_{LV}), the solid/vapor surface tension (γ_{SV}) and the liquid/solid surface tension (γ_{LS}), each represented by a vector at Figure 3.[24]

The vectors represent the balance of the forces acting in the triple point interface, and their relation is given by Young's equation:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}}$$

Equation 1

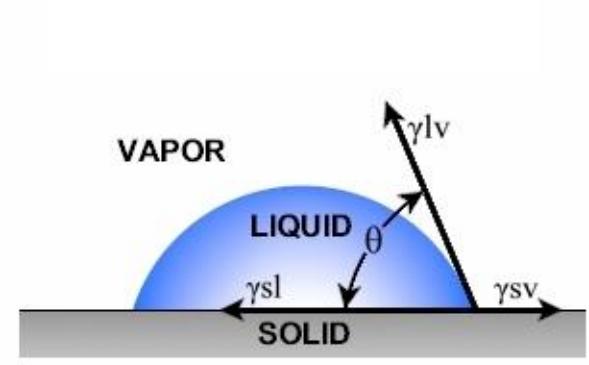

Figure 3. Balanced contact angle between a triple interface between the liquid (L), the solid (S) and the surrounding vapor (V). (adapted from Ref. 25)

From a macroscopic viewpoint, the wettability of a surface can be determined by the contact angle which is the measurement of the angle formed between the liquid and the solid.

Regarding wettability, and when using water as a liquid, the surfaces can be classified as hydrophobic if the contact angle is higher than 90° or hydrophilic if the surfaces with contact angles higher than 180° are classified as superhydrophobic and if the contact angle is 0° then the surface is called superhydrophilic.[26]

Table 1. Wettability conditions of a surface by contact angle (θ) measurements (Figures and table concept has been taken from Ref. 26)

Optical Representation	Macroscopic Result	Contact Angle	Energetic Relationship
	Non-wettability (Superhydrophobic)	$\theta = 180°$	$\gamma_{SV} - \gamma_{LS} = -\gamma_{LV}$
	Low wettability (Hydrophobic)	$90° \leq \theta \leq 180°$	$\gamma_{SV} - \gamma_{LS} < 0$
	High wettability (Hydrophilic)	$0° \leq \theta \leq 90°$	$\gamma_{SV} - \gamma_{LS} > 0$
	Complete wetting (Superhydrophilic)	$\theta = 0$	$\gamma_{SV} - \gamma_{LS} = \gamma_{LV}$

2.4. IMPACT OF SURFACE ROUGHNESS ON WETTABILITY

Superhydrophobicity, or non-wetting surfaces, can be obtained by conjugating two parameters: the increase of surface roughness and the lower low surface energy.[27]

Despite Young's equation being considered assuming a flat, rigid, smooth and chemically homogeneous surface, the reality is that there are few solid surfaces that represent these properties at once. In fact, surface roughness is one of the most significant properties that should be taken into consideration when it comes to superhydrophobic behaviour of surfaces.[28]

Two different theoretical models stand out on explaining the superhydrophobicity phenomenon using roughness as a variable: Wenzel model and Cassie-Baxter model.

2.4.1. WENZEL MODEL

This model was described in 1936 by Robert Wenzel and suggests that when a water drop gets in touch with a rough surface, it will fill all its voids. Therefore, the surface area available to be in contact with the water is larger than if the surface was completely smooth[29,30], as it can be observed in Figure 4.

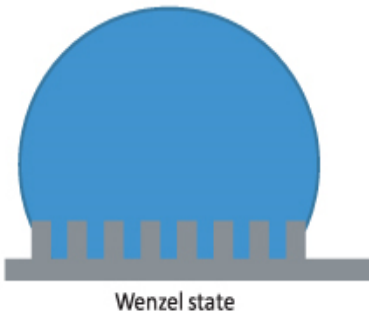

Figure 4. Wenzel model. (adapted from Ref. 31)

According to Wenzel, the roughness of a surface is a variable capable of increasing or decreasing the wettability of a surface. This model applies to static contact angle measurements and assumes that with an increase in the roughness of the surface area, the contact angle will also increase when compared to a smooth surface.[8,28]

In his research, Wenzel defines the roughness factor (r) as the ratio between the total area that is what the surface area would be if it was completely smooth and the projected area that is the area of the rough surface.[8,32]

$$r = \frac{real\ area}{projected\ area}$$

Equation 2

If the surface is rough, then $r > 1$ and if a surface is totally smooth then $r = 1$.

Wenzel defined the contact angle on a rough surface as:

$$\cos\theta_{rough} = \frac{r\,(\gamma_{SV} - \gamma_{LS})}{\gamma_{LV}} = r\cos\theta$$

Equation 3

where θ_{rough} represents the apparent static angle that is the angle associated to the rough surface. r represents the roughness factor, and θ represents Young's contact angle (the angle formed if the surface was totally smooth).[28,29]

2.4.2. CASSIE-BAXTER MODEL

Cassie-Baxter model was proposed in 1944, and it assumes that when water gets in contact with a rough surface, it relays on air that gets trapped between the water and the surface as it can be observed on Figure 5.

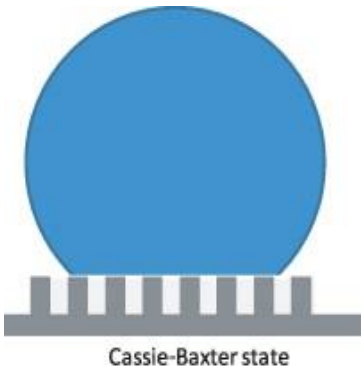

Figure 5. Cassie-Baxter model. (adapted from Ref. 31)

According to Cassie-Baxter model, the liquid interface consists in two different interfaces: the liquid-solid interface and the liquid-vapor interface and each interface presents a different contact angle.[32,6] Therefore, the apparent contact angle is the sum of these different contributions, and it is given by the Cassi-Baxter equation:

$$\cos\theta_{app} = f_s cos\theta_s + f_v cos\theta_v$$

Equation 4

where θ_{app} is the apparent angle, f_s and f_v represent the area fractions of solid and vapor on the surface and θ_s and θ_v represent the contact angles for the liquid-solid and liquid-vapor, respectively.

For superhydrophobic surfaces, $\theta_v = 180°$ because the water drop is in contact with the surface fractions and the air pockets between the roughness of the surface. As f_s and f_v are the fractions that compose the surrounding and that have contact angles θ_s and θ_v respectively, it can be concluded that $f_s + f_v = 1$.[8] Therefore, the equation can be written as:

$$\cos\theta_{app} = f(1 + \cos\theta) - 1$$

Equation 5

where f represents the surface fraction that is in contact with the water drop and θ represents Young's contact angle.[28,29]

2.5. CONTACT ANGLE HYSTERESIS

A contact angle can be dynamic while it is spreading onto a surface. Hysteresis means the capacity of a system to preserve a deformation induced by a stimulus. The contact angle hysteresis is the measurement of the adhesion of the drop to the surface.

There are two ways that can be used to measure the contact angle hysteresis: the first is a volume changing method, done on a horizontal plan and measures the difference between the advancing and receding contact angle; the second is done on tilting support and measures the sliding angle.

On the first case, the advancing and receding contact angle is measured on a horizontal plan, and the difference between the expansion and the contraction of the drop is calculated.

The advancing contact angle is obtained by measuring the contact angle of the drop until it hits its maximum value before the liquid-solid interfacial area increases, and the receding angle is measurement until the minimum value is obtained when pressure is applied. This schematic can be observed in Figure 6.

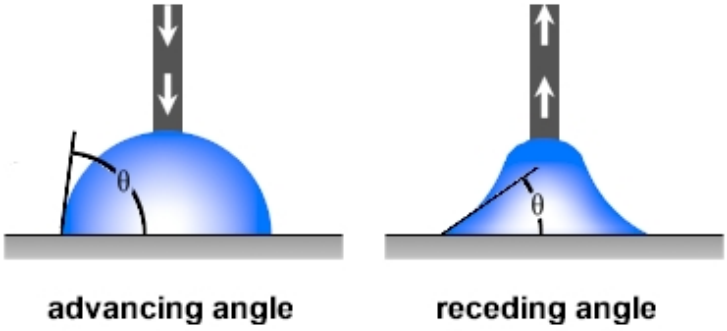

Figure 6. Advancing and receding contact angle measurement (adapted from Ref. 25)

Another way of measuring the contact angle hysteresis is by measuring the sliding angle. In this case, a drop is placed onto a tilted surface, and the sliding angle will be the minimum angle needed for the drop to start sliding. The lowest the angle, the poorer the adhesion of the drop to the surface and vice-versa.

A representation of the sliding angle hysteresis and contact angle can be observed in Figure 7 and its correlation can be quantified by the Equation 6:

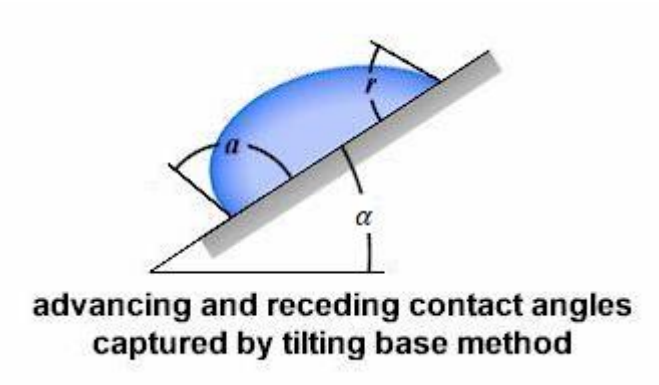

Figure 7. Sliding angle hysteresis on tilted support. (adapted from Ref. 25)

$$\frac{m\,g\,(sin\alpha)}{d} = \gamma_{LV}(cos\theta_r - cos\,\theta_a)$$

Equation 6

where α is the sliding angle, g is the gravitational acceleration, m is the mass of the droplet, d is the diameter of the droplet, γ_{LV} is the surface tension of the liquid, θ_r is the receding angle and θ_a is the advancing angle.

Thus, by analysing equation 6, it can be concluded that the sliding angle is dependent on the mass and diameter of the droplet. The lowest the sliding angle, and therefore the lowest hysteresis of contact angle, is translated as higher hydrophobic surfaces with a low tilted angle of the surface due to low adhesion of the droplet to the surface.[8]

2.6. CONTACT ANGLE MEASUREMENT

2.6.1. TECHNIQUES FOR CONTACT ANGLE MEASUREMENT

A variety of techniques are available for contact angle measurement and choosing between one of them can be a difficult task.

The techniques can be divided into two major groups: direct optical methods and indirect force methods.

The direct optical methods are methods that, as the name states, measurements that are made visually with the help of equipment and software. The equipment generally consists of a horizontal stage where the sample is assembled, a micro-needle used for drop deposition, light source and a camera with zoom.

In this category, it can be distinguished two types of methods as explained in Figure 8.

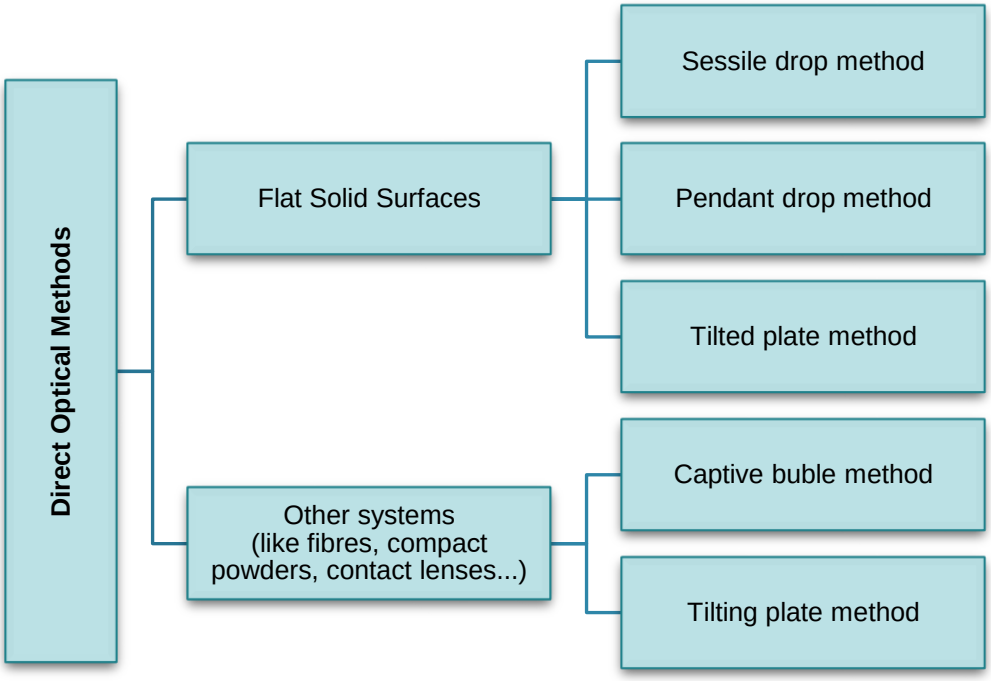

Figure 8. Schematic of the different types of direct optical methods for contact angle measurements. (adapted from Ref. 33)

When it comes to contact angle measurements, sessile drop method is the most commonly used method due to its simplicity, quickness and because it uses very small amounts of liquid as small surfaces are required. This method calculates the contact angle by the direct measurement of the tangent angle at the interface point on a static drop. However, because it can be performed using very small quantities of liquid and sample, it is more exposed to the interference of impurities. Several measurements should be made using this method and the value for contact angle is the average value.[29,33,34]

Pendant drop method consists of the deposition of a hanging drop as large as possible onto the sample[34], and it is used to measure the contact angle hysteresis. The tilted plate method is used to measure the sliding angle of a drop on a tilted plate, as the name implies.[33]

Captive bubble method and tilting plate methods are two different methods used to measure the contact angle of non-flat surfaces. The captive bubble method consists of immersing the sample in the liquid where an air bubble forms underneath the solid sample and the contact angle of the air bubble is measured.[33] This method applies to high-energy surfaces.[34]

The tilting plate method consists in having the plate sample rotating above the liquid surface, with one end gripped and allowed the plate to rotate towards the liquid. Once it gets immersed, with the gripped end outside, it will form a meniscus on both sides of the plate. The rotation should be made slowly until one of the meniscus gets horizontal on one side of the plate. (see Figure 9) The contact angle is the angle formed between the plate and the horizontal.[33,35]

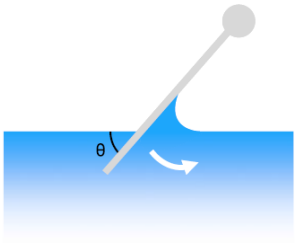

Figure 9.Tilting plate method. (adapted from Ref. 33)

For the indirect force methods, there are several approaches for the different applications namely Wilhelmy balance method; capillary rise at vertical plate method; individual fibre method; capillary tube method and capillary penetration method for powders and granules. The indirect force methods are used when the direct measurement of the contact angle is not viable because of the nature of the sample.[33,35]

2.6.2. DROP SHAPE ANALYSIS

When using a direct optical method, it is necessary to perform a drop shadow analysis (DSA). Most of the equipment is linked to software that does image analysis and measures the contact angle through the shadow image of a sessile drop. To do this measurement, a geometrical model describing the drop shape is fitted.[36]

To apply the geometric model and calculate the contact angle it is necessary to choose from different DSA models. The most common are the Circle method, the Conic section method, the Polynomial method, and the Young-Laplace method.[37]

The circle method assumes a drop shape in the form of a circular arc. For the conic section method, an elliptical drop shape is assumed. The polynomial method, also known as tangent method adapts to any drop shape as it assumes that the shape of any curve that can be thought of at the three-phase contact point. The Young-Laplace method fits symmetrical drop shapes considering the influence of gravity.

To choose between them it is necessary to evaluate the angle measuring range, the drop weight allowed, the deposition type and the contour shape of the drop as it can be seen in Table 2.

Table 2.Overview of the procedures to choose the most suitable DSA method. (adapted from Ref. 34)

		Circle method	Conic section method	Polynomial method	Young-Laplace-Fit
Assumed drop shape		Circular arc	Ellipse	No prior assumption	Ideal sessile drop
Recommended measuring range	0-20°	X			
	10-100°		X	X	X
	100-180°			X	X
Drop weight (Volume*Density)	Low	X	X	X	X
	High		X	X	X
	Very High			X	X
Dosing	Static (contour without needle)	X	X	X	X
	Dynamic (contour with needle)		X	X	
Contour shape	Symmetrical	X	X	X	X
	Slightly asymmetrical		X	X	
	Very asymmetrical			X	

2.7. CREATION OF SUPERHYDROPHOBIC SURFACES

Hydrophobic and superhydrophobic surfaces can be obtained through a wide range of methods as long as two premises are verified: the surface must be rough, and the coating should grant low surface energy.

Different methods are available for so, such as dip coating[38–40], physical or chemical etching[41–43], chemical bath deposition[44], electrospinning[45], lithography[46,47], templating[48], chemical vapor deposition[49,50], sol-gel processes[51], layer-by-layer deposition[47,52], spray coating[47,53–55], spin coating[52], brush coating[56,57], like many others.

For this work, the chosen methods were the chemical etching, dip coating and spray coating due to its simplicity and easy way of applying which meet the project requirements.

2.7.1. SILICON DIOXIDE (SiO_2)

Silicon dioxide, also known as silica, is a chemical compound composed of one atom of silicon and two atoms of oxygen, with a chemical formula of SiO_2. Being the most abundant mineral on Earth, it can be found as sand, quartz, or even as part of cell walls.

Taking into consideration the silica atoms arrangement, as it can be found in many different forms but always with same composition silica can be divided: crystalline or amorphous.

Crystalline silica has structures that form patterns that repeat themselves. Consists of a three-dimensional polytetrahedral structure ($[SiO_4]^{4-}$) where two oxygen atoms of one SiO_2 molecule are associated with the silicon atom of another SiO_2 molecule by Si-O-Si bridge. Amorphous silica has a more randomly linked chemical structure.[58,59,60]

The silanol groups existing on the surface of silica (i.e., Si-OH) are responsible for the silica reactivity.

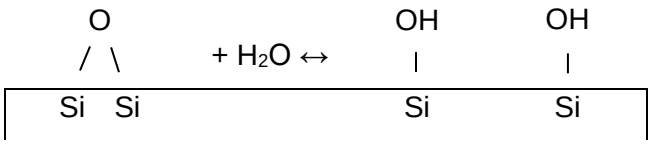

Figure 10. Representation of the equilibrium reaction on silica surface (adapted from Ref. 58)

Silica particles can be functionalized to become hydrophobic. Generically, this functionalization happens by the dehydration of the silanol groups and its substitutions with silanes. (See Figure 11). Hydrophobic silica is a form of silicon dioxide where hydrophobic groups can be chemically attached to its surface. These hydrophobic groups are normallyalkylorpolydimethylsiloxanechains.[61]

Figure 11. Representation of the dehydration reaction between the silica silanol groups and a silane forming hydrophobic silica.(adapted from Ref. 58)

2.7.2. POLYDIMETHYLSILOXANE

Polydimethylsiloxane (PDMS) is a polymer assembled by dimethylsiloxane monomers ($[SiO(CH_3)_2]$) (see Figure 12). Is part of the group of organosiloxanes also known as silicones and its chemical formula is $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$, where *n* is the number of repetitions of the monomer.

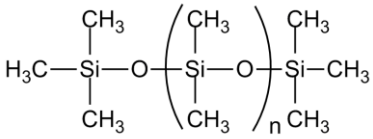

Figure 12. Structure of polydimethylsiloxane. (adapted from Ref.62)

PDMS is hydrophobic, inert, thermally stable and viscoelastic. Methyl groups (CH_3) can be found at its surface what confers it a low energy surface and also hydrophobic properties. Consequently, because of having low surface energy it also has poor adhesion to surfaces.[63]

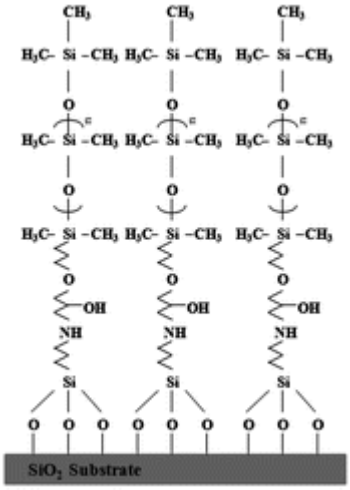

Figure 13. Schematic description of a PDMS layer coated onto the surface of SiO_2 substrate. (adapted from Ref.64)

3. MATERIALS AND METHODS

In this chapter, the materials and methods that were used in this project will be briefly described as well as the equipment and methodology applied for the experiments and contact angle measurements. The coating process and systematic experiments will be explained. Non-systematic experiments and general recipes can be found in Appendix A.

For practical experiments, some assumptions had to be considered: Extermínio wanted to use as many of their products, techniques and existing equipment as possible and the investigation should target the client's existing materials, as most of the clients would not want to invest in new materials, being textiles or glass. Therefore, different approaches were followed when taking these premises into consideration.

3.1. MATERIALS

3.1.1. SAMPLES

Two types of samples were used in this project: textiles, more precisely table linen and commercial window glass.

Three different table linens were tested: 100% cotton white coloured (100% CW) with flower patterns, 100% cotton light pink coloured (100% CC) with flower patterns and 50/50%polyester/cotton white coloured plain (50/50% PCW). These textiles were chosen because they are the most common in table linen used by hotels and the choice of testing white and coloured was to see if the coatings would stain the textiles.

All the textile samples were 20cmx20cm. Cotton samples (100% CW and 100% CC) had flower patterns on them, and the 50/50% PCW was plain.

Figure 14. Images of the textiles samples used in all systematic experiments. a - 100% Cotton (white); b - 100% Cotton (colour) and c - 50/50%Polyester/Cotton (white).

The glass samples used were from commercial windows, which are also known as flat glass. This type of glass is one of the most common and is called soda-lime silicate glass. Its composition is 16% sodium oxide (Na_2O) commonly added in the form of "soda" (sodium carbonate), 10% calcium oxide (CaO) commonly termed lime and 74 % silicon dioxide (SiO_2) also called silica. The SiO_2 is the glass former, the Na_2O is used as a flux to reduce the melting temperatures of silica, and the CaO is used as a stabilizer. Other additives can be found but in very small amounts. These proportions are in weight percentage and are an approximation.

3.1.2. MATERIALS

For this project, three types of silicon dioxide were acquired from PlasmaChem with the following specifications accordingly to the Technical Datasheet:

- SiO_2 - Nanoparticles, 10 nm, 30% aqueous suspension (SiO_2 10nm): Primary particle average size: ca.10 nm; Specific surface: ca. 320 m^2/g; Density: ca. 1,2 g/cm^3; Purity of solid component: > 99.5%; Admixtures: Na ca. 0,45%

- SiO_2 - Nanoparticles, 20 nm, 50% aqueous suspension (SiO_2 20nm): Primary particle average size: ca.20 nm; Specific surface: ca. 140 m^2/g; Density: ca. 1,4 g/cm^3; Purity of solid component: > 99.5%; Admixtures: Na ca. 0,25%

- Fumed silica, nanopowder, hydrophobic (SiO_2-PDMS): Primary particle average size: ca. 14 nm; Specific surface: ca. 100 m^2 /g; Bulk Density: ca. 0,05 g/cm^3; Purity: > 99,8% Modified by polydimethylsiloxane (PDMS)

As solvents, a 60/40% ethanol/2-propanol mixture commercially called ““Brenntsolv ML” (Brenntsolv) acquired from Brenntag (provided by Extermínio), and Tetrahydrofuran (stabilized with ~ 300 ppm of BHT for analysis) (THF) developed by PanReac were used. The water used in all experiments was obtained through reverse osmosis filters and is the water used at Extermínio for their productions, being called Production Water (H_2Op). Other solvents were tried such as Ethanol (Pro Analysis, 99.5%) from PanReac, 2-propanol (≥99.0%) from VWR, Triethanolamine (85%) from Univar and gamma-Butyrolactone from Acros Organics on SiO_2-PDMS solutions.

Meant for the etching process of the samples, for textiles, it was used sodium hydroxide pearls (NaOH) acquired from Brenntag, and for the glass surface etching, it was used a commercial product categorized as a surface cleaner developed by Extermínio called Destart. This product is composed manly by Hydrofluoric acid (up to 25%), ethoxylated alcohol (up to 10%) and a non-ionic surfactant.

3.2. METHODS

3.2.1. PRE-TREATMENT OF SAMPLE SURFACE

For most of the textile samples, the only pre-treatment performed was the cleaning of the textile with tap water and allowing it to dry at air temperature. Another approach was tried by chemically etching the textile fibres with a highly concentrated solution of sodium hydroxide (NaOH).

For the etching, previously cleaned textiles were dipped into a 380g/L NaOH solution for ten minutes and placed in an oven to dry at 120°C for four minutes. After, the textiles were washed abundantly with tap water to neutralize the NaOH solution and let dry at room temperature. This approach was adapted from Ref.[65].

For glass surfaces, the pre-treatment consisted of washing the surfaces with tap water and, in some cases, spraying them with Destart at 10% in H_2Op, allowing to settle for thirty seconds. After that application, they were abundantly washed with tap water to neutralize the product and let to dry at room temperature.

3.2.2. COATING METHODS

Due to the established premises, the coating methods available were limited. Therefore, dip coating (immersion) and spray methods (trigger spray) were the selected methods. For textiles, both methods were applied while on glass surfaces only the spray method was experimented.

Dip coating method was performed by immersing the textile on the chosen solution for about 5 minutes and allowing it to dry for at least 1hour at room temperature.

Spray method was applied by a traditional trigger spray, and the application pattern was according to the Figure 15.

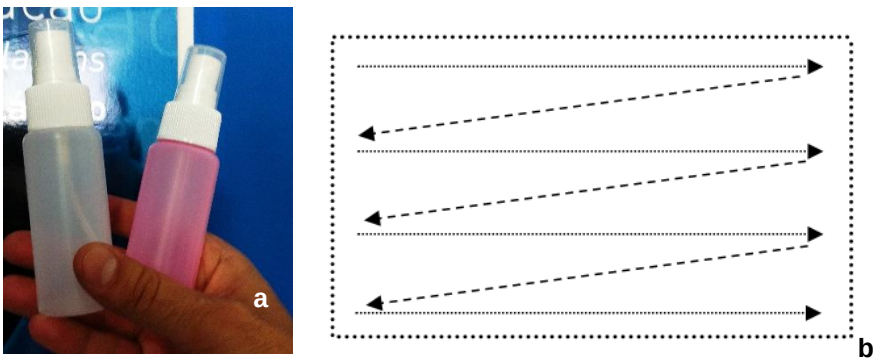

Figure 15. a) traditional trigger spray used on spray applications. b) application pattern applied in all experiments using spray coating method.

The influence of spraying distance was also tested on textiles.

The number of coating layers was another parameter tested. All the samples were able to dry for at least one hour before applying the next layer. On textile experiments, both methods were tried on different layers on the same sample.

Between layers, hydrophobicity was tested by applying a water drop on the sample with a Pasteur pipette and observing its behaviour. After applying the layers, the hydrophobicity tests were performed after one hour, twenty-four hours, five days and two months.

3.2.3. METHODOLOGY OF EXPERIMENTS

Non-systematic experiments trying different material/solvent systems were tried before choosing a systematic composition for textile and glass surfaces. Those experiments are documented in Appendix 1.

Due to the difference between samples, different approaches had to be taken, and different tests were applied.

3.2.3.1. TEXTILES SAMPLES

For textiles, the selected solutions were all tried on the three different types of textiles (100% CW, 100% CC and 50/50% PCW).

Different samples were prepared, to test variables such as different coating methods, the concentration of solutions, the distance of spray application and chemical etching of the textile.

Two layers of coating were applied to create a more homogeneous coating. After the application of each layer, the samples were allowed to dry at open air for at least one hour until the application of the next layer. Macroscopic tests done by naked eye were performed by laying a drop of water with the help of a Pasteur pipette and observing its behaviour on the textile's surface, for each layer. Contact angles were measured twenty-four hours after the last layer was applied and the again, two months after the coatings were applied.

After the tests and contact angle measurements, the textile samples that showed good hydrophobic effect were reproduced and washed with abundant tap water twenty-four hours after the last coating to see if they would maintain the acquired properties.

The methods are presented in table 3. Note that all these experiments were tried on the three types of textiles.

Table 3. Methodology used on textile coatings

Textile coatings						
Samples	**#**	**Application Method**	**Materials (% w/v and v/v%)**	**Solvent**	**Nº of coating layers**	**Experimental**
100% Cotton White 100% Cotton Coloured 50/50% polyester/cotton white	**A**	Spray method	SiO_2-PDMS 0.5%	"Brenntsolv"	1 2	- Application 15cm distance from sample; - 1 hour drying between layers
	B	Spray method	SiO_2-PDMS 0.5%	"Brenntsolv"	1 2	- Application near the sample; - 1 hour drying between layers
	C	Spray method	SiO_2-PDMS 0.25%	"Brenntsolv"	1 2	- Application 15cm distance from sample; - 1 hour drying between layers
	D	Spray method	SiO_2-PDMS 0.25%	"Brenntsolv"	1 2	- Application near the sample; - 1-hour drying between layers
	E	Dip Coating method	SiO_2-PDMS 0.5%	"Brenntsolv"	1 2	- Immersion for 5 minutes - 1hour drying between layers
	F	Dip Coating method	SiO_2 (20nm) (aqueous) 1% SiO_2-PDMS 0.5%	H_2Op "Brenntsolv"	1 2	- Immersion for 5 minutes - 1hour drying between layers
	G	Dip Coating method	SiO_2 (10nm) (aqueous) 1% SiO_2-PDMS 0.5%	H_2Op "Brenntsolv"	1 2	- Immersion for 5 minutes - 1hour drying between layers
	H	Spray method	SiO_2-PDMS 0.5%	"Brenntsolv"	1	- The textiles were chemically etched as pre-treatment - Application near the sample; - 1-hour drying between layers
	I	Dip Coating method	SiO_2-PDMS 0.5%	"Brenntsolv"	1	- The textiles were chemically etched as pre-treatment - Immersion for 5 minutes - 1 hour drying between layers

3.2.3.2. GLASS SAMPLES

For glass surfaces, the first solutions prepared were similar to the ones used on textiles, but protocol adapted fro Ref. 66 was also tested using ethanol and THF as co-solvents. For this approach, different proportions of the solvents were tested, as well as the order of solvent addition. Every test was performed on surfaces with no pre-treatment (not etched) and on surfaces that were chemically etched.

Only SiO_2-PDMS was tested for obvious reasons as the composition of glass is mainly SiO_2. Therefore, no different results should be expected from applying solely SiO_2 coatings on SiO_2 subtracts. The reason for not testing the distance of application is related to the mixture consistence and will be explained in results.

Due to the premises set beforehand, the coating method had to be spray coating as applying dip-coating, or other methods to a glass assembled on a wall or any other structure was not feasible. Due to the same reasons, curing the coating with heat or pressure was not viable.

Two layers of coating were applied to create a more homogeneous coating. A third layer was applied to perceive if more layers would make some change in the hydrophobicity of the surface. After the application of each layer, the samples were let to dry at open air for at least one hour until the application of the next layer. After the last layer, the samples were allowed to rest for twenty-four hours and then cleaned with a microfibre cloth.

Macroscopic tests done by naked eye were performed by placing a drop of water with the help of a Pasteur pipette and observing its behaviour on the surface. Contact angles were measured after twenty-four hours and two months after the coatings.

When the samples showed good hydrophobic effect, new samples were prepared using the same procedure and were washed abundantly twenty-four hours after the coating to test if the hydrophobic effect were resistant to washing or not.

The methodology used on glass surfaces can be seen on table 4.

Table 4. Methodology used on glass coatings

Glass Coatings				
#	Pre-treatment	Material (% w/v)	Solvents	Nº of coating layers
A	-	SiO_2 - PDMS 0.5%	Brenntsolv	3
B	Chemical etching	SiO_2 - PDMS 0.5%	Brenntsolv	2
C	-	SiO_2 - PDMS 3%	50% THF + 50% Brenntsolv	2
D	-	SiO_2 - PDMS 3%	33% THF + 66% Brenntsolv	2
E	-	SiO_2 - PDMS 3%	66% Brenntsolv + 33% THF	2
F	Chemical etching	SiO_2 - PDMS 3%	66% Brenntsolv + 33% THF	2
G	-	SiO_2 - PDMS 3%	80% Brenntsolv + 20% THF	2
H	Chemical etching	SiO_2 - PDMS 3%	80% Brenntsolv + 20% THF	2
I	-	SiO_2 - PDMS 2%	80% Brenntsolv + 20% THF	2
J	Chemical etching	SiO_2 - PDMS 2%	80% Brenntsolv + 20% THF	2
K	-	SiO_2 - PDMS 1%	80% Brenntsolv + 20% THF	2
L	Chemical etching	SiO_2 - PDMS 1%	80% Brenntsolv + 20% THF	2
M	-	SiO_2 - PDMS 0.5%	80% Brenntsolv + 20% THF	2
N	Chemical etching	SiO_2 - PDMS 0.5%	80% Brenntsolv + 20% THF	2

Since it was available at Extermínio, two glass samples were prepared with commercial products: one with CeNano Primer Sealant (V_A) acquired from “CeNano GmbH & Co. KG” and other with Nanopreserv CV (V_B) acquired from “NanoPreserv - Nanotecnologia aplicada, unipessoal, Lda”. Later, it was found out that this last company was no longer operational. Both solutions are specific for the use on glass surfaces. All the samples were prepared according to manufacturer instructions. Contact angles for these samples were obtained and compared with the glass experiments.

3.2.4. EQUIPMENT

The wettability of the surfaces was analysed by contact angle measurements performed by a KRÜSS DSA-100B Drop Shape Analyzer from KRÜSS GmbH and its DSA software (V1.92).

After the assembling of the sample on the stage, a drop of distilled water (volume of the drop = 5µL) was deposited on the top of the sample surface by a micro syringe coupled to the equipment and controlled by the software.

After the deposition, a picture was taken with the digital camera of the equipment, and the contact angles were found and calculated by the DSA software. The method for contact angle measurement used was the sessile drop method, and the contact angle calculations were made by the Young-Laplace fitting method. It was not possible to perform the contact angle hysteresis since the equipment was not prepared for so.

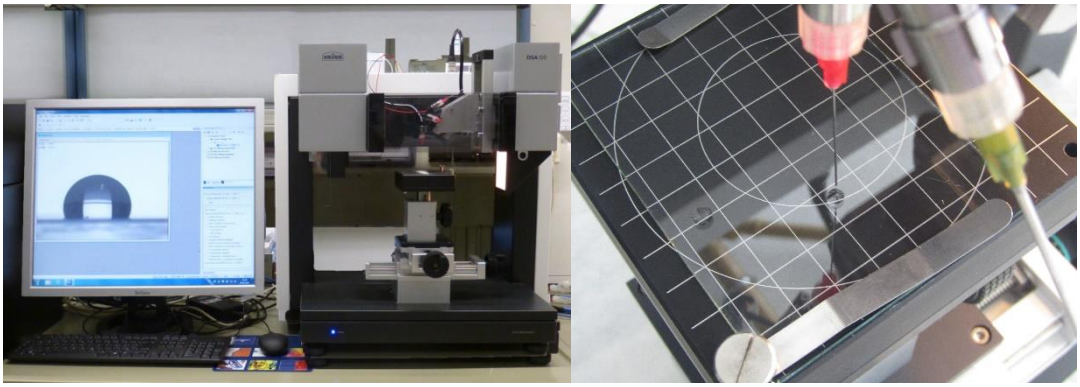

Figure 16. Kruss DSA 100 equipment.

Inverted Microscope Nikon Eclipse TE2000-E was also used to examine the dispersion of the textile fibres in each type of textile sample.

4. RESULTS & DISCUSSION

Different solutions were tried to find the most suitable system particles-solvent to apply the coatings. The method that raised more concerns was the spray method as some solutions clogged the spray.

SiO_2 10nm and 20nm were used as aqueous solutions. Although several attempts were performed for the preparation of a SiO_2-PMDS solution, most were unsuccessful. As solvents ethanol, 2-propanol, triethanolamine, and gamma-butyrolactone were tried. The last two solvents showed no satisfactory results because of the agglomeration levels of the powder in solution. When using ethanol and 2-propanol, it was possible to obtain a dispersion. As Brenntsolv is a 60/40% ethanol/2-propanol mixture and is available at the company, this was the solvent used for most of the experiments.

4.1. TEXTILES

The choice of solutions to use was a matter of available techniques, materials, and solvents.

Three types of silica were available: SiO_2 10 nm and SiO_2 20 nm, both in aqueous solutions, and SiO_2 modified by PDMS in the powder form. Finding a suitable solvent for the SiO_2-PDMS turned out to be a challenge as normally they are acquired in separate for hydrophobic coating purposes and then mixed.

After trying different solvents, some proposed by the manufacturer, others available at CQM and others from Extermínio, no stable solution was obtained. The best results obtained were by preparing a suspension composed by SiO_2-PDMS and “Brenntsolv”. The maximum concentration of SiO_2-PDMS that was able to be used with a trigger spray was 0,5% (% w/v). When the concentration was higher than this value, the trigger spray would clog. The obtained suspension was whitish, opaque and it was possible to observe powder sedimentation after some time. Therefore, the suspensions were always shaken before use to obtain the closest to a homogeneous dispersion as possible. The final look of the suspensions can be observed in Figure 17.

The three different textiles types were observed under the Inverted Microscope to closely observe how the fibres were dispersed in the textile. As the cotton textiles had flower patterns, those sections were also examined to see if there was a difference in the pattern of the fibres. The images were obtained in the bright field and with a 10X objective.

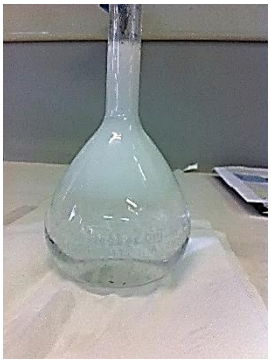

Figure 17. Photo was taken from the suspension of SiO_2-PDMS 0.5% in “Brenntsolv”.

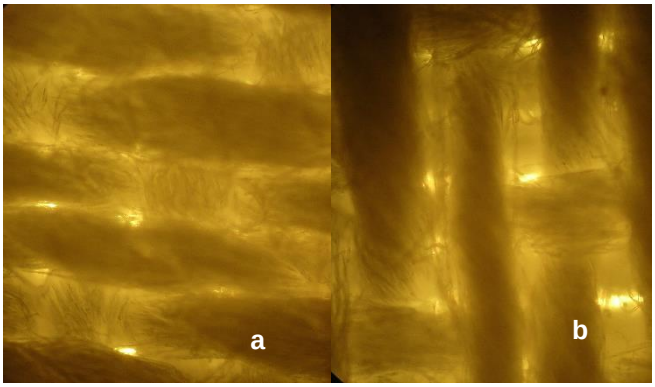

Figure 18. Images from 100% cotton (white) textile: a) general fibre b) flower motif at Inverted microscope (Bright filed, 10X).

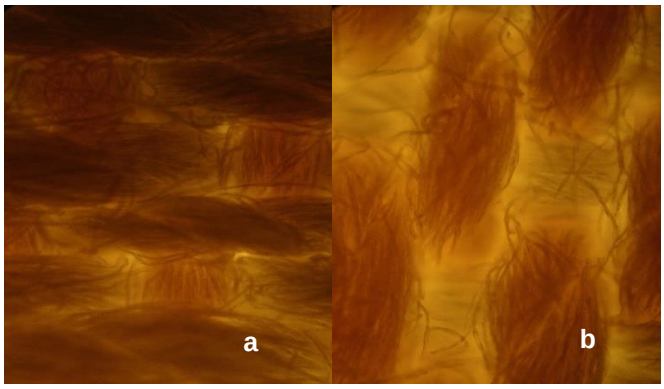

Figure 19. Images from 100% cotton (coloured) textile: a) general fibre b) flower motif at Inverted microscope (Bright filed, 10X).

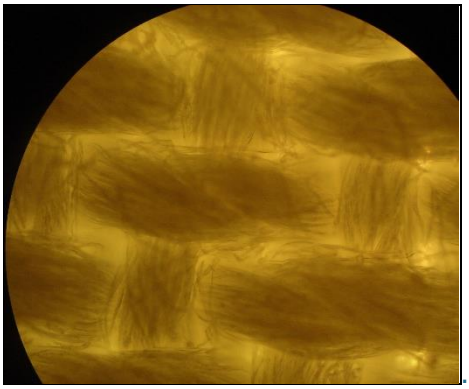

Figure 20. 50/50%polyester/cotton textile. at Inverted microscope (Bright filed, 10X)

As it can be observed, the fibres from all the textiles are intertwined, and no remarkable difference can be observed from the flower motifs and the general textile. Thus, no different results should be expected from these regions.

Behaviour analysis by simple eye inspection methods and contact angle measurements were performed to evaluate the wettability. The results of the measurements are summarized on table 5 for 100% Cotton White samples, on table 6 for 100% Cotton Coloured and on table 7 for 50/50% Polyester/Cotton White samples.

It is noteworthy that when the macroscopic tests were performed, and the results were “Medium”, the water drops were absorbed by the textile after a few seconds. The difference between marking a result as “Medium” or “Good” was whether the drops were absorbed or not. When possible, the contact angles for “Medium” samples were measured before absorption and gave similar values to the “Good” samples. When the macroscopic results are marked as “No” was because the drop was immediately absorbed by the textile or within few seconds after the drop deposition, which was the average time needed to measure the contact angle. The “Low” results are applied when the water drop was almost immediately absorbed by the textile, and therefore no contact angle measurement was possible.

Table 5. Resume of the results on hydrophobicity tests on textile 100% Cotton White

	#	Application Method	Solution	Nº coatings layers	Results observed with the naked eye after:				Contact angle	
					1 hour	*24 hours*	*5 days*	*2 months*	*24 hours*	*2 months*
100% COTTON WHITE	A	*Spray (15 cm distance)*	SiO_2-PDMS 0.5% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	B	*Spray (near the sample)*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	106°	110°
				2	Medium					
	C	*Spray (15 cm distance)*	SiO_2-PDMS 0.25% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	D	*Spray (near the sample)*	SiO_2-PDMS 0.25% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	E	*Dip Coating*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Good	Good	Good	118°	122°
				2	Good					
	F	*Dip Coating*	SiO_2 (20nm) 1% in H_2Op	1	Medium	Good	Good	Good	120°	125°
			SiO_2-PDMS 0.5% in Brenntsolv	2	Good					
	G	*Dip Coating*	SiO_2 (10nm) 1% in H_2Op	1	No	Medium	Medium	Medium	109°	115°
			SiO_2-PDMS 0.5% in Brenntsolv	2	Medium					
	H	*(Chemically etched previously)* *Spray near*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	*	*
	I	*(Chemically etched previously)* *Dip Coating*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	*	*

No - No hydrophobicity observed (immediately absorbed);

Medium - Some hydrophobicity was observed but the drops were partially or **totally absorbed by the textile** after a few seconds;

Good- Good hydrophobicity;

* - no contact angle measurement was possible because the textile absorbed the water drop too quickly.

Table 6. Resume of the results on hydrophobicity tests on textile 100% Cotton Coloured

	#	Application Method	Solution	Nº coatings layers	Results observed with the naked eye after:				Contact angle	
					1 hour	24 hours	5 days	2 months	24 hours	2 months
100% COTTON COLOURED	A	*Spray (15 cm distance)*	SiO_2-PDMS 0.5% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	B	*Spray (near the sample)*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	98°	110°
				2	Medium					
	C	*Spray (15 cm distance)*	SiO_2-PDMS 0.25% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	D	*Spray (near the sample)*	SiO_2-PDMS 0.25% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	E	*Dip Coating*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Good	Good	Good	120°	121°
				2	Good					
	F	*Dip Coating*	SiO_2 (20nm) 1% in H_2Op	1	Medium	Good	Good	Good	115°	119°
			SiO_2-PDMS 0.5% in Brenntsolv	2	Good					
	G	*Dip Coating*	SiO_2 (10nm) 1% in H_2Op	1	No	Medium	Medium	Medium	109°	118°
			SiO_2-PDMS 0.5% in Brenntsolv	2	Medium					
	H	*(Chemically etched previously)* *Spray near*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	*	*
	I	*(Chemically etched previously)* *Dip Coating*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	*	*

No - No hydrophobicity observed (immediately absorbed);

Medium - Some hydrophobicity was observed but the drops were partially or totally **absorbed by the textile** after a few seconds;

Good- Good hydrophobicity;

* - no contact angle measurement was possible because the textile absorbed the water drop too quickly.

Table 7. Resume of the results on hydrophobicity tests on textile 50/50%Polyester/Cotton White

	#	Application Method	Solution	Nº coatings layers	Results observed with the naked eye after:				Contact angle	
					1 hour	24 hours	5 days	2 months	24 hours	2 months
50/50% POLYESTER/COTTON WHITE	A	*Spray (15 cm distance)*	SiO_2-PDMS 0.5% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	B	*Spray (near the sample)*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	110°	115°
				2	Medium					
	C	*Spray (15 cm distance)*	SiO_2-PDMS 0.25% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	D	*Spray (near the sample)*	SiO_2-PDMS 0.25% in Brenntsolv	1	No	No	-	-	*	*
				2	No					
	E	*Dip Coating*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Good	Good	Good	122°	126°
				2	Good					
	F	*Dip Coating*	SiO_2 (20nm) 1% in H_2Op	1	Medium	Good	Good	Good	121°	123°
			SiO_2-PDMS 0.5% in Brenntsolv	2	Good					
	G	*Dip Coating*	SiO_2 (10nm) 1% in H_2Op	1	No	Medium	Medium	Medium	113°	117°
			SiO_2-PDMS 0.5% in Brenntsolv	2	Medium					
	H	*(Chemically etched previously)* *Spray near*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	*	*
	I	*(Chemically etched previously)* *Dip Coating*	SiO_2-PDMS 0.5% in Brenntsolv	1	Medium	Medium	Medium	Medium	*	*

No - No hydrophobicity observed (immediately absorbed);

Medium - Some hydrophobicity was observed, but the drops were partially or absorbed by the textile after a few seconds;

Good- Good hydrophobicity;

* - no contact angle measurement was possible because the textile absorbed the water drop too quickly.

As it can be observed in the tables 5, 6 and 7, the results for the different textiles types did not differ much from one to another. It was expected that the results were different for the 50/50% Polyester/cotton as the composition of the textile was different (at least 50% different) and because polyester is a hydrophobic polymer in nature. The only noticeable difference between the cotton textiles and polyester/cotton textiles was that on these textiles, when the drops were absorbed, it would take longer but even so, they would end up being absorbed not accomplishing the intended purpose.

When applying the spray method, two variables were tested: the spraying distance (15cm of distance from the textile or near the textile) and different concentrations (0,5% SiO_2-PDMS and 0,25% SiO_2-PDMS). Using the 0,5% concentration, when the spray was applied at 15 cm distance no hydrophobic effect was observed. Probably because at this distance, the suspension did not impregnate the textile deep enough to induce the hydrophobic effect. When the spray was applied near the textile, some hydrophobic effect was noticeable, but after a few seconds, the drop was absorbed by the textile. When testing the 0,25% concentration no hydrophobic effect was observed when using the spray method. No spray method was efficient to induce a lasting hydrophobic effect.

For dip coating methods, three different solutions were tested on different layers. When using two layers of SiO_2-PDMS at a 0,5% (% w/v) concentration and two layers, one of SiO_2 20nm at 1% (% v/v) followed by a layer of SiO_2-PDMS at a 0,5% (% w/v) concentration the final results were “Good” showing a lasting hydrophobicity. When using two layers, one of SiO_2 10nm at 1% (% v/v) followed by a layer of SiO_2-PDMS at a 0,5% (% w/v) the results were not satisfactory as hydrophobic effect was only noticeable when applying the second layer and the results were “Medium” as the drop was absorbed after a while. This leads us to assume that the hydrophobic effect was possibly induced by the second layer and the SiO_2 10nm solution had no influence. It was assumed that the nanoparticles were too small and went through the textile fibres.

The approach of chemically etching the fibres had the purpose of roughening the textile and consequently increasing the adherence and mechanical stability. However, this approach was not suitable for these kinds of textiles because after the etching and washing them abundantly with tap water, the aspect of the textiles was much different from the pristine textiles as it can be observed on Figure 21. In fact, all the textile samples shrank, become yellowish coloured and stiff. The stiffness decreased after abundantly washing them but not going back to pristine standards. The 50/50% Polyester/Cotton White sample was “rubbery” to the touch. Still, macroscopic tests were performed after the dip coating method with SiO_2-PDMS at a 0,5% (% w/v) concentration. This method induced a “Medium” result as the drops were absorbed after a while. Contact angle measurements were not possible to perform because the textiles were too much wrinkled and not easy to smooth and therefore it was not possible to distinguish the water drop from the background on the DSA software.

Concerning the number of coating layers, two showed good results and no more layers were tried because the textiles started to show some stiffness.

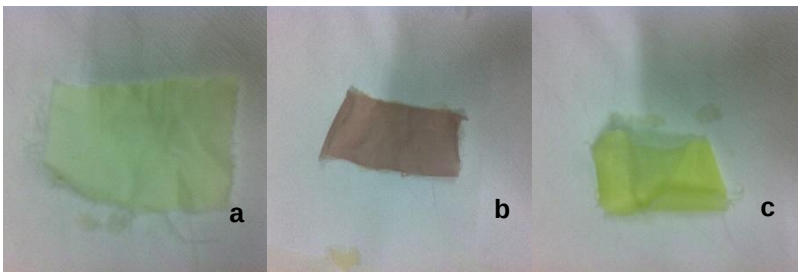

Figure 21. An aspect of the textiles after chemical etching. a) 100% Cotton White sample; b)100% Cotton Coloured sample; c) 50/50% Polyester/Cotton White sample.

The samples that showed good results were sampled E and F. Both samples were coated by dip coating method and had two layers. The first layer of the samples was different as E had a SiO_2-PDMS 0,5% coating and F had a SiO_2 20 nm coating, but both showed “Medium” results after the first layer. The second layer was equal for both samples.

After two months, the samples maintained the hydrophobic effect. Some images of the hydrophobic effect can be observed in Figure 22.

After all the tests, the textiles that showed “Medium” or “Good” results (samples B, E, F, and G) were hand washed like normal laundry to see if they would sustain the results. After washing, macroscopic tests were performed, and none of the samples preserved the results, absorbing the drop. This lets us conclude that the materials were not permanent bonded to the fibers.

No more tests were performed on textiles surfaces because the results were not the desirable regarding the durability after washing. THF approach was also not tested because of its toxicity and the use given to this kind of textiles would be a high risk if impregnated with THF.

Figure 22. Pictures of the hydrophobic effect on a sample of: a) 100% Cotton White sample; b)100% Cotton Coloured sample; c) 50/50% Polyester/Cotton White sample

4.2. GLASS SURFACES

For glass surfaces, only SiO_2-PDMS was tested.

Concerning the coating methods, spray coating was the chosen method as dip coating methods were not viable for the commercial application intended for these coatings mainly because most of the glass surfaces would already be assembled on an existing structure. The biggest concern for this application method was that the prepared solutions were, in fact, suspensions and when using higher concentrations than the ones that were used the trigger sprays clogged.

The first suspension chosen to try on glass surfaces was the one with better results on textiles (SiO_2-PDMS 0.5% in Brenntsolv). These tests were performed both on pre-treated (by chemical etching) and non-treated surfaces and both show very low hydrophobicity, probably because there was no adhesion of the suspensions to the glasses. (sample A)

New approaches were tried, being a big concern finding a solvent that would allow some dissolution of SiO_2-PDMS. After some research and due to availability, THF was tried as a co-solvent. In fact, the use of THF helped to form suspensions with a more homogeneous aspect. THF has a capacity to cause swelling of PDMS, but it had been used in other researches using SiO_2 and PDMS as a coating for superhydrophobic surfaces[66].Also, it has been studied that when in contact with an organic solvent with swelling capacity as THF, PDMS has the higher swelling rates during the first 15min and the rate of swelling decreases gradually until it reaches a steady state after 40 min. After the volatilization of the solvent, PDMS deswells[67,68].

When adding THF to SiO_2-PDMS powder, it would form a slurry, and when the Brenntsolv was added, the final suspension presented some clots (See Figure 23). The presence of the clots was not desirable; thus, another approach was tried.

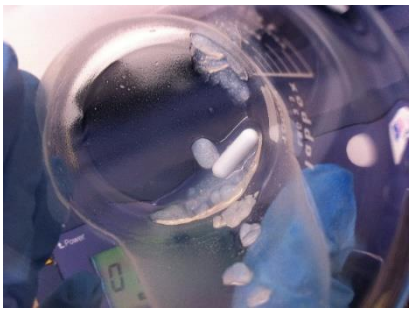

Figure 23. Clots presented on the suspension when THF was added before Brenntsolv.

It was decided to change the order of solvent addition by adding first the Brenntsolv and then the THF. When adding the Brenntsolv, the formed suspension was, like the textiles experiments, whitish, opaque and with sedimentation of particles. When adding the THF, it would become more

viscous and with a more homogeneous aspect (see Figure 24). Using this formula, the maximum concentration (% w/v) of SiO_2-PDMS allowed by the trigger spray was 3%.

Figure 24. An aspect of the suspension when using Brenntsolv and then adding THF.

After spraying the suspension onto the glass surface, a detail was observed: when spreading the suspension with the trigger spray, the coating was whitish and opaque (see Figure 25) in opposition to the commercial products available to test which were transparent and leaving no macroscopic residue. Despite it, the aspect of the prepared suspension was positive as it could be evaluated if the coating was homogenously distributed on the sample. Because of this aspect, different spray coating distances were not tried. All the samples were sprayed at 15 cm distance because if the distance were shorter the coating would be too much concentrated on the centre of the spray range and if it were farther, a full coverage would not be possible.

Figure 25. Aspect of the glass surface after the application of the coatings made of SiO_2-PDMS/Brenntsolv/THF

Between layers and after the last layer, a macroscopic test was performed by applying a water drop on the surface and evaluating its behaviour. The observations were recorded as “Low” if the drop spread easily, “Medium” if the drop showed some beading and “Good” if the drop was beaded. After the last layer coating, contact angles were measured. The results of the experimental tests are in table 8.

Table 8. Resume of the results on hydrophobicity tests on glass surfaces

#	Pre-treatment	Material	Solvents	Nº of coating layers	Hydrophobic behaviour examined by naked eye				Contact angle	
					1 hour	24 hours	5 days	2 months	24 hours	2 months
A	-	SiO_2 - PDMS 0.5%	Brenntsolv	1	Low	Low	-	-	29°	24°
				2	Low					
				3	Low					
B	Chemical etching	SiO_2 - PDMS 0.5%	Brenntsolv	1	Low	Low	Low	Low	40°	38°
				2	Low					
C	-	SiO_2 - PDMS 3%	50% THF + 50% "Brenntsolv"	1	Low	Low	Low	Low	81°	79°
				2	Low					
D	-	SiO_2 - PDMS 3%	33% THF + 66% "Brenntsolv"	1	Low	Low	Low	Low	80°	79°
				2	Low					
E	-	SiO_2 - PDMS 3%	66% "Brenntsolv" + 33% THF	1	Medium	Medium	Medium	Medium	86°	88°
				2	Medium					
F	Chemical etching	SiO_2 - PDMS 3%	66% "Brenntsolv" + 33% THF	1	Medium	Good	Good	Good	103°	101°
				2	Good					
G	-	SiO_2 - PDMS 3%	80% "Brenntsolv" + 20% THF	1	Medium	Medium	Medium	Medium	86°	83°
				2	Medium					
H	Chemical etching	SiO_2 - PDMS 3%	80% "Brenntsolv" + 20% THF	1	Good	Good	Good	Good	126°	119°
				2	Good					
I	-	SiO_2 - PDMS 2%	80% "Brenntsolv" + 20% THF	1	Medium	Medium	Medium	Medium	82°	80°
				2	Medium					
J	Chemical etching	SiO_2 - PDMS 2%	80% "Brenntsolv" + 20% THF	1	Medium	Medium	Medium	Medium	98°	92°
				2	Medium					
K	-	SiO_2 - PDMS 1%	80% "Brenntsolv" + 20% THF	1	Low	Low	Low	Low	38°	20°
				2	Low					
L	Chemical etching	SiO_2 - PDMS 1%	80% "Brenntsolv" + 20% THF	1	Medium	Medium	Medium	Medium	80°	76°
				2	Medium					
M	-	SiO_2 - PDMS 0.5%	80% "Brenntsolv" + 20% THF	1	Low	Low	Low	Low	28°	28°
				2	Low					
N	Chemical etching	SiO_2 - PDMS 0.5%	80% "Brenntsolv" + 20% THF	1	Low	Low	Low	Low	27°	30°
				2	Low					
V_A	-	CeNano Primer Sealant	Commercial	1	Good	Good	Good	Good	134°	132°
V_B	-	Nanopreserv CV	Commercial	1	Good	Good	Good	Good	121°	123°

Low - Low hydrophobic effect was observed;

Medium - Some hydrophobic effect was observed;

Good - Good Hydrophobic effect was observed

By examining the table 8 and the figure 26, it can be concluded that all the samples that were chemically etched had higher results than the ones that had no pre-treatment. The chemical etching had the goal of increasing the surface roughness and therefore the hydrophobicity effect, what seems to be accomplished. Regarding the concentration of the suspensions applied to the surfaces, there is a tendency of obtaining higher contact angles when the concentration is also higher.

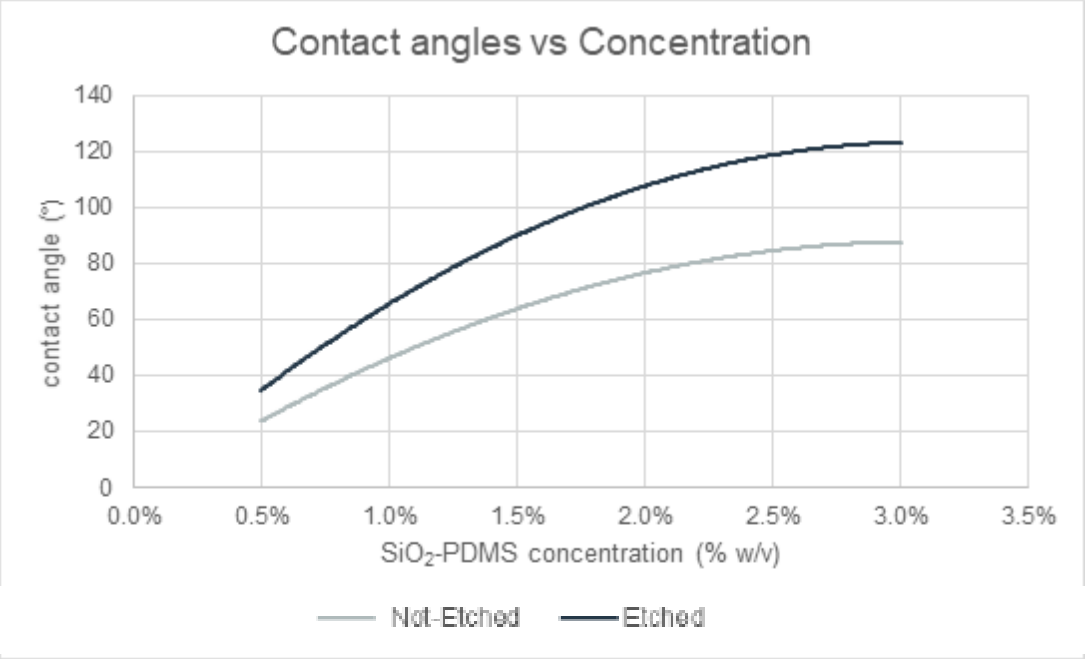

Figure 26. Development of contact angles with the increasing of the concentration of SiO_2-PDMS of etched and not-etched surfaces.

The very low hydrophobic effect was obtained when using only Brenntsolv as a solvent, in disagreement to what occurred on the textile samples. The reason for such was, probably, due to the fact of the textile's surface having a higher roughness and therefore this product would be enough to show some hydrophobicity on them. When using THF as a co-solvent, the hydrophobic effect increased but, despite helping the suspension aspect, altering the addition order of solvents did not have much impact on the contact angle.

The highest contact angles were obtained on sample F (SiO_2-PDMS 3% + 66% Brenntsolv + 33% THF with a contact angle of 103°) and on sample H (SiO_2-PDMS 3% + 80% Brenntsolv + 20% THF with a contact angle of 126°). When decreasing the THF percentage in the suspension, the contact angle increased. Probably because of the swelling effect that THF has on PDMS. Nevertheless, the data shows that the presence of THF is needed to induce a hydrophobic effect on these conditions possibly because of the swelling. To know the exact role of THF on the process, more characterization procedures should have been done. The hydrophobic effect is given by the

increase of the surface roughness and the use of PDMS that has low surface energy. Lower concentrations of SiO_2-PDMS like the ones used on samples M and N (0.5%) are not enough to grant hydrophobicity to the surfaces.

Regarding samples V_A and V_B, it was expected that those samples exhibited contact angles higher than 150°, once they were commercial products that claimed to be superhydrophobic. Remarkably, sample H had a contact angle within the contact angle range of these products.

Samples F and H were reproduced and washed abundantly under tap water twenty-four hours after applying the last layer. After washing, the samples remained with hydrophobic effect although with a lower value. Sample F showed a contact angle of 95° and sample H showed a contact angle of 111°. This demonstrates that there is some attachment, probably by electrostatic forces, between the coating and the surfaces. It is known that the coatings were not permanently bonded as for that to happen a cure of the coating should have been applied, probably by heating but this approach was not viable for commercial purposes as it would imply a much more complex method of application and waiting periods.

Although high hydrophobic results were attained on textiles and on glass surfaces, no superhydrophobicity was accomplished. Therefore, it is not expected for these coating to exhibit good self-cleaning properties.

Regarding glass surface characterization on Inverted Microscope, no image was obtained as it was not possible to observe anything pertinent for this study.

5. CONCLUSIONS AND OUTLOOKS

This project had the goal of developing superhydrophobic coating products for textiles and glass surfaces to be commercialised by the company Extermínio. These products should exhibit self-cleaning properties, and therefore, the consumption of chemical cleaning products to maintain these surfaces cleaned would be much reduced.

The premises for the project were to develop the coatings using as much of the available resources and technique existent in the company and that the products should be able to apply in situ, meaning, directly on client's facilities. Therefore, the materials and solvents used were the ones available that presented the best result possible.

The available materials for the hydrophobic coatings were SiO_2 10nm, SiO_2 20nm, and SiO_2-PMDS. SiO_2 is not hydrophobic by nature while PDMS is hydrophobic. Regarding the targeted textiles surfaces, 100% cotton textiles do not present any hydrophobicity on its own, while 50/50%polyester/cotton textiles should present some water absorbing resistance due to the presence of polyester. The use of SiO_2nanoparticles on textile coatings had the intention of allowing the SiO_2-PDMS to bind easily. The glass surfaces, mainly composed of SiO_2, are also not hydrophobic.

SiO_2 10nm and 20nm were already aqueous solutions, but using them without any other component was not a possibility because as it was not supposed to be used with heat or any other cure method, they would not link with the surfaces.

It was challenging to find a solvent that would allow the formation of a clear solution using the SiO_2-PDMS particles. Even after contacting the manufacturer and trying their proposed resolution, it revealed not being a viable approach. Different solvents were tried, but the best suspensions were obtained when using alcohols. As ethanol and 2-propanol did not show much difference when the suspensions were prepared, it was decided to use the Brenntsolv because of the availability of this product at the company. The solutions were in fact suspensions and using this solvent by itself, the maximum allowed concentration of SiO_2-PDMS usable was 0.5% (%w/v) before the trigger spray clogged. For textile surfaces, it was not an issue because when using this suspension on textiles, hydrophobic effect occurred and therefore no other solvents were tried. For glass surfaces, it was not the case. Thus, THF was added to the suspension. THF has the ability of swelling PDMS, but it is also extremely volatile. Its addition proved to help to form a slurry suspension and allowed to solve higher concentrations, up to 3% (w/v) of SiO_2-PDMS with no clots. However, the addition order of solvents played an important role as clots were formed when adding the THF before adding the Brenntsolv.

Dip coating methods and spray methods also showed different results on textiles. Dip coating method could not be tried on glass surfaces because it is not considered a practical method for surfaces already mounted on structures. For textiles, although spray coatings had some results when applied near the textiles, these results were not satisfactory as the water drops were absorbed after some time. Dip coating method revealed to be the best option for textiles exhibiting contact angles measurements of 120° and 115° when applying two layers of 0,5% SiO_2-PDMS in Brenntsolv or when applying the first layer of SiO_2 20nm followed by a second layer of 0,5% SiO_2-PDMS.

It was a concern if the textiles patterns would interpose on the coatings behaviours but they did show any different result from the textiles with no pattern. Also, no remarkable difference was noted on the various types of textile samples.

Regardless of having high contact angle results on textile samples, superhydrophobicity was not attained although hydrophobicity was observed. After washing the textiles with abundant water, the samples did not sustain the effect letting to conclude that there was no strong binding of the coatings and that this option is not feasible.

On the other hand, spray methods proved to be a good option for glass surfaces as high hydrophobic results were attained on some samples. The coatings composition of these samples is the same only changing the solvent ratios. It was concluded that when the lowest THF proportion was added, a higher contact angle was obtained. The reason for so is attributed to the influence of the swelling effect as less THF would lead to less swelling and ease the assemblage of the particles on the surface.

The approach of chemically etching also shows results on glass surfaces because they increase the surface's roughness. For textiles, this etching approach was not adequate as it damaged the textiles irreparably.

Regarding number of coating layers, two layers showed to have good results on both types of samples.

For textiles, the results were not the expected as the samples did not preserve the hydrophobic effect after being washed. For glass samples, even after washing, they were able to sustain the hydrophobic effect so it can be concluded that the coatings were linked to the substrate, probably by electrostatic forces as no pressure or heat was applied.

Without performing more assays, it is difficult to conclude about the relation between the surface and the coatings. Therefore, it is suggested that more characterization studies should be made:

- UV/vis Spectrometry should be performed to evaluate the produced samples transmittance and photocatalysis;

- FTIR analysis should be made to verify which compounds are present on the surface of the sample;
- SEM images should be observed to evaluate the roughness of pre-treated and not pre-treated surfaces if there is an aggregation of particles and the particles size;
- Contact angle hysteresis should be measured to complement the wettability studies.

Nevertheless, it is also suggested that for textile samples and glass samples, some premises should be changed, namely:

- SiO_2 and PDMS should be acquired separately and assembled as there remains the doubt of how the SiO_2-PDMS particles used on this project were modified;
- Air brush spraying should be applied to increase the dispersion of the particles;
- Heat should be tried, integrating it into the process to promote the cure and bonding of the coatings onto the substrate.

Future work based on the suggestions would be interesting to develop as it is a promising project.

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APPENDIXES

APPENDIX 1

Textile (Non-systematic experiments)

	Type	Color	Fibers	Acronym
1)	100% Cotton	White	Intertwined	100% CW
2)	100% Cotton	Color		100% CC
3)	50%-50% Polyester/Cotton	White		50/50% PCW

Sample Number	Sample Material	Layers	Method	Solutions Used	Results
1	100% CW	1	Spray	SiO_2-PDMS 1% in Ethanol	No Hydrophobicity
2	100% CW	1	Spray	SiO_2-PDMS 1% in Ethanol	No Hydrophobicity
3	100% CW	1	Spray	SiO_2-PDMS 0,5% in Ethanol	No Hydrophobicity
4	100% CW	1	Spray	SiO_2_PDMS 0,5% in Ethanol	No Hydrophobicity
5	100% CW	1	Immersion	SiO_2-PDMS 0,5% in Ethanol	No Hydrophobicity
6	100% Cw	1	Immersion	SiO_2 0,5% in Brenntsolv	No Hydrophobicity
7	100% CW	2	Immersion	1- SiO_2 0,5% in Brenntsolv 2- SiO_2 0,5% in Brenntsolv	No Hydrophobicity
8	100% CW	3	Immersion + Heat	1- SiO_2 20nm 1% in H_2Op 2- SiO_2-PDMS 0,5% in 2-propanol 3- SiO_2-PDMS 0,5% in 2-propanol	No Hydrophobicity
9	100% CW	3	Immersion + Heat	1- SiO_2 20nm 1% in H_2Op 2- SiO_2-PDMS 0,5% in Brenntsol 3- SiO_2-PDMS 0,5% in Brenntsolv	Low Hydrophobicity
10	100% CW	1	Spray	SiO_2-PDMS 0,5% in Trietanolamine + Brenntsolv	No Hydrophobicity
11	100% CW	1	Spray	Solugard®	Hydrophobic
12	100% CW	3	Immersion	1- SiO_2 20nm 1% in H_2Op 2-SiO_2-PDMS 0,5% in Brenntsolv 3- SiO_2-PDMS 0,5 in Brenntsolv	Low Hydrophobicity

Sample Number	Sample Material	Layers	Method	Solutions Used	Results
13	100% CW	1	Spray	SiO_2-PDMS 0,5% in 2-propanol	No Hydrophobicity
14	100% CW	1	Immersion	SiO_2-PDMS 0,5% in 2-propanol	No Hydrophobicity
15	100% CW	2	Spray + Heat	1- SiO_2 20nm 1% in H_2Op 2- SiO_2-PDMS 0,5% in 2-propanol	No Hydrophobicity
16	100% CW	2	Immersion + Heat	1- SiO_2 20nm 1% in H_2Op 2- SiO_2-PDMS 0,5% in 2-propanol	No Hydrophobicity
17	100% CW	2	Spray (apllyed 15cm from fabric)	1- Solugard® 2- Solugard®	Hydrophobic
18	100% CW	3	Immersion + Heat	1- SiO_2 20nm 1% in H_2Op 2- SiO_2-PDMS 0,25% in 2-propanol 3- SiO_2-PDMS 0,25% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
19	100% CW	3	Immersion + Heat	1- SiO_2 10nm 1% in H2Op 2- SiO_2-PDMS 0,25% in 2-propanol 3- SiO_2-PDMS 0,25% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
20	100% CW	3	Spray (near fabric)	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2-PDMS 0,5% in 2-propanol 3- SiO_2-PDMS 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
21	100% CW	3	Spray (apllyed 15cm from fabric)	1- Solugard® 2- Solugard® 3- Solugard®	Hydrophobic
22	100% CC	3	Spray (near fabric)	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2-PDMS 0,5% in 2-propanol 3- SiO_2-PDMS 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
23	50/50% PCW	3	Spray (near fabric)	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2-PDMS 0,5% in 2-propanol 3- SiO_2-PDMS 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)

Sample Number	Sample Material	Layers	Method	Solutions Used	Results
24	100% CW	3	Spray (apllyed 15cm from fabric)	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2-PDMS 0,55% in 2-propanol 3- SiO_2-PDMS 0,55% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
25	100% CC	3	Spray (apllyed 15cm from fabric)	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2-PDMS 0,5% in 2-propanol 3- SiO_2-PDMS 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
26	50/50% PCW	3	Spray (apllyed 15cm from fabric)	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2-PDMS 0,5% in 2-propanol 3- SiO_2-PDMS 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
27	100% CW	3	Spray (near fabric)	1- SiO_2-PDMS 0,25% in 2-propanol 2- SiO_2-PDMS 0,25% in 2-propanol 3- SiO_2-PDMS 0,25% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
28	100% CC	3	Spray (near fabric)	1- SiO_2-PDMS 0,25% in 2-propanol 2- SiO_2-PDMS 0,25% in 2-propanol 3- SiO_2-PDMS 0,25% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
29	50/50% PCW	3	Spray (near fabric)	1- SiO_2-PDMS 0,25% in 2-propanol 2- SiO_2-PDMS 0,25% in 2-propanol 3- SiO_2-PDMS 0,25% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
30	100% CW	2	Immersion	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
31	100% CC	2	Immersion	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
32	50/50% PCW	2	Immersion	1- SiO_2-PDMS 0,5% in 2-propanol 2- SiO_2 0,5% in 2-propanol	Some Hydrophobicity (absorbed after few seconds)
33	100% CW	3	Immersion	1- SiO_2 20nm 1% in H_2Op 2- SiO_2-PDMS 0,5%% in 2-propanol 3- SiO_2-PDMS 0,5% in 2-propanol	Hydrophobic

Sample Number	Sample Material	Layers	Method	Solutions Used	Results
34	100% CC	3	Immersion	1- SiO_2 20nm 1% in H_2Op	Hydrophobic
				2- SiO_2-PDMS 0,5% in 2-propanol	
				3- SiO_2-PDMS 0,5% in 2-propanol	
35	50/50% PCW	3	Immersion	1- SiO_2 20nm 1% in H_2Op	Hydrophobic
				2- SiO_2-PDMS 0,5% in 2-propanol	
				3- SiO_2-PDMS 0,5% in 2-propanol	
36	100% CW	2	Spray	SiO_2-PDMS + Y-butyrolactone 10% in H_2Op	No Hydrophobicity
37	100%CW	3	Spray	1-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	No Hydrophobicity
				2-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Very low hydrophobicity
				3-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Low hydrophobicity
38	100%CW	3	Immersion	1-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	No Hydrophobicity
				2-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Very low hydrophobicity
				3-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Low hydrophobicity
39	100%CC	3	Spray	1-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	No Hydrophobicity
				2-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Very low hydrophobicity
				3-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Low hydrophobicity
40	100%CC	3	Immersion	1-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	No Hydrophobicity
				2-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Very low hydrophobicity
				3-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Low hydrophobicity
41	50/50% PCW	3	Spray	1-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	No Hydrophobicity
				2-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Very low hydrophobicity
				3-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Low hydrophobicity
42	50/50% PCW	3	Immersion	1-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	No Hydrophobicity
				2-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Very low hydrophobicity
				3-SiO_2-PDMS 0,25% + Y-butyrolactone + H_2Op	Low hydrophobicity
43	100% CW	2	Immersion	1- Etching with NaOH	Low hydrophobicity
			Spray	2- SiO_2-PDMS 0,5% in 2-propanol	

Sample Number	Sample Material	Layers	Method	Solutions Used	Results
44	100% CC	2	Immersion	1- Etching with NaOH	Low hydrophobicity
			Spray	2- SiO_2-PDMS 0,5% in 2-propanol	
45	50/50% PCW	2	Immersion	1- Etching with NaOH	Low hydrophobicity
			Spray	2- SiO_2-PDMS 0,5% in 2-propanol	
46	100% CW	2	Immersion	1- Etching with NaOH	Low hydrophobicity
			Spray	2- SiO_2-PDMS 0,25% in Y-butyrolactone + H_2Op	
47	100% CC	2	Immersion	1- Etching with NaOH	Low hydrophobicity
			Spray	2- SiO_2-PDMS 0,25% in Y-butyrolactone + H_2Op	
48	50/50% PCW	2	Immersion	1- Etching with NaOH	Low hydrophobicity
			Spray	2- SiO_2-PDMS 0,25% in Y-butyrolactone + H_2Op	

TEXTILES: NON-SYSTEMATIC EXPERIMENTS – OBSERVATIONS AND CONCLUSIONS								
Textile	**Tested Liquid**	**Application Method**	**Solution**	**Procedure**	**Layers**	**Observed Effect**	**Conclusion**	**OBS**
100% cotton	Water	Spray	Ethanol +SiO_2-PDMS 1%	spray + 30 min to dry in hood	1º) SiO_2-PDMS 1%	Some hydrophobic effect but absorbed a few seconds later	Coating not strong enough; nanoparticles nor dispersed evenly along the textile sample; nanopowder not completely dissolve in ethanol	
		Spray	Ethanol +SiO_2-PDMS 1%	2x spray + 30 min to dry in hood	1º e 2º) 2x SiO_2-PDMS 1%	Some hydrophobic effect, some water drops rolled off the textile but absorbed a few seconds later	Better than the previous one but not enough	
		Spray	Ethanol +SiO_2-PDMS 0,5%	spray + 30 min to dry in hood	1º) SiO_2-PDMS 0,5%	No hydrophobic effect	Let more 10 min of drying. Still no effect. Seems the distribution of nanoparticle to be the major fact of not getting satisfactory results	Detected some yellow spots on the textile: textile was not clean.
		Immersion	Ethanol +SiO_2-PDMS 0,5%	Immersion 1 min + 40 min dry in the hood	1º) SiO_2-PDMS 0,5%	Some hydrophobic effect but not significant		
		Spray + Spray + Immersion	Brenntsol (ethanol 60%+2-propanol 40%) + SiO_2-PDMS 0,5%	spray + 40 min to dry in hood	1º) SiO_2-PDMS 0,5%	No hydrophobic effect		
				spray + dry in hood	2º) SiO_2-PDMS 0,5%	Some hydrophobic effect in some areas, but some drops were absorbed		
				Immersion 5 min	3º) SiO2-PDMS 0,5%	No significant changes		
		Spray + Spray + Spray	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,5%) in Brenntsolv + SiO_2-PDMS (0,5%) in Brenntsolv	spray + 2h to dry in oven 100º at horizontal position + 2h cooled ate open air at the bench	1º) SiO_2 20nm 1% PW	No test was taken	It was expected that SiO_2 would give textile more roughness, thus, more hydrophobic effect	Tested days after and still showing hydrophobic effect. Immersion Method showed amazing results after 3 days
				spray + 40 min to dry in hood	2º) SiO_2-PDMS 0,5%	Some hydrophobic effect but some drops were absorbed and others rolled off the textile		

TEXTILES: NON-SYSTEMATIC EXPERIMENTS – OBSERVATIONS AND CONCLUSIONS								
Textile	**Tested Liquid**	**Application Method**	**Solution**	**Procedure**	**Layers**	**Observed Effect**	**Conclusion**	**OBS**
				Spray + dry	3º) SiO_2-PDMS 0,5%	Results improved a lot. Showing great hydrophobic effect. Drops remained at textile surface longer and some rolled off	Better results than the immersion test taken after although it's believed that spray method does not distribute the solution uniformly	
		Immersion + Immersion + Immersion	SiO_2 solution (1%) in Production Water (PW) + SiO_2-PDMS (0,5%) in Breentsolv + SiO_2-PDMS (0,5%) in Breentsolv	Immersion in 5min + drying 1h on oven 100ºc	1º) SiO_2 20nm 1% PW	No test was taken	After each layer, the textile was leaving to rest for 30min on a bench; A powder deposition was observed on the Petri dishes in all cases	
				Immersion + 40min in hood	2º) SiO_2-PDMS 0,5%	No significant hydrophobic effect was noticed		
				Immersion + 40min in hood	3º) SiO_2-PDMS 0,5%	Better hydrophobic effect than with 2 layers, but not better than the spray test		
		Spray	SiO_2-PDMS 0,5% in Thriethanolamine + Brenntsolv	Spray + 2h30 dry at hood	1º) SiO_2-PDMS 0,5%	No hydrophobic effect after	Because of its viscosity, and it didn't improve the SiO2-PDMS dissolution. Thriethanolamine was no longer used from now on.	
	Water, Juice, Red Wine	Spray + Spray	Commercial Solution	Spray + 24h dry	1º) Commercial Solution	No hydrophobic effect	It's believed that the bad results were due to the type of sprayer or the application method. Afterwards, it was find out that the product was expired.	
				Spray + 24h dry	2º) Commercial Solution	The drops of water, juice and wine remained for a bit in surface but were easily absorbed		
	Water, Juice, Red Wine, Milk and Coffee	Immersion + Immersion + Immersion	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,5%) in Breentsolv + SiO_2-PDMS (0,5%) in Breentsolv	Immersion 5min + 24h dry	1º) SiO_2 20nm 1% PW	No test was taken	With the 3 layers application, the drops remain ate the textile surface much longer before they were absorbed. Juice and Red wine stains were smaller than on non-treated cotton. After a few hours, the test was repeated and with juice the results remained good but not with wine.	The test was taken 7 days after and the results were still good. Milk was also tested with good results. When absorbing the wine drops with a tissue, small stains were left
				Immersion 5min + 24h dry	2º) SiO_2-PDMS 0,5%	No significant hydrophobic effect was observed		
				Immersion 5min + 24h dry	3º) SiO_2-PDMS 0,5%	Significant hydrophobic effect was remarked		

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Textile	**Tested Liquid**	**Application Method**	**Solution**	**Procedure**	**Layers**	**Observed Effect**	**Conclusion**	**OBS**
		Spray + Spray	SiO_2-PDMS 0,5% in 2-Propanol	Spray + 40min dry	1º) SiO_2-PDMS 0,5%	No Hydrophobic effect was observed	The teste was taken a few hours after with better results but not good as other cases. Increasing time fo textile to dry or review the application method is suggested	Wine and juice were tested. Juice had better results than wine. The dispersion pf nanoparticles is still a problem, as in some parts of the textile the sample is absorbed faster than in others.
				Spray + 40min dry	2º) SiO_2-PDMS 0,5%	Better hydrophobic effect but not significantly		
		Spray	SiO_2-PDMS 0,5% in 2-Propanol	Immersion 5min + 24h dry	1º) SiO_2-PDMS 0,5%	With Water the results were good, but when juice and red wine are applied the results aren't good, being worse for wine	The juice drops remain longer, and red wine drops were almost absorbed right after the deposition	
		Spray + Spray + Spray	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,5%) in 2-propanol+ SiO_2-PDMS (0,5%) in 2-propanol	Spray + 1h oven 100º + 40min cooled at open air in hood	1º) SiO_2 20nm 1% PW	No test was taken		
				Spray + 40min dry	2º) SiO_2-PDMS 0,5%	No hydrophobic effect was observed		
				Spray + 40min dry	3º) SiO_2-PDMS 0,5%	Better results for water and juice but not for red wine		
		Spray + Spray	SiO_2-PDMS 0,5% in 2-Propanol	Spray + 40min dry	1º) SiO_2-PDMS 0,5%	4 days after the treatment, a reasonable hydrophobic effect was achieved		Water and juice got good results and so did the milk. Red wine didn't get good results
				Spray + 40min dry	2º) SiO_2-PDMS 0,5%			
		Spray + Spray	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,5%) in 2-propanol	Spray	1º) SiO_2 20nm 1% PW	3 days after the treatment, the results improved but no significantly		Water and juice got good results and so did the milk. Red wine didn't get good results
				Spray	2º) SiO_2-PDMS 0,5%			
		Spray + Spray + Spray	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,5%) in 2-propanol+ SiO_2-PDMS (0,5%) in 2-propanol	Spray + 1h oven 100º + 40min cooled at open air in hood	1º) SiO_2 20nm 1% PW	3 days after the treatment, the results improved a little bit	Shows some improvement	
				Spray + 40min dry	2º) SiO_2-PDMS 0,5%			
				Spray + 40min dry	3º) SiO_2-PDMS 0,5%			

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Textile	**Tested Liquid**	**Application Method**	**Solution**	**Procedure**	**Layers**	**Observed Effect**	**Conclusion**	**OBS**
		Immersion + Immersion	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,5%) in 2-propanol	Immersion 5 min + 1h oven 100ºC + 30min cooling in open air	1º) SiO_2 20nm 1% PW	After 24h, the results with water, juice and milk were reasonable. Collecting the drops of milk and juice after the test, they still left small stains. With red wine, drops didn't hold much time at textile surface	It's believed that if it were applied another layer of SiO_2-PDMs, the results would be better	
				Immersion 5min + 24h dry in hood	2º) SiO_2-PDMS 0,5%			
		Spray + Spray	Commercial Solution	Spray with 15cm distance+ 24h dry in hood	1º) Commercial Solution	No hydrophobic effect	The results were worse than the first ones	No reason was found to this result at this point.
				Spray with 15cm distance+ 24h dry in hood	2º) Commercial Solution	No hydrophobic effect		
		Immersion + Immersion + Immersion	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,25%) in Propanol + SiO_2-PDMS (0,5%) in 2-propanol	Immersion 5min + 1h in oven 100ºC + 30min cooling	1º) SiO_2 20nm 1% PW	No test was taken	This experiment allowed to conclude that the textile patterns from 0,5% of SiO_2-PDMS and 0,25% SiO_2-PDMS were different. In first, it was squared and the second were lines.	5 days later the results were reasonable but not better than 0,5%. The patterns for 0,25% and 0,5% were different
				Immersion 5min + 24h dry	2º) SiO_2-PDMS 0,25%	No test taken		
				Immersion 5min + 24h dry	3º) SiO_2-PDMS 0,25%	Reasonable hydrophobic effect with milk, water, liquid and thicker juice, white wine and tea, but no significant effect for red wine, and coffee with or without milk		
		Immersion + Immersion	SiO_2 solution (1%) in Production Water + SiO_2-PDMS (0,25%)	Immersion 5min + 24h dry	1º) SiO_2 10nm 1% PW	No test taken	The better results were with juice with 2 layers. In the end of the process (3	After a few hours, the test was taken again and a low hydrophobic

TEXTILES: NON-SYSTEMATIC EXPERIMENTS – OBSERVATIONS AND CONCLUSIONS								
Textile	**Tested Liquid**	**Application Method**	**Solution**	**Procedure**	**Layers**	**Observed Effect**	**Conclusion**	**OBS**
		+ Immersion	in 2-propanol + SiO_2-PDMS (0,25%) in 2-propanol	Immersion 5min + 24h dry	2º) SiO_2-PDMS 0,25%	No significant hydrophobic effect was observed	layers) the general hydrophobic effect was reasonable but didn't exceed the results of the 0,5% 20nm. Although the drops seemed almost perfect, when absorbed with a pipette,little stains were left.	effect was noticed. After 4 days the results remain reasonable but the stains left by red wine were more noticeable
				Immersion 5min + 24h dry	3º) SiO_2-PDMS 0,25%	Significant hydrophobic effect was remarked		
		Spray + Spray + Spray	Commercial Solution	Spray with 15cm distance+ 1h dry on a bench	1º) Commercial Solution	No test was taken	It was expected better results than the ones obtained as it is a commercial product	It was found out that the product was expired
				Spray with 15cm distance+ 24h dry on a bench	2º) Commercial Solution	No test was taken		
				Spray with 15cm distance+ 24h dry on a bench	3º) Commercial Solution	The results were slightly better than the previous ones for water and thick juice. For liquid juice and red wine almost, no hydrophobic effect was noticed		

Glass: Non-Systematic Experiments

Sample Number	Layer	Solutions Used	Results
VA		Water	No Hydrophobicity
VB		Cenano Primer Sealant	Very good Hydrophobicity
VC		Nanopreserv CV	Very good Hydrophobicity
V0	1	SiO_2-PDMS 0,25% in Ɣ-butyrolactone + H_2Op	No Hydrophobicity
	1	SiO_2-PDMS 0,5% in 2-propanol	No Hydrophobicity
V1	1	SiO_2-PDMS 0,5% in 2-propanol	No Hydrophobicity
	2	SiO_2-PDMS 0,5% in 2-propanol	Some Hydrophobicity
V2	1	SiO_2-PDMS 0,25% in Ɣ-butyrolactone + H_2Op	No Hydrophobicity
	2	SiO_2-PDMS 0,25% in Ɣ-butyrolactone + H_2Op	No Hydrophobicity
V3	1	SiO_2-PDMS 0,5% in Brenntsolv	No Hydrophobicity
	2	SiO_2-PDMS 0,5% in Brenntsolv	No Hydrophobicity
V4	1	SiO_2-PDMS 0,5% in Trietanolamine+ Brenntsolv	No Hydrophobicity
	2	SiO_2-PDMS 0,5% in Trietanolamine+ Brenntsolv	No Hydrophobicity
V5	2	SiO_2-PDMS 2,5% + THF + Brenntsolv	Some Hydrophobicity
V6	2	SiO_2(20nm + 10nm) 10% + THF + Brenntsolv	Very Low Hydrophobicity
V7	2	SiO_2-PDMS 3% + THF + Brenntsolv	Very Low Hydrophobicity
V8	2	SiO_2(20nm + 10nm) 20% + THF + Brenntsolv	Very Low Hydrophobicity
V9	2	SiO_2-PDMS 3% + Brenntsolv + THF	Good Hydrophobicity
V10	2	SiO_2-PDMS 2% + Brenntsolv + THF	Very Low Hydrophobicity
V11	2	SiO_2-PDMS 1% + Brenntsolv + THF	No Hydrophobicity
V12	2	SiO_2-PDMS 0.5% + Brenntsolv + THF	No Hydrophobicity
V13	2	SiO_2-PDMS 1.5% + Brenntsolv + THF	No Hydrophobicity
V14	2	SiO_2-PDMS 2.5% + Brenntsolv + THF	Low Hydrophobicity
V15	2	SiO_2-PDMS 0.25% + Brenntsolv + THF	No Hydrophobicity
V16	2	SiO_2-PDMS 5% + Brenntsolv + THF	Could not spray. Solution too thick
V17	2	SiO_2-PDMS 3,5% + Brenntsolv + THF	Good Hydrophobicity
V18	2	SiO_2-PDMS 3,3% + Brenntsolv + THF	Good Hydrophobicity
V19	2	SiO_2-PDMS 3% + Brenntsolv + THF	Good Hydrophobicity
V20	2	SiO_2-PDMS 3.2% + Brenntsolv + THF	Good Hydrophobicity

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