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Publisher *Taylor & Francis*

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The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

The Implications of Surface Energy in Ice Adhesion

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To cite this Article Itagaki, K.(1983) 'The Implications of Surface Energy in Ice Adhesion', *The Journal of Adhesion*, 16: 1, 41 – 48

To link to this Article: DOI: 10.1080/00218468308074903

URL: <http://dx.doi.org/10.1080/00218468308074903>

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NOTE

The Implications of Surface Energy in Ice Adhesion

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(Received June 29, 1981; in final form February 10, 1983)

A simple experiment indicates that the effect of the surface energy of a substrate can be detected through a thin grease layer by spreading water drops. The effect of the surface energy on the adhesive strength of ice can be described qualitatively based on this fact with the use of a schematic diagram.

Hydrophobic materials and coatings have long been considered effective ice removal agents, and an extensive search has been conducted in the hope of finding a "miracle coating" that would allow effortless ice removal. Bascom *et al.*¹ performed a series of carefully prepared experiments, and found no clear correlation between the contact angle of water and the adhesive strength of ice, despite the generally accepted notion that adhesion of ice is weaker on a hydrophobic surface. The observations reported here may shed some light on the mechanism of bond weakening by hydrophobic coating and the contributions of various parameters to the adhesive strength of ice.

A circular area on a glass plate was treated with silane (SiH_4) vapor to make it hydrophobic. The silane-treated area was outlined on the back side of the glass. Water drops subsequently placed inside the circle assumed hemispherical shapes, while others placed outside it became

Presented at the Annual Meeting of The Adhesion Society, Savannah, GA, U.S.A., February 22-25, 1981.

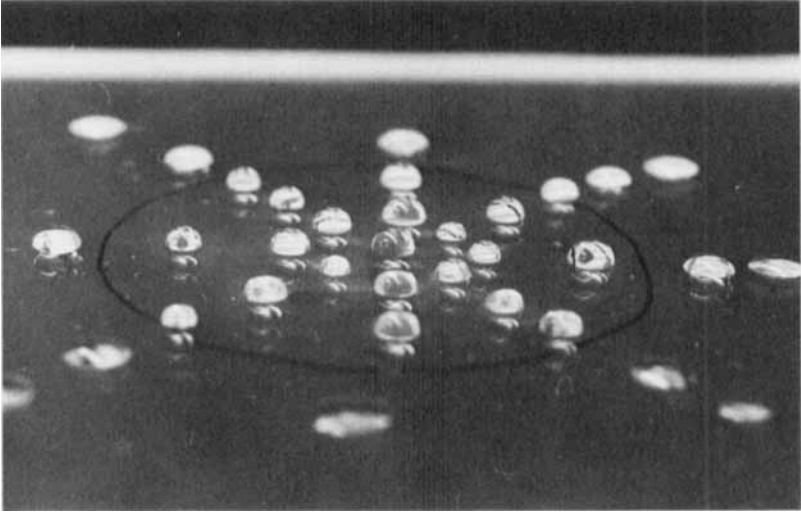


FIGURE 1 The rounded tops of the water drops inside the circle show that the silane-treated glass surface has a lower surface energy than the untreated area outside the circle.

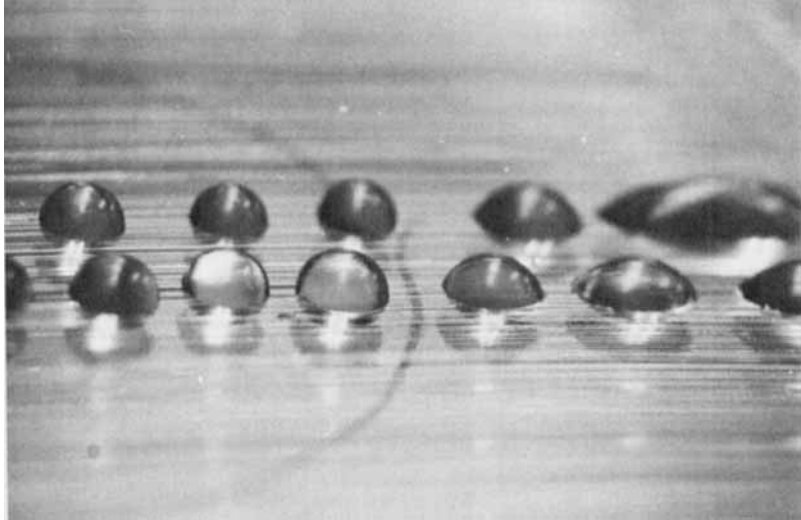


FIGURE 2 The same silane-treated glass plate shown in Figure 1 coated with silicone grease. Note that the drops outside the circle are still slightly flatter than those inside.

flatter and more irregular (Figure 1). The same glass plate was later entirely coated with about a 5- to 10- μm -thick layer of grease. Water drops about 3 mm in diameter were then placed in a regular array on the plate. Figure 2 shows the drops 3 minutes after placement. Drops placed outside of the circle became somewhat flatter while the drops placed in the silane-treated area remained hemispherical. Three greases—Dow Corning High Vacuum, Primer Industrial Corporation Rotorium Multi-Purpose Blue Grease 35342, and Cheseborough Pond Inc. Vaseline—were tested. All gave similar results.

Ring-shaped traces left on the grease layer after the drops were shaken off from the glass are shown in Figure 3. Sharp, distinct rings were left in the silane-treated area. But in the untreated area, where the grease layer had been removed by the drops and excess grease accumulated towards the centers of the rings, less distinct traces were left.

Apparently, the edges of water drops can attack and penetrate a grease layer through the surface tension effect, until they reach the substrate surface. Since interfacial tension between grease and water γ_{gw} is smaller than water/air interfacial tension γ_{wa} the grease tends to spread out over the water drop. However, the supply of grease available to the drop

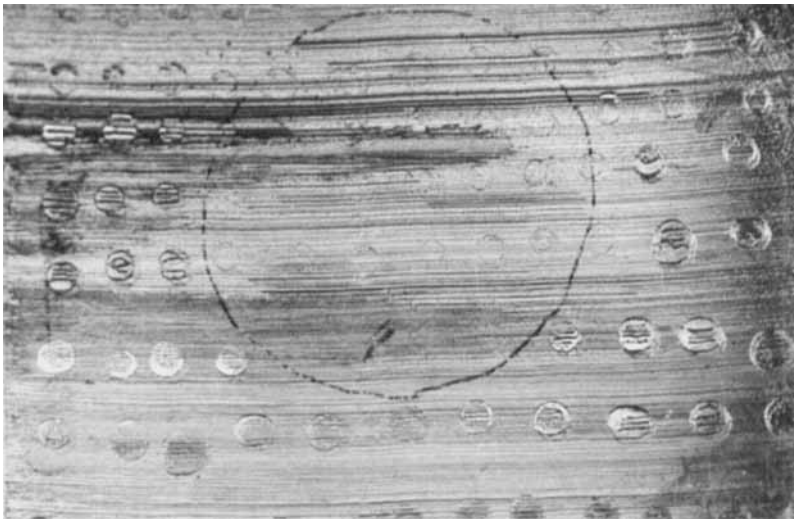


FIGURE 3 Traces left after water drops were shaken off the plate. Note the well-defined ring-shaped traces inside the circle in contrast to the wide grease-free areas observable outside the circle.

surface is limited to the grease layer near the edge of the drop. As the grease spreads over the drop the grease layer near the edge of the drop is depleted until the edge of the drop makes "real" contact with the glass surface. Detailed discussion of the observation of this process will be given elsewhere. Additional pressure exerted by the weight of the drop could accelerate the process but it is not the primary driving force since similar phenomena have been observed with the drop in the inverted position. If the interfacial tension between the substrate and the grease γ_{sg} is lower than the water/substrate interfacial tension γ_{sw} , as it was on the silane-treated surface, the left-hand side of the Young and Dupré equation

$$\gamma_{sg} - \gamma_{sw} = \gamma_{gw} \cos \theta \quad (1)$$

becomes negative, making the contact angle θ over 90° , as shown in Figure 4a. Thus no more spreading occurs. When the surface energy of the substrate is high the contact angle becomes smaller and the water drops spread, as shown in Figure 4b, until equilibrium force is established by Eq. (1).

One interesting finding is that the grease layer was displaced at the centers as well as at the edges of the water drops. Figure 5a shows the

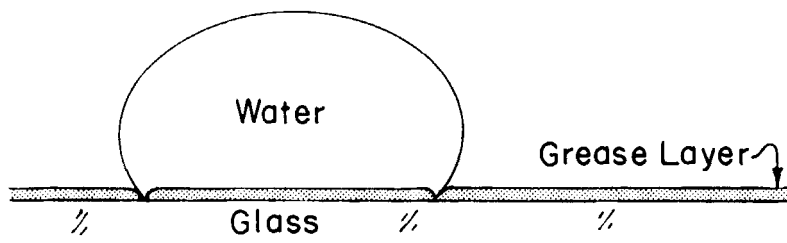


FIGURE 4a Water drop on grease-coated, low-energy surface keeps its shape.

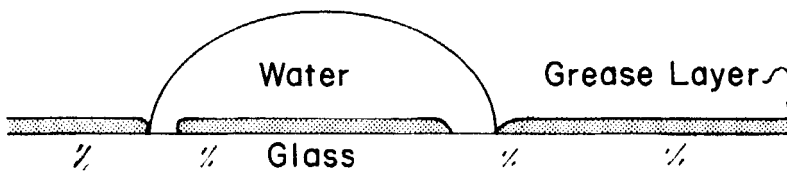


FIGURE 4b Water drop spreads by displacing grease layer on high-energy surface.

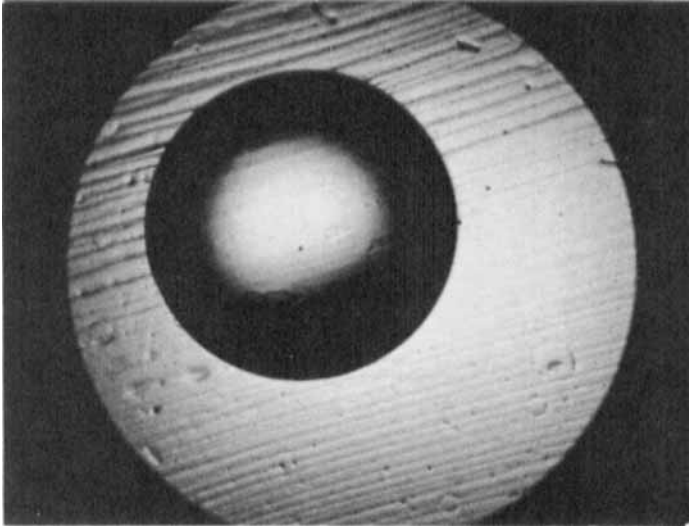


FIGURE 5a Grease layer under drop starting to be displaced.

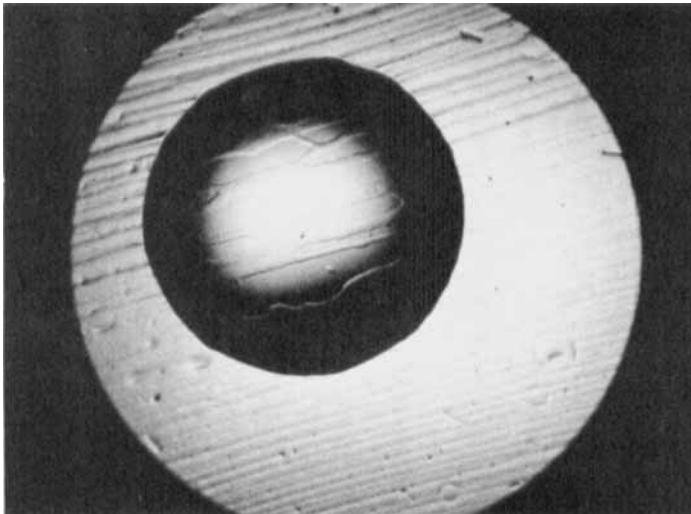


FIGURE 5b A considerable portion of the grease removed.

initial stage of grease removal and Figure 5b shows the final stage. The appearance of the plate indicates that a direct interaction occurred

through the thinner part of the grease layer caused by the curvature due to variation in the thickness.

When some reasonable assumptions are combined with these findings, the rather complex feature of ice adhesion seems explainable. The assumptions are:

- 1) Water can penetrate an oil or grease layer before it freezes.
- 2) An oil or grease layer usually exists on a substrate unless its surface has been very carefully cleaned.
- 3) The adhesive strength of the frozen bond is dependent on the "real" contact area.

When a substrate is hydrophobic the actual contact of a drop of water with its surface is limited to the edge of the drop. "Real" contact area A_r , as shown schematically in Figure 6, between ice and substrate is limited to the small area around the edge of the drop when the drop is frozen. Area A_g makes indirect contact through the grease layer. Under a static load most of the force F is supported by the "real" contact area, since the grease layer could produce resistance force by viscous flow only. The stress σ_r within the "real" contact area is therefore $\sigma_r = F/A_r$, which can be much higher than the stresses within bulk ice $\sigma_i = F/A_i$ or the substrate $\sigma_s = F/A_s$ when the "real" contact area is small.

We do not expect that the strength of the ice in the "real" contact area is much greater than the strength of bulk ice, and the strength

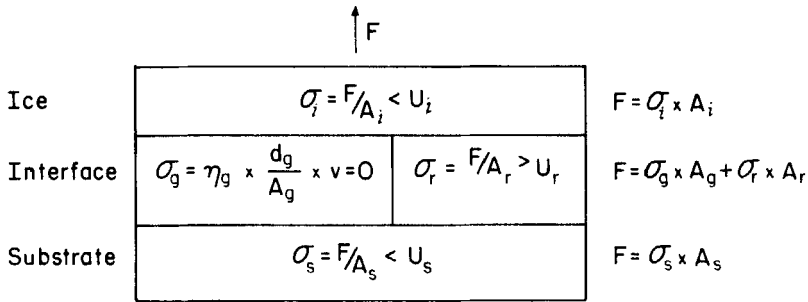


FIGURE 6 Stress levels of ice, interface and substrate zones are schematically indicated. Stress within the ice and substrate zones is lower than the ultimate strengths U_i and U_s , respectively, since they are uniformly distributed over the cross-sectional areas A_i and A_s . Since the grease layer offers no resistance without motion, all force has to be supported by the real contact area A_r , making the stress higher than the ultimate strength of the real contact area.

of the substrate is usually much higher than the strength of the ice. Therefore the main factor contributing to the overall system is the "real" contact area A_r , which would be a complex function of many elements.

The area of contact A_r may grow to the full drop size when the substrate is hydrophilic and the time before the drop freezes (rest time) is sufficiently long. The adhesive strength when the drop is frozen will, therefore, become higher as the surface energy of the substrate becomes higher, simply because A_r is larger. This growth rate of A_r is controlled by many factors, such as the surface energy of the substrate, the thickness and viscosity of the oil/grease, the size of the drop, etc.

The longer the rest time, the larger the area of "real" contact will be until a complete balance of force between the water drop and the substrate surface is established, resulting in higher adhesive forces as the unfrozen state lasts longer.

The increase in adhesive strength by the rest time, observed by Baker *et al.*², supports this notion. Table 1 indicates the conceivable effects of various properties on the adhesive strength and its rate of increase. The effect of temperature during the rest time may appear through the interface energies and the viscosity of the grease/oil. Although other factors such as test temperature, surface roughness, and elastic constants of the substrate should affect the adhesive strength, these factors should be discussed elsewhere since they are not directly related to the present topic of surface energy.

TABLE I

Conceivable effects of various properties on the rate of strengthening and the final adhesive strength.

Increase in	Rate of strengthening	Final adhesive strength
Interface energy between:		
substrate and water	faster	stronger
substrate and oil/grease	slower	weaker
water and oil/grease	faster	stronger
Viscosity of oil/grease	slower	unchanged
Rest time ^a	slower	stronger
Thickness of oil/grease ^b	faster at start	weaker

^a Discussed in Ref. 2.

^b Experiments indicated that if the grease is thicker than about 10 μm the edge of the water drop cannot penetrate through the grease layer.

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2. H. R. Baker, W. D. Bascom and C. R. Singleterry, *J. Colloid Sci.* **17**, 477–491 (1962).