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Lubricant Impregnated Surfaces for Mitigating Asphaltene Deposition

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Abstract

Asphaltenes are heavy aromatic components of crude oil. Their complex chemical makeup - an aromatic core surrounded by aliphatic side-chains - enables them to adhere to most surfaces. Their buildup in pipes can result in clogging and lead to interruption of production operations and expensive mechanical cleaning. We demonstrate the use of liquid impregnated surfaces (LIS) to prevent asphaltene deposition and buildup on substrates. Indeed, these surfaces expose a liquid interface to the working fluid which combines the benefits of a dynamic defect-free surface and a tunable interfacial tension. In contrast to bulk additives that are typically mixed into the bulk oil phase, the impregnating liquid also provides the great benefit of protecting the underlying solid surface with a stable and minimal layer of lubricant, thereby reducing costs and eliminating the need for subsequent downstream removal. We first select and confirm the thermodynamic stability of a suitable lubricant and its lack of interaction with asphaltenes. By using a carefully-selected system composed of a textured and functionalized solid substrate in conjunction with a fluorinated lubricant, we show that asphaltene adsorption is prevented over long timescales. We further demonstrate the possibility of building such a system with representative industrial materials such as aluminum and expose the resulting substrate to an external shear flow to simulate pipe flow conditions.

Introduction

Asphaltenes are amongst the components of crude oil most known for their remarkable affinity with interfaces (1–4). While their exact chemical composition varies depending on the source of the oil they are extracted from, most varieties exhibit multi-aromatic cores with aliphatic side chains and polar substitutions such as nitrogen and sulfur (5,6). This complex structure enables them to readily adhere on solid surfaces through both polar and apolar interactions (7–10) which leads to fouling – and eventually pipe clogging (10–12) – requiring costly interruption of production and, often, mechanical scrubbing or ‘pigging’ of the pipes. Several strategies have been proposed to mitigate asphaltene deposition: the use of chemical additives has been extensively studied but their performance depends on the composition of the oil; in addition, large quantities are necessary, and they must then be removed in downstream processing (13–15). Anti-fouling coatings and functionalizations have also been proposed (16) but none have succeeded at completely preventing the adsorption of these contaminants (17). The ability of asphaltenes to adsorb on almost any surface is due to their dual molecular morphology which enables the combination of π - π , polar, and apolar interactions with a substrate (18). Here, we report a robust and versatile approach to mitigate asphaltene fouling. Through the use of liquid impregnated surfaces and a careful choice of lubricant, we show that we can prevent the adsorption of asphaltenes under both static and dynamic flowing conditions.

Liquid impregnated surfaces (LIS) are hybrid surfaces consisting of a porous or textured solid matrix impregnated with a liquid lubricant (19–24). Such surfaces exhibit the mechanical robustness of a solid substrate while also presenting a slippery liquid interface to contacting liquids (19,22). Sessile droplets on such surfaces exhibit a high mobility with low liquid-solid adhesion (i.e. low contact angle hysteresis). LISs can also repel a variety of complex liquids by carefully choosing an appropriate lubricant (21,25). The adsorption of complex particles suspended in

liquids can also be mitigated such as cells and proteins in blood (20,26), bacterial suspensions (27), or algae (28).

Asphaltenes, defined by their solubility in toluene and their insolubility in n-alkanes (5,29), present further challenges in the design of a robust LIS due to their great affinity for interfaces. In this study, we consider solutions of asphaltenes in toluene as a model system to abstract the variability of crude oil. Indeed, the low surface tension of toluene and its ability to solubilize most other organic oils require careful design of the solid-liquid composite surface to ensure that a stable lubricant layer can be maintained. Here, we show the stable impregnation of a textured commercial aluminum substrate with a lubricant that does not interact with asphaltenes. Finally, we evaluate the dynamic stability of this materialsystem under an external shear stress.

Results and Discussion

Due to its low surface tension ($\gamma \approx 28\text{mN/m}$), toluene spreads readily on most solids. In particular, Figure 1a shows a $2\mu\text{L}$ drop of toluene deposited on a polished and cleaned aluminum surface (see Methods). The liquid spreads as a puddle of diameter $2R \approx 3\text{ mm}$. Upon tilting the surface, the drop starts moving at the roll-off angle, $\alpha_c = 7^\circ$. This critical angle, defined at the onset of gravity-driven motion, is a measure of the adhesion of the $2\mu\text{L}$ drop to the surface. As it is rolling, the drop exhibits an asymmetric shape from which we can measure the advancing contact angle (at the leading edge), $\theta_a = 13^\circ \pm 2^\circ$, and the receding contact angle (at the trailing edge), $\theta_r \approx 0^\circ$. The difference between these angles gives rise to an adhesion force that scales with the radius R and the contact angle hysteresis $\Delta\cos\theta = \cos\theta_r - \cos\theta_a$ (30).

Figure 1: Characterization of asphaltene behavior on functionalized aluminum. **a)** 2 μL drop of toluene on a plain aluminum substrate tilted at the roll-off angle $\alpha_c = 7^\circ$. **b)** 2 μL drop of toluene on a porous aluminum solid impregnated by a lubricant (LIS), at the roll-off angle $\alpha_c = 3^\circ$. **c)** A 20 μL drop of an asphaltene solution (300 mg/L) in toluene is deposited on both plain aluminum (top row) and LIS substrate (bottom row) tilted by an angle of $\alpha = 20^\circ$.

When an identical volume of toluene is deposited on a functionalized impregnated porous aluminum substrate (LIS), the resulting drop shape is dramatically different as depicted in Figure 1b: the drop exhibits an almost perfectly symmetrical shape on the lubricant impregnated substrate. The advancing and receding contact angles are close ($\theta_a = 67^\circ \pm 2^\circ$ and $\theta_r = 64^\circ \pm 2^\circ$) which leads to a low value of the contact angle hysteresis, $\Delta\theta = 3^\circ$. Moreover, the contact area is decreased by a factor 3 ($2R \approx 1 \text{ mm}$) compared to the plain aluminum substrate. The combination of these two effects leads to significantly lower adhesion between the droplet and the substrate. This is demonstrated by the drop starting to roll at a lower tilt angle ($\alpha_c = 3^\circ$) compared to the plain untextured aluminum substrate. In addition, the liquid-impregnated substrate leads to more localized wetting, which could potentially reduce the effect of any contamination.

In the presence of dissolved asphaltenes, these key observations are maintained as shown in the pictures of the Figure 1c. A 20 μL drop of a concentrated asphaltene solution in toluene (300 mg/L)

is deposited on plain aluminum (top row, and Movie S1) and on an LIS (bottom row, and Movie S2). Both substrates are tilted at an angle $\alpha = 20^\circ$, which exceeds the roll-off angles of both surfaces. The sequence of images in Figure 1c shows that the drop spreads and leaves a trail when rolling on plain aluminum due to the affinity of the solvent in the drop with the underlying substrate. When this trail evaporates, a deposit of asphaltenes is formed on the surface which permanently fouls the surface and changes the wetting properties of the solid, thus enabling subsequent adsorption. By contrast, the drop deposited on the LIS remains essentially a spherical cap and rolls down the substrate without leaving any apparent residue, even after drying (Figure 1c, right panel). This indicates a lower affinity of the lubricated substrate for the asphaltene solution. Conversely, when a droplet is deposited on porous aluminum without chemical treatment or impregnation, the wetting of toluene is enhanced and the toluene-aluminum contact area is greatly increased (see Movie S3).

Figure 2: Thermodynamic stability of LIS with toluene. **a)** Schematic of the silicon-based lubricant impregnated surface. Two kinds of posts were investigated: smooth and nanotextured. On the right, SEM images of an impregnated surface (top) and close up of the top of a nanotextured post (bottom). **b)** Stability diagram of the LIS as a function of the spacing b between two posts and the contact angle of the lubricant on a smooth solid in a bath of the working fluid. Black dots (smooth posts) and stars (nanograin posts) correspond to post spacings of 5, 10, 25, and $50\mu\text{m}$. Vertical line corresponds to the contact angle of Krytox on fluorosilane in toluene ($\theta_{o/s(l)} \approx 55^\circ$). **c)** Contact angle of water (in blue) and toluene (in red) on a lubricant impregnated surface before and after immersion in toluene for 72 hours as a function of post spacing b on smooth posts. For large spacings (25 and $50\mu\text{m}$) the change in contact angles indicate an unstable situation in good agreement with figure 2b (yellow squares). **d)** On nanograin posts, contact angles are identical to the control for every spacing.

Selecting an appropriate lubricant is key to enable the use of lubricant impregnated surfaces for industrial applications. Indeed, the lubricant must be retained within the texture despite the presence of other liquids, exposure to contaminants, and the presence of an external shear flow. We will first consider the problem of static stability when exposed to other liquids. To remain in the texture, the lubricant must be immiscible with the outer liquid phase and have an appropriate

value of the interfacial tension with the solid substrate such that it remains thermodynamically stable in the impregnated configuration and is not displaced from the texture by the working fluid. Both of these criteria are difficult to achieve in the context of crude oil due to the presence of very low surface tension components, that have a strong tendency to spread on solids, and a combination of both aqueous and organic liquids, that can dissolve most other liquids. To study the thermodynamic stability of lubricants in this context, we chose toluene as a model working fluid due to its low surface energy and high affinity for many other solvents. In addition, because the texture of the underlying solid plays a significant role, we elected to use surfaces consisting of microtextured silicon post arrays in order to have precise control over both the Wenzel roughness r - the ratio of the total surface area over the projected surface area - and exposed solid fraction, ϕ , of the substrate. An array of square posts of side length a , height h , and spacing b was fabricated using photolithography on the surface of a silicon wafer as sketched in Figure 2a. The height and side length were kept constant across this study both equal to 10 μm while the spacing, b , was varied from 5 to 50 μm . In addition, two kinds of posts were investigated: posts with flat faces and posts that display an additional roughness on the scale of 100 nm, commonly referred to as ‘nanoglass’, that is obtained by directional reactive ion etching in the presence of SF_6 and O_2 gas (31,32).

The lubricant impregnates the texture if it wets the surface in the presence of the working fluid. This configuration is thermodynamically stable when the interfacial energy per unit area of the solid is lower when fully wetted by the lubricant in an environment of toluene than it is when the toluene directly wets the porous solid (21,33). This criterion can alternatively be expressed by a condition on the contact angle $\theta_{\text{os(l)}}$ of the lubricating liquid on a flat solid of identical chemistry immersed in the working liquid, toluene. Specifically, it corresponds to an upper limit for the contact angle $\theta_{\text{os(l)}}$ expressed as a critical angle $\theta_c = \arccos \frac{1-\phi}{r-\phi}$ where r is the Wenzel roughness and ϕ is the solid fraction of the top of the posts. When $\theta_{\text{os(l)}} < \theta_c$, the lubricant is thermodynamically stable in the solid. In the opposite case, progressive flooding of the texture and displacement of the impregnated lubricant by the external working fluid is energetically favorable.

Given these constraints, we selected Krytox 1506, a fluorinated commercial vacuum oil, as the lubricant for our system. Indeed, it is immiscible with toluene – and other organic solvents - and

exhibits a low surface tension that is well-suited to wetting the substrate. Guided by the chemistry of the lubricant, we functionalized the silicon substrate with a perfluorinated alkane: (1H, 1H, 2H, 2H)-perfluoro-octylsilane. This combination leads to $\theta_{os(l)} = 55^\circ \pm 2^\circ$, suggesting that stable impregnation is possible, for instance with flat posts of spacing $b = 10 \mu\text{m}$, for which $\theta_c \approx 65^\circ$. An SEM micrograph of such a surface ($b = 10\mu\text{m}$) is shown in Figure 2a. The noisiness of the signal is due to the presence of the lubricating oil between, and on top of, the posts.

These thermodynamic considerations enable us to build the phase diagram in Figure 2b showing the influences on the thermodynamic stability of an LIS of both (i) the surface chemistry of the solid (through the contact angle $\theta_{os(l)}$ of the lubricant on a flat solid substrate of the same chemistry in the presence of the working fluid) and also (ii) its roughness (captured here by the post spacing b). Considering Krytox as the lubricant, the contact angle $\theta_{os(l)}$ exhibits a strong dependence on the external working fluid, varying from a low value ($\cos \theta_{os(w)} \approx 0.99$) for water to an intermediate value ($\cos \theta_{os(t)} \approx 0.57$) for toluene (solid black vertical lines). The green solid line in Figure 2b represents the stability criterion for smooth micro-posts: $\cos \theta_c = (1 - \phi)/(r - \phi)$ where $r = 1 + (4ah) / (a + b)^2$ is the Wenzel roughness and $\phi = a^2/(a + b)^2$ the solid fraction (21,33). Similarly, the orange solid line denotes the stability criterion for posts covered with nanograss where the critical contact angle for the lubricant in toluene can then be expressed as $\cos \theta_c = (1 - \phi \phi_{ng}) / (r r_{ng} - \phi \phi_{ng})$ where $r_{ng} = 3.4$ and $\phi_{ng} = 0.09$ are the additional hierarchical levels of roughness and reduced surface fraction conferred by the nanograss texture, as experimentally determined from AFM micrographs of the surface. This phase diagram allows us to predict the maximal pitch between two posts for different working fluids. Specifically, the green region indicates the thermodynamic stability of the lubricant in a substrate consisting of smooth posts, the orange region the extended region of stability with nanograss-covered posts and the red region indicates thermodynamic instability of the system.

To validate this phase diagram for Krytox in toluene, we use textures with a range of post spacings $b = 5, 10, 25$, and $50 \mu\text{m}$ respectively. The round and star-shaped points on Figure 2b show the critical values of $\cos(\theta_{os(l)})$ for each of these cases with both smooth posts and posts textured with nanograss, respectively. To evaluate the stability of the lubricant, we measure the contact angle of water and toluene on these different LIS before and after immersion in a bath of toluene for 72h.

Immediately after impregnation of the LIS surfaces, both advancing and receding contact angles of water and toluene do not depend on post spacing. This case is referred to as *Control* in Figure 2c where the contact angles are shown using a rectangular bar for which the upper value corresponds to the advancing angle θ_a and the lower value represents the receding angle θ_r . The absence of significant change in advancing and receding contact angles after immersion in toluene demonstrates that the lubricant remains stably impregnated in the textures with spacings of $b = 5$ and $10\ \mu\text{m}$ as predicted from the thermodynamic stability analysis above. By contrast, the samples with post spacing $b = 25$ and $50\ \mu\text{m}$ show a marked decrease in the receding contact angles. This is characteristic of a progressive loss of lubricant leading to the exposure of the top of the posts which then act as pinning sites and defects leading to low receding contact angle as the drop has to depin at the contact line before moving.

Conversely, in the case of nanoglass covered posts, the contact angles of water and toluene do not change after immersion in toluene for 72h as reported in Figure 2d. Even the LIS with the largest $50\ \mu\text{m}$ spacing between posts remains stable. These experimental results are plotted in Figure 2b as squares on the vertical line defining the chemistry of the system consisting of Krytox placed on fluorosilane-coated substrates immersed in toluene. The green squares show stability in all cases (smooth and rough posts) while the orange squares denote stability only in the case of nanoglass-coated posts. These results are in good agreement with the domains represented in Figure 2b and defined by the thermodynamic stability analysis discussed above.

This demonstrates that Krytox can be used as a stable lubricant in contact with a working liquid phase of toluene as long as the underlying texture exhibits roughness on a sufficiently small scale to make the impregnation thermodynamically stable.

Figure 3: Interfacial activity of asphaltenes. **a)** Interfacial tension measured between a solution of 300mg/L of asphaltenes in toluene and either a water phase or Krytox 1506, respectively, as a function of the age of the interface. **b)** Contact angle of water and toluene on lubricant impregnated surfaces that have been exposed to a solution of toluene containing 0, 50, 300 and 1,000 mg/L of asphaltenes, respectively, for 21 days.

In addition to being stably impregnated in the textured surface, the lubricant should also exhibit as little interaction as possible with contaminants present in the working fluid. Indeed, these contaminants can act as surfactants at the lubricant-working fluid interface and modify the thermodynamic balance keeping the lubricant stably impregnated. Specifically, we consider here the case of asphaltenes as surface-active contaminants present in toluene. To study the affinity of asphaltenes for the lubricant-toluene interface, we measure the interfacial tension γ_i between the two liquids as a function of the age of the interface. A solution of asphaltenes in toluene was freshly prepared at a concentration of 300mg/L in a quartz cuvette. A drop of the opposing fluid (water or Krytox, respectively) was then created in the asphaltene solution and its shape was continuously measured by a Ramé-Hart goniometer enabling the calculation of the interfacial tension (see Methods).

Figure 3a shows the time evolution of the Krytox-toluene interfacial tension γ_{k-t} (in orange) and the water-toluene interfacial tension γ_{w-t} (in blue) in the presence of 300mg/L of asphaltenes dissolved in the toluene phase. The water-toluene interfacial tension exhibits a marked decline from the value expected for pure liquids ($\gamma_{w-t}^0 = 36$ mN/m). This decrease can be attributed to the adsorption of asphaltenes at the water-toluene interface, reducing the interfacial energy by acting as surfactants. It can be fitted by an exponential law such as $\gamma_{w-t}(t) = \gamma_{w-t}^0 \exp(-t/\tau) + \gamma_{w-t}^\infty$ with γ_{w-t}^∞ the equilibrium interfacial tension and τ the time constant of the adsorption process. This fitting enables us to evaluate the timescale of the asphaltene adsorption as $\tau = 350$ seconds. Conversely, in the case of the Krytox-toluene interface, no change in the interfacial tension was observed over a time of 1,200s. These results demonstrate that asphaltenes have very little affinity for the Krytox-toluene interface and do not alter the interfacial tension term of the thermodynamic balance. We can therefore expect the Krytox lubricant to remain stable indefinitely in the textured substrate.

To study the long-term resistance of Krytox lubricant to asphaltenes, we designed an experiment consisting of immersing liquid impregnated surfaces in toluene containing between 50 and 1,000 mg/L of asphaltenes for 21 days. After the 3-week immersion period, the samples were recovered and tested. In order to limit the potential loss of asphaltenes during the removal of the samples, a more viscous Krytox oil was selected: Krytox GPL 107 with a viscosity of 10,000 cSt. Figure 3b shows the post-immersion contact angle of water (in blue) and toluene (in red) on these samples as a function of the concentration of asphaltenes in the toluene they were exposed to. The results show that all the samples exhibit the same contact angle as the control, which was immersed in pure toluene and not exposed to asphaltenes. This demonstrates that the surface energy of the Krytox/toluene interface has not changed during the experiment. Furthermore, the contact angles measured were significantly different than those expected on a surface contaminated with asphaltenes: 100° for water and 0° for toluene (18). These results suggest the absence of asphaltene deposition on the LIS substrate.

Figure 4: Long term interfacial activity of asphaltenes. **a)** X-ray photoelectron spectroscopy survey spectrum on a bare silicon surface and a lubricant impregnated surface (LIS) exposed to a solution of 300mg/L of asphaltenes for 21 days. **b)** High resolution Sulfur 2p spectrum on a bare silicon surface and a lubricant impregnated surface exposed to a solution of 300mg/L of asphaltenes for 21 days.

To further evaluate the presence of asphaltenes on the uppermost layer of the viscous Krytox, X-ray photoelectron spectroscopy (XPS) measurements were performed in a low vacuum environment on the surfaces post-exposure to asphaltenes. XPS measurements provide highly sensitive detection of the elemental composition of the surface of a material. The maximum sampling depth is around 10 nm making this surface-sensitive technique ideal to detect deposition of contaminants such as asphaltenes. In addition, the detection limit of XPS is on the order of 0.1 to 1 atomic percent (34) allowing it to detect minute amounts of deposition at the surface. The technique can be used to detect asphaltenes because of the presence of large amount of sulfur, 8 wt. % for the asphaltenes studied here (see Methods), which is otherwise absent from the surface under examination (35,36).

A representative survey spectrum of the LIS as well as a control silicon surface (flat and chemically unmodified) exposed to 300 mg/L of asphaltenes in toluene for 21 days are shown in Figure 4a. The survey shows the presence of fluorine, carbon and oxygen from the Krytox oil on the LIS. The control surface, on the other hand, only exhibits carbon, oxygen and a small sulfur peak. The absence of a silicon peak indicates the control surface is covered with contaminants. A high resolution Sulfur 2p spectrum, shown in Figure 4b, further demonstrates the contrast between the pronounced S 2p peak observed on the control surface and the absence of signal on the liquid impregnated surface. This demonstrates the absence of asphaltene on the LIS down to the detection limit of XPS.

These results demonstrate the long-term resistance of Krytox impregnated surfaces to fouling by asphaltenes suggesting their potential use in industrial applications. However, additional complexity in practical applications arises from exposure to shear-flow. To this end, we studied the dynamic stability of a Krytox-impregnated textured aluminum rotor exposed to shear-stress in toluene in a Taylor-Couette cell.

A custom rheometer rotor was fabricated from Aluminum 6061 stock obtained from McMaster-Carr. The rotor was then cleaned thoroughly (see Methods). To generate the microtexture necessary for lubricant impregnation, the aluminum was etched in HCl for 15 minutes resulting in a microscopic roughness on the order of 10 μ m (Figure 5a and c). To further increase the level of textural roughness, the rotor was then immersed in boiling water for 20 minutes. The oxidation resulting from the boiling step leads to the formation of boehmite platelets which provide an additional level of nanoscale roughness (37,38). This double treatment leads to a hierarchical micro-nano texture with a high roughness capable of stabilizing a lubricant.

The surface of the rotor was further functionalized with (1H, 1H, 2H, 2H) – perfluorooctylsilane (pFOTS) by vapor deposition and then dip coated in Teflon (2% in FC70). The Teflon coating was then cured on a hot plate to evaporate the solvent and homogenize the coating by reflowing the Teflon above its glass transition temperature. Figure 5c shows the surface texture following the Teflon coating, demonstrating the presence of significant surface roughness and the absence of

excess Teflon. The rotor was finally dip-coated in Krytox to impregnate the texture with lubricant and form a stable LIS. Lubricants of two different viscosities but with similar chemical characteristics were used to study the effect of viscosity on the stability: Krytox 1506 (62 cSt at 20°C) and Krytox GPL107 (1535 cSt at 20°C). The static stability of the lubricant was verified in a similar manner to that described in Figure 2. Immersing the rotor in toluene for 72 hours followed by removal, drying and then measurement of the contact angle of a small drop placed on the LIS-coated rotor resulted in no change of the contact angle for water or toluene droplets indicating good thermodynamic stability of the lubricant in the texture. This confirmed that the scale of the roughness was sufficiently small to ensure stable impregnation of the Krytox lubricant.

To study the dynamic stability under shear, we placed the rotor in a wide gap geometry as sketched in Figure 5b and rotated it in a toluene environment for 24 hours at a steady angular velocity of $\Omega = 100$ rad/s. The Taylor-Couette geometry shown in Figure 5b ($D = 28$ mm and $D_{out} = 68.6$ mm) leads to a high-Reynolds number shear flow ($Re \approx 44000$). The torque measured ($\Gamma \approx 225$ μ N.m) during the experiment allows us to estimate the wall shear stress ($\sigma_w \approx 4$ Pa) much larger than the range of expected pipe wall shear stress in common light crude operations (30-500 mPa).

Over the course of the experiment, the rotor was removed from the toluene bath periodically and the contact angles of both water and toluene were measured to evaluate the loss of lubricant. Figure 5d shows the resulting measurements. For the less viscous Krytox, the receding contact angle of toluene droplets started to decline after 4 hours followed by changes in the advancing and receding contact angles of water after 6 hours. Both contact angles reached steady-state values after 8 hours and then remained constant until the end of the experiment. This indicates that the top portion of the lubricant was progressively removed with time under shear, exposing the underlying Teflon surface. In fact, the contact angle of toluene reverted to that on the underlying superhydrophobic surface (SHP, in the absence of lubricant). However, in the case of the more viscous Krytox oil, the contact angles of both toluene and water droplets remained significantly more stable throughout the experiment demonstrating that the use of a higher viscosity lubricant leads to improved dynamic stability under a strong shear flow.

While dynamic stability is known to be a possible limitation for application of LIS (39,40), these experiments show that increasing the viscosity of the lubricant can lead to extended metastability for intermittent applications. Conversely, impregnation with low viscosity oil can promote self-healing properties in an LIS by enhancing capillary wicking through the porous substrate, provided a reservoir of lubricant is provided at regular intervals.

Figure 5: Dynamic stability of an aluminum/Krytox LIS immersed in toluene under exposure to a steady shear stress. **(a)** sequence of steps in the aluminum texturing, functionalization and impregnation process. **(b)** Schematic of the wide-gap Taylor-Couette setup used to probe the dynamic stability of the lubricant under turbulent flow operations. A rotor of diameter $D = 28$ mm rotates at an angular velocity $\Omega = 100$ rad/s within a cylindrical stator of diameter $D_{out} = 68.6$ mm. **(c)** Pictures of an aluminum rotor that was textured and impregnated with Krytox 1506 (top). SEM images of the rotor showing the microtexture at progressive levels of magnification (bottom). **(d)** Contact angle of water (blue, cyan) droplets and toluene droplets (red, orange) measured on the rotor after exposure to a turbulent shear flow in a toluene environment as a function of time elapsed for two different viscosities of the lubricant: 62 cSt and 1535 cSt respectively at 20°C. The contact angles of water and toluene droplets in air on a dry (non-lubricant impregnated) superhydrophobic surface (SHP) with the same surface texture and functionalization are shown for reference as the rightmost bars in the plot.

In conclusion, we have designed and characterized a lubricant impregnated and surface-textured superhydrophobic surface system that enables prevention of the adsorption of asphaltenes on aluminum surfaces. The chosen lubricant was demonstrated to remain stably impregnated within the texture provided the substrate is provided with sufficient roughness to satisfy the thermodynamic stability criterion. We also demonstrated the lack of interfacial activity of asphaltenes at the lubricant-toluene interface, both on the short timescale of diffusion as well as on longer timescales. Even after 3 weeks of immersion in an asphaltene solution, the interface of the lubricant-impregnated surface (LIS) was asphaltene-free within the detection limit of x-ray photoelectron spectroscopy. While this study was conducted in a model system of asphaltenes dispersed in toluene, we expect our results to remain valid even in the case of more complex solutions composed of other organic and aqueous solvents. Finally, we demonstrated a proof-of-concept approach enabling the scalable production of asphaltene-phobic surfaces from typical aluminum substrates which remain stable even when exposed for extended durations to the range of wall shear stresses relevant to turbulent flows encountered in pipelining operations. This composite material system can prevent the adsorption of asphaltenes without the use of bulk chemical additives and requiring minimal use of lubricant (sufficient to only the hierarchically-textured surface of the solid substrate).

Methods

Asphaltenes – The asphaltenes used in this study were provided by ExxonMobil. They were extracted from Cold Lake Vacuum Residue by dissolution in toluene and precipitation in n-heptane (C7-Asphaltenes). Their elemental composition is reported in Table 1 below.

Element	Unit	Value
Carbon	[wt%]	80.30
Hydrogen	[wt%]	7.58
Nitrogen	[wt%]	1.33
Sulfur	[wt%]	8.12
Oxygen	[wt%]	1.34

Table 1: Elemental composition of the asphaltenes used in this study. Only elements with >1 wt% are shown.

Krytox – Krytox 1506 and Krytox GPL107 commercial oils were obtained from Chemours and used ‘as is’ as impregnating lubricants. While their exact composition is proprietary, the primary chemistry is based around perfluoro-polyethylene (PTFE). Krytox was chosen as a model lubricant in this study for its lack of chemical interaction with water and organic solvents and its low surface tension.

Aluminum surface preparation – Polished aluminum 6061 coupons were obtained from McMaster-Carr and cut to a size of 1” x 1” with a shear. The surfaces were then thoroughly cleaned to remove the processing oils by manual cleaning with industrial detergent followed by sonication for 15 minutes in ethanol and 15 minutes in water. Finally, the coupons were rinsed with acetone, isopropyl alcohol and water. The polished samples were then used as is while the textured samples were further treated by etching and chemical functionalization (see *Rheometer rotor etching and impregnation* below for the procedure).

Silicon-based Liquid Impregnated Surface (LIS) preparation – Micro-patterned surfaces were prepared from silicon wafers (University Wafers) using photolithography to create a pattern of square posts of side length 10 μ m with a post spacing varied from 5 to 50 μ m. Reactive-ion etching following the Bosch process was used to etch the posts into the silicon to a depth of 10 μ m. The surfaces were then cleaned, activated in an oxygen plasma and functionalized with 1H,1H,2H,2H perfluorooctylsilane (Sigma Aldrich) in vapor phase for 4 hours. The surfaces

were then dip-coated in the lubricant, Krytox, and withdrawn at a slow speed such that the capillary number $Ca = \mu v / \gamma \ll 1$ to ensure no excess lubricant was withdrawn during the coating process. These surfaces were then used as is.

Contact angle measurements – Contact angles were measured with a Ramé-Hart (500-F1) goniometer with a 30Ga disposable dispensing needle. The advancing and receding angle measurements were made by injecting and withdrawing liquid from a droplet formed on the surface at a rate low enough to ensure a quasi-static contact angle was obtained. The angles reported here are the average of a minimum of at least three measurements at different positions on the sample. Error bars represent the standard deviation of the measurement which was below $\pm 3^\circ$ for almost all measurements.

Interfacial tension measurements – The water-toluene and Krytox-toluene interfacial tension measurements were obtained with a Ramé-Hart (500-F1) goniometer using the pendant drop method by suspending a drop of water / Krytox in a bath of toluene containing asphaltenes. The shape of the drop was evaluated and used to compute the interfacial tension every 0.5 seconds.

X-ray spectroscopy (XPS) measurements – XPS measurements of silicon and LIS samples were made using a Thermo-Scientific K-Alpha XPS system. Each surface was probed in 3 different locations in survey mode and then in high-resolution sulfur S 2p mode. The spectra shown in Figure 4 are representative of the results obtained.

Rheometer rotor etching and impregnation – A liquid impregnated rheometer rotor was custom built from Aluminum 6061. The aluminum surface was textured with a combination of acid etching in HCl (2.5M) for 15 minutes and boiling in deionized water for 20 minutes. The resulting surface exhibited a roughness on the order of $10\mu\text{m}$. The rotor was then functionalized, first with 1H,1H,2H,2H perfluoro-octylsilane and then with Teflon (2% in FC-70) resulting in a high contact angle in water and low roll-off angle. Finally, the rotor was immersed in Krytox and again withdrawn at low capillary number to ensure a minimal equilibrium lubricant thickness was achieved.

Shear stress sensitivity measurements – A TA Instruments AR-G2 rheometer was used with a Taylor-Couette cell of outer diameter 68.6mm, rotor diameter 28mm and rotor length 42mm. The cell was filled with toluene and the textured rotor was spun at $\Omega = 100$ rad/s for 2 hours at a time before being withdrawn for contact angle measurements.

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Supplementary Information

Supplementary movies are available online, showing a drop of asphaltene solution in toluene deposited on one of three substrates at an angle: polished aluminum (Movie S1), a liquid impregnated aluminum surface (Movie S2), and a porous aluminum surface (Movie S3).

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