TP 12860E

ADHESION OF FREEZING PRECIPITATES TO AIRCRAFT SURFACES

Prepared for

Transportation Development Centre
on behalf of
Civil Aviation

Safety and Security
Transport Canada

by

Optima Specialty Chemicals and Technology Inc.

November 1996

TP 12860E

ADHESION OF FREEZING PRECIPITATES TO AIRCRAFT SURFACES

by

Y. Boluk
Optima Specialty Chemicals and Technology Inc.

November 1996

Since the accepted measures in the industry are imperial, they are used equally with metric measures in this report.

OPTIMA SC&T PROJECT TEAM

Dr. Y. Boluk	Project Leader
Dr. E.M. Berksoy	Research Scientist
Mr. A.M. Haine	Research Scientist

Un sommaire français se trouve avant la table des matières.

Transport Canada Transports Canada

PUBLICATION DATA FORM

1. Transport Canada Publication No.
TP 12860E

2. Project No.
8896

3. Recipient's Catalogue No.

4. Title and Subtitle
Adhesion of Freezing Precipitates to Aircraft Surfaces

5. Publication Date
November 1996

6. Performing Organization Document No.

7. Author(s)
Y. Boluk

8. Transport Canada File No.
D-1455-14

9. Performing Organization Name and Address
Optima Speciality Chemicals & Technology Inc.
2203 Beaconsfield Ave., Suite 2
Montreal, Quebec
H4A 2G9

10. PWGSC File No.
XSD-5-01692

11. PWGSC or Transport Canada Contract No.
T8200-5-5547/001-XSD

12. Sponsoring Agency Name and Address
Transportation Development Centre (TDC)
800 René Lévesque Blvd. West
6th Floor
Montreal, Quebec
H3B 1X9

13. Type of Publication and Period Covered
Final

14. Project Officer
B. Myers

15. Supplementary Notes (Funding programs, titles of related publications, etc.)
This report was produced for the Transportation Development Centre on behalf of Civil Aviation.

16. Abstract

A review of the ice adhesion studies in the literature was undertaken, followed by a study of the adhesion process of freezing precipitates on aircraft surfaces and an investigation of factors affecting ice adhesion.

The adhesion strength of ice depends upon the material type and roughness of the surface, presence of lubricating surface layer, type of ice, nature of ice formation and purity of freezing ice. The adhesive strength of ice was 1.65 MPa on steel surfaces. The adhesive strength was as low as 0.07 MPa on polished steel surfaces. Adhesion of ice to clean bulk plastics such as nylon and polyethylene was low (0.32-0.08 Mpa) compared with metals but still too high for those plastics to be recommended as icephobic surfaces. However, ice could be removed easily from lubricated plastics surfaces. Lubricants such as silicone grease and petroleum grease reduced the ice adhesion strength to plastics to zero. The lowest ice adherant material was heterogenous polymers. Surfaces of organopolysiloxane modified with lithium compound (SIII), organopolysilixane grafted fluoro polymer (FX) and polyperfluoroalkyl acrylate combined with hydrophobic silicium dioxide (NX) almost completely prevented the ice adhesion.

Deicing and anti-icing fluids, even after their failure, reduce the adhesive strength of ice and freezing precipitation. Anti-icing fluids are more effective than deicing fluids to lower the adhesive strength of ice. The adhesive strength of ice and failed de/anti-icing fluids would be in the order of 10^{-3}-10^{-1} MPa. Aircraft wings are subject to a maximum shear stress of 10^{-4} MPa before rotation. This level of shear stress is not sufficient to clear the wing from ice, slush and failed fluid mixtures just before take-off. The low adhesion strength of slush and ice on failed fluids make consecutive deicing operations speedy and easy. Caution must be exercised in case of a non anti-iced dry snow operations if the aircraft is refuelled with warm fluid and there is no wind.

17. Key Words
Ice, adhesion, freezing, glycol, deicing, anti-icing

18. Distribution Statement
Limited number of copies available from the Transportation Development Centre

19. Security Classification (of this publication)	20. Security Classification (of this page)	21. Declassification (date)	22. No. of Pages	23. Price
Unclassified	Unclassified	—	xviii, 44	—

Canada

Transports Canada Transport Canada

FORMULE DE DONNÉES POUR PUBLICATION

1. N^{o} de la publication de Transports Canada TP 12860E	2. N^{o} de l'étude 8896	3. N^{o} de catalogue du destinataire

4. Titre et sous-titre

Adhesion of Freezing Precipitates to Aircraft Surfaces

5. Date de la publication

Novembre 1996

6. N^{o} de document de l'organisme exécutant

7. Auteur(s)

Y. Boluk

8. N^{o} de dossier - Transports Canada

D-1455-14

9. Nom et adresse de l'organisme exécutant

Optima Speciality Chemicals & Technology Inc.
2203 Beaconsfield Ave., Suite 2
Montreal, Quebec
H4A 2G9

10. N^{o} de dossier - TPSGC

XSD-5-01692

11. N^{o} de contrat - TPSGC ou Transports Canada

T8200-5-5547/001-XSD

12. Nom et adresse de l'organisme parrain

Centre de développement des transports (CDT)
800, boul. René-Lévesque Ouest
6^{e} étage
Montréal (Québec)
H3B 1X9

13. Genre de publication et période visée

Final

14. Agent de projet

B. Myers

15. Remarques additionnelles (programmes de financement, titres de publications connexes, etc.)

Ce rapport a été produit pour le Centre de développement des transports au nom de l'Aviation civile.

16. Résumé

Recherche documentaire sur les ouvrages traitant du phénomène d'adhésion des précipitations givrantes; description du phénomène d'adhésion du givre sur les surfaces des aéronefs et étude des paramètres régissant ce phénomène.

La force d'adhésion des précipitations givrantes dépend de la nature du matériau sur lequel il se forme, de l'état du fini superficiel, de la présence ou de l'absence d'une couche lubrifiante, de la forme de précipitation givrante, de la nature du givre qui se forme et de la pureté de celui-ci. La force d'adhésion du givre sur l'acier inoxydable a été établie à de 1,65 MPa; sur l'acier poli, elle est très faible, pouvant tomber à 0,07 MPa. Sur le plastique de grande consommation en état de propreté, tel que le nylon et le polyéthylène, les valeurs d'adhésion sont faibles (0,32 - 0,08 MPa) comparativement à celles sur les métaux, mais quand même trop élevées pour qu'on puisse recommander ces matériaux comme surfaces empêchant la formation de givre. Il a cependant été constaté que le givre s'enlevait facilement des surfaces plastiques si elles étaient lubrifiées par un produit tel que la graisse de silicone ou de pétrole, qui a la propriété de rendre nulle la force d'adhésion du givre sur le plastique. Le matériau sur lequel le givre adhère le moins est le polymère hétérogène. Les matériaux tels que les polyorganosiloxanes modifiés aux composés de lithium (SIII) ou sur lesquels on greffe un polymère fluoré (FX), ainsi que les acrylates de polyperfluoroalkyl associés au dioxyde de silicium hydrophobe (NX), ont empêché la formation de givre presque complètement.

Même inopérants, les liquides dégivrants ou antigivrage abaissent la force d'adhésion des précipitations givrantes telles que le givre, bien que les liquides antigivrage soient plus efficaces en ce sens que les dégivrants. La force d'adhésion mesurée est de l'ordre de 10^{-3} à 10^{-1} MPa, alors que les forces de cisaillement aérodynamique maximales agissant sur les ailes d'un aéronef sont de l'ordre de 10^{-4} MPa avant le cabrage. Celles-ci ne sont donc pas assez puissantes pour que le givre, la neige fondue et les résidus du liquide dégivrant/antigivre ayant perdu son efficacité se détachent durant le décollage et avant le cabrage. L'abaissement de la force d'adhésion du givre et de la neige fondue aux surfaces des aéronefs recouvertes d'un liquide dégivrant/antigivre même inopérant facilite les opérations de dégivrages subséquentes. Cependant, des précautions s'imposent dans le cas d'une neige sèche sur des surfaces non recouvertes d'un antigivre, lorsqu'on fait le plein avec un carburant tiède et que le vent ne souffle pas.

17. Mots clés

Givre, force d'adhésion, gel, glycol, dégivrage, antigivrage

18. Diffusion

Le Centre de développement des transports dispose d'un nombre limité d'exemplaires.

19. Classification de sécurité (de cette publication) Non classifiée	20. Classification de sécurité (de cette page) Non classifiée	21. Déclassification (date) —	22. Nombre de pages xviii, 44	23. Prix —

ACKNOWLEDGEMENTS

Optima SC&T Inc. would like to thank Scientific Authority Mr. Barry Myers of the Transportation Development Centre of Transport Canada and Mr. Frank Eyre for their guidance and assistance in coordination of the project.

EXECUTIVE SUMMARY

Optima Specialty Chemicals and Technology Inc. undertook this study to investigate the adhesion of freezing precipitates to de/anti-iced and non-deiced aircraft surfaces at the request of the Transportation Development Centre (TDC) of Transport Canada.

The research activity focussed on two types of freezing precipitation adhesion:

1. The adhesion of slush, ice and snow which are formed on and in a de/anti-icing fluid subject to freezing precipitation.

2. The adhesion of dry snow on warm aircraft surfaces.

1. Background study

A background study was performed to establish the present state of research and knowledge on the adhesion of freezing precipitation on aircraft surfaces. It included:

1.1 Literature Review

Literature on ice adhesion was reviewed and a summary presented. According to the studies in the literature, adhesive strength of ice on stainless steel was quite high, up to 1.65 MPa. On polished steel surfaces, the adhesion strength of ice was as low as 0.07 MPa. Adhesion of ice to clean bulk plastics such as nylon and polyethylene is low (0.32- 0.08 MPa) compared with that to metals but still too high for those plastics to be recommended as icephobic surfaces. However, ice was removed easily from lubricated plastics surfaces. Lubricants such as silicone grease and petroleum grease reduced the ice adhesion strength of plastics to zero.

1.2 Research Activities

Studies and theoretical models developed on physics of ice adhesion, lubricity of failed de/anti-icing fluid between ice and aircraft surfaces were reviewed. Test methods on ice adhesion were investigated.

1.3 Research at MIT

Research activity at Massachusetts Institute of Technology (MIT) was reviewed.

2. Fluid failure definition

The mechanisms of de/anti-icing fluid failure under conditions of freezing precipitation were described.

3. Definition of adhesion

The technical definitions of adhesion for the deposition of slush, ice and snow in the presence of de/anti-icing fluids were developed. The shear strength of ice adhesion on aircraft surfaces was interpolated based on adhesion values in the literature. The conditions needed to remove the failed fluid under the aerodynamic shear stress at take-off before rotation were described.

4. Factors affecting adhesion

The principal independent variables which affect the adhesion were identified. They are:

4.1 Hydrophobic nature of surfaces

Treatment of wing surfaces with anti-icing fluids causes surface hydrophobicity and reduces wetting and adhesive bonding characteristics. The hyrophobicity and surface finish as factors affecting adhesion of failed fluid and ice were investigated.

4.2 Temperature

The effect of temperature on the rheology of failed fluid, lubricity of a thin fluid layer between ice and surfaces, and shear strength of freezing contamination were investigated.

4.3 Surface Profile

The effects of aircraft wing surface profiles and joints on adhesion were investigated.

4.4 Lubricity of thin de/anti-icing fluid layer

5. Conditions for adhesion in the absence of protective fluid

The limiting conditions for the adhesion of frozen precipitation on an aircraft surface were outlined. A schematic representation was postulated showing maximum air temperature at which there is no adhesion.

SOMMAIRE

À la demande du Centre de développement des transports (CDT) de Transports Canada, la firme Optima Specialty Chemicals and Technology Inc. a mené une étude sur l'adhésion de certaines formes de précipitations aux surfaces d'un aéronef arrosées et non arrosées d'un liquide dégivrant et (ou) antigivrant.

La recherche s'est concentrée sur les deux formes principales d'adhésion, à savoir :

1. Adhésion de givre, de neige et de neige fondante qui s'accumulent sur le liquide dégivrant/antigivrant ou qui existent à l'intérieur de celui-ci.

2. Adhésion de neige sèche sur des surfaces d'aéronef chaudes.

1. Recherches préliminaires

Des recherches préliminaires ont été faites pour déterminer l'état de la recherche et du développement dans le domaine de l'adhésion de certaines formes de précipitations givrantes aux surfaces des aéronefs, à savoir :

1.1 Une recherche documentaire

Les études traitant de l'adhésion du givre, consultées dans le cadre de la recherche documentaire, montrent que les valeurs d'adhésion du givre sur l'acier inoxydable sont très élevées, pouvant atteindre 1,65 MPa, et que sur l'acier poli elles sont très faibles, pouvant tomber à 0,07 MPa. Sur le plastique de grande consommation en état de propreté, tel que le nylon et le polyéthylène, les valeurs d'adhésion sont faibles (0,32 - 0,08 MPa) comparativement à celles sur les métaux, mais quand même trop élevées pour qu'on puisse recommander ces matériaux comme surfaces empêchant la formation de givre. Il a cependant été constaté que le givre s'enlevait facilement des surfaces plastiques si elles étaient

lubrifiées par un produit tel que la graisse de silicone ou de pétrole, qui a la propriété de rendre nulle la force d'adhésion du givre sur le plastique.

1.2 Des recherches

Examen des études menées et des modèles théoriques élaborés concernant les principes physiques expliquant l'adhésion du givre et sur l'effet lubrifiant du liquide dégivrant/ antigivrant agissant comme interface entre le givre et les surfaces d'aéronefs quand ce liquide a cessé d'être efficace. Examen des méthodes pour mesurer la force d'adhésion du givre.

1.3 Examen des recherches menées au MIT

Des recherches au Massachusetts Institute of Technology (MIT).

2. Description de la cessation d'efficacité

Le mécanisme par lequel un liquide dégivrant/antigivrant cesse d'être efficace dans des conditions de précipitations givrantes a été décrit.

3. Définition du phénomène d'adhésion

Définition du phénomène d'adhésion dans le cas de l'accumulation de givre, de neige et de neige fondante en présence d'un liquide dégivrant/antigivrant. La résistance au cisaillement, ou cohésion, du givre aux surfaces des aéronefs a pu être obtenue par interpolation, à partir des valeurs d'adhésion données dans les ouvrages publiés. Description des conditions dans lesquelles les forces de cisaillement aérodynamique durant le décollage et avant le cabrage font se détacher les résidus du liquide qui a cessé d'être opérant.

4. Paramètres régissant les forces d’adhésion

Les principales variables indépendantes régissant les forces d’adhésion ont été reconnues. Ce sont :

4.1 L’hydrophobicité des surfaces

L’arrosage des ailes avec un liquide antigivrant rend celles-ci hydrophobes et abaisse le pouvoir mouillant ainsi que la force d’adhésion. L’action de l’hydrophobicité et de la finition superficielle sur l’adhésion du givre en présence d’un liquide antigivre inopérant a été approfondie.

4.2 La température

L’influence de la température sur la rhéologie d’un liquide antigivre inopérant, sur l’effet lubrifiant de l’interface de ce liquide et sur la cohésion des précipitations givrantes a été examinée en profondeur.

4.3 L’état des surfaces

L’effet de l’état des surfaces et des joints sur l’adhésion a lui aussi été examiné.

4.4 L’effet lubrifiant du liquide dégivrant/antigivrant

5. Conditions aux limites

Le rapport esquisse les conditions aux limites de l’adhésion des précipitations givrantes aux surfaces des aéronefs et fixe les idées au sujet de la température maximale de l’air à laquelle le risque d’adhésion devient nul.

CONTENTS

Page

Page

LIST OF FIGURES

Page

LIST OF TABLES

1. INTRODUCTION

The formation of ice deposits on aircraft surfaces can adversely affect the aerodynamic characteristics of airfoils. Therefore, Canadian Air Regulation 540.2(2) requires that wings, control surfaces and propellers of an aircraft must be free from adhesion of frost, ice or snow before take-off. Aircraft ground deicing/anti-icing fluids play a vital role in cold weather procedures to ensure that an aircraft is free of ice, frost and snow contamination at takeoff.

There are two kinds of fluids airlines use during ground deicing operations. Those are: aircraft deicing fluids (Type I) and aircraft anti-icing fluids (Types II, III, IV). Aircraft deicing fluids are used to remove the accumulated ice contamination and to clean aircraft surfaces. Because deicing fluids have low viscosities, they offer very little protection time against continuing precipitation.

Aircraft anti-icing fluids are used to prevent ice, snow or frost build-up on aircraft surfaces during precipitation. The protection time of those fluids depends on precipitation conditions in addition to fluid properties. Under conditions of freezing precipitation, visual inspection is required to make a decision as whether the applied de/anti-icing fluid on the aircraft surfaces has failed. In some cases, such as at the gate or at the time of de/anti-icing, ground crew personnel are present to advise to the pilot. However, in other cases the tactile and visual inspections required by the regulations pose problems. It is difficult to visually identify the true fluid failure when the rate of absorption of falling precipitate by an anti-icing fluid is low. Slush, ice or snow may be present in the fluid which has not failed. The ultimate problem is to ascertain the adhesion of precipitate, which determines true failure point of de/anti-icing fluid.

Precipitation temperature, ambient air temperature, water content of precipitates, wing surface temperature, and wind velocity play a decisive role on the adhesive nature of freezing precipitates. The adhesive properties of freezing precipitates increase around freezing point. On the other hand, if the ground ambient temperature is very low, freezing precipitation becomes dry and does not adhere on the surfaces. However, the adhesion limits of precipitates are not well known. For example, the adhesion of dry snow might indeed be possible on warm aircraft surfaces.

The objective of this project was to review the literature and develop an understanding of the mechanism of the ice adhesion on aircraft surfaces. Since the adhesion of ice to surfaces has many practical and safety aspects, the literature search included the studies of ice on paints, naval vessels, bridges, road pavements, and electrical transmission lines in addition to fundamentals of adhesion. Chapter 2 presents the literature survey on ice adhesion. Chapter 3 describes the fluid failure from the view of ice adhesion. The ice adhesion process is presented in Chapter 4, and factors affecting ice adhesion are reviewed and discussed in Chapter 5. The adhesion conditions of dry snow are discussed in Chapter 6.

2. BACKGROUND STUDY

2.1 Literature review

There are numerous studies in the literature which have investigated the adhesion of ice on various substances. The experimentation of ice adhesion under controlled conditions with natural ice is sometimes difficult, therefore some of the studies in the literature used artificial ice. Investigations have focussed on ice adhesion to ships, bridge decks, highways, electrical switches, lubricated machinery, aircraft and helicopters. Greater effort was put into the study of aeronautical icing problems, which includes aircraft, helicopters and runways. In addition to fundamental works on the adhesion of ice, extensive searches have been conducted in the hope of finding a “miracle coating” that would allow effortless ice removal from surfaces. The results and conclusions of those studies will be reviewed in this section.

The instability of ships in icing conditions has been recognized for hundreds of years, but it was only after the loss of the British trawlers “Lorella” and “Roderigo” in the early 1950s the British Shipbuilding Research Association carried out cold room model tests and investigated the effects of ship design on ice build-up. The former USSR had carried out much work on the theoretical aspects of ship icing but no practical solutions were developed. Those studies were reviewed by Minsk in “Icing on Structures”(1)[*] and Sawyard in “Seeking Low Ice Adhesion”(2). The U.S. Navy decided there was no strong need for icephobic coatings. However, the U.S. Navy later changed its position (3). Ono also studied the conditions of icing and accreted ice weights on ships (4). He was unable to pin down the relationship between the latent heat balance and the weight of pure ice formed, but he discovered that it was necessary to take the weight of ice accretion as roughly twice the weight of pure ice formed from the captured spray.

The adhesions of ice to electrical switches and electrical power conductors were investigated by Mundon (5), Druez et al. (6), Phan et al. (7) and Laforte et al. (8). Studies measured the adhesive strength of natural rime and glaze impact ice on aluminum electrical power conductor cables. In

***** *References are listed in Section 8* those works, the adhesive shear strength was shown to vary from 0.067 MPa to 0.40 MPa, and appeared to increase with both wind velocity and surface roughness. The greatest variation in adhesion was observed with surface roughness. The adhesive shear strength was found also to increase with wind velocity.

One of the earliest works on the adhesion of ice to various surfaces-related aeronautical icing was done by Lougborough and Haas (9). The shear strength of refrigerated ice was found to reach 1.72 MPa. Adhesion of artificial ice to metals and polymers was also studied. They found the adhesive shear strength varied from 1.52 MPa for aluminum to 0.85 MPa for copper. Those relatively high adhesion strength values were probably due to the nature of artificial ice. Artificial ice is by nature more homogeneous and hard solid and gives higher interfacial contact areas with test substrates. Beams et al.(10) used the first rotating rotor centrifugal force technique to measure adhesive and tensile strength of thin films of ice on metal. Raraty and Tabor (11) used the same method to measure the adhesive shear strength of ice, on polished, cleaned stainless steel. They measured the shear strength of ice as 1.96 MPa at 10°C. Jellinek (12) studied the adhesive and cohesive strength of a snow-ice sandwiched between polished circular 304 SS plates approximately 0.3 cm apart. Shear stresses were developed from torsional loads. Using the “sandwich” technique he found the adhesive strength of ice on stainless steel to be quite high, up to 1.65 MPa at –14°C. Bascom et al. (13) and Ford and Nichols (14) measured somewhat lower values of 1.63 MPa and 0.24 MPa, respectively, for polished stainless steel. Kuroiwa (15) attempted to measure the adhesive shear strength of natural impact ice from the top of Mt. Nisekoan-Nupuri. The calculated strength was quite high, 2 MPa at –10°F and 3 MPa at –5°C.

On the other hand, Stallabrass and Price (16), and more recently, Itagaki (17,18) found the adhesive shear strength of ice to be quite low, ranging from 0.03-0.07 MPa at -6°C and 0.03-0.16 MPa at the temperature range from -1 to -15°C. Those investigators used another measurement technique, the dynamic rotating rod centrifugal force technique.

Kozitsokii (21) studied the effect of surface roughness on 304 SS plates. He investigated three types of surfaces: a machined surface, a mat surface finish, and a mirror polish 127-178 µm. Mean adhesive shear strengths were 0.6 MPa, 0.26 MPa, 0.07 MPa respectively, for a snow-ice layer 0.1-0.2 cm thick and a cross section of 0.26 cm^2. Thus, increasing surface roughness can increase the shear strength by a factor of 10.

One of the most extensive studies on ice adhesion was conducted by Chu and Scavuzzo (20). T hey investigated the adhesive strength of impact ice formed in an icing tunnel as a function of tunnel temperature, wind speed, water droplet size, substrate material (aluminum vs. steel), substrate surface roughness and substrate/impact ice temperature. The NASA Lewis Research Center Icing Research Tunnel (IRT) was used for testing. IRT is a closed-return low speed refrigerated wind tunnel. Its test section is 1.83 m high and 2.74 m wide. The airspeed in the test section can be varied from 30 km/h to 480 km/h, and the tunnel temperature can be varied from above 0 °C down to about −30 °C. More than 200 points were collected. In general, the adhesive shear strength of impact ice is found to be highly stochastic in nature. It is independent of substrate material, tunnel temperature T<-7 °C and ice thickness. It has weak linearly increasing correlation with droplet momentum. On the other hand, it has strong correlations with the following factors: the shear strength linearly decreased with increasing ice/substrate surface temperature at T>-4°C, and there was a marked linearly increasing correlation with substrate surface roughness. It was found that the adhesive strength was 0.12 MPA for rime ice and 0.41 MPa for glaze ice. Therefore, it was concluded that the adhesive shear strength of rime ices is much weaker than that of glaze ices. While glaze ice is a homogeneous transparent hard continuum solid, rime ice is nonhomogeneous, consisting of powdery ice particles, shaped into finger-like structures.

An early literature review on coating materials to prevent ice adhesion was given by Porte et al. (21). Ahlborn et al. (22) and Dohaney et al. (23) investigated methods to reduce the adhesion of ice onto pavements and highways. Those studies were directed specifically to the development of hydrophobic material coatings for highway surfaces to reduce the adhesion of ice of such surfaces. Polymers having low critical surface tension such as organopolysiloxane and tetrafluoroethylene were tried. The applied cost of those polymers ranged from 0.08 $/m^2 to 0.69 $/m^2 . Those coatings exhibited satisfactory traction on wet roads, produced very low runoff water contamination, and demonstrated a significant reduction in ice adhesion. However, the coatings were unsuccessful because of their very short service life. They did not meet the goal of one season long effective service life. Keyser (24) studied the role of deicing chemicals on the adhesion of ice to pavements. The positive impact of deicing chemicals on ice release was found due to the ice melting characteristics of such chemicals. Croutch and Hartley (25) investigated more than 50 paint formulations in an effort to minimize ice adhesion. Those studies involved alkyd coatings, silicone coatings, fluorinated coatings, latex paints and polyethylene glycol PEG 400. Fluorinated and polysiloxane modified surfaces showed the poorest wetting by water and the best candidate for icephobic coatings. Latex paints, because of their hydrophilic nature, gave the higher ice adhesion values. Differences in ice adhesion were observed for ice produced from natural seawater, synthetic seawater, fresh distilled and boiled distilled water.

Murase et. al. (26) investigated the adhesion of ice on heterogeneous polymer systems. Surfaces of organopolysiloxane modified with lithium compound (SIII), organopolysilixane grafted fluoro polymer (FX) and polyperfluoroalkyl acrylate combined with hydrophobic silicium dioxide (NX) were used in the study. It was found that ice adhesion can be almost completely prevented by the composite material (SIII).

Baker et al.(27) and Ford and Nichols (14) researched the adhesion of ice to lubricated surfaces. According to those studies, adhesion of ice to clean bulk plastics such as nylon and polyethylene is low (0.32- 0.08 MPa) compared with that to metals but still too high for those plastics to be recommended as icephobic surfaces. However, ice was removed easily from lubricated plastics surfaces. Lubricants such as silicone grease and petroleum grease reduced the ice adhesion strength of plastics to zero.

The difference in values of the adhesive shear strength measured by various investigators could be attributed to many factors. The most significant ones are:

- the types of ice used in the experiment (natural, wind tunnel, refrigerated, rime, glaze);
- the conditions of substrate surfaces (clean, lubricated, rough, smooth, hydrophobic);
- the methodology of measurements (static, quasistatic, dynamic);
  and
- statistical adequacy of data points collected, which is necessary because of the inherent highly stochastic nature of properties of ice.

Further investigations are necessary to collect more extensive data and investigate the effects of wind speed, drop size, and water content on ice adhesion.

2.2 Research activities

The research activities on ice adhesion are reviewed in two domains. Those are: 1) test and evaluation methods; and 2) search for material and conditions which minimize ice adhesion.

2.2.1 Test and evaluation methods

1. Method used by Murase et al.(26)

For the evaluation of adhesive forces of ice, Murase et al. built a test device which consists of temperature-regulated chamber, process controller, load cell and recorder. The stainless-steel metal ring with inside section area 5 cm^2, height 1.5 cm, was set on a polymer surface of test plates and precooled for 90 minutes at the predetermined temperature: then 2 ml of distilled deionized water stored at 25°K was poured into the ring. After 3 hours at that temperature, shear strength of ice adhesion was measured. A substrate of test pieces made of stainless steel was 70x90x10 mm in size, and with this apparatus, the adhesion of ice on polymers with heterogenous chemical structures was tested.

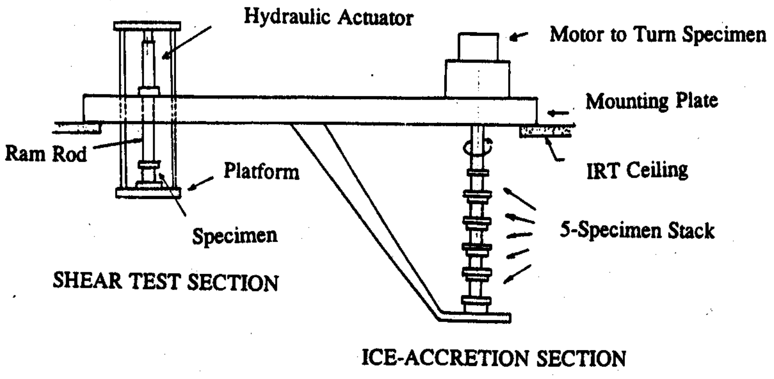
ii. Adhesion-shear test apparatus

Ford and Nichols(14) used adhesion-shear apparatuses which consists of a specimen holder, plunger, jack support and hydraulic jack. The specimen was prepared with an ice formation on a test substrate. With this apparatus they measured the adhesion bond of ice on clean and lubricated brass, stainless steel, nylon, teflon and polyethylene surfaces.

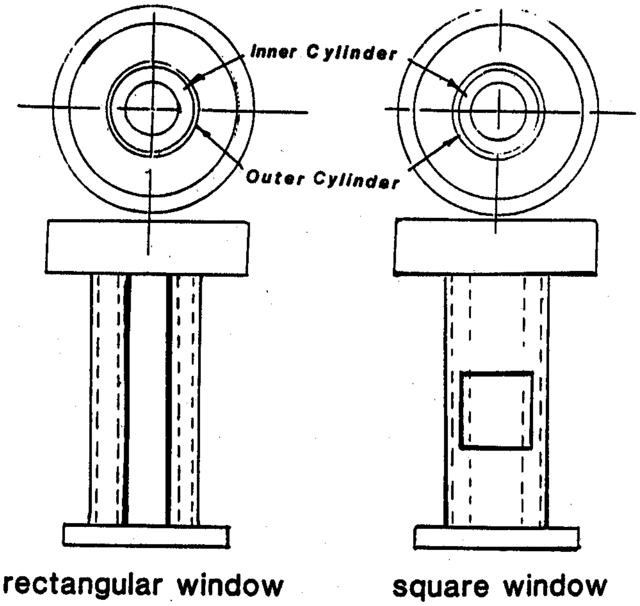
iii. Shear strength test apparatus

One of the common apparatus for adhesion testing of impact ices, uses cylindrical specimen ice holder geometry. It was used by Chu (20) and others. Figure 1 shows a schematic diagram of test apparatus to determine the adhesive shear strength of impact ices. As shown, the equipment has two main sections 1) the ice forming section where impact ices are accreted on the test specimens, and 2) the test section where the adhesive shear force is measured. The device is placed in the cold room. Instrumentation of the test section stays outside the cold room. The test specimen (see Figure1) consists of a thin outer cylinder with window and end flanges and a hollow inner rod. The impact ice is accreted through the window on the inner rod. The material to be tested must be fabricated in hollow rod forms as test specimens.

Such particular geometry was useful to measure the adhesion of rime ice on various machined metal cylinders. However, it is not be appropriate for the adhesion measurement of snow or other precipitations with and without de/anti-icing.



(a)



(b)

Figure 1. Common apparatus for adhesion testing of impact ices

a) Test apparatus; b) Ice specimen holder

iv. Centrifugal apparatus

Stallabrass and Price used a whirling arm apparatus(16). This apparatus consisted of a two-bladed, 9- foot diameter rotor situated in a 10 foot x 10 foot cold chamber. Test specimens were basically 1/2 inch diameter cylinders, 3 inches long. To ensure a constant area of ice accretion, two parallel flats 0.375 inches apart were milled on opposite sides of the cylinder, parallel to the relative air flow, thus confining the ice accretion to the forward facing curved surface having an area of 1.27 square inches.

The centrifugal force exerted by the ice at the moment that the ice/specimen interfacial bond breaks down is the adhesive shear force of the bond. The centrifugal load of the specimen was measured by strain gauges.

2.2.2 Materials and conditions

The studies in the literature were focussed on ice adhesion on various metals and plastics. Some of the studies investigated the effects of lubricants on metal surfaces and freezing point depressants such as salt in freezing water. The ice adhesion characteristics of various surfaces are presented in Table 1.

Various investigators studied the dependence of the adhesive strength with various factors:

- air temperature
- wind speed
- water droplet size
- substrate material
- substrate surface roughness; and
- substrate/impact ice temperature.

The adhesive shear strength of impact ice was found to be highly stochastic in nature.

No study was found in the literature on the subject of ice adhesion on aircraft wings after the failure of de/anti-icing fluids.

Table 1. Comparison of ice adhesion characteristics of surfaces

Surface	Type of ice	Shear Strength, MPa	Reference
Aluminum	Artificial ice	1.52	9
Aluminum	Rime ice	0.60	16
Titanium	Rime ice	0.30	16
Copper	Artificial ice	0.85	9
Aluminum	Rime and glaze impact ice	0.067-0.40	8
Stainless steel	Snow-ice	1.65	12
Stainless steel	Natural ice	1.63	10
Stainless steel	Artificial ice	1.96	11
Nylon	Artificial ice	0.325	25
Polyethylene	Artificial ice	0.08	25
Teflon	Artificial ice	0.025	14
SIII	Artificial ice	0.0	26
Silicone grease	Artificial ice	0.0	14

Note: By comparison, the applied aerodynamic shear stress on a wing during rotation is less than 10^{-4} MPa.

In the literature the problem of ice adhesion was described by the following features:

- One of the components (ice) is close to its melting point

- Either phase transition or very fast mass transfer on the surface makes the contact area grow quickly to a size comparable to that of one of the components (ice).

Such conditions are closer to bonding by an adhesive than to adhesion between two solids in contact, in which case the contact area is pretty much limited and considerable internal stress exists within the contact area. Therefore the ice adhesion was treated as liquid (adhesive) spreading and liquid/solid interfacial interaction phenomena in the literature. Itagaki (17,18) and Murase et al. (26) have used a surface energetics approach in their studies to the adhesion problem. Those studies can be named as one of the key researches to the ice adhesion problem. We have chosen the same approach to explain the ice adhesion on top of failed de/anti-iced fluids and non deiced surfaces in the preceding sections.

2.3 Research at MIT

A research group directed by Hansman has been investigating various aspects of aircraft icing process since the 80s. The group started to work on flight icing and later focussed on ground icing as well.

Hansman (27) studied droplet size distribution effects on aircraft ice accretion. The impinging mass flux distribution which determines an aircraft ice accretion rate was shown to be related to the atmospheric droplet size distribution through the droplet collection efficiency of the body. Collection efficiency was studied be means of a two-dimensional droplet trajectory code which includes the effect of nonspherical droplet shape due to hydrodynamic deformation. The intermittent maximum icing envelope of Federal Aviation Regulation, Part 25 was also modelled.

In another study (28), a series of experimental investigations focussed on isolating the primary factors that control the behaviour of unfrozen surface water during glaze ice accretion. Detailed micro video observations were made of glaze accretions on 2.54 cm diameter cylinders in a closed loop refrigerated wind tunnel.

Recently Hansman has been investigating the adhesion of ice using a centrifugal apparatus, similar to that described in Section 2.2.1.

3. DEFINITION OF FLUID FAILURE

Canadian Air Regulation 540.2(2) requires that wings, control surfaces and propellers of an aircraft must be free from adhesion of frost, ice or snow before take-off. The rationale behind this concept is that the presence of even minute amounts of contamination in form of frost, ice, or snow on aircraft surfaces can cause a dangerous degradation of aircraft performance. The regulations are very clear in terms of the definition of contamination and zero tolerance policy. However, the term “adhering” in the regulations lacks a clear description. The meaning of adhesion is especially important in the case of an anti-icing fluid failure under precipitation. A fluid must be accepted as failed when the precipitates start to adhere to surfaces. Therefore, the adhesive property of precipitation/failed fluid mixture onto surfaces needs a better description.

3.1 Fluid failure

Aircraft anti-icing fluids are used to prevent the deposition and adhesion of ice, snow and frost on aircraft surfaces for a certain period of time under continuous precipitation. The protection time which is usually referred as Holdover Time is defined by the duration of time. During the holdover time, an anti-icing fluid resists freezing precipitation. The failure point marks the end of the holdover time. An anti-icing fluid must be considered as failed, once the precipitation starts to adhere to the aircraft surfaces and degrades the aerodynamic properties. Therefore, the three phenomena are:

- the fluid failure;
- adhesion of precipitated contamination; and
- the aerodynamic performances are directly related to one another.

The physical state of precipitation contaminated anti-icing fluid can be characterized in various forms, such as “loss of gloss”, snow build-up, slush, and ice. The formation of those forms depends on the precipitation conditions, such as precipitation density, temperature, type of precipitation, water content of precipitation, in addition to the exposure time of the fluid to the precipitation. The exposure time of fluid with the rate of precipitation determines the fluid film thickness and freezing point depressant glycol concentration. To define the fluid failure and adhesion of precipitation contaminated (failed) anti-icing fluid, one has to describe the freezing process of a precipitation diluted anti-icing fluid mixture.

3.2 Growth of ice crystals and slush formation

Prior to examining the adhesion of ice from failed de/anti-icing fluids, the work was carried out to investigate the ice formation and freezing processes in the fluid during failure.

Aircraft anti-icing fluids are used to protect aircraft surfaces against on-going precipitation. With appropriate flow properties, aircraft anti-icing fluids adhere to the aircraft surfaces and attain thicknesses of typically 0.1-1 mm. The fluid film thicknesses vary with time, location on the inclined surface and precipitation intensity. As time passes, the fluid film gets thinner and the glycol (freezing point depressant) concentration in the fluid decreases. Since the mixing of fluid and precipitation is not instantaneous, the deicing fluid becomes heterogeneous. The most common observation of this point is a “loss of gloss” in the fluid. This happens when the fluid saturates with precipitates.

Figure 2 shows schematically the freezing process in the fluid. During the snowing process, ice crystals first start to grow out of the fluid. They are not attached to the metal surface but mobile within the fluid layer.

It is important to characterize the nature of freezing in mixtures of precipitation and glycol solutions. Contrary to common belief, a single freezing temperature cannot describe a freezing process of any liquid. In some cases pure water can be supercooled to temperatures of -20°C to -40°C before solidification. Precipitation of droplets in the 20 micron-diameter range commonly exists in the supercooled state down to temperatures as low as -20°C. The rate of heat transfer

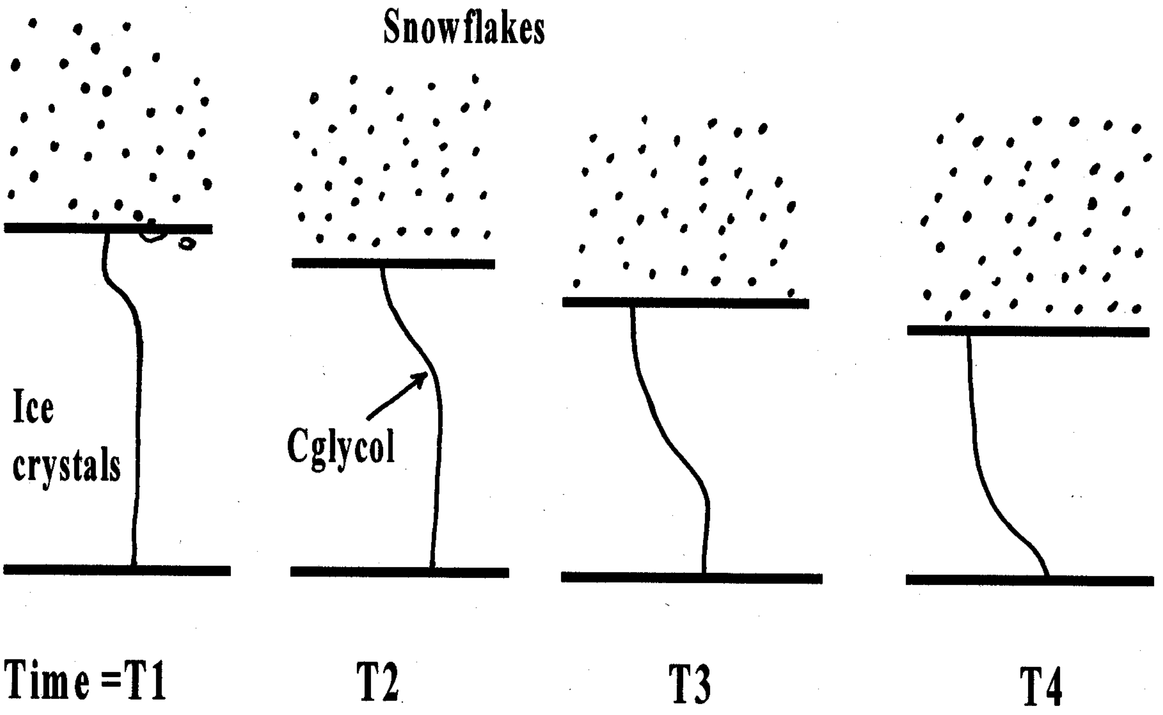


Figure 2. Formation of ice crystals in a de/anti-icing fluid.

also has an impact on freezing point. Lowering the rate of cooling favours the formation of small grain crystals and surface disclocations and should lower adhesion values. Therefore, the inhibition of freezing of ice has far-reaching ramifications to control the adhesion of ice in the field of aviation.

In physical chemistry, there are two points which describe the freezing nature of glycol solution de/anti-icing fluids. Those are: freezing point and pour point.

Freezing point is the onset of crystallization. It is defined by the appearance of the first crystal. The freezing point determination uses ASTM method D 1177. The maximum temperature in the cooling curve gives the freezing point. The ice crystals form on cooling at the freezing point.

Figure 3 shows the freezing diagram of a typical deicing fluid (29). Unlike single component liquids, chemical solutions do not completely freeze and solidify at their freezing points. They start to form non-rigid "slush" below freezing points.

The transformation point from slush to a solid state is called pour point. Unlike a freezing point, a pour point cannot be clearly described with a sudden phase change. Below pour point, slush becomes more solid than liquid.

The glycol solutions in precipitation contaminated anti-icing and deicing fluids exist in slush form between freezing and pour points. During the freezing process of an anti-icing fluid, pure water crystals are initially formed with pockets of concentrated glycol solutions between crystals (30). Under shear, slippage between crystals can occur leading to lower shear adhesion values.

The shear adhesion in failed anti-icing fluids is lower than failed deiced fluids because of their formulations. Unlike deicing fluids, anti-icing fluids contain more complex thickener and surfactant additives (31,32). Those additives can work as lubricants between ice crystals in the slush and cause lower shear adhesion values.

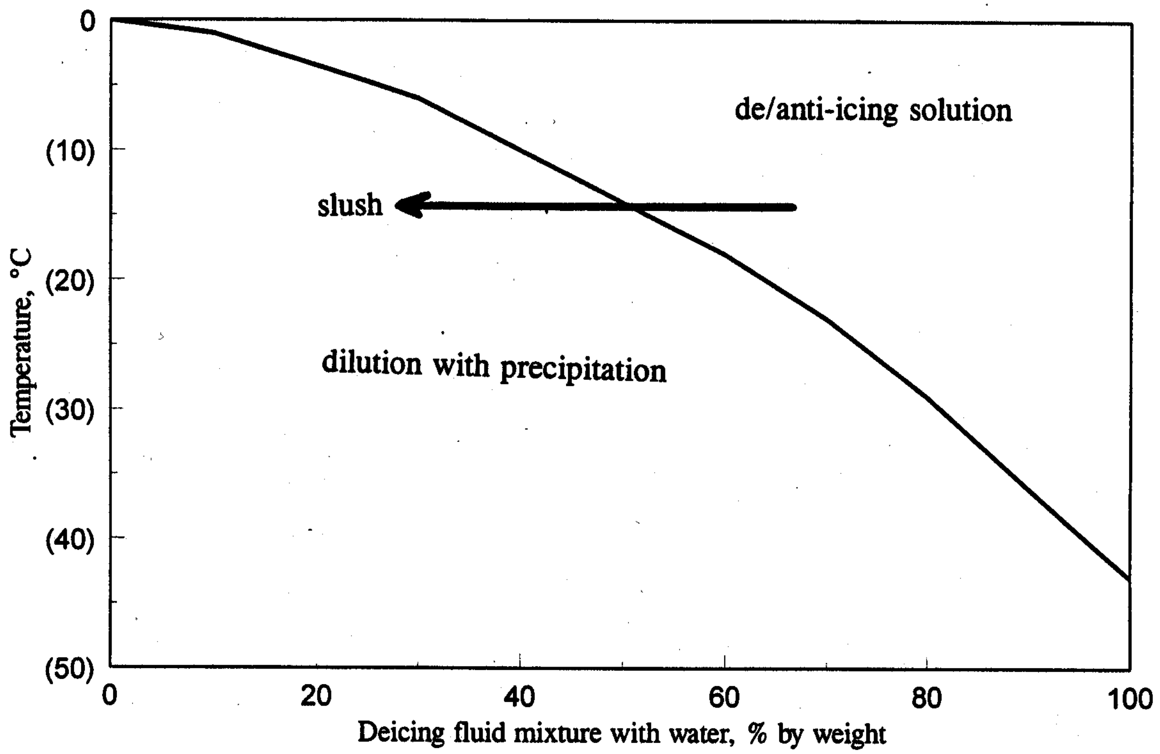


Figure 3. Freezing diagram of deicing fluid/water mixture

4. DEFINITION OF ADHESION

Adhesion is a physical-chemical process in which two surfaces are held together by interfacial interactions. It may consist of intermolecular forces or mechanical interlocking action, or both. This chapter* presents the theoretical aspects and applied surface physics of adhesion. It specifically addresses the adhesion of ice and snow to a wing surface with and without de/anti-icing fluid.

4.1 Wetting theory

In order for ice to adhere to a surface, it is necessary for liquid water to spread on a surface or to "wet." Wetting means to replace the solid substrate/air interface with a substrate/water interface.

The tendency of water to wet the surface can be determined by measuring the contact angle of a water drop on the substrate. When water is at equilibrium with solid substrate and air, we can diagram the contact angle Θ as shown in Figure 1. At point A, the three surface tensions are in equilibrium. Therefore, the force balance gives:

$$\gamma_{LA} \cos \Theta = \gamma_{SA} - \Gamma_{sl}$$

[1]

Equation [1] is generally called Young's equation and where

γ_{SA} = the surface tension at the solid-air interface,
γ_{SL} = the surface tension at the solid-liquid interface,
γ_{LA} = the surface tension at the liquid-air interface.
Θ = Contact angle.

* *Task 3.3 Definition of Adhesion in the Contract*

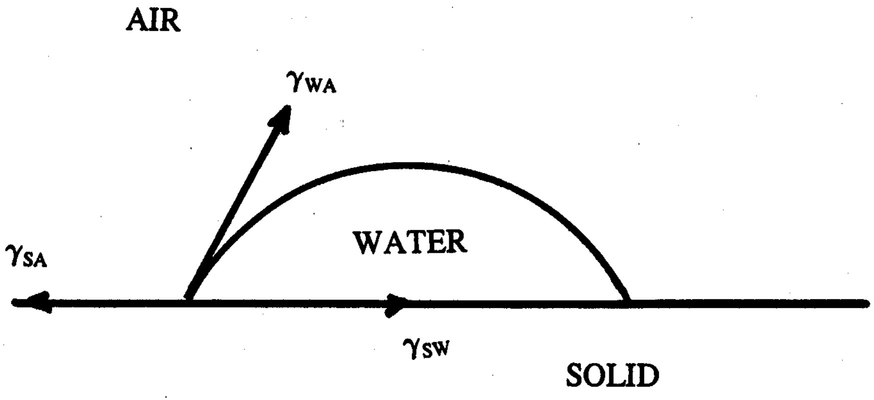


Figure 4. Contact angle and surface energies

The quantity known as the work of adhesion, W_A, between water phase, L and solid substrate, S is given by

$$W_A = \gamma_{LA} + \gamma_{SA} - \gamma_{SL} \qquad [2]$$

Combination of Equations [1] and [2] gives:

$$W_A = \gamma_{LA} (1 + \cos \Theta) \qquad [3]$$

The description of contact angle and theory of adhesion in detail can be found in the literature (35). From Equation [3] it can be seen that when $\Theta = 0°$ then $W_A = 2\ \gamma_{LA}$ and complete wetting occurs with perfect adhesion. When $\Theta = 180°$ then $\cos \Theta = -1$ and so W_A becomes zero with wetting and no adhesion. When $\Theta = 90°$, $W_A = \gamma_{LA}$, with poor wetting and poor adhesion. However, it is impossible to reach $\Theta = 180°$ because the London (see Section 4.2) and dispersion intermolecular forces still act at the interface and hydrophilic sites are still present in hydrophobic surfaces. Therefore it is not possible to produce a surface which water would not wet at all and to which ice would not adhere.

Consequently, for a practical icephobic surface, it is necessary to obtain a surface with $\Theta > 90°$ and with little or no tendency for water to spread spontaneously. For the latter to occur, the work of adhesion W_A must overcome the cohesion to the liquid drop and this can be expressed as

$$S = W_A - W_C \qquad [4]$$

Where S is the spreading coefficient and W_C is the work of cohesion of the liquid. It can be shown that $W_C = 2\ \gamma_{LA}$ and the equation [4] become

$$S = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) \qquad [5]$$

and a liquid will spread on a solid when $S > 0$.

The difficulty here is that γ_{SA} and γ_{SL} cannot be determined using equation [1] alone. This was solved by considering the relationship between the free energy of adhesion, the attractive energy between liquid molecules, dipole moments, polarizability, and ionization energy. The result is given by:

$$\gamma_{SA} = \gamma_{LA} (1 + \cos \theta)^2/4 \qquad [6]$$

Consequently, surface-free energies have been determined for a wide range of metals, oxides, salts, and polymers (33,34,35) and some polymer values are shown in Table 1. Since water has a surface energy of 72 mNm^{-1}, it will not readily wet the various surfaces which have surface energies lower than 72 mNm^{-1}. This would result in poorer adhesion.

Table 2. Surface tensions of substrates

Surface	**Free surface energy mNm^{-1}**
Polyvinylchloride	45
Polystyrene	42
Teflon	20
Polymethyl siloxane film	24
Aluminum	>100
Steel	>100

4.2 Interfacial forces and work of adhesion

Two types of bonds exist in the nature which holds atoms and molecules together. First there are primary chemical bonds (covalent, ionic, and metallic) which hold atoms in the molecules. There are also secondary intermolecular forces which hold molecules together. These types of intermolecular forces at solid/water interface play a key role in the adhesion process.

Intermolecular forces are much weaker secondary forces compared to primary chemical bonds. Two neutral molecules, interacting with little electron orbital perturbation or electron redistribution, can be attracted to each other if an instantaneous fluctuation in one molecule polarizes electrons in the second molecule. This instantaneous dipole-induced dipole is the London dispersion force which acts over an extremely short range. Similar electron polarizations occur with permanent dipoles (including hydrogen bonds) and when dipole-induced dipole (Debye force) interact.

The binding energies involved are 40 to 400 kJ mol^{-1} for covalent and ionic bonds, 4 to 8 kJ mol^{-1} for London dispersion forces, and 8 to 35 kJ mol^{-1} for hydrogen bond forces. The most important force at the solid surface is London dispersion force. The strength of London dispersion forces for adhesion is 30 MPa at a distance of 5 nm from the surface. London dispersion forces are relatively short-range forces. They are effective in the range of a molecular monolayer. However, permanent and induced dipole forces and hydrogen bonds have effects thicker than monolayer. Water is in this category and this explains the strong adhesion of ice onto surfaces. The adhesive bonding of ice and effects of failed de/anti-icing fluid layers are discussed in the following sections.

4.3 Adhesion of ice

While ice is a special case in which the practical emphasis is on good abhesion (i.e., the opposite of adhesion), the principles involved are similar to those in conventional adhesion processes described in the previous section. First water must wet and spread onto the substrate prior to the freezing process. For the start of freezing, nucleating spots at the interface must cause a structural match of water molecules and ice nucleation.

Ice adhesion in terms of wetting theory can be explained as follows. The interfacial tension between water and solid surface was expressed by the equation of Girifalco and Good (36):

$$\gamma_{SL} = \gamma_{SA} + \gamma_{LA} - 2 (\gamma_{SA} \times \gamma_{LA})^{1/2} \qquad [7]$$

Thus the interfacial tension between water and Teflon for example can be found 16.6mNm^{-1}, assuming that the surface tension of Teflon is 20 (Table 1) and the surface tension of water is 72 mNm^{-1}. The interfacial tension is then smaller than the surface tension of Teflon, making spreading of water on Teflon surface energetically favourable. Since the surface energy of ice is 109 mNm^{-1} and much higher than that of water, the interfacial tension becomes 35.6 mNm^{-1}, which is much higher than the surface tension of Teflon, making a smaller interface energetically favourable. If this simplified explanation is applicable further, water may not stay on a substrate having surface tension lower than the interfacial tension γ_{SL}. From Equation [7] the value was calculated to be $\gamma_{SL}/4 = 18.5$ mNm^{-1} or less. If such a low interfacial energy surface was available, water would not stay on the surface and no adhesion would be expected (37).

The ice nucleation is sensitive to nature and orientation of surface groups. Those groups organize water molecules at interfaces and start nucleation of ice. It was observed that at first large crystals were formed and within a few hours smaller polygonal grains were produced by recrystallization(38).

Like any other adhesive layers, the theoretical adhesive strength of ice at the solid interface is expected to be stronger than the bulk strength of ice (39). Nevertheless, the experimental adhesion values of ice on surfaces are an order of magnitude lower than theoretically expected values. In addition, it was found that the adhesion strength of ice varies on different surfaces. For example, with metals, adhesion is good, while with tetrafluoroethylene (Teflon) it is poor. The reason, apparently, is that freezing against a surface that it wets only poorly, air bubbles are produced at the ice-substrate interface(40). These allow stress concentration to lead interfacial crack propagation.

Ice adhesion failures occur due to crack initiation at stress points and are not the results of breakage of chemical bonds. Therefore, it is very difficult to correlate basic theoretical adhesion values with practical adhesion and the difference can be very large. In fact, adhesion values of ice measured on the same type of surfaces by different groups show wide variations. This is in fact due to the method of water and surface preparations, thermal history and test methods.

4.4 Failed de/anti-icing fluids and ice adhesion

Field experiences and climatic chamber tests have shown that the adhesion of ice on deiced and anti-iced surfaces are weaker than non de/anti-iced surfaces. Based on our investigation on ice adhesion, we can outline several one mechanisms that reduce the adhesion of failed de/anti-icing fluids onto aircraft surfaces. They are:

4.4.1 Slippage of ice crystals in the slush

Prior to examining the failed fluids and slush bonding onto surfaces, we have investigated the effect of the type of freezing medium to the ice form.

The freezing and adhesion of boiled distilled water, synthetic seawater, and natural seawater on an uncoated brass rod were used as examples (25). The results are given in Table 3.

Table 3. Shear adhesion of various types of ice to uncoated brass rods

Water used	Temperature, °C	Average shear adhesion, MPa	Standard deviation
Boiled distilled water	-20	1.542	0.4
Synthetic sea water	-20	1.055	0.2
Natural sea water	-20	0.483	0.7

In the case of boiled distilled water, the torque adhesion is higher than the two saline water, with a 31% reduction for synthetic seawater and a 68% reduction for natural seawater. The reason for this is that during freezing, pure water crystals are initially formed with pockets of concentrated salt solution between the crystal phases (24). So under shear, slippage between crystals occurs leading to lower shear adhesion values. The large difference between the natural and synthetic seawater can be explained by the presence of hydrophilic polymeric substances from various plant, animal, and bacterial species, e.g. alginate, fulvates, polysaccharides, etc. These substances would also tend to concentrate in the saline solution between the crystal phases and, since they are related to friction reducing polymers, extra slippage can occur.

The adhesion of a failed de/anti-icing fluids resembles adhesion of frozen salt water. Like boiled distilled water, precipitates without any de/anti-icing fluids freeze homogeneously at 0°C. Therefore, adhesion of such solid ice will be strong. On the other hand, de/anti-icing fluids and precipitate mixtures start to freeze once the liquid temperature is below the freezing point of failed fluid solution. The freezing process does not transform all of the liquid into a solid phase (Section 3.2). As it was described previously, during the freezing, pure water crystals are initially formed with pockets of concentrated glycol solution between the crystal phases. This is what we called slush. Under shear, slippage between crystals occurs, leading to lower shear adhesion values for slush.

Again with a natural vs. synthetic seawater analogy one would expect different adhesion values for the failed deicing fluids and anti-icing fluids. A lower adhesion value of a failed anti-icing fluid than the failed deicing fluid can be explained as follows. Unlike deicing fluids, anti-icing fluids contain more sophisticated thickener and other additive systems. These substances would also tend to concentrate in the glycol solution between the crystal phases and, since they are related to friction reducing polymers. Therefore extra slippage can occur in anti-icing fluids and cause lower adhesion values. Thus, adhesion of failed anti-icing fluid is expected to be lower than failed deicing fluid.

4.4.2 Adsorption of additives to surfaces

The adhesive strength of ice at the surface and the cohesive strength in the ice near to the surface is controlled by crystallization of water near the surface. Crystallization is accompanied by structure formation, in which the form and location of the ice grains depend on the adsorbed species onto surfaces.

Density, viscosity and other properties of failed de/anti-icing fluid near the wing surface differ significantly from the bulk properties of liquid. Surface active species and thickeners in deicing and anti-icing fluids migrate and are adsorbed onto aircraft surfaces. After the failure of the deicing and anti-icing fluids failure under precipitation, those adsorbed species still reduce the bond strength of ice to the surface and lower the adhesion. Thus one would expect lower adhesion values for failed anti-icing fluids than failed deicing fluids because of more sophisticated formulations of anti-icing fluids.

4.4.3 Lubricating effect of a thin layer of fluids

In most cases, precipitation builds up at the surface of an anti-icing fluid. A glycol concentration gradient in the fluid forms in the direction of thickness. The glycol concentration decreases from the solid interface to the air interface. After the failure of the fluid, a thin film of anti-icing fluid exists between slush/ice and wing surface. This layer works as a lubricating layer between ice and wing surface and reduces the adhesion.

A similar example was found in the literature. The U.S. Naval Research Laboratory investigated the adhesion-shear strength of ice frozen to clean and lubricated surfaces. Table 4 shows the effectiveness of silicon grease on the three bulk plastics: nylon, polyethylene, teflon.

Table 4. Adhesion strength of ice to clean and lubricated bulk plastics at -1°C

Surface	**Lubricant**	**Average shear adhesion, kPa**	**Standard deviation**
Nylon	None	325	214
	Silicon grease		
	J941-C-5000	1	0
Polyethylene	None	76	62
	Silicon grease		
	J941-C-5000	0	0
Teflon	None	0	0
	Silicon grease		
	J941-C-5000	0	0

5. FACTORS AFFECTING ADHESION

Factors affecting the adhesion of ice after the failure of a deicing or anti-icing fluid are listed as follows:

5.1 Hyrophobicity of surfaces

Aluminum, made aircraft surfaces have a hydrophobic nature. They have high affinity to water, therefore they make strong adhesive bonds with ice. Wing surfaces treated with anti-icing fluids causes surface hydrophobicity and reduced wetting and adhesive bonding characteristics.

5.2 Effect of temperature

The temperature at which freezing starts and the place it starts in a body of failed de/anti-icing fluid are important because these factors influence crystal structure and the direction of growth. The temperature effect plays a role together with glycol concentration for ice bonding. The solidification of glycol water mixture slush increases with lowering temperature and bonding becomes stronger below -10°C.

5.3 Surface profiles

Surface profile has a significant impact on ice nucleation start-up and bonding strength. Edges and protrusions reduce bonding of ice on surfaces. In addition, recesses retain anti-icing fluids and delay ice formation and bonding.

5.4 Lubricity of thin de/anti-icing fluid layer

The presence of a thin film of de/anti-icing fluid between ice/precipitation build-up and wing surface works as a lubricating layer and reduces the adhesion. The type and intensity of precipitation and type of fluid whether deicing fluid or anti-icing fluid are critical factors in determining the efficiency of the lubricating layer. This type of adhesion reduction is greater than an anti-icing fluid.

5.5 Fluid formulations

The type of fluid and formulations with thickeners and surface active agents affects the additive adsorption and thin lubricity layers. Therefore, the type of fluid affects the adhesive strength. The climatic chamber experiments and field experiences showed that lower adhesion is obtained on anti-icing fluids than deicing fluids. Nevertheless, deicing fluids still reduce the adhesion compared to a bare wing surface.

5.6 Ice adhesion shear strength vs. shear stress at rotation

In the literature there is no measurement of ice adhesion in the presence of failed de/anti-icing fluids. Nevertheless, based on other adhesion values, we can postulate that the adhesion in the presence of failed de/anti-icing fluids would be in the range of 1 - 100 kPa. This is significantly lower than the adhesion values of ice on the non de/anti-iced surfaces. Aircraft wings are subject to shear stresses around 0.1 kPa before rotation. This level of shear stress is not sufficient to clear the wing from ice, slush and failed fluid mixtures just before take-off.

6. CONDITIONS FOR ADHESION IN THE ABSENCE OF PROTECTIVE FLUID

Snow is a precipitate of porous, unstable aggregate mixture of ice particles and air. It is formed directly from the water vapour in air at a temperature less than 0°C. At temperatures higher than -5°C, the crystals are generally clustered to form snowflakes. The most frequently occurring temperature range of wet snow fall is 0 to -10°C. At temperatures lower than -10°C, snow becomes dry.

Under dry snow condition, if the wing surface is dry and cold, snow does not adhere to the surface. Dry snow particles flow freely. Strong blowing wind and shear forces at take-off minimize the particle-particle and particle-wing surface contact times. Snow is easily blown off and cleared from wing surfaces. Therefore, dry snow at lower temperatures does not as require anti-icing.

Adhesion and cohesion of ice and snow particles are of fundamental importance and have received attention in recent years, but in 1858 Tyndall (41) and Faraday(42) proposed that ice was covered by a water film at temperatures just below the freezing point. Their suggestion was based on the observation that two pieces of ice brought in contact at 0°C freeze together, even in vacuum and with the least possible contact pressure. Tyndall called this phenomenon “regelation.” This view was vigorously opposed by Thomson(43) who ascribed regelation to a melting produced by stress, followed by solidification upon removal of the stress.

Recently Weyl (44), Nakaya and Matsumoto (45) and Jellinek (46) have given renewed support to the liquid- like layer theory. Jellinek estimates the thickness of the layer at -4.5°C to range from 10^{-6} (100 Angstrom) to 10^{-5} cm (1000 Angstrom). This represents a layer 30 to 300 water molecules thick. Theoretical investigations of the stability of the liquid-like layers by Fletcher (47) led him to suggest that water layer exceeds 100 Angstrom in thickness just below the freezing point of water and that it disappears at about -30°C.

The adhesion and cohesion phenomena of snow particles could be conveniently explained if there were a liquid-like film surrounds snow particles. Air and surface temperatures and water content of particles affect the thickness of liquid-like layers. Sintering of snow particles results in cohesion phenomena and size growth and accumulation. Refreezing of liquid-like water film around snow particles on wing surfaces cause adhesion. The sintering process is shown in Figure 5.

The primary criteria for the adhesion of snow particles is the melt and formation of a thin water layer around particles. If wing surface temperature is sufficiently warm, snow particles melt and fuse together and adhere to wing surfaces.

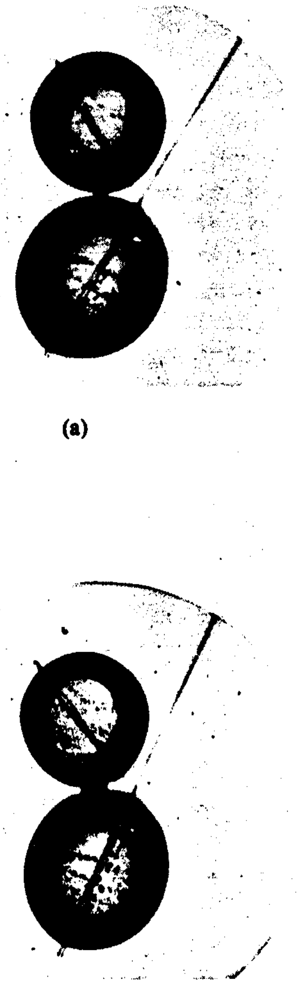
The two conditions for the adhesion of dry snow particles on aircraft wing surfaces can be described as follows:

1. Warm aircraft wing surface

    In the cases of interest in the winter, wing surfaces are either at or above ambient air temperature (parked aircraft) or at very low temperatures (recently landed aircraft). Most of the fuel tanks are located in aircraft wings and after landing the wings stay cold because of the heat sink effect of structure and fuel tanks. Nevertheless, the wing temperature might change if there is a refuelling. Warm fuel goes on top of the cold fuel with very little mixing and contact to the top of the tank. In this case the wing surface might become warm.

2. Absence of blowing wind

    Dry snow particles do not accumulate on wing surfaces because of their low cohesive properties. A strong wind can easily blow free-flowing dry snow particles. However, if there is no wind and wing surface is warm liquid layers around snow particles might form and bond snow particles together and to the wing surfaces.



(a)

(b)

Figure 5. Sintering of dry snow particles with liquid-like layers

A schematic diagram of a temperature profile from a warm surface to the covered snow layer is given in Figure 6. The heat flux density from a warm aircraft wing to the dry snow pile layer is Q_w, taken as positive if heat is added to the snow layer. After melting, snow particles refreeze and bond to surface. The partial melting process can last longer by the insulating influence of a snow cover.

The preceding analysis showed that the adhesion of dry snow on wing surfaces is not likely unless a wing surface becomes warm on a calm (not windy) day.

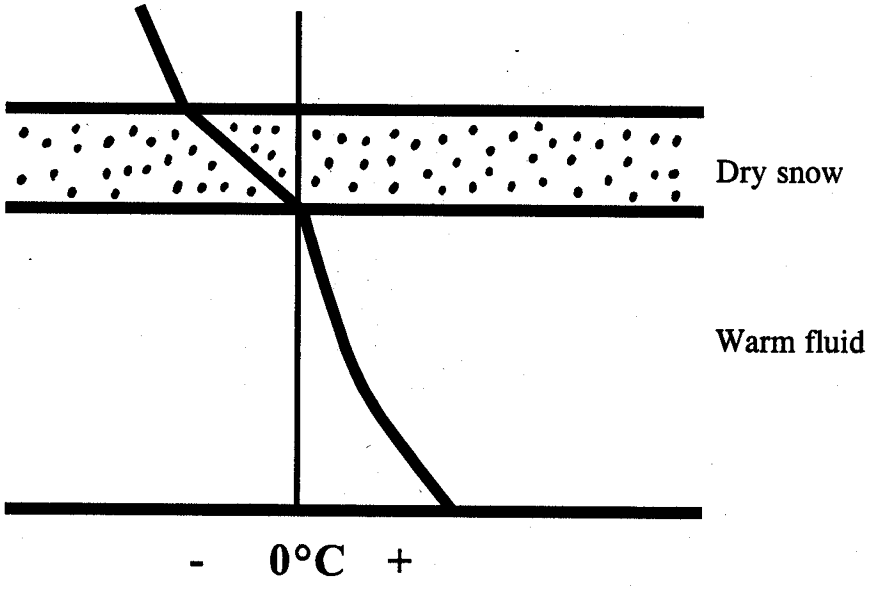


Figure 6. A schematic diagram of a temperature profile

7. CONCLUSIONS AND RECOMMENDATIONS

Deicing and anti-icing fluids, even after their failure, reduce the adhesive strength of ice and freezing precipitation. Anti-icing fluids are more effective than deicing fluids to lower the adhesive strength of ice.

The adhesive strength of ice and failed de/anti-icing fluids would be in the order of 10^{-3}-10^{-1} MPa. Aircraft wings are subject to a maximum shear stress of 10^{-4} MPa before rotation. This level of shear stress is not sufficient to clear the wing from ice, slush and failed fluid mixtures just before take-off.

The low adhesion strength of slush and ice on failed fluids make consecutive deicing operations speedy and easy.

Caution must be exercised in case of non anti-iced dry snow operations if the aircraft is refuelled with warm fluid and there is no wind.

8. REFERENCES

(1) Minsk, L.D., “Icing on Structures.” Report 80-31, Cold Regions Research and Engineering Laboratory, Hanover, NH, December 1980.

(2) Sawyard, J.M.,“Seeking Low Ice Adhesion.” Report SR79-11, Cold Regions Research and Engineering Laboratory, Hanover, NH, April 1979.

(3) Hearst P.J., “Coating Material for the Prevention of Ice and Snow Accumulations - Further Investigations”, Appendix to Report TN 541, U.S. Naval Civil Engineering Laboratory, Port Hueneme, CA, 1964.

(4) Ono, N, “Studies of Ice Accumulation on Ships, Conditions of Icing and Accreted Ice Weights.” Technical Translation 1319, National Research Council of Canada, 1968.

(5) Mundon, J.L.,“Ice-Release Coating for Disconnect Switches”, Report EL-1330, Electric Power Research Institute, Palo Alto, CA., March 1980.

(6) Druez, J., Phan, C.L., Laforte, J.L., and Nguyen, D.D., “The Adhesion of Glaze and Rime on Aluminum Electric Conductors”, Transactions CSME, Vol 5, No 4, 1979, pp. 215-220.

(7) Phan, C.L., McComber, P. and Mansianx, A., “Adhesion of Rime and Glaze on Conductors Protected by Various Materials”, Transactions CSME, Vol 4 No 4, 1976-1977, pp. 204-208.

(8) Laforte, J.L., Phan, C.L., Felin, B. and Martin, R., “Adhesion of Ice on Aluminum Conductor and Crystal Size in the Surface Layer”, CRREL Special Report, 83-17, 1983, pp. 83-91.

(9) Loughborough and Hass, E.G., “Reduction of the Adhesion of Ice to De-Icer Surfaces”, journal of Aero.Sci., **13**, 126-134 March (1946).

(10) Beams, J.W., Breazeale, J.B., and Bart, W.L., “Mechanical Strength of Thin Film of Metals”, Physical Review, Vol 100, 1955, pp. 1657-1661.

(11) Raraty, L.E. and Tabor, D. “The Adhesion and Strength properties of Ice”, research Laboratory for the Physics and Chemistry of Surfaces, department of Physical Chemistry, University of Cambridge, March (1957).

(12) Jellinek, H.H.G. et al., “Ice Releasing Block Copolymer Coatings”, Colloid and Polymer Sci., **256**, 544-551 (1978).

(13) Bascom, W.D., Cottington, R.L., and Singleterry, C.R. “Ice Adhesion to Hydrophilic and Hydrophobic Surfaces”, J. Adhesion, **1,** 246-263 (1969).

(14) Ford, T.F. and Nichols, O.D., “Adhesion-Shear Strength of Ice Frozen to Clean and Lubricated Surfaces”, Naval Research Lab. Report. 5832, 1962.

(15) Kuroiwa, D., “Icing of Aeroplane Propeller of Real Size”, Low Temperature Science, No 6, pp. 11-22.

(16) Stallabrass, J.R. and Price, R.D., “On the Adhesion of Ice to Various Materials”, NRC Report LR-350, July 1962.

(17) Itagaki, K. “Adhesion of Ice to Polymers and Other Surfaces”, Physicochemical Aspects of Polymer Surfaces, 1981.

(18) Itagaki, K., "The Implications of Surface Energy in Ice Adhesion", J. Adhesion, **16** 41-48 (1983).

(19) Kozitsokii I.E., "The Shear Strength of Ice", Metoralgiya I. Gidrolgiya, No 3 1978, pp. 103-105.

(20) Chu, M.C.and Scavuzzo, R.J., "Adhesive Shear Strength of Impact Ice", AIAA Journal, **29**, 1921-1926 (1991).

(21) Porte, H.A. and Nappier, T.E., "Coating Material for Prevention of Ice and Snow Accumulations - A Literature Survey", U.S. Naval Civil Eng. Lab., Port Hueneme, CA, TN-541, November 12, 1963.

(22) Ahlborn, G.H. and Poehlmann H.C., "Development of a Hyrophobic Substance to Mitigate Pavement Ice Adhesion." Report EPA-600/2-76-242, December 1976.

(23) Dohaney, W.J. and Innes, J.D., "Ice Free Pavement-Evaluation of Verglimit as a De-Icing Agent", Materials Protection, 20, 3, 39, March 1981.

(24) Keyser, J.H., "Selection and Use of Deicing Chemicals and Abrasives in North America and Overseas." paper No 780907, Society of Automotive Engineers, 1978.

(25) Croutch, V.K., Hartley, R.A., "Adhesion of Ice to Coatings and the performance of Ice Release Coatings", J. Coatings Technology, **64**, 41-53 (1992).

(26) Murase, H., Nanishi, K., Kogure, H.,Fujibayashi, T., Tamura, K., and Haruta, N. "Interaction Between Heterogeneous Surfaces of Polymers and Water", J. of Applied Polymer Science, **54**, 2051-2062 (1994).

(27) Baker, H.R., Bascom, W.D., and Singleterry, C.R., “The Adhesion of Ice to Lubricated Surfaces”, N.R.L. Report 5429, U.S. Naval Res. Lab., Washington, DC. February 9, 1960.

(28) Hansman Jr. R. J., “Droplet Size Distribution Effects on Aircraft Ice Accretion”, J. Aircraft, **22**, 503-508 (1985).

(29) Hansman, Jr. R. J., “Investigation of Surface Water Behaviour During Glaze Ice Accretion”, J. Aircraft, 140-147 (1989).

(30) ABC-3 Aircraft De/Anti-icing Fluid Literature, Kilfrost Ltd., 1989.

(31) Glycol Product Literature, Union Carbide Corporation, 1978.

(32) Nieh, E., U.S. Patent 5,118,435 6/1992.

(33) Salvador, R., U.S. Patent 4,744,913 5/1988.

(34) Rance, D.G., “Thermodynamics of Wetting: From its Molecular Basis to Technological Application”, Surface Analysis and Pretreatment of Plastics and Metals, Brewis, D.M.(Ed.), **6**, 121-151, MacMillan, New York, 1982.

(35) Zisman, W.A., “Relation of Equilibrium Contact Angle to Liquid and Solid Constitution ”, in Advances in Chemistry: Contact Angle, Wettability and Adhesion, Am. Chem. Soc., Washignton, DC. 1964.

(36) Fowkes, F. M., “Attractive Forces at Interfaces”, Chemistry and Physics of Interfaces Symposium, 1-12, Am. Chem. Soc., Washighton, DC, 1965.

(37) Girifalco, L.A. and Good, R.J., J. Phys. Chem., 61, 904, 1957.

(38) Landy, M. and Freiberger, "Studies of Ice Adhesion", Colloid and Interfacial Science, **25**, 231-244 (1967).

(39) Bolger, J.C., and Micheals, A.S., "Molecular Structure and Electrostatic Interactions at Polymer-Solid Interfaces", Interface Conversion for Polymer Coatings, Weiss, P and Cheever, G.D. (Eds.), 3-52, Am Elsevier Publisher Inc., New York, 1968.

(40) Mittal, K.L., "Adhesion Measurement: Recent Progress, Unsolved Problems and Prospects, Adhesion Measurements of Thin Films, Thick Films and Bulk Coatings", ASTM Special Tech. Publ., 640, 18-26, Philadelphia, PA, 1976.

(41) Tyndall, J., Proc. Roy. Soc. London, **9**, 76 (1858).

(42) Faraday, J., Proc. Roy. Soc. London, **10**, 440 (1860).

(43) Thomson, W. (Lord Kelvin), Proc. Roy. Soc. London, **9**, 141 (1858).

(44) Weyl, W.A., J.Colloid Science, **6**, 369 (1951).

(45) Nakaya, U., and Matsumoto, A., J. Colloid Science, **9**, 41 (1954).

(46) Jellinek, H.H.G., J. Applied Physics, **31**, 833 (1960).

(47) Fletcher, N.H., Phil. Mag. **7**, 255 (1962).

Other literature on ice adhesion and mechanical properties

"Adhesion and Shear Strength of Ice Frozen to Clean and Lubricated Surfaces", NRL Report 5832, August 30, 1962.

Andrews, E.H. and Lockington, N.A., "The Cohesive and Adhesive Strength of Ice", Journal of Material Science, **18**, 1983.

Andrews, E.H., Majid, H.A. Lockington, N.A., "Adhesion of Ice to a Flexible Substrate", Journal of Material Science, Chapman and Hall 1984.

Anon., "A Review of Problem of Adhesion", Report 52-69 Wright Air Development center, December 1952.

Anon., "A Study of Chemical-Physical Nature of Adhesion of Ice to Solid Surfaces", WADC Technical Report 53-461, October 1953.

Anon., "mechanical measurement of Interatomic Bonding Energies at Interfaces", Journal of Material Science,London, England: Plenum Publishing Company (1984).

Asswfpour-Dezfuly, M., Vlachos, C. and Andrews, E.H., "Oxide Morphology and Adhesive Bonding on Titanium Surfaces", Journal of Material Science, Chapman and Hall 1984.

Dryden, H.L., "review of Published Data on the Effect of Roughness on Transition from Laminar to Turbulent Flow", Jour. Aero. Sci., **20(7)**, 477-482 (1953).

Eskin, S.G., Fontain, W.D. and Witzell, O.W., "Strenght Characteristics of Ice in Contact with Various Kinds of Surfaces", Purdue University.

Hawkes I. and Mellor, M., "Deformation and Fracture of Ice under Uniaxial Stress", US Army Cold Regions research and Engineering Laboratory, Journal of Glaciology (1972).

Jellinek, H.H.G., "Adhesive properties of Ice", Research Report 38, U.S. Army Snow and Ice and Permafrost Research Establishment, September 1957.

Lange, M.A. and Thomas, J. Ahrens, "The Dynamic Tensile Strength of Ice and Ice-Silicate Mixtures", Journal of Geophysical Research, **88(B2)**, February 10, 1988.

Meyer, W.R. and Foley, Jr., E.F., "Ice Adhesion Tests on Films of Organic Polar Materials", WADC Technical Report 56-591, March 1957.

Minsk, L.D., "Some Snow and Ice properties Affecting VTOL Operation", AHS, AIAA, and U. of Texas, Proc. of the Joint Symposium on Environmental Effects on VTOL Designs, Arlington, Texas, Nov. 16-18, 1970.

Murphy, W.J.H. and Waterman, T.E., "Glaze Ice-Forming Characteristics of Various Structural Shapes", RADC TN 59-411, June 1959.

Raraty, L.E. and Tabor, D. "The Adhesion and Strength properties of Ice", research Laboratory for the Physics and Chemistry of Surfaces, department of Physical Chemistry, University of Cambridge, March 1957.

Rothrock, A.M. and Selden, R.F., "Adhesion of Ice in its Relation to the De-icing of Airplanes", NACA TN 723, August 1939.

Scavuzzo, R., "Presentation of Shear Test Data from NASA Icing Research Tunnel", University of Akron, Ohio, September 1984.

Smith-Johannsen, “Effect of Impurities in Water on Ice Adhesion”, Basic Icing Research by General Electrics., Co., Fiscal Year 1946, U.S. Air Forces, tech. Rept. 5539 (1947).

Stallabrass, J.R. and Price, R.D.,“ On the Adhesion of Ice to Various Materials”, Canadian Aeronautics and Space Journal, **9**, 199-204 (1963).

Tint, L.M., “Determination of Tensile and Shear Strength of Ice and Its Adhesion to neoprene”, Ames Aeronautical Laboratory, NACA, Moffet Field, California, June 18, 1943.