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Development of a range of hydrophobizing aerosols and the process for their manufacture

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"…por donde pasa, moja."

Frase popular

Por un lado me gustaría agradecer a mi tutor, José María Gutiérrez González, por su ayuda y por transmitirme pasión y curiosidad por la química.

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SUMMARY

The development of formulated products is based on transform one or several needs detected in society into a commercial product for consumers. Many of the products we see in the market have been based primarily on events of nature. That's why hydrophobic and self-cleaning property are inspired by nature, surfaces that show a non-wetting behaviour due to a "microrugous" morphology with hydrophobic character present in the lotus flower, wings of birds, in spider webs, etc. Water is essential for life on earth and for human life but it can become one of the main inconveniences for the proper functioning and useful life of certain material and tools necessary in at the present time. Due to these inconveniences that water presents us in certain situations, some products have been created and currently are in the market, each one with its own particular applications. The advantages that provide cover economic and environmental aspects due to the decrease in periodic maintenance of surface and / or reducing the use of cleaning products (self-cleaning) besides achieving anti-humidity, anti-corrosion, anti-freeze and anti-pollution on different surfaces. This kind of products can be applied in the electronics, marine, paint and construction industries, biomedical and biological sector and very commonly at home nowadays.

The present work begins with the intention of developing a range of hydrophobizing aerosols with one or several applications each. An extensive market study focused on these was carried out that led to the final choice of super-hydrophobic sprays to differentiate ourselves from the competition, providing water repellency and dirt repellency (self-cleaning). The product was conceptualized, choosing the surfaces where they could be applied; and the quality factors were determined, some of them experimentally. In addition, certain ingredients that were used for the development of the products to be developed were observed in the present patents and the packaging related to them was chosen. At the end of this work, it describes the design of the manufacturing process and its method of operation for 12 tons of each of the aerosols per year, 4 tons of each per year. This describes the different operations and their conditions, the factors to be taken into account to obtain the desired product, and the required equipment.

Keywords: Formulated product development, hydrophobic surfaces, super hydrophobic surfaces aerosols, process synthesis.

RESUMEN

El desarrollo de productos formulados se basa en la transformación de una o varias necesidades detectadas en la sociedad en productos comerciales para los consumidores. Muchos de estos productos que vemos en el mercado han sido basados primordialmente en sucesos de la naturaleza. Por ello las propiedades de auto limpieza e hidrofóbica han sido inspiradas en la naturaleza, superficies que muestran un comportamiento de no “mojabilidad” debido a una morfología micro rugosa con un carácter hidrofóbico presente en la flor de loto, en las alas de ciertos pájaros, en las telarañas de las arañas, etc.

El agua es esencial para la vida en la tierra y para la vida de los humanos pero puede ser uno de los principales inconvenientes para el buen funcionamiento y la vida útil de ciertos materiales y herramientas necesarias en la actualidad. Debido a estos inconvenientes que el agua nos presenta en determinadas situaciones, se han creado productos que tenemos actualmente en el mercado, cada uno para su particular aplicación. Las ventajas que proporcionan cubren tanto aspectos económicos como medioambientales por la disminución en el mantenimiento periódico de las superficies y / o la reducción del uso de productos de limpieza (auto limpieza) además de lograr antihumedad, anticorrosión, antihelio y anticontaminación en diferentes superficies. Este tipo de productos pueden ser aplicados en la industria electrónica, la marina, la de pinturas y la construcción, en el sector de la biomédico y biológico y muy comúnmente en el hogar hoy en día.

El trabajo presente se inicia con la intención de desarrollar una gama de aerosoles hidrofobizantes con una o varias aplicaciones cada uno. Se realizó un amplio estudio de mercado centrado en éstos que derivó a la elección final de realizar aerosoles super-hidrofobizantes para poder diferenciarnos de la competencia, proporcionando repelencia al agua y a la vez repelencia a la suciedad (autolimpieza). Se conceptualizó el producto, escogiendo las superficies donde se podrían aplicar; y se determinaron lo factores de calidad, algunos de ellos experimentalmente. Además, se observaron en las patentes presentes ciertos ingredientes que nos sirvieron para la elaboración de los productos a desarrollar y se escogió el “packaging” relacionado con éstos. Al

final del presente trabajo describe el diseño del proceso de fabricación y su método de operación para 12 toneladas de cada uno de los aerosoles al año, 4 toneladas de cada uno al año. En éste quedan descritas las diferentes operaciones y sus condiciones, los factores a tener en consideración para obtener el producto deseado, y los equipos requeridos.

Palabras clave: Desarrollo de productos formulados, superficies hidrofóbicas, superficies hidrofóbicas, síntesis de procesos.

1. JUSTIFICATION AND OBJECTIVES

Water is essential for life on earth but presents certain inconveniences for the proper functioning and useful life of certain materials and tools necessary in our days.

The development of human beings goes hand by hand with the development of new products in their daily lives and sometimes that entails entering into conflict with nature and with physics, so we must develop additives and complements that confer new properties to the products already invented to continue develop ourselves.

Water usually generates moisture due to capillarity, condensation, absorption of the environment or breakage of installations on porous surfaces, being essential for the life of fungi, lichens and other microorganisms under conditions of optimum temperature and nutrients, thus degrading the material as shown in *Humedad (2019).*

This is why hydrophobic aerosols are an essential part of the market. There are currently a wide variety of products that confer hydrophobicity and the amount of options that consumers have in terms of application is very wide too. But as the years go by, research and human development produce new types of surfaces and new materials. All this entails a greater demand in terms of properties, in terms of features that the product offer us, so that the coating must evolve in a solidary way with the products and materials. That is why industries are increasingly innovation in terms of new surfaces properties to the point of achieving super hydrophobicity.

Referring to *Zhang et al. (2018),* hydrophobicity is seen when water droplets in contact with the surface form an angle greater than 90º and if it's greater than 150º it's called super hydrophobicity. It is still difficult for these coating technologies to provide permanent hydrophobic properties and their duration depends on their chemistry, application method and environmental conditions such as temperature and surface.

According to *Carmona (2009)*, this property used as a coating is widely used in the manufacture of fabrics (water and dirt repellents), construction work (clean surfaces, anti-graffiti), for vehicles (antifouling, antifreeze, anti-fog) or in engineering processes (reduction of biofilm in pipes). Moreover it is expected to provide economic and social benefits such as reducing the costs of maintaining equipment in the processes, minimizing the risks of transmitting infectious surface agents in sanitary environments such as hospitals, etc.

So that work about hydrophobic aerosols is a product engineering work, that's why includes all the steps from when the need is detected until the formulated product is ready to be sold, which includes the design, development, selection of materials, and transition from the prototype stage to the manufacture of the product as shown in *Cantero et al. (2019).* All these steps are really important to improve the quality and optimize the cost of production among other properties to be able to differentiate itself from the other companies in the sector.

As we have said before, the main objective of the industry that produces hydrophobic and super hydrophobic aerosols will be to design a product that meets the needs of the consumer in terms of the hydrophobic capacity of the product (mainly) and other characteristics that will be described later in the quality criteria section ; product conceptualization, analysis of the quality factors, the section of the ingredients and the microstructure of the product and the design of the manufacturing process.

This work addresses the invention and subsequent development of a range of aerosol formulated products that can be sprayed on different materials to make them super hydrophobic. It includes all stages in product development: product conceptualization, definition of quality criteria, ingredient selection, process synthesis for product manufacturing; and will also include the design and/ or selection of equipment for its manufacture as shown in *Cambray et. al (2019).* It is very important to first carry out an in-depth market study of the formulated product that it wants to develop. In this way find what the market offers, the needs that are covered and those that are not and based on that the type of product that is wanted to make will be chosen. After conducting this market study, the ingredients of the formulated product that will give those desired properties and/or requirements will be decided. Finally, the chemical process and the corresponding equipment selected to produce the desired product will be designed. The procedure described above can be divided into four sections:

Product conceptualization: In this first section, a study of the possible formulated products to be developed will be carried out, detecting those needs that we want to know which are covered or not in the market. For this, a thorough analysis of similar products is carried out in the market, comparing and studying very diverse patents, encyclopaedias and documents and the main characteristics of the product are defined to choose those that interest us.

Establishment of quality factors: Once the product has been conceptualized and its characteristics and properties have been detailed, it is necessary to identity the quality factors which will allow us to define the formulated product and see if these are complemented or not with the needs to satisfy. These quality factors jointly with the product conceptualization made before, will condition completely the next section of this work: the selection of ingredients and structure.

Selection of ingredients and structure: This part focus on the formulation of super hydrophobizing aerosols. A thorough analysis and selection of the active ingredients, propellants, solvents and/or additives and their quantity and the microstructure that the formulated product must have is made.

Manufacturing process synthesis: Here the production processes of the super hydrophobic aerosol range will be described, explaining the unit operations and the necessary equipment for this.

2. PRODUCT CONCEPTUALIZATION

The first step to make a product is its conceptualization and the scope of the project. The needs to be satisfied, the purpose of the formulated product and the set of intangible characteristics and attributes (brand, company image, service…) and tangible (shape, dimensions, colour, texture, etc.) that make it attractive to the consumer. That's why making a research of market trends it's very important to understand the concept of the product.

The first intention at the beginning of this work is to develop a range of hydrophobic aerosols, the conceptualization of the product will begin first with the market analysis to know what the different brands of the market offer us. As they are aerosols that give a layer to a surface (coating), the first thing that should be observed is what surfaces they are used for and thus perform an analysis and a choice of the surfaces where we want the product to be developed to be applied. Next, emphasis will be placed on the selection of the ingredients that form it, in this way, by fully understanding the supply and demand of the sector that belongs to the product to be developed, the product can be highlighted over the other competitors in the market.

In addition to the choice of the surfaces where you want to apply, the ingredients that you want to use, services and needs that you want to satisfy, the choice of the container where the product will be contained has a great importance since it influences the application of this and not less important, in the visual perception of the potential buyer. After performing this entire analysis process, you are fully trained to make a difference with existing products and succeed in the industry.

After the market analysis has be done, the next section is about product functionality, where the basic concepts of hydrophobic aerosols and surfaces where they will be applied are explained to better understand this work.

And finally, the last step to understand the whole product, the concepts of packaging and the choice of the appropriate packaging for the aerosols developed will be explained due to the requirements of this.

This process about this entire analysis and comparison made to conceptualize the product that is wanted to be developed is called *benchmarking.*

T*he benchmarking* is a process of gathering information and obtaining new ideas by comparing services, processes or products that are taken as a reference and that belong to leading companies and/ or stronger competitors that demonstrate best practices in the area of interest for the purpose of make improvements and implement them.

2.1. MARKET ANALYSIS

Initially this work was carried out with the objective of developing a range of hydrophobic product. For this reason, a thorough market analysis was carried out and thus see what products should be manufactured.

Initially the search was focused on patents of affected products in the market which were hydrophobic and water repellent with very diverse applications. The most common and most found products were manufactured in liquid phase, such as paints, and especially for the maintenance of surfaces related to the construction sector and marine industry as shown in *Star brite waterproofing with PTEF.* Given that there was a lot of competition and many type of applications, it was decided to further reduce the spectrum and focus the search on aerosols sprays that granted this hydrophobic property to the desired surfaces.

Some of the patents of hydrophobic aerosols and sprays were intended for the protection and conservation of artworks such as *Krylon UV-Resistant Clear Coating, Clear Gloss 1305*, others like *Permatex No Touch Instant Rainshield* to favour the route of the raindrops ad thus the vision through the glasses related to the automotive industry, the *Thompsons WaterSeal Clear Muti-Surface Waterproofer* intended for different surfaces and others such as *Kiwi Camp Dry Performance Fabric Protector* for the care of all types of clothing and accessories that are going to be exposed to dirt, mud and rain. These patents are shown in *Table 1.*

Table 1. Patents of hydrophobizing aerosols

Product	**Ingredients**	**Content (%)**
Krylon UV-Resistant Clear Coating, Clear Gloss, 1305,	Acetone	41.07
	Propane	13.79
	Naphthalene	0.39
	Butane	13.25
	Toluene	16.57
	Ethyl 3-ethoxy propionate	4.01
	Solvent naphtha, petroleum, heavy aromatic	2.52
Permatex No Touch Instant Rainshield Windshield Coating	Isopropanol	75.0 - 85.0
	Propane	1.0 - 10.0
	Isobutane	1.0 -10.0
	2-Butoxyethanol	< 3.0
	Water	1.0 - 10.0
Thompsons WaterSeal Sport Seal Outdoor Fabric & Leather Protector	Acetone	25.0
	Propane	14.0
	Butane	6.0
	Distillates, petroleum, hydrotreated light	49.0
	Solvent naphtha, petroleum, medium aliphatic	2.0
Kiwi Camp Dry Performance Fabric Protector	Propane	7.0 - 12.0
	Isobutane	12.0 - 19.0
	Butylacetate	1.0 - 3.0
	Heptane	27.0 - 34.0
	Stoddard solvent	1.0 - 3.0
	Naphta, petroleum, heavystraight run	

The market of hydrophobic coatings is a market that has gone from being entirely destined to serve the requirements of the industries to be increasingly important as a product of use (or consumption) *in situ* in the home. This can be observed with the appearance, in recent years, of hydrophobic aerosols whose objective is the care of fabric and more specifically those fabric that fashion shoes and clothes. That is, products with a more or less periodic use to preserve the properties of the surfaces of garments that everyone has at home. This type of care products for footwear and clothing has become popular due to the increase in the consumption of clothing and sneakers by young people, and that aesthetics is increasingly important for all types of social class.

Once a number of patents have been analysed, certain aspects can be affirmed:

The proportions of the ingredients that formed the formulated products of the patents that were found at the beginning had very large ranges.

On the other hand, in a first search, it was observed that in the vast majority of the patents that were found, the only ingredients that appeared were propellants and solvents that evaporated (such as butane, hexane, propane, naphtha, etc.). Therefore, they could not confer hydrophobic capacity on the surface since the entire product would evaporate in a matter of minutes and even seconds.

These two facts are very common and are intended to protect the formula by the developer.

These data do not give enough information to make a product with similar properties and characteristics, so we continued the search until it came up with a patent that had hydrophobized silica particles, the *Kiwi Camp Dry Heavy Duty Water Repellent*. Their ingredients are shown in *Table 2.*

Table 2. Patent with hydrophobicized silica particles

Product	**Ingredients**	**Content (%)**
Kiwi Camp	Propane	10.0 - 30.0
Dry Heavy Duty	Isobutane	10.0 - 30.0
Water Repellent	Ethylbenzene	0.1 - 1.0
	2-Ethylhexyltitanate	5.0 - 10.0
	Xylene (mixed isomers)4	1.0 - 5.0
	Naphta, petroleum,	60.0 -100.0
	heavy alkylate	
	Trymethylated silica	5.0 - 10.0

After this search, it was concluded based on what was found at the moment in the market analysis that the range of hydrophobic aerosols would consist of three types of aerosols: some could be “simple products” such as those whose patents simply contain solvents and propellants; and the other two types would be those that already have a particularly hydrophobic agent and, therefore, remain on the surface on which it is permanently applied for a considerable time, such as silanes or fluorides.

$$\begin{cases} A\ hydrophibizing\ aerosol\ that\ simply\ contains\ solvents\ and\ propellants \\ A\ hyrophobizing\ aerosol\ containing\ silica \\ A\ hydrophobizing\ aerosol\ containing\ fluorinated\ produccts\ (fluorocarbons) \end{cases}$$

Figure 1. Scheme of the “prototype” range of the hydrophobic aerosol range work

After conducting all these searches and finding several different product patents, we should focus attention on the first question that this work was aimed at solving: “what should we manufacture?” All patent analyses served, not only to have a conceptual idea of the product, but also to understand that this question is entirely conditioned by two concepts:

1. The surface on which you want to apply.
2. How hydrophobic this one wants to do.

So as the desire was to make a product for footwear, three types of surfaces were chosen where each of the hydrophobizing aerosols that had the range would be effective and these surfaces were leather, suede and nubuck

At this point we have the three surfaces on which you want to apply and the developed formulated product and the three types of aerosols with different ingredients and hydrophobic capacities will be effective.

Non-compliant with the patents found, research was conducted more deeply on hydrophobic property and more specifically on super-hydrophobicity. Property that gives the surface in addition to water repellency, self-cleaning ability against all types of fats.

So having this concept in mind, subsequent market analyses were conducted focusing on this property. Products like *C.N. Pat. No.101962514A* and a like the *Ultra Ever Dry* were found, self-cleaning aerosols and super hydrophobic to apply on all types of surfaces

At this point in the market analysis we had two “approaches”: hydrophobizing aerosols and super-hydrophobizing aerosols, so returning to the question “what should we manufacture?” It was solved with another: “what differentiates us from others?” and in this way we can succeed in the industry. In order to know “what differentiates us from the others”, the different patents that were found were gathered, the different surfaces and sectors where these products are used and it was observed that there were no super-hydrophobic aerosols for footwear. So, from the market analysis carried out together, it was concluded that a range of super-hydrophobic footwear aerosols would be carried out for the here surfaces chosen above and thus differentiate the product form the other competitors. That is, the range would be better than those on the market and depending on how hydrophobic the product will be, it will be more or less expensive. Furthermore, two of these three aerosols will be for a domestic purpose and the other, which only has fluorides, for a more industrial use. The durability component is added to this economic component, related to the degree of lipophobicity. This durability is a very important property that will differentiate the product from more industrial use from the others, the aerosol composed mainly of fluorides, since this product will form covalent bonds with the surface where it is applied. Producing a great adhesion of the hydrophilic chains and leaving out the hydrophobic chains of the surfactant, as will be better explained in section 4 of this work. Therefore this greater or lesser lipophobic (self-cleaning) and hydrophobic capacity will be given by the amount of fluorides that compose it, so finally the range that consumers would have at their disposal would be:

$$\begin{cases} \text{Superhydrophobizing aerosol with silanes} \\ \text{Superhydrophobizing aerosol with silanes plus fluorides} \\ \text{Superhydrophobizing aerosol with fluorides} \end{cases}$$

Figure 2. Final scheme of the hydrophobic aerosol range before it will be carried out

2.2. PRODUCT FUNCTIONALITY

After making a market study, the next step in terms of product conceptualization is to determine the main function of the range of aerosols. The function performed by each product helps us understand its nature and that is why this section explains certain necessary concepts. As mentioned in *section 2.1. Market Analysis*, the product to be developed is conditioned by how hydrophobic a surface is to be achieved and the type of surface to which this water repellency is to be given.

This last aspect will be the one that will be explained in this section. The characteristics of the substrate (the surface) where the product will be applied should be understood and studied since the type of surface is totally linked with the hydrophobic property that it confers to it and therefore for its proper functioning. The surfaces where the formulated product will be applied as discussed above will be leather, nubuck and suede, therefore, an explanation will be made of each of them.

Leather

Leather is one of the oldest materials and has a vital importance in our lives, this importance of leather is very evident: humans needed protection against cold, moisture and mechanical influences and hunted animals had hides and skins (base of the first shoes, clothing, gloves, etc.). Despite the fact that its importance initially was for protective purposes, its aesthetic qualities as a fashion material are of great relevance today.

It is important to know the topographic structure of skins and leather as this is where the products to be developed are going to be applied. Thus, this topography consists of three main layers: the epidermis, the dermis (corium or cutis) and the hypodermis (subcutis).

Figure 3. *Topographic structure of skins and leather*
(image taken from Leather. Ullmann's Encyclopedia of Chemical Technology, 7th ed, Vol. 20*)*

Moreover, each of these three layers can be divided into several sub-layers.

The epidermis is a cellular tissue that contains the hair of animals or the sales of fish or reptiles.

Referring to *Leather. Ullmann's Encyclopedia of Chemical Technology* The hair is embedded in the hair follicles. The hair roots are found in the border layer between the epidermis and the dermis (only the bristles of the pig skins cross the entire cutis). After removing the epidermis and hair before tanning by chemical hair removal, you can see the characteristic structure of the grain, which is caused by the actual arrangement of the hair according to the type of animal. The "grain" of the final leather surface is a typical characteristic of natural leather.

According to *Leather. Ullmann's Encyclopedia of Chemical Technology* the main protein of the hairs and the epidermis is keratin. This protein has a high content of cysteine, an amino acid with a disulphide bridge –S-S- that stabilizes its structure. So the processes of "hair removal" of the leather are based on the destruction of this bridge through alkaline, reducing, oxidative or even enzymatic treatments to dissolve or damage the hairs and achieve a smooth skin.

The subcutis consists of two layers, the papillary and the reticular layer. Both layers contain the fibrous collagen network (the papillary layer is less dense than the reticular layer, and the fibers are thinner and the density of the fiber network, the diameter of the fiber and the angle of tissue depends on the topographic position in the skin), and very small amounts of other collagens, proteoglycans, elastin, some fats, blood cells, etc. and mainly water (>70%).

Leather is primarily a hydrophilic substrate due to the porous structure of collagen and its hydrophilic groups. For some purposes like a specifically permanent waterproofing required for certain leather sports shoes. This motive, was the main driver in carrying out this work.

There are some possibilities to achieve the described properties. The simplest is the spray coating of leather finished with polymer solutions containing fluorine and / or silicone, which can protect the surface for a longer time, such as the product to be developed in this work. This procedure can be repeated later, when the properties are finished, by the consumer himself. Total water absorption is minimally reduced with a spray coating. Referring to *U.S. Pat. No. 13/849740*, leather has microdepressions 130 µm. As will be discussed in *section 3. Quality Factors,* the roughness of the material plus the nanoparticles that are applied with the aerosol of the range developed in this work, will generate the super-hydrophobic capacity

To guarantee a lasting and effective waterproofing, the aerosols to be developed are composed of hydrophobic substances that when applied on the surface reacting as ligands to the chromed tannins attached within the leather. Stearates are a good example, but recently highly sophisticated polymers such as those detailed in the next section referring to ingredients are often used. Some of these products, which will be used in this work, are acrylate-based products that contain COOH functional groups capable of binding to chromium complexes and long alkane chains, modified with silicone and / or fluorine derivatives. It is often said that such polymers are amphiphilic, that is, that they have a hydrophilic end, another hydrophobic one. In this way they make the fiber surfaces water repellent without closing the pores and intermediate spaces ("open hydrophobicization"), not like certain waxes that clog all the pores causing the leather to lose its breathability and ability to absorb water vapour ("closed hydrophobicization") as shown in *Leather. Ullmann's Encyclopedia of Chemical Technology pp 649-650.* As the superhydrophobic sprays to be developed have the objective of repelling water from the surfaces of footwear, this will mean that in addition to offering this property they are still breathable. Helping sweating and good foot care, an added value that can be largely differential from other competitors.

Nubuck

The nubuck is cowhide with velvet-like surface. This velvety surface is due to the sanding of the leather on the side of the grain, thus giving a surface of slight short protein fibers. As remarkable features it has great wear resistance and can have colour or not as mentioned in *Tanning and Leather Finishing. Encyclopedia of Occupational Health and Safety. 2000.*

This is very similar to the suede but, while the nubuck is created from the outside of the skin, the suede is not. This sanding or polishing gives it a greater resistance and thickness due to the fine grains that are received as shown in *American Leather Chemists Association ALC (1906). The Journal of the American Leather Chemists Association*. Due to these properties and to finish the sanding process it should be dyed, in general, it is more expensive than suede.

Referring to *Suede - Nubuck - Buckskin (2019),* other characteristics of the nubuck will be that it is soft to the touch, scratches easily and raindrops obscure it. This last feature is what we want to improve by applying the products that are going to be developed in this work, but it is known that the older the surface of the leather, nubuck or suede, the waterproofing properties decrease and drops can penetrate and expand on the surface.

Suede

According to *Tanning and Leather Finishing. Encyclopedia of Occupational Health and Safety. 2000,* Suede is a type of leather made from the lower part of the skin (mainly lamb, although goat, veal and deer are specifically used). Thus, giving greater properties of flexibility, thinness and softness, although not as durable as those with the outer layer of the skin. Therefore, it is usually used for delicate garments.

Due to presenting open pores and their textured nature, the range can get dirty and absorb liquids quickly and easily, so it is expected that the aerosols developed in this work will be used more for this type of surface than for the other two proposals.

Super-Hidrophobizing aerosols

They are aerosols of the type of coating aerosols which aim to provide different types of surfaces with a hydrophobic and lipophobic capacity.

They contain various combinations of propellants, solvents, nanoparticles and active ingredients of all kinds (surfactants, siliconized or fluorinated compounds that are responsible for water repellency) to achieve these effects on the surface, which makes a wide variety of formulations available.

According to *Shepherd (1961),* the active ingredient is the material that really does the job for which the product is designed. It determines the effectiveness of the product and is the base ingredient on which the entire aerosol formulation is constructed. If the active ingredient itself is not effective, the combination with the others will not. But the application method can increase its effectiveness or help in its application, as is the case with the type of aerosols to be designed. You could have chosen another type of application for the same product, such as applying the product by brush, but aerosols allow you to create a thin layer of product and a better extension of it, thus increasing the effectiveness of the active ingredient.

Super-hydrophobic aerosols currently use as active ingredient to achieve super-water repellent polymers with fluorine side chains, also known as fluorocarbons, whose repellency is generated by its good surface activity and its hydrophobic and oleophobic properties due to interactions between fluorine atoms and water and fat atoms. Perfluorocarbons, such as perfluoroalkyl acrylate, perfluoropolyether (PFPE), perfluorosulfoamides, perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and derivatives are some of the best known and most applied according *C.N. Pat. No.101962514A.* In addition to fluorocarbons, fluorosilicone resins are found as hydrophobic agents (*C.N. Pat. No.110054915A)* and the most commonly used although with less water repellency, the siliconized compounds that carry polydimethilsiloxane and which are also shown in the patent *C.N. Pat. No.101962514A.*

In order for the active ingredients mentioned above to leave the can and can be applied, other compounds, called propellants, are needed. These are an integral part of the aerosol formula and are essentially formed by propane-butane mixtures. According to *Shepherd (1961),* they fulfill a double function: on the one hand, as mentioned, they provide the necessary force to push the product out of the container. On the other hand, once the product has been expelled, the liquefied gas on the applied surface undergoes an instant evaporation that leaves the active ingredient in a unique, especially effective state. *Sciarra and Stoller (1974)* comments that they should have a mutual solubility with solvents since the combination of both should serve as a solvent for the active ingredients.

Solvents or dissolvents are substances that allow the dispersion of another in it at the molecular or ionic level (it surrounds it but does not react with it), so they have different applications in different articles intended for cleaning, paints and adhesives among others as shown in *Los solvents (2019).* In this work, combinations of glycerine, propylene glycol, ethanol or acetone are taken into account; and on the other, of a single compound.

Nanoparticles or nanomaterials are also added, on the one hand, to increase the surface roughness; and on the other, they help to bind the surface with the active ingredient. The most common and studied nanoparticles are those of silica (silicon oxide) and those of titanium (titanium oxide), but there are also others with similar properties, for example zinc and zirconium oxides.

3. QUALITY FACTORS

Once the market study is done on the different brands that we can find in the market, the quality factors of the formulated products to be made must be defined. These quality factors are the requirements that the product must achieve, satisfying the needs that have been detected and in turn make it attractive and differentiating it from its competitors. Depending on the shape of the product, these factors could be different. In addition, quality factors must be specified before the ingredients are selected in the next step. Quality factors directly condition the ingredients that will be used to make the desired formulated product, which is why making a through and compete choice of quality factors is necessary first.

The quality factors are quantified with the quality indices, which are properties of the product. In this chapter, some experiments carried out with hydrophobic products available in the market will be mentioned to have a reference and to be able to predict, together with the patents found, the quality indices and the properties that the aerosols that are going to develop in the present work.

But it will be in the next chapter *Selection of the ingredients and microstructure* where information will be discussed to select the most suitable ingredients for the formulated product.

Listed below are the different quality factors that products must have and that will be specifically explained in the next subsection of this section. In addition some of these will be determined experimentally and will be shown in the *Appendix* figures.

The ***relative amount deposited*** is important since it gives us the information of the amount of product that is retained in the form of a film on the desired surface, which directly influences the hydrophobic properties at the microscopic level as will be explained below.

The most important objective when developing a hydrophobic aerosol is to ensure that it gives us the ***hydrophobic capacity***, the main action that this product should perform. Calculated with the ***contact angle***, the quality index.

On the other hand, the ***adhesion to the surface or degree of adhesiveness***, which will be related to another quality factor that we will mention next, the durability. Totally related to the ***degree of self-cleaning*** that could be another quality index

The ***hiding power*** is very important, since the developed aerosols will be colourless (transparent) so they should not change the colours of the surface where they are applied. Calculated with the quality index ***alteration of the colour.***

Durability, a very important factor to consider in order to calculate the time that the hydrophobic property on the desired surface can be had. It will affect us directly in the time of use we want to perform on that surface.

It is also very important the ***drying time***, the speed and evaporation when spraying it, since it dries in a reasonable time the product is a very important aspect in terms of products in the form of spray.

Last, but not least, the ***sprayed capacity*** or rather ***sprayability*** is a very important factor since our product is a spray and there must remain as a thin film.

3.1. QUALITY ÍNDEX

When determining the quality index, the form of the product to be developed, its status, the way of applying it and the quality factors that we have taken onto account for it have been taken into account.

It should be noted that to determine these quality indices, the relevant experiments were carried out with two hydrophobic products that can be found in the market. Although the formulated products that are going to be developed in this work are not the same as those used for the experiments, since they are similar applications and products, they will serve as a model to find these indexes.

A first quality index has been referred as the ***relative deposited quantity*** that gives us the information of the quantity of product that is retained in the form of a film above the desired surface and, therefore, of the maximum limit of the quantity of product it can hold. This quality index will be determined experimentally in the steps described below:

Experiment to determinate the relative deposited quantity

First, a piece of square cloth is available on a scale with sufficient precision. The weight of the piece of cloth alone is recorded and considerable amount of hydrophobic product is sprayed on top of it. Just after spraying the desired amount, the stopwatch is started and the weight of the deposited product evolves over time. In this way it can be seen how the weight decreases progressively until it reaches a point that there is no variation in weight over time and remains constant for a long time. Once we have this data for a considerable time, we can end the experiment. After the experiment, if we make the difference between the final weight of the product on the fabric and the initially recorded weight of the fabric, we will obtain a weight, which will be our ***relative deposited quantity***.

The second quality index that was proposed was the most important and that is related to the ***hydrophobic capacity*** quality factor, this index is the ***contact angle.***

When talking about hydrophobic property, the first thing that is generally thought of is in the way we see water (small droplets), but what is really important in this phenomenon are the physical-chemical properties of the surface where the water is deposited. The assumption to understand this phenomenon is to consider an ideal surface, that is, smooth and chemically homogeneous. A drop is placed on it, which will be under the influence of the forces created by the different tensions generated in the interfaces. From this first assumption, the first characteristic parameter of this property, the contact angle (θ), was determined.

According to *Barjola et. al (2007)*, the contact angle is the angle formed between the surface and the line tangent to the drop contact point.

On this surface the energy will be:

$$G = \gamma_{SV} A_{SV} + \gamma_{SV} A_{SL} + \gamma_{SV} A_{LV} \quad (1)$$

Where:

γ_{SL}: Solid-liquid interface stress [N / m]

γ_{SV}: Solid-vapour interface stress [N / m]

γ_{LV}: Liquid-vapour interface stress [N / m]

G: Gibbs energy, surface energy [J]

A: stress direction

So the most stable state will be the one with the lowest free energy, so in the equilibrium the change of free energy will be zero and deriving equation 1 and equalizing it to zero we get:

$$\Delta G = \gamma_{SV}\Delta A_{SV} + \gamma_{SV}\Delta A_{SL} + \gamma_{SV}\Delta A_{LV} = 0 \quad (2)$$

Substituting ΔASV = -ab, ΔASL = ab and ΔALV = ab cos θ (considering “a” the origin point at the point where the three phases are located and “b” as a point farther between the solid and the gas phase) in the previous equation we arrive at the following result:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (3)$$

Where:

cosθ: Cosine contact angle function

By making the arcs θ of equation 2 the contact angle is calculated that for an angle less than 90° the wet will be favourable and if the angle is greater than 90° the wet will be unfavourable.

If we look at the equation, for positive cosθ values (low γ_{SL} values) we will have surfaces that will facilitate the spread of the liquid on them, these are called hydrophilic, but for negative cos (values (high γ_{SL} values) we will have surfaces that they will make it difficult to spread the liquid on them, reducing the contact between the liquid and the solid, resulting in practically spherical drops, these surfaces are called hydrophobic. This type of surfaces will be those that focus the interest of this work since from these it will be possible to design the super-hydrophobic aerosols with a self-cleaning behaviour.

$$\begin{cases} If\ \theta < 90^{o} \ \rightarrow hydrophilic\ surface \\ If\ \theta > 90^{o} \ \rightarrow hydrophobic\ surface \end{cases}$$

The contact angles obtained experimentally by using a hydrophobic aerosol on a cloth are shown in Figures 4 and 5

Figure 4. Hydrophilic surface (fabric), contact angle less than 90º

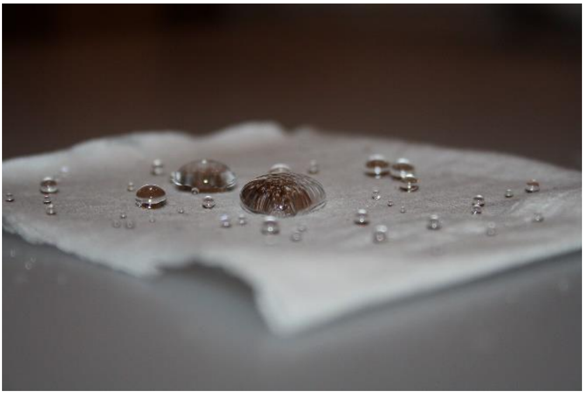

Figure 5 Hydrophobic surface (cloth + hydrophobic spray), contact angle greater than 90º

But as reality is more complex, really those rough surfaces (some more than others) and chemically heterogeneous (in terms of composition) are what will give us a good approximation to reality. This variation in surface chemistry or roughness may not be obvious and / or relevant to the naked eye but is of great importance on a microscopic scale.

Real surfaces are characterized precisely by these irregularities that form a profile of peaks and valleys of varying sizes.

This does not mean that all the surfaces that surround us have an important roughness on a microscopic scale but that they will hardly be completely smooth since there can be some impurity on the surface. This will create some local peak on the surface observable by microscopy. These surfaces whose microscopic roughness is insignificant can be modelled through Young's equation, although this theoretical value may not coincide exactly with the contact angle obtained experimentally.

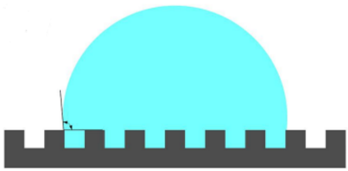

Figure 6 Water drop partially penetrating the depressions of roughness

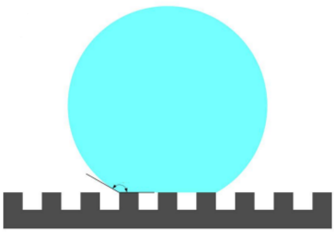

Figure 7 Water drop resting on the peaks of the roughness

It is precisely these peaks and valleys, this microscopic roughness, responsible for increasing hydrophobic properties. These can give rise to two different situations: that the liquid drop partially penetrates the depressions (*Figure 6*) or rests on the top of the peaks (*Figure 7*).

In Figure 6 the liquid will be exposed to a greater hydrophobic area, the roughness provides a greater area on a microscopic scale than on a macroscopic scale, thus causing a greater contact angle than that same liquid would have on a smooth surface of the same composition. This arrangement of the drops on the surfaces is a clear example of hydrophobic surfaces.

But the case observed in Figure 7, the liquid drop rests on the peaks of the rough hydrophobic surface, so that it is in contact with two surfaces of different wettability: a surface that is that of the hydrophobic solid (with peaks and valleys generating that microscopic roughness discussed above); and then the surface generated by the air that is in the depressions of the solid. In this way the hydrophobic properties will increase, giving a contact angle of 150º-180º, giving rise to super-hydrophobic surfaces.

These are two clear examples of the models that were based on different geometric parameters to characterize the roughness, the Wenzel model and the Cassie model.

The first Model described in Figure 6 is the Wenzel model (also called wet contact), which dates back to 1936 and is based on the assumption that liquid droplets partially penetrate the depressions and interstices of a rough surface.

Since the roughness has a larger area on a microscopic than macroscopic scale, the contribution of the surface energy of the solid (γ_{SL} - γ_{SV}) to the total energy of the system will be greater, so this difference in energy is multiplied by a roughness factor, r, defined as the ratio between the current area of the rough surface (contact area that provides the surface roughness) and the projected solid surface area (contact area that provides the smooth surface). How logical is this factor it will always be greater than one (provided the surface is rough) since the area contributed by the roughness will be greater than the area contributed by the smooth surface.

Following the same approach as the one made to establish Young's equation, in the equilibrium the free energy change will be zero:

$$\Delta G = r(\gamma_{SV} - \gamma_{SV})ab + \gamma_{SV}(ab)\cos\theta = 0 \qquad (4)$$

Getting the Wenzel equation:

$$\cos\theta_r^w = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r\cos\theta_e \qquad (5)$$

Where θ_e it will be equal to Young's contact angle, it will be the roughness factor, superscript "w" will indicate Wenzel's contact angle and subscript "r" will indicate rough surface.

According to *Barjola et. al (2007)*, knowing that with an increase in roughness there will be an increase in the contact angle, if it is multiplied by a value greater than one (roughness factor) it will result in a larger value. So, the contact angle will be larger the more negative the product between r and cos θ_e.

On the other hand, the Cassie model (1944), also called composite contact, as can be seen in Figure 7 it assumes that the drops of liquid rest on the tops of the peaks of the protuberances, giving rise to a heterogeneous chemical composition where it enters a third phase represented by the air that is maintained between the drop of liquid and the solid is added.

Following the same approach as the one used to establish Young's equation, Gibbs' energy is:

$$\Delta G = \varphi(\gamma_{SL} - \gamma_{SV})(ab) + (1-\varphi)\gamma_{LV}(ab)\cos\theta = 0 \qquad (6)$$

Where φ is the fraction of solid in contact with the liquid.

In equilibrium G it will be minimal and we get Cassie's equation:

$$\cos\theta = \varphi\left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} + 1\right) - 1 \qquad (7)$$

$$\cos\theta_r^c = -1 + \varphi(\cos\theta_e + 1) \qquad (8)$$

Where θ_e will be Young's contact angle, superscript "c" indicates Cassie and subscript "r" rough surface.

So, the smaller φ, the less contact between the solid surface and the liquid and the greater the Cassie contact angle.

Initially it was unknown when one or the other model was to be applied since the two predict high contact angles, but the tracking of one or the other determines the behavior of the drop on the substrate: for example, the Cassie model shows a low adhesiveness which favors a self-cleaning capacity while the Wenzel model does not. Therefore, due to the formulated products to be developed in this work, Cassie's model should be taken into account for experiments related to contact angle and hydrophobic capacity.

It should be said that this roughness can also produce different angles for the same contact line, this phenomenon is called ***hysteresis of the contact*** angle and is very important on super-hydrophobic surfaces (it is another important quality factor for the aerosol range in develop).This phenomenon occurs when a liquid travels over a surface, a clear example is the drops of water that fall on the windshields of cars. These drops while traveling on the surface form a small angle at its final part (backward angle θ_R) and a larger angle at the leading front (forward contact angle, θ_A) as shown in *Fernández et. al (2013).* In displacement, gravity is creating a leading front and the tail of the drops (falling back) are resting on an area of the surface that has already been wet, which gives it greater hydrophilic properties and therefore, the contact angle found is smaller in the tail.

The advance angle is defined as the contact angle that has a drop of liquid that advances on a dry surface; and the recoil as the contact angle of a drop that advances through a previously wetted area due to the path of the drop. The contact angle may vary between these two limits and the difference between them is called the contact angle hysteresis:

$$\Delta\theta = \cos\theta_A - \cos\theta_R \quad (9)$$

What is really useful for this work is that we can increase this difference between forward and reverse contact angles to a greater extent by thinking again about microscopically rough surfaces.

The hysteresis found on these surfaces will depend mainly on the type of contact established between the drop and the surface.

On the one hand, if the droplet penetrates the microscopic depressions of the surface in question, the hydrophilic contribution that will determine the recoil contact angle will be greater causing it to offer a smaller contact angle. On the contrary, if the surface of the drop rests on the top of the peaks, the recoil front will be exposed to a smaller area with hydrophilic properties compared to the situation previously exposed, so it is expected that this hysteresis will be less.

So the hysteresis of the contact angle gives us the ***degree of adhesiveness*** (that is another quality factor of the super-hydrophobic of this work) between the drop and the surface. The lower the contact between the solid surface and the liquid in the drop, the lower the hysteresis and the adhesiveness. This fact is of the utmost importance in the design of super-hydrophobic surfaces, since they are characterized by the fact that water droplets roll easily across a surface due to poor contact between the liquid and the substrate (surface).

In turn, this difference in angles determines the angle of sliding that determines the degree of inclination to which we must subject a surface so that the droplets roll over it and drag dirt particles in its path giving us the ***degree of self-cleaning*** (it is another quality factor that is integrally related to the degree of adhesiveness).

In short, the contact angle is a measure of static hydrophobicity while the hysteresis of the contact angle and the sliding angle are dynamically mediated. As super-hydrophobic surfaces are to be achieved, they must meet the different points: that the contact angle formed by the liquid with the substrate is greater than 150°and that the hysteresis of the contact angle and the sliding angle are less than 10°.

Experiment to determine the contact angle:

The materials that were necessary to carry out the experiment to determine the contact angle are a piece of cloth or Surface that can be moistened, some water contained in a drop count and the hydrophobic product that you want to use to see the hydrophobic effect.

The first step is to drop a drop on the surface of the fabric without prior treatment and see how the drop of water stays on the surface, if it is completely dispersed by the fibers of the fabric or on the contrary it looks how it retains a part on the surface and the angle that is formed.

The second step is to treat the surface of the fabric with the product and after allowing the product to dry, drop a drop with the drop count on the surface. Once this was done, we it was observed that the drop was not completely dispersed as in the previous case but that it was observed how the drop was “suspended” on the surface and it was found that the angle of contact of the drop with the surface was greater.

This second step was carried out with different amounts of product applied on top of the surface in this way it was observed that the more quantity of the product, the greater the contact angle and therefore the greater the hydrophobic capacity. But it should be said that, as in the previous experiment, there is a limit quantity of product that can be supplied from which that angle no longer increases and therefore we will also have a limit of hydrophobic capacity.

A fifth quality factor would be the ***hiding power*** determined by the quantity of pigment or the active ingredient, as in this case, in the formulation and which can modify the colour of the surface where it will be applied is calculated with the quality index ***alteration of the colour***. This parameter is important above all for suede surfaces, as mentioned *in section 2 of this work (Product Functionality*), since they have a higher porosity, they can absorb stained liquids more easily and therefore, change their default colour.

Experiment to determine if there are some alteration of the surface colour

As in the previous case, a piece of cloth or surface that could be moistened, some water contained in a drop count and the hydrophobic product to be used were necessary.

First you would see the colour of the piece of cloth or surface where it is to be sprayed. Then, a first test would be done leaving a drop of water on the surface without being treated to see what colour the surface ends up having with the drop. Once the colour is noted and the surface is dried, we treat the surface with the product and see if there is a change in surface colour or not. That colour is noted and then a drop is dropped on the hydrophobic surface to see if there is another colour change. Having done these steps, the colours obtained are analysed and if the colour changes from the beginning to the end of the experiment are observed.

Another of the most important quality factor is the ***durability*** of the product. Practically the most important property for consumers. As it has been commented at the time of conducting the market analysis, this property is entirely related to the amount of fluorinated and more specifically acrylates. These when applied on the surface create covalent bonds with the hydrophilic chains of the surface, making it very difficult to detach it and leaving its hydrophobic part towards the outside of the surface. These acrylate properties will be detailed in detail in the next section, in relation to the *Selection of the ingredients and microstructure.*

Drying time is also an important quality factor, which is determined by the choice of the component that forms the hydrophobic film, that is, the active ingredient. Consumers have learned to associate aerosol coatings with quick drying time, and as a result the majority of coatings sold of less than 30 min as shown in *Sciarra, Stoller (1974).* However, generally speaking, the slower-drying coatings are more durable than very-fast-drying ones. What explains a great relationship this factor with the durability factor, previously commented. Therefore, the two most commercial use aerosols are expected to have drying times of about 20 minutes, while the most commercial use has a drying time of about 50 minutes.

But above the other quality factors, that essential element that distinguishes an aerosol coating from those coatings that are applied by brush is the **sprayability**. This characteristic can be defined as the ability to apply small droplets on a surface with minimal finger fatigue and, after drying the drops, produce an attractive appearance. Spraying can be divided into two parts: application and appearance. The viscosity, the coating / propellant ratio of the solvent mixture, spray head selection and valve clogging freedom are the variables that affect this quality factor according to *Sciarra and Stoller(1974).*

4. SELECTION OF THE INGREDIENTS AND MICROSTRUCTURE

Referring to *Aerosols. Kirk-Othmer Encyclopedia of Chemical Technology, 5th ed. Vol. 1,* aerosols are a unique type of product. This is because not only the formulation is important, but all the components of the product are, in the same mediated, important and related to each other. Therefore, in this section, in addition to explaining the structure and formulation that the contents of the can will have, the packaging will also be chosen.

The product to be developed, being an aerosol, will be considered a two-phase system. One phase will be the liquid / solid mixture; and the second will be the gas phase composed of the propellant (located in the upper space above the mixture) as discussed in *Sciarra and Stoller (1974).* What makes us think that the structure of the product will be a homogeneous liquid in terms of the expelled ingredients remain in the form of a film on the desired surface and the solvents have evaporated. As mentioned in the section on quality factors, both the free energy of the surface of the material and the microscopic roughness of the surface determine the hydrophobic capacity. The lower the free energy and the rougher the surface, the stronger the hydrophobicity.Water is a substance with a relatively high surface energy. Therefore, in order to achieve great hydrophobicity, substances whose surface energy is less than that of water must be sought. These types of substances are those that contain silicon and fluorine, exhibiting great hydrophobicity, causing the water to reduce spherically on the surface of said substance.

Although in the present work different products are going to be developed, they must have similar functions, there are components that are common in all three; and others that are not. Therefore, the characteristics of the ingredients that make up the range of hydrophobic aerosols and the characteristic function of each of them are explained. These ingredients will be the hidrophobizing ingredients (silicone components, fluorinated or the mixture of the two), propellants, solvents and nanomaterials.

Finally, the composition of each of them will be reflected in Table 3, Table 4 and Table 5.

4.1. INGREDIENTS

Fluorine-containing compounds

Fluorinated substances are those organic and inorganic substances that have at least one fluorine atom, with very different physical, chemical and biological properties (*Banks et al. 1994*). Of these substances, the subset of the highly fluorinated aliphatic substances, also called perfluorinated, is taken into great consideration in this work. These may contain one or more carbon atoms in which all substituents are formed by fluorine, whereby a structure of the C_nF_{2n+1} type is obtained and are more specifically referred to as perfluoroalkyl or polyfluoroalkyl (PFAS) *(Buck et al. 2011).*). An example of them is shown in Figure 8.

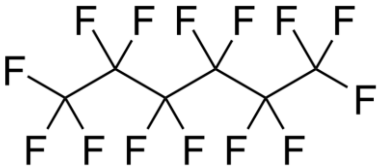

Figure 8. Perfluorohexane structure

(Edgar181, 17/09/07, Wikimedia Commons, Creative Commons Attribution)

According to *Kissa (2001)*, since 1950, PFAS and surfactants and polymers manufactured with the help of PFAS have been widely used in numerous industrial and commercial applications. The C-F link is extremely strong and stable as shown in *Smart (1994)*. The chemical and thermal stability of perfluoroalkyl, in addition to its hydrophobic and lipophobic nature, leads to highly useful and long-lasting properties in surfactants and polymers in which these are incorporated *(Kissa 1994, 2001).* Polymer applications include the repellency of stains, greases and dirt in fabrics as shown in *Rao and Baker (1994).*

All these properties make perfluoroalkyls the active ingredients that you want to use for the most lipophobic and industrial use aerosol, but in particular a perfluoroalkyl acrylate was selected for the formulation as in the *C.N. Pat. No.101962514A*. Perfluoroalkyls, being completely formed by fluorine atoms, these atoms will not react with water but in turn also with the surface where they will be applied, so they will not adhere to it. So to solve this, a hydrophilic part is added. In our case, the acrylate was selected, because its double bond is very reactive, it can adhere strongly to the hydrophilic chains of the surface, leaving the hydrophobic part (the perfluoroalkyl) towards the outside of the surface and thus giving water repellency. In this way they make the fiber surface water repellent without closing the pores and intermediate spaces as commented at *section 2.2. Product functionality*.

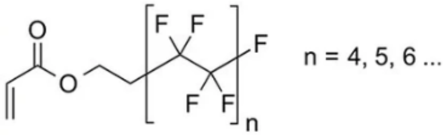

Figure 9. 2-perfluoroalkyletyl acrylates
(image taken from https://fluoryx.com/products/65605-70-1)

Silicon-containing compounds

In addition to fluorocarbons, siloxanes, commonly known as silicones, also have very low surface energies so they are also used so they will be used in this work to achieve water repellent surfaces as shown in *C.N. Pat. No.101962514A.*

According to *Fromme (2019)*, siloxanes, often also described as silicones, are molecules with an oxygen-silicon skeleton (Si-O-Si) where each Si atom carries two organic groups, mainly methyl, ethyl or phenyl groups, the structure is shown in *Figure 4*. Depending on their molecular weight, siloxanes can be characterized as linear or cyclic volatile methylsiloxanes, polydimethylsiloxanes (PDMS) or polyethermethylsiloxanes (PEMS).

The siloxane functional group forms the backbone of silicones, whose main example (and one of the most used) is polydimethylsiloxane (PDMS) as shown in *Röshe and Reitmeier (2003).* The functional group R_3SiO- (where the three Rs can be different) is called siloxy.

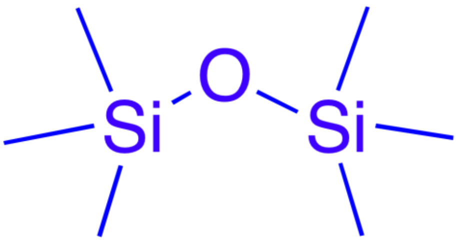

Figure 10.Siloxane structure
(Smokefoot, 02/01/13 via Wikimedia Commons, Creative Commons Attribution)

According to *The unique physico-chemical properties of siloxanes article*, although carbon and silicon share a group in the periodic table, the latter has a greater chemical affinity for oxygen compared to carbon. This difference is reflected in the strength of the bonds (higher link energies, higher link angles and shorter than expected link lengths) associated with the silicon-oxygen bond compared to that of carbon-oxygen. The silicon-oxygen bond angle confers a particular geometry, presenting low barriers for rotation around them due to the low steric hindrance, thus allowing rotation around the link and a more linear arrangement of the system. This geometric characteristic is the basis of the useful properties of some materials containing siloxane, such as its hydrophobic capacity, certain compounds, low glass transition temperatures, and its flexibility as shown in *Siloxane (2019).*

On the other hand, silicon has a moderate capacity to form bonds with hydrogen, but carbon has a very high affinity for hydrogen, with which it forms very strong and stable bonds.

To this is added that the large size of the silicon atoms weakens the silicon-silicon bond, while the carbon-carbon bond is well known for its strength. Thus, giving the structures of siloxane that we know. One of the most used is polydimethylsiloxane (PDMS). But for the hydrophobizing aerosol that only contains silanes as an active component of the range developed in this work, polymethyltriethylsiloxane is used, it is believed to be effective due to its use in *C.N. Pat. No.101962514A.*

Fluorosilicones

According to *Mistri et. al (2015),* fluorosilicones (FLS) are polymeric compounds of siloxane skeleton and fluorocarbon pendant groups The flexibility of the Si-O skeleton and the fact that the outermost surface of fluorosilicone is closely packed with polyfluoroalkyl side groups makes that have a low surface energy. This combined effect of siloxane and fluorinated polymers not only gives low surface energy but also gives integral properties such as weather resistance, chemical resistance, thermal stability, flame resistance, etc. So these materials have been used as surface modifying agents to improve surface properties in the fields of coatings, adhesives, films, fibers and moldings, etc. This low surface energy is the most important characteristic that is taken into account for your choice in this work, since it provides a great water repellency due to the migration of silicone to the surface as shown in *Kozakiewic et. al (2015)* being very useful for its application in antigraffitis or antieaderentes. In addition to these, there are other applications of fluorosilicones: they can be antifoaming agents for organic liquids, cosmetics and other formulations for the use of the skin in which long-lasting repellency of oil and water is desired, release agents for pressure sensitive adhesives in PDMS, coatings and antifouling lubricants, and even aerospace applications that can determine good performance even at extremely low temperatures up to -70 °.

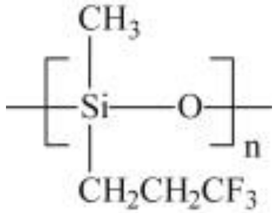

Figure 11. Fluorosilicone structure

The primary and most commonly used commercial fluorosilicone is poly (3,3,3-trifluoropropyl methyl siloxane (PTFPMS). This is used in several applications, particularly where there is a need for resistance to fuel, oils and hydrocarbon solvents. Examples are lubricants in bearings exposed to such materials and sealants and elastomers for automotive fuel systems as shown in *Mistri et. al (2015).*

Propellants

According to *Aerosols. Kirk-Othmer Encyclopedia of Chemical Technology, 5th ed. Vol. 1,* the propellant maintains adequate pressure inside the container and expels the product once the valve is opened. The propellants can be a *liquefied* halocarbon, a hydrocarbon or a mixture of halogenated hydrocarbons, or a *compressed gas* such as carbon dioxide, nitrogen or nitrous oxide.

Liquefied gas propellants (chlorofluorocarbons, hydrocarbons and hydrofluorocarbons): One of the advantages of using a liquefied gas propellant is that the pressure in the aerosol container remains constant until the content is completely expelled. The disadvantages are that hydrocarbons are flammable. In addition, aerosols have earned a reputation for being harmful to the environment and the ozone layer because they are related to chlorofluorocarbons (CFCs) that were their base in the past, but are now banned. Manufacturers eliminated the use of CFC almost 40 years ago (the United States banned the use of CFC in 1978).

Aerosol products now use propellants, such as hydrocarbons and compressed gases that do not deplete the ozone layer, but still have a negative effect on the carbon footprint. These propellants, since they contain compressed hydrocarbons and gases, emit volatile organic compounds (VOCs) that are also harmful emissions to the environment as shown in the article *Chlorofluorocarbons and Ozone Depletion (2017)*

These types of propellants are usually soluble, so they must be stirred before use so that the propellant is dispersed in the liquid concentrate. Dissolved gas tends to escape into the atmosphere, dispersing the liquid into fine particles. The pressure inside the container decreases as the product disperses because the volume occupied by the gas increases. Then, part of the gas leaves the solution, partially restoring the original pressure. To be aware of that fact, *Sciarra and Stoller (1974)* comment that propellants must have a mutual solubility with solvents since the combination of both must serve as a solvent for the active ingredients.

In the formulation of the two aerosols of more general use to the public this type of thrusters will be used. More specifically butane-propane mixtures will be used, this type of propellants are simpler and do not need as much pressure as the product with a more industrial approach might need, such as the super hydrophobic spray with fluorides.

Compressed gas propellants (carbon dioxide, nitrous oxide, nitrogen): Compressed gas propellants, so named because they are gaseous in conventional aerosol containers, are very inert, non-toxic and non-flammable. But as a disadvantage they have that when used in aerosols, the pressure in the container drops as the contents run out, thus making the expulsion of the contents out of the container more complicated. Although the problem decreases when the contents are materials in which the propellant is somewhat soluble, this pressure drop can cause changes in the speed and characteristics of the aerosol.

In the formulation of the fluoride-only aerosol, carbon dioxide, a compressed gas propellant, will be used, since it is the most superhydrophobic product in the range that the concentrate in liquid form is expected to be immiscible with the propellant inside the aerosol. This super-hydrophobicity means that higher pressure and technology are required, which can be achieved with this type of thruster. In addition, these types of thrusters are inert, non-toxic and non-flammable, which makes them very stable products for any type of industry.

Solvents

Shepherd (1961) tells us that in addition to the active ingredients and the propellant, most aerosol formulations contain a solvent or a mixture of them. The solvent is included for one or more of the following reasons: to produce a compatible formulation; to increase its effectiveness; to reduce the pressure.

As a general rule, all these solvent effects occur at the same time, although the main reason for adding the solvent may have been limited to one or two. The choice of solvent can have an important effect on the properties of the complete formulation and more specifically, on the active ingredient or propellant that is used.

According to *Sciarra and Stoller (1974),* if the active ingredient has infinite dilution characteristics with low solvent solvents, the choice of solvent is based almost exclusively on the evaporation rate. However, if the tolerance of the active ingredient to the solvent of low solvency is limited, then it will be necessary to choose strong solvents so that the solvent power of the propellant / solvent mixture is high enough to keep the active ingredient accommodated to the large volume of propeller.

It must produce a formulation that, on the one hand, does not react the solvent with the container, the valve components and other materials; and on the other, it remains the effective product during temperature changes and during long storage periods, as showed in Shepherd (1961). Finally, based on this information and the modifications by the patents *C.N. Pat. No.101962514A* and *C.N. Pat. No.110054915A*, the integration of ethanol and acetone as solvents for the products to be developed was proposed. Ethanol for more personal use products and acetone for more industrial use.

Nanomaterials

In addition to the roughness of the material on which aerosols, leather, nubuck and suede will be applied, we also superimpose another roughness based on nanoparticles. In this way, different hierarchies of particle sizes, large and small, are obtained, one over the other, generating the superhydrophobic capacity of the surface as discussed in *Barjola et. al (2007).*

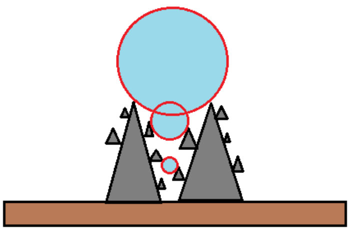

Figure 12. Nanoparticles of diferent sizes on the surface.

As shown in Figure 12, due to these nanoparticles of different sizes, the deposition of the drops on the surface is difficult, regardless of the size of the drops. A large drop will be retained by the larger particles, while a small drop will be retained between the small particles.

These nanomaterials, or nanoparticles, are titanium oxides, silicon oxides, zinc oxides and zirconium, but in this work we have chosen to work with titanium oxide for the three aerosols. Titanium oxides have been chosen over other oxides because it is cheaper and they all have very similar properties. According to *Hanaor, Dorian A.H. and Sorrell, Charles C (2011),* titanium has the ability to catalyze the decomposition of organic compounds by oxidizing them when exposed to sunlight and lower surface energy on the surface. Which make it useful as an additive in construction materials, for example in antifogging coatings and self-cleaning windows. These titanium oxide nanoparticles can be hydrophobicized and sold hydrophobicized as mentioned in *Jang, Hee Dong et. al 2010 10th IEEE Conference, ,* but the characteristics we need are their hydrophilic character and the nanoroughness they provide, so they will be received with small different particle sizes ranging between approximately 5 to 0.5 µm without being treated as shown in *C.N. Pat. No.110054915A*. When these oxides are not treated, they are hydrophilic, due to the humidity of the air they end up being hydroxides, which will help their adhesion (once applied to the desired surface) with the fluorinated surfactant. With these nanoparticles completely covered by the component that will give us hydrophobicity.

Patents like *C.N. Pat. No.101962514A*, had lanthanide oxides in their formulation but this option was rejected. This decision was made because the function that lanthanide oxides could provide in the final product would be a catalytic activity that degraded the possible dirt that would remain on the surface of the material but that property also has titanium, as previously mentioned. In short, it was a choice not to add more complexity to the formulation or more economic investment to, after all, obtain similar properties

Final proposed composition

Next table details the final formulation proposal for all the super-hydrophobic aerosol of the range. The proportions of the ingredients of each product have been chosen based on those shown in the patents *C.N. Pat. No.101962514A* and *C.N. Pat. No.110054915A.*

Table 3. Final formulation proposal for the super-hydrophobizing aerosol with silanes

Super-hydrophobizing aerosol with silanes	
Ingredients	**Content (%)**
polymethyltriethylsiloxane	1.0%
nano titanium dioxide	15.0%
ethanol	20.0%
propane	35.0%
butane	29.0%

Table 4. Final formulation proposal for the super-hydrophobizing aerosol with fluorinates.

Super-hydrophobizing aerosol with fluorinates	
Ingredients	**Content (%)**
perfluoroalkyl acrylate	5.0%
nano titanium dioxide	5.0%
acetone	45.0%
nitrogen	45.0%

Table 5. Final formulation proposal for the super-hydrophobizing aerosol with fluorosilicone

Super-hydrophobizing aerosol with fluorosilicone	
Ingredients	**Content (%)**
fluorosilicone copolymer	15.0%
nano titanium dioxide	1.0%
ethanol	5.0%
propane	55.0%
butane	24.0%

4.2. PACKAGING

Although the packaging is also part of the conceptualization of the product, it was decided to include it in this section due to the importance it has in the formulation. In addition to its importance in containing the product in optimal conditions and its application being effective, the product packaging is a decisive factor because it's the first thing that the consumer perceive of the product. It's a sensorial experience, engaging us through sight and touch by the first impression. These details could make understand to the consumer what the enclosed product is for, how it should use it and who should use it. All these details could be the determining factor when choosing a product or another.

According to *The ultimate guide to product packaging design (2019),* before starting to design the packaging of the products to be developed, three questions must be answered:

1. What is the product?
2. Who's buying the product?
3. How are people buying the product?

Answering the questions, the product is a hydrophobic aerosol, intended for any type of public who wants to take care of their footwear and clothing.

So, in this section we will talk about the definition of aerosol referring to the container and how to apply the product, not the product itself.

Referring to *Aerosols. Kirk-Othmer Encyclopedia of Chemica Vol. 1, pp 769-786*, aerosols developed in the early 1940s due to the development of an insect repellent spray during World War II. Already in the 1950s it had had commercial success and it was evolving both the compounds they contained, as well as the dimensions, materials and technologies of which they were made.

This success was partly thanks to various advantageous features available to the container itself: one of them was that being sealed tightly, there was no risk of dripping, spillage or contamination. Thing that made it proof of external manipulations. Another was the ease offered by its application. The product can be applied directly without contact by the user, in an efficient way even in hard-to-reach places, due to the volume per second ejected, the spray pattern and the particle size control.

But these properties cannot be achieved if the product does not have the necessary components that make that product, an aerosol.

Currently the aerosols have very advanced technologies, but ultimately, they have three main parts that make them common to the other aerosols, these parts are the valve, the actuator and the container. Each of the parts will be explained below.

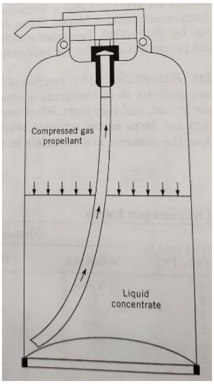

Figure 13. *Compressed gas aerosol using insoluble gas as propellant*
(image taken from Aerosols. Kirk-Othmer Encyclopedia of Chemica Vol. 1)

Container

The container is the container where the valve, the actuator and the ingredients (propellants and the concentrated product) are arranged as commented in *Revathi et. al (2012).* Mainly they are characterized by the material of which they are composed and the capacity they have, both are a function of the pressure they must withstand. Usually, they are made of metal or glass and plastics, depending on certain requirements that the product has, although the latter are more commonly used in the pharmaceutical and cosmetic industry. That is why, in this work we will study the type of container made of metallic materials that best suits the range of hydrophobic sprays to be developed, then the types are listed and finally the most suitable one will be chosen.

According to *Aerosols Kirk-Othmer Encyclopedia of Chemica vol. 1, pp 769-786*, an example of metal composite containers is those formed by steel. These are usually cylindrical in shape and with a concave (or flat) bottom and a top convex dome with a circular opening finished to receive a valve with an opening of about 2.54 cm. They have three pieces (body, bottom and top), contain an amount of between 100-150 ml of product, a diameter of 54.0 mm and a height of approximately 141.3 mm.

A subgroup, tinned steel containers, is obtained from the steel containers. Which have a tin coating that provides protection to both the inside and the surface and are welded by a side seam thus giving greater security against leaks. In addition, welding eliminates the need for a certain amount of tin, which translates into less financial investment. Desirable and welding does not weaken during prolonged storage at elevated temperatures. In addition, an inert internal organic coating can be applied to protect the product from any unwanted reaction within the container.

Another option that was raised was the use of an aluminium container with one-piece construction (monobloc) as shown in *Shepherd (1961)*. These containers are widely used for many products and are available in a wide range of heights and diameters. Due to the great versatility in terms of its shape, several unusual shapes can be found in the market, they can also be coated. These types of containers due to the oxide coating have great hardness and corrosion resistance, making them a good choice for a wide variety of applications. But on the other hand, they have the disadvantage that if the container is hit and the coating has been penetrated, the corrosion on the aluminium will accelerate.

After shuffling the different options listed, a tinned steel container of 120 ml capacity was chosen.

On the one hand, the formulation gives us a stable product that we believe may not require more complexity than that provided by steel. In addition, it is believed that steel against aluminium may be more resistant, containing the high pressure that the aerosol for more industrial use may have inside, in addition to the resistance to shocks it may receive and the possible corrosion that may occur.

On the other hand, the choice of capacity was based on the fact that the most common hydrophobic shoe sprays in the market generally have a capacity of 200 ml and we believe that having this smaller size would be a more attractive product for those people who They want to take these products with themselves or they don't have much space at home. Despite this, we have two options in terms of construction material or composition of the container once its capacity has been determined. For that reason, it is necessary to compare the two remaining options to choose the one that is most suitable for the range of hydrophobic sprays to be developed.

Valve

There are two quality factors that are directly related to the packaging and even more specifically with the valve, which are the speed of spraying, the spread of the aerosol and the size of the particles:

On the one hand, the spray rate is a direct function of the valve that is crimped on the inner edge of the can, so the design of this component is very important for the realization of formulated products.

On the other hand, the particle size in the aerosol and the extent of spraying depend on the shape and size of the nozzle.

The dispersion valve and the actuator serve to close the opening through which the product and often the impeller enter the container, to retain the pressure inside the container and to dispense the product in the precise form and dosage provided by the manufacturer and expected by the consumer. Referring to *Aerosols. Kirk-Othmer Encyclopedia of Chemica Vol. 1,* there are many variations but in essence an aerosol valve consists of the following components:

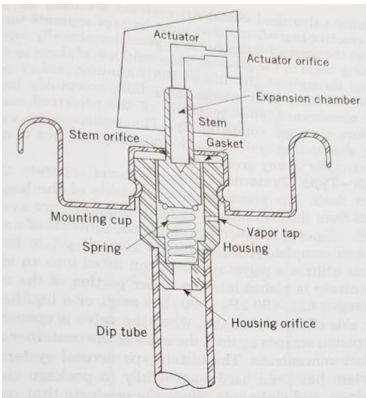

Figure 14. *Aerosol valve components*

(image taken from Aerosols. Kirk-Othmer Encyclopedia of Chemica Vol. 1)

The *mounting cup*, mechanically joins the valve to the container and is usually made of tinned steel at the bottom (but it can be made of a variety of materials such as coated aluminium). It contains a (polymer) gasket that provides the seal.

The *housing* physically keeps the valve parts together by means of crimping by fitting on the pedestal of the mounting cup and is made of several common thermoplastics. A steam tap may also be present to reduce the flammability of the product when emitted or to produce a finer and drier spray.

The plastic *stem* is the mobile segment of the valve. It provides the opening mechanism and generally contains other measuring holes.

The *spring* ensures a solid closing action and is usually wound with stained steel wire.

The *immersion tube* conducts the product from the container to the valve and serves to reduce the flow rate and can operate at the rate of the liquid measuring hole in the valve housing.

The *actuator* contains the end hole and a finger pad or a mechanical link for on and off control. The spray pattern is greatly affected by the construction of the actuator, particularly by the chamber that precedes the hole.

5. DESIGN OF THE MANUFACTURING PROCESS

The last step, once the microstructure and the ingredients of the formulated product have been determined, design its manufacturing process.

The process design establishes a series of chemical and physical operations, operating conditions, equipment necessary to guarantee the operation of the plant and construction materials of all process equipment, line sizes and main instrumentation. This section will not only explain the operating conditions, but also a theoretical production will be designed for a given population.

The manufacturing process of the range of super-hydrophobic aerosols will be carried out as a batch process. A batch process is the process in which a sequence of operations is executed over a certain period of time, providing a specific raw material input to the system, a product output is obtained after a certain time. Batch processing is a very common production method in the chemical process industries, such as pharmaceuticals, agrochemicals, perfumes and many more.

The batch process for the aerosol range is the option chosen, firstly because a large production of the product is not going to be generated, which adding that this type of production has lower capital costs than in continuous will be a key point in the investment. In addition to the fact that in the developed range the products do not have large differences in terms of composition, working in batches gives the flexibility to produce a wide variety of different product types in the same system, so that the place of optimization is optimized production.

The products developed are superhydrophobic aerosols, which have few differences between them in terms of the compositions. These products were conceived with the idea of supplying a large population but which could have around 100,000 consumers. Assuming that each of these people consumed an aerosol per year, taking into account that these products as mentioned in the section referring to packaging will be available in 120 ml containers, an amount of 12,000,000 ml per year of aerosol should be produced. The final density of each of the aerosols is approximated to 1 kg/L, knowing the density of the ingredients that the components, a production of 12,000 kg per year is calculated, or what is the same, 12 tons per year of aerosols, 4 tons per year of every aerosol.

But to reduce the stock and not make all the production at the beginning of the year with the result of having a product stored, batches of 3,000 kg of spray (1000 kg of each, which is the same, 1 m^3 of each that is the reactor capacity) will be established. So, if the desired production is 12,000 kg in batches of about 3,000 kg, the number of lots will be four, one every four months. It must be said that this is an approximate quantity because the number of lots will depend on demand, in addition this production will also be conditioned by the type of plant where they will be produced. When working in batches it has been decided to work in a multiproduct plant (the recipes of the products are different but the manufacturing process is similar) not only focuses on the manufacture of this range of aerosols, but others are manufactured in the same plant while aerosol batches are not carried out (due to the similarity in product compositions there will be no need to worry about cross contamination). In addition to this, the equipment will be available for products that may need more thorough cleaning after carrying out the lots belonging to the aerosols. That is, a batch of 1m^3 of each product will be manufactured every four months, but this can be modified depending on demand. To produce these batches, the quantity of each ingredient will be adapted to 1m^3 which is the capacity of the reactor where the mixture is to be carried out.

A unique manufacturing process has been designed since there are no differences in the process flow chart for each aerosol, the only difference there are certain ingredients in the recipe to make each product, but its function is the same. So for the three aerosols the same equipment will be used that are essentially a reactor and a packaging machine.

5.1. FLOWSHEET PROCESS

The flow chart for the aerosol manufacturing process generally consists of only a few unit operations. In essence it can be divided into two steps. First a batch of the desired quantity of raw materials is made, and then the batch is introduced into the cans by a packaging machine. (*How products are made Volume 3 Mosquito repellent).* But being so few, more steps will be described below:

According to *C.N. Pat. No.101962514A*, first we must weigh the raw materials according to the formula; secondly, all raw materials, except the propellant, are stirred and mixed evenly, and then placed in a can; the valve is then inserted into the can, sealed and filled with a propellant and finally, the canned aerosol is subjected to online weighing, water bath leak detection and labelling.

No pre-treatment step is included, since there is no need, all ingredients are ready to use. The nanoparticles, for example, have the size and shape that is required on demand.

Mixing

All ingredients, except the propellant, are added to a stainless steel reactor or tank and mixed. Silanes and fluorides can be incorporated into the reactor in different ways, but being as an oil, an oil phase, it is best to add them to the reactor as the first ingredients. Next, the nanoparticle set will be loaded. To the oil phase formed by the silanes and / or fluorinated the nanoparticles will be added and slowly while stirring to achieve homogenize the mixture perfectly.

Since some of the materials in this process are flammable, spark-proof electrical outlets and explosion-proof walls will be used. Once the batch is finished, a small sample is sent to the laboratory, to the quality department and there they will ensure that the product meets the established standards *(How products are made Volume 3).*

Filling

After including all the ingredients and mixing, the aerosols will finally be packed in 120 ml containers, as mentioned in Chapter 2, referring to the packaging.

Aerosols will be produced by a pressure-filling process, the usually method in the industry as shown in the *Aerosols. Kirk-Othmer Encyclopedia of Chemica Vol. 1, pp 769-786,* first, the content is introduced, generally, a concentrate is prepared which is filled into the aerosol container and then the valve is added. This pressure filling will be carried out through the valve but could be carried out too by an under-the-cup filler where a vacuum is drawn, the propellant is added (under the valve cup), and then the valve is sealed in place.

As the filling through the valve stem is the selected method for this process, the product is first filled into the container, a valve is crimped into the place, and, at the same time, a vacuum is drawn in the can. The propellant filler then forms a seal around the head of the can and under high pressure the propellant is forced through the actuator and valve stem into the container. The contents are then checked for leaks and an overcap is added to complete the process.

These compressed gases (propellants) like nitrogen, carbon dioxide, and nitrous oxide are added through the valve using a gasser-/shaker-type filler.

5.2. SELECTION OF THE EQUIPMENT UNITS

As commented in the section *4. Selection of the ingredients and microstructure*, we have products with different ingredients, but the function is the same, in addition, due to the nature of these and the quantities that are desired to produce, the optimal selection of equipment will be to choose common equipment for the three types of aerosol. In addition, therefore, there is no need to worry about cross contamination and then equipment that meets the range of requirements demanded by each aerosol will be chosen. This equipment consists of a stirred tank reactor and a packaging machine.

At the time of selecting the equipment, a search was also carried out in parallel of the way in which the first subjects are distributed to make a further explanation of carving. In this search you will find the solid particles of titanium oxide will be sold in bags of 25 kg so they will be stored in the warehouse that has the plant as shown in *Dióxido de titanio 25 kg (2019)*. It was also found that liquefied gases that act as propellants in our product, such as propane and butane, are usually marketed in 12.5 kg butane cylinders and between 11 kg and 35 kg propane. Therefore, 12.5 kg butane bottles and 35 kg propane bottles will be stored as mentioned in *Propano y Butano envasados (2019).*

As you work in batches and do not have a large amount of production, it is interesting to be able to store the products in a comfortable way such as in sacks or in drums, as long as you take into account the stock.

Mixing

Mixing is the first large part of the production process and to make the selection of the equipment involved in this process we first look for the proposals that the program *Aspen Batch Process Developer* offered us. Reactors of various capacities were observed under DIN Europe standards which are technical standards for the quality assurance of industrial and scientific products as discussed in *Deutsches Institut für Normung (2019*). We observed that Aspen *Batch Process Developer* works with two brands, De Dietrich and Pfaudler. The most suitable among the possible ones was sought and this last brand offered the Pfaudler DIN Reactor BE 12500 reactor that has a capacity of 12500 L which we thought was more suitable for the production process. The choice of this reactor was based on the volume of ingredients to be loaded (1 m^3), in addition, despite assuming a density of 1 kg / L of product the silicones will make it denser so the reactor must be larger than the volume loaded. Add to this discussion the fact of the pressure conditions that will be generated inside by adding the propellants and good homogenization, which will be done with less volume occupied by the ingredients.

Figure 15. Pfaudler DIN Reactor BE 12500 reactor

(image taken from Catalogue Pfaudler DIN BE reactors)

As in this mixing step we will have various liquids with gases, among the different options the axial flow or hydrofoil agitators were chosen as the most suitable. The reactor already has its agitation system, but these obligations must be according to the requirements of the product, so that types of agitators were observed in the model to choose the suitable one for the process. With the search we observe that the best agitator would be the TBF *(Catalogue Pfaudler DIN BE reactors).* These types of impellers have high axial flow, a low torques/low power consumption, very versatile and have great mixing efficiency. When working in a multiproduct plant this is an important factor since it can work for turbulent regimes of low viscosity and laminar regimes of high viscosity.

Figure 16. TBF agitator

(image taken from Catalogue Pfaudler DIN BE reactors)

Filling

For filling a B-GS-700K model of the Dawsom brand, shown in *Dausom filling machine (2019)*, was chosen as it is designed for a wide range of applications. This is a Semi-automatic butane gas cartridge filling machine mainly for small scale production. In principle it is designed to fill the can of butane gas, but in our process, it will also be used for the other desired propellants. The filling system starts with vacuuming the aerosol can, then crimps the can, and then fill the gas into the can through the valve stem. It is 100% pneumatic (no need for electricity) and super easy for operation and maintenance.

Figure 17. Semi-automatic Butane Gas Cartridge Filling Machine B-GS-700K
(image taken from Dausom filling machine (2019))

Furthermore, to the filling machine a boosted pumb gas spray, shown in *Booster Pump Dawsom (2019*), also of the Dawson brand, will be available to ensure that the gas is filled in the can in liquid phase. This pump also maintains a desired and constant gas pressure. Thus, more stable, accurate and fast fillings can be obtained, making it a very important factor in aerosol production.

Figure 18. Aerosol Gas Booster Pump

6. CONCLUSIONS

Three types of superhydrophobic sprays have been developed establishing their quality factors, selecting the right ingredients and the product delivery vehicle and, finally, designing their manufacturing process and equipment selection. The three aerosols developed are a superhydrophobic aerosol composed of silanes, a superhydrophobic aerosol composed of silanes and fluorine and a final superhydrophobic aerosol formed by fluorides. The differences between them are that the more fluorides they have, the more hydrophobic and more oleophobic they will be. That is, the one that is only composed of silanes will produce little lipophobicity while the fluorinated compound will be very lipophobic.

The selection criteria for surfactants, propellants, solvents or solvents were based on the study of different articles and patents in addition to taking into account the typical market trends. As the characteristics and objectives of the three products are very similar, similar ingredients were chosen.

The hydrophobizing spray composed of silanes provides the surface with a hydrophobic capacity characterized by a contact angle (o) of 155 ± 3 and a contact angle with vegetable oil (o) of 141 ± 3. The hydrophobic spray composed of silanes and fluorides provides the surface with a hydrophobic capacity characterized by a contact angle (o) of 164 ± 3 and a contact angle with vegetable oil (o) of 146 ± 3. The fluorinated compound hydrophobic spray provides the surface with a hydrophobic capacity characterized by a contact angle (o) of 169 ± 3 and a contact angle with vegetable oil (o) of 151 ± 3. These data are approximate in reference to those obtained by *C.N. Pat. No.101962514A et. al (2019).*

It has been decided to work as a batch process with an approximate production of 1,000 kg of each aerosol per batch and with a total production of 12,000 kg of aerosols per year, 4,000 kg of each aerosol per year. Changes in production were considered as it depends by demand. To carry out the manufacturing process, a hermetic stirred tank type reactor and a bottling machine were chosen to refill the cans. In addition, the equipment will be the same for all three aerosols.

Table 6. Final composition of the range of hidrophobizing aerosols

	Super-hydrophobizing aerosols		
	with silanes	**with fluorides**	**with silanes and fluorides**
Hydrophobizer	polymethyltriethylsiloxane (1.0%)	perfluoroalkyl acrylate (5.0%)	fluorosilicone copolymer (15.0%)
Nanomaterial	nano titanium dioxide (15.0%)	nano titanium dioxide (5.0%)	nano titanium dioxide (1.0%)
Solvent	ethanol (20.0%)	acetone (45.0%)	ethanol (5.0%)
Propellant	propane (35.0%)	nitrogen (45.0%)	propane (55.0%)
	butane (29.0%)		

From the work done, it can be concluded that this project has certain advantages:

The production process is simple, it has no temperature or use requirements. As mentioned in patents *C.N. Pat. No.101962514A et. al (2019)*, it is assumed that it will be colourless, odourless, with great adhesion (therefore long useful laminate) and frictional resistance. In addition, due to the high reactivity of the acrylate-containing aerosol, its application is expected to serve not only for shoes, but to have a wide range of application.

Finally, as a summary of the work done in this work, it has been observed that this "technology" is not mature as a whole. At present, there are scientific research institutions and companies developing superhydrophobic materials and technologies and there are many methods to prepare superhydrophobic surfaces, but it is not yet economical and comprehensive enough.

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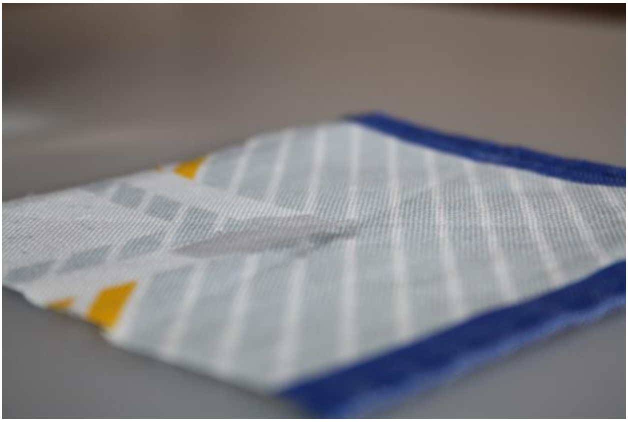
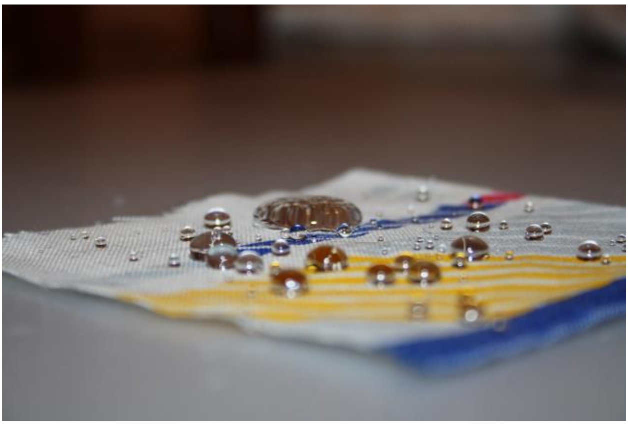
APPENDICES

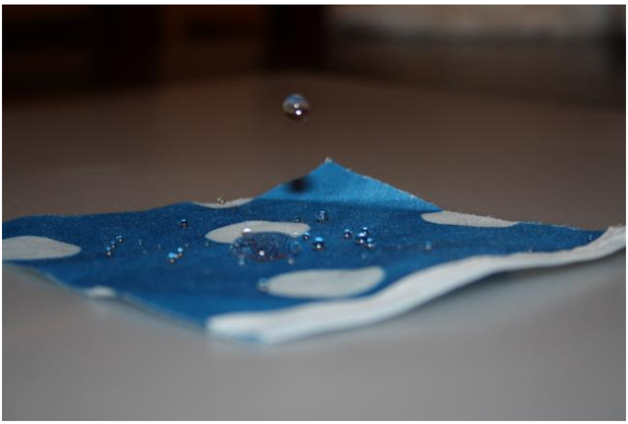
APPENDIX : RESULTS OF THE EXPERIMENTATION

EXP1: HYDROPHOBIC COATING ON 67% POLYESTER, 33% COTTON

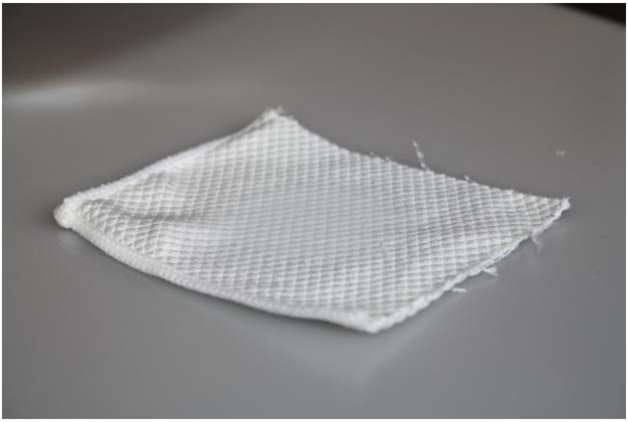




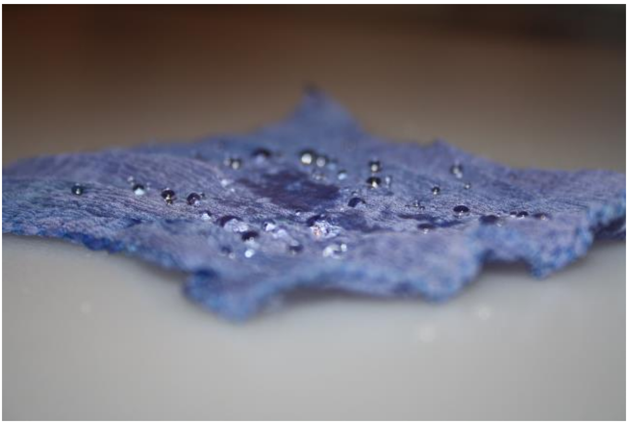
EXP2: Hydrophobic coating on 80% polyester, 20% cotton



EXP3: Hydrophobic coating on 82% polyester, 18% polyamide



EXP4: Hydrophobic coating on 100% viscose



EXP5: Hydrophobic coating on 55% polyester, 45% SLK