Progress in anti-ice technologies – coating concepts and evaluation

Nadine Rehfeld, Dr. Björn Weber, Fraunhofer IFAM, Germany
Wiener Str.12, 28359 Bremen, web@ifam.fraunhofer.de

Abstract - The prevention of ice accretion on surfaces has been investigated for a long time by work groups all over the world. There has only been limited success to date. A more realistic current goal is the production of durable, industrially-viable coatings which function by reducing ice adhesion forces rather than by completely preventing the formation of ice. Besides carrying out research on these (passive acting) coatings, specialists at the Fraunhofer IFAM are developing temporary, active anti-ice coatings and are working on a biomimetic coating concept which uses a biological model for technical coatings.

The work on the development of anti-ice coating concepts is carried out by the Paint Technology department of the Fraunhofer IFAM. For this research different types of icing need to be taken into account. Reliable test methods had to be developed to evaluate icing behaviour, including ice chamber tests, adhesion tests and investigations under real icing conditions. This paper summarises the work that has been completed with the latest results. The following approaches are described:

- Temporary anti-ice coatings with freezing-point depressors
- Biomimetic anti-ice coatings with the inclusion of anti-freeze proteins
- Hydrophobic coatings, mainly combined with
- Surface structuring via nanoparticles or micro-scale particles

I. Introduction

1. Why are anti-ice technologies so important?

The prevention of icing on surfaces is an aim in many technical fields because this would ensure the operability and reliability of engines and constructions, even in cold climates. Furthermore, currently employed de-icing procedures are associated with increased energy consumption due to heating, use of chemicals and additional mechanical actions. The prevention of surface icing or (at least) the reduction of ice formation is therefore of great interest in order to reduce costs.

Effective anti-ice technologies would not only improve the operability of means of transportation such as aircraft, cars and trains but would also minimize adverse icing effects on bridges, transmission lines and road surfaces. Furthermore, the prevention of ice formation on, for example, cooling units or wind turbines would save a great amount of energy. These selected examples already show the great importance of effective anti-ice measures.

Figure 1: Icing on a car, cooling units and wind turbines

The Fraunhofer IFAM has been working on icing issues for a number of years. Several ongoing projects are developing anti-ice coatings for various technical applications. As part of this challenging work, efforts were made to understand the mechanisms of icing and the interactions between ice and solid surfaces. Furthermore, tests that can differentiate the icing behaviour on coatings were developed.

II. Work Preparation

1. How to evaluate anti-ice coatings?

In order to evaluate anti-ice coatings, the environmental and technical conditions as well as general requirements need to be taken into consideration. This includes the application properties of such coatings as well as the paint and coating properties (e.g. toxicity, weather stability, abrasion resistance, flexibility). Last but not least, the ability of the coating to prevent icing or reduce ice adhesion has to be investigated, including assessment of the duration of the anti-icing effects.
Bearing in mind that the properties of ice depend on the ambient conditions, the following points need to be taken into consideration for evaluating anti-ice coatings:

- The test parameters for assessing icing behaviour should be carefully selected and should represent real conditions as much as possible.
- Even small parameter variances could lead to different results and hence misinterpretation.
- The sensitivity of the icing process means that there is a relatively high risk of the test results not correlating with icing behaviour under real conditions.

As a consequence of these issues, it is advisable to perform a broad range of tests under different lab-conditions and then perform the tests under real conditions.
Tests in the IFAM ice chamber are the first step for evaluating icing behaviour under controlled conditions. In general, two different icing scenarios are investigated first of all:

1. Ice rain test, which simulates the run-off behaviour of water as well as the subsequent formation of clear ice.
2. Rime test, which simulates the formation of rime under test conditions.

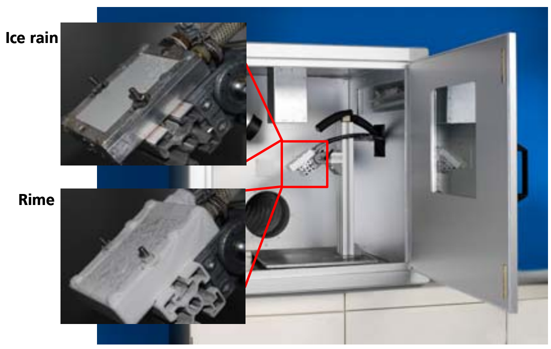


Figure 3: IFAM ice chamber

The features of the IFAM ice chamber allow different test scenarios to be studied as well as the inclusion of additional test devices. In general, tests can be performed at temperatures down to -10°C at a relative humidity of up to 70%. The test surface can additionally be cooled down to -30°C and a wind speed up to a maximum of 30 m/s can be applied. Additionally, rain can be simulated and a camera allows visual inspection of the test surface during test runs.
The Fraunhofer IFAM is also working on reliable tests for the assessment of ice adhesion. Once again, two main types of ice (clear ice, rime) are considered in the test design. The tests are based on measuring the force that is needed to completely remove the ice from the surface. The results of the individual tests allow coatings to be differentiated, and comparison of the measurement data gives an indication of the relative reduction of ice adhesion.

Coatings with promising results in IFAM laboratory tests are then tested under real winter conditions on a test rig positioned on Mount Brocken. Here, tests are carried out under harsh winter conditions over a long time period. The coatings are inspected for ice accretion and ice adhesion on a regular basis. It could be shown that results of IFAM laboratory adhesion tests actually correlate with observed anti-ice effects under real conditions. This is an important finding and proves the developed methods.

Figure 4: Test rig on Mount Brocken

1. What kind of anti-ice technologies are available?

In this paper, anti-ice technologies are considered to be technologies that prevent ice formation at the initial stage or that remove ice after it has formed. Most technologies use ACTIVE methods, which include thermal, chemical and biochemical as well as mechanical means.
The heating of a structure is widely known to be an effective anti-icing method and is used in many industries (e.g. the automotive and aviation industries). Also widely used are chemical actions that lead to a lowering of the freezing point of water. Such chemicals can be used, for example, on aircraft by spraying a mixture of alcohols – and so forming a protective film of glycol [1].
A relatively new approach is the use of biological strategies for the prevention of ice formation on technical surfaces. This biochemical method is being investigated in an ongoing research project at the Fraunhofer IFAM and involves coupling anti-freeze proteins to coatings [2].
Mechanical means include the familiar scraping of ice from the windows of cars. Also, electromechanical systems can be used to remove ice from surfaces. This active method can be supported by a PASSIVE method which leads to reduction of ice adhesion and subsequently to easier ice removal. Another passive method involves changing the wetting behaviour of surfaces so that most of the water rinses off before freezing. The following table summarises all the anti-ice methods and the highlighted items represent the approaches being studied by experts at the Fraunhofer IFAM in ongoing projects.

Active methods	Passive methods
Thermal	Ice adhesion reduction
Chemical	
Biochemical	Change of wetting behaviour
Mechanical	

3. Active coating concepts

The first active coating concept being investigated by the Fraunhofer IFAM is chemical freezing point depression which is based on the leaching of depressors out of the paint matrix [3]. Due to the leaching aspect, this effect is only temporary and is only suitable for technical applications that require ice free surfaces for a short time.
The first step was to formulate suitable coatings which contained freezing point depressors, without there being any negative effects on the coating properties. The subsequent leaching of the depressors out of the paint matrix had to be guaranteed. Water-based PUR dispersions were selected as the most suitable coating formulations for this work. They showed good compatibility with different glycol types as well as with selected salts. The maximum concentration of each freezing point depressor to achieve the maximum anti-ice effect was defined. Results of the initial IFAM rime test showed significant reductions in rime formation: For example, for a PUR dispersion without depressor the rime thickness was measured as 900 µm, whilst with added freezing point depressor no rime was observed after the test period.
These promising results have resulted in further investigations being conducted on the long-term performance of the coatings and the minimum temperatures at which these coatings are effective. Also, the combination of different freezing point depressors will be studied as part of further research.

Besides the chemical method, which suppresses the freezing point due to the presence of dissolved particles (colligative properties), there is a further strategy for preventing ice formation. This biochemical method is used by organisms in polar and sub-polar regions and is the reason for the survival of, for example, fish, amphibians, plants and insects [4]. It is based on substances with constitutive properties that cause freezing point depression due to the configuration and conformation of the molecules. Such molecules selectively depress the freezing point, but have no effect on the melting point of ice. This leads to a temperature difference between melting point and freezing point and is called “thermal hysteresis” [5]. These molecules are described as thermal hysteresis proteins or (more commonly) anti-freeze proteins (AFPs).
The Fraunhofer IFAM is currently working on the synthesis of anti-freeze proteins and the subsequent coupling of the proteins, without loss of their activity, to suitable coatings. The figure below schematically shows this approach.

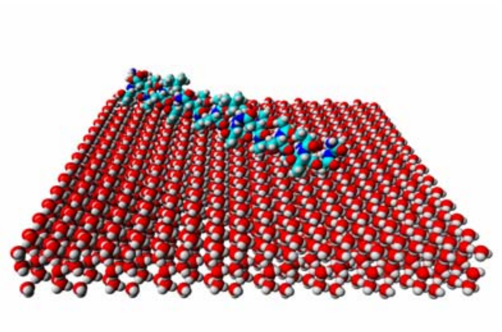


Figure 5 – Scheme of AFPs on coatings

A research project "Biomimetische Frostschutzoberflächen auf Basis Peptid-funktionalisierter Lack (AFPII)" is being funded by the BMBF (Federal Ministry of Education and Research, Germany) and is a continuation of a study that showed the feasibility of this approach. It was demonstrated that the synthesis of relevant protein-sequences is possible. Thereafter, three strategies for coupling the synthesized sequences to the coatings were investigated:

1. Application to coatings with reactive groups using an ultrasonic atomiser, and subsequent polymerization within the paint matrix;
2. Covalent linkages
3. Use of additional linking molecules between the coating and protein-sequences.

All three strategies were essentially successful and are further investigated with regards to maximizing flexibility and the effectiveness of the proteins. In this context, coupling strategies with varying reactive chemical groups were performed for immobilization of the proteins. First tests in the IFAM ice chamber showed promising results as rime accretion was reduced under certain test conditions. As part of the current project, further development work will be performed to investigate the suitability of this biomimetic approach.

4. Passive coating concepts

Over recent years, much emphasis has been placed on the development of coatings that act as passive anti-ice surfaces. Most products that are available are hydrophobic coatings that prevent the water from settling on the surface and subsequently reduce the ice formation. In general, organic fluorine compounds and silicone resins / compounds are the most commonly used hydrophobic chemicals. The hydrophobic property of a surface can be expressed as the contact angle of water, which indicates the interaction between water and the surface. Hydrophobic surfaces have contact angles greater than 90°, whilst super hydrophobic coatings have angles greater than 140°.

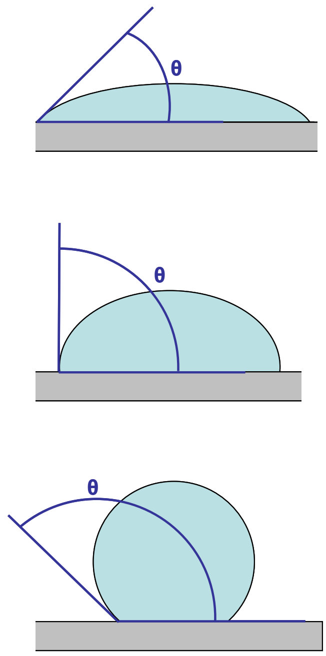
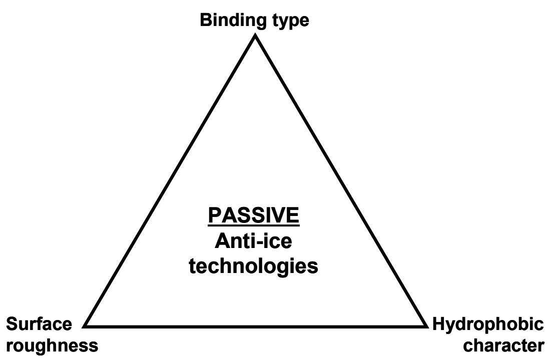


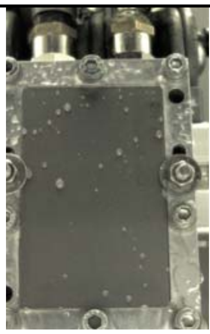
Figure 6: Principle of water contact angle with hydrophilic (left) to super-hydrophobic surface (right)

The key parameters for passive anti-ice coatings are the types of bonding that are available (in order to allow interactions between the water molecules and the solid surface), the surface roughness and the hydrophobic characteristics. Furthermore, these parameters interact with each other, for example the surface roughness has an influence on the water contact angle.



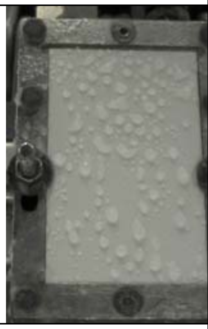
The Lotus effect is an example of surfaces that prevent wetting due to the combination of nano-scale and micro-scale surface structures and hydrophobic wax crystals. This leads to super-hydrophobic surfaces with water contact

TABLE I: Systematic study of polysiloxane additives in PUR coatings

Parameter	**2% additive**	**4% additive**	**6% additive**
Water contact angle [°]	98	104	106
Roughness Ra [µm]	0.12 (±0.01)	0.14 (±0.07)	0.16 (±0.04)
Pictures of the ice rain test			
Description of result	Low Ice formation after rain contamination at -5°C	Clearly increased ice formation	Maximum ice formation

angles of more than 140°. No water can adhere to these surfaces and contamination is easily removed.
On first thought, (super-) hydrophobic coatings should improve the anti-icing behaviour due to the reduced wetting. Nevertheless, it has been shown in comprehensive studies performed by the Fraunhofer IFAM that the hydrophobicity is only one of the determining factors for predicting anti-ice properties – and furthermore, a hydrophobic coating is not necessarily an anti-ice coating. A systematic study showed that with increasing the hydrophobicity of a coating with polysiloxane additives, an increase of ice formation occurs (Table I). That's a clear hint on H-bonding interactions between the silicon surface and water which was also found in investigations of other groups [6].

Another influence on ice formation on surfaces is the roughness of the surface, which can allow the anchoring of water. In such cases, ice adhesion increases due to the increased contact area, the formation of rime, which forms from water vapour in the air, cannot be prevented by such passive coatings.
The development of passive anti-ice coatings was also carried out by the paint technology department of Fraunhofer IFAM. Here, a coating was developed with a balance of surface roughness and hydrophobicity and a minimum of available sites for interaction with water molecules. This coating showed reduced ice adhesion in both laboratory and field tests. Beforehand, the reduced wettability of the coating, compared to unmodified coatings, was demonstrated in the IFAM ice rain test. The test conditions were set as follows: temperature -5°C, relative humidity 66%, wind speed 9 m/s, rain duration 10 s. The pictures below show the test surfaces 10 minutes after raining:

Parameter	**Unmodified top coat**	**Passive anti-ice coating**
Water contact angle [°]	82	124
Roughness Ra [µm]	0.17 (±0.01)	0.64 (±0.07)
Pictures of the ice rain test		
Description of result	Ice formation after rain contamination at -5°C	Clearly reduced ice formation due to improved water run-off ability

A further approach is the development of coatings that contain hydrophilic centres in a hydrophobic environment. This allows water molecules to adhere to certain sites, yet the hydrophobic surroundings of these sites promote the removal of ice crystals.

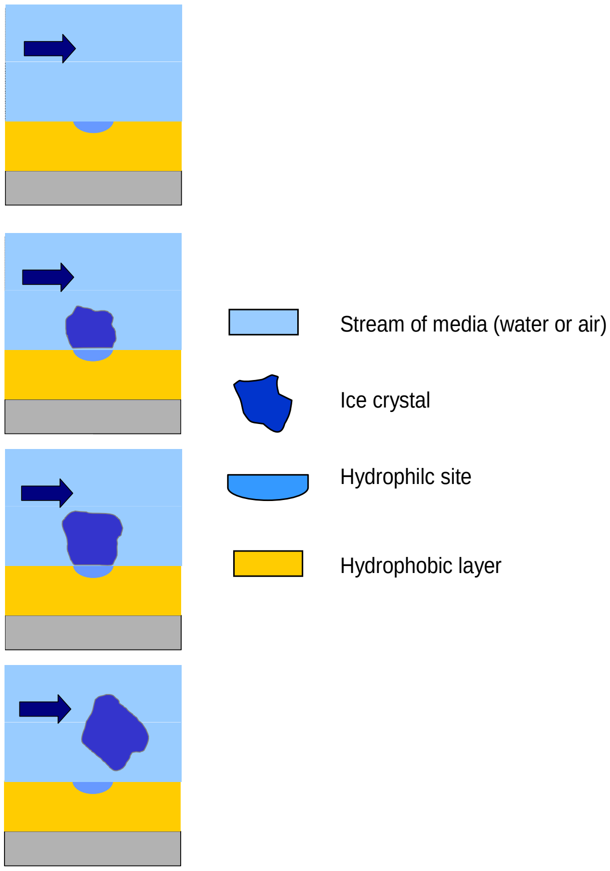


Figure 7: Scheme of hydrophobic / hydrophilic coating approach

This approach is being investigated in a BMBF funded project (in cooperation with Leibniz-Institute of Polymer Research Dresden, Germany and industry partners), and involves different technical strategies. One interesting technique is the use of laser radiation for coating modification. First results showed that this is feasible at a micro-scale level. Finer structuring is currently under investigation. Furthermore, the use of nanoparticles and micro-scale particles in appropriate coating formulations is being studied at the Fraunhofer IFAM. In this context, micro-scale particles have been investigated for their ability to enhance the hydrophobic character without adversely affecting ice adhesion due to the increased contact area. After surface modifications that ensure the availability of uncoated particles at the surface, tests have shown that the water preferably adheres to the hydrophilic anchoring points – but the particles were too large meaning that no positive effect on ice adhesion due to the hydrophobic surrounding area could be observed.

The use of nanoparticles is also being investigated by the Fraunhofer IFAM in this project. Nanoparticles of $BaSO_4$ were selected as these show polar, hydrophilic properties and are insoluble in water. These will lead to preferred interaction of the water molecules with the nanoparticles at the surface. To guarantee the mode of action, the availability of the uncoated particles needed to be guaranteed. XPS (X-ray photoelectron spectroscopy) showed that 10% of the total amount of particles in the formulation was available at the surface. Further investigations showed promising anti-ice effects in terms of ice formation and ice adhesion on specially designed surfaces with additional hydrophobic character.

III. Outlook

The Fraunhofer IFAM has invested a lot of work in the development and evaluation of anti-ice coatings for different kinds of technical applications. The first stages of the development work, including test development, gaining fundamental understanding of icing mechanisms and experience with suitable paint formulations, have been completed. Promising coating approaches were identified and focus is placed on the optimization of anti-ice coatings for technical applications. This work will be undertaken in ongoing projects.

IV. Acknowledgement

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