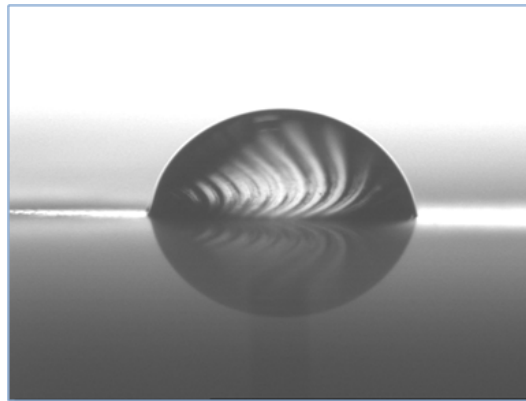


CHALMERS



Methods for preventing the sticking of crude oil on radar antennas used for oil level measurement in oil tanks

Master's Thesis in Applied Physics

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Department of Applied Physics
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2011
Master's Thesis 2011:1

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Abstract

This master thesis have investigated a problem arising on oil tankers in rough sea and cold weather; water and oil sticks to radar antennas used for level measurements in their tanks and prohibits operation of the radar system.

Limiting factors from safety rules on tankers placed the focus on chemical treatments which gives hydrophobic and superhydrophobic properties to the surface. However another lead was also investigated further, were the ability to create and maintain a thin water film to protect a surface from crude oil was researched.

A firm root in the physics of the process, when a liquid meets an interface, is discussed before experiments are conducted and results presented. The best case solutions are proposed based on the experimental data, also possible future studies to verify that the solutions work in the real application.

Today's best commercial repellent coating is not able to withstand the worst of the oils transported in tankers, but they are able to withstand some of the more refined products. The only options available for protecting an antenna from the worst oil product is using a thin water film sustained through a hydrophilic coating.

Keywords: hydrophobic, hydrophilic, surface tension, contact angle, hysteresis, repellent, VGO, titanium dioxide and radar antenna.

Preface

Early in September we initiated our project together with our main supervisor at Emerson, Lennart Almegård. Emerson gave us free rein to plan and carry out the project. We have during the time elapsed encountered problems and limitations that made us change our planning. Though we feel very satisfied with the project and its results and hope that Emerson will benefit from our findings.

The first part of the autumn we spent on literature search and understanding the problem. We were fortunate to, together with a service engineer, visit a tanker transporting oils in the northern Baltic sea. This gave us great insight of the problem at hand. Further on, in the darkness of the winter we began experimenting and measuring in a laboratory at Chemical Physics department of Chalmers University of Technology.

This thesis has been written together and with an equal contribution from us both. A few times during the thesis there were parts that have been worked upon more by one of us; Linus have gotten more results produced in the laboratory while Mattis have done more of the data analysis.

We are very grateful to announce that this thesis ended up in a patent application and hopefully further field tests will eventually realize a launch of a product utilizing our idea.

Acknowledgements

There are many people we would like to thank for our upbringing, education and support during this thesis work. First we would like to thank our families and friends for whom we are, Chalmers and our many teachers we had there which made it possible for us to start and finish this master thesis. During our this thesis work we have had contact and help from many sources and instances, but we would like to especially thank Igor Zoric and Lennart Almegård which have been our examiners from Chalmers and Emerson respectively. Their great knowledge and experience have helped us avoid many first time mistakes. We would also like to thank Emerson for giving us the opportunity for taking a real world engineering problem and letting two fresh students giving it a go.

*Mattis Sunesson and Linus Eklund
Göteborg February 16, 2012*

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1

Introduction

WHAT DO LOTUS LEAVES, insect eating plants and a radar antenna got in common? They all want to remain clean, but whereas the plants and leaves do this just fine due to their natural self-cleaning abilities the radar antenna does not. This thesis investigates and presents different solutions of a self-cleaning radar antenna.

1.1 Reading directions

This report is divided into five chapters where the reader is guided through the problem description in the first chapter. The chapter Theoretical Background represents the theoretical study that was carried out during the initial part of this thesis. The most important concept to grasp for understanding the results presented in chapter 4 is the contact angle. The chapter Laboratory Procedures presents the used equipment and our laboratory approach. Chapter 5 concludes this thesis and the reader only interested in main conclusions should read the introduction and concluding remarks.

1.2 Background

Emerson Process Management Rosemount Tank Radar AB is one of the world leading companies in the field of level measurements using radar technique and has its main office in Gamlestaden, Gothenburg. They operate in three main business areas; Marine, Process and Tank Gauging. In the Marine applications there are strong demands on robust and durable equipment. The company has a goal to be able to deliver tank radars which does not demand service. In 1.1b the system is shown; in Figure 1.1a, the radar unit on top of the tank with a parabolic antenna inside sends out an electromagnetic wave which bounces back. The signal is analyzed through various electronic and software calculations and the radar unit then determines where the surface is down to a few mm. Note that radar echoes and noise from many sources exists so there is a moderate amount of data analysis needed to follow the echo that represents the surface.

1.2.1 Problem background

During cold weather and rough sea measurement problems have arisen at oil tankers with crude oil cargo. The electromagnetic (EM) wave, sent out to measure the oil level

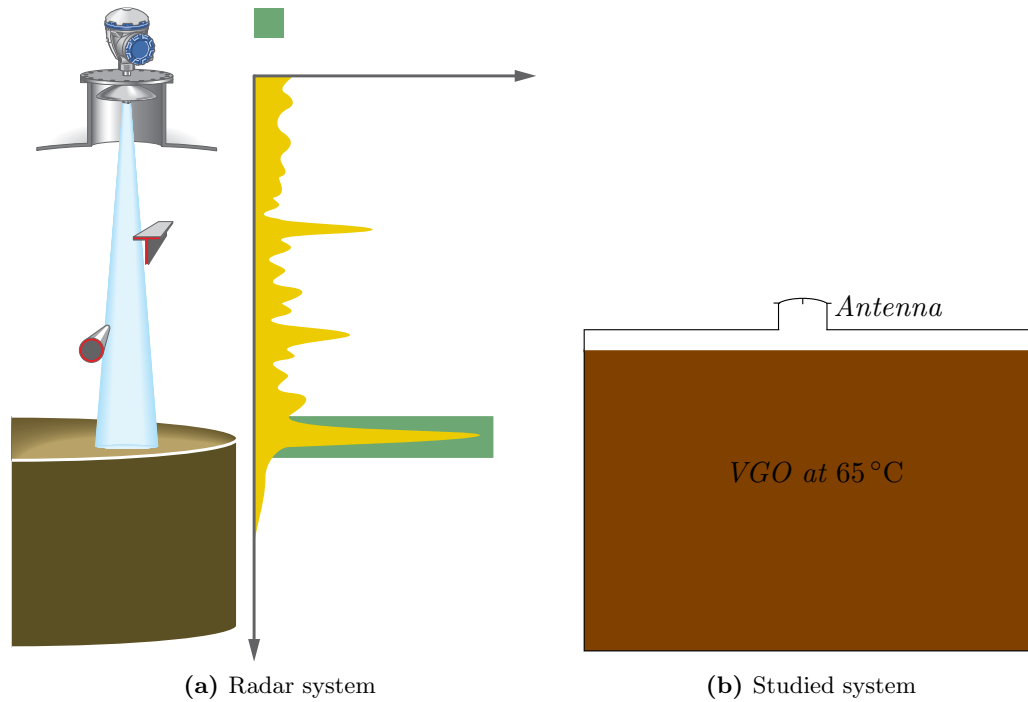


Figure 1.1: a) A radar level measurement system, note the radar spectrum on the right side of the figure where smaller radar echoes from other surfaces such as pipes can come into play. b) A typical tank system where the problem occurs. Heavy crude oils are almost always transported heated to 60-70°C.

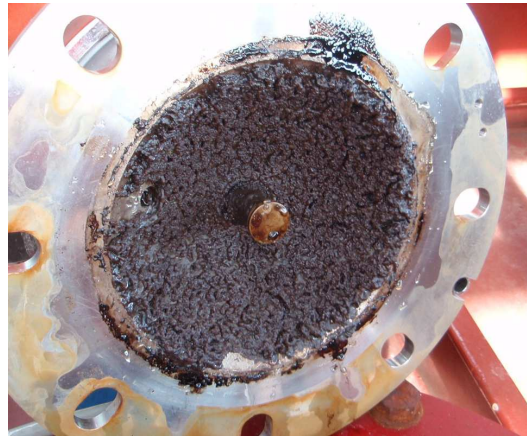


Figure 1.2: An antenna covered in oil and water, these conditions causes a loss of signal.

in the tank, bounces against the parabolic antenna which focuses both the outgoing and incoming EM-waves. Oil and water adheres on the antenna, which lowers the amplitude of the signal until it is lost during cold weather. The adhering of oil and water is an ongoing process that gets worse and worse until manual removal of the residue is the only solution. The problem only occurs during temperatures below 10°C, above this temperature only a few problems arise which do not disable the system. In Figure ?? an antenna covered in oil and water is shown, this is a typical problem situation where the signal is lost. The antenna is made of stainless steel and is mounted on a 150 mm high flange on top of the tank. The radar unit is operating at 26 GHz which corresponds to a wave length of 11.5 mm.

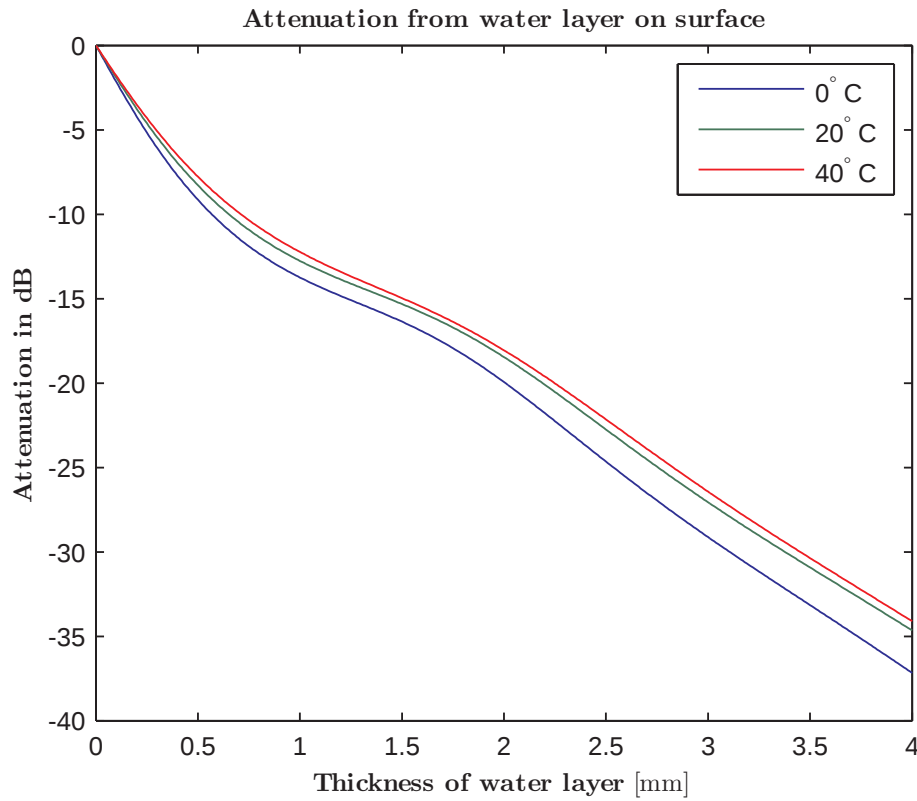


Figure 1.3: Damping of EM-waves in water layer of different thicknesses at 26 GHz and three different temperatures. [1]

The signal damping due to a alien material layer on the antenna is a function of the dielectric constant and the layer thickness. In Figure 1.3 the damping for different thicknesses of a water layer is shown. Note that a higher temperature gives higher damping and that a thicker layer implies higher damping. An attempt to mitigate the problem through creating a repellent coating with nickel nano particles have been tried prior to this thesis, but was never field tested or explored further. We investigated this further in our thesis and evaluated the idea.

1.2.2 Project goal

The goal with this thesis is to explain the physical processes leading up to the problem described above and possibly propose suitable solutions through different materials, surface treatments or similar.

1.3 Project approach

This thesis was initiated by a thorough study on the material available to us through Chalmers, it was evident that most work on repelling surfaces was done experimentally due the difficulties in measuring and characterizing a macroscopically sized surface.

Hence the decision was made to reach results and understanding of the situation at hand experimentally. Plans were made for a testing apparatus consisting of a heated tank containing roughly 100 L of oil, but due to financial reasons and the difficulties in restricting the atmosphere amongst other variables in this tank these plans were scrapped.

The focus then shifted wholly onto contact angle measurements which is the industry and scientific standard of doing measurements of surfaces.

First different grades of roughnesses through lathing were produced, a trend could be identified, where a larger roughness created more and more tendency for the droplets formed on these surfaces to flow out into the tracks and lock into place.

The last steps of measurements were made on electropolished, nickelplated and lathed species of steel disks. The lathed disks had been coated with Titania TiO_2 , where the purpose was to try the possibility of a hydrophilic surface to capture enough water to create a protective layer from the oil. The electropolished and nickelplated disks were made as hydrophobic as possible to avoid water and oil buildup.

1.3.1 Limitations

During the time frame of this thesis there was no possibility to test new materials or coatings in the real application, this was due to the nature of modern marine transport. Ships carry a variety of cargo from point to point to optimize revenue. Thus it is very hard to predict when or where it would be suitable to install a new antenna with the coating of our choice.

An issue that we brought up during the first meeting with the company, and many more has done to us when we presented the problem, is if there is no possibility to heat the antenna since the temperature is an inherent cause to the problem. Due to safety of electrical installations and carrying of volatile cargo the safety rules prohibit the power of heaters to such low numbers that it would not be feasible. One could imagine a type of installation where the humongous latent heat of the carried oil is used, but there are a number of factors limiting and thereby minimizing the installation options for the company.

There could also be a number of mechanical solutions available. The directions of this thesis were not about to solve the issue, but rather research and understanding the feasibility of using coatings or surface structure to avoid issues as these. This knowledge could then be used in different areas of the company.

1.4 Results in short

The surface roughness caused by the lathing of the antenna was investigated, it had no impact on the hydrophobicity but a larger lathing showed improved hydrophilicity. Several commercial repellent coatings were examined, among them a superhydrophobic. Our investigation concludes that no repellent coating is repellent enough to repel the heaviest crude oils transported in tankers, however are lighter oils as cooking oil and diesel easily repelled by a superhydrophobic surface. The temperature of the antenna surface has a large impact on the contact angle since the studied oil (VGO) has a phase transition at $\sim 20^\circ\text{C}$. A hydrophilic material which will let water adhere first and keep the water between the antenna and the oil seems an excellent candidate for further studies and field tests.

2

Theoretical Background

THIS chapter presents the basic theory which will be needed and that we have acquired during this thesis. We begin by discussing forces acting between molecules and a surface of solids, continue with how surfaces interact with liquids and what determines the interaction forces between a solid surface and a liquid.

2.1 Forces between liquids and solids

The problem we are addressing deals with the issue of how to prevent sticking of heavy hydrocarbon molecules (present in crude oil) to a surface of stainless steel 316L. In the first section we describe what forces act between these materials.

2.1.1 Adhesion to surfaces

Surface properties are important for variety of applications; among them are the catalysis on a surface, Teflon frying pans, Gore Tex etc. When a molecule from a gas or liquid phase impacts on a solid surface there are three different scenarios for outcome of the molecule-surface collision event.

1. Adsorption onto the surface
2. Absorption into the material
3. Reflection into the gas/liquid phase

A molecule or atom can be adsorbed onto a surface in two different ways; via physisorption or via chemisorption. Physisorption is an abbreviation of physical adsorption and is characterized by Van der Waals and polar forces. Chemisorption (chemical adsorption) is characterized by a formation of a strong chemical bond. There are different theoretical descriptions for adsorption isotherms when small molecules are adsorbed on surfaces at a given applied pressure (Langmuir and the BET isotherms are just two examples how to describe the buildup of adsorbed layer). [2]

2.1.2 Physisorption - Van der Waal

The Van der Waals (VdW) force is the sum of intermolecular forces other than those due to covalent bonds or electrostatic interaction. For an atom or molecule on a surface

the VdW forces are.

- Forces between a permanent dipole and a corresponding induced dipole. This part of the VdW forces is called the Debye force or mirroring and is shown in Figure 2.1.
- Forces between two instantaneously induced dipoles. This is also known as London dispersion forces, and is shown in Figure 2.2.

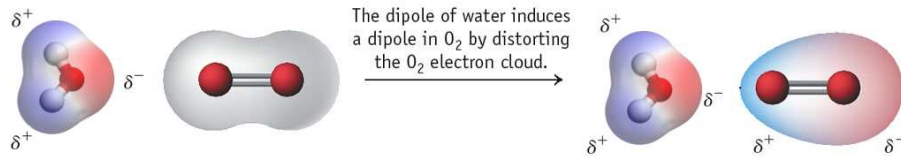


Figure 2.1: The figure illustrates the inducement of VdW forces through mirroring, a permanent dipole affects the electron cloud of another molecule and induces a dipole.

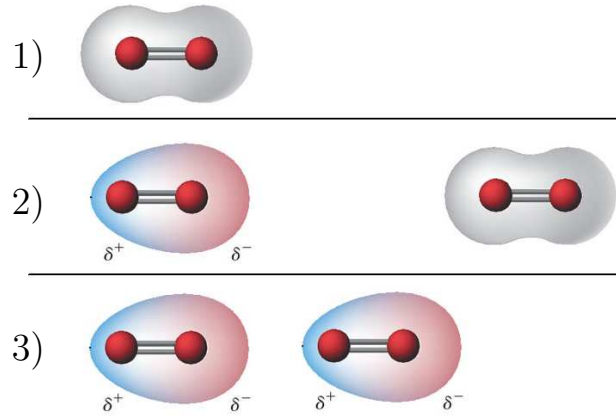


Figure 2.2: The figure illustrates the inducement of VdW forces between molecules. **1)** A perturbation causes the electron cloud to oscillate. **2)** If this molecule is close enough to another molecule this will start correlated movement of the electrons in both molecules. **3)** The electrons will feel each other and want to avoid each other at short intermolecular distances.

VdW forces are relatively weak compared to chemical bonds, typically they are roughly meV while chemical bonds are on the order of several eV. The VdW interaction is increasingly attractive, as the adsorbed atom moves closer to the surface, however when the electron wave functions starts to overlap with the tails of the electron wave functions sticking out from the surface then the energy of the system will increase due to the requirement of orthogonality between the wave functions of the approaching atom and electron wave functions at surfaces. This is a consequence of the Pauli exclusion principle that prevents double occupancy of the same quantum state for fermions. Thus, the Pauli exclusion principle causes an increase in the energy of the system at short distances i.e. it leads to strong repulsive interaction. The latter is particularly strong for atoms with closed valence shells interacting with metallic surfaces. As a result, the minimum in total energy of the physisorbed system occurs at some finite distance which is an equilibrium distance for adsorbed atom on the surface. [3]

2.1.3 Chemisorption

Chemisorption is characterized by the forming of new electronic bonds; a new chemical species is created at the surface where the chemisorption occurs and covalent bonds are created. Unlike the physisorption process, chemisorption does not leave atoms or molecules impinging onto the surface unaffected. A very common reaction apparent everyday is metallic oxidation (rust). As mentioned before chemisorption bonds are in all cases much stronger than physisorption bonds, typically they are in the order of several eV, which is two or three orders of magnitude larger than the physical bonds which lets us make the distinction between them. This also means that the distance between the surface and the closest adsorbate atom is much smaller than for physisorbed atoms or molecules. Chemisorbed molecules may be torn apart at the demand of the unsatisfied valencies of the surface atoms, and the existence of molecular fragments on the surface as a result of chemisorption is one reason why solid surfaces catalyse reactions. [3]

2.1.4 Surface Tension

To describe the interactions between liquid phase substances and a solid surface the concept of surface tension has to be introduced. Two concepts are common in the literature; the surface tension and the surface energy. The surface energy is defined as *The free energy change when the surface area of a medium is increased by unit area* [4]. If a force is applied to increase the surface area of a medium a tension within the medium will rise counteracting the applied force. The surface tension γ is then, in similar to the surface energy, said tension and has the unit J/m² or N/m. The surface energy is related to the surface tension as the tension per area.

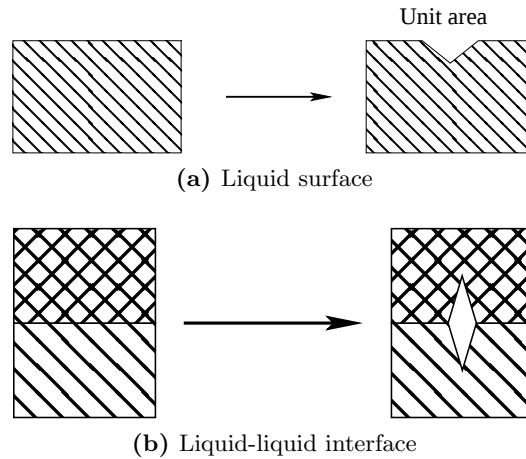


Figure 2.3: a) Breaking the surface by enlarging the exposed area by unit area. b) The interfacial tension of two liquids is determined by the surface tension between said liquids.

The interface between two immiscible liquids can be characterized by an interfacial tension, in similarity to surface tension it is the tensions created upon expanding their interfacial area, see Figure 2.3b. Interfacial tension is defined by the Dupree-equation

$$\gamma_{12} \approx \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d}$$

and the Interface energy is then given by

$$W_{12} = 2\gamma_{12}A \tag{2.1}$$

2.1. FORCES BETWEEN LIQUIDS AND SOLIDS

where the superscript d denotes dispersion force, i.e. Van der Waals forces, contributions to the total surface tension and A denotes the area of applied force. For example water has 27 % dispersion force contribution to the total. Some for this thesis relevant surface tensions are shown in Table 2.1.

Table 2.1: Some for this thesis relevant surface tensions at room temperature [5][4]. Values for stainless steel were averaged from two different publications [6][7]. Eicosane is here used to represent crude oils.

	Dispersion Component (mN m ⁻¹)	Total surface tension (mN m ⁻¹)
Water	20	72.8
316L	40	60
Eicosane (C ₂₀ H ₄₂)	28.9	28.9

The surface tension has a temperature dependency; for liquid compounds the temperature has a higher impact on the surface tension compared to solids. In Figure 2.4 is the surface tension plotted for the temperatures between 20 °C to 100 °C. The surface tension for solids is proportional to $e(-1/T)$ [8], but the temperature dependency for liquids has only been determined by experiments [9].

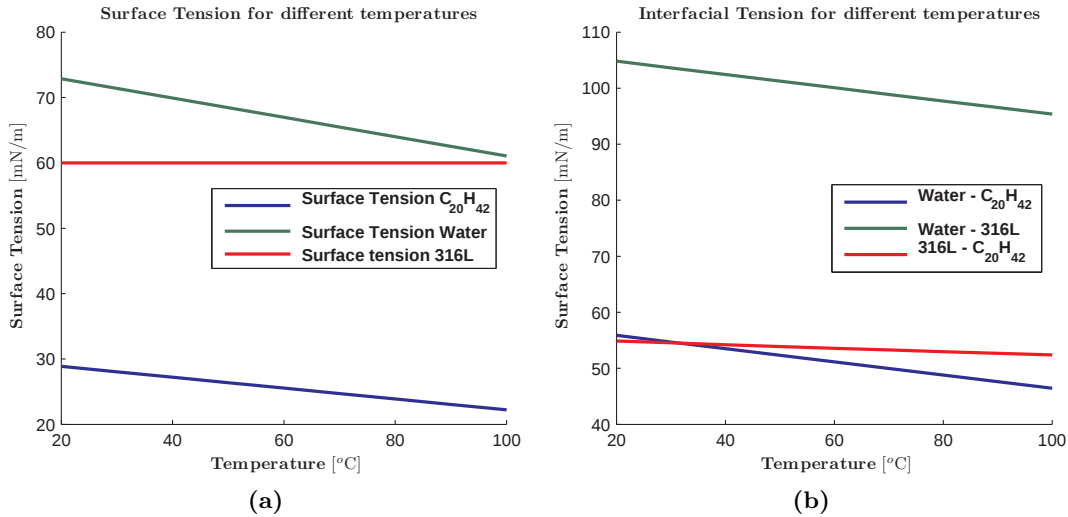


Figure 2.4: a) Surface tension for different temperatures and materials. b) Interfacial tension for 316L, Water and C₂₀H₄₂ for different temperatures, calculated from Equation 2.1.

Interfacial tensions for variable temperatures for different combinations of water, oil and steel are shown in Figure 2.4b. So far only the interfacial tension between two interfaces has been studied, however when an adhesion process takes place in a third medium a different interfacial tension is obtained. It is now convenient to use the concept of interfacial energy instead or work of adhesion.

$$W_{132} = W_{12} + W_{33} - W_{13} - W_{23} = (\gamma_{13} + \gamma_{23} - \gamma_{12}) A \quad (2.2)$$

From Equation 2.2 the graph in Figure 2.5a is obtained. The calculations are based upon an assumption that steel and oil/water is totally surrounded by the third medium (water/oil), see Figure 2.5b and Figure 2.5c. From the interfacial energies in a third medium conclusions can be drawn whether the liquid will wet the steel or not.

When W_{132} is negative it means that medium 1 and 2 repels each other and when positive an attraction occurs. This can be interpreted as that when W_{132} is negative medium 3 will displace medium 2 and thus totally wet the surface of medium 1. When W_{132} is positive a partial spreading of medium 2 and 3 on the surface of medium 1 is obtained. From this reasoning another conclusion may be drawn; the configuration in Figure 2.5c is more likely to occur than the configuration in Figure 2.5b and the system will tend to reach this state since the energy for 316L-water- $C_{20}H_{42}$ is extensively lower than for the system 316L- $C_{20}H_{42}$ -water.

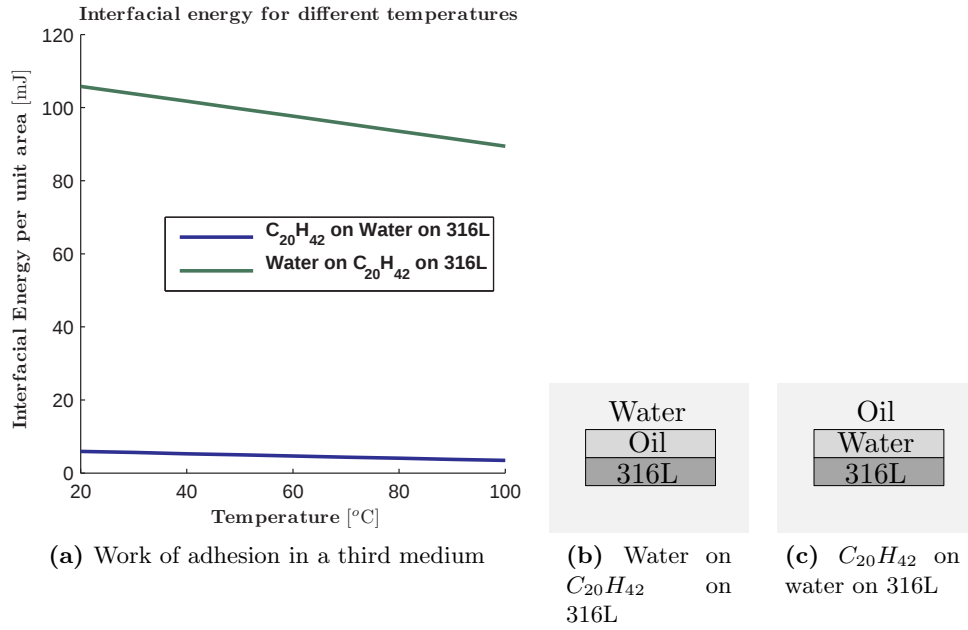


Figure 2.5: a) Interfacial energy in a third medium for different temperatures, calculated from Equation 2.2. b and c) Specification.

2.2 Contact Angle

What determines whether a fluid on a surface spreads out as a thin film or stays in drop like shape? This following section discusses the principles and theory of drop formation and its characteristics.

When a small volume of liquid encounters a solid surface, for example a raindrop on glass, a drop is formed. The drop is a sphere of water sectioned by the surface at a discrete, measurable contact angle. The contact angle is a thermodynamic quantity; a drop surrounded by a gaseous phase will reach the lowest energy possible by forming itself into a sphere. The energy minimized by forming the drop into a sphere is the interfacial energy of the drop and its surrounding medium. Said energy can be related to the interfacial tension, see previous section.

If a fluid is in contact with a surface and surrounded by an inert atmosphere the Young-Dupré equation, Equation 2.1, becomes the Young equation

$$\begin{aligned}\gamma_{12} + \gamma_2 \cos(\theta_c) &= \gamma_1 \\ \theta_c &= \arccos\left(\frac{\gamma_1 - \gamma_{12}}{\gamma_2}\right)\end{aligned}\tag{2.3}$$

where γ_{12} denotes the interfacial tension between solid and liquid, γ_1 and γ_2 is the surface tension of solid and liquid respectively. The contact angle is the limit for wetting and is defined as the angle inside the liquid from the surface to the gas-liquid interface, see Figure 2.6.

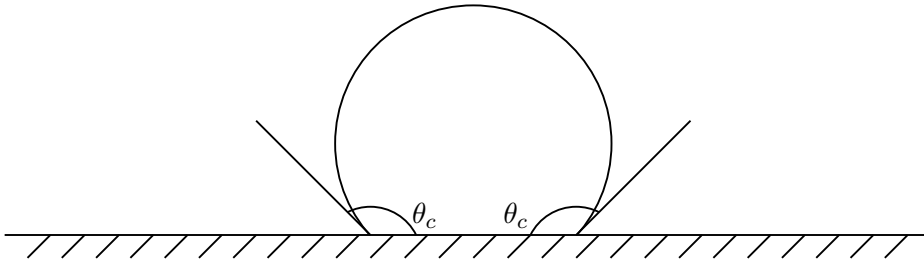


Figure 2.6: Contact angle definition.

The work demanded to disconnect a drop from a surface can thus be related to the contact angle, see Equation 2.1. Thus the work needed to separate an ideal drop from a solid surface without deforming the drop is

$$W = 2\gamma_{12}A = 2(\gamma_1 - \gamma_2 \cos(\theta_c))A\tag{2.4}$$

where A is the contact area between the solid surface and the liquid. However, this is an ideal situation and normally the drop is deformed due to what will in the next section be referred to as *contact angle hysteresis*.

2.2.1 Contact Angle Hysteresis

An ordinary drop is characterized by the three-phase contact line, which for the example of a drop on glass consists of the interfaces between the three materials glass, water and air. Each of these materials and their characteristics will influence the drop's contact angle on the surface, the surface in particular and the topology of it will cause drop deformation or contact angle hysteresis.

The contact angle, as previously mentioned, is a thermodynamic quantity, thus has a unique value for each system. But in most cases it is found that when a drop or interface advances along a surface, even on atomically smooth surfaces, there is a difference in the advancing angle θ_A and the receding angle θ_R , see Figure 2.7; this is known as *contact angle hysteresis*. The hysteresis can be induced by either physical roughness (discussed in the following section) or by chemical heterogeneity. Effects such as surfactants from the advancing liquid adsorbing on the surface cannot be wholly dismissed either.

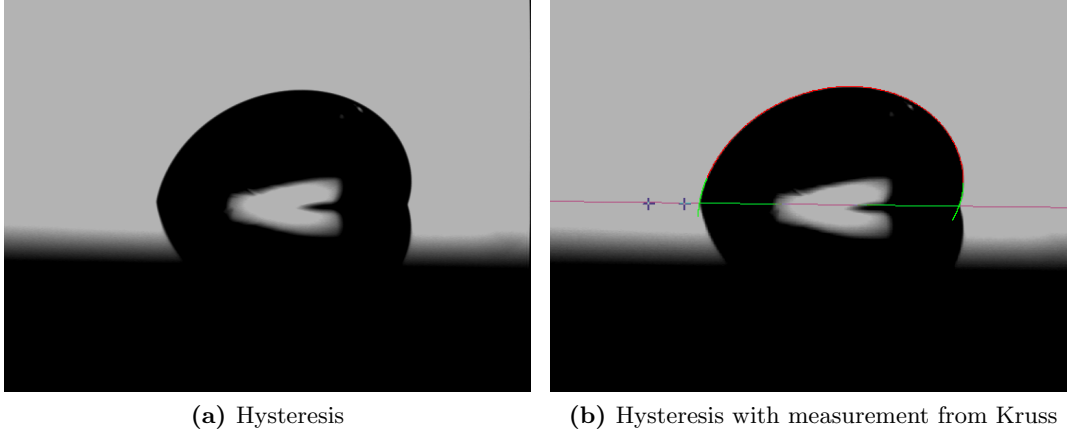


Figure 2.7: **a)** The figure shows a tilted plate of 316L stainless steel with a drop on top, note that the right and left angle are very different due to hysteresis which locks the drop in place. **b)** This is the same image but with the calculation interpolation from a Kruss software. The measured angles are; left side 80.5° and right side 108.9° .

Hysteresis is always present but never desired and it causes the drop to have metastable contact angles between two extremes, θ_A and θ_R . Hence the shape of a droplet is not reproducible. On most metal surfaces, that seems smooth to the human eye and touch, the contact angle will still vary by 20° or more due to hysteresis.

Important to note is that a high contact angle (CA) hysteresis lowers the drop's mobility (i.e. the ability to move along the surface) and a low CA hysteresis increase it. The energy needed to move the drop is also the same energy needed to deform the drop into a shape complying with the advancing and receding contact angles for that liquid on the surface. Hence it is a thermodynamic activation energy. Furmidge proposed a simple equation in the 1960's for relating the hysteresis to the gravitational forces acting on the drop which has been the basic concept for all later research [10].

$$\frac{mg \sin \alpha}{w} = \gamma_2 (\cos \theta_R - \cos \theta_A) \quad (2.5)$$

where m denotes the mass of the drop, g the gravitational acceleration, α the sliding angle, w the width of the drop and γ_2 the surface tension of the liquid, see Figure 2.7. Hence, the hysteresis indicates how strongly bound a drop is to a surface.

2.2.2 Wenzel and Cassie-Baxter states

If a roughness is induced on the surface, the Wenzel model introduced in 1936 by Wenzel describes the how a liquid homogeneously wets a rough surface, see Figure 2.8a [11]. Equation 2.6 describes the apparent contact angle in this case, where θ^* is the apparent contact angle and r is the roughness ratio. The apparent contact angle indicates when the system is in equilibrium, i.e. when the energy is minimized. The roughness ratio

measures how much the surface roughness affects the contact angle and is the ratio between the true solid surface area and the apparent one.

$$\cos \theta^* = r \cos \theta \quad (2.6)$$

Wenzel's model was further improved by Cassie and Baxter. In 1944 they introduced the Cassie-Baxter (CB) model, see Figure 2.8b [12]. In the CB model r_f is the roughness ratio of the wet surface area and f is the fraction of solid surface area wet by the liquid. Note that when $r_f = f = 1$ the CB model reverts back into the Wenzel model. The important part of the CB model is that it describes how vapor can be trapped under a liquid on a rough surface. A liquid resting on a surface in the CB state is more mobile than a liquid in the Wenzel state.

$$\cos \theta^* = r_f f \cos \theta_Y + f - 1 \quad (2.7)$$

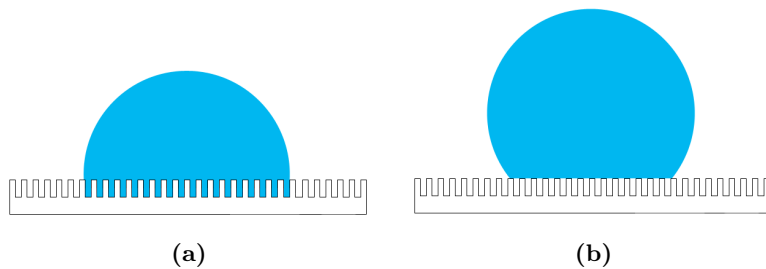


Figure 2.8: Wetting states models. **a)** Wenzel model. The liquid penetrates the rough features and wets the surface. **b)** Cassie-Baxter model. The liquid does not penetrate the rough features and rests on top of them; thus do not wet the surface.

2.2.3 Hydrophobicity

The definition of a hydrophobic material is still debated, but Israelachvili defines it as a material with a contact angle (CA) greater than 90° [4]. Such a large CA can be obtained in two different approaches; by chemically manipulating the surface thus lowering the surface energy and/or by changing the geometry of the contact area thus achieve a higher apparent CA. The most common chemical treatment of materials is to adsorb some kind of fluoropolymer, such as polytetrafluoroethylene (PTFE) which is widely known as Teflon. But only modifying the chemical structure of the surface cannot increase the contact angle above 115° . To achieve really high CAs and avoid wetting of the surface in question, modification of the surface topology is needed. Surfaces showing extreme CAs (above 140°) are henceforth referred to as superhydrophobic.

2.2.4 Lotus effect

A contact angle higher than 115° cannot be achieved by chemical modification. Thus the latest research has been focused on changing the surface topology instead. Researchers has discovered that the nature can offer some solutions to this problem, where the most known is the *Lotus effect*. This effect is based on that the liquid on the surface will never enter the Wenzel state, see subsection 2.2.2, by having small topological structures in the range of micrometers.

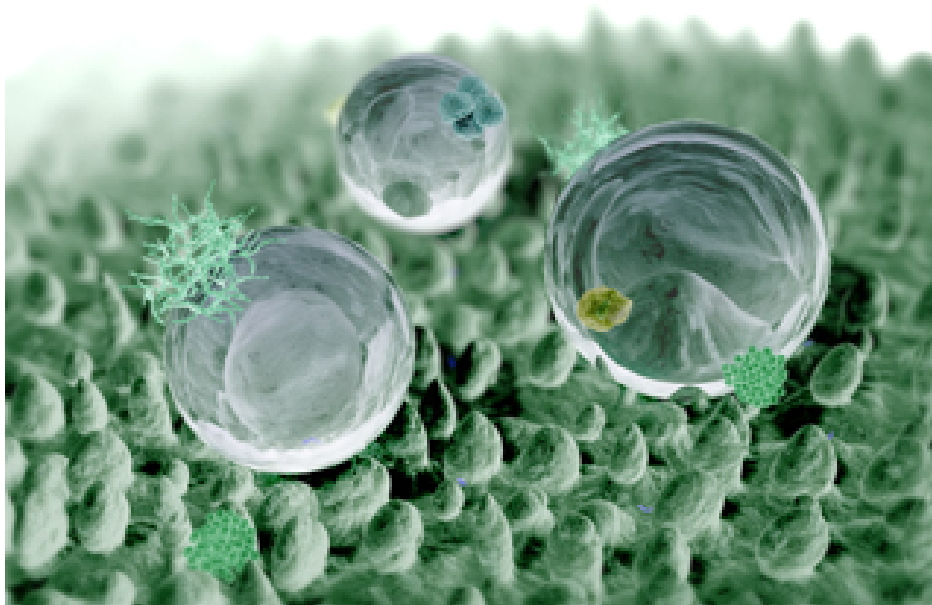


Figure 2.9: An illustration of the lotus leaf's superhydrophobicity.

Barthlott and Neinhuis published their findings of how the lotus leaf have a self cleaning mechanism due to its hydrophobicity in 1997 [13]. The water forms near perfect drops on the surface and those drops attracts dust particles and then roll of due to the high hydrophobicity of the leaf surface creating a self-cleaning mechanism, see Figure 2.9. Since then there have been many successful attempts to recreate a surface which have the lotus leaf characteristics [10] [14].

2.2.5 Omniphobicity

Omniphobicity means the ability to repel all liquids, not just water. In general other liquids will be harder to repel, water has a high surface tension and phase transitions in temperatures which are easy to control. Other liquids will in general have a lower surface tension, which will let them completely or partially wet a surface. There are also liquids with particles in colloidal suspension, these colloidal particles can physisorb or chemisorb and inhibit omniphobic properties.

Self-cleaning is an very interesting characteristic of superhydrophobic surfaces, however most hydrocarbons have a lower surface energy than water, so for this thesis there is a need to find a surface which is very oil repellent (superoleophobic). It has however been proven to be difficult to create surfaces that are superoleophobic and very few publications exists dealing with superoleophobic materials in comparison to superhydrophobic [15]. Another difficulty to overcome is how to obtain a stable surface that can be exposed to hard weather conditions and tough environments. Though some examples of very successful attempts are published [15][16].

2.3 Transport theory

The following section will describe the macroscopic view of gaseous molecules in contact with a surface.

2.3.1 Evaporation

Evaporation is a type of vaporization that only occurs at the surface of a liquid. On average a particle of a liquid will not have enough energy to leave the surface, but since the energy is distributed over a wide interval some molecules will have higher energy and some lower. The molecules in the liquid with enough energy and travelling in the right direction will then have a probability to leave the surface and form a vapor above the surface. Different substances have different boiling points and hence different temperature regimes where evaporation is quicker or slower. For the substances dealt with in this thesis evaporation is a slow process but it is nevertheless occurring. Evaporative equilibrium is when the vapor above the surface is saturated with the molecules from the surface. Hence this occurs when the same number of molecules is leaving the surface as the number of molecules that are returning. This occurs at a certain temperature and pressure which is dependent on the molecules that are evaporating.

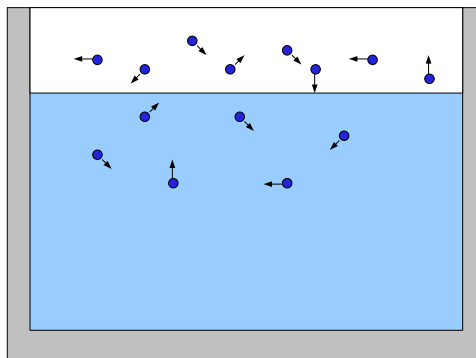


Figure 2.10: The random motion of particles is illustrated, the particles with the highest energy has the highest probability to leave the surface.

2.3.2 Condensation

Condensation is the reverse process of evaporation, where matter goes from gaseous phase to the liquid phase. When a particle impinges upon a solid surface and if the attractive forces are as large as the kinetic energy or comparable, there is a probability that the particle will stick to the surface. The particle will then lose one or several degrees of freedom; this means that the kinetic energy the particle was carrying will have to be transferred away through the material that the particle condensed upon.

2.3.3 Sticking coefficient

The sticking coefficient is a term used to describe the ratio of the number of particles adsorbed on a surface to the total impinging particles. The ratio is calculated with a value between 1.00 (all impinging particles stick) and 0.00 (none of the particles stick). The coefficient is a function of surface temperature, surface coverage and structural details as well as the kinetic energy of the impinging particles.

2.4 Mixing water and oil

Oil and water in general do not mix, the reason for this can be explained easily in thermodynamic terms. Imagine a closed ideal system, in which a hydrocarbon molecule (of any sort or size) is taken from a reservoir of hydrocarbons and placed into a reservoir of water. The mixing of the two increases the total free energy of the system, and the entropy for the system is also increased.

The system cannot return to a state where the lowest free energy is found due to the caused increase in entropy, that is when oil and water are in distinct separate macroscopic phases and not mixed. But one other interaction needs to be taken into account, the hydrophobic¹ effect which is the ability of the hydrogen bonds to create networks. This means that for a reservoir of water there is a configurational entropy from how each water molecule aligns to its nearest neighbors. When we immerse one molecule of hydrocarbon into our system of water molecules we lower the total number of configurations available for the hydrogen bond network of water. With the hydrophobic effect taken into account the total entropy of the system is lowered and it explains how the system can return to a state with lower free energy where oil and water are separated. Is it due to this entropic effect that water and oil do not mix [17].

¹This unluckily named interaction is not the same hydrophobicity as the one discussed in further detail later on.

3

Laboratory Procedures

EARLY IN THIS THESIS we concluded that an experimental approach was the only satisfactory way to achieve results. We wanted to characterize the surface and the treatments which we would coat the surfaces in, as well as to characterize the heavy oils that sticks to the surface. A goniometer sessile drop experiment was chosen, described below (section 3.4), where the temperature of the sample could be controlled. Basic experiments with hydrocarbons were conducted with visual results.

3.1 Crude and heavy fuel oils

Oils of interest in this thesis were all of the heavier type typically with a high viscosity at room temperature, thus a very low flow velocity. The oil chosen as testing stock, Vacuum Gas Oil (VGO) contains hydrocarbons of all sizes but mostly from C_{20} and larger. VGO is mainly used as fuel for heat plants and other types of permanent installations. When transported it is heated to approximately 70°C , which makes it easier to handle and it can be pumped using ordinary equipment for petroleum transport.

The oil is produced by vacuum distillation; the oil is at an atmosphere with pressure below its vapor pressure, thus will the parts of the oil with the lowest boiling point evaporate, leaving heavier parts. In this way heavy oils are obtained.

Table 3.1: Some of the for this thesis relevant characteristics of VGO [18].

Property	Value
Boiling point	180 – 550 $^{\circ}\text{C}$
Density (15 $^{\circ}\text{C}$)	900 kg/m^3
Viscosity (40 $^{\circ}\text{C}$)	10 – 40 mm^2/s
Water content	< 0.1 %

3.2 The mechanism behind VGO transport in this project

There was from the beginning a need to characterize which method or sort of transport that allowed the oil in a tank to reach the antenna mounted on top of the tank (According to 1.1b). A reasonable first guess would be that evaporation and condensation of the oil would let it reach the antenna. To investigate if this could be the case, the results found by Kudchadker *et al.* were used [19]. They derived corrections for the constants

B and C in the Antoine Equation 3.2 for the vapor pressures of normal alkanes in the range of C_{21} to C_{100} .

$$P = 10^{A - \frac{B}{C+T}} \cdot 133.322(\text{Pa}) \quad (3.1)$$

Since it is very difficult to characterize VGO we have chosen to approximate VGO with a combination of several heavy alkanes. The result from a calculation done with the corrections from Kudchadker *et al.* with the Antoine equation for several different sizes of hydrocarbons is shown in Figure 3.1. Figure 3.1 shows that the partial pressure is very low for heavy alkanes in the relevant temperature regime. At this pressure and a sticking coefficient of 1 it would take approximately 1 second to build a monolayer of particles on the surface, however each monolayer is only a few Ångström (10^{-10}m) thick. At this growth rate it would take ~ 100 days to condense a layer 1 cm thick.

Hence we can conclude that the partial pressure from VGO in an oil tank is still very low even if heated, this means that the main transport mechanism for VGO to the antenna in the problem we are investigating is in all likelihood not oil evaporating and condensing.

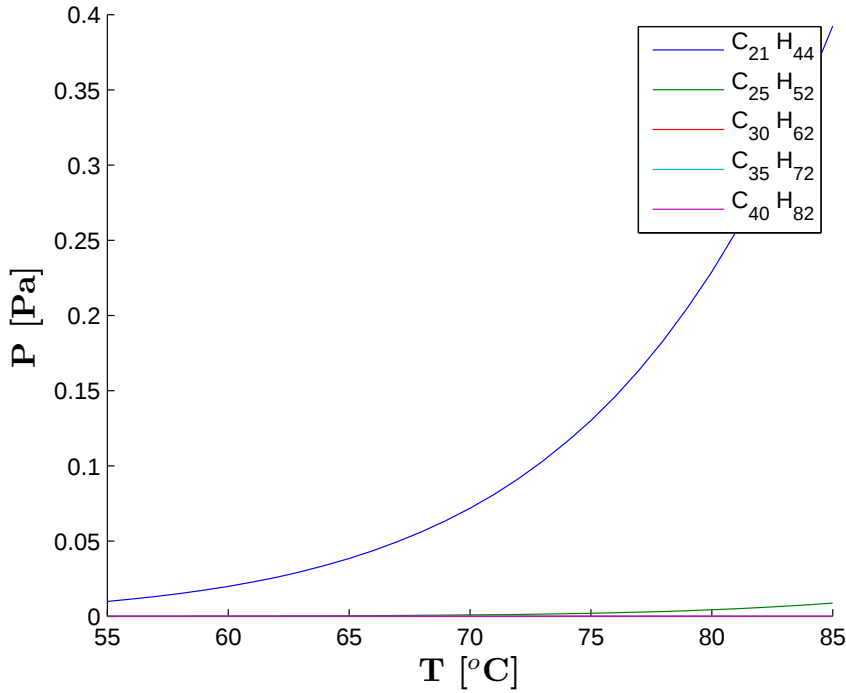


Figure 3.1: The vapor pressure for different hydrocarbons in a temperature interval relevant for this thesis.

3.2.1 Slushing

When talking to the crew of an oil tanker a transport mechanism called slushing seems more appropriate. For normal transport purposes the tank is filled to 98% capacity. When the ship is travelling in waves, the movement will cause the oil in the tank to slush around and splash up into the antenna mounted at the top of the tank. The idea of slushing is described in Figure 3.2.

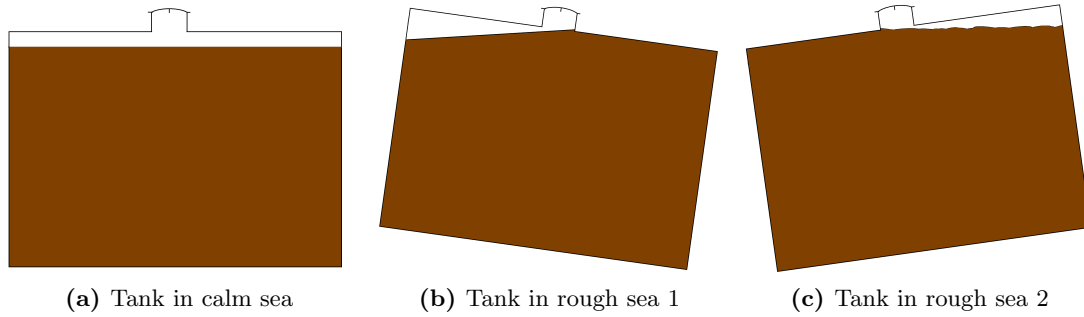


Figure 3.2: a) One of the oil tanks on a tanker in calm sea, filled to 98% capacity of the tank which is standard operating procedure. b) and c) The tank tilted at 8° , note how the oil almost reaches the antenna and most likely will splash oil towards it in those scenarios

3.3 Equipment

The basic equipment for the contact angle experiments performed is the Kruss DSA10 goniometer, which combined with its software provides easily recognizable and reproducible results. Temperature control was achieved by using a current controlled power supply coupled to a Peltier element; a Eurotherm 3216 temperature controller sent signals to the power supply using a thermoelectric couple in contact with the sample as reference. Deionized water was mainly used as test fluid, however in later stages of the experimental phase VGO and other hydrocarbons were also used to test the surface. Diiodmethane was meant to be used to calculate the surface energy, however it is difficult to handle and was not used to the extent originally planned.

Equipment list:

- Machined stainless steel samples of 316L, machined in nine varying roughnesses. Ten electropolished plates of stainless steel 316L.
- Kruss DSA10 goniometer, including a camera capable of 25 fps.
- Eurotherm 3216 temperature controller.
- Powersupply, Delta Elektronika ES 030-5, capable of 0 – 30V and 0 – 5A.
- Peltier element 38W
- Water and diiodmethane, other fluids for testing.
- Stylus profilometer for measuring the surface roughness.

3.3.1 Peltier elements

A Peltier element is used for heating and cooling and is often used in freezing boxes. The principle of a Peltier element is that an electrical current creates a shift in the charge distribution creating a p-n transition. A change between cooling and heating is thus easily done by shifting the polarity of the current.

3.4 Experimental Setup

In this section the setup of the experiments are explained in short terms, for more information there are photos in ??.

3.4.1 Sample plates

To study the wetting of water and VGO on stainless steel 316L standardized sample plates were constructed. In Figure 3.3 a sample plate with dimensions is shown. The sample plates were cut from a sheet of 316L stainless steel, and holes were drilled for the ability to secure them during the temperature controlled experiment.

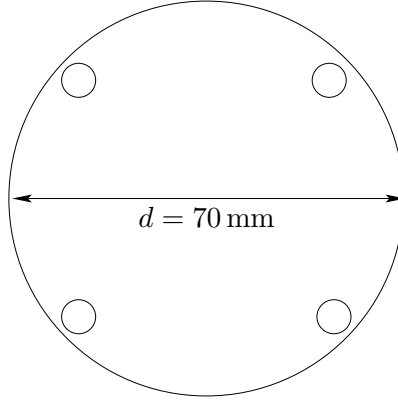


Figure 3.3: The sample plate.

3.4.2 With and without cooling

The principal setup of the experiment is shown in Figure 3.4. The goniometer is used for measuring the contact angle. The sample holder was modified to enabling temperature control.

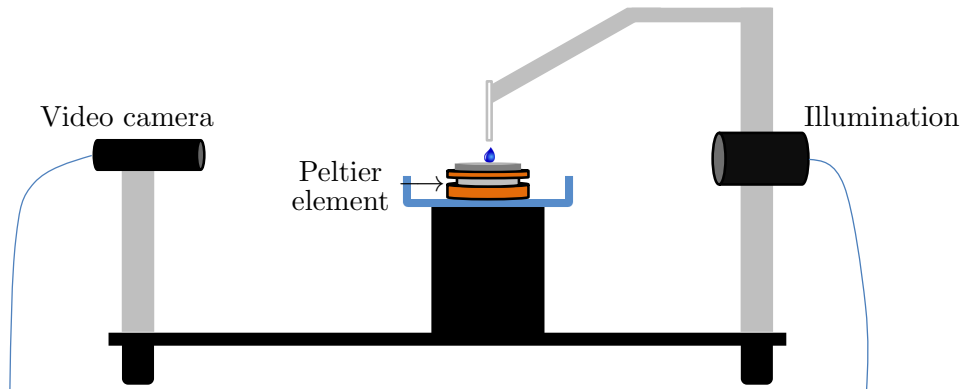


Figure 3.4: Schematics of goniometer.

A temperature control system was built since we wanted to vary the temperature of the surface experiment. The temperature was measured on the sample and given as

input to the Eurotherm which was set to cool. A control voltage from the Eurotherm was connected to a power supply which powered the Peltier element.

3.5 Sessile drop technique

To characterize the wetting properties of the surfaces examined the sessile drop technique was chosen in this thesis. By placing a drop of liquid onto a surface with known surface energy or a drop of a liquid with known surface tension surface information can be obtained. The contact angle as previously mentioned in section 2.2 is the parameter measured during these experiments. In Figure 3.5 images from a measurement is shown, in this case the two measurements are dynamic and evidently hysteresis is present.

To examine whether the forces were polar or dispersive, different kinds of liquids are used. In this thesis we used deionized water and diiodmethane.

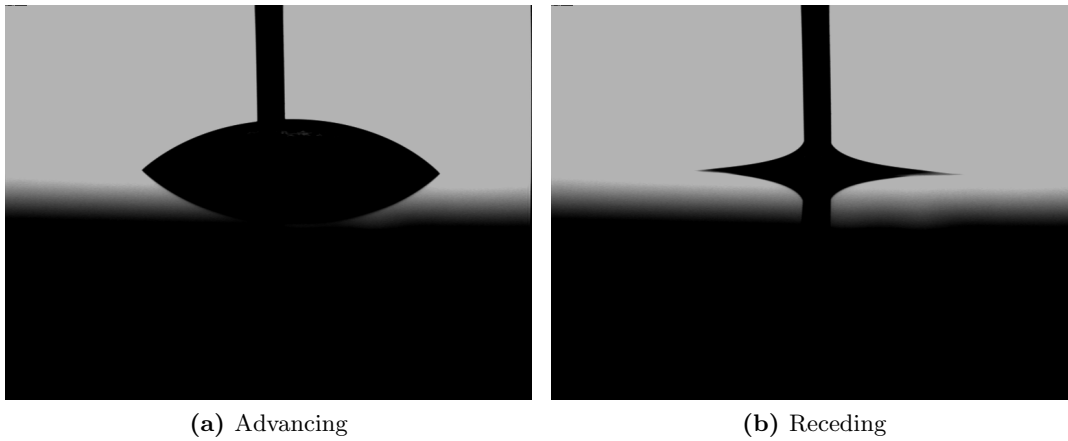


Figure 3.5: **a)** An advancing drop in a dynamic measurement. **b)** A receding drop in dynamic measurement. Note the large difference between the two, indicating a large hysteresis.

3.5.1 Curve fitting methods

When a picture/frame of a drop has been obtained the contact angle is to be calculated. This can be done by the use of several different curve fitting methods. A baseline is placed in the picture to represent the substrate surface and then a drop shape analysis software (Kruss Software Version 1.80.0.2) finds the drop edge. Then a curve is fitted to the drop and the contact angle is calculated. Throughout this work a polynomial curve fitting method has been applied.

3.5.2 Fowkes theory

To fully characterize a solid surface both the polar and dispersive components of the surface tension have to be examined. The basic theory for this was developed by Fowkes in 1964 who presented a two-component experimental model [20].

$$\gamma_{sl} = \gamma_l + \gamma_s - 2(\sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p}) \quad (3.2)$$

In the equation above γ_{sl} is the interfacial tension between the solid and the liquid and the superscripts d and p denotes dispersive and polar components respectively. The idea is that measurements with two different liquids are performed. The first liquid should be

completely, or almost completely, dispersive and the second should contain both polar and dispersive parts. Typically is deionized water used as liquid two and diiodmethane (CH_2I_2) used as dispersive liquid. γ_s^d is easily calculated from the measurements with the dispersive liquid, since $\gamma_s = \gamma_s^p + \gamma_s^d$. Then γ_s^p is determined from the second measurement with water [21].

3.6 Sample preparation

To prepare the steel disks used for measurements several different methods are presented in few details here. The interested reader will find more information following the references in this section.

3.6.1 Electropolishing

Electropolishing is an electrochemical process that removes material from a metallic piece. It is used to polish, passivate and deburr metal parts. Electropolishing is a common treatment in the industry, especially in areas having high requirements for hygiene. The principle of electropolishing is shown in Figure 3.6, the piece is immersed in an electrolyte bath and a current runs through the system. This means that the work piece on the rack in Figure 3.6 will have material removed from the surface, this removes impurities and smoothes out artifacts on the surface. The electropolished disks used during this thesis had approximately $25\text{ }\mu\text{m}$ removed from the surface.

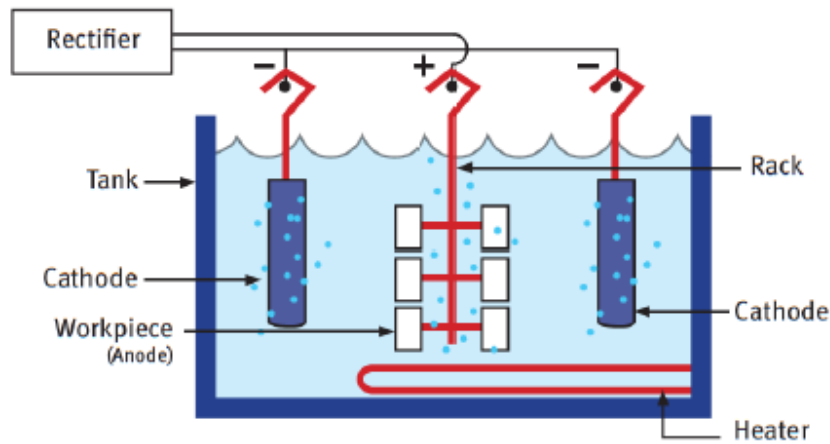


Figure 3.6: A principle figure of electropolishing. The work piece is the anode of the electrochemical process, which means that material is being removed from the surface.

3.6.2 Electroplating

Electroplating is similar to electropolishing, with the work piece being the cathode instead and metal nano particles in the bath instead of electrolyte. In this way the metal particles will instead adhere to the surface and create a rough surface on a nanoscale. The point being that this roughness on a nano scale will induce hydrophobicity or even superhydrophobicity. In this thesis we electroplated nickel, henceforth called nickelplated.

3.6.3 Lathing

Lathing¹ is a very common way to machine industrial items and has been so for roughly the last 150 years. There are different ways to characterize the precision of the lathing. One of the most used specifications is R_A , which is empirically defined as

$$R_A = \frac{1}{7} (R_Y - 0.2) \mu\text{m} \quad (3.3)$$

where R_Y denotes the maximum vertical deviation in μm on the surface [22]. Traditionally there are two ways to modify the surface roughness in lathing; the cutting speed and the radius of the lathe tool. There is an empirical formula which relates R_A to those parameters

$$R_A = \frac{1}{7} \left(\frac{f^2}{8 * r_\epsilon} - 0.2 \right) \mu\text{m} \quad (3.4)$$

where f denotes the cutting speed and r_ϵ the radius of the cutting tool [22].

Eight different lathings were studied during this thesis ranging from $R_A = 0$ to $R_A \approx 3.8$, see table Table 3.2. In Figure 3.7 the theoretical roughness from the earlier equation is compared to the value measured upon the surfaces with a stylus profilometer, data can be seen in ??.

Table 3.2: Different turnings used in this thesis. With $r_\epsilon = 0.2 \text{ mm}$

Cutting speed [mm/rev]	Measured R_A [μm]
0.04	0.15
0.050	0.28
0.075	0.62
0.010	1.03
0.0125	1.44
0.015	1.88
0.0175	2.62
0.020	3.80

Two more lathings were analyzed; one blank electropolished surface and one matching the antenna lathing.

3.6.4 Coatings

In Table 3.3 coatings that were used in experiments are listed. Most of them are commercially available of the shelf. TiO_2 and the electroplating of nickel combined with PFTS were ideas from the thesis and are novel combinations for solving the problem.

Below follows a list of the applying techniques used for applying the coatings used during this thesis.

Titanium dioxide A thin layer of approximately 50 nm TiO_2 was deposited in a clean room on three different samples using physical vapor deposition; electropolished, $R_A = 0.8$ and $R_A = 3.8$ plates. Physical vapor deposition (PVD) takes place in a vacuum chamber where an amount of the material, in this case TiO_2 is evaporated and allowed to condense on the surface of our sample.

Vendado The sample coating from Vendado was applied according to their instructions; wet a non-fuzzing rag with their product and swipe our sample, repeat

¹In Swedish: svarvning

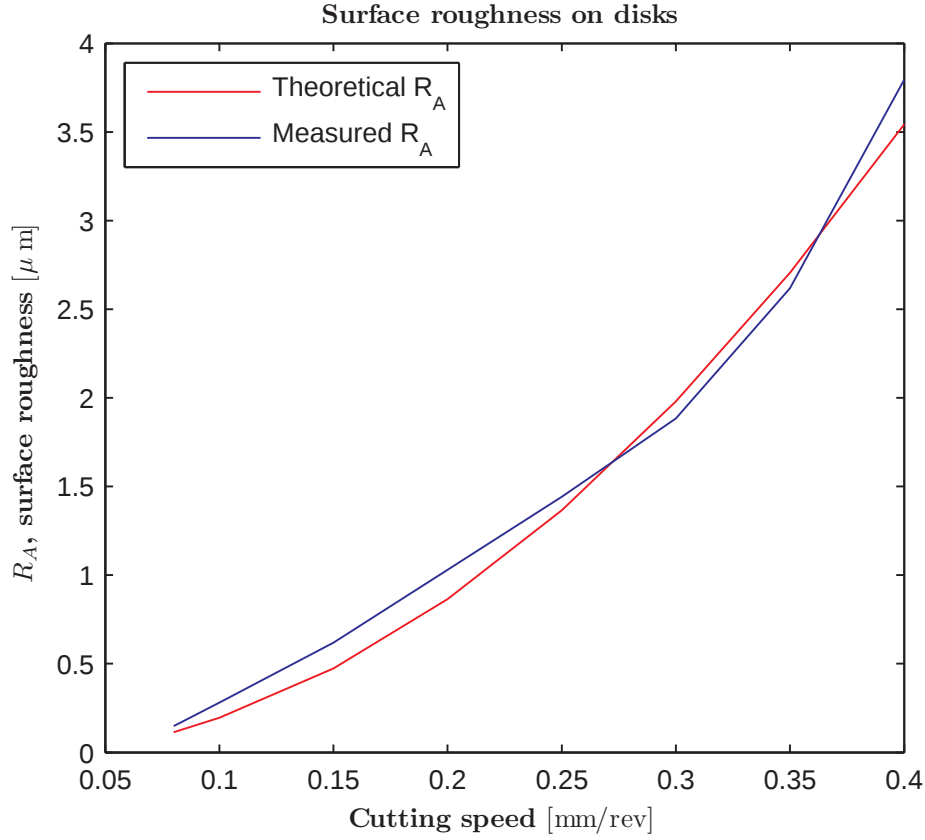


Figure 3.7: The theoretical roughness for lathed surfaces compared to the roughness measured with the stylus profilometer.

Table 3.3: Coatings and their application methods.

Coating	Application	Can withstand wash
TiO ₂	Vapor deposition	Yes
Vendado	Spray and rubbing	Yes
Daikin - TG581	Dip and curing	No
Daikin - TG5601	Dip and curing	No
Hirec	Painting	Yes, but not repeatedly
Aculon	Unknown	Yes
Electroplated nickel	Electroplating	Yes
Electroplated nickel and PFTS	Electroplating and Self Assembled Monolayer	Yes

process and then wipe a clean non-fuzzing rag over sample. Let the sample dry for 8 hours before testing.

Daikin TG581 and TG5601 Both the coating from Daikin were applied to the sample plates through dip coating, dried in a cabinet at 100 °C for 60 minutes and cured at 160 °C for one minute. When dip coating the entire sample is immersed in the coating and then pulled out at a constant velocity, the velocity then determines how thick the layer of coating becomes.

Hirec The sample plate covered in Hirec 450 provided from NTT AT² was already

²NTT Advanced Technology Corporation

prepared with their product Hirec 450. But according to the manufacturer the coating is painted onto the surface that is to be coated with a special roller supplied from them. Smaller areas can also be covered with a spray solution.

Aculon The sample plate covered with Aculon's solution was already prepared with their product. Best guess is a similar applying as Vendado.

Nickel Three different samples were treated with nickel nano particles, mimicking the procedure presented by Hang *et al.* [23]. Said nano particles were electrodeposited in a manner similar to electropolishing, however reversed. The treatment was performed by Provexa AB³ who is specialized in surface treatments.

PFTS Two sample plates were treated with 1H,1H,2H,2H-Perfluorododecyltrichlorosilane (PFTS), one of the plates was electropolished 316L and the other that was covered was electroplated nickel. The two plates were cleaned according to the ordinary cleaning method and then also immersed in piranha solution (base/basic piranha) to make sure the surface was as clean as possible. 0.4 g of crystalline PFTS was solved in 50 ml of toluene which is 1% of PFTS. The sample plates were then put in a drying cabinet for 5 hours at 80 °C. This mimicked the procedure presented by He *et al.* [15].

3.7 Methods and procedures

The following methods and procedures were used throughout the project to ensure that bias during all measurements would be minimized.

3.7.1 Washing and preparing

The sample plates were washed with the same technique and chemicals each time. The process used is a laboratory standard procedure, although some alternatives for the chemicals used are common i.e. isopropanol instead of methanol. The sample plates are handled in normal room temperature and atmosphere.

1. Sample is handled using pincers and latex gloves.
2. Washing of the sample commences with a cleaning using ordinary house ware dishwashing fluid and is lightly brushed to remove large fat cluster and impurities.
3. Sample is flushed using ample amounts of deionized water.
4. Sample is placed in beaker containing acetone and placed in ultrasonic bath for 5 minutes.
5. Sample is removed from beaker and then placed in second beaker containing methanol and placed in ultrasonic bath for 5 minutes.
6. Sample is dried using nitrogen flow in a fume cupboard and then placed in a plastic container to keep it reasonably protected.

3.7.2 Static measurements

There are two different methods of measurements that can be performed with the goniometer in use for this project; static and dynamic measurements. The static contact angle was measured in the following manner.

³Gamlestadvägen 303 SE-415 25 Göteborg

1. Make the goniometer level.
2. Adjust focus and illumination.
3. Place a drop on substrate.
4. Take a snapshot with the camera.
5. Analyze the snapshot and calculate the contact angle using a suitable curve fitting method.
6. Store data in a result file.

Data was collected from the positions marked in Figure 3.8, where the numbers indicate the numbering used further on.

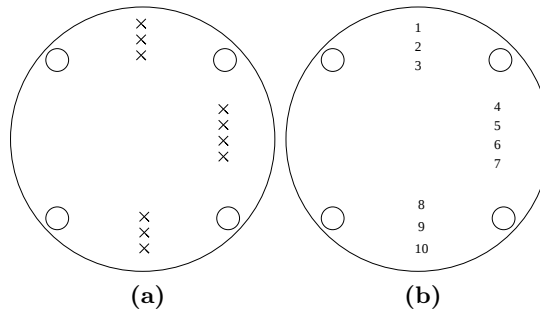


Figure 3.8: Measurement points for static measurements.

3.7.3 Dynamic measurements

Dynamic measurements, as the name indicates, describes the contact angles when a drop is moving across the substrate. The difference between the two methods is described in subsection 2.2.1. The procedure for measuring dynamic contact angle was as follows.

1. Make the goniometer level.
2. Adjust focus and illumination.
3. Place the needle near the substrate.
4. Start pumping out/sucking liquid from/to syringe with constant flow rate 12 $\mu\text{L}/\text{min}$.
5. A movie is recorded with the existing camera as the drop grows from $\sim 2\mu\text{L}$ to $\sim 20\mu\text{L}$ (or reversed for receding).
6. Analyze each third (8.33 fps) frame of the movie and calculate contact angle for each and every frame (length of movie is 30 s)
7. Remove badly calculated contact angles.
8. Store data in result file.

Data was collected from the positions marked in Figure 3.9.

During the initial measurements on lathed stainless steel 9 different measurement points was used in the same manner as for the static contact angle measurements (see Figure 3.8). The drop size was also reduced to 10 μL .

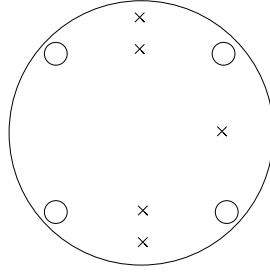


Figure 3.9: Measurement points for dynamic measurements.

3.7.4 Temperature dependence measurements

An interesting part from the beginning was the influence of temperature of how much VGO would stick to the antenna. Using our temperature control earlier mentioned contact angle measurements were taken for water on electropolished sample plates. Measurements were taken at all temperatures found in Table 3.4. Measurements were also

Table 3.4: Temperatures that were measured upon are found in this table.

Temperatures measured upon:	3°C	4°C	6°C	8°C	10°C	12°C	15°C	21°C
	22°C	27°C	30°C	35°C	37°C	40°C	50°C	

performed with VGO drops placed onto all coating at both 5° and 20° to measure if the temperature had any effect on the contact angle of VGO. A 15 μL drop of VGO was then placed onto the surface with a pipette.

3.7.5 Drop size dependence

Due to high inaccuracy in the first batches of measurements from the goniometer there was a need to eliminate as many possible sources of errors as possible. Due to this static measurements of the impacts of drop size on contact angle were conducted the drop size was varied at 1 – 3 – 5 μL .

3.7.6 Titanium dioxide experiments

The protective properties of Titania and water on steel had to be measured in another way since the oil could not be heated and handled easily due to odor and rapid cooling. Three different plates of different roughness were examined; electropolished, $R_A = 0.8$ and $R_A = 3.8$. Different experiments were performed on the Titanium dioxide coated samples.

Initially; to mimic the antenna, and examine the ability to maintain a water film, the sample plate was placed up-side-down above a beaker of water heated to 80 °C.

A sample plate covered in TiO_2 was fully or partially covered in small amounts of water, VGO drops at 65 °C were placed onto the plate in sized from 10 – 20 μL with a pipette. In Figure 3.10 a drawing of the principle is shown. The setup for controlling the temperature of the sample plate (the same setup as the one used together with the goniometer) is shown in Figure 3.11. In the case where contact angle is to be measured the sample plate was cooled to the desired temperature and then the oil drops were dripped onto the water film; the sample plate was then transferred to the goniometer and measured upon. Other data during these experiments was recorded by a camera either filming or taking photographs of the process.

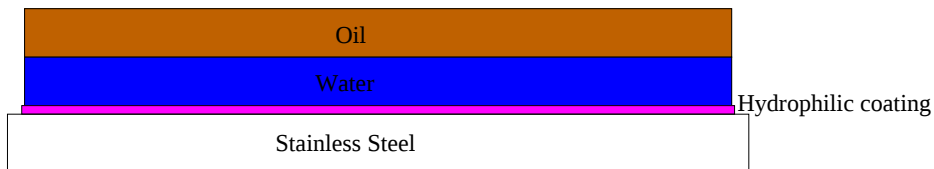


Figure 3.10: The figure shows the idea of the hydrophilic TiO_2 coating on steel and how it would protect the steel by keeping a film of water between it and the oil.

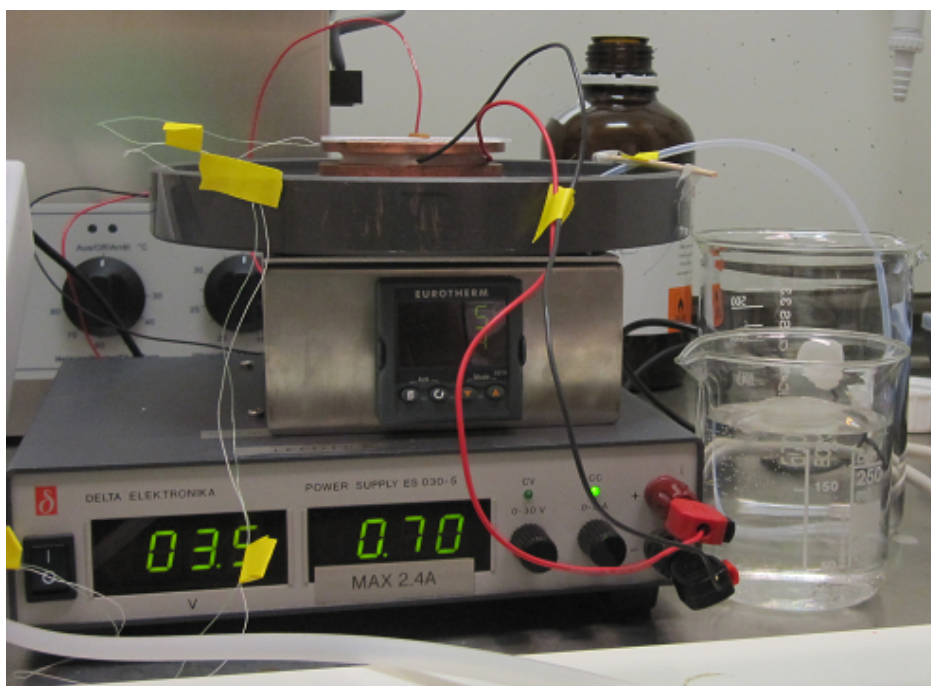


Figure 3.11: Experimental setup for the temperature controlled TiO_2 measurements. A thermo couple probe is connected to the copper plate on top of the peltier element. The thermo couple probe serves as input for the Eurotherm temperature controller which in turn gives a control signal to the power supply. The power supply powers the peltier element.

3.7.7 Scanning electron microscope imaging

The microscope used was a FEI Quanta 200 ESEM. Two different sample types were investigated; one electropolished stainless steel 316L sample plate and two different nickel-plated samples. Different magnifications were used during the imaging process; e.g. 50000X, 30000X, 15000X and 2000X magnification were used during the comparative experiments of nickelplated surfaces.

3.7.8 Hydrocarbons on repellent coating

A superhydrophobic coating's ability to repel hydrocarbons was tested with VGO, palm oil, cooking oil, diesel and gasoline. The results were recorded with a digital camera by filming the process.

4

Results

THIS section presents the results from the experiments performed during this thesis. The results are presented in graphical form and in some cases where appropriate also in tables. Some of the experiments performed were filmed or photographed due to their nature, in these cases the results are discussed a bit more in depth and the situation at hand described in more detail since no numerical comparison can be made. In the graphs showing contact angle the vertical axis is sometimes named left or right; left and right corresponds to the left and right side of the drop measured upon.

4.1 Static Contact Angle

Static measurements were performed on sample plates prepared in a number of different ways presented in the following sections. Due to the nature of contact angle hysteresis, static measurements are inherently prone to a large margin of error. In Figure 4.1 results from static CA measurements are shown; note the large standard deviations shown as error bars and these error bars remain large even though a large number of measurements were performed. The CA at $R_A = 0$ was obtained from an untreated (i.e. not electropolished) smooth surface of stainless steel 316L. The large deviations that appear during static CA measurements prompted us to do dynamic CA measurements during the remainder of this thesis.

4.1.1 Varying drop size

There was initially a question if the size of the drops put on the samples would affect accuracy of measurements. In Figure 4.2 measurements of three different drop sizes put on a smooth glass surface are shown. If there was an effect from drop size it would increase or decrease the CA with increasing or decreasing drop size. There is no linear relationship between drop size and CA, since the drop of $3\ \mu\text{L}$ has the lowest contact angle in the measurement.

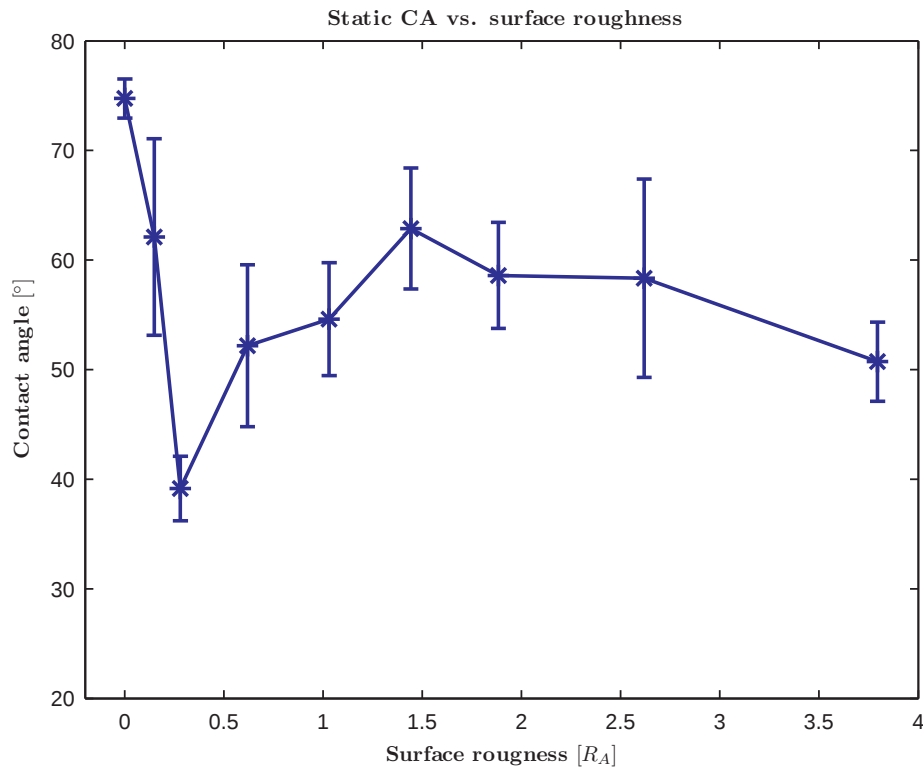


Figure 4.1: Mean CA from static measurements with a varying roughness on the surface. Note the large standard deviations presented as error bars at every measured roughness.

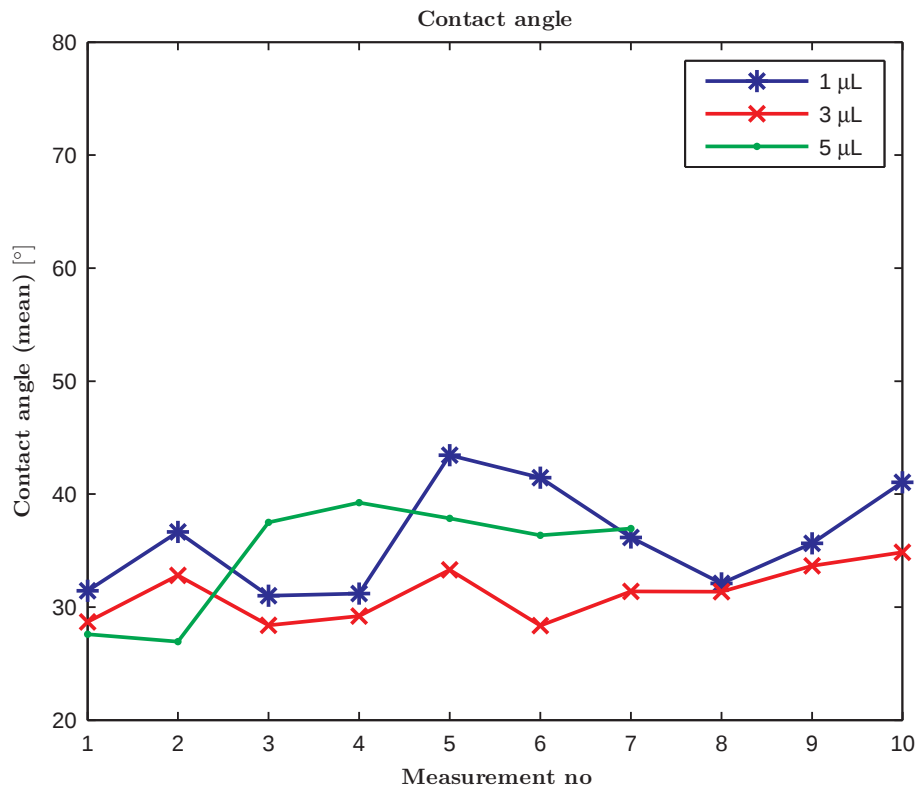


Figure 4.2: CA for different drop sizes, mean contact angle. Note that there is no linear relationship between drop size and CA.

4.2 Dynamic measurements

The principle of dynamic measurements has been explained earlier and in Figure 4.3 the typical results from such measurements are shown.

Note that the almost periodic dips in Figure 4.3a is taken from a sample plate with the drops placed along the lathing; the dip in contact angle is when a drop climbs above a valley and expands into the next. This can be compared to the smooth measurement of an advancing drop on an electropolished plate in Figure 4.3b. Lastly, in Figure 4.3c a typical measurement of the receding angle on a sample plate is shown; the liquid on the surface will not move and stays locked in place until the receding angle is reached which is the semi-apparent and steady contact angle on the end of that measurement.

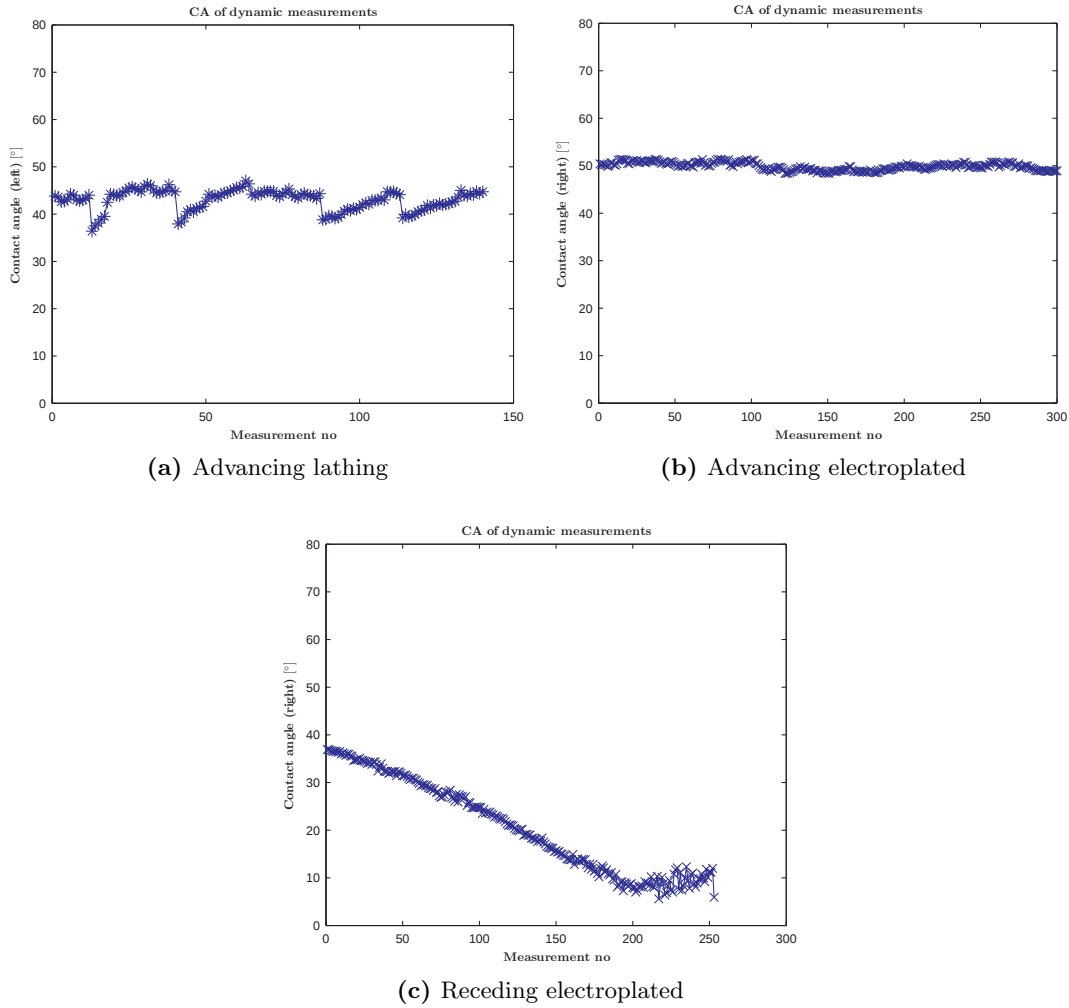


Figure 4.3: Raw data from dynamic measurements. Note the saw tooth like behavior in **a**), the smoothness in **b**) and the receding angle which is the last CA reached in **c**).

4.2.1 Different roughnesses

Dynamic CA measurements with an advancing drop on sample plates lathed to varying degrees of roughness were made and the result can be found in Figure 4.5 and Figure 4.6; the drops were placed along the lathing and perpendicular the lathing respectively.

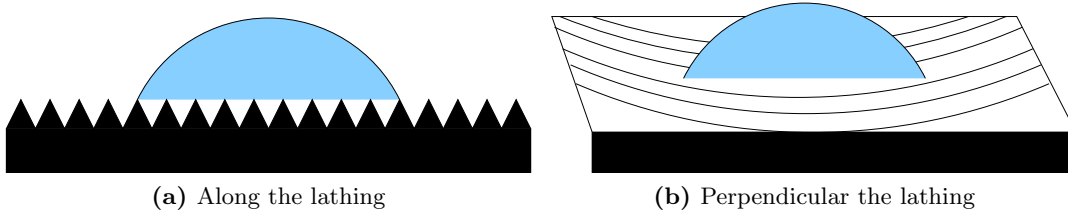


Figure 4.4: Along and perpendicular the lathing explained

We expected the resulting CA from a measurement along the lathing to rise in correlation with a higher roughness, this is consistent with the wetting theory of Wenzel (Equation 2.6). In Figure 4.5 a rising trend for the contact angle with higher roughness can be noted. This can also be derived from the situation at hand, when the lathing becomes coarser the drops need to reach a higher CA to wet the next groove in the lathing.

In Figure 4.6 the largest contact angle is found with the smallest roughness, this indicates that the drop is more willing to flow out into the grooves. The CA for all measurements above roughness $R_A = 0.25$ could be considered constant, $R_A = 0$ is from an electropolished plate. One interesting comparison is between Figure 4.6 and the static measurements in Figure 4.1, they show the same behavior even if the contact angles are lower for the dynamic measurement.

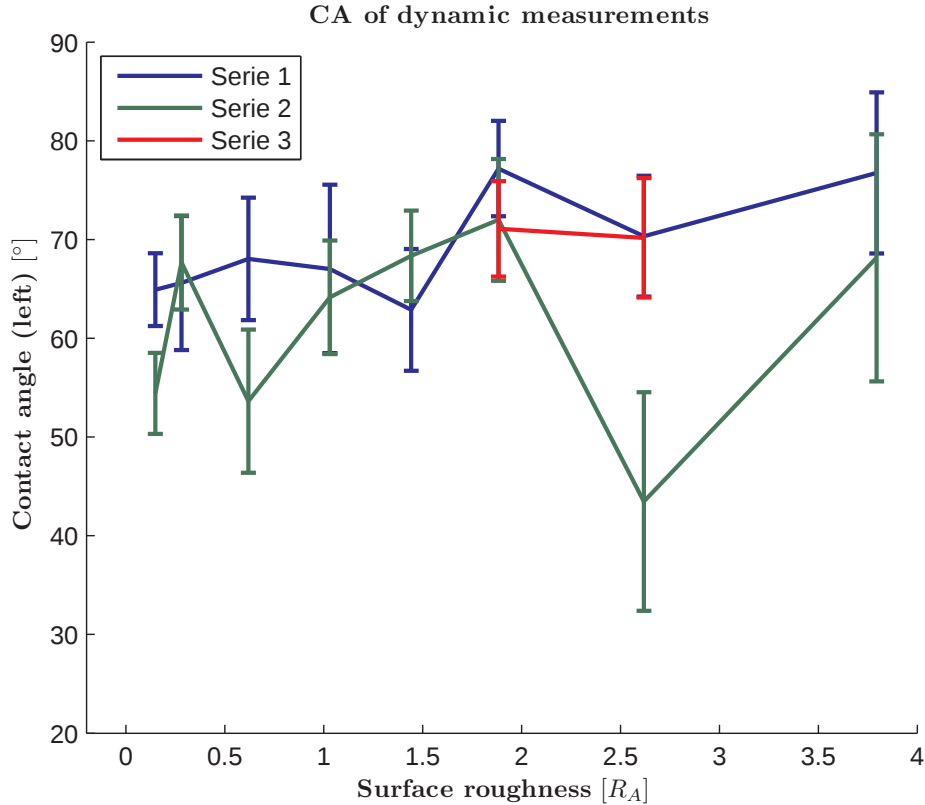


Figure 4.5: Mean contact angle of drops on varying roughness. All drops are placed along the lathing. A rising trend for the contact angle with higher roughness can be noted. The error bars represents the standard deviation of measurements.

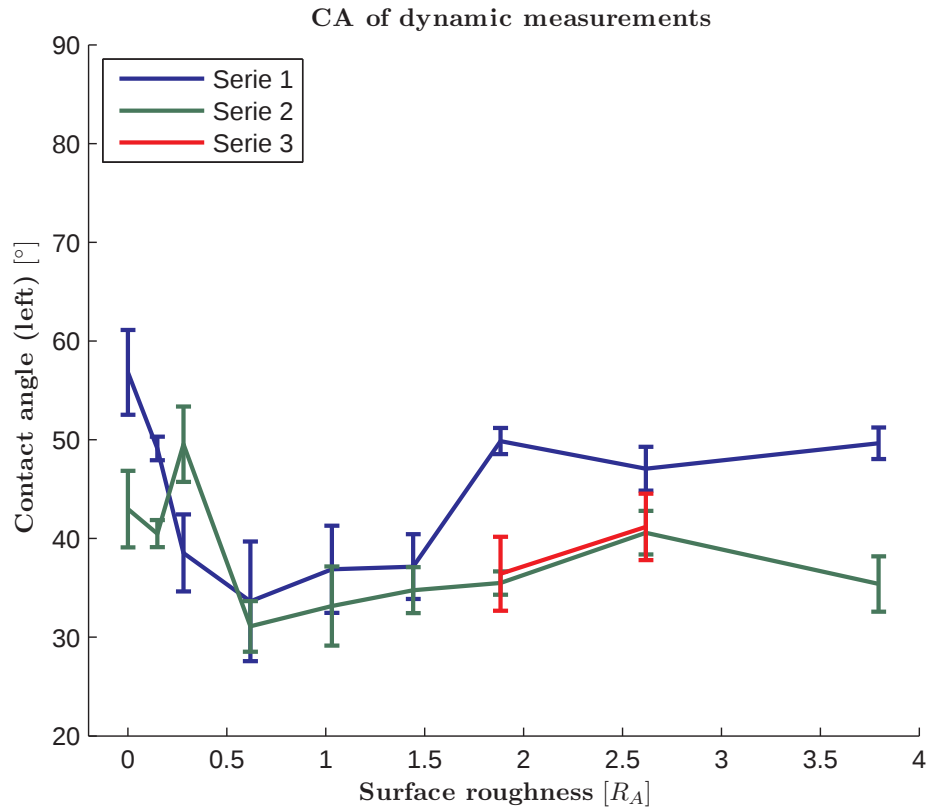


Figure 4.6: Mean contact angle of drops on varying roughness. All drops are placed perpendicular the lathing. The largest contact angle is found with the smallest roughness. Except for the smallest roughnesses, the CA can be considered constant. The error bars represents the standard deviation of measurements.

Plotted for each measuring point

Drops were put on sample plates with varying roughness according to Figure 3.8, by measuring the advancing contact angle on each plate and then plotting for each point and each individual measurement the result in Figure 4.7 was obtained. Note how points 1-3 and 8-9 are similar due to the orientation of the lathing where they were placed, there are also similarities as this for points 4-7. In Figure 4.7 point 1-3 and 8-9, the results show larger disparity than for measurements shown in point 4-7. Point 1-3 and 8-9 can also be compared to Figure 4.5 but the resulting rise in CA is harder to observe. Figure 4.7 Point 4-7, where a lower CA in general can be noted together with higher values for the smallest roughnesses, can in the same way be compared to Figure 4.6.

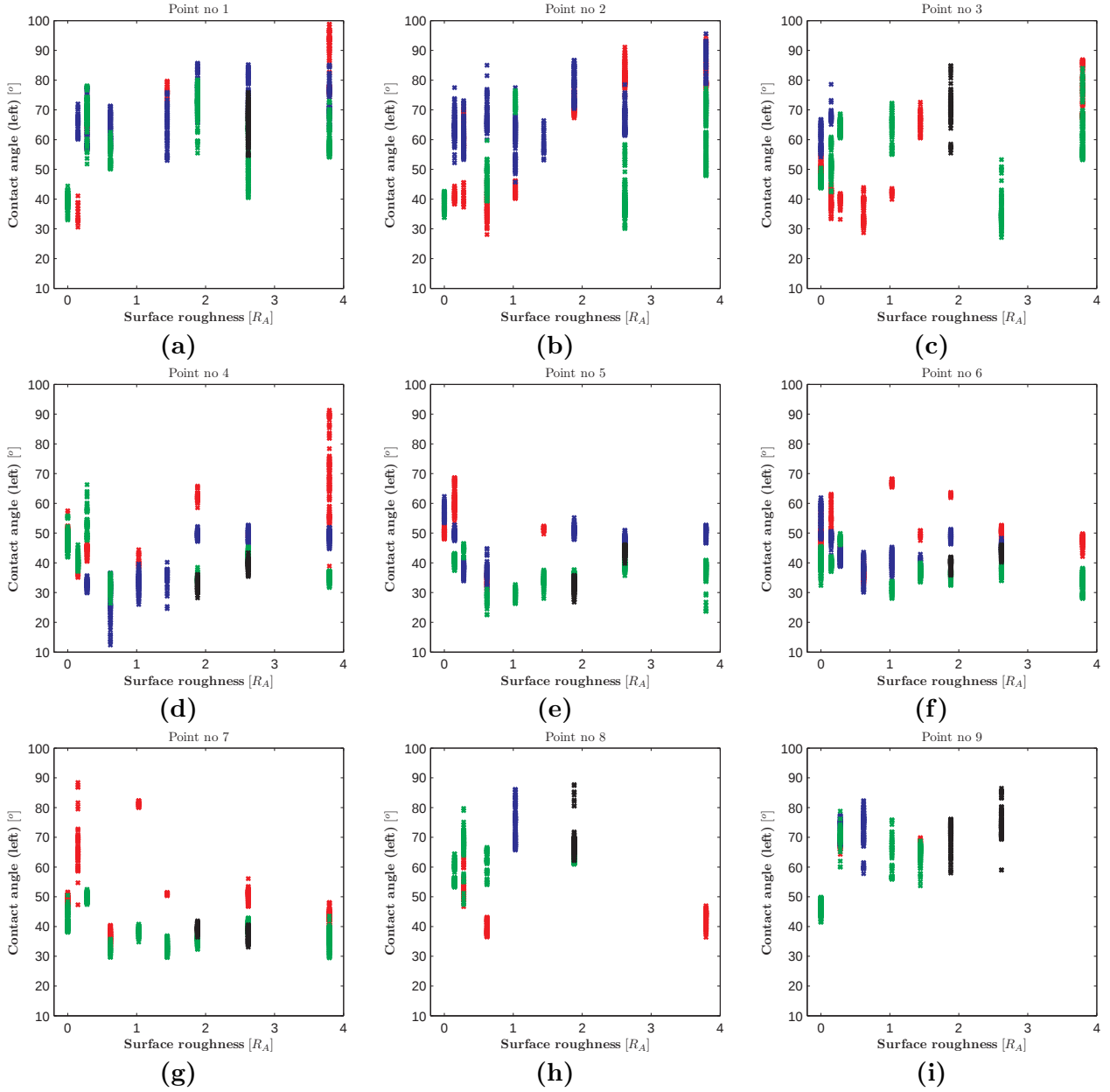


Figure 4.7: Comparison of different measurement points. The different colors represent different measurement series. Note how points 1-3 and 8-9 are similar due to the orientation of the lathing where they were placed, except seeing similarities as this for points 4-7 as well.

4.2.2 Electropolished plates

In Figure 4.8 the results from dynamic measurements with advancing drops on electropolished sample plates are shown. There is a surprising amount of disparity between the samples; the expected result was that the plates should have a CA within the error margin of each other. However the results are consistent for each individual plate. This is discussed further in section 4.6 where scanning electron microscope (SEM) images were taken from the surfaces of electropolished plates. The results are consistent with other CA measurements on stainless steel 316L [6] [24].

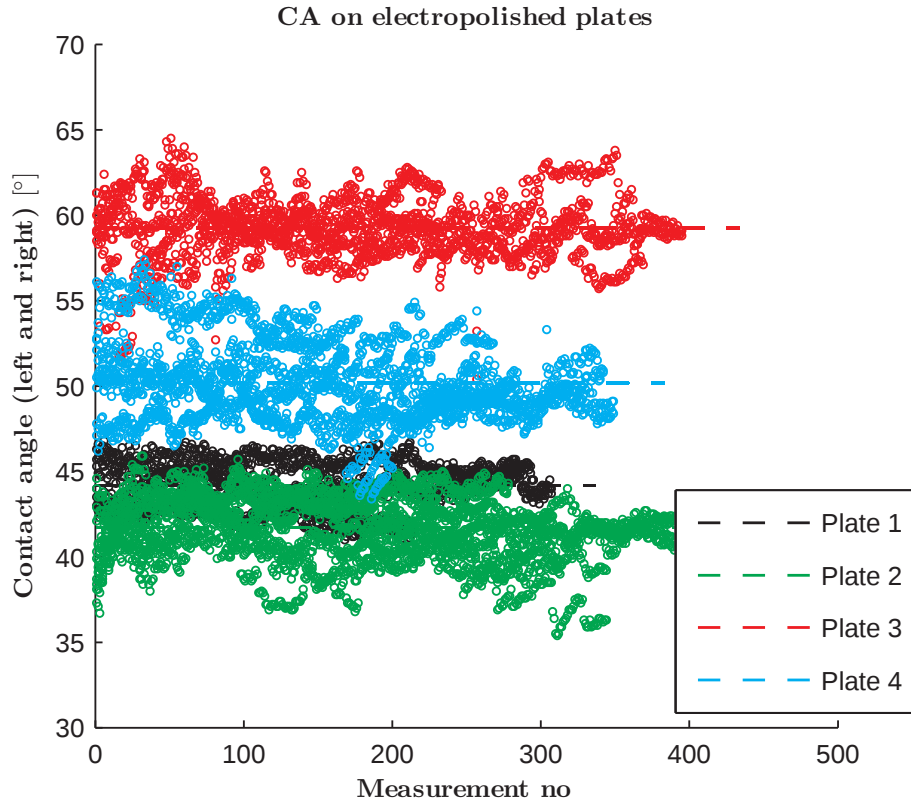


Figure 4.8: Contact angle of electropolished stainless steel 316L sample plates, left and right on y-axis means that both the left and right contact angle measurements are included in the figure. Each measurement point is the resulting CA from a frame of the movie recorded. Note that the results are consistent for each individual plate.

4.2.3 Nickelplating

Before this thesis began there were some trials done with nickelplated nanoparticles on an antenna, during measurement of this antenna it showed a very high contact angle but also a high hysteresis. In Figure 4.9 the results for the antenna and our sample plates are shown, note the very high hysteresis for the antenna but also a very large difference between the antenna and the sample plates. This large difference prompted us to examine the surfaces with SEM imaging, the results from this imaging is shown and discussed in section 4.6.

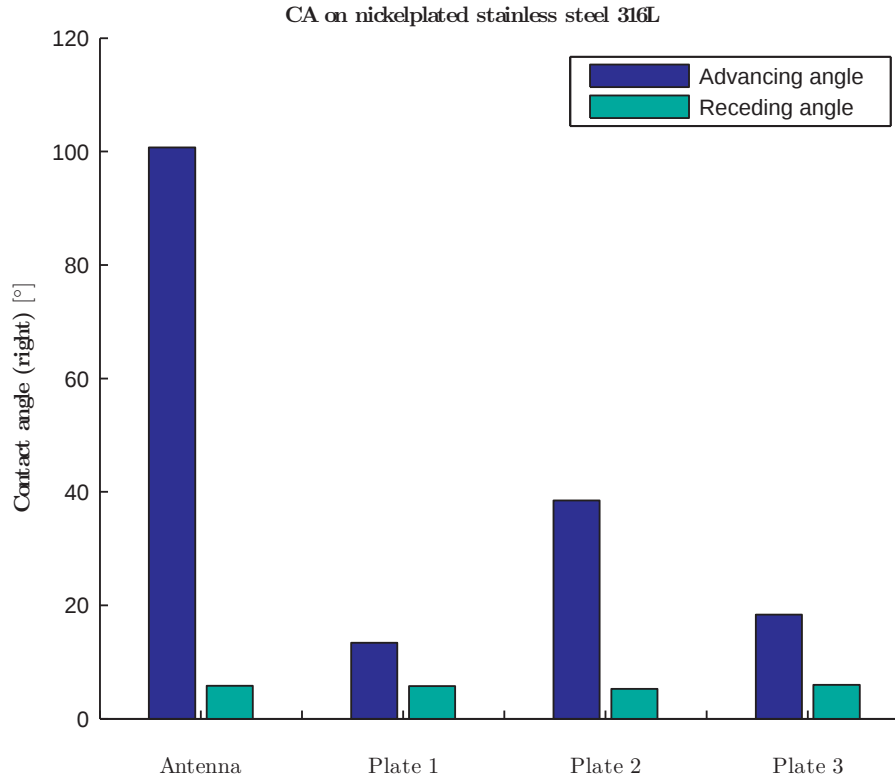


Figure 4.9: Contact angle on our nickelplated sample plates and the antenna previously mentioned. Note the very large difference in contact angle between the two.

4.2.4 Repellent Coatings

Commercial repellent coatings and coatings of our own design were tested first for their hydrophobic properties, the result is presented in Figure 4.10 while the numerical values from the measurements can be found in Table 3.3.

The highest values for both advancing and receding contact angle for coatings belong to the Hirec treatment, coincidentally the hysteresis for Hirec is also the smallest. This means that water drops have a very high mobility on the Hirec treatment, it is enough to tilt the surface less than 5° for water drops to roll off. The second highest advancing angle measured is for the sample plate with nickel and PFTS, however the hysteresis is immense here and drops show poor mobility. The third highest advancing angle and second lowest hysteresis is Aculon's treatment, the low hysteresis gives water drops on this treatment a good mobility as well. All of the other treatments show an improvement for both contact angles and the hysteresis on stainless steel 316L but the improvements are not expected to yield results for VGO.

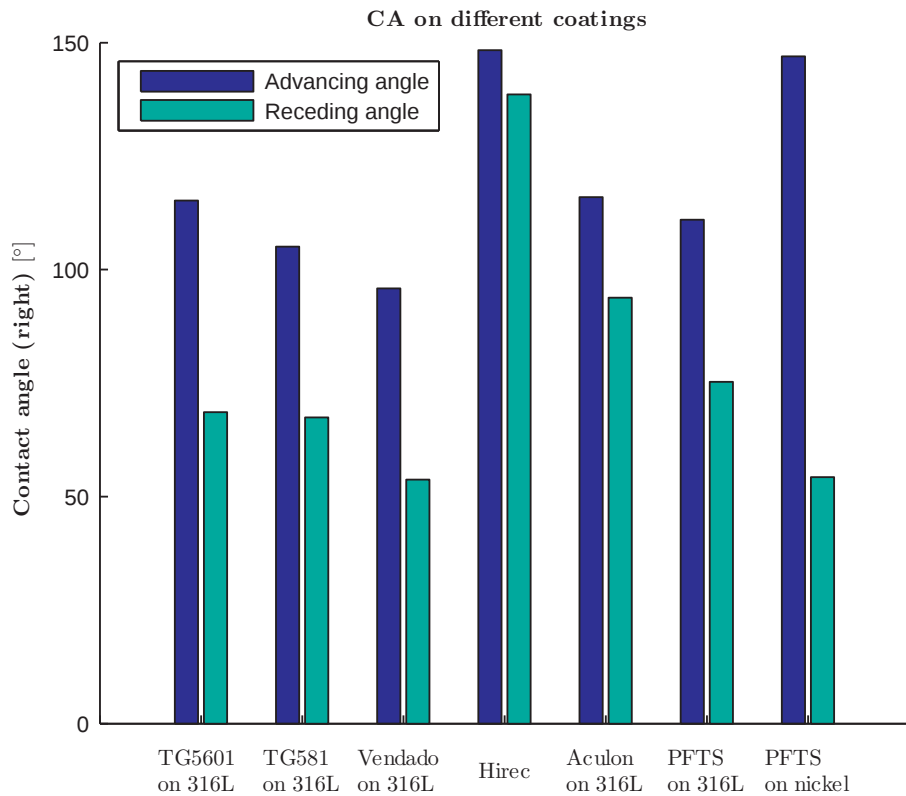


Figure 4.10: Contact angle of different repellent coatings. Data which the graph is based upon is shown in Table 4.1. The best values for contact angles and hysteresis belong to the Hirec treatment, the second best treatment seem to be Aculon since the hysteresis is huge for Nickel and PFTS.

Table 4.1: Data for the results presented in Figure 4.10. All results are based upon 5 successful measurement points.

<i>Coating</i>	<i>Mean advancing CA (Standard deviation)</i>	<i>Mean receding CA (Standard deviation)</i>	Hysteresis
TG5601	115.2 (2.48)	68.6 (11.5)	46.6
TG581	105.1 (5.78)	67.4 (8.72)	37.6
Vendado	95.8 (4.96)	53.7 (8.92)	42.1
Hirec	148.3 (2.03)	138.6 (13.6)	9.73
Aculon	115.9 (1.81)	93.8 (9.19)	22.1
PFTS on 316L	111.0 (4.47)	75.3 (3.74)	35.7
PFTS on nickel	147.0 (1.41)	54.3 (14.4)	92.6

4.3 Temperature Dependence

The temperature dependence was investigated during this work and in the following section results from measurements on the contact angle temperature dependence are presented. The studies have been performed on stainless steel and coated surfaces with both VGO and water.

4.3.1 Water on electropolished sample plates

The temperature dependence of the advancing CA for water was investigated on electropolished steel, the result is presented in Figure 4.11 while the numerical values from the measurements can be found in Table 4.2. There seems to be no apparent effect from the temperature in Figure 4.11. The theoretical temperature dependence of a metal sample is, described in subsection 2.1.4, negligible for such small temperature interval. Water do have a stronger temperature dependence, but within this interval the surface tension varies $\sim 10\%$ (Figure 2.4a) which is within the measurement error. Thus no temperature dependence conclusions can be drawn from these measurements.

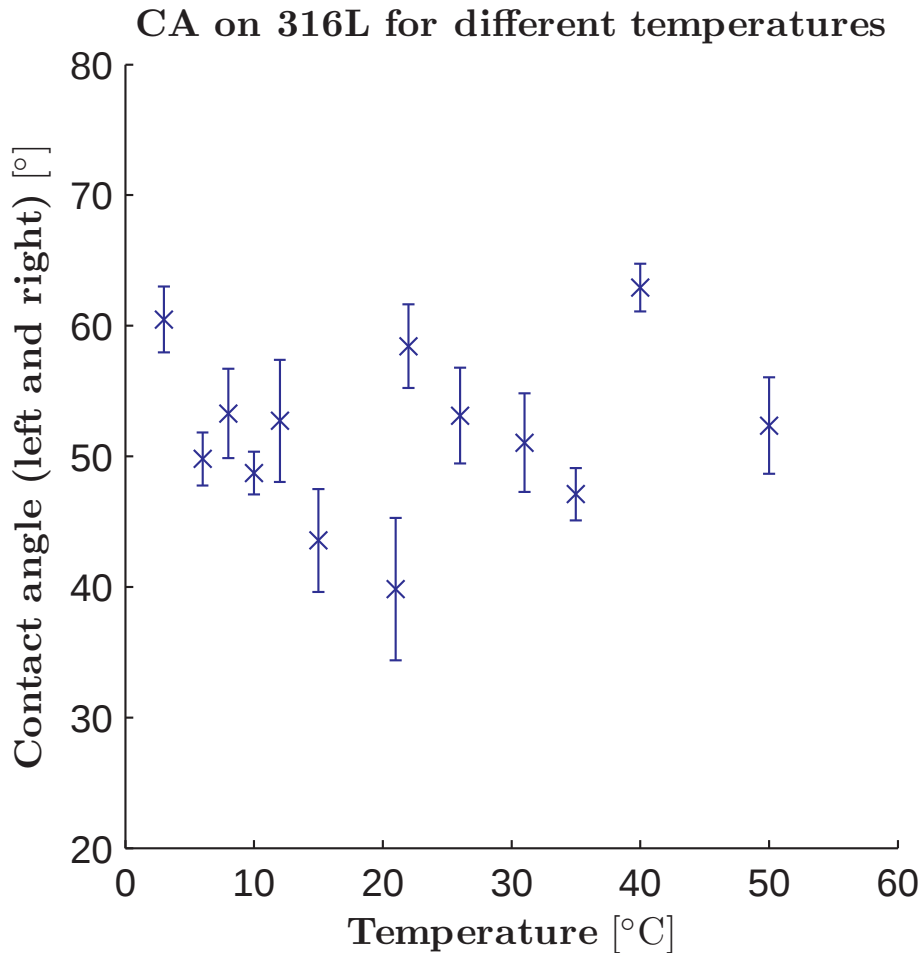


Figure 4.11: Mean advancing CA (based on both left and right CA) of water on electropolished stainless steel 316L is plotted against different temperatures. The error bars indicate the standard deviation in the measurements. Data which the graph is based upon is shown in Table 4.2.

Table 4.2: Data for the results presented in Figure 4.11.

<i>Temperature</i>	<i>Mean contact angle (Standard deviation)</i>	<i>Number of successful measurement points</i>
3	60.5 (2.52)	3
6	49.8 (2.03)	4
8	53.3 (3.42)	4
10	48.7 (1.63)	3
12	52.7 (4.68)	5
15	43.6 (3.94)	4
21	39.8 (5.45)	4
22	58.4 (3.20)	3
26	53.1 (3.65)	5
31	51.0 (3.78)	5
35	47.1 (1.99)	4
40	62.9 (1.82)	5
50	52.4 (3.69)	3

4.3.2 VGO on repellent coatings

VGO at 65 °C was placed on the samples and the static CA was measured; the obtained results are shown in Figure 4.12. In contrast to the results for water a strong temperature dependence can be observed. VGO, in similarity to water, in theory has a temperature dependence (Figure 2.4a) but also a phase transition in this temperature regime.

However, the most likely scenario is that the oil solidifies upon surface contact since the phase transition temperature for VGO between liquid and solid phase is higher than room temperature. The time required for this process will be reduced when the surface which the oil lands upon is cooler. Thus will the spreading velocity decrease and a smaller contact area is obtained; since the same amount of VGO is applied the drop will have a more spherical form, implying higher contact angle.

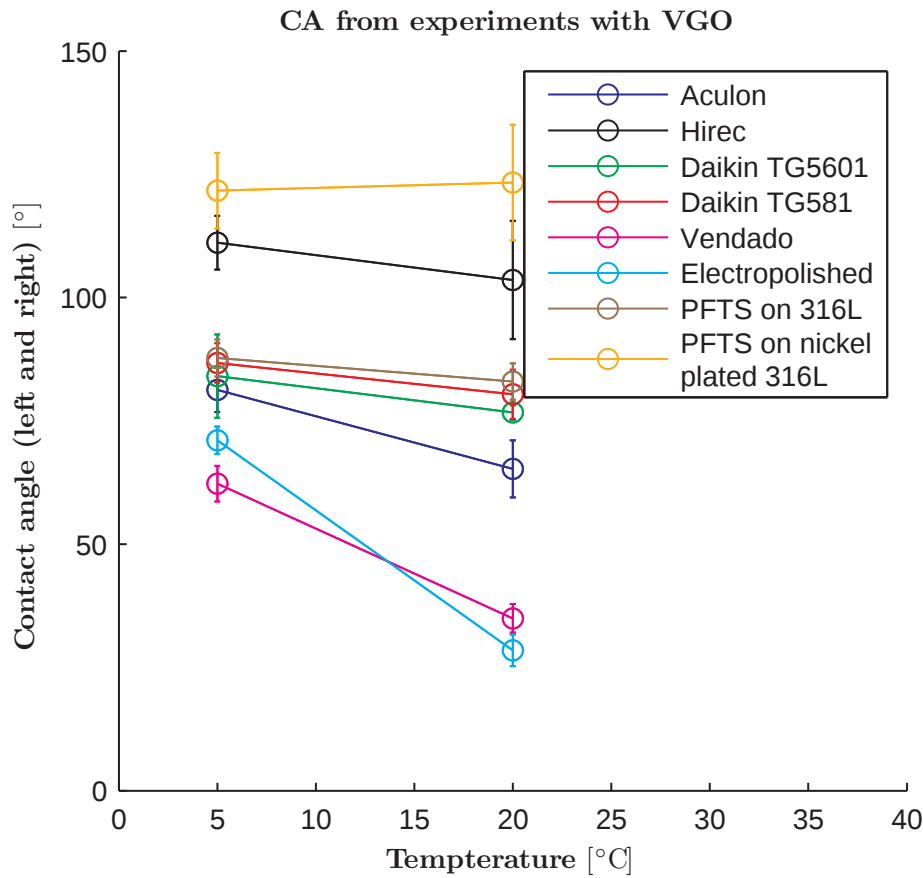


Figure 4.12: Mean static contact angle (based on both left and right CA) of VGO on different coatings is plotted against different temperatures. The error bars indicate the standard deviation in the measurements. Data which the graph is based upon is shown in Table 4.3.

Table 4.3: Data for the results presented in Figure 4.12.

<i>Coating</i>	<i>Temperature</i>	<i>Mean contact angle (Standard deviation)</i>	<i>Number of successful measurement points</i>
Aculon	5 °	81.3 (4.46)	5
	20 °	65.2 (5.80)	5
Hirec	5 °	111.1 (5.46)	5
	20 °	103.5 (12.0)	5
TG5601	5 °	84.1 (8.45)	5
	20 °	76.7 (1.46)	5
TG581	5 °	86.7 (4.00)	5
	20 °	80.4 (5.00)	5
Vendado	5 °	62.2 (3.62)	5
	20 °	35.0 (2.87)	5
Electropolished	5 °	71.1 (2.80)	5
	20 °	28.4 (3.20)	5
PFTS on 316L	5 °	87.8 (3.76)	5
	20 °	83.0 (3.68)	5
PFTS on nickel plated 316L	5 °	121.7 (7.69)	5
	20 °	123.3 (11.7)	5

4.3.3 VGO on water film

VGO at 65 °C was placed on a water film on the hydrophilicly coated sample plates (TiO_2) and the contact angle was then measured; the obtained results are shown in Figure 4.13. In similarity to the obtained results in subsection 4.3.2 a higher contact angle is obtained for lower temperatures.

Three different roughnesses were examined and they all show a similar dependence, there seems to be no major contribution from the roughness. This is to be expected since the goal with this treatment is to keep VGO away from the metal surface and the water film in each case is a smooth liquid surface. The diverging value at 20 °C for $R_A = 3.8$ in Figure 4.13 can be explained by either a bad measurement or that the water film at this rough surface was not thick enough to cover all the sharp edges of the grooves.

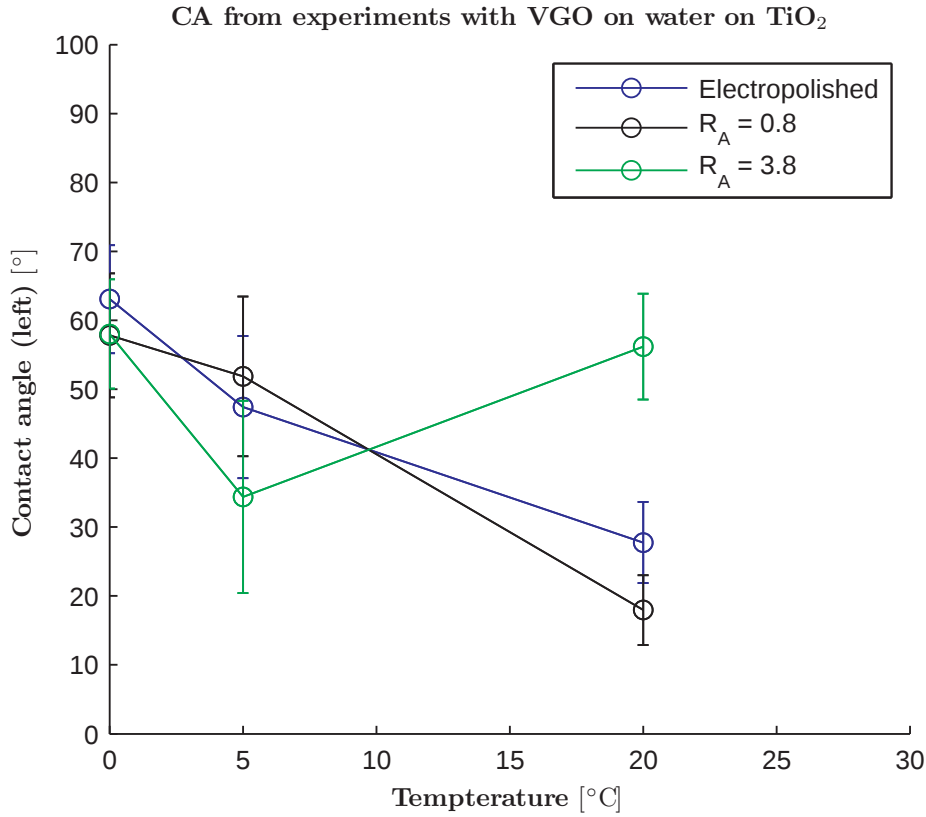


Figure 4.13: Static contact angle of VGO on TiO_2 with water film plotted against different sample plate temperatures. The error bars indicate the standard deviation in the measurements.

4.4 Hydrocarbons on superhydrophobic coating

From the measurements in subsection 4.2.4 Hirec seems to be the best candidate for repellent coating, also the temperature dependent tests showed promising results for Hirec. Hence it was interesting to measure how different heavier hydrocarbons would behave on this coating.

In Figure 4.14 the results from the static measurements are shown, note how the CA is much lower for the smaller hydrocarbons in diesel and gasoline. Worth to mention is that gasoline dissolved the coating and should be considered as inaccurate.

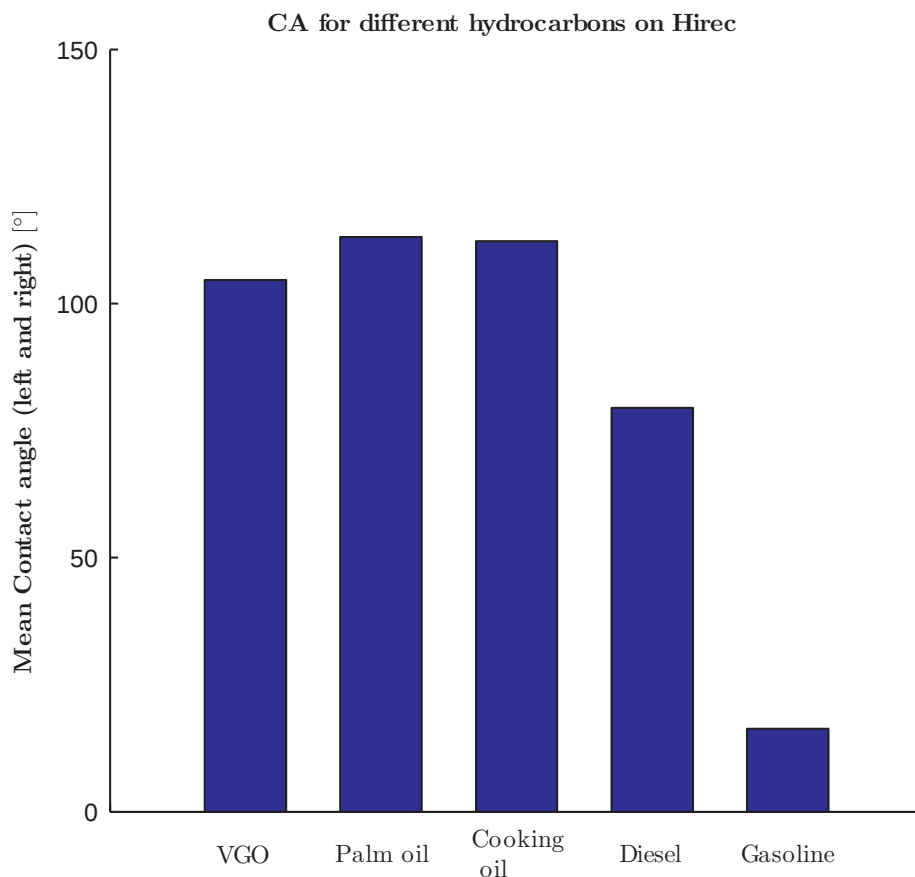


Figure 4.14: Static contact angle of different types of hydrocarbons on the Hirec treatment. Note how the CA is much lower for the smaller hydrocarbons in diesel and gasoline.

In Figure 4.15 palm oil, cooking oil and diesel are placed on the Hirec plate tilted to $\sim 45^\circ$. Neither palm oil nor cooking oil did stain the surface; in this specific example Hirec serves as an oil repellent surface. Diesel, however, completely wets the surface.

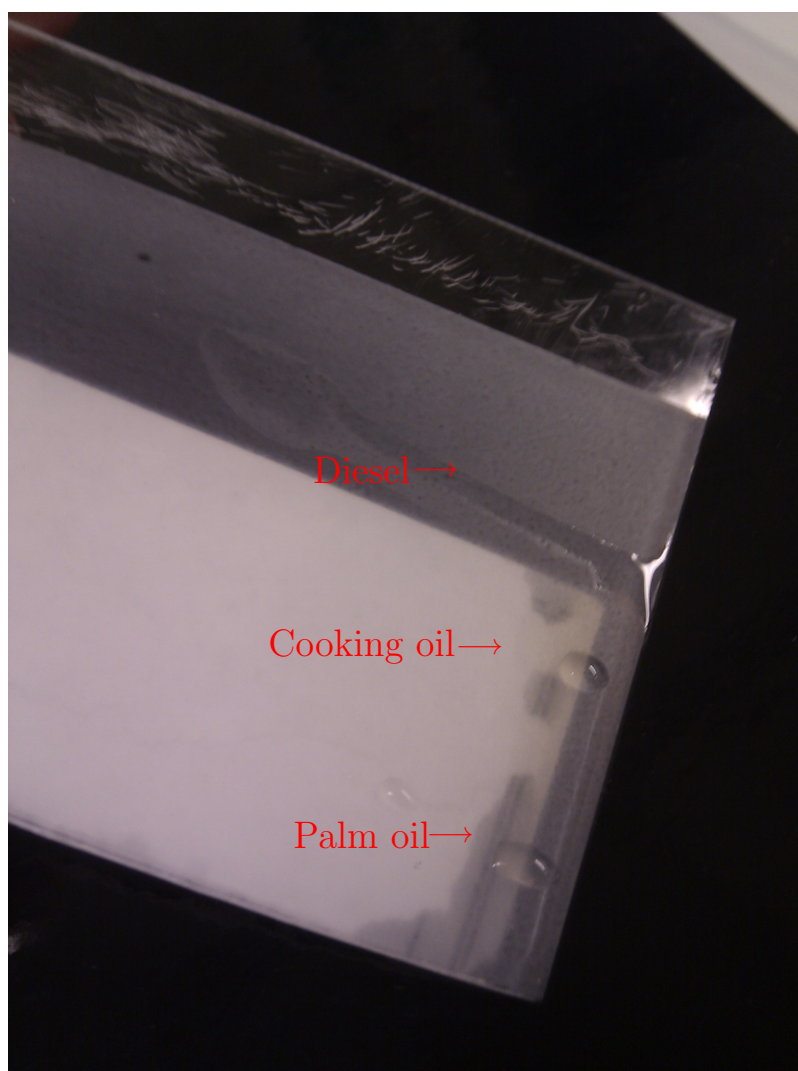


Figure 4.15: Each drop corresponds to palm oil, cooking oil and diesel. Notice how both palm oil and cooking oil fail to stain Hirec but diesel completely wets the surface.

VGO at 65 °C was dripped onto a plate coated in Hirec, the plate was tilted to $\sim 45^\circ$; the results are shown in Figure 4.16 in time-lapsed steps. In Figure 4.16 there is a large amount of VGO which flows off the plate; but in contrast to palm oil and cooking oil there is a significant amount of smearing which sticks to the surface and will impair the future performance of the surface.

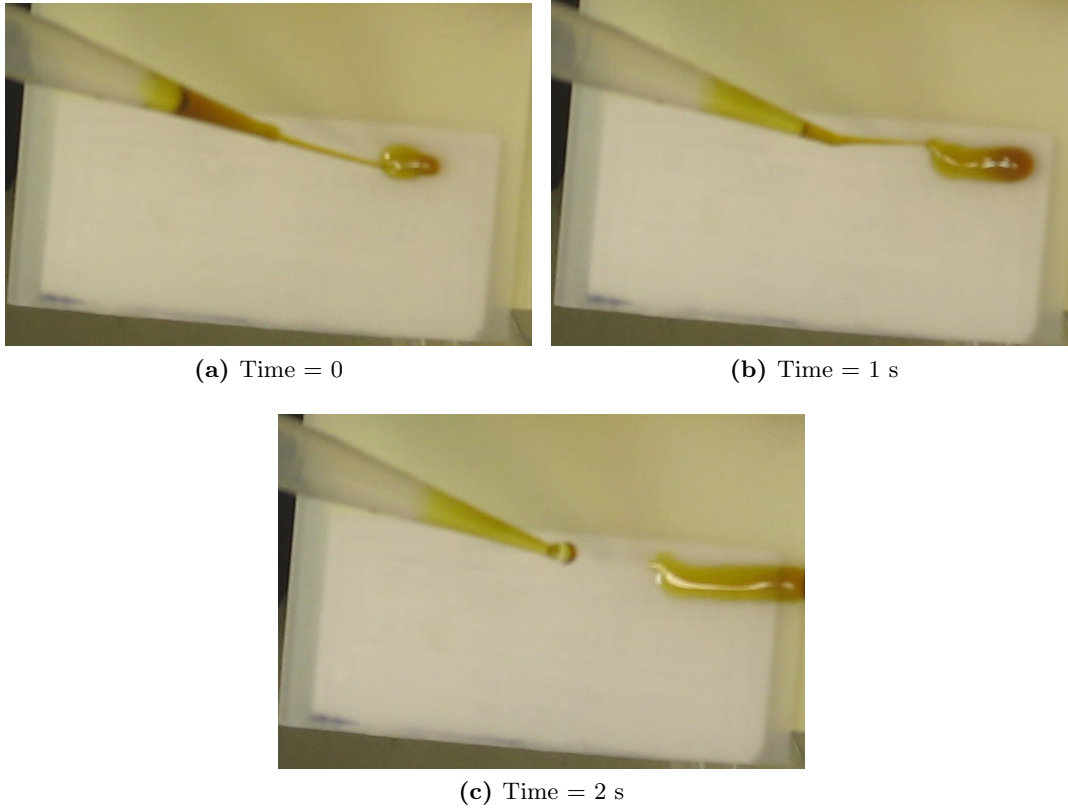


Figure 4.16: VGO at 65 °C, note that there is a large amount of VGO which flows off the plate, but there is also a significant amount of smearing which sticks to the surface and will impair the future performance of the surface.

4.5 Titanium dioxide

In this section the results from the experiments with a hydrophilic coating are presented. The idea is described in a previous section (subsection 3.7.6); using a hydrophilic coating to create a thin water film which protects the antenna from ever coming into contact with oil.

4.5.1 Condensing water on Titanium dioxide

The first test deemed appropriate was whether condensing water would cover a sample plate treated with TiO_2 in a thin water film or if drops would form instead. A beaker of water heated to 80°C was placed below a sample plate treated with TiO_2 , the results are shown in Figure 4.17. The result in Figure 4.17d tells us that condensing water will form a film on TiO_2 after sufficient time, in this case 15 minutes.

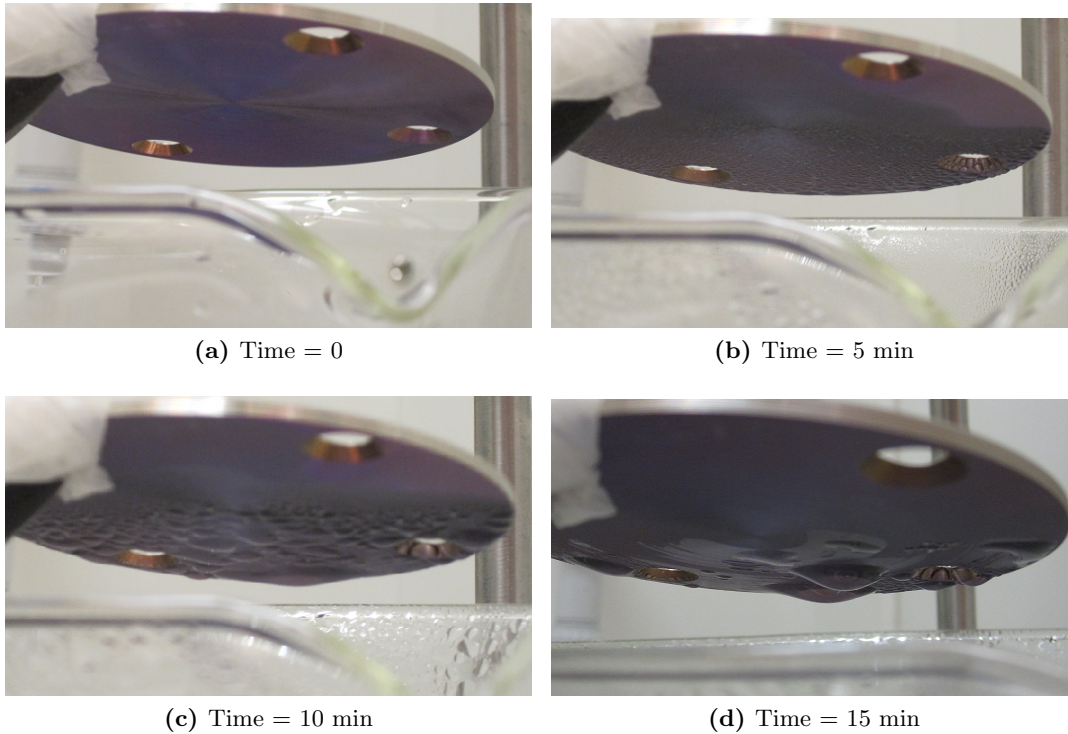


Figure 4.17: Results from water condensing experiments on TiO_2 . Note how the water forms a film after sufficient time.

4.5.2 VGO on TiO_2 covered with water film

A sample plate treated with TiO_2 was covered in a thin water film and VGO at 65°C was dripped onto the surface in drop sizes of approximately $15\ \mu\text{l}$. The result is shown in Figure 4.18, note how the drops move between Figure 4.18a, 4.18b and 4.18c due to the tilting done before each photo was taken. The drops showed good mobility during experiments and we observed complete roll-off from the surface.

The achieved results are in good accordance with the theory in subsection 2.1.4, where the conclusion is that a configuration where oil is on top of the water on stainless steel is energetically favorable in comparison to the configuration where water is on top of the oil on stainless steel (Figure 2.5a). This is however the case for untreated stainless steel 316L, the surface in this case has been treated with TiO_2 ; our conclusion is that this reasoning also holds for TiO_2 treated surfaces. The high mobility may be explained from that there is a liquid-liquid interaction and thus no surface roughness. An existing surface roughness would have increased the hysteresis and by that decrease the mobility.

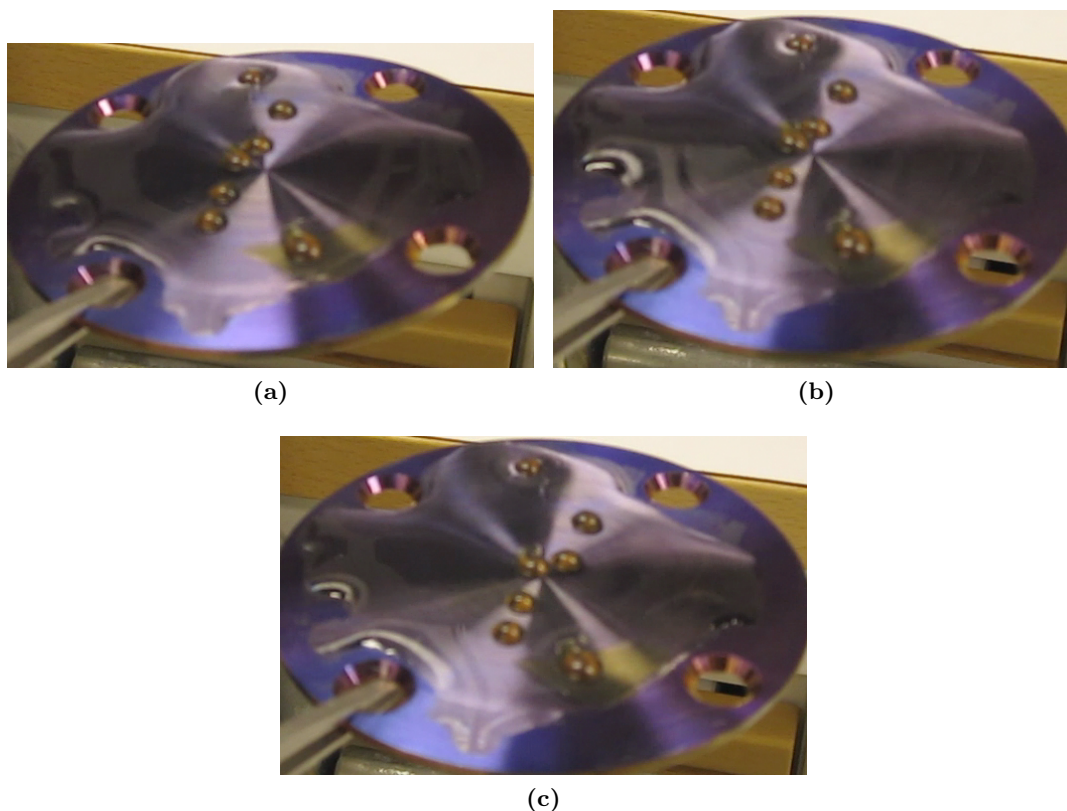


Figure 4.18: Showing mobility of oil drops on water film at three different angles.

4.6 SEM images

Figure 4.8 showed a large difference in contact angle between the electropolished plates; the expected result was that the plates should have a CA within the error margin of each other. Therefore scanning electron microscope (SEM) images were taken from the surface to identify and explain the unexpected result. There was also a difference in the results we obtained from an antenna earlier coated with nickel nano particles and the sample plates we coated, SEM images were taken from these surfaces as well.

4.6.1 Electropolished

In Figure 4.19 an electropolished sample plate has been imaged in a SEM at four different magnifications. At the largest magnification in Figure 4.19d the surface seems smooth. In the second largest magnification Figure 4.19c scratches appear, in the two least magnified images Figure 4.19a and Figure 4.19b a cratered landscape appears and it is apparent that the surface that was expected to be smooth on a μm scale after electropolishing is not. These micro sized scratches, holes and ridges explains the difference in measurement values obtained in Figure 4.8. The conclusion from these images is that the surface is not as smooth as we had hoped for after electropolishing.

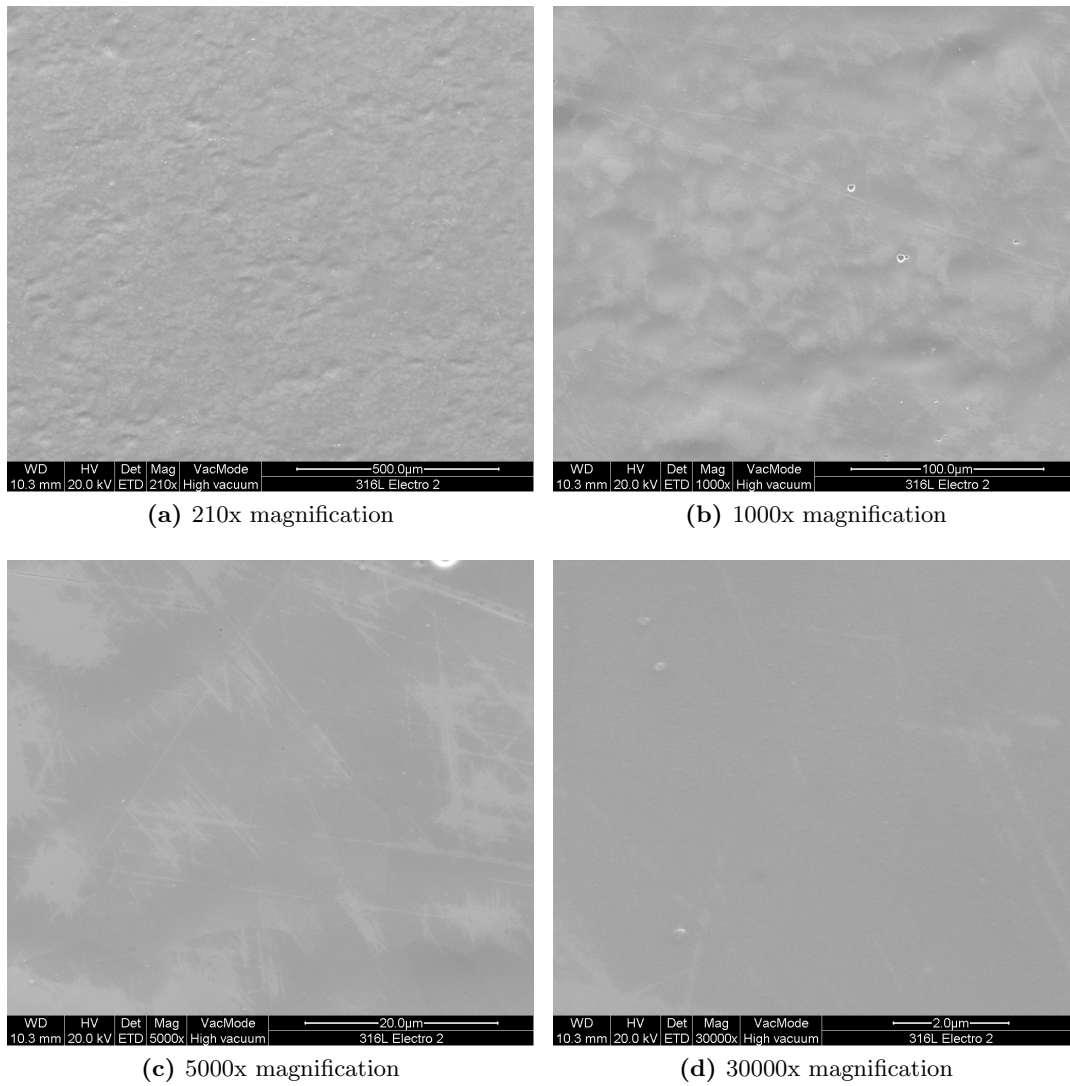


Figure 4.19: An electropolished sample plate is imaged in a SEM at four different magnifications. At the largest magnification the surface seems smooth but as the larger areas are viewed in smaller magnification micro sized scratches and other topological defects appear and affect the CA.

4.6.2 Nickel plated antenna and sample plates

In Figure 4.20 and Figure 4.21 SEM images from an antenna electroplated with nickel particles and an electropolished sample plate treated with the same process are shown. On the right side the sample plate is shown and on the left is the antenna, all magnifications are at equal level. From the largest magnification in Figure 4.21 it seems that the sample plate exhibits a smaller structure than the antenna.

The idea to coat a surface in nickel nano-particles was presented by Hang *et al.* [23]. When comparing SEM-images from their article to ours neither the antenna nor the sample plate shows a surface structure similar to the best one from the report. But the antenna's surface structure is similar to one of the surfaces produced by Hang *et al.* which showed improved contact angles, as do the antenna. The sample plate does not appear to be similar to any surface produced by Hang *et al.*, which not showed any improvements in contact angle (Figure 4.9).

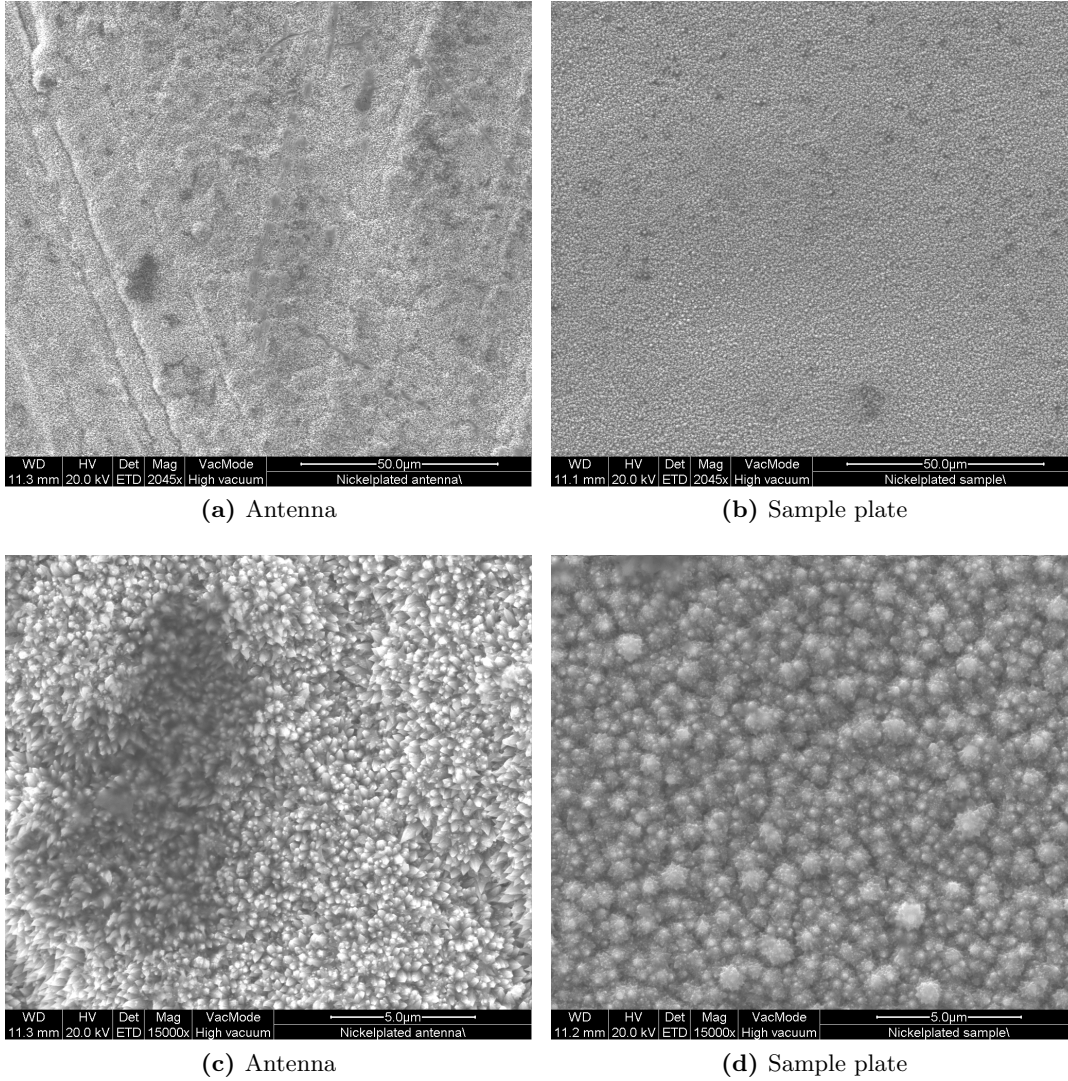


Figure 4.20: SEM images from the antenna coated in nickel nano-particle and the sample plate at 2045x and 15000x magnification.

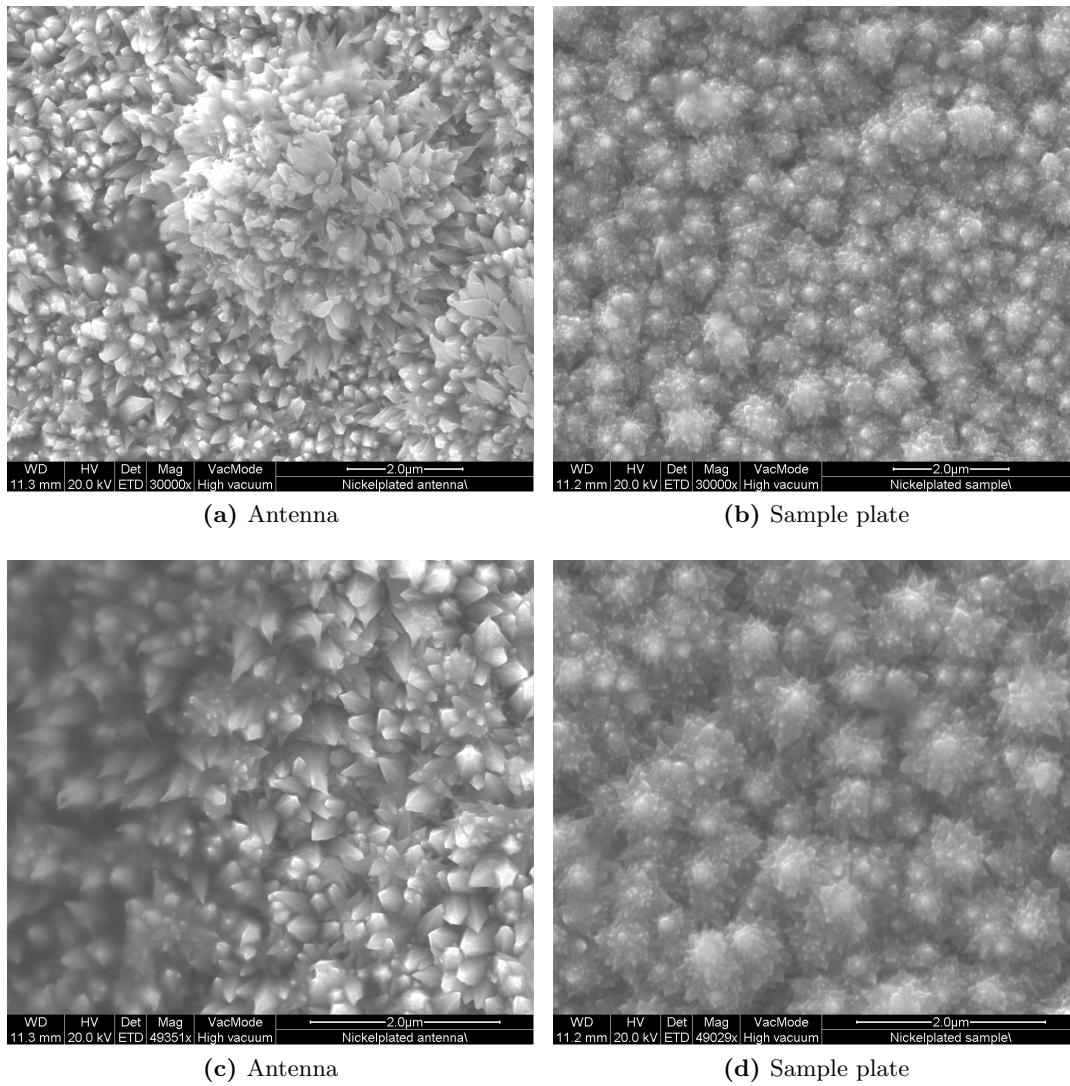


Figure 4.21: SEM images from the antenna coated in nickel nano-particle and the sample plate at 30000x and 49351x magnification.

4.7 Discussion of error sources

During the course of experiments there has been a large disparity in some measurement values, in this section we will discuss the reason behind these errors.

Hysteresis

The measurement on the lathed surfaces and also on the electropolished sample plates showed large hysteresis and this is an inherent problem for getting reliable CA measurements. Surface features on the nanoscale and microscale affect the contact angles greatly, an attempt to mitigate this by electropolishing failed. But we have not found a definitive surface energy value for stainless steel 316L in the literature and different articles present different values [6] [7] [24], which is in itself not surprising. Even if stainless steel 316L was polished smooth on the atomic level it is an alloy (it consists of several different elements). To ensure that the same situation was present in all measurements we would then have to ensure consistency on an atomic level.

Cleaning

The cleaning procedure before each measurement was handled with the utmost care, however there is a possibility that particles and residues from earlier measurements remained. These impurities would have an effect on each contact angle. Since the impurities would be heterogeneously spread over the surface they will increase the disparity from each measurement on the surface in question.

There are ways to clean a surface to ensure that it is even cleaner than the method we used, for example with strong acids or bases. But each of these presents new problems and they might affect the surface much more than the cleaning presently used. The SEM images taken from an electropolished surface was taken after cleaning was performed. In Figure 4.19d only two particles that were left after cleaning can be observed. Thus we believe that our cleaning method worked as intended and harsher cleaning is not necessary before taking other measures or actions as ensuring the surface topology through better electropolishing.

Small angles

There was a problem in measuring small angles with the goniometer, the manual from Kruss describes this situation. It instructs the operator to change the fitting method. In most cases we observed the fitting to small angles difficult since the drop has a very flat cone like shape flowing towards the needle as in Figure 3.5b. These conditions made it very hard to determine the exact angle when the CA was below 10° . Though it is very probable that the drop completely wetted the surface (according to Wenzel's theory). A similar problem occurred when a CA over $\sim 140^\circ$ was observed, where it was hard to separate the surface from the drop due to inadequate illumination. However such a high CA is indicative of superhydrophobicity regardless.

Applying technique

Another possible source of errors is how the different repellent coatings were applied to the sample plates, even though the instructions from each company was followed strictly. We are not experts at performing coatings and do not have much experience, this could in all likelihood have decreased the measured contact angle for the coatings we applied.

Hirec and Aculon was not applied by us, they were delivered applied on a substrate to us, they are in all likelihood applied by experts and are almost best cases for the coating they represent.

4.7.1 In experiments

There are conditions that we removed or mitigated during the course of experiments, they will be discussed here.

Static measurements

When measuring a static contact angle the measured value will be intermediary between the advancing and receding angle due to hysteresis. Since we confirmed this early in the project we changed our experimental method to dynamic experiments with advancing and receding measurements. The results from static measurements should always be considered to be inaccurate in our notion. This is the case also for surfaces treated and believed to be hydrophobic or superhydrophobic as is the case with our combination of PFTS and nickelplating (see Figure 4.10) which showed a hysteresis over 90° ; this coating locked the water drop in place and hindered all mobility on the surface. Nakajima proposes in his review that drop mobility and hysteresis is more important than the contact angle itself for useful hydrophobic surfaces; we are inclined to agree with him [10].

Dynamic measurements

The effect of drop size on static CA was investigated in subsection 4.1.1 and no effect was found, in all measurements following the same drop size was used to ensure that no bias between surfaces were present. In all following experiments that were dynamic we ensured that the same flow rate was kept and drop size was reached at the final stage of the measurement. There is a recommended maximum flow rate from the Kruss manual to $15 \mu\text{L}/\text{min}$ which we kept below at all times, how this is related to the size of the needle used is unknown to us. But the flow rate used will affect the stability of the measurement, a large enough flow rate will push the boundaries of the drop out over the surface quicker than a stable increase will allow. This will cause extreme values, either larger or smaller than typical for the surface, to appear in the measurement.

The needle will also have an effect on the measurement, during the measurements on superhydrophobic surfaces it was apparent that the drops clung to the needle which is made of some sort of stainless steel instead of dropping to the surface. This was expected but the size of the needle is not always negligible to the size of the drops placed on the surface. A smaller needle would be preferred in future work.

Transport

The temperature dependence experiment with hydrocarbons had to be performed under a fumehood, but the goniometer was not placed in the same area which necessitated that the samples were moved between the drop placement and measuring of contact angle during these experiments. The samples were handled with the utmost care, but temperature could not be controlled during transport which might have affected the measurements even if the delay was kept minimal. No observable difference (to the

naked eye) occurred during these transports, but a better experimental setup would remove this issue.

Laboratory environment

The condensation experiment in subsection 4.5.1 was performed in a fumehood in an open atmosphere, is quite far from the conditions in the tank carrying VGO on a ship. The experiment was still a success, the limited condensing on the sample plate at room temperature was enough to create a film.

5

Concluding Remarks

THIS chapter concludes our thesis with drawn conclusions and we propose what can be done for future work to improve or solve the problem.

In our problem definition we were limited to only use surface treatments to solve the problem, as this was of most interest for Emerson. Other solutions to the problem still exists though. One of the most obvious is a mechanical solution to screen off the antenna from the tank during transport with e.g. a knife valve, since the level measurement in almost all cases only takes place during loading and unloading of the tanks.

During the early stages of our work we concluded that within an oil tank, on an oil tanker, the problem arises from slushing. The condensation of oil is an ongoing process, however the time frame for condensing large amount of oil is large in comparison with the time it takes before problems occur, according to tanker personnel.

5.1 Repellent coatings

From our experimental research we draw the conclusion that there is no industrially available coating that is repellent enough to protect a surface from VGO sticking to the surface (subsection 4.3.2). In other words the worst case scenario during winter and rough sea, when a layer of water and VGO is built up on the antenna surface, will still create problems or even failure of the radar system. However, a repellent coating will in most cases ease the maintenance of the antennas. In our results the best repellancy was found on Hirec 450, it also showed good oleophobic properties for palm oil and food oil. However, our experiments showed that gasoline dissolved the coated layer and in a tank environment where diesel and gasoline might be present this coating may not withstand the wear. The coating from Aculon did however show better wear abilities and fairly low hysteresis for water (subsection 4.2.4) and therefore might be the best solution of repellent coatings. Worth to mention is that even if many of the coatings has simple application methods it may be hard to achieve the optimal repellency promoted by the manufacturer.

In conclusion we would like to mention that it is almost 15 years since the lotus effect was discovered by Barthlott and Neinhuis, and today only a few products available on the market utilizes this effect. In the last years the number of journal articles about

extremely repellent coatings has increased immensely. Our estimation is that the area of superhydrophobic and super oleophobic coatings has yet another decade before a commercial and robust coating will be available for this application.

5.2 Titanium dioxide

The option of using a hydrophilic TiO_2 coating to create a thin water film the is main solution we propose to solve the problem. In this case water serves as sacrificial material between the antenna and the oil in question. A thin water film may be corrected for in the radar software but cannot be too thick because of the significant intensity attenuation of EM-waves in water films (subsection 1.2.1). The proposed hydrophilic TiO_2 coating is a cheap coating which is easily accessible.

TiO_2 showed good abilities to create water films upon exposure of condensing water and from our own experience there is even more water condensing on the antenna during normal operation. The water content of the heavy oils is hard to measure, but for e.g. VGO Preem ensures that the water content is below 0.1 %. A typical oil tank in an oil tanker has a volume of $\sim 1000 \text{ m}^3$ implying at maximum 1000 L water in one tank which is an extensive amount if in gaseous phase. This means that if an antenna is treated with TiO_2 and put in a tanker a thin film of water is highly likely to form on the antenna. The mobility of VGO on a water film is high according to our results (subsection 4.5.2) since there is a liquid-liquid interaction instead of liquid-solid interaction. These results indicate that a thin water film covering the antenna surface would protect it from coming into contact with VGO and a potential oil residue buildup on the water surface would easily roll off the surface due to the up-side-down mounting of the antenna.

Our presented solution with a hydrophilic TiO_2 coating will definitely prevent oil condensation on the antenna. If oil splashes the antenna the water layer will act as sacrificial surface, however from our experiments it is not possible to estimate whether a water layer can withstand a powerful splash or not.

5.3 Surface roughness modifications

The evaluation of different lathings (subsection 4.2.1) showed that it is not possible to hinder wetting or extensively increase the contact angle due to surface roughness achieved by lathing. Though if an increase in wetting is wanted to increase the hydrophilicity of a surface, a roughness caused by lathing may very well be suitable. Thus by combining TiO_2 coating with a lathed surface the proposed solution is enhanced even further.

Nickelplated surfaces or other surface roughness modifications are hard to produce with good result. The resulting surface is dependent of a successful application process, but it is hard to tell whether an application was successful or not without measuring upon the surface. Our evaluation of nickelplated stainless steel showed a large disparity in the results (subsection 4.6.2 and subsection 4.2.3). If a surface roughness modification is to be applied it would have to be a very simple process with easily reproducible results. Too high hysteresis was observed on the nickelplated surfaces to recommend this surface treatment for further field tests.

5.4 Temperature dependent problem

In section 4.3 a clear temperature dependence for VGO can be seen and higher contact angles are observed for lower temperatures. The main reason for this is that VGO has a phase transition in this temperature regime. There are two sides of this result; the higher contact angle observed do help to obtain larger aggregates of oil which hopefully will detach/roll off from the surface due to gravitation or the lower temperature will increase the adhesion to a point where the surface is sufficiently covered to dampen the radar performance. Since VGO has a phase transition in this regime an easy solution would be to heat the antenna to a temperature above the melting point, as mentioned in the limitations this is unfortunately not possible.

5.5 Future work

There are substantial suggestions for what future actions should be conducted based on this thesis. Our suggestions are divided into two parts in this section; what should be done as a follow up to this thesis to mitigate or solve the problems occurring and what should be done in the long term.

We propose that field testing of the repellent and hydrophilic coatings is commenced to evaluate their effectiveness in the real application. There are some problems occurring with tankers carrying palm oil in the north sea area, therefore the repellent coating can be tested in this area while the hydrophilic coating should be tried on a ship carrying crude oil or VGO. This presumes that the cargo for each ship is known well ahead of time which unfortunately is difficult to predict.

5.5.1 Long term

We have a number of suggestions for what actions should be investigated or conducted in the future, we list them here in no particular order.

Water film thickness We have not investigated how thick a water film needs to be for protecting the surface from different kinds of oils on different roughnesses in detail.

Covering the development The technology for superhydrophobic coatings is still in its infancy, we estimate that there will be industrial products within a decade or two which will resist any liquid trying to smear the surface. To this end we believe it would be interesting and therefore propose that Emerson follows the development in this area.

Defining oil Oil is hard to describe, oils have different components whether it is pumped up in Norway or Saudi Arabia. We have not made an effort to describe the physics of VGO, this could be investigated in more detail. The enthalpy of fusion is of particular interest, if VGO can be kept above its melting point it will probably not cause disruptions in the system.

Heat conduction The problem is as previously mentioned temperature dependent, the heat conduction from the entire system should therefore be simulated. This could let small adjustments be made to the mechanical design to ensure that the temperature

never drops below the phase transition temperature of VGO.

Surface energy We did not measure the surface energy as close as we intended from the beginning of this thesis, this is partly due to the large hystereses we found and also from the difficulty of handling diiodomethane which is a dangerous substance. Measurements with diiodomethane will also show hysteresis on surfaces which will result in an surface energy interval rather than a definite value.

5.6 Final words

We did file a patent request to the committee handling those issues on Emerson. And they decided to file a patent application....

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