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Enhancement of Drain-Down Capabilities of Submarine Antennae

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Maritime Platforms Division
Defence Science and Technology Organisation

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ABSTRACT

Water droplets on submarine antennae degrade signal transmission and increase signature. To improve antennae coating performance a surface which repels water is required. In this study several experimental coatings were compared for their ability to remove water droplets from their surface. The contact angle of a drop of water on each surface was recorded as well as the hysteresis, which is a measure of how easily a droplet will roll off an inclined surface. It was found that the experimental coatings from the University of NSW had the highest contact angles and lowest hysteresis over a 1 week period of immersion in seawater. These coatings may provide far better drain-down capabilities than the standard polyurethane coatings presently used. Other coatings such as *Intersleek*[®] and *Rain-X*[®] provided short-term improvements in drain-down efficiency, with the added advantage of easy application.

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Enhancement of Drain-Down Capabilities of Submarine Antennae

Executive Summary

Water droplets and films on the surfaces of submarine antennae degrade signal transmission and increase signature. Performance can therefore be enhanced if water drains rapidly off the antennae surfaces when deployed. The characteristic of a surface that influences drain down is the hydrophobicity or, conversely, the wettability of that surface. On a hydrophobic surface, water droplets will bead. In contrast on hydrophilic surfaces droplets will spread out over the surface. Hydrophobicity can be quantified by measuring the contact angles of water droplets on a test surface. Equally important is the hysteresis of the surface, which measures whether a droplet will stick to an inclined surface (high hysteresis) or roll off (low hysteresis).

Currently submarine antennae are coated with polyurethane paint. Little is known about the drain down efficiency of this coating, how it performs over periods of immersion and what other coating systems are available which could provide better drain down capabilities.

This report measures the wettability and hysteresis of the polyurethane coating and compares it to three commercially available coatings (*Intersleek*[®], *RainX*[®] and *Broadshield*[®]) and three experimental coatings from the University of NSW (UNSW). The wettability of each surface was measured by examining the contact angle formed from a drop of water on the surface using a goniometer. Hysteresis was calculated by examining the change in contact angle when the surface is tilted.

It was found that the UNSW coatings had the highest contact angles (least wettable), greater than 150°. In contrast all the other coatings, including the control polyurethane, had contact angles less than 90°. The UNSW coatings also had the lowest hysteresis values (best drain down capabilities), far lower than the control polyurethane, which remained low after 1 week of immersion.

Two of the commercial coatings, *Intersleek*[®] and *Rain-X*[®], provided short-term improvements in drain-down efficiency compared to the polyurethane control. However the improvements diminished after 168 hours of immersion. These coatings have the advantage of easy application.

The UNSW coatings appear to provide far better drain down capabilities than the standard polyurethane paint system currently applied to submarine antennae. The UNSW coatings are superhydrophobic, which means they are extremely repellent to water. Droplets roll off these surfaces even at slight inclination angles. It is recommended that the UNSW coatings are assessed for longer periods of immersion and monitored for other mitigating effects such as biofouling.

Reductions in drain down characteristics of the coating will indicate that cleaning of the coating is required. If cleaning no longer regains drain-down characteristics re-coating may be required. The ease of application of the UNSW coatings (spray on) will need to be considered, however if not commercially available it is recommended that the *Intersleek*[®] treatment will provide better drain-down than the standard polyurethane paint.

This study has assessed the drain down capabilities of alternative submarine antennae coatings. It has demonstrated that the present coating system has poor drain down characteristics and that other available coatings may provide far superior drain down performance.

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Jim started working in DSTO in 1987 as a trainee technical officer. He completed his traineeship in 1990 after gaining his Associate Diploma (Laboratory Technology) at the Northern Melbourne Institute of TAFE. In the same year he started working in the Ballistic Protection and Survivability area within the then Materials Division. In 1998 he gained his BSc (Applied Chemistry) at RMIT University. In 2000 he transferred to the Environmental Compliance and Biotechnology Group within the Maritime Platforms Division. In 2002 he completed his Certificate of Surface Coatings, (Surface Coatings Association Australia Inc SCAA) at Victoria University. Currently he is working on novel antifouling strategies.

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Since 1977, after completing BSc (Hons) and MSc degrees in marine biology at the University of Melbourne, John Lewis has worked as a scientist in the Defence Science & Technology Organisation, with primary research interests in marine biofouling and its prevention, and the effects of RAN activities on the marine environment. John currently heads the Environmental Compliance and Biotechnology Group, within the DSTO Maritime Platforms Division, and leads a team investigating new, environmentally acceptable methods of biofouling control, biofouling and marine pest management, environmental compliance of naval vessels, and other environmental aspects of navy operations.

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1. Introduction

Water droplets and films on the surfaces of submarine antennae degrade signal transmission and increase signature. Performance can therefore be enhanced if water drains rapidly off the antennae surfaces when deployed. The characteristic of a surface that influences drain down is the hydrophobicity or, conversely, the wettability of that surface. On a hydrophobic surface, water droplets will bead and run off vertical or inclined substrates. Hydrophobicity can be quantified by measuring the contact angles of water droplets on a test surface.

As illustrated in Figure 1, when a drop is placed on a horizontal surface its shape can vary when viewed from the side and the shape represents how well the droplet wets a surface. The angle between a line tangent to the surface of the droplet where it touches the substrate, and the substrate, is the contact angle. If the contact angles are 90° the drop resembles a perfect hemisphere; if angles are $< 90^\circ$, the surface is hydrophilic and easily wetted (Figure 1a); if the angles are $> 90^\circ$, the droplet appears spherical, the surface is hydrophobic and does not wet easily (Figure 1b). The extremes of these two states are superhydrophilicity and superhydrophobicity.

When a surface is tilted, the droplet deforms and the contact angles on each side of the droplet change. The angle on the downward side of the droplet right before the droplet starts to move is termed the advancing contact angle (ACA); that on the upper side is the receding contact angle (RCA). Hysteresis is the parameter calculated by subtracting RCA from ACA, and this can be used to compare drain down characteristics of a surface. A surface with a positive hysteresis causes poor drain characteristics and the RCA will 'stick' to the surface as the droplet rolls off the surface (Figure 1c). In contrast a hysteresis approaching zero has favourable drain down characteristics as droplets will easily roll off the surface (Figure 1d). When there is no tilt on a surface the two angles formed from a droplet are also referred to as the apparent contact angle rather than ACA and RCA (Figure 1a & b).

Antennae housings are constructed of glass-reinforced polyester (GRP) and coated with a polyurethane paint system (PPS). The present study was undertaken to assess and compare different coatings and surface treatments for their ability to enhance drain down characteristics of this type of surface when compared to the standard PPS.

2. Methodology

2.1 Test materials

Two coatings and two surface treatments were evaluated and compared to uncoated polyurethane (Table 1). *Intersleek*[®] is a silicone-based, three-pack elastomeric paint marketed as a non-toxic fouling release coating for ship hulls and other underwater surfaces. *Rain-X*[®] is a commercial surface treatment for enhancing water repellence and run-off from, primarily, vehicle windscreens. *Broadshield*[®] is a similar treatment, but for shower screens and other bathroom applications. The experimental coating, from the University of New South Wales, is a silicone surface nano-modified to exhibit superhydrophobicity (CA $> 150^\circ$). There were three superhydrophobic coatings (SHCs) used which differed in their physical architecture. The SHCs are referred to as UNSW 1, UNSW 2 and UNSW 3.

Table 1: Test materials

System No.	Material Type	Material Name	Manufacturer
1	Coating	<i>Intersleek</i> [®]	International Paints
2	Surface treatment	<i>Rain-X</i> [®]	SOPUS Products
3	Surface treatment	<i>Broadshield</i> [®]	Showa Technocoat
4	Coating	Experimental Superhydrophobic	University of New South Wales

The test coupons were made of GRP and measured 75 mm x 150 mm x 3 mm. One set of three coupons was painted with polyurethane paint which acted as controls, and one set of three coupons prepared of each of the test materials.

Material application

The *Intersleek*[®] system is a two coat system: a tie coat and a finish coat. Each is a three pack product, consisting of a base, a hardener, and an accelerator. Each coat was applied by brush. *Rain-X*[®] and *Broadshield*[®] were applied with a polishing cloth as per manufacturer's instructions. Coupons of the experimental superhydrophobic coating were prepared at the University of New South Wales. These coatings are sprayed onto the surface (Lamb *et al.*, 1997).

2.2 Immersion procedure

To assess performance after seawater immersion, test coupons were immersed in seawater for 24 h, 96 h and 168 h. Immersion was performed in a glass aquarium, approximately 20 L in capacity, filled with artificial seawater (*Instant Ocean*[®]). After each period of immersion the coupons were air dried before measurements were taken. This procedure simulates the condition of a recently surfaced submarine antenna.

2.3 Measurement

Contact angles were measured with a Rame-Hart Model 100 goniometer. This is a manual instrument equipped with a 20" rail, 3 stage axis, tilt base, microscope, eyepiece and light source.

The coupons were attached to the tilting base of the goniometer by clamping the coupons onto the base using small vices. A 0.5 ml droplet of artificial seawater was placed onto the surface of the coupon using an auto-pipette, and droplets placed at three positions on the coupons: centre left, centre, and centre right. The advancing and receding contact angles were recorded manually at tilt angles of 0, 10, 20, 30, and 40 degrees. It was not possible to obtain reliable contact angle measurements at higher tilt angles, as droplets would roll off the coupons between angles of 40 – 90°. The results of the advancing and receding contact angles were averaged for each of the three droplets for each angle of tilt. Measurements were taken on each material before immersion, and after each successive period of immersion.

3. Results

Results are presented graphically in Figures 3 – 8. Figure 3 shows the contact angles on a horizontal surface and Figures 4 – 8 the corresponding hysteresis versus the base tilt. In graphs of contact angles, a guidance line crosses the y-axis at 90° , to clearly illustrate the shape of the bead. In graphs of hysteresis vs. tilt angle, a guidance line crosses the y-axis at the point equivalent to the control to clearly illustrate the performance of the treatments relative to the control. Standardised hysteresis values are presented. It should be noted that whilst standardised values of hysteresis range from -2 to 2, in real terms hysteresis values are never negative. Actual values would be very close to zero.

3.1 Contact angles versus the base tilt

No tilt (0°)

On a horizontal surface with no tilt the most hydrophobic surfaces were the experimental coatings from UNSW (CAs $> 120^\circ$, Figure 2). In contrast the *Intersleek*[®], Polyurethane, *Rain-X*[®] and the *Broadshield*[®] surfaces were all hydrophilic with CA $< 90^\circ$ (Figure 2). Most surfaces became more hydrophilic with increasing immersion time (Figure 2). The UNSW1 coating lost hydrophobicity from 120° to 95° over 1 week and the Broadband surface treatment changed from 75° to 35° after 4 days of immersion.

3.2 Hysteresis – Advancing contact angle (ACA) versus Receding contact angle (RCA)

No tilt (0°)

The UNSW coatings all had low hysteresis values which indicates that the ACA was similar to the RCA. The hysteresis increased with increasing periods of immersion. All the UNSW coatings regardless of exposure time had lower hysteresis values than the control (Figure 3). In contrast the *Intersleek*[®], Polyurethane, *Rain-X*[®] and the *Broadshield*[®] surfaces had more positive hysteresis values, which means the ACA were larger than the RCA. Hysteresis also became more positive with increasing exposure times on these treatments. Of the non-UNSW coatings only the *Intersleek*[®] 24 h treatment had a lower hysteresis than the Polyurethane control after immersion (Figure 3).

Hysteresis 10° - 40° tilt

There was a similar trend for surface hysteresis with all tilt angles tested. The UNSW SHCs all had lower hysteresis values than the control for all immersion periods. In contrast all the other coatings and surface treatments had higher hysteresis values. None of these other surfaces had lower hysteresis than the control after immersion.

4. Discussion

Measuring advancing and receding angles, and using these to calculate hysteresis, provides a measure of the hydrophobicity of the surface and the likelihood that water droplets will roll off a vertical or steeply inclined surface. The smaller the hysteresis value, the more likely this will occur. The UNSW samples were the most hydrophobic of the surfaces tested and

performed the best overall. Other surfaces showed various degrees of hydrophilicity and hydrophobicity. The UNSW surfaces had the lowest hysteresis which remained lower than the control after one week of immersion.

The other treatments, in order of decreasing performance, were *Intersleek*[®], *Rain-X*[®], *Broadshield*[®] and Polyurethane (control). Both the *Intersleek*[®] and *Rain-X*[®] treatments provided short-term improvements in drain-down capacity. However, these improvements relative to the Polyurethane control, diminished after 168 hours of immersion.

It should be noted that generally advancing and receding angles are measured at the moment before a droplet rolls off a surface, and hence only one hysteresis value is reported. With the goniometer used in this study it was not possible to measure the angle at the exact moment the droplet rolled off an inclined surface as the goniometer was not equipped with a computer controlled X-Y stage. Therefore several angles at intermediate stages of the droplets deformation were recorded. It is likely that maximum possible ACA and RCA were not recorded, as such the true hysteresis values for each surface may be slightly higher.

All the treatments suffered some degradation in hydrophobicity with increasing immersion in seawater. This was greatest in the UNSW1 coating and *Intersleek*[®] and least in *Broadshield*[®] and Polyurethane. However, the UNSW coatings were still the best performed overall and had consistently lower hysteresis than the controls through all immersion periods. Loss of hydrophobicity has also been reported on Mechanically Assembled Monolayers (MAMs) over 1 week of submergence (Genzer & Efimenko, 2000). These changes in hydrophobicity are not drastic (5-20°) and tend to level out after 5 days. In a recent study Zimmermann et al. (2006) demonstrated that silicone superhydrophobic coatings, not too dissimilar to those used in this study, retained their superhydrophobic properties for up to 6 months immersion in a variety of different aqueous media. However, this media was abiotic and as such was not influenced by biofilms. Submarine antennae would quickly become exposed to biofilms which may alter the wettability of the surface. Improvements in surface coating design allow greater interlocking of molecules which will reduce surface changes upon immersion and lead to increased longevity of surface hydrophobicity (Genzer & Efimenko, 2000). Further improvements in the design of the experimental coatings may lead to increased drain-down performance for extended periods of immersion.

Applications based on superhydrophobic surfaces have grown considerably in recent years (reviews Sun et al 2005; Marmur, 2006; Genzer & Efimenko, 2006). These surfaces have begun to be utilised in textiles, agriculture and medical devices. Superhydrophobic surfaces are often inspired from natural surface features such as on the leaves of the Lotus plant (Barthlott & Neinhuis, 1997), the desert beetle (Zhai et al. 2006) and the water strider (Gao & Jiang, 2004). All these natural surfaces facilitate self-cleaning. It is this type of technology that can be of use in drain-down applications.

From this study it is recommended that applying the UNSW 3 coating to antennae surfaces will enhance drain down characteristics. The UNSW coatings are the only superhydrophobic coatings and therefore had the highest contact angles. The UNSW 3 coating is recommended above the others as it was able to maintain the lowest hysteresis values over longer periods of immersion. The drain down performance will degrade with increasing immersion time. However, the performance may still be better than the current polyurethane coating.

Although untested in this study, initial performance could be regained, in the case of *Intersleek*[®], by cleaning the surface. A gentle non-abrasive wipe of the surface would remove excess slime which may be contributing to the reduction in hydrophobicity and an increase in hysteresis.

Future work will need to assess the performance of the UNSW or *Intersleek*[®] coatings over longer time periods of immersion. Any mitigating effects of surface fouling will also need to be monitored in the long term. However, it is known that surfaces with low hysteresis have better release properties and higher biofouling resistance (Schmidt et al. 2004). Reductions in drain down characteristics of the coating will indicate that further cleaning of the coating is required. If cleaning no longer regains drain-down characteristics re-coating may be required. The ease of application of the UNSW coatings (spray on) is favourable. However, if not commercially available, it is recommended that the *Intersleek*[®] treatment will provide better drain-down than the standard polyurethane paint.

5. Acknowledgements

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7. Figures

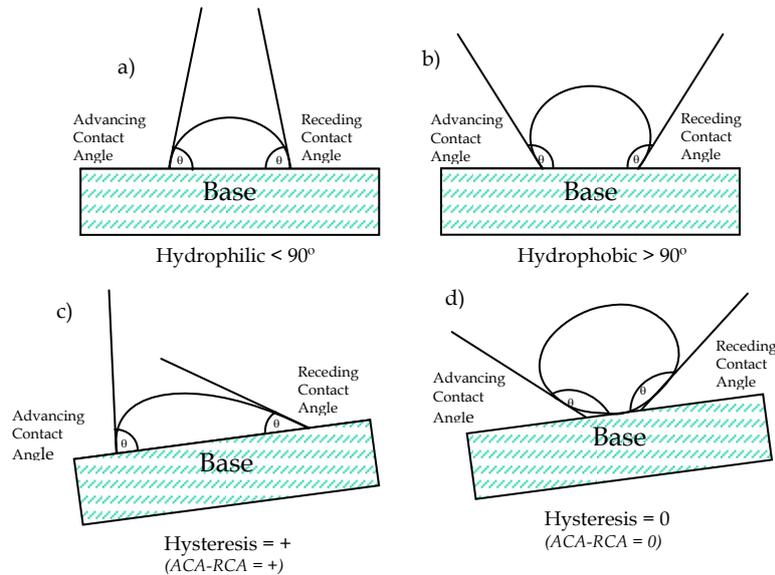


Figure 1. Diagrams showing characteristic shapes of droplets on surfaces of varying hydrophobicity; a) a hydrophilic surface b) a hydrophobic surface c) a positive hysteresis on a tilted surface d) a negative hysteresis on a tilted surface

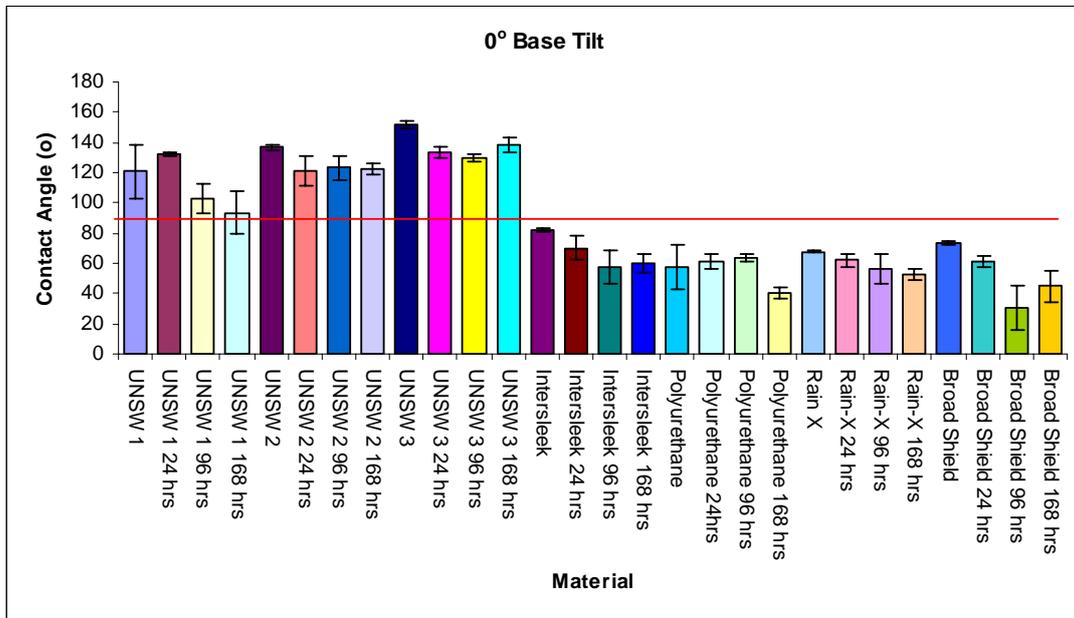


Figure 2. Mean contact angles measured at 0° tilt for each treated coupon and Polyurethane control \pm one standard error. Contact angles are recorded prior to immersion and after 24 h, 96 h and 168 h. Coupons with contact angles above the red line (90°) are considered hydrophobic whilst those with contact angles below the red line are hydrophilic.

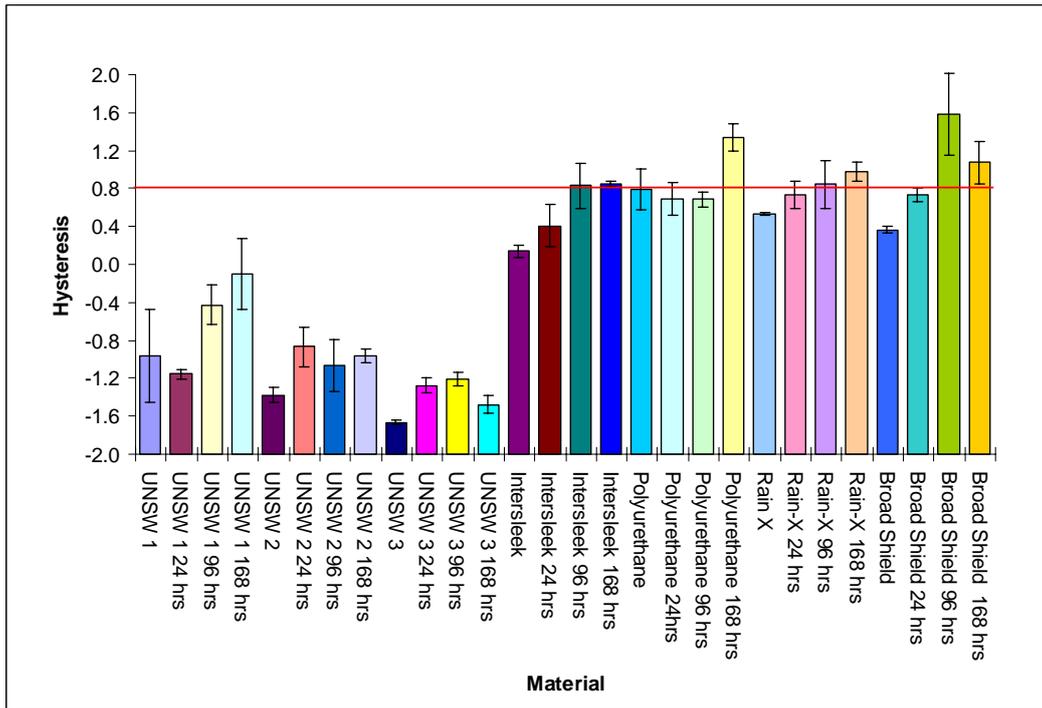


Figure 3: Standardised mean hysteresis values for treated coupons and Polyurethane control with no tilt \pm one standard error. Lower values results in greater drain down performance. In contrast highly positive hysteresis values are due to smaller RCA values than ACA. The red line indicates the hysteresis value of the Polyurethane control.

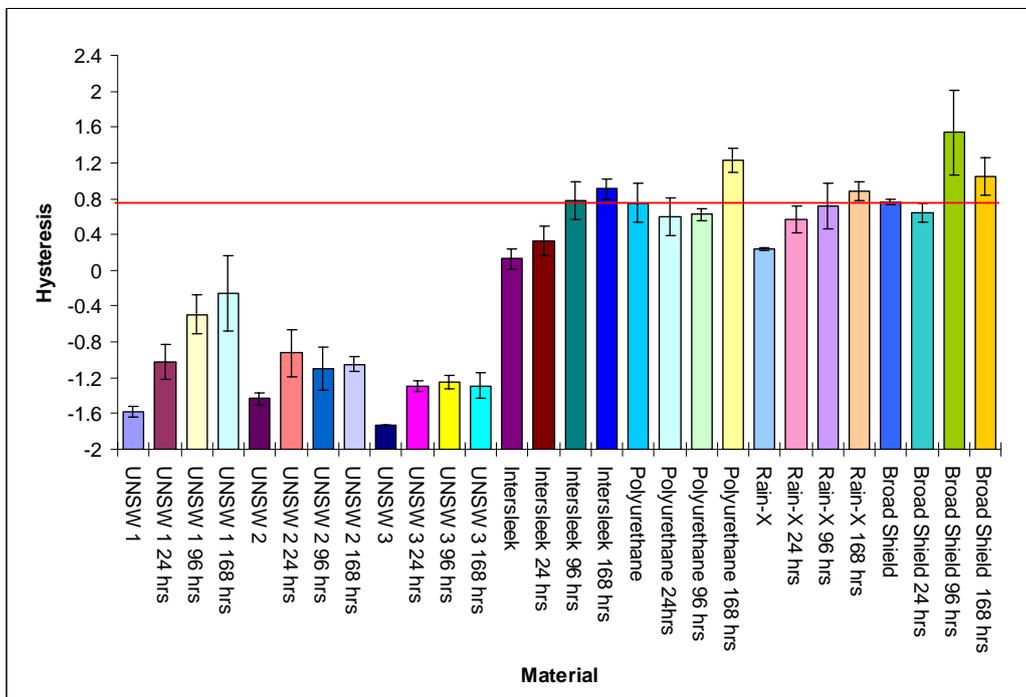


Figure 4: Standardised mean hysteresis values for treated coupons and Polyurethane control with 10° tilt \pm one standard error. Lower values results in greater drain down performance. In contrast highly positive hysteresis values are due to smaller RCA values than ACA. The red line indicates the hysteresis value of the Polyurethane control.

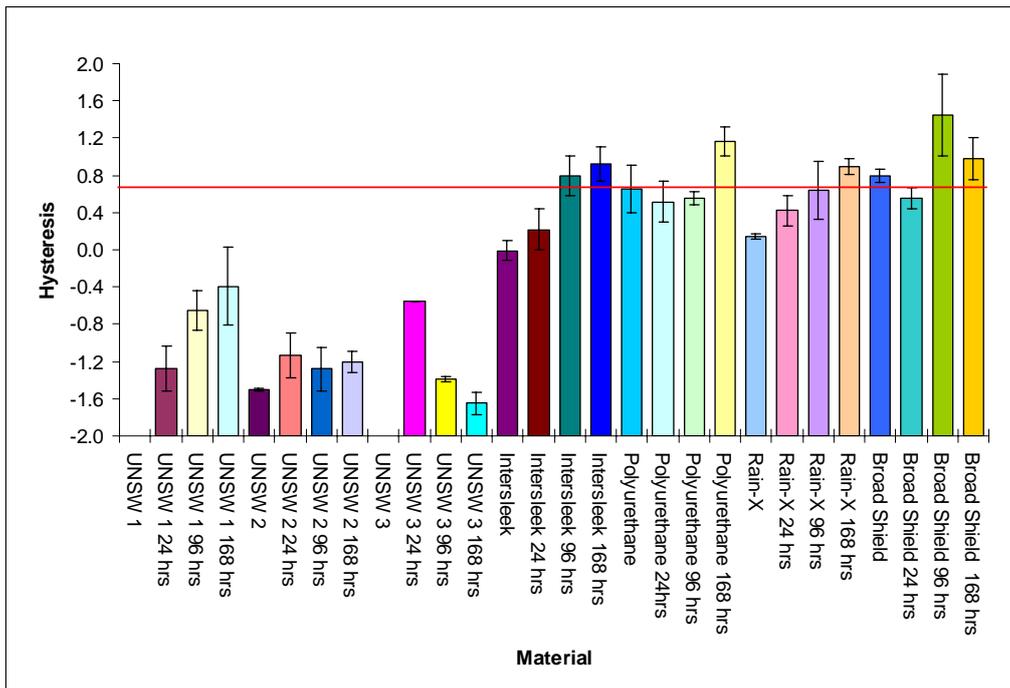


Figure 5. Standardised mean hysteresis values for treated coupons and Polyurethane control with 20° tilt ± one standard error. No value indicates that the droplets rolled off the test surface. Lower values results in greater drain down performance. In contrast highly positive hysteresis values are due to smaller RCA values than ACA. The red line indicates the hysteresis value of the Polyurethane control.

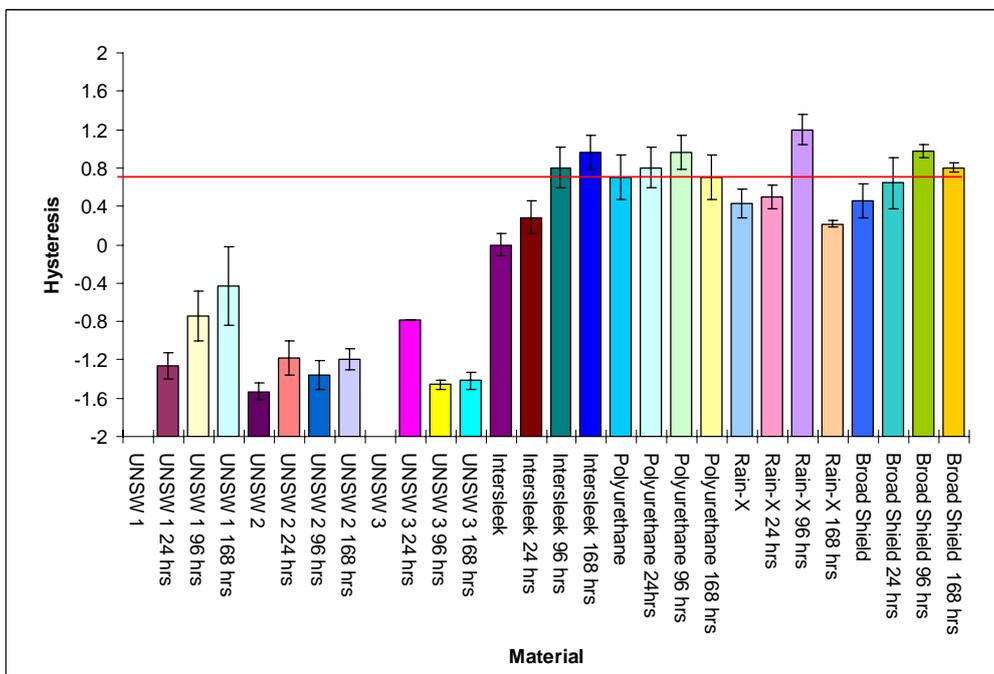


Figure 6. Standardised mean hysteresis values for treated coupons and Polyurethane control with 30° tilt ± one standard error. No value indicates that the droplets rolled off the test surface. Lower values results in greater drain down performance. In contrast highly positive hysteresis values are due to smaller RCA values than ACA. The red line indicates the hysteresis value of the Polyurethane control.

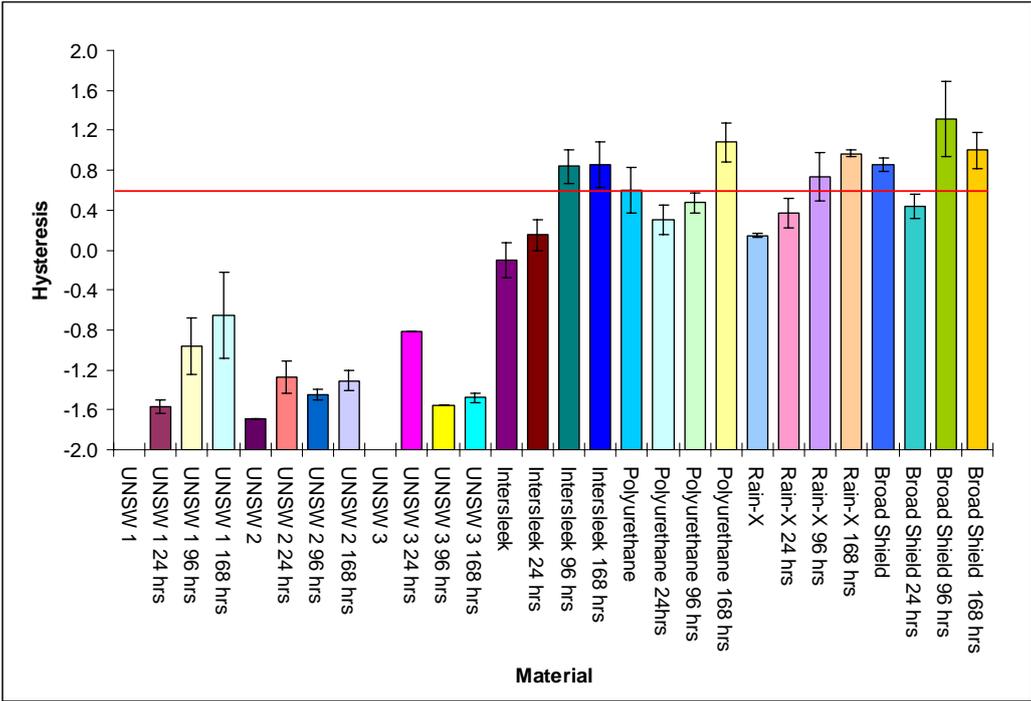


Figure 7. Standardised mean hysteresis values for treated coupons and Polyurethane control with 40° tilt ± one standard error. No value indicates that the droplets rolled off the test surface. Lower values results in greater drain down performance. In contrast highly positive hysteresis values are due to smaller RCA values than ACA. The red line indicates the hysteresis value of the Polyurethane control.

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