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The properties of polyethylene glycol (PEG) as a sacrificial ice control coating are discussed. PEG is effective longer than many single component coatings, and it has low toxicity and a high flash point. The results of preliminary experiments on PEG's ability to control snow accumulation on a panel and ice accumulation on a cryogenic tank are also discussed.
PREFACE

This report was prepared by Dr. Kazuhiko Itagaki, Research Physicist, Snow and Ice Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided partly by DA Project 4A161102 AT24, Research in Snow, Ice and Frozen Ground; Task C, Research in Terrain and Climatic Restraints Environment; Scientific Effort 01, Cold Environment Factors; Work Unit 002, Adhesion and Physics of Ice, and partly by the U.S. Air Force Space Center through MPR FY76 168200394 (6 January 1982).

The author thanks D. Minsk and S.F. Ackley of CRREL for the technical review of this report.

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POLYETHYLENE GLYCOL AS AN ICE CONTROL COATING

Kazuhiko Itagaki

INTRODUCTION

Extensive efforts to find a “miracle coating” to prevent ice formation on cold surfaces have met with little success. Theoretical calculations have indicated that the weakest molecular bonds between water molecules and molecules of any known solid surface can be stronger than the strength of ice itself. Therefore, we cannot expect to find a universal solution that prevents ice formation permanently. Individual problems have to be attacked differently in a case-by-case approach. Some of the possible approaches include thermal methods as well as replaceable and sacrificial coatings.

Recently, my work (Itagaki 1983a,b) has indicated that when a low energy surface is contaminated by a grease layer, the adhesive strength of ice can be reduced through the reduction of “real” contact area. If such a grease layer can be replenished, we can obtain an ice release coating that is relatively long lasting.

Also, some freezing point depressants can be used as sacrificial coatings. Among the various freezing point depressants, such as salt, alcohol, and dimethyl sulfoxide, polyethylene glycol (PEG) deserves special attention for space and aeronautic applications because it is safe (CRC 1971) (low toxicity, high flash point; see Appendix A).

PROPERTIES OF POLYETHYLENE GLYCOL

According to Billmeyer (1962) polyethylene glycol is one of the earliest polymers synthesized. It is constructed by a linear chain of ethylene glycol, and its chemical structure is

\[ \text{HO} - (\text{CH}_2\text{CH}_2\text{O})_n - \text{H}. \]

Products with a wide range of molecular weights (200–20,000) are available. They have a wide range of properties at room temperature, ranging from a liquid to a greasy paste to a flaky solid (see Appendix A).

Commercially available PEG is a mixture of polymers having a relatively narrow range of molecular weights. Examples of melting points and physical properties are shown in Table 1. A user can select the substance with the most suitable molecular weight for a particular application and use it alone or impregnated with materials of low surface energy.

Miyachi (1975) observed that frost did not form on the surface of a freezer that was coated with PEG (molecular weight 1020). He also qualitatively examined the effectiveness of PEG samples of various molecular weights. His method of examination was to sprinkle iodine powder on an ice surface and then to place a sample of PEG on top of the powder and ice. When PEG of a certain molecular weight was dissolved on the ice at the test temperature, the iodine powder also dissolved in the solution and it left a red stain on the ice surface. This showed that there was a liquid layer at the ice/PEG interface. No iodine trace was left if the eutectic point of the PEG was higher than the test temperature, because there was no liquid at the interface. Properties of samples used in his study are listed in Table 2. The effective temperatures, which depend on the molecular weight of the PEG, indicated the existence of the liquid interface layer that helps make ice removal relatively effortless.

There are two ways to remove ice with little effort by using PEG. When the rate of ice accumulation is higher than the rate of dissolution at the PEG/ice interface, ice builds up. The interface, however, stays liquid, as long as the ambient tem-
Table 1. Physical properties of PEG.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Molecular weight</th>
<th>Melting point (°C)</th>
<th>Appearance (at room temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG 300</td>
<td>285–315</td>
<td>—</td>
<td>Colorless transparent liquid</td>
</tr>
<tr>
<td>400</td>
<td>380–420</td>
<td>—</td>
<td>Colorless transparent liquid</td>
</tr>
<tr>
<td>600</td>
<td>570–630</td>
<td>20–25</td>
<td>Colorless transparent liquid</td>
</tr>
<tr>
<td>1000</td>
<td>950–1050</td>
<td>39–40</td>
<td>White grease-like consistency</td>
</tr>
<tr>
<td>1500</td>
<td>Mixture of 300 and 1540</td>
<td>38–41</td>
<td>White grease-like consistency</td>
</tr>
<tr>
<td></td>
<td>1300–1600</td>
<td>42–46</td>
<td>White wax-like texture</td>
</tr>
<tr>
<td>4000</td>
<td>3000–3700</td>
<td>—</td>
<td>White flaky powder</td>
</tr>
<tr>
<td>6000</td>
<td>6000–7500</td>
<td>—</td>
<td>White powder</td>
</tr>
</tbody>
</table>

Table 2. Limit of PEG effectiveness by molecular weight and physical properties (after Mlyauchi 1975).

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Limit of effective temperature (°C)</th>
<th>Appearance</th>
<th>Melting point (°C)</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>below -20</td>
<td>Colorless transparent liquid</td>
<td>6.0</td>
<td>1.126</td>
</tr>
<tr>
<td>1020</td>
<td>-14</td>
<td>White solid</td>
<td>37.1</td>
<td>1.100</td>
</tr>
<tr>
<td>2000</td>
<td>-11</td>
<td>White solid</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3110</td>
<td>-7</td>
<td>White flaky powder</td>
<td>53.0</td>
<td>—</td>
</tr>
<tr>
<td>7500</td>
<td>-5</td>
<td>White flaky powder</td>
<td>56.5</td>
<td>—</td>
</tr>
</tbody>
</table>

Temperature is higher than the eutectic point of the PEG used, hence little effort is needed to remove the ice. When the accumulation rate is lower than the rate of dissolution, the surface is always covered by the solution and no ice can build up. However, moisture is absorbed, the coating dissolves, and the solution will eventually drip down by gravity and wash away.

Since very little research has been done on the ice control capability of PEG, it is difficult to predict its performance as well as any possible problems with it.

However, two preliminary qualitative studies were made at CRREL of the general characteristics of PEG's ice control capability. One tested PEG's ability to control snow accumulation on a horizontal flat surface and the other to prevent frost and ice formation on a simulation of the space shuttle external fuel tank (Ferrick et al. 1982).

The former study is shown in Figure 1. The right half of a galvanized steel sheet was coated by a thin layer (143 g/m²) of PEG (mixture of PEG 1000 and PEG 400 by the weight ratio of 3.2:2) and was dry before the test. Figure 1a shows the panel a few minutes after the test started. About 40 minutes after exposure, with about 2 cm of snow accumulation, the coating was still effective to some extent (Fig. 1b). The coating was melting the snow but the rate of melting couldn’t follow the precipitation rate. Since the rate of precipitation was rather high, (roughly 4 cm/hr) and remained constant, snow covered the coated surface in about 2 hours (Fig. 1c). But a liquid layer still existed at the PEG/snow interface, and the snow on the surface slid off when the panel was placed in an upright position (Fig. 1d). The effectiveness was almost gone after 4 hours (Fig. 1e).

On a level surface, the effectiveness of a freezing point depressant is determined by the amount of snow or ice it can melt at a prescribed temperature. On a sloped or vertical surface, the requirements for an effective freezing point depressant are rather conflicting. In order to make the snow
a. Beginning of test. Right half of the panel is coated by 200 g/m² of a mixture of 32 parts PEG 1000, 20 parts PEG 400 and 20 parts water.

b. Forty minutes after start of test.

*Figure 1. Snow control test.*
c. Two hours after start of test—no more slush is visible on the PEG-coated surface.

d. Two hours after start of test—most of the accumulated snow falls off when the panel is raised to vertical.

Figure 1 (cont'd). Snow control test.
slide off easier, the viscosity of the solution has to be low. However, such a solution tends to drip faster, losing its effectiveness quicker. More detailed studies are needed to optimize the coating properties.

In the second study, the space shuttle's external fuel tank was simulated by a cryopanel coated with Spray On Foam Insulation (SOFI) covered with three grades of PEG. They were a mixture of molecular weights 400 and 1000 (3:2:2) for test 5, 4000 for test 9, and 6000 for test 11. Water solutions of those PEG grades were sprayed on a nominally 1.9-cm-thick SOFI layer on the cryopanel in a 36- by 457-cm strip at a rate of 275 g/m² (Fig. 2). The panel was filled with liquid nitrogen and watched to see if frost and ice would form. As the frost or ice accumulated on the untreated surface, PEG started to work, keeping the treated surface ice free. The PEG-treated surface, except for those portions having very thin SOFI layers, remained ice-free for 5 hours. However, a certain amount of PEG was lost by dripping. The PEG that dripped down was collected in a plastic tray as shown in Figure 3. The concentration was measured by taking a refractive index of the collected samples every 30 minutes. By comparing these with the refractive index of a solution of known concentration, the concentration of PEG in the drip pan could be determined. The measured result is shown in Table 3. The concentration in the drip decreases monotonically, except after 270
Figure 3. Drops containing PEG are collected below cryopanel.

Table 3. PEG concentration in drop from cryopanel.

<table>
<thead>
<tr>
<th>Time from start (min.)</th>
<th>Test 5</th>
<th></th>
<th>Test 9</th>
<th></th>
<th>Test 11</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount of drip (g)</td>
<td>PEG conc. (%)</td>
<td>PEG loss (g)</td>
<td>Amount of drip (g)</td>
<td>PEG conc. (%)</td>
<td>PEG loss (g)</td>
</tr>
<tr>
<td>60</td>
<td>1.2</td>
<td>58.7</td>
<td>0.7</td>
<td></td>
<td>0.4</td>
<td>55.8</td>
</tr>
<tr>
<td>90</td>
<td>4.5</td>
<td>52.5</td>
<td>2.36</td>
<td></td>
<td>5.8</td>
<td>45.8</td>
</tr>
<tr>
<td>120</td>
<td>9.6</td>
<td>51.5</td>
<td>4.94</td>
<td></td>
<td>11.0</td>
<td>43.4</td>
</tr>
<tr>
<td>150</td>
<td>11.9</td>
<td>47.7</td>
<td>5.67</td>
<td></td>
<td>32.5</td>
<td>40.4</td>
</tr>
<tr>
<td>180</td>
<td>6.5</td>
<td>44.7</td>
<td>2.90</td>
<td></td>
<td>55.2</td>
<td>39.9</td>
</tr>
<tr>
<td>210</td>
<td>1.2</td>
<td>44.8</td>
<td>0.54</td>
<td></td>
<td>39.6</td>
<td>39.1</td>
</tr>
<tr>
<td>240</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
<td>53.6</td>
<td>35.2</td>
</tr>
<tr>
<td>270</td>
<td>0.3</td>
<td>74.1</td>
<td>0.22</td>
<td></td>
<td>41.3</td>
<td>32.5</td>
</tr>
<tr>
<td>300</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
<td>40.8</td>
<td>29.9</td>
</tr>
</tbody>
</table>

minutes in test 5, which indicated that water in the drip evaporated because of a change in ambient conditions as shown in Figure 4. On the other hand, the rate of total PEG loss peaked 120-180 minutes after the dripping began (Fig. 5). The whole coating started to move at about this time. Probably moisture penetrated through the coating by then and made the whole layer into a viscous liquid.
POSSIBLE METHODS OF COATING APPLICATION

Various organic solvents, as well as water, can be used to dilute PEG, making spraying or brush painting feasible. However, a thick coating of diluted PEG tends to leave spherulite type crystals after the solvent has evaporated (Fig. 6). For example, mixtures of PEG 300 and 1540 (designated as PEG 1500) and an ethylene dichloride solution left large spherulites, and gaps between the crystals were filled with a thin oil-like layer. Apparently, PEG of low molecular weight makes the coating surface very rough.

Generally, PEG of molecular weight of 1000 to 2000 is the most convenient since it has a waxy or grease-like consistency at room temperature and it

Figure 4. Concentration of PEG in drips. It continuously decreased, except for last of test because of a very slow drip rate.

Figure 5. Time variation of PEG loss rate.

Figure 6. Spherulite crystals left after thick diluted solution of PEG 1500 has evaporated.
can be applied either by spraying it hot or diluted by a solvent. In the case of a mixture of PEG of two molecular weights, such as PEG 1500 (Table 1), its consistency is close to grease and it can be smeared on the surface. Low molecular weight PEG is liquid at room temperature and the surface temperature has to be kept lower than the melting point of the PEG to keep the coating from dripping away. Since the PEG coating is sacrificial, longer operation requires a thicker coating. After prolonged exposure to icing conditions, the thicker coating would roughen by wash out.

Although higher molecular weight PEG is a slightly more resistant coating, single-component coatings will not last for long operations under severe conditions. A coating having a low surface energy matrix impregnated with PEG may be a good approach.

COST

It is very difficult to compare the cost of PEG with that of other icing control substances because no reasonable base exists for comparing their effectiveness. The closest substance whose cost can compare with the cost of PEG is the ethylene glycol monomer of the same grade ("Baker" grade). The price of 19 L (5 gal.) of Baker grade PEG 1000, in the 1982/1983 VWR Scientific Inc. catalog, is $151.75, while the same amount of Baker grade ethylene glycol is $87.85; PEG costs 73% more. However, such comparison may be meaningless, since ethylene glycol loses its effectiveness within a short time by dripping while PEG stays effective for hours. In the CRREL studies previously mentioned, the cost of coating was about $1/m² for the snow panel and $2/m² for the cryopanel. Lower grade PEG may be used to reduce the cost considerably.

SAFETY

According to the Merck Index (Weinholz 1976) the toxicity of PEG when given orally to rats (LD₅₀) is 40-50 g/kg, depending on its molecular weight. PEG is used in food processing as well as in cosmetics and ointments, indicating that PEG is a very safe substance.

The CRC Laboratory Safety Handbook (1971) listed a wider range of hazards. On a scale of 1 (low) to 5 (high), the relative health hazards for various modes of exposure were mostly 1, except for ingestion. The flash point is listed at 111°C. Unfortunately, only ethylene glycol is listed, but values for the monomer could serve as a reasonable basis for evaluation.

CONCLUSIONS

Polyethylene glycol could be applied to almost any surface. However, because it is translucent, application on windshields or optical surfaces is probably not a good idea. Also, even the PEG with the highest molecular weight is relatively soft and applications under abrasive conditions as a single-component coating, such as on helicopter rotor blades, which are subjected to rain erosion, are not feasible. Impregnation of PEG in a low surface energy matrix of greater durability may considerably improve its performance under abrasive conditions. In any case, the limited effective life of a PEG solution has to be taken into account for all applications.

In consideration of the above constraints, the single-component PEG coating is effective under short-term "moderate" environmental conditions. A possible application is on the space shuttle's external cryogenic fuel tank. Conditions there are not too abrasive and effectiveness needs to be only short-term. However, possible contamination to the cargo bay of the shuttle and an insufficiently low flammability have precluded using PEG on the space shuttle under its current operating restrictions.

A second possible application is short-term ice prevention for aircraft. Usually, liquid anti-icing agents are sprayed on aircraft before takeoff. However, their effectiveness is quickly lost by dripping while the aircraft is parked, or the coating is blown away when the aircraft takes off. According to the investigations made by the National Transportation Safety Board of the 13 January 1982 Air Florida crash at Washington National Airport (NTSB 1982a-f), the main cause was errors by the pilots and the operator of the hot ethylene glycol spray rig. However, stall caused by accumulated snow near the wing tip after the long delay following deicing may have aggravated the problem since air speed at takeoff was reasonably high (NTSB 1982a). If a longer lasting deicing agent, such as PEG, had been used in place of the simple ethylene glycol solution, wing tip contamination may have been reduced and the worst case might have been avoided.

A temporary remedy for frost problems on the third rail of an electrified railway may be another possible application.
PEG is by no means a panacea for icing problems. However, it can solve certain problems relatively easy and inexpensively, if we understand the properties of PEG and the mechanisms of ice control.

LITERATURE CITED


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National Transportation Safety Board (1982e) NTSB investigates runway conditions. Aviation Week and Space Technology, 117(18), November 1, pp. 92-95.


Appendix A

The following is an excerpt from the Merck Index (Weiholz 1976).

7349. Polyethylene Glycol. $\alpha$-Hydro-$\omega$-hydroxy-poly (oxy- 1,2-ethanediyl); macrogol; PEG; Carbowax; Nycoline; Puracol E; Poly-G; Polyglycol E; Solbase. Liquid and solid polymers of the general formula $\text{H(OCH}_2\text{CH}_2\text{)}_n\text{OH}$, where $n$ is greater than or equal to 4. In general, each PEG is followed by a number which corresponds to its average molecular weight. Synthesis: Fordyce, Hibbert, J. Am. Chem. Soc. 61, 1905, 1910 (1939).


Polyethylene glycol 400, average value of $n$ between 8.2 and 9.1, molecular weight range 38-420. Viscous, slightly hygroscopic liquid; slight characteristic order; d$_{20}^\circ$ 1.110-1.140. Freezing range 4-8°C. Viscosity (210°F): 6.8-8.0 centistokes. LD$_{50}$ orally in rats: 43.6 g/kg.

Polyethylene glycol 600, average value of $n$ between 12.5 and 13.9, molecular weight range 570-630. Viscous, slightly hygroscopic liquid; characteristic odor; d$_{20}^\circ$ 1.126. Freezing range 20-25°C. Viscosity (210°F): 9.9-11.1 centistokes.

Polyethylene glycol 1500, average value of $n$ between 29 and 36, molecular weight range 1300-1600. White, free-flowing powder; d$_{20}^\circ$ 1.15-1.12. Freezing range 44-48°C. Viscosity (210°F): 25-32 centistokes.

Polyethylene glycol 4000, average value of $n$ between 68 and 84, molecular weight 25 range 3000-3700. White, free-flowing powder or creamy-white flakes; d$_{20}^\circ$ 1.20-1.21. Freezing range 44-58°C. Viscosity (210°F): 76-110 centistokes. LD$_{50}$ orally in rats: 59 g/kg (divided doses).

Polyethylene glycol 6000, average value of $n$ between 158 and 204, molecular weight range 7000-9000. Powder or creamy-white flakes; d$_{20}^\circ$ 1.21. Freezing range 56-63°C. Viscosity (210°F): 470-900 centistokes. LD$_{50}$ orally in rats: > 50 g/kg.

Use: As water-soluble lubricants for rubber molds, textile fibers, and metal-forming operations. In food and food packaging. In hair preparations, in cosmetics in general, and in ointments. Also in water paints, paper coatings, polishes and in the ceramics industry. Caution: Solvent action on some plastics!

Therapeutic Category: Pharmaceutical aid (ointment and suppository base).

Therapeutic Capacity (Veterinarian): Ointment base.

* Note some discrepancy in PEG 1500 in freezing point and appearance with Table 1.