

Ice Adhesion and Abhesion: A Survey

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Understanding adhesion is essential for solving problems of ice adhering to aircraft, runways, ships, and all kinds of solid surfaces. These problems have not been solved satisfactorily in many cases; frequently mechanical devices rather than principles of interfacial physical chemistry have to be used for minimizing ice adhesion. This paper discusses some of the fundamental parameters in adhesion, recent work on ice adhesion, application of fundamental principles of interfacial physical chemistry, effects of mechanical, rheological, and morphological properties of ice and its substrates, transition layer in the ice-air or ice-solid interfaces, and significance of some recent developments in interfacial physical chemistry for the problem of ice adhesion.

Ice is one of the best adhesives in nature as people in cold regions are well aware. This property of solid water substance is of great fundamental interest for surface science and has been studied quite thoroughly under well-defined conditions in the laboratory. Many of the general fundamental principles connected with adhesive properties of materials on a macroscopic and molecular scale are apparent in the case of ice. However, there are also many abnormal features peculiar to this substance, which have to be considered in detail in order to understand ice adhesion fully.

The problems of ice adhesion—or ice abhesion, which is a more apt term in this connection—encountered in practice are quite different in nature from those studied in the laboratory. Still, the principles of ice adhesion can be discerned in many practical problems, although they are often nearly completely obscured and are not of main significance.

It is quite feasible to choose satisfactory substrates of sufficiently hydrophobic nature to diminish ice adhesion to an acceptable extent, but the main problem here is that such substrates become contaminated after a few adhesions and become useless. The same is true for special interfacial films (e. g., monolayers); these not only deteriorate but are removed on repeated adhesion. Thus, the problem here is to find not so much a suitable hydrophobic surface, which can be achieved fairly easily, but a surface that renews itself during use and that remains efficient. Thus icing of aircraft, ships, vehicles, instruments, and windows is the problem in ice adhesion or abhesion, and it is here that satisfactory long-lasting solutions have to be found.

Thus, there are 2 large areas in ice adhesion: the fundamental area, where the principles of surface science can be directly utilized to a large extent, and the practical area, which in the past was almost completely divorced from the fundamental aspects and which presents additional problems of a special type. Recently progress has been made by Zisman's discovery of the critical surface tension and by using lubricants and self-healing films, which may well further advance the solution of the practical ice abhesion problems (1, 2, 3).

A brief survey of fundamental aspects of ice adhesion and principles underlying the practice of ice abhesion is presented here. First, a short summary of general theoretical principles of adhesion is given to place ice adhesion in the general context of the field of adhesion.

SOME FUNDAMENTAL CONCEPTS

Thomas Young introduced the contact angle θ in 1805 (4, 5). Complete wetting of a surface takes place if $\theta = 0$ or $\cos \theta = 1$; a liquid cannot spread on a surface if $\theta > 0$.

The contact angle is always smaller than 180 deg; thus any liquid wets any solid to a certain extent. θ is independent of drop volume, if the surface is ideally smooth. θ is an inverse, while $\cos \theta$ is a direct measure of wettability (Fig. 1). Although there is not always a unique relation between adhesive strength and θ , it can serve as a useful guide in adhesion work. Surface roughness, r , can have an appreciable effect on the contact angle. The ratio of the geometrical area to the apparent area (i. e., envelope covering all peaks) is given by (6)

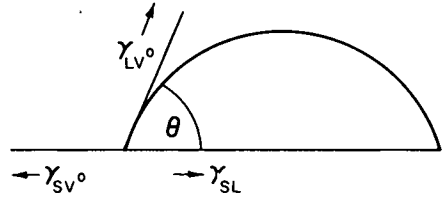


Figure 1. Contact angle between a liquid and a solid substrate (89).

$$r = \frac{\cos \theta'}{\cos \theta} \quad (1)$$

Here θ' is the contact angle of the rough surface. Equation 1 implies that for $\theta < 90$ deg, $\theta' < \theta$, and for $\theta > 90$ deg, $\theta' > \theta$ respectively.

The equilibrium for all surface tensions acting at a phase boundary of a drop is given by Young's equation

$$\gamma_{SV}^0 - \gamma_{SL} = \gamma_{LV}^0 \cos \theta \quad (2)$$

where the subscripts SV^0 and LV^0 refer to the solid and liquid tensions respectively in equilibrium with the vapor of the liquid; SL signifies the solid-liquid interfacial tension.

The reversible work of adhesion, W_A per unit surface area, is given for 2 liquids or 1 liquid and 1 solid respectively by (7)

$$W_A = \gamma_{S^0} + \gamma_{LV}^0 - \gamma_{SL} \quad (3)$$

S^0 refers to the solid in vacuum. If, however, a monolayer of the liquid is left on the solid surface on removal of the liquid, the reversible work of adhesion W_A^* is

$$W_A^* = \gamma_{SV}^0 + \gamma_{LV}^0 - \gamma_{SL} \quad (4)$$

Hence, combination of Eqs. 2 and 4 gives,

$$W_A^* = \gamma_{LV}^0 (1 + \cos \theta) \quad (5)$$

or

$$W_A = (\gamma_{S^0} - \gamma_{SV}^0) + \gamma_{LV}^0 (1 + \cos \theta) \quad (6)$$

The first term in Eq. 6 can be written

$$f_{SV}^0 = W_A - W_A^* \quad (7)$$

f_{SV}^0 is always positive. In general

$$W_A > \gamma_{LV}^0 (1 + \cos \theta) \quad (8)$$

or

$$W_A > W_A^* \quad (9)$$

If S , the initial spreading coefficient, is defined as

$$S = \gamma_{S^{\circ}} - (\gamma_{LV^{\circ}} + \gamma_{SL}) \quad (10)$$

then for organic liquids spreading on organic surfaces, γ_{SL} is negligible compared with $\gamma_{LV^{\circ}}$; hence,

$$S = \gamma_{S^{\circ}} - \gamma_{LV^{\circ}} \quad (10a)$$

For $S > 0$, spreading occurs; if $S < 0$, spreading is not possible. Zisman (1) identifies these as high and low energy surfaces respectively. The former are surfaces of solids having large specific free surface energies ($>100 \text{ erg/cm}^2$, e.g., metals, metal oxides, nitrides, silica, and diamond; these range from 500 to 5,000 erg/cm^2). The latter belong to soft organic solids and most polymers ($<100 \text{ erg/cm}^2$). Thus liquids with low energy surfaces can easily spread on solids with high energy surfaces.

Zisman found interesting and very important relationships for liquids of a homologous series (e.g., alkanes) on a particular solid (e.g., polytetrafluoroethylene or polyethylene). $\cos \theta$ is directly proportional to the surface free energies of the liquid

$$\cos \theta = a - b \gamma_{LV^{\circ}} \quad (11)$$

where a and b are constants characteristic of the system (e.g., alkane plus polymer). If $\cos \theta = 1$ or $\theta = 0$, then $\gamma_{LV^{\circ}} = \gamma_C$ and Eq. 11 becomes

$$\cos \theta = 1 + b (\gamma_C - \gamma_{LV^{\circ}}) \quad (12)$$

γ_C is the important term designated as critical surface tension (CST). Equation 12 shows that only liquids that have a free surface energy, $\gamma_{LV^{\circ}} < \gamma_C$, can spread on the respective solid. Equation 12 is of great significance for the selection of hydrophobic

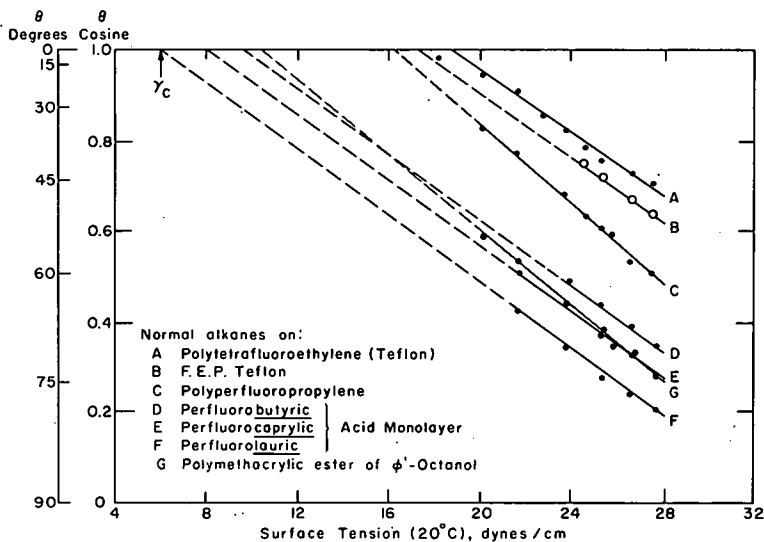


Figure 2. Contact angles formed by a series of n-alkanes on various fluorinated low energy solid surfaces (1).

surfaces. Water cannot spread on solid surfaces that have a γ_C value smaller than the surface tension of water. The lowest γ_C value known today is given by surfaces consisting of close packed $-\text{CF}_3$ groups (6 dyne/cm). A consequence of Eq. 12 is the following relationship:

$$W_A^* = (2 + b \gamma_C) \gamma_{LV}^0 - b \gamma_{LV}^0{}^2 \quad (13)$$

Equation 13 represents the equation of a parabola and has been verified repeatedly (Fig. 2).

Some brief remarks may be made about the forces acting near an interface on an atomic or molecular scale. One has to deal with interfacial and cohesive forces and with materials under stress. There are quite a number of different adhesion theories based partly on the type of molecular or macroscopic forces involved; each has some justification under definite conditions. The mechanical theory ascribes adhesion to the flow of the adhesive into pores of the substrate, where solidification takes place. The adhesive is mechanically anchored to the substrate. The molecular aspect of the mechanical theory is in essence dealt with in the diffusion theory; polymer molecules diffuse to the interface and are absorbed. This theory is important for flexible linear polymers as adhesives, preferably mutually soluble. The chemical or molecular theory is important in dealing with forces at an interface. These forces can be of short- or long-range molecular interaction. Primary or short-range forces are due to highly directional covalent bonds (rupture energy 40 to 100 kg-cal/mole, e.g., diamond, cross-linked polymers). Another type of force is ionic (electrostatic force). This is less directional than the covalent bond. Metallic bonds are due to nonlocalized mobile electrons; these bonds are of similar strength as covalent bonds. Image forces are produced in metals when a permanent dipole approaches. Hydrogen bonds are important in many cases. They are of longer range than most polar forces or van der Waals forces (dispersion forces about 10 kg-cal/mole). Permanent dipoles are somewhat stronger than van der Waals (dispersion) forces. Oriented dipoles exert an influence over many atomic layers. The secondary or van der Waals forces are very important and always present; they are also referred to as dispersion forces and are due to temporary dipoles of relatively short range (about 3 Å) and of 2 to 4 kg-cal/mole strength. They account for 75 to 100 percent of molecular cohesion in most cases. The magnitude of these forces is proportional to the number of electrons in a chemical group. Thus, the dispersion forces are all similar for the following chemical groups: NH_3 , OH , $-\text{CH}$, $-\text{NH}$, $-\text{O}-$, and $-\text{CH}_3$. These forces decrease with the sixth power of the distance. The interaction of different groups 1 and 2 is given by the geometric mean between 1 and 1 and 2 and 2; i.e.,

$$D_{12} \sim \sqrt{D_{11} D_{22}} \quad (14)$$

Fowkes developed a theoretical approach to the problem of surface energies of solids (8, 9, 10, 11, 12). It was assumed that the contribution of dispersion forces to free surface energies is additive. The attraction between 2 unlike compounds per unit area is given by $(\gamma_1^d \gamma_2^d)^{1/2}$, where d indicates the contribution of dispersion forces. Hence, if these forces contribute the major part to interfacial free energy, a relationship should hold as follows:

$$\gamma_{12} - \gamma_1 - \gamma_2 = -2(\gamma_1^d \gamma_2^d)^{1/2} \quad (15)$$

This equation is obeyed quite frequently, especially if one of the compounds is nonpolar or nonhydrogen bonding. In this context, it means that in such a case only dispersion forces are operative. For example, only dispersion forces are assumed to be operative in the paraffin-water system; γ_{12} , γ_1 , and γ_2 are known for this system. Hence, one has, according to Young's equation (here $\gamma_S = \gamma_1$, $\gamma_L = \gamma_2$, and $\gamma_L > \gamma_S$),

$$\gamma_L (1 + \cos \theta) = 2 \left(\gamma_L^d \gamma_S^d \right)^{1/2} \quad (16)$$

or

$$\cos \theta = 2 \left(\gamma_S^d \right)^{1/2} \frac{\left(\gamma_L^d \right)^{1/2}}{\gamma_L} - 1$$

Cos θ plotted versus $\left(\gamma_L^d \right)^{1/2} / \gamma_L$ for a series of nonpolar liquids gives γ_S^d by extrapolation to $\theta = 0$. The slope of the straight line is $2 \left(\gamma_S^d \right)^{1/2}$ and its origin $\cos \theta = -1$. This is somewhat similar to Zisman's γ_C (CST), if only dispersion forces are involved. (γ_C : F < H < Cl < O < N.)

Fowkes (8, 9) refined this treatment recently as far as the summation of the forces is concerned. This summation was carried out in the past according to Polanyi and London (13). Their treatment caused quite a substantial error in the result. Crowell (14) used a model in which the dispersion energy involving molecules is "smeared out" uniformly over planes parallel to the surface. The calculation is relatively simple and yields more accurate results.

ICE ADHESION (FUNDAMENTAL STUDIES)

Fundamental investigations concerning ice adhesion are not too numerous, although some of them are very detailed. The theoretical principles of adhesion are often obscured by imperfections in the ice, which decrease the theoretically expected tensile and adhesive strengths. However, this is a general phenomenon of materials; their experimental strength is only a small percentage of that theoretically possible. Forces in the interface on a molecular scale not only play a role in general adhesion and in particular ice adhesion but also are often overshadowed by the plastic-elastic and thermal properties of ice and those of the substrate. Severe stress concentrations can be set up partly conditioned by the geometry of a particular joint; adsorption of gases can interfere. Thermal expansion coefficients and thermal conductance of the materials are also of significance.

Thus adhesion, and in particular adhesion of ice, deals with a very complex situation, which frequently makes it quite difficult to recognize the underlying fundamental principles. In particular ice, as will be seen later, has very peculiar interfacial properties, which influence its adhesive behavior and make its interfacial properties of special importance to surface science. A number of workers have attempted to investigate the adhesive properties of ice from a fundamental point of view by systematically collecting experimental data under rigidly standardized conditions and attempting to interpret them with the help of known principles or by developing new hypotheses and theories. The types of experiments usually performed are tensile and shear tests; the latter are sometimes performed by applying a torque. The conditions are systematically altered, as will become apparent later, in the hope of ascertaining generally valid relationships. Working with ice presents quite formidable experimental problems, and establishing really satisfactory techniques is not an easy task. Strength measurements have always to be performed in large numbers. The results are statistical in nature and have to be evaluated on this basis. Thus, all final results are average values of a more or less wide distribution of individual values. In comparing work of various authors, one has to carefully ascertain the degree to which such results have been obtained by comparable experimental methods and what their limits of error are. Even slight variations in the preparation of ice may produce marked differences in experimental results (e. g., the presence of gas or air in ice is very significant, and the technique of preparing an adhesive joint is important for whether the air is driven away from the interface or not). It is quite surprising that various workers nevertheless obtain experimental results that show similar regularities.

The most important and extensive work is contained in publications by Berghausen et al. (15, 16, 17, 18), Bascom et al. (19), Ford and Nichols (22, 23), Jellinek, (24, 25, 26), Landy and Freiberger (27, 28), and Raraty and Tabor (29, 30), and, to a

lesser extent, Sellario (31), Loughborough (32), Brunner (33), and Hunsacker et al. (34). Only Berghausen et al. and Jellinek among these authors performed tensile experiments, whereas the others carried out shear (or torque) tests only.

Tensile Experiments

For details of apparatus, reference should be made to the original papers. Berghausen et al. constructed a very elaborate tensile strength apparatus, where ice could be sandwiched between metal cylinders, which formed the substrate. These metal pieces could be directly refrigerated in situ, and the gap width could be adjusted from about 5×10^{-3} cm to larger widths. Water was double distilled and had a specific conductivity of not more than 2×10^{-6} mhos. The lowest temperature that could be reached with this apparatus was -35 C, and the rate of freezing could be varied. Usually the water was saturated with air or helium, but freezing was so arranged that gas was driven away from the interface and accumulated as bubbles in the middle of the ice specimen. The rate of force application could also be varied from 1.4 to 22.7 kg/sec. The technique was rigidly standardized. Berghausen's most important results from tensile tests are as follows:

1. Only cohesive breaks were observed at all gap widths with metals as substrates. Ice prepared from helium-saturated water showed smoother breaks than ice prepared from air-saturated water. Helium-saturated ice showed tensile strength (35 kg/cm^2) higher than that of air-saturated ice (stainless steel-ice); it was independent of gap width and temperature (-5 to -15 C, area 7 to 2 cm^2 , and gap width 5×10^{-3} cm to 4.5×10^{-2} cm). With aluminum as substrate, the cohesive strength was again larger in the case of the helium-saturated ice, but here the slopes of the strength versus gap width plot have different values in each case, indicating a common or crossover point near very small gap width for the helium and aerated ice.

2. The tensile strength increases with decreasing ice volume; this is a phenomenon common to all ordinary materials (this was also found for ice by Jellinek, as discussed later). The curve obtained indicates that it may go through a maximum at very small gap widths (volumes); the subsequent decrease in strength at still smaller widths may be due to unfrozen water and to radial stresses in the sandwiched ice. Air bubbles may also be responsible for this maximum. At -15 C, the tensile strength found was 91.4 kg/cm^2 for a volume of $3.26 \times 10^{-3} \text{ cm}^3$, and 21.1 kg/cm^2 for a volume of $6.52 \times 10^{-2} \text{ cm}^3$.

3. Ice in small gap widths indicated a negative temperature coefficient, whereas the trend was in the opposite direction for larger widths.

4. According to these authors, the differences in strength found for aluminum, mild steel, and stainless steel substrates are not due to the different elastic properties of these metals but rather to their different thermal properties. There is always an oxide film on aluminum, which is a good heat insulator; mild steel tends to rust, and this also provides thermal insulation. On the other hand, stainless steel is a good heat conductor. Thus the rate of freezing will differ for each of these metals. It was also observed that, for a given frozen ice volume, the tensile strength increases with decreasing diameters (i. e., with larger gap width). This increase is believed to be due to the slower overall rate of cooling of the wider gaps.

5. Metals covered by monolayers of stearic and perfluorodecanoic acid (hydrophobic surfaces) still gave cohesive breaks. However, when thicker layers were deposited on the substrate surfaces, failure occurred, for instance, in the stearic acid layer. Thus, the cohesive break shifted to the mechanically weaker material. Adhesions were repeated about 12 times by using the same coating. The strength of the first break amounted to 1.9 kg/cm^2 and of the eleventh break, to 35.2 kg/cm^2 ; obviously, the layer was progressively removed by repeated adhesions of the ice (-16 C, gap width 2.54×10^{-2} cm).

6. Tests were also performed with low density polyethylene (2.54×10^{-2} cm in height) having smooth surfaces. The polymer was especially fixed by suitable chemicals to the aluminum substrate. The ice was helium saturated. Adhesive breaks were observed; whether a monolayer was removed with the ice—a cohesive break taking

place—was not investigated. This is true for most investigations. Though adhesive breaks are referred to here, breaks are meant that may have removed a monolayer of one or the other component. Strictly speaking such breaks are also cohesive. At a gap width of 46.23×10^{-3} cm and at -15 C, the adhesive strength found was 21.82 kg/cm²; on extrapolation of the strength values to zero gap, it increased to 44.65 kg/cm². This increase may actually indicate that cohesive breaks are still involved rather than adhesive ones. For a slight increase in diameter (from a diameter of 0.95 cm to one of 1.27 cm), a mixture of adhesive and cohesive breaks is obtained. The tendency for cohesive breaks actually increases for small gap widths.

Jellinek had not so elaborate an arrangement as Berghausen, but conditions could be exactly reproduced and the rate of load application could be varied. The lowest temperature that could be reached was about -45 C. Highly polished stainless steel disks were used. Double distilled water was passed through exchange resin and continuously boiled to remove air. Mounting was rigidly standardized and was performed so that any residual air was driven away from interfaces. Thick layers of ice were prepared with snow-ice. Gap widths were measured with a Starrett gage to 2.5×10^{-4} cm. Tensile strength was measured with a 500 lb Baldwin cell, and the output was traced on a recorder. All breaks were cohesive (though some breaks left part of the substrate surface bare). Most took place near one of the interfaces at an angle of about 20 deg. These breaks were quite jagged. Less frequently, smooth breaks occurred at right angles to the interface. The experimental results can be summarized as follows:

1. Tensile strength increases linearly with stress rate, passes through a maximum, and comes to a plateau corresponding to the bulk tensile strength of ice ($\epsilon \approx 15.8$ kg/cm²). Typical values are given in Table 1. At least 12 tests were carried out at each rate.

$$\bar{S} = C \left[\left(\frac{v\epsilon}{\epsilon v_m - 1} \right) e^{-\epsilon v} + 1 \right] \quad (17)$$

where ϵ is the inverse stress rate, C is a constant, and v_m is the rate of loading at maximum tensile strength. All subsequent experiments were carried out in a range where tensile strength is independent of stress rates and areas (Fig. 3).

2. Similarly, as was found by Berghausen et al., the tensile strength increases rapidly with decreasing ice volume. However, each cross-sectional area gives a separate curve. Logarithmic plots of tensile strength versus volume give parallel straight lines. A single straight line is obtained, including all areas, by plotting $\log [(\bar{S} - C)/A]$ versus $\log V$ over a thousandfold range of volumes. C is a constant, \bar{S} the tensile strength, and A and V area and volume respectively. In the specific case investigated here, the relationship is (Fig. 4)

$$\bar{S} = (2.74AV^{-0.84} + 9.4) \quad (18)$$

3. The theoretical tensile strength value of ice is given by

$$\bar{S} = \frac{2\gamma_i}{d} \quad (19)$$

TABLE 1
TENSILE STRENGTH AS FUNCTION OF STRESS RATE—
 -4.5 C, AREA 3.14 cm², AND HEIGHT 2 cm

Stress Rate, v (kg-cm ² /sec)	Mean Strength, S (kg/cm ²)	Standard Deviation (\pm kg/cm ²)	Standard Error of Mean (\pm kg/cm ²)
0.051	14.7	2.6	0.7
0.110	16.7	2.5	0.7
0.210	17.0	3.9	1.2
0.570	15.6	2.2	0.6
1.100	16.1	2.1	0.8

Here γ_i is the surface free energy of ice, recently determined by Hobbs (35) as $\gamma_i = 109$ erg/cm². If d is taken as 2×10^{-8} cm, a value of $\bar{S} = 10,900$ kg/cm² results. The actual tensile strength of ice is only a small fraction of this value (15.8 kg/cm²). Czysak (36) calculated the cohesive strength of ice by classical and quantum

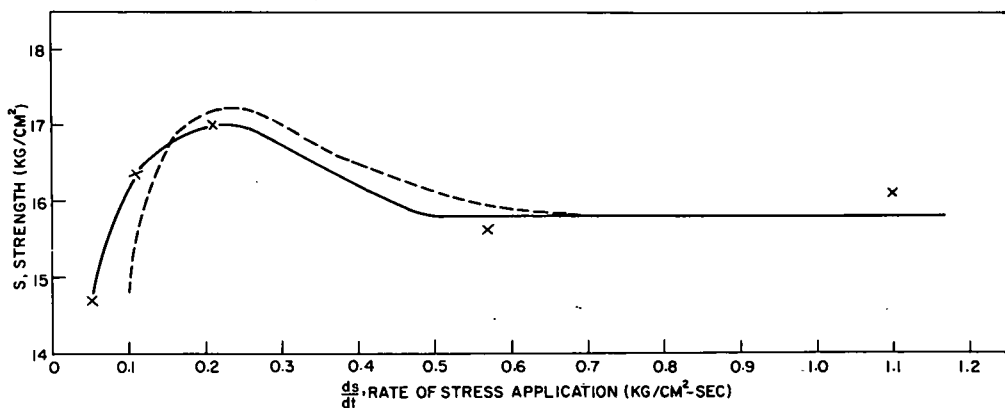


Figure 3. Average tensile strength as a function of rate of stress application for snow-ice cylinders 2 cm in height and 2 cm in diameter (5). Dotted line calculated according to Eq. 17.

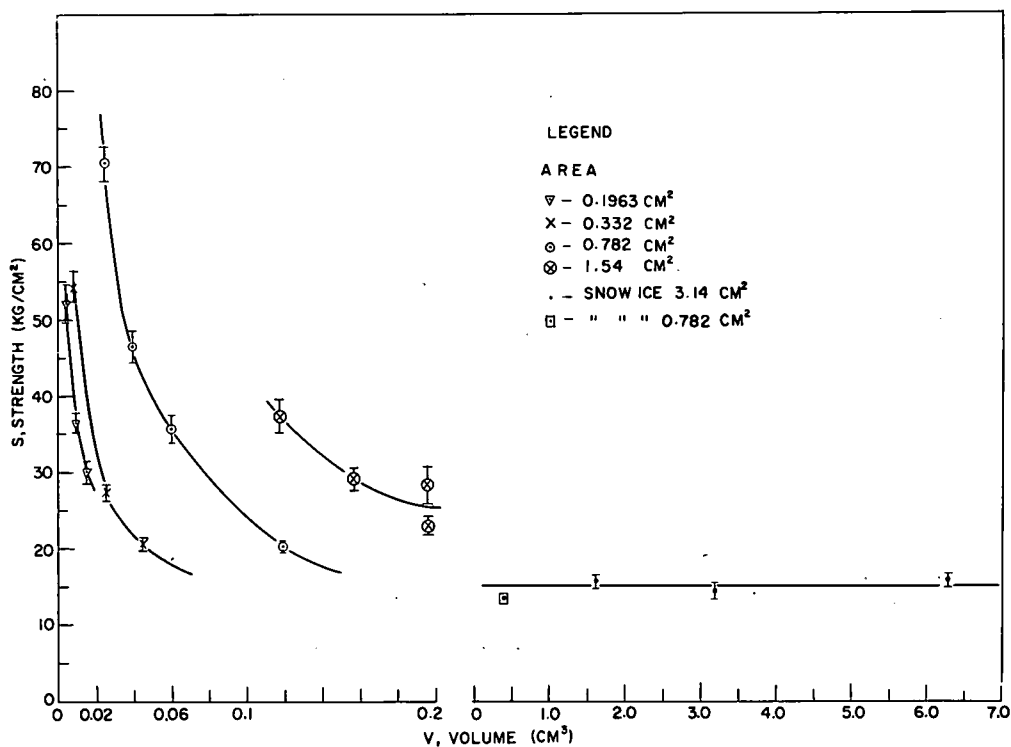


Figure 4. Average tensile strength as a function of ice volume (5, Fig. 7). Each point represents average value of at least 12 tests, and ranges indicated are standard errors of the mean.

mechanical methods, and obtained 6,770 and 13,050 kg/cm² respectively. This discrepancy of experimental and theoretical strength is usually ascribed to imperfections in the substance under consideration and is a general phenomenon. The probability of finding an imperfection decreases with the volume of the substance under test. Jellinek succeeded in deriving this increase with decreasing volume on a statistical basis, obtaining an expression in agreement with experimental data.

$$\bar{S} = k A^{1/\beta} V^{-1/\beta} + C \quad (20)$$

Here k , C , and β are constants; A and V are the cross-sectional area and volume of ice respectively. Equation 20 fits the experimental data except for a small discrepancy believed to be due to stress concentrations influencing the purely statistical aspect of the derivation.

4. There is an indication that tensile strength decreases slightly with decreasing temperature (-11 to -45 C).

5. Experiments with polystyrene and polymethylmethacrylate as substrates were also performed. These polymers were cast sheets and had very smooth surfaces. Mainly adhesive breaks were obtained. The adhesive stress for polystyrene-ice as a function of temperature gave a straight line to -25 C (this was the lowest temperature investigated; the area was 1.54 cm² and the height 0.1 cm). This line is given by

$$\bar{S}_A = -0.173 t^0 + 1.81 \quad (21)$$

6. Cross section and rate of stress application in the range investigated have no effect. A mean adhesive strength of 4.4 kg/cm² (standard deviation ± 2.9 kg/cm² and standard error of mean ± 0.7 kg/cm²) was obtained for the polymethylmethacrylate-ice system (cross-sectional area 0.785 cm², height 0.1 cm, temperature -5 C); 19 adhesive breaks and 4 border-line cases were observed. The adhesive strength for this system is larger than for the polystyrene-ice system. This is understandable because polymethylmethacrylate is a polar compound, whereas polystyrene has only a very small dipole moment. The surfaces of these polymers become cloudy and crazed after 3 tests, and test pieces have to be renewed. Whether a real adhesive break takes place or whether a polymer monolayer or a very thin layer is removed is not known.

In summary, it can be stated that similar relationships, not numerical but in type, are found in the studies of both Berghausen et al. and Jellinek. The increase in tensile strength with decrease in volume is similar in both cases, and so is the area relationship. Only cohesive breaks were found in both studies with metal substrates, whereas polymer layers thicker than a monolayer gave predominantly adhesive breaks. The temperature coefficient with metals as substrate (cohesive breaks) showed a negative trend in both cases. The tensile and adhesive strength values were only small fractions of the corresponding theoretical values, indicating the presence of imperfections in ice.

Shear Tests

Shear tests were carried out by several workers: Bascom et al. (19), Ford and Nichols (22, 23), Loughborough (32), Brunner (33), and Hunsacker et al. (34). Shear apparatus was used in which, in principle, a prism of ice is sheared off a flat surface, the force acting in the ice-substrate interface. Some workers used torque devices such as napkin joints and also centrifugal methods. Some of the results of these workers are considered and compared.

Table 2 gives some comparable test results obtained by Sellario (31) using the torque method and Loughborough using the centrifugal method. Sellario's method gives higher adhesive values than Loughborough's centrifugal apparatus.

Table 3 gives a summary of some of the results of some experiments performed by Brunner.

TABLE 2
ABSOLUTE AND RELATIVE SHEAR STRENGTH OF
METAL-ICE INTERFACES

Metal or Ice	Loughborough		Sellario	
	kg/cm ²	Relative Values ^a	kg/cm ²	Relative Values ^a
Copper	8.72	1.0	22.36	1.0
Steel(iron)	13.01	1.5	26.58	1.2
Aluminum	15.47	1.8	24.68	1.1
Ice (cohesion)	17.58	2.0		

^aRelative values are referred to ice-copper adhesive strength taken as one.

TABLE 3
RESULTS OF EXPERIMENTS BY BRUNNER

Substrate	Percentage of Total Which Gave Adhesive Breaks	Adhesive Strength ^a (kg/cm ²)
Metal	17	9.5
Oxidized metal	39	8.8
Metal as obtained from factory	37	7.2
Ski-lacquer	35	6.3
Mainly consisting of polystyrene	39	5.9
Paraffin	50	4.6
Silicone grease	79	3.1

^aIncludes breaks leaving four-fifths of surface bare.

Raraty and Tabor (29) employed torque, studying the effect of various substrates on adhesive strength. Ice annulus and cylinders were investigated. A paper by Bowden and Tabor (30) is of interest in this connection.

1. The experiments indicated that creep of ice takes place. This creep remained small until a critical torque was reached; the torque was applied in small increments. The primary cause determining failure is strain rate at the interface and not the magnitude of strain. In all subsequent experiments, torque was applied in increments and adhesive strength in kg/cm² was expressed as the torque at failure divided by the area of ice-solid interface being sheared. Air bubbles were formed relatively far away from the interface.

2. Rate of freezing did not affect the adhesive strength, which increased with decreasing height of the cylindrical specimens. This is similar to the observations made on cohesive breaks (tensile).

3. The adhesive strength for cylindrical and annulus specimens decreases linearly with decreasing temperature down to -25 C for cylinders; however, the strength values become constant below about -7 C for annulus specimens and only cohesive breaks take place. Similar results are obtained for ice in the form of an annulus as for complete napkin ring joints. The fracture plane lies at 45 deg to the interface. Above -7 C, the break is ductile and adhesive, and creep and yielding take place in or near the interface. These authors try to explain the tests on the basis of creep as determined by Glen (37) or Jellinek and Brill (38); the agreement is only approximate.

4. The adhesive fracture range for the annulus specimens is appreciably extended to lower temperatures for contaminated surfaces (e.g., stearic acid monolayer, silvered surface, and the like); the slope of the straight line parts increases, but otherwise the type of relationship is preserved for the various covered surfaces.

5. Aluminum gave only cohesive breaks.

6. The range of adhesive fractures is extended for polymers as substrates to about -10 C.

7. Addition of salts decreases the mechanical strength of ice and increases its creep rate.

Ford and Nichols (22, 23) carried out well-controlled shear experiments, most of them at -6 C. The rate of loading was approximately 1.41 kg-cm²/sec. Brass and stainless steel were electrolytically polished. Water was triple distilled and boiled before being applied to the substrate. This procedure was used for thin ice specimens. Bulk shear strength was measured differently; details are given in their paper.

1. Bulk experiments were carried out over a temperature range of -2 to -21 C. The corresponding average shear strengths range from 25.3 to 31.5 kg/cm². There is a slight trend to higher values with decrease in temperature.

2. Cohesional breaks (average strength 43.7 kg/cm²) were obtained with ice-stainless steel (ice height 1.27 cm, -6 C); mixed cohesional-adhesional break (strength

76.6 kg/cm²) occurred with an ice height of 0.1 cm. Apparently the average strength value increases with decreasing height of the ice specimen. Brass, aluminum, and Teflon with ice of 0.1 cm height also gave mixed cohesive-adhesive breaks at -6 C. The strengths were 88.6 and 47.1 kg/cm² respectively. The values agree closely with those of Freiburger and Lacks (39).

3. Lubricated surfaces scarcely show a difference in type of break and magnitude of strength on repeated adhesions from those given by bare surfaces; however, if surface active agents are added, adhesive breaks are obtained. In the case of Teflon it is not necessary to have additives; lubrication is sufficient to obtain adhesive breaks only.

The second part of Ford and Nichols' paper deals with adhesion of ice to bulk polymers, polymer films, lubricated polymers, and lubricated metals at 3 temperatures.

4. Adhesive strength was measured with bare nylon, polyethylene, and Teflon surfaces, and surfaces covered with silicone grease at -1 C. The adhesive strength dropped from a finite value to practically zero, although in the case of Teflon its unlubricated surface already showed zero strength. At -6 C, the drop in strength is very dramatic on lubrication with silicone and petroleum grease (this latter grease contained lithium stearate, basic barium dinonylnaphthalene sulfonate, and 1-phenylnaphthylamine). At -20 C the results are similar; the adhesive strength of the uncovered polymer surface scarcely changes with temperature.

5. Unlubricated polymer films on metal substrates behave differently at -20 C; here the adhesive strength remains finite (about 1.4 to 2.8 kg/cm²).

6. The adhesive strength increases dramatically with the number of adhesions performed with the lubricated bulk polymer. The ease of increase of strength depends on the lubricant; silicone grease (J941-C-5000) lasts many more cycles than other lubricants. The increasing values tend eventually to those of the uncovered polymer, which is independent of the number of adhesions as long as the surface is kept clean (-20 C).

7. Lubricated metal surfaces initially show low adhesive strengths, but not zero (about 0.5 to 1.6 kg/cm²) as is the case with polymers. Here, loss of effectiveness is also observed with repeated adhesions.

Landy and Freiburger (27) studied the adhesion of ice to polymers by carefully performing shear tests. All measurements were carried out at -12.2 ± 1 C.

1. All adhesive tests with Teflon showed a strength of about 17.6 kg/cm² even after repeated adhesions. These were the lowest values found for polymers. Polymethylmethacrylate showed the highest value (87.9 kg/cm²), this value remaining the same after 10 adhesions. The authors could not discover any correlation of the strength values of all the numerous polymers investigated with Zisman's critical surface tension (CST), γ_C , with contact angles, thermal conductivity, thermal expansion, porosity, and dielectric constant. They found some correlation with flexibility of the substrate. However, the extent of correlation is not sufficient to explain the behavior of the polymers completely. There are one or two additional factors of importance in this connection. If polymers of the same thickness having the same type of chemical bonding are grouped together, then it was observed that the ice adhesion in each group increases with the flexural modulus of the polymers. Hence for each such group, the mechanical deformation theory is followed quite satisfactorily.

2. The adhesive strength increased with thickness.

3. The results do not agree well with those of Ford and Nichols (22, 23). This may be due to the history of the polymers and to adhesion technique. Age of the ice-substrate bond also affects the strength somewhat.

4. Ice adhesion was also measured on ice-polymer systems immersed in water. In some cases, the adhesive strength passed through a maximum with time, in others the reverse took place.

5. It was expected that the adhesive strength would increase by decreasing the flexibility of the polymer. Preliminary experiments showed that addition of fillers and pigments, which decrease the flexural modulus, actually showed higher adhesive strength. Plasticizer may show the opposite effect. This has not yet been studied.

Bascom, Cottingham, and Singleterry (19) also studied adhesion by shear. The influence of hydrophobic and hydrophilic surfaces was investigated. Permanent records of the rupture surfaces were obtained by making replicas. Contact angles were measured by the sessile drop method at 25 C. Shear strengths were measured at -6 C in the same apparatus as that previously used by Ford and Nichols. Ice was made in Teflon-coated foil molds. The water was redistilled from a quartz still. Air was removed by boiling (conductivity 1×10^{-6} ohm⁻¹ cm⁻¹). The adhesive strengths of highly polished steel and steel covered by monolayers were compared. The ice was allowed to recrystallize overnight before the test was started. Results are given in Table 4. The hydrophobic monolayers decrease the adhesive strengths.

TABLE 4
CONTACT ANGLE AND SHEAR STRENGTH OF
POLISHED AND COVERED STEEL

Surface	Contact Angle With H ₂ O	Shear Strength (kg/cm ²)	Type of Break
Steel	0	94.9	Cohesive-adhesive
Steel plus			
Octadecylamine	104	49.9	Adhesive
Stearic acid	104	61.2	Adhesive
Perfluorodecanoic acid	97	69.6	Adhesive
Polymethylsiloxane	103	69.6	Adhesive

6. Emery-abraded surfaces showed increased adhesive strength. The failure was always cohesive whether the metal was bare or covered by a monolayer.

7. Polymer coatings decrease the adhesive strength except for some of the siloxanes. Thick layers are more effective than monolayers.

8. The authors could not find a clear correlation between contact angle and adhesive strength.

9. Replicas were made of sheared surfaces and examined microscopically. Imposition of a hydrophobic monolayer between steel and ice reduced adhesive strength by about 30 percent and changed the break from cohesive to adhesional. The work of adhesion of water to a monolayer is low (the contact angle is high), but apparently this is not enough to actually give a low adhesive strength. Crystal defects seem to be present in greater concentration at an ice-monolayer interface than at an ice-hydrophilic steel interface.

10. Polymers tend to fail cohesively very near the interface as indicated by replicas; appressional relaxation is not fast enough. The macroscopic break "appears" to be adhesional. It is important to note that the rate of stress application in this work was 1.4 kg-cm²/sec, whereas Jellinek used 0.7 kg-cm²/sec.

11. Generally the impression was gained from replicas that adhesional breaks occur very near the interface in the case of polymer coatings and monolayers. Thus it appears that these adhesional breaks are rather cohesive breaks taking place in the substance of weaker mechanical strength (monolayer, polymer). This was assumed generally to be the case by Bikerman (40). Actually evidence was found of polymer fragments adhering to ice after rupture. The authors point out that with smaller stress application, the ice has sufficient time to relax by dislocation slip and various mechanical processes on a microscale; however, when force is applied very rapidly, there is not sufficient time for relaxation to occur before rupture.

12. Thin layers of water freezing on steel were investigated with polarized light during their formation. Initially, large crystals were formed that subsequently recrystallized into smaller polygonal grains. The authors assume that a similar process takes place during the formation of ice test blocks. However, recent experience shows that in ice, usually, small grains are first formed that then grow into larger ones (41). The authors assume further that the recrystallization and polygonization process creates a high density of dislocations at ice surfaces. The driving force for this dislocation movement to the surfaces or interfaces is, according to these authors, due to stress produced by the difference in thermal coefficients of expansion between ice and substrate. Thus adhesional failure is explained by high dislocation density in the interface, which leads to easy deformation by prismatic slip parallel to the interface.

Jellinek (24, 25, 26) also performed accurately controlled shear experiments. The water was treated as indicated before.

TABLE 5
ADHESIVE SHEAR STRENGTH OF SNOW-ICE AT -5 C
AS FUNCTION OF CROSS-SECTIONAL AREA

Area (cm ²)	Adhesive Strength (kg/cm ²)	Standard Deviation (±kg/cm ²)	Time of Load Application (sec)
1.54	5.44	0.40	14
3.14	5.50	0.72	23
4.91	5.32	1.14	28
6.61	5.41	0.49	41

Note: All breaks adhesive; thickness of ice 0.2 to 0.4 cm.

1. First, snow-ice, sandwiched between polished stainless steel plates, was investigated at -5 C as a function of cross-sectional area. Results are given in Table 5.

2. Adhesive strength (stainless steel/snow-ice) as a function of temperature at constant height of ice (0.2 to 0.4 cm) and constant cross-sectional area can be expressed by a straight line until -13 C is reached where a sudden kink occurs and the adhesive breaks go over into cohesive breaks. The cohesive breaks are only very slightly dependent on temperature, decreasing slightly with decreasing temperature. The adhesive breaks as a function of temperature can be expressed by

$$\bar{S}_A = 1.24 t^0 - 0.18 \tag{22}$$

The magnitudes of strengths of the cohesive breaks obtained by shear tests are similar to those produced by tensile experiments. Also the type of break is similar (height 0.2 to 0.4 cm, area 1.52 cm²). Hunsacker et al. (34), using brass-ice napkin joints, also found a similar trend in their shear experiments. Adhesive breaks occurred until -13 C was reached; at this temperature the breaks become cohesive and less dependent on temperature (Fig. 5).

3. Shear tests were also performed with ice frozen to smooth polystyrene. The rates of stress application for these experiments were from 0.3 to 1.0 kg-cm²/sec.; these rates had no influence on the results. All breaks were adhesive.

4. The temperature relationship of the adhesive strength (0 to -16 C, area 9.61 cm², height 7.6 × 10⁻² cm) for ice-polystyrene is given by

$$\bar{S}_A = 2.8 \times 10^{-2} t^0 \tag{23}$$

The rate of stress application was practically constant. Further work is described in a second paper (42) in which the shear apparatus was modified. The rate of stress application could be varied over large ranges.

5. Surface roughness had an appreciable effect on adhesive strength (Table 6). The average rate of linear travel up to maximum strength was 5.9 × 10⁻³ cm/sec while the average rate of stress application was 0.27 kg-cm²/sec (stainless steel -4.5 C, height of snow-ice 0.1 to 0.2 cm, density 0.888 g/cm³). Profilometer readings showed unevenness of 1.3 × 10⁻² cm to 7.2 × 10⁻² cm.

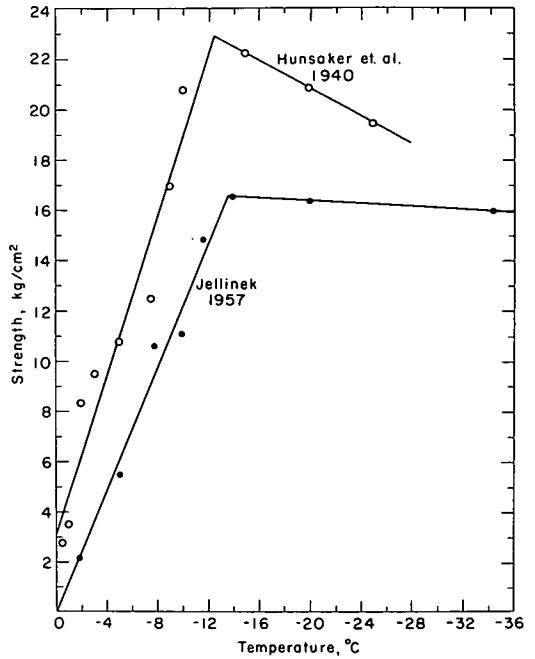


Figure 5. Strength as a function of temperature for snow-ice/steel and ice-brass obtained by shear for cross-sectional area 1.54 cm² and 0.2 to 0.4 cm in height. Adhesive breaks only down to -13 C, and cohesive breaks only below -13 C.

TABLE 6
SURFACE ROUGHNESS OF SUBSTRATE AND ADHESIVE STRENGTH, -4.5 C

Surface	Avg. Rate of Travel to Max. Strength (cm/sec)	Avg. Rate of Stress Application (kg-cm ² /sec)	Mean Adhesive Strength, 12 Tests (kg/cm ²)	Standard Deviation (±kg/cm ²)
Rough plates	5.9×10^{-3}	0.27	6.1	1.46
Polished, mat finish	5.4×10^{-3}	0.16	2.7	0.37
Bright mirror finish	5.8×10^{-3}	0.12	0.6	0.24

6. The stress versus time curves differ for the various degrees of roughness (Fig. 6). The rough surface shows a linear increase of stress with time up to a maximum value of 6.1 kg/cm², when the ice is suddenly released and the stress decreases very rapidly to zero. The mat finish only rises somewhat more slowly than in the previous case to a maximum of 2.7 kg/cm², when it drops very fast to zero. The mirror polish rises still more slowly to 0.45 kg/cm², or in another experiment to the same value with

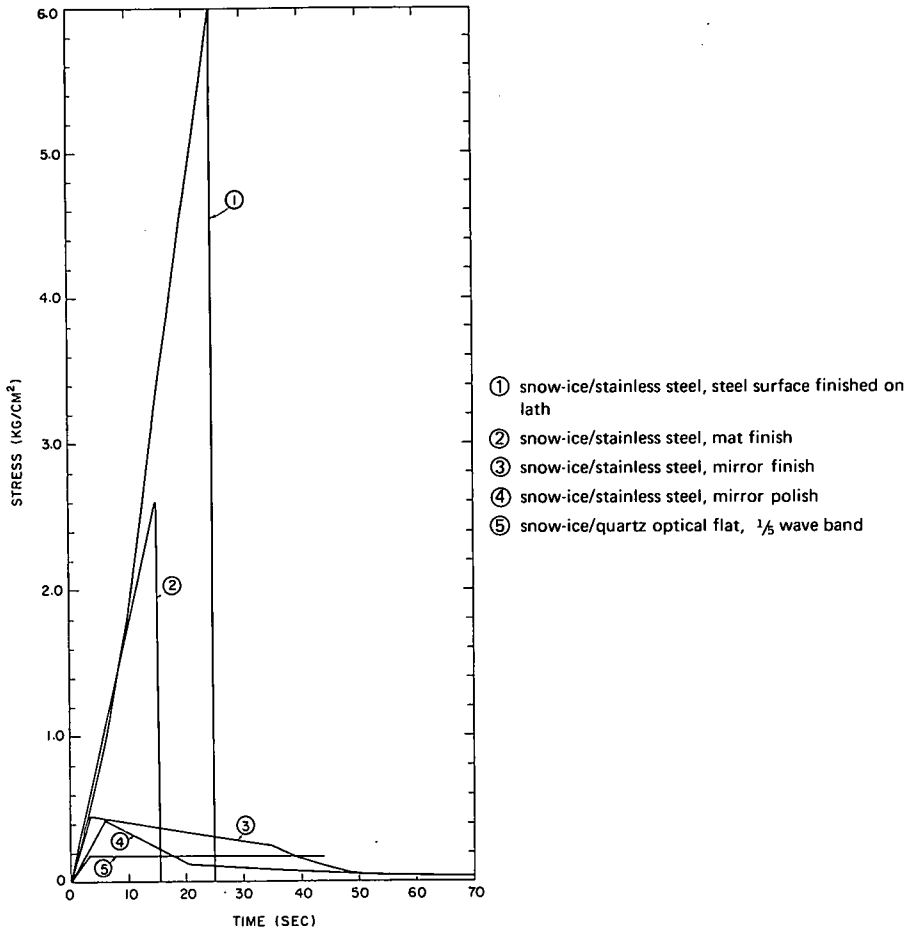


Figure 6. Typical stress versus time curves for stainless steel disks of different roughness and for fused quartz optical flat, -4.5 C (43, Fig. 2). Rates of shear are similar in all cases.

a slightly smaller slope than in the first experiment. However, after the maximum value, the stress drops quite slowly (the ice glides on the substrate surface) and eventually reaches zero or almost zero stress. An experiment was also carried out with an optical quartz flat as substrate. Here the stress rises still more slowly to 0.2 kg/cm² after which it remains constant with time; steady travel (gliding) of the ice over the quartz surface takes place.

7. A number of tensile experiments were performed using mat and mirror-polished stainless steel. The types of cohesive breaks obtained were similar and of similar magnitude as those obtained previously. The mirror-polished steel showed a somewhat smaller value for the cohesive strength. The mean tensile strength for mirror-finished sheets was 9.9 ± 1.7 kg/cm² (-4.5 C, area 3.14 cm², height 1 cm). For mat finish, a value of 12.2 ± 3.2 kg/cm² was obtained.

8. Shear experiments as a function of rate of shear were also carried out. The adhesive strength increases linearly with rate of shear (-4.5 C, snow-ice/mirror-finish stainless steel). The relationship is as follows

$$\bar{S}_A = 69.9v + 0.22 \quad (24)$$

where v is the rate of shear in cm/sec. It is interesting to note that this straight line has an intercept on the adhesive strength axis of 0.2 kg/cm², the same value as that obtained with optically flat quartz (Fig. 7).

9. Quite a number of experiments were carried out with optically flat quartz as substrate (flat within one-third of a light band). The ice cross section was made somewhat smaller than the quartz area to allow for movement of the ice or vice versa.

Adhesive strength was measured as a function of average rate of travel of the quartz flat (cm/sec). Ice was snow-ice (0.888 g/cm³, -4.5 C, area about 5 cm², height 0.1 to 0.2 cm). At least 11 tests were made for each rate of travel. The results are given in Table 7.

The adhesive strength plotted against the rate of shear gives a straight line with an intercept for zero rate of shear at about 0.07 kg/cm². The equation for the straight line is

$$\bar{S}_A = 15.1v + 0.07 \quad (25)$$

where v is rate of shear in cm/sec (Fig. 8).

10. Tensile tests were also carried out with optical quartz flats as substrates (height 1 cm, diameter 2.3 cm, -4.5 C). Breaks were cohesive and similar to those

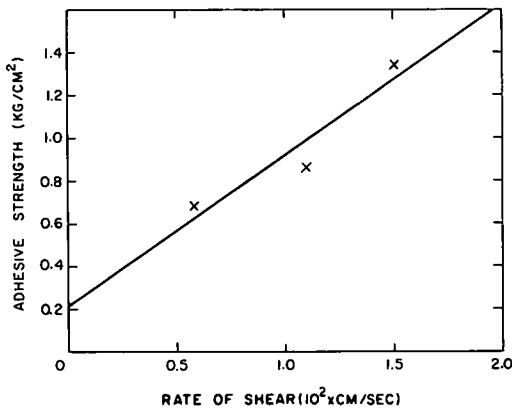


Figure 7. Relationship between average adhesive strength and rate of shear for snow-ice/stainless steel, mirror polish, -4.5 C (43, Fig. 3).

TABLE 7
ADHESIVE STRENGTH OF SNOW-ICE/OPTICAL QUARTZ FLAT AS FUNCTION OF RATE OF TRAVEL

Average Rate of Travel (cm/sec)	Mean Adhesive Strength (kg/cm ²)	Standard Deviation (±kg/cm ²)
0.53 × 10 ⁻³	0.074	0.020
1.10 × 10 ⁻³	0.120	0.059
6.30 × 10 ⁻³	0.184	0.083
1.20 × 10 ⁻²	0.194	0.063
1.60 × 10 ⁻²	0.355	0.105
2.50 × 10 ⁻²	0.402	0.130
4.10 × 10 ⁻²	0.720	0.190

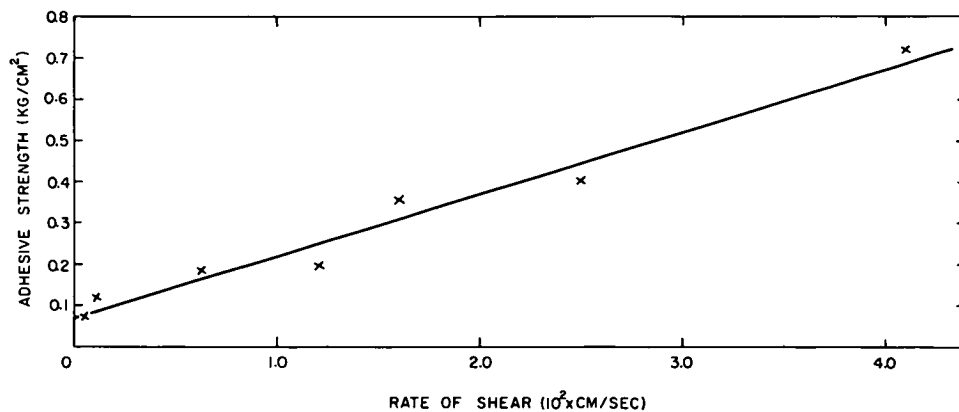


Figure 8. Relationship between average adhesive strength and rate of shear for snow-ice/fused quartz optical flat, -4.5 C (43, Fig. 5).

obtained with stainless steel. The mean tensile strength amounted to 10.6 kg/cm^2 with a standard deviation of $\pm 2.7 \text{ kg/cm}^2$.

11. Frictional properties of thin water films sandwiched between optical flat glass plates were investigated (44). One of the plates was slid very carefully over the water film. The thickness of the films was measured by optical interference and ranged from 0.2 to 1μ (0.2×10^{-4} to $1 \times 10^{-4} \text{ cm}$). The shear stress at constant shear rate

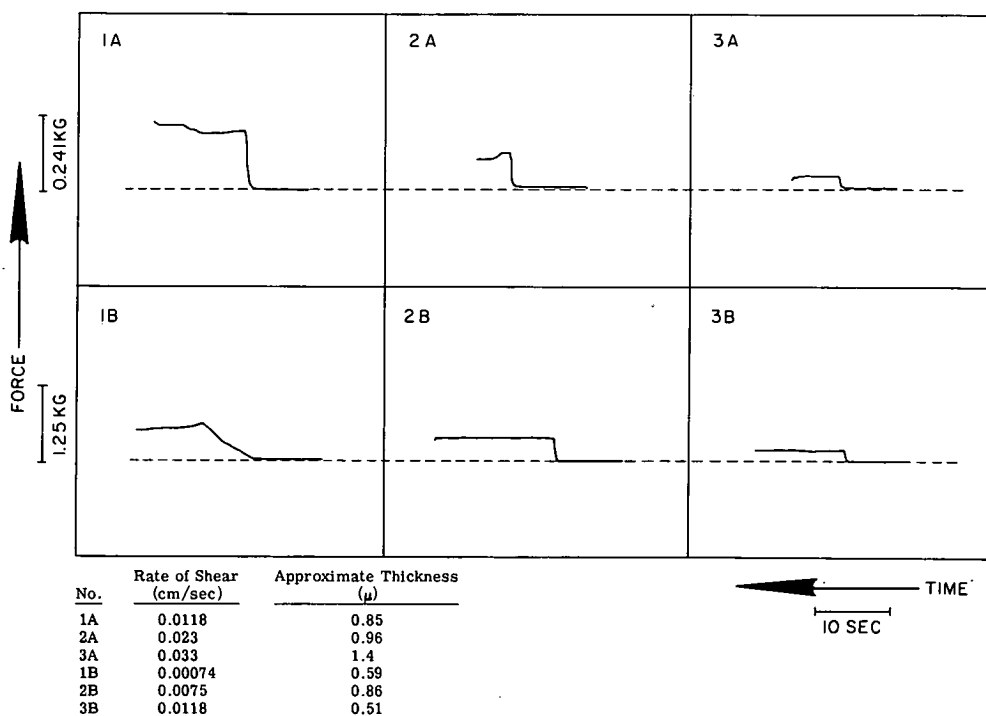


Figure 9. Recordings of force versus time for water films between glass plates, -5 C (44, Fig. 13).

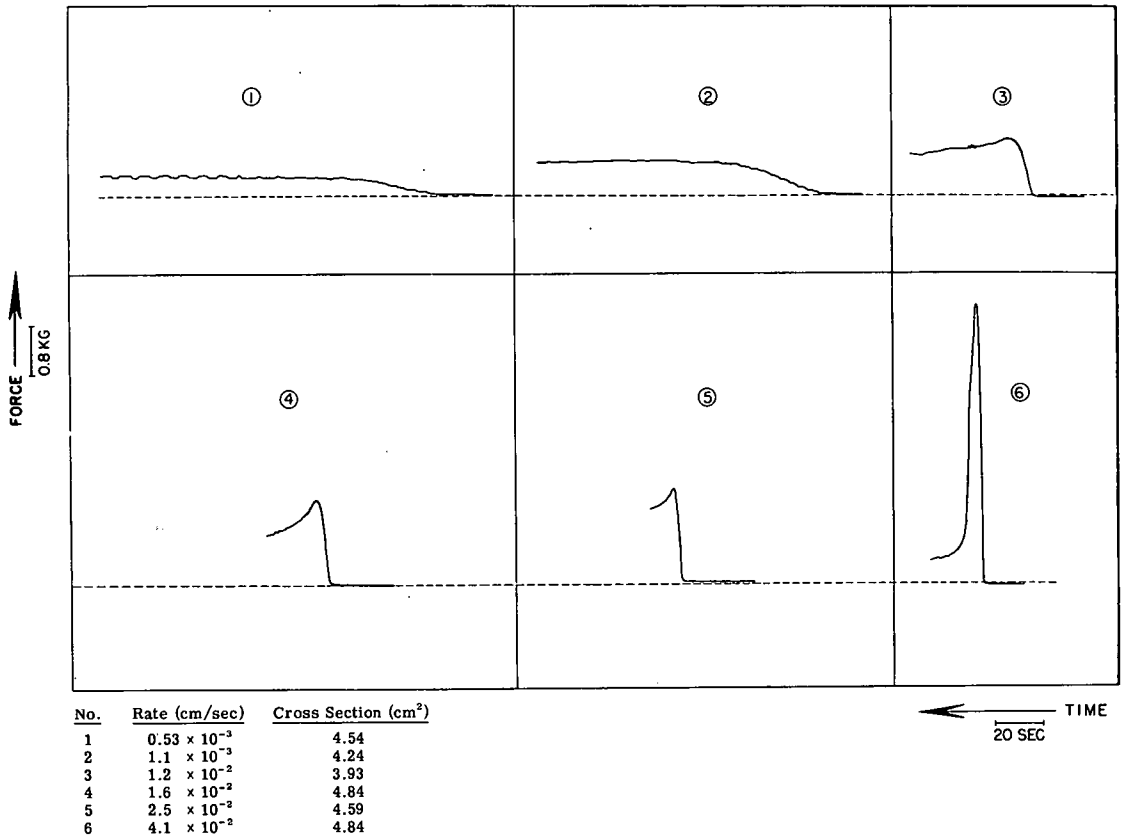


Figure 10. Typical recordings of force as a function of time at different rates of shear for snow-ice/fused quartz optical flat at -4.5 C (43, Fig. 6).

was found to be a linear function of the reciprocal film thickness. The frictional force dropped rapidly for thicknesses larger than $1 \mu\text{m}$ to such low values that they could not be recorded with the equipment available. Recordings of force versus time are very similar to the recordings obtained with ice-quartz; at high rates of shear a very sharp maximum was quickly reached, whereas at low values lines almost parallel to the time axis are obtained (Figs. 9 and 10).

Comparing the plot of stress versus reciprocal thickness of the water film at -5 C obtained for a rate of shear of 0.0114 cm/sec with the results for quartz/snow-ice gives a thickness of water film of $0.2 \mu\text{m}$ behaving almost the same as the snow-ice/quartz at -4.5 C.

DISCUSSION OF TESTS

The general features of ice adhesion found by the various investigators are similar in general outline and type, although they differ in some details and in their numerical values. Cohesive breaks using uncovered metal substrates were generally found in tension experiments; also, the observation that monolayers are not sufficient in changing cohesive to adhesive breaks is also a general feature. Thicker coatings, however, give rise to adhesive breaks. Lubricants alone are also not very effective unless surface active agents are added, but this addition is not necessary for hydrophobic surfaces such as polytetrafluoroethylene (Teflon).

The increase of tensile strength with decreasing ice volume is part of a general property of materials. Height and cross-sectional area are also generally found to have an effect on the strength. Those polymers that have been investigated in tension and shear usually show adhesive breaks that are temperature dependent; cohesive breaks are not or are only slightly dependent on temperature. Adhesive breaks with polymers or coatings as substrates often give an indication that the break has really taken place very near the interface in the weaker material (usually the polymer). Thus, in the strict sense of the word, cohesive breaks take place—temperature dependence of these breaks also suggests that. However, the macroscopic appearance of the breaks gives the impression of an "adhesive" break. It is doubtful whether adhesive breaks actually can take place at all. For convenience, one talks about cohesive and "adhesive" breaks, even if the latter are most likely "special" cohesive breaks, which probably take place within about one monolayer of the interface. There is no exact correlation between contact angles of water and various substrates, but the general trend is roughly followed, namely that hydrophobic substrates (θ large) give relatively low strength values, while strength values increase with the hydrophilic nature (θ small) of the substrate. Stress concentration, thermal expansion, and conductance effects were found by all workers. The history of the ice influences the numerical values obtained, but the type of relationship is often preserved.

The most remarkable feature in ice adhesion work is the very large strength differences found for tensile and shear experiments. This will be discussed later; a detailed discussion was given in a previous paper (45, 46). The shear experiments are characterized by the following features: The adhesive strength decreases linearly with temperature for stainless steel substrates; however, at a certain temperature the adhesive breaks change quite suddenly to cohesive breaks, which are only very slightly temperature dependent. This occurred at -13 C for Jellinek's tests (24); Hunsacker et al. (34) observed this at about -12 C and Raraty and Tabor (29) at about -7 C. Quartz-ice joints give the definite impression of ice gliding across the quartz surface or vice versa. This glide can be accomplished by almost zero rate of shear application. If the stress rates are increased, the impression is gained that the system cannot relax quickly enough and a fairly fast release (break) is observed.

Tensile strength experiments on bare metals and on optical flat quartz surfaces as substrates show cohesive breaks of normal magnitude. If the ice volume is made small enough, of the order used in many of the shear experiments, the tensile stress increases enormously. In Jellinek's experiments 70 kg/cm^2 were reached, but there is no reason why still higher tensile strength values could not be obtained. It is impossible to explain these profound differences of tensile and shear tests by easy creep of solid ice along the substrate interface and by very much less creep in the ice perpendicular to the interface. This does not actually throw any doubt on the replica technique observations made by Bascom et al. (19). However, it must be concluded that their technique is not suitable for solving the problem encountered here. The replica method actually misses the clue for this discrepancy as will become clear in the following.

Ackley and Itagaki (20) also investigated defects in the transition zone during adhesion processes and came to the conclusion that this zone is crowded with defects. Murrmann, Anderson, and Peek (21) studied the ionic surface diffusion of ice. These authors attempted to combine the various views concerning the nature of the transition zone. Thus, they suggest that it starts with bulk ice, then goes over into a region rich in defects and misorientation and eventually nears the properties of water in its uppermost ranges. This seems to be a reasonable and fruitful approach. One type of experimental method can only detect the defects, missing the more liquid-like part, whereas other methods can mainly locate the liquid-like part and not the defective zone. It is very likely that both parts are present in the various regions of the transition layer and there is no real contradiction between these apparently opposing views.

The assumption that actually accounts best for all the observed facts regarding the difference of tensile and shear experiments is that of a viscous or plastic transition layer in the ice-air and ice-solid interfaces respectively in the range from the ice melting point to lower temperatures. The properties of this layer are dependent on the particular ice-solid interface as far as thickness, viscosity, temperature range,

and the like are concerned. In this way, the vastly different behavior of ice-solid systems on tension and shear can be accounted for. This assumption was treated in detail in a previous paper and its exhaustive discussion will not be repeated here. The term "liquid-like," used previously, led to some misunderstandings in the past and is best to be avoided. Hence, we refer here rather to a viscous or plastic transition layer. This means that there is a gradual transition from bulk ice or far from the interface to water-like substance at the interface itself. The side of the transition layer directly adjacent to the substrate surface resembles liquid water more than ice. A molecular structure different from water or ice, such as the case for so-called "anomalous water" discovered by Derjaguin (47), is not envisaged here. Actually, Hori (49) in 1956 seems to have experimented with such anomalous water without realizing its real significance.

The picture of such a transition layer does not contradict any of the results of other ice research workers. It is also not intended here to go into any detailed history of this transition layer, which originated with Faraday (50, 51, 52, 53) in 1856 and the phenomenon of regelation. Such famous scientists as the Thomson brothers, Lord Kelvin (54) and J. Thomson (55), Tyndall (57), and Helmholtz were involved in a controversy about pressure melting of ice. This type of melting cannot be involved here (590 atm are needed to depress the melting point of ice to -5°C). Jensen (58, 59) presented quite conclusive evidence against pressure melting in this connection. Bowden and coworkers (60, 61, 62) discussed melting by friction. There is, of course, a possibility of obtaining melting by friction in shear experiments, if the stress rates are very high. However, this possibility recedes more and more the slower the stress rate, and can safely be excluded for small rates. In more recent times, Weyl (63) wrote a theoretical paper on the transition layer and Nakaya and Matsumoto (64) were the first to present experimental evidence for such a layer. Thus, in summary, the different properties of tensile and shear tests can be explained as follows: A cylindrical ice specimen adhering to stainless steel as substrate, for instance, has a transition layer of definite thickness that depends on the temperature (Fig. 11). It is assumed that this layer forms a zero contact angle with stainless steel. On tension a pressure difference due to the curvature of the transition layer has to be overcome; its magnitude is (4, 65)

$$\Delta P = \gamma_t \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (25)$$

Here ΔP is the pressure difference across the transition layer-air interface, γ_t is the transition layer surface tension, and r_1 and r_2 are the radii of curvature, $r_2 \gg r_1$; hence,

$$\Delta P = \frac{2\gamma_c}{d} \quad (26)$$

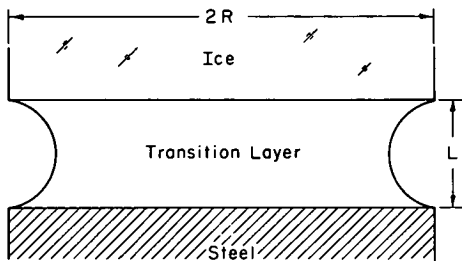


Figure 11. Transition layer between ice and solid substrate, metal or polymer (46, Fig. 9).

where d is the diameter of the smaller curvature. Hence, if d is small enough (about 10^{-6} cm at -5°C), the ice ruptures cohesionally long before adhesive failure can take place ($\Delta P = 7 \times 10^7$ dyne/cm², $\gamma = 76.4$ dyne/cm). However, in shear, only viscous or (if non-Newtonian) plastic forces have to be overcome in the transition layer. If the surface of the substrate is smooth enough, as is the case with optically flat quartz, the smallest stress will cause continuous gliding of the ice across the substrate as is actually observed with quartz-ice. There may be a small yield point needed to overcome the structure of the transition layer. All experiments reviewed in this paper can be

explained consistently on this basis. The average viscosity of the transition layer was estimated for ice-steel at about 70 to 700 poises and for ice-quartz, 15 to 150 poises for a layer thickness of 10^{-5} to 10^{-6} cm, at -4.5 C.

Quite a number of papers were discussed previously (45, 46), which add evidence for the existence of such a transition layer. This discussion will not be repeated here; however, some of these papers and some new ones will be mentioned briefly. In addition to those of the last century, the contributions of Weyl (63), Nakaya and Matsumoto (64), and Jensen (58, 59) were already mentioned. Jellinek and Ibrahim (66) sintered very small (radii 0.5μ) ice spheres at various temperatures, following surface area changes by the BET method. The results are compatible with the assumption of a transition layer. Kingery (67) also carried out sintering experiments, which are also consistent with the assumption of a transition layer. A paper by Telford and Turner (68) explains the slow migration of wires through ice in terms of the transition layer. Similar experiments were carried out by Townsend and Vickery (69) and by Nunn and Rowell (70). The results do not agree with Nye's theory (71) of regelation based on pressure melting. The latter came to the conclusion that regelation based on pressure melting shows many discrepancies with experimental data. Mason, Bryant, and van der Heuvel's paper (72) on growth habits and surface structure of ice crystals is of relevance here.

Fletcher (75) was the first to elaborate the existence of a transition layer on thermodynamic grounds. His first treatment contained some fairly rough approximations. Since then, he has revised this theory (78, 79). New information on quadrupole moments of water molecules and on liquid water structure has been utilized. Electrostatic forces are taken into account in this revised paper. The main driving force for molecular orientation near the water surface is the interaction between quadrupole moments and molecular dipoles. As far as ice is concerned, the free energy available from surface polarization leads to a change of phase in the ice surface over a range of temperatures near the melting point. The conclusion is reached that at temperatures larger than about -5 ± 3 C a transition layer exists on ice. Its thickness is calculated, as about 10 to 40 Å at -5 C, increasing rapidly with temperature (Fig. 12). The electric conductivity of this layer is quite large, based on this theory. It may also be mentioned here that Jellinek and Nagarajan (80) carried out some rough contact angle

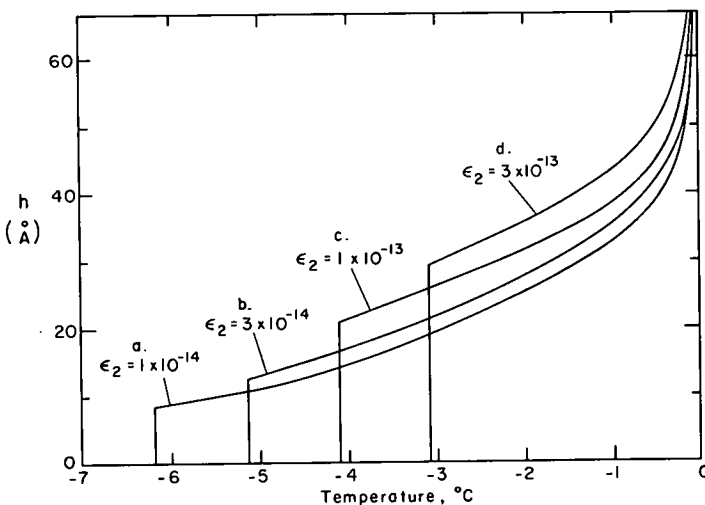


Figure 12. Calculated transition layer thickness on ice, h , for various assumed values of ϵ_2 , energy of formation of diffuse L defects at the ice-water interface (78, Fig. 2, p. 1287).

measurements with paraffin and carbon disulfide on ice. These angles did not change over a large range of temperatures down to liquid nitrogen temperature. It is possible that, even on disappearance of the transition layer at lower temperatures, the uppermost water molecule layer does not take up a random arrangement again. The size of the contact angle is practically conditioned only by the first surface layer.

ICE ABHESION

There appear to be about 3 possible modes of attack on the problem of ice adhesion. In some respects, considerable success has been achieved in formulating effective ice releasing compositions and surfaces. But, there still may be room for improvement in certain areas. The 3 approaches to the ice adhesion problem, which can be pursued and which under favorable conditions may reinforce each other, are as follows.

Self-healing films have surface active additives that diffuse preferentially into the interface between the substrate and ice, forming highly condensed hydrophobic monolayers. If such a layer has been removed because of repeated adhesions, it can reform by diffusion of an additional agent from the bulk film to the interface. The main problem here is the role of diffusion, whose magnitude is dependent on the viscosity, structure, and temperature of the film. The second and third alternatives are somewhat similar. Decrease of shear strength of the layer near the ice interface in the substrate can be achieved by a liquid-like or pasty layer such as an oil or a grease, which has low shear strength. These substances should preferably be hydrophobic and often contain surface active agents to decrease interfacial free energies. Appreciable success has been achieved with such systems. Weakening of mechanical (shear) strength of ice near the interface can be achieved by inorganic and organic substances added in small amounts to the substrate. These compounds are soluble in water and pass preferentially into the crystal grain boundaries, enlarging the latter and weakening the ice structure. These 3 aspects of ice adhesion are discussed in detail in the following sections.

Self-Healing Films

Perfluorolauric acid gives the lowest CST, γ_C , value known so far. The surface, in this instance, consists of a closely packed condensed monolayer of $-\text{CF}_3$ groups. Unfortunately, these layers are removed on repeated adhesion and are only effective a limited number of times.

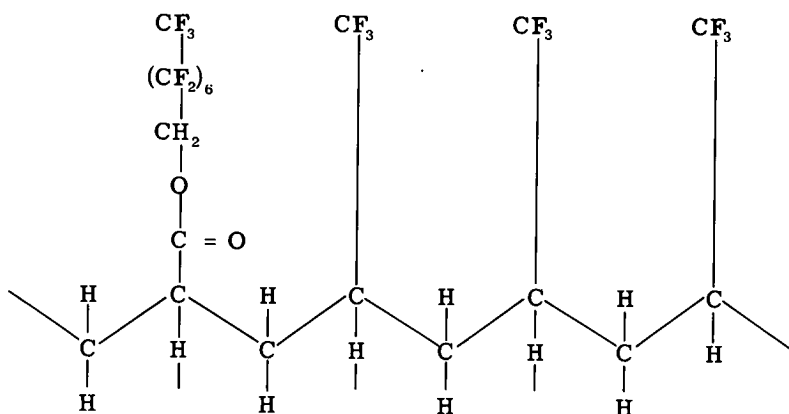
However, there is a way of regenerating such a monolayer; so-called "self-healing" films can be prepared. The same principle is operative here as that encountered in the formation of monolayers on water surfaces. To obtain a monolayer on a clean water surface in a Langmuir trough requires that molecules be spread on such a surface. These molecules must have such a structure that there is a sufficient balance between the water-soluble (polar) part of the molecule and its water-insoluble chain (hydrocarbon) part. If this balance is right, a monolayer is formed on the water surface. The polar groups dip into the water and the hydrocarbon tails stick almost vertically out of the surface in the monolayer, if it is closely packed. Thus a hydrophobic surface is created. The surface area occupied by each oleamide molecule, for instance, in a closely packed monolayer, is 28 \AA^2 . Water is not necessarily the only surface on which monolayers can be formed. Polymers can also have highly condensed monolayers on their surfaces, for instance, polyethylene (carefully protected from surface oxidation). Allan (81) has demonstrated the formation of monolayers on polyethylene by surface active agents. Such agents must have the right balance between polar and nonpolar groups. Examples of molecules are stearamide, oleamide, palmistamide, and myristamide. Oleamide was found to be the most effective in this group. The agents are either milled into the polymer or are present in polymer solutions from which films are cast. The polar groups are oriented toward the medium of higher dielectric constant (i. e., polyethylene). The free energy of the system becomes a minimum for such a configuration.

The amount of surface active agent for a given amount of polymer has to be increased if the surface-volume ratio increases or if the film thickness is decreased. Thus for

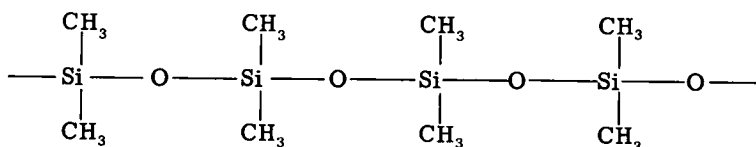
agents such as those employed in Allan's work give the lowest critical surface tensions, γ_C , as the surfaces are composed of $-\text{CF}_3$ or $-\text{CF}_2$ groups.

An interesting study of self-healing films was undertaken by the American Association of Textile Chemists and Colorists, Piedmont Section (83). Water-repellent films were mixed with fluorocompounds as surface active additives. These fluorochemicals are oil and water repellent. "Quarapel," for instance, which was developed by the U.S. Army Quartermaster Corps for textiles, consists of a pyridinium fatty water repellent containing a fluorocarbon. This study of textiles was based on Zisman's research (1) resulting in the formulation of critical surface tensions, γ_C .

It was recognized that a most effective fabric treatment would consist of producing a closely packed monolayer of $-\text{CF}_3$ groups or of the somewhat less efficient $-\text{CF}_2$ groups. Only smooth, nonporous surfaces were investigated. The fluorochemical chosen for this investigation was FC-208, available as a nonionic emulsion containing 28 percent solids. Its structure is representative of types of compounds used commercially, and is most likely a polymer or copolymer of vinyl-perfluoro-acid or perfluoro ester of acrylic acid.

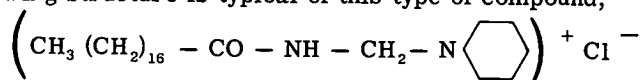


The silicone compound used was an emulsion of dimethyl and methylhydrogen siloxanes (Sylmer 72). The exact nature of this "silicone" has not been released, but it is of the following types:



Two fatty, wax-like water repellents were also employed in this work; these are generally applied in conjunction with fluorochemicals. The repellents were metallic soaps or film-forming polymers. Phobotex, FTC, a triazine fatty water repellent (TFWR) was also used in this research. It is a mixture of various fatty acids and alcohols attached somehow to methylolmelamine. Curing leads to cross-linking.

Last, a pyridinium-fatty-water repellent (PFWR) was chosen (Zelan AP). It is a pyridinium acid chloride derivative of stearamide, sold in the form of a preemulsified solid. The following structure is typical of this type of compound,



The emulsions were spread on the substrate and air dried (5 percent of total solids used). The films were then cured in an oven. Films of a number of substances were prepared by cross-linking various emulsions. Critical surface tensions, γ_C , were determined with alkanes.

<u>Repellent</u>	γ_C (dynes/cm)
Fluorochemical	13 to 16
Silicone	18 to 20
TFWR	about 21
PFWR	about 21

All these preparations are commercially available.

The CST values, γ_C , were plotted against the composition of the mixture; they decrease with decreasing fluorochemical concentration. TFWR is an exception; it shows a CST-minimum at about 0.5 percent w/w of fluorochemical. This may have something to do with the solubility of the fluorochemical in the film. Investigation showed that the 90-10 (TFWR-FC) mixture is uniform throughout the whole film, while the 99.5-0.5 mixture has most of the fluorochemical located at the film surface. The underlying substrate, glass or any other material, has no effect on the CST. If the surface of the film is abraded, the CST value increases. However, it can be decreased again by heating the film. Self-healing then takes place by reforming the monolayer by diffusion of the fluorochemical to the surface.

Decrease of Shear Strength in the Nonice Interfacial Layer (Lubrication)

This section deals with improper adhesive joints or with improper adhints. The latter term was coined by Bikerman (40). This approach to ice adhesion has been successful in many cases. An interfacial layer of relatively low shear strength such as an oil (lubricant) or grease is used to decrease the interfacial shear strength. In this category belongs also the transition layer on ice, which was dealt with at length in this author's fundamental studies on ice adhesion (42, 43, 45, 46). It is not necessary that a lubricant have a particular hydrophobic nature, although this is of advantage. The layer of oil, however, that is removed with each act of ice adhesion will probably be smaller if the oil is hydrophobic. The major condition is that the shear strength be low. Baker, Bascom, and Singleterry (84) studied the adhesion of ice from lubricated surfaces. Oil, to be really effective, should not be replaceable by water. Here again, addition of surface active agents up to about 1 percent is beneficial, decreasing the oil substrate interfacial tension. These additions appreciably decrease the adhesive strength of ice, for instance, in the case of diester oil (bis-2-ethyl-hexyl-sebacate) on steel (-25 to -30 C). Barium-phenylstearate proved very effective, more so than phenylstearic acid. Additives did not, however, improve the Diester-Teflon surface. Mineral oil (Nujol)-Teflon also proved fairly effective without additive.

Quite extensive work was carried out by Plump and coworkers (85) with lubricated surfaces. A large number of substrates, oils, and additives were tried. The most efficient combination consisted of a silicone layer (Dow-Corning XZ8-3057) covered by pristane oil, a pure hydrocarbon found in sharks. Ice adhesion was very low for this system under various conditions tested in the laboratory and outdoors; the lubricant was effective for a number of adhesions. The rate of shear used in the laboratory apparatus was usually fairly high: 0.05 cm/min. Some results are given in Table 9.

A comparison of unoled polymers and polymers oiled with pristane is of interest (Tables 10 and 11). These experiments were carried out at a shear rate of 0.5 cm/min. It seems that in the case of pristane also, the replaceability of the oil by water plays an important role.

Landy and Freiberger (27) also experimented with lubricants. A number of substrates were tested in the absence of surface active agents; in such cases the lubricated surfaces showed similar adhesive strength as the untreated surfaces. Only when surface active agents were added, a substantial reduction in adhesive strength took place. Thus only cohesive breaks were observed with bis (2-ethyl-hexyl-sebacate) alone; however, the addition of barium phenylstearate decreased the adhesive strength appreciably. The most efficient additive proved to be sodium di-nonyl-naphthalene-sulfonate. Only adhesional breaks were taking place when this additive was present;

TABLE 9

SHEAR ADHESIVE STRENGTH OF ICE ON SILICONE XZ8-3507, LOT K2, OILED (PRISTANE) AND UNOILED

Rate (cm/min)	Temperature (deg C)	Strength (psi)	
		Oiled	Unoled
0.005	-7.7	<0.10	4.1
0.05	-7.5	<0.15	5.5
0.5	-8.0	0.42	7.1
5.0	-7.3	1.50	2.8
0.05	-3.0	<0.45	3.4
0.05	-7.5	<0.15	5.5
0.05	-11.0	<0.41	>5.7

TABLE 10

UNOILED POLYMERS, -10 C, SHEAR STRENGTH IN psi

Freeze-on	Polyethylene (high density)	Polypropylene	Kel-F
1	<1.0	3.9	14.8
2	<10.0	13.7	10.4
3	3.9	11.7	—
4	5.5	14.1	—
5	<5.0	4.0	—
6	7.4	5.9	—
7	6.7	13.8	—
Avg.	<5.6	9.6	12.6

TABLE 11

OILED POLYMERS (PRISTANE), -10 C,
SHEAR STRENGTH IN psi

Freeze-on	Polyethylene	Polypropylene	Kel-F
1	<0.1	<0.1	11.0
2	<0.1	14.1	<17.8
3	<<5.5	8.1	<19.7

the strength was reduced from 80 to 5 psi with steel as substrate. Also in the cases of brass and aluminum as substrates, the sodium compound was the most effective additive; however, a layer of bis (4' -C₅) glutarate without any additive was found to be best for Teflon. Here again those additives that are effective prevent the displacement of oil by water, thus preventing wetting of the substrate.

In another series of experiments Teflon, polyethylene, and nylon were

taken as substrates. The lubricants were various silicone greases and petroleum grease. Repeated adhesion tests were performed. Also additives were used in quite a number of cases.

The shear strength of ice for lubricated nylon, polyethylene, and Teflon was zero for several cycles of adhesion. After a definite number of cycles, however, the shear strength rises sharply if the surfaces are not relubricated. If a grease rather than an oil is used for coating these polymers, the number of cycles having zero adhesion increases.

During 12 cycles with polyethylene coated by silicone grease (J941-C5000), no increase in strength took place. Nylon is not so good. The number of effective cycles increases with decreasing temperature indicating that the higher the viscosity of the oil (within limits, of course) the more efficient it seems to be. Thus an oil should have a fairly high viscosity and a grease a high apparent viscosity index.

The general conclusion was arrived at that coating materials showing negligible adhesion with respect to ice must be liquid- or grease-like and must not be displaced by water or easily removed by repeated adhesions. These properties should not be too temperature sensitive. The nature of the solid substrate is also of importance, as it plays a role in the displacement of the oil by water. Hence, a low energy surface material such as polyethylene or Teflon is required. The reversible work of displacement of the oil by water is given by

$$W'_D = \gamma_{OW} (1 - \cos \theta) \quad (27)$$

Equation 27 indicates that the greater the contact angle of water on the oil the more energy is needed to displace the latter by water. Maximum protection is afforded if $\theta = 180$ deg. The work of displacement of oil by water from a solid surface (Eq. 27) is also a function of the free surface energy of the solid. Baker et al. (quoted in 22) measured the effect of a number of sulfonate soaps on the contact angle of water on steel. They found, for instance, from Eq. 27, that $W'_D = 5.6$ erg/cm² for a sodium

sulfonate and $W'_D = 20.5 \text{ erg/cm}^2$ for a corresponding barium compound. In accordance with the theory, it was found that the barium compound is superior in reducing the adhesive strength of ice. Thus these surface active agents are adsorbed at the oil-solid (e.g., steel) interface. [There seems to be some contradiction to Ford and Nichol's (22, 23) results.]

Oil is not as easily displaced from polymers, i.e., from low energy surfaces, as from high energy metal surfaces.

Adhesion of ice to grease-coated metal surfaces is higher than that to grease-coated polymer surfaces. It is believed that water can, to some extent, penetrate the grease and wet the metal surface.

Weakening of Ice Near the Interface

Extensive work has been carried out on this by Smith-Johannsen (86). He found that small amounts of water-soluble compounds appreciably reduced the strength of ice adhesion. These substances have to be insoluble in organic materials such as waxes or greases. Instantaneous freezing is a requirement for minimum adhesive strength. Thus solutions were usually cooled to 0 C before rapid freezing. Table 12 gives the values for the adhesive strength of 10^{-3} M solutions frozen to very thin wax films.

New surface coatings were elaborated on the basis of these results especially for aircraft propellers. A number of surfaces were tested, such as untreated wood, General Electric Antipastes (No. 87 and No. 89), and Teflon foil. Impure ice looks quite opaque and cloudily in contrast to pure ice. The reduction of ice adhesion by impurities was observed both for hydrophilic and hydrophobic surfaces such as glass, aluminum, chromium, copper, and also for these surfaces treated with waxes and lacquers.

It is of interest to consider the freezing process of impure ice more closely. The salt solution follows the phase rule on freezing, i.e., the solution becomes more concentrated as ice is frozen out according to its phase diagram. Hence, as long as the temperature is above the eutectic, one has a definite salt solution in equilibrium with ice. Quick freezing produces small grains. It was found that in the presence of impurities the adhesion is small only if a fine granular ice is formed. On quick freezing, the impurity distributes itself evenly over the whole ice sample; in other words, the impurity is trapped in the many grain boundaries existing in the fine-grained ice. The distribution of grains does not depend on the impurity or its amount but only on the rate of freezing. However, the widths of the grain boundaries are dependent on the type of salt solution and its concentration. These widened grain boundaries weaken the ice structure and contribute to easy adhesion. If the temperature is lower than that of the eutectic point, the grain boundary will be solid. The adhesion below the eutectic temperature of the added salt is lower than that without the impurity, but considerably higher than for impurities above their eutectic points. Exothermic heats of solution, low eutectic temperatures, and high water solubility are usually favorable properties. The adhesion decreases with increasing salt concentration to about 10^{-3} M , and, as pointed out, the grain boundary width increases with salt concentration.

A great number of solvents and substrates were tested. The best substrate was Formvar for wet outdoor conditions. The salt and Formvar were finely ground to a powder (about $1 \mu\text{m}$) of uniform size distribution.

Pounder (87) performed some interesting experiments on the mechanical strength of ice frozen from impure melts, and also of ice layers that were sprayed with contaminants. Small amounts of alcohols, ketones, and ethers are very efficient in lowering the mechanical strength of ice. Alginic and stearic acids are also effective. One gram

TABLE 12
ICE ADHESION OF 10^{-3} M SOLUTIONS ON VERY THIN WAX FILMS MEASURED AT -15 C

Solution	γ/cm^2	Solution	γ/cm^2
Distilled H ₂ O	4,250	MgAc ₂	850
SnCl ₄	2,800	Glycerine	790
NH ₄ Cl	2,775	Na-Silicate	770
NaCl	2,400	KAc	750
Calgon	2,375	CaAc ₂	750
BaCl ₂ , pH 2.6	2,250	NH ₄ Ac	700
KCl	2,200	K ₂ SO ₄	690
Aerosol OT 100	1,940	BaCl ₂	660
BaAc ₂	1,665	NaNO ₃	650
Ca(NO ₃) ₂	1,375	CaCl ₂	390
MgCl ₂	1,300	Th(NO ₃) ₄	110

Note: Solution bp about 0.005 C.

TABLE 13
FRACTURE LOADING PRESSURES OF IMPURE ICE

Additive in 25 Percent Alcohol Solution	P_F	Average Percent Deviation
Pure water (no alcohol)	1.000	9
20 ml of 25 percent C_2H_5OH	0.263	18
20 ml LiCl	0.139	15
20 ml methyl cellulose	0.180	8
10 ml sodium stearate + 10 ml PVM	0.185	0
10 ml PVM + 10 ml D-235	0.185	16
20 ml T-253	0.202	18
20 ml PVM	0.211	17
20 ml ethyl cellulose	0.221	12
10 ml sodium stearate + 10 ml D-235	0.224	6
10 ml PVM + 10 ml L-245	0.255	20
20 ml soluble starch	0.262	5
10 ml sodium stearate + 10 ml agar-agar	0.274	6
10 ml soluble starch + 10 ml D-235	0.288	3
20 ml sodium stearate	0.302	29
20 ml agar-agar	0.325	29
10 ml sodium stearate + 10 ml sodium alginate	0.345	28

of each additive was dissolved in 75 ml of water and 25 ml of industrial alcohol. Of the resulting solution, 20 ml was sprayed on water of 800 cm^2 surface area; the total volume of distilled water was 25.0 liters. The concentration of the additive was thus 2.5 grams of solid and 50 grams of ethyl alcohol for each cm^2 . Freezing was carried out at about -25 C for 60 hours. Ice sheets of 7 mm thickness of pure water and 8 to 10 mm thickness containing various additives were obtained in this way. The results are given in Table 13.

Impure ice is opaque, and the top surface is slightly roughened. Here again, it was observed that the grain boundaries increased in width and were responsible for the decrease in mechanical strength of the ice. Thus these observations agree with those of Smith-Johannsen (86).

Recently Jones and Glen (88) found appreciable lowering of shear strength of single ice crystals due to the addition of small amounts of hydrogen fluoride. Fluoride ions can be incorporated into the ice lattice. A few ppm of HF are effective. Thus 0.03 ppm HF decreases the shear strength of ice by half. The effectiveness decreases with increase in temperature.

CONCLUSION AND SUMMARY

The fundamental aspects of ice adhesion have been studied quite thoroughly in the past. However, ice adhesion from a practical standpoint has to deal with quite different conditions from those encountered with fundamental studies carried out under laboratory conditions. Although, the principles operative for ice adhesion are also valid in practical tests, they are often completely obscured under actual practical conditions. Contamination of surfaces and removal of substances may take place. Hence, an approach has to be made with respect to the practical problem of ice adhesion by considering 3 main avenues of attack: (a) preparation of self-healing films, (b) formation of interfacial areas of low shear strengths (oils and lubricants), and (c) weakening of the mechanical strength of ice near the interface. These 3 approaches have been discussed in some detail. Quite a large measure of success has been reported in some of these areas, which will probably not be surpassed in the future. However, an important shortcoming of the systems so far used is apparent. The drawback is the relatively low number of adhesions that can be carried out with these systems before the adhesive strength starts to rise appreciably. This is due to loss of material on adhesion; it presents one of the main areas where more research is needed.

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Informal Discussion

H. R. Kivisild

We have actually made some tests on the commercial surfaces mentioned using actual field materials. The tests were conducted in the form of the shear tests mentioned by Professor Jellinek. The main aim was to find out the relationships between the adhesion of ice to structural surface, temperature, and the properties of the material. Some observations were available on ice slipping on concrete and steel structures, and we also had laboratory tests to verify our findings from the field. We ran tests with rough steel, which gave something like a constant effect, or a cohesive break, all the way through at a temperature range from quite cool down to roughly 0.1 to 0.2 deg from the freezing point. The experiments were not really suited to cover any higher accuracy in temperature measurements. These were followed by tests on corroded steel, concrete, abraded concrete, and freshly poured concrete right out of molds, untouched. We even tried various coatings, like coal tar epoxy coating on the steel surface, and they all came up to a more or less constant cohesive figure almost independent of the temperature or of the properties of the surface. Only when we polished the steel surface was there a change with a rise in temperature from about -20 to -10 C from cohesive break to adhesive failure, and the adhesive failure seemed to occur as in the lubricating layer mentioned. This phenomenon was only observed on very smooth steel faces. There was no comparable effect on rough surfaces, which showed little reduction in shear strength at the face with increasing temperature. I wonder whether the tests on commercial and polished surfaces are in disagreement with Professor Jellinek's earlier work or whether they actually fall in the same pattern.

Jellinek

That is very similar to the work that I have done. If you measure the adhesive strength and shear of a smooth steel surface and go down in temperature, you get adhesive breaks down to -13 C. Then suddenly you get cohesive breaks, almost independent of temperature. Other people have also found this. Andecker at M. I. T., for instance, found this also at -13 C. Taking rate of loading, Raraty and Tabor in England found this at -7 C. If you take surfaces of various roughness, you can get something like this.

J. W. Renahan

What happens to the ice under compression?

Jellinek

How much compression?

Renahan

Any amount.

Jellinek

If you get too much, you get pressure melting.

Renahan

Then just enough compression to break the ice.

Jellinek

You get a certain compressive strength that is usually different from the tensile strength but not too much.

Renahan

I am referring to compression on top with this adhesion that is underneath.

Jellinek

I didn't do that, but I think you would get a cohesive break.

Renahan

In other words, would it move and break free?

Jellinek

It would not move because you have to press directly vertical to the substrate. The ice would break. You would get some movement in the ice, and you would get a cohesive break.

Renahan

Would it break the adhesive bond?

Jellinek

No, I do not think so. Before it melts, the cohesive strength will be reached.

Malcom Mellor

If we are talking about something like a roller running over a coating of ice on a solid substrate, I think we are dealing with a structural problem and the actual properties of the ice are secondary. Incidentally, I would take issue with the remark that the compressive strength and the tensile strength of ice are about equal. This is only true if you have a very poor loading technique.