Melting the ice

Efforts to prevent ice accretion on surfaces have had limited success to date. A more realistic goal is the production of durable, industrially viable coatings that reduce ice adhesion rather than completely prevent its formation. Besides carrying out research on these "passive" coatings, specialists at the Fraunhofer IFAM are developing novel nano-structured surfaces with outstanding anti-ice effects, as well as temporary anti-ice coatings and a biomimetic concept based on a biological model.

New anti-frost technologies
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Tackling the ice problem
Ice formation on surfaces and structures severely impairs the functionality of equipment, endangering property and even life in some cases. That is why current methods of preventing ice formation on aeroplanes, vehicles, wind turbines, trains, traffic signalling devices, windows and building surfaces, weather stations and also refrigerators need to be improved. For example, aircraft are today de-iced using liquids with a low freezing point; this procedure increases costs and down time and causes environmental problems. During flight, anti-icing is achieved with hot bleed air from the engine, which uses about 5 % machine power and the additional equipment required adds to the total weight of the aircraft. New hydrophobic, functionalised layers with a nano-structure are one prospective technology for developing better, durable, reliable and cost-saving solutions. They will enhance product value, increase safety in critical applications such as aerospace and also be of benefit to a large number of other technical areas and applications.

Reliable test methods
The Fraunhofer IFAM has for several years been developing both anti-ice coatings for various technical applications and tests that can differentiate icing behaviour on coatings.

For development of new functional coatings with improved ice-phobic properties, it is necessary to understand ice formation mechanisms and ice adhesion as well as their interaction. Differential scanning calorimetry (DSC) allows investigation of the influence of surface functionalisation on the phase transition between water and ice (crystallisation and melting). A special test chamber enables the freezing process of water droplets on different (coated) surfaces to be observed via optical microscope or infra-red camera. To assess anti-ice coatings, environmental and technical conditions as well as general requirements must be taken into account, including the durability of anti-icing effects. The following points need to be taken into consideration:

Test parameters for assessing icing behaviour should be carefully selected and reflect real conditions as far as possible. Even small parameter variances could lead to different results and hence misinterpretation. The icing process is very sensitive, which means that there is a fairly high risk that the test results will not correlate with icing behaviour under real conditions. A broad range of tests under different laboratory and real-life conditions therefore has to be performed.

The ice chamber (Figure 1) allows variation of ambient conditions, enabling different scenarios to be tested as well as the inclusion of additional test devices. Tests can generally be performed at temperatures down to -10 °C and a relative humidity of 80 %. Additionally, the test surface can be cooled down to -40 °C and a wind speed of up to 30 m/s applied. Rain can also be simulated, and a camera allows visual inspection of the test sample.

In general, three different tests are performed:
1. The ice rain test, which simulates the run-off behaviour of water as well as subsequent formation of clear ice.
2. Rime formation.
3. Run-back ice formation. This generally occurs after de-icing of leading edges such as aircraft wings and wind turbine blades, where melted ice freezes again in other areas.

The Fraunhofer IFAM is also developing reliable tests for assessing clear ice and rime adhesion. The tests involve measuring the force needed to remove ice or rime completely from a surface. The results of individual tests allow coatings to be differentiated, and comparison of the measurement data gives an indication of the relative reduction of ice adhesion.

To verify the results, promising coatings are tested under real winter conditions on a rig (Figure 2). The important finding is that the laboratory test results correlate with anti-ice effects under real conditions.

Anti-ice technologies
The technologies described could either prevent initial ice formation or remove ice after it has formed. There are two distinct anti-ice technologies: active and passive (Table 1).

Chemical
Chemicals that reduce the freezing point of water are also widely used. For example, a mixture of alcohols can be sprayed on aircraft, forming a protective glycol film [1]. Another method is to incorporate freezing point depressors in paint matrices. Since these depressors leach out, however, this effect is only suitable for technical applications that require rime-free surfaces for a short time.

Biochemical
The use of biochemical technologies for the prevention of ice formation on technical surfaces is a relatively
new approach. This method involves coupling anti-freeze proteins to coatings [2].

Mechanical
Mechanical and electromechanical methods include scraping ice from car windows. Active methods such as these can be supported by passive ones via reduction of ice adhesion.

Active coating concepts
Synthesizing anti-freeze proteins from fish, amphibians, plants and insects in polar and sub-polar regions use biochemical methods to survive [3]. One method of preventing ice formation is based on anti-freeze proteins with constitutive properties that cause freezing point depression due to the configuration and conformation of their molecules, but have no effect on the melting point of ice. This leads to a temperature difference between freezing point and freezing point, known as "thermal hysteresis" [4]. The molecules are called thermal hysteresis proteins (or more commonly) anti-freeze proteins (AFPs).

Work is currently being carried out to synthesise anti-freeze proteins and couple them on paint matrices without loss of activity (Figure 3). The ice chamber test for a coating that contains AFPs shows reduced rime formation. A research project, "Biomimetic anti-frost surfaces based on peptide-functionalised coating" ("Biomimetische Frostschutzoberflächen auf Basis Peptid-funktionalsierter Lack (AFPIL)"), funded by the BMBF (Federal Ministry of Education and Research), Germany, is the continuation of a study that demonstrated the feasibility of synthesising relevant protein sequences. Three methods of coupling the synthesized sequences to the coatings were subsequently tested:
1. Application to coatings with reactive groups using an ultrasonic atomiser, and subsequent polymerisation 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 further investigated with the aim of maximising flexibility and the effectiveness of the proteins. Coupling tests with varying reactive chemical groups were performed for immobilisation of the proteins. Initial tests in the ice chamber showed reduced rime accretion under certain conditions. Further tests will be carried out to determine the technical feasibility of this biomimetic approach.

Temporary anti-icing
Another active coating concept is the use of chemical freezing point depressors in paints. Since it is based on the leaching of depressors out of the paint matrix [5], this effect is temporary and only suitable for technical applications that require rime-free surfaces for a short time.

The first step was to formulate suitable coatings containing freezing point depressors that did not impair coating properties and were certain to leach out of the paint matrix. Water-based polymer dispersions that are compatible with different glycol types as well as with selected salts were selected as paint matrices. The initial test results showed significant reductions in rime formation, some coatings preventing it completely for a certain period (Figure 4). These promising results led to investigations of the long-term performance of the coatings and the minimum temperatures at which they are effective. Combinations of different freezing point depressors are also being investigated.

Passive coating concepts
Passive methods are those that use energy only from natural forces such as wind, gravity and temperature variations. Most anti-icing coatings currently available are hydrophobic. They prevent water from settling on surfaces and subsequently reduce ice formation. The hydrophobic property of a surface can be expressed as the contact angle of water, which indicates the interaction between water and surface. Hydrophobic surfaces have contact angles greater than 90°, whilst super hydrophobic coatings have angles greater than 140°. Organic fluorine compounds and silicone compounds are the most commonly used hydrophobic chemicals.

The key parameters for passive anti-ice coatings are the types of bonding available (in order to allow interactions between the water molecules and the solid surface), surface roughness and hydrophobic characteristics. These parameters interact with each other, for example surface roughness affects water contact angle (Figure 5). It would seem logical that (super) hydrophobic coatings should improve anti-icing behaviour, because they reduce wetting. However, comprehensive studies have shown that hydrophobicity is only one of the factors determining anti-ice properties. Furthermore, a hydrophobic coating is not necessarily an anti-ice coating. A systematic study has shown that polysiloxane additives in coatings increase hydrophobicity, but, surprisingly, also increase ice formation. This depends, among other things, on the roughness of the surface. Rime formation, caused by water vapour in the air, cannot be prevented by passive coatings either.

Fraunhofer IFAM has developed a passive anti-ice coating that achieves a balance between surface roughness and hydrophobicity and minimises available sites for interaction with water molecules. This coating showed reduced wettability in the ice rain test and also reduced ice adhesion in laboratory and field tests.

A further approach is the development of coatings that contain hydrophilic centres in a hydrophobic environment (Figure 6). This allows water molecules to adhere to certain sites, but the hydrophobic surroundings of these sites promote the removal of ice crystals. This approach is being investigated in a BMBF funded project (in cooperation with the Leibniz Institute of Polymer Research, Dresden, Germany and industry partners), and involves different technical strategies. The Fraunhofer IFAM is studying the use of nano- and micro-scale particles in appropriate coating formulations. Micro-scale particles have been investigated for their ability to enhance hydrophobic character without adversely affecting ice adhesion as a result of increased contact area. After surface modifications that ensure the availability of uncoated particles at the surface, tests have shown that water preferentially adheres to the hydrophilic anchoring points but since the particles were too large, no positive effect on ice adhesion due to the hydrophobic surrounding area could be observed.

The most recent development is a coating that contains nano-hydrophilic centres in a hydrophobic environment. This pure organic coating can be applied by spraying. The structure allows water molecules to adhere to hydrophilic centres and the hydrophobic surroundings of these sites...
promote the removal of ice crystals. Rime formation can clearly be reduced compared to surfaces without anti-ice coatings. Further investigations will show to what extent other required coating properties like durability, adhesion etc. can be achieved.

A promising start development work to continue
New, more effective, durable, reliable and cost-efficient methods of reducing ice formation on different surfaces are being developed that will enhance product value, increase safety in critical applications such as aerospace and also be of benefit to a large number of other technical areas and applications. These novel technologies include hydrophobic, functionalised layers with a nano-structure, the synthesis of anti-freeze proteins and their coupling to paint matrices to produce biomimetic anti-ice coatings, the use of chemical freezing point depressors to produce temporary anti-ice coatings, and passive coatings that reduce ice formation through nano-hydrophilic centres in a hydrophobic environment. The first stages of the development work, which include investigation of icing mechanisms and setting up test procedures and experiments with suitable paint formulations, have been completed.

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REFERENCES

Results at a glance
Surfaces have been developed to obtain anti-ice effects. The synthesis of anti-freeze proteins and their coupling to paint matrices has been used to produce biomimetic anti-ice coatings. Using chemical freezing point depressors, temporary anti-ice coatings have been developed. Passive coatings that reduce ice formation through nano-hydrophilic centres in a hydrophobic environment have been produced.

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Table 1: Anti-ice technologies. Experts at the Fraunhofer IFAM are investigating the highlighted methods
Figure 1: The IFAM ice chamber allows icing behaviour to be tested under controlled conditions Maximum wind speed of 70m/sec
Figure 2: The IFAM test rig on Mount Brocken provides real winter conditions
Figure 3: Linkage of anti-freeze proteins (AFPs) to suitable coatings
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unmodified coating</th>
<th>Modified coating</th>
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<tbody>
<tr>
<td>Pictures of the Rime test</td>
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<td>Description of result</td>
<td>Rime formation after 20 min 400 µm</td>
<td>Rime formation after 20 min 100 µm</td>
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Figure 4: Rime test with unmodified (left) and modified coatings (right) on glass substrate
Figure 5: Key parameters for passive anti-ice coatings
Figure 6: Hydrophobic / hydrophilic coating approach