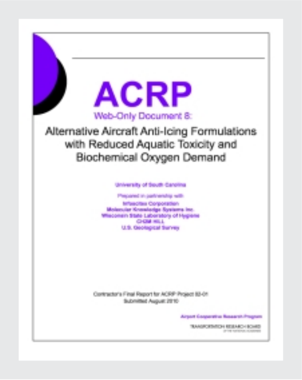

ACRP

Web-Only Document 8:

Alternative Aircraft Anti-Icing Formulations with Reduced Aquatic Toxicity and Biochemical Oxygen Demand

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Alternative Aircraft Anti-Icing Formulations with Reduced Aquatic Toxicity and Biochemical Oxygen Demand

University of South Carolina

Prepared in partnership with

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Wisconsin State Laboratory of Hygiene
CH2M HILL
U.S. Geological Survey

Contractor's Final Report for ACRP Project 02-01
Submitted August 2010

Airport Cooperative Research Program

TRANSPORTATION RESEARCH BOARD
OF THE NATIONAL ACADEMIES

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Appendices

The information in this document is summarized in *ACRP Research Results Digest 9: Alternative Aircraft and Pavement Deicers and Anti-Icing Formulations with Improved Environmental Characteristics*. Readers can purchase or read *ACRP Research Results Digest 9* at http://www.trb.org/Publications/Blurbs/163408.aspx.

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ACRONYMS AND ABBREVIATIONS

µg/L	micrograms per liter
µL	microliter
µM	micromolar
AAF	aircraft anti-icing fluid
ACRP	Airport Cooperative Research Program
ADF	aircraft-deicing fluid
AMS	Aerospace Material Specification
ASTM	American Society for Testing and Materials
BOD	biochemical oxygen demand
BOD_5	5-day biochemical oxygen demand
CAS RN	Chemical Abstracts Service Registry Number
CMC	critical micelle concentration
COD	chemical oxygen demand
cP	centipoise
DEG	diethylene glycol
DO	dissolved oxygen
EC_{50}	half maximal effective concentration
EPA	U.S. Environmental Protection Agency
FPD	freeze-point depressant
HLB	hydrophilic-lipophilic balance
HOT	holdover time
L	liter
LC_{50}	50 percent lethal concentration
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
PDM	pavement-deicing materials
Q-TOF	quadropole time of flight
rpm	revolutions per minute
SAE	Society of Automotive Engineers
TEA	triethanolomine
TIE	toxicity identification evaluation
ThOD	theoretical oxygen demand
UM-BDD	University of Minnesota-Biocatalysis/Biodegradation Database
wt%	percent by weight

SECTION 1

INTRODUCTION

The current research was conducted to identify alternative aircraft and pavement deicer and anti-icer formulations with improved environmental characteristics compared to currently used commercial products (2007). The environmental characteristics of primary concern are the biochemical oxygen demand (BOD) and aquatic toxicity of the fully formulated products. Except when the distinction among products is necessary for clarity, "deicer" will refer to aircraft-deicing fluids (ADFs), aircraft anti-icing fluids (AAFs), and pavement-deicing materials (PDMs).

A previous report presented the results of the first phase of the research, consisting of a review of available literature and data, and the results of laboratory analyses of commercial aircraft and airfield pavement deicers*(1)*. These analyses characterized the oxygen demand and aquatic toxicity of the commercial products, and identified the relative contribution of constituent components to these characteristics.

This current report presents the results of the second phase of the research, wherein candidate alternative components were evaluated and mixtures were built up through a progressive series of performance and environmental testing and down-selecting. At the direction of the research panel, the research objectives in this phase were the development of a Type IV aircraft anti-icing fluid formulation with reduced toxicity compared to commercially available products, and identification of an additive for solid pavement deicers to reduce caking. The following activities were conducted to achieve these research objectives:

- Candidate freezing-point depressants (FPDs), thickeners, surfactants, and corrosion inhibitors with improved environmental qualities were identified and compared to components of commercial aircraft deicers and anti-icers.
- Laboratory analysis of the candidate components were conducted for oxygen demand and toxicity.
- Candidate components were down-selected to identify a subset for use in building candidate formulations.
- A series of testing and down-selecting of increasingly complex mixtures was conducted to arrive at a final formulation that is equivalent to, or better than current commercial formulations in terms of deicing performance and environmental characteristics.
- Candidate anti-caking agents were identified and tested in solid FPD formulations to evaluate performance.
- The environmental characteristics of the final formulations were determined.

The procedures developed and applied in this research would be applicable to developing additive packages for formulations based on other FPDs.

Background

The aviation industry faces a formidable combination of tasks in ensuring the safety of winter flight operations. These include removing ice and snow from aircraft surfaces, preventing ice and snow from accumulating on aircraft surfaces before takeoff, maintaining ice- and snow-free taxiways and runways, maintaining flight schedules, and minimizing the environmental impact of aircraft and airfield deicer and anti-icer formulations through deicer-runoff management programs. The industry has made steady progress over the past two decades in collecting and containing deicing runoff; however, a more comprehensive and more practical approach to reducing the environmental impacts of deicers includes reducing BOD and the potential toxic impact of components in the products and, by extension, in discharges to the environment. Deicer manufacturers have made progress to reduce these impacts in formulations within recent years, but BOD and aquatic toxicity in deicing runoff entering receiving waters continues to be a concern.

FPDs in ADFs and AAFs are most commonly propylene glycol or ethylene glycol, or, rarely, diethylene glycol (DEG). New formulations have appeared in recent years using glycerol and 1,3-propandiol, although their use is currently limited. ADFs and AAFs also contain water and various additives, collectively referred to as the “additive package,” which enhance the fluids’ performance and are required to meet strict Society of Automotive Engineers (SAE) international performance standards*(2)*. Classes of chemicals in additive packages include corrosion inhibitors, surfactants, thickeners, dyes, flame retardants, defoamers, and pH buffers *(3, 4)*.

Although it is recognized that the primary source of BOD in all aircraft and airfield deicers is the FPD, the source of toxicity has not been as clear. The first phase of this research found that aquatic toxicity in aircraft deicers is associated with additives, principally polyethoxylated nonionic surfactants, including both alkyphenol ethoxylate surfactants and aliphatic alcohol ethoxylate surfactants. In the case of one Type IV aircraft anti-icer, triazole-based corrosion inhibitors were also implicated as contributing significantly to toxicity, although this class of chemicals is being phased out of commercial formulations. Toxicity in pavement deicers was found to be associated primarily with the FPDs in those products.

Objectives of the Phase 2 Research

The primary objective of the Phase 2 research was to identify and characterize commercially viable alternative deicing formulations with reduced aquatic toxicity and BOD and to generate a data base for use by the air transport industry. Another objective was to present this information to chemical manufacturers so they could use it to produce more environmentally friendly deicing formulations and to aircraft operators so they could look at alternatives for meeting discharge requirements.

Report Structure

Section 2 presents a summary of the rationale for the selection of alternative candidate aircraft and runway deicing/anti-icing components evaluated in the test program. The components included FPDs, thickeners, surfactants, corrosion inhibitors, anti-caking agents and other additives.

A summary of the test plan used to evaluate the alternative components is presented in Section 3. The test program was divided into two parts: Tier 1 and Tier 2. Tier 1 testing evaluated pure components and mixtures of pure components with water. Candidate components were down-selected for Tier 2 testing that involved more-complex mixtures. After evaluation of the Tier 1 results, Tier 2 tests were redirected to focus on aircraft Type IV anti-icing formulations and sodium formate runway deicers.

Details of the Tier 1 experimental results are presented in Section 4 and the Tier 2 results in Section 5, including a summary of the aquatic toxicity results for the final Type IV formulation. Degradation pathways for the deicing components are detailed in Section 6. Conclusions of the study are presented in Section 7, and suggested future research topics are provided in Section 8.

SECTION 2

SUMMARY OF CANDIDATE DEICER COMPONENTS EVALUATED IN TEST PROGRAM

The initial phase of the research focused on identifying alternatives for four major deicer components based on their contributions to BOD and toxicity:

- FPDs: 26 candidates
- Thickeners: 5 candidates
- Surfactants: 19 candidates
- Corrosion Inhibitors: 17 candidates

Also identified were two candidate anti-caking additives for use in sodium formate runway deicers and one candidate antifoam for use in deicing formulations.

A combination of molecular modeling, database searches, and literature searches were used to identify candidates for each of these component classes. The selection approach and recommended candidates are detailed in the following subsections.

FPD Candidates for ADFs and AAFs

The following chemicals were identified in the literature as either current or proposed FPDs in ADFs or AAFs:

- 1,2-Propylene glycol
- 1,3-Butanediol
- 1,3-Propylene glycol
- Diethylene glycol
- Dipropylene glycol
- Erythritol
- Ethyl lactate
- Ethylene glycol
- Glycerol
- Mannitol
- Pentaerythritol
- Sorbitol
- Triethylene glycol
- Urea
- Xylitol

The general characteristics of viable FPDs were identified by examining this list and considering some of the fundamental relationships between chemical structure and physical properties. These characteristics include:

- FPDs have low molecular weight. The largest molecule contains six carbon atoms. This makes sense because freezing point depression is related to molar concentration.
- FPDs exhibit strong hydrogen bonding because of the presence of alcohol or amine groups. The presence of these bonds increases non-ideal solution behavior, which enhances the performance of the FPD.

- FPDs contain several oxygen atoms. This increases the hydrogen bonding and polar interactions with water, in addition to lowering the chemical's BOD.
- FPDs used on aircraft are typically nonionic compounds. Although various salts have been proposed, the intimate contact of FPD with the variety of materials and electrical systems found on aircraft tends to favor the use of non-ionic compounds.
- Except for a carbonyl group, all the FPDs contain only single-bonded atoms. This is probably because of a requirement for high thermal stability and low chemical reactivity.
- The use of amine groups in FPDs is limited. This is probably the result of the increased toxicity of amine-containing compounds and their potential for contributing to eutrophication of receiving waters.

Using these general characteristics, a set of molecular structure constraints was developed to guide the search for candidate FPDs. The search was limited to those candidates whose molecular structure can be constructed from the following groups:

>C< –H –O– –CO–

Groups containing nitrogen were excluded because of concerns that they could contribute to eutrophication. Table 2-1 shows how the molecular structure of some of the FPDs listed above can be represented by these groups.

TABLE 2-1. Structural group representation of FPDs.

FPD	Formula	Groups
1,2-Propylene glycol	$C_3H_8O_2$	3 >C<, 8 –H, 2 –O–
Ethyl lactate	$C_5H_{10}O_3$	4 >C<, 1 –CO–, 10 –H, 2 –O–
Ethylene glycol	$C_2H_6O_2$	2 >C<, 6 –H, 2 –O–
Glycerol	$C_3H_8O_3$	3 >C<, 8 –H, 3 –O–
Triethylene glycol	$C_6H_{14}O_4$	6 >C<, 14 –H, 4 –O–

Group representation enabled the computational generation of chemical structures for all candidate FPDs. The first step was to limit the number of carbons in a structure to a minimum of one and a maximum of six. A constraint also was imposed that at least two oxygen atoms be present in the structure. All possible combinations of groups satisfying these structural constraints were generated, and then the chemical formula for each of these combinations was generated. This procedure resulted in a total of 160 candidate chemical formulas. The following are examples of these candidate formulas:

$C_2H_2O_2$	$C_3H_2O_3$	$C_3H_6O_3$
$C_4H_2O_6$	$C_4H_{10}O_4$	$C_5H_2O_{10}$
$C_5H_{12}O_5$	$C_6H_4O_6$	$C_6H_{14}O_6$

Each of these 160 candidate chemical formulas was used to search for commercially available chemicals using the National Institute of Standards and Technology Chemistry WebBook *(5)*. The WebBook contains more than 70,000 chemical species. Candidates that contained chemical reactive groups such as acids or peroxides were excluded from consideration. Appendix A lists the 419 chemicals found in this search. Although any database search is limited to the extent of the database, the effectiveness of this search was validated because it found all the FPDs currently in use or being considered for use.

Availability and Pricing

Not all of the chemicals listed in Appendix A are available in commercial quantities. To determine commercial availability, the research team searched the online version of the *Aldrich Chemical Catalog (6)*. The online catalog contains more than 40,000 commercially available chemicals. If a candidate was found in the online catalog, it was retained for further examination. If a candidate was not found in the online catalog, it was considered to be commercially unavailable and was rejected. This screening process yielded 219 candidate FPDs.

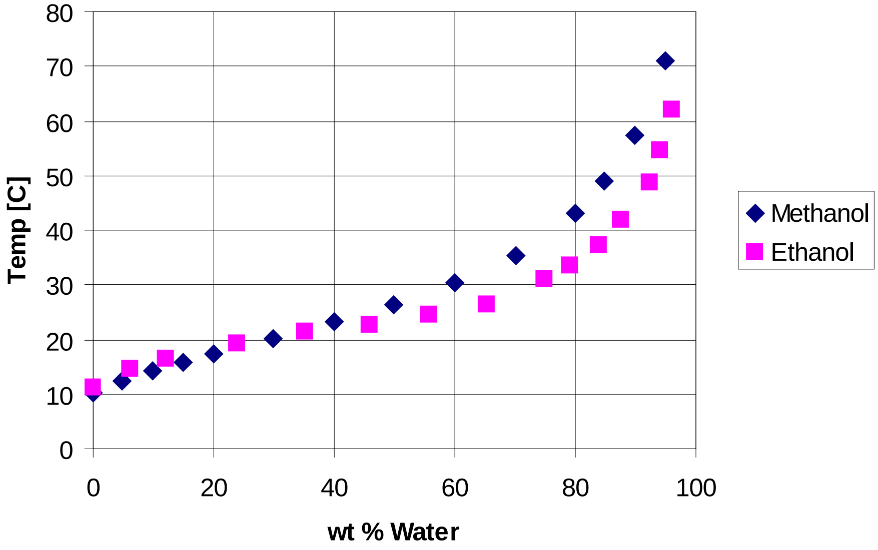
Although some candidates were commercially available, their high price would prohibit use in a deicing or anti-icing fluid. Because these chemicals are available solely for research purposes, the prices in Aldrich Chemical Catalog are primarily for laboratory quantities and purities. These prices are often ten times greater than bulk prices. Because of these considerations, price was used very conservatively as a constraint. Only those chemicals whose price was greater than $750 per kilogram were eliminated from consideration. This screening step eliminated 87 candidates, leaving 132 for further consideration.

Flash Point

Paragraph 3.2.1 of the Aerospace Material Specification (AMS) 1424G states that fluids that are used as supplied must have a flash point not lower than 100°C. Although many deicing and anti-icing fluids are supplied mixed with water, this dilution has little effect on the FPD's flash point. Figure 2-1 shows the flash points for methanol-water and ethanol-water mixtures *(7)*.

As Figure 2-1 shows, even at 60 percent water by weight, the flash points of the alcohol mixtures have increased by less than 20°C over the flash point of the pure alcohols. Using this observation in a conservative manner, the research team rejected all candidate FPDs with flash points below 75°C. This eliminated 79 candidates from further consideration. The flash points for 21 candidates were not available; however, these candidates all had high melting points, making them room-temperature solids. As such, their flash points would satisfy the constraint and they were included in the list of candidates for further consideration.

Figure 2-1. Flash points for mixtures of alcohol and water.



Biological Oxygen Demand

BOD is a major environmental concern with deicers, and candidate FPDs were constrained to a BOD of the same general magnitude or lower than currently used FPDs. Quantifying this constraint is complicated by the effect of time, temperature, acclimation of microorganisms and extent of biodegradation on BOD test results. To overcome this difficulty, theoretical oxygen demand (ThOD) was used as the metric for quick screening. ThOD is the amount of oxygen needed to convert a chemical entirely into carbon dioxide, water, and other "final" combustion products. For candidate FPDs, ThOD can be computed by Equation 2-1.

$$ThOD = \frac{(32C + 8H - 16O)}{Mw} \tag{2-1}$$

In Equation 2-1, C is the number of carbon atoms in the candidate, H is the number of hydrogen atoms, and O is the number of oxygen atoms. The right-hand-side of the equation is equal to the grams of oxygen needed for complete oxidation per unit weight. The coefficients in Equation 2-1 give ThOD in units of grams of oxygen per gram of candidate. Table 2-2 gives the ThOD for several currently used FPDs.

Considering the ThODs of current FPDs, all candidates with ThOD values greater than 2.0 were rejected. This criterion further reduced the list of candidates to 41.

Freezing Point Depressant

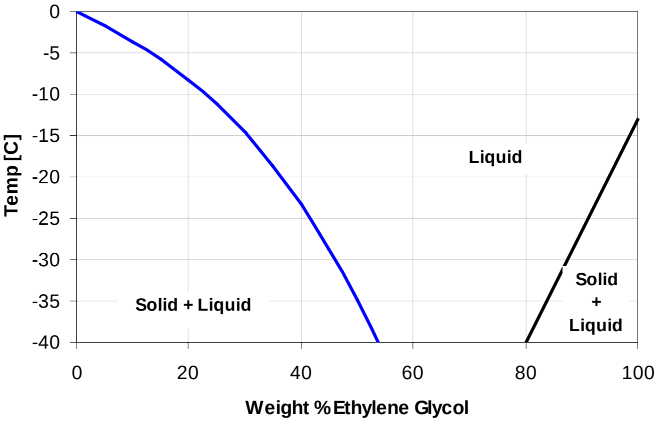
Paragraph 3.5.1 of AMS specification 1424G states that candidate deicing fluids must have a freezing point below -20°C when diluted 1:1 by volume with water. Figure 2-2 shows the freezing point curves for mixtures of ethylene glycol and water *(8)*. The figure shows that mixtures with ethylene glycol concentrations between 36.5 and 94.8 percent will have freezing points below -20°C.

TABLE 2-2. ThOD of some current FPDs.

FPD	ThOD (kg/kg)
Glycerol	1.216
Ethylene glycol	1.288
DEG	1.508
Triethylene glycol	1.598
Propylene glycol	1.682

kg/kg = kilogram per kilogram

Figure 2-2. Freezing point curves for mixtures of ethylene glycol and water.



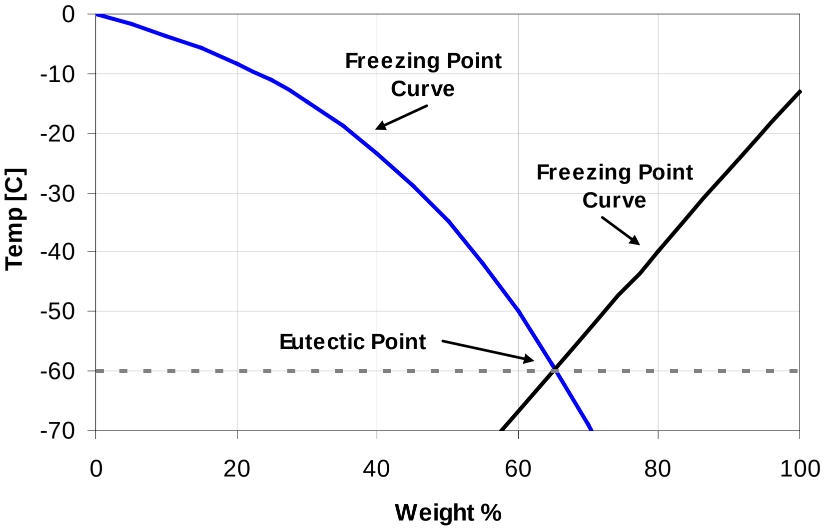
The freezing point curves of candidate mixtures can be predicted from thermodynamics. If it is assumed that all candidate mixtures form simple eutectics and solid-solid phase transitions are ignored, then their freezing point curves are given by Equation 2-2.

$$\ln(\gamma x) = -\frac{\Delta H_m}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) \tag{2-2}$$

In Equation 2-2, x is the mole fraction of the concentrated species, γ is the activity coefficient—a measure of solution non-ideality, ΔHm is the enthalpy of fusion, R is the ideal gas constant, T is the initial melting point of the mixture, and T_m is the melting point of the pure compound.

Equation 2-2 is only applicable for the concentrated portion of the phase diagram. To generate the complete phase diagram, Equation 2-2 is plotted for the concentrated water region first and then for the concentrated FPD region. Figure 2-3 shows such a construction. The intersection of the two curves denotes the eutectic point. The region above the two intersecting curves denotes the liquid phase. The region below the eutectic point, indicated by the horizontal dashed line, denotes the solid phase. The regions below the curves but above the eutectic point indicate two phase regions—a mixture of solid and liquid phases.

Figure 2-3. Construction of a hypothetical freezing point curve.



This analysis was used as the basis for computationally evaluating the eutectic point for each of the candidate FPDs. Unfortunately, enthalpy of fusion values were found for only 16 candidates. Values were estimated for the remaining candidates, but review of these predictions raised concerns about their accuracy. As an alternative, a single, conservative value was chosen for the enthalpy of fusion in the analysis. This value was used to evaluate all candidates, including those for which experimental values were known.

Figure 2-4 shows how varying the enthalpy of fusion affects a mixture's eutectic point and thus its acceptability as a FPD. It was assumed that the FPD had a freezing point of 10°C and the solution exhibited ideal behavior. (For ease of computation, Figure 2-4 displays FPD concentration in mole percent.)

Figure 2-4. Variation of eutectic point with variation in enthalpy of fusion (ΔHm is given in units of kJ/mol).

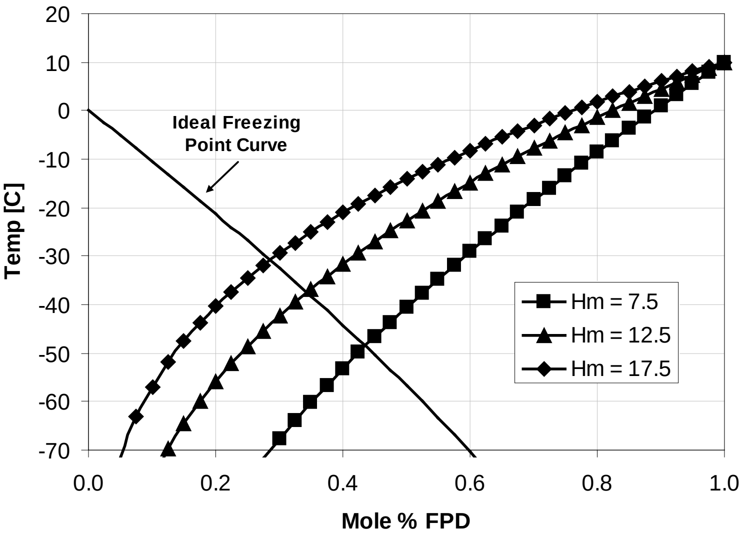


Figure 2-4 shows that as the enthalpy of fusion increases, the mixture's freezing point decreases. A lower value of the enthalpy of fusion is thus preferable in candidate FPDs. The lowest enthalpy of fusion values found for candidate FPDs was 7.5 kJ/mol. This was therefore chosen as the single, conservative value to use in the continued analysis.

Using a value of 7.5 kJ/mol for the enthalpy of fusion, Figure 2-5 shows how the eutectic point varies as a function of FPD melting point.

Figure 2-5. Variation of eutectic point with variation in FPD freezing point (A ΔHm of 7.5 kJ/mol assumed).

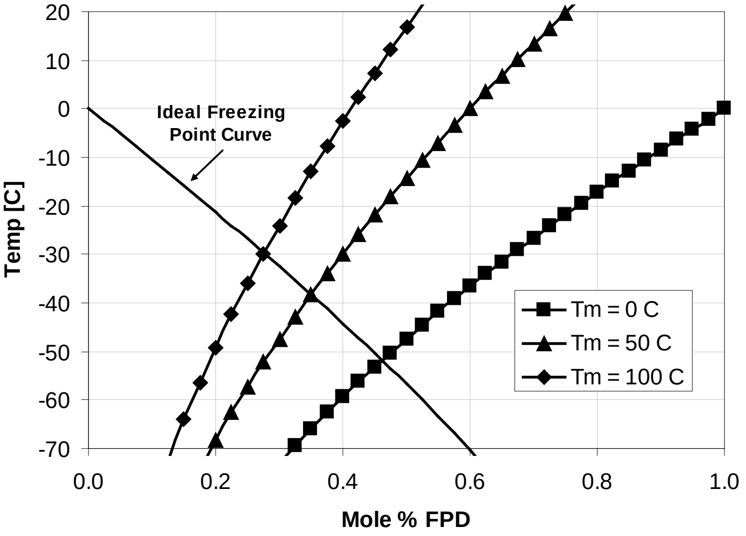


Figure 2-5 shows that an FPD with a melting point of 100°C has a eutectic temperature near -30°C. This value satisfies the specifications. However, the liquid range for such an FPD is very narrow. This means that any preferential evaporation of water or FPD could move the fluid into the two-phase, solid-liquid region, which could result in formation of residuals on the aircraft surface.

From this analysis, an upper limit of 50°C was set on the freezing point of candidate FPDs. This freezing point results in a eutectic temperature near -40°C and a narrow, but acceptable, liquid range. Candidates with freezing points above this limit were eliminated from further consideration.

Seven candidates did not have known freezing points. Values were estimated for these candidates using Joback's group contribution method *(9)*. Using these estimates and literature values for candidate melting points, the number of candidates was reduced to 27.

Aquatic Toxicity

One of the major goals of this project is to develop deicing and anti-icing fluids with lower aquatic toxicity than currently used products. Toxicity analyses conducted during this project identified the aquatic toxicity range for several current products *(1)*. Tables 2-3 and 2-4 show the aquatic toxicity toward *Ceriodaphnia dubia* and *Pimephales promelas*, respectively. Products are designated by letter (A–N) to maintain anonymity.

TABLE 2-3. 96-hour *C. dubia* LC_{50} of some current deicing/anti-icing products.

	Product	**Type**	**Toxicity Limit [mg/l]**
1	D	Type I	33,977
2	C	Type I	26,517
3	E	Type I	11,468
4	A	Type I	7,747
5	N	Runway	4,547
6	K	Type IV	2,600
7	N	Runway	2,437
8	L	Runway	1,302
9	H	Type IV	948
10	I	Type IV	662
11	J	Type IV	528

LC_{50} = 50 percent lethal concentration.
mg/L = milligrams per liter

TABLE 2-4. 96-hour *P. promelas* LC_{50} of some current deicing/anti-icing products.

	Product	Type	Toxicity Limit [mg/l]
1	D	Type I	32,256
2	C	Type I	20,800
3	E	Type I	12,172
4	A	Type I	10,893
5	M	Runway	6,757
6	N	Runway	4,708
7	H	Type IV	2,666
8	J	Type IV	1,041
9	L	Runway	960
10	K	Type IV	888
11	I	Type IV	219

Tables 2-3 and 2-4 are sorted in increasing order of toxicity. Sorting in this manner for the products investigated shows that Type I fluids have the lowest toxicity; Type IV fluids have the highest toxicity; and runway deicers are in between. This is a very interesting result because Type I and Type IV fluids often use the same FPDs, surfactants, and even corrosion inhibitors.

To screen candidate components, the following toxicity goals were established for new complete formulations, based on the objective to improve toxicity over current products:

- New Type I fluids will have a 96-hour LC_{50} in excess of 35,000 mg/L.
- New runway deicing chemicals will have a 96-hour LC_{50} in excess of 7,500 mg/L.
- New Type IV fluids will have a 96-hour LC_{50} in excess of 5,000 mg/L.

These limits would be applicable to both *Ceriodaphnia dubia* and *Pimephales promelas* species. (Although these limits were established for screening purposes, the goal is to develop new products with the lowest toxicities possible.)

If it is assumed that no synergistic or antagonistic effects occur between the components of a formulation, these formulation toxicity limits can be used to establish toxicity limits for pure, candidate FPDs. For example, a mixture containing a minimum of 38.9 wt% 1,2-propylene glycol in water is needed to meet the -20°C freezing point requirement. At this concentration, the toxicity limit of the FPD must be greater than

$$35{,}000 \text{ mg/L} \times 0.389$$

or 13,615 mg/L to satisfy SAE's AMS 1424 Type I fluid toxicity constraint of 4,000 mg/L. 1,2-Propylene glycol has a reported 96-hour LC_{50} of 55,700 mg/l for *Pimephales promelas (10)*.

Because this LC_{50} is greater than the toxicity constraint, 1,2-propylene glycol was retained for further consideration.

Unfortunately, aquatic toxicity data were found for only 12 of the remaining 27 candidates. Two of these candidates had 48-hour LC_{50} values for carp below 280 mg/L *(10)*. One of these candidates had a 96-hour LC_{50} value for bluegill of 90 mg/L *(10)*. Although these species are different than those set in the constraints, they are representative of generally high toxicity and as a result were eliminated from further consideration. This lack of aquatic toxicity data clearly demonstrates the need for the experimental portion of the project.

Mammalian Health Effects

Deicing and anti-icing fluids may be accidentally inhaled or ingested and may come in contact with skin and eyes during application. As a result, the acute toxicity and irritation potential of the candidate FPDs must be low. For each of the remaining 24 candidates, health effect data from Sax's handbook *(11)*, the National Library of Medicine's Hazardous Substances Data Bank (HSDB) website *(12)* and individual material safety data sheets (MSDSs) were examined. Analysis of these data eliminated 7 candidates based on oral toxicity values for rat and mouse species.

Summary of Candidates

Table 2-5 lists the 17 candidate FPDs that satisfy all of the selection constraints. Several of these candidates are commonly used in current deicing fluids. For example, 1,2-propylene glycol evaluated well against all selection constraints and is a major component in commercially available fluids.

TABLE 2-5. Candidate FPDs recommended for further evaluation.

Project ID	Formula	Candidate	CAS RN
027.01	$C_3H_4O_3$	Ethylene carbonate	96-49-1
039.03	$C_3H_8O_2$	1,2-Propylene glycol	57-55-6
039.04	$C_3H_8O_2$	1,3-Propylene glycol	504-63-2
040.01	$C_3H_8O_3$	Glycerol	56-81-5
059.02	$C_4H_6O_3$	Propylene carbonate	108-32-7
071.02	$C_4H_{10}O_2$	2,3-Butanediol	513-85-9
071.04	$C_4H_{10}O_4$	1,3-Butanediol	107-88-0
071.12	$C_4H_{10}O_2$	2-Methyl-1,3-propanediol	2163-42-0
072.01	$C_4H_{10}O_3$	Diethylene glycol	111-46-6
097.05	C_5H8O_2	4-Methyl-γ-butyrolactone	108-29-2
099.01	$C_5H_8O_4$	Dimethyl malonate	108-59-8
111.02	$C_5H_{12}O_3$	2-(2-Methoxyethoxy)-ethanol	111-77-3
145.01	$C_6H_{10}O_4$	Dimethyl succinate	106-65-0
151.16	$C_6H_{12}O_3$	2,2-Dimethyl-1,3-dioxolane-4-methanol	100-79-8

TABLE 2-5. Candidate FPDs recommended for further evaluation.

Project ID	Formula	Candidate	CAS RN
157.01	$C_6H_{14}O_3$	2-(2-Ethoxyethoxy)-ethanol	111-90-0
157.09	$C_6H_{14}O_3$	Dipropylene glycol	25265-71-8
158.01	$C_6H_{14}O_4$	Triethylene glycol	112-27-6

CAS RN = Chemical Abstracts Service Registry Number

Appendix B provides detailed information for each of these candidate FPDs.

Freezing Point Depressant Candidates for PDMs

The following chemicals were identified in the literature as either current, past, or proposed FPDs for PDMs:

1,2-Propylene glycol
Potassium formate
Sodium acetate
Magnesium acetate
Calcium acetate
Diethylene glycol

1,3-Propylene glycol
Potassium acetate
Sodium formate
Urea
Ethylene glycol
Triethylene glycol

Many of the same chemicals used to remove ice and snow from aircraft are also used to remove ice from runways. This is reasonable because similar constraints apply to both operations. The list above includes several metallic salts that are used for runway deicing. Using salts as FPDs has the advantage that each ion contributes on a molar basis to the lowering of the mixture's freezing point. As a result, adding one mole of a monovalent salt to water actually contributes two moles of ions to the solution, assuming the salt completely dissociates.

A search of the literature did not find runway deicing chemicals based on cations other than sodium, potassium, calcium, and magnesium anions. The use of other period 4 elements—specifically scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc—was investigated. A search of the *Alfa-Aesar Chemical Catalog (6)* and *Sax's Dangerous Properties of Industrial Materials (11)* found only organic salts of these elements with adverse health effects, high cost, or instability. Based on these observations, it was decided to limit the cations to sodium, potassium, calcium and magnesium.

The anions found in PDMs include formates, acetates, lactates, and carbonates. All of these anions have a negatively charged oxygen molecule, which forms an ionic bond with the cation. This observation was used to generalize the search for PDMs whose molecular structure can be constructed from the following groups:

>C< –H –O– –CO– KO– NaO– –OCaO– –OMgO–

Groups containing nitrogen or phosphorus were not included because of environmental concerns. Groups containing silicon were not included because of health concerns. Groups containing sulfur were not included because of corrosion concerns. Table 2-6 shows how the molecular structure of some of the FPDs listed above can be represented by these groups.

TABLE 2-6. Structural group representation of FPDs potentially useful for PDMs.

FPD	Formula	Groups
1,2-Propylene glycol	$C_3H_8O_2$	3 >C<, 8 –H, 2 –O–
Potassium acetate	$C_2H_3KO_2$	1 >C<, 1 –CO–, 3 –H, 1 KO–
Calcium pyruvate	$C_6H_6CaO_6$	2 >C<, 4 –CO–, 6 –H, 1 –OCaO–
Magnesium lactate	$Mg(C_3H_5O_3)_2$	4 >C<, 2 –CO–, 10 –H, 2 –O–, 1 –OMgO–
Triethylene glycol	$C_6H_{14}O_4$	6 >C<, 14 –H, 4 –O–

As before, the number of carbons in a structure was limited to a minimum of one and a maximum of six. At least two oxygen atoms were also required to be present in a structure. The number of metallic cations was limited to a minimum of one and a maximum of three per molecule. (One cation was required because non-ionic candidates have already been identified in the search for ADF and AAF FPDs.) All possible combinations of groups satisfying these structural constraints were generated, and then the chemical formula for each combination was generated. This procedure resulted in a total of 2,172 candidate chemical formulas. The following examples illustrate some of these candidate formulas:

$CHKO_2$	$C_2H_2CaO_4$	$C_5H_7NaO_3$
$C_4H_5KO_4$	$C_6H_6CaO_6$	$C_6H_9NaO_3$
$C_5H_4Na_2O_5$	$C_4H_6MgO_4$	$C_3Na_2O_5$

Each of these 2,178 candidate chemical formulas was used to search for commercially available chemicals using the Aldrich Chemical Catalog *(6)* and the Alfa-Aesar Chemical Catalog *(13)*. Candidates that contained chemical reactive groups such as acids or peroxides were excluded from consideration because of safety or material compatibility concerns. Appendix C lists the 59 chemicals found in this search. Although any database search is limited to the extent of the database, the search found all the FPDs currently in use or being considered for use in PDMs.

Availability and Pricing

Not all of the chemicals listed in Appendix C are available in commercial quantities at reasonable prices. To determine commercial availability the online version of the Aldrich Chemical Catalog *(6)* was searched. Again using price as a very conservative constraint, only those chemicals whose price was greater than $750 per kilogram were eliminated from consideration. This screening step eliminated 28 candidates and left 31 for further consideration.

Another 132 candidates identified in the search for ADFs and AAFs also had acceptable pricing and were considered possible PDM candidates. These previously identified non-ionic candidates were combined with the current 31 ionic candidates to produce a compilation of 163 candidates that were investigated further.

Flash Point

Paragraph 3.2.1 of AMS specification 1435A states that runway deicing fluids must have a flash point not lower than 100°C. Paragraph 3.2.2 of AMS specification 1431B states that runway deicing solids must have a flash point not lower than 93°C. Because some of the candidates may be applied as mixtures with water, these constraints were relaxed slightly, and all candidate FPDs with flash points below 75°C were rejected. This eliminated 80 candidates from further consideration. The flash points for 37 candidates were not available. However, these candidates all had high melting points, making them room-temperature solids. It is therefore reasonable to assume that their flash points would satisfy the constraint, so they were included in the list of candidates for further consideration.

Biological Oxygen Demand

ThOD was again used to screen candidates for low BOD. Equation 2-1 shows that only carbon, hydrogen and oxygen were used in the calculation of ThOD. Metallic cations were assumed to make no contribution to ThOD. Twelve nonionic candidates with ThOD values greater than 2.0 were rejected. This reduced the current list of 83 candidates to 71. None of the ionic candidates were eliminated.

Note on the Definition of BOD

It is generally assumed that elements such as sodium, potassium, calcium, or magnesium are not oxidized by biochemical means. As a result, the amount of oxygen needed to degrade one molecule of sodium acetate is the same as the amount needed to degrade one molecule of potassium acetate. However, because potassium acetate has a higher molecular weight than sodium acetate, its ThOD is lower by 16 percent. Table 2-7 shows the calculations for these two chemicals.

TABLE 2-7. ThOD values for FPDs.

FPD	**Molecular Weight**	**ThOD (g O_2/g FPD)**
Sodium acetate	82.03	0.68
Potassium acetate	98.14	0.57

g O_2/g FPD = gram of oxygen per gram of FPD

By the same calculation, cesium acetate has a ThOD of 0.29 g O2 / g FPD even though on a molecular basis the same amount of oxygen is needed for degradation.

A thorough comparison of runway deicing chemicals must also consider their ability to melt ice, penetrate ice, and disrupt the adhesion of ice to pavement. A deicing chemical's freezing point depression is a major factor in all of these attributes. Therefore, comparing the freezing point depression of runway deicing chemicals should provide a fair prediction of actual performance.

Table 2-8 shows the freezing points for aqueous solutions of sodium acetate and potassium acetate *(14)*. Figure 2-6 shows the same data plotted on a molar basis.

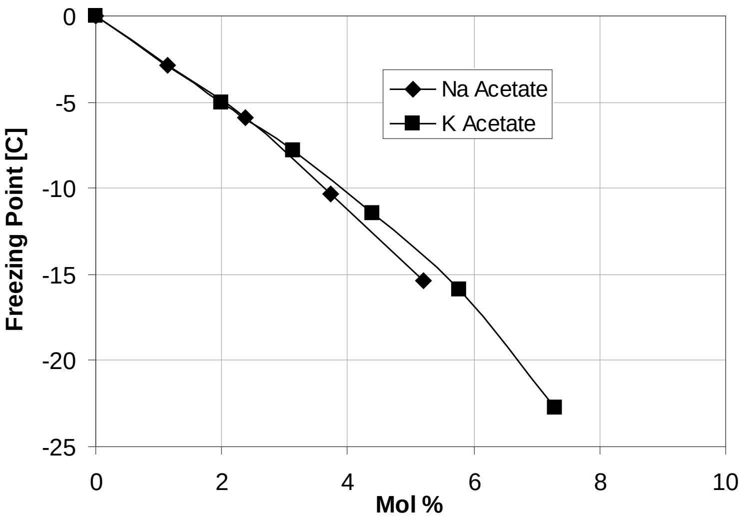
TABLE 2-8. Freezing points of aqueous deicing chemical solutions.

	Sodium Acetate		**Potassium Acetate**	
Weight %	**Mole %**	**Tm [°C]**	**Mole %**	**Tm [°C]**
5	1.1	-2.9	1.0	-0.2
10	2.4	-5.9	2.0	-5.0
15	3.7	-10.3	3.1	-7.8
20	5.2	-15.4	4.4	-11.5
25	—	—	5.8	-15.9
30	—	—	7.3	-22.7

Figure 2-6 shows that slightly more potassium acetate is needed than sodium acetate to achieve the same freezing point depression. For example, to melt 1 kilogram of ice at -15°C would require 2.98 moles of sodium acetate and 3.23 moles of potassium acetate.

To oxidize these quantities of deicing fluid would take 166.9 grams of oxygen for sodium acetate and 180.9 grams of oxygen for potassium acetate. The sodium acetate requires less oxygen. This is the opposite conclusion that is drawn from comparing ThOD values.

Figure 2-6. Freezing point depression on a molar basis.



This analysis shows that simply comparing oxygen demand parameters is insufficient for evaluating the environmental impact of PDMs. Additional parameters such as molecular weight, freezing point depression, application rates, and runoff must be considered. The following metric is proposed for evaluating environmental impact:

> Grams of oxygen needed to oxidize the chemicals needed to achieve and maintain one square meter of runway free of ice for one hour.

Melting, Penetration, and Undercutting

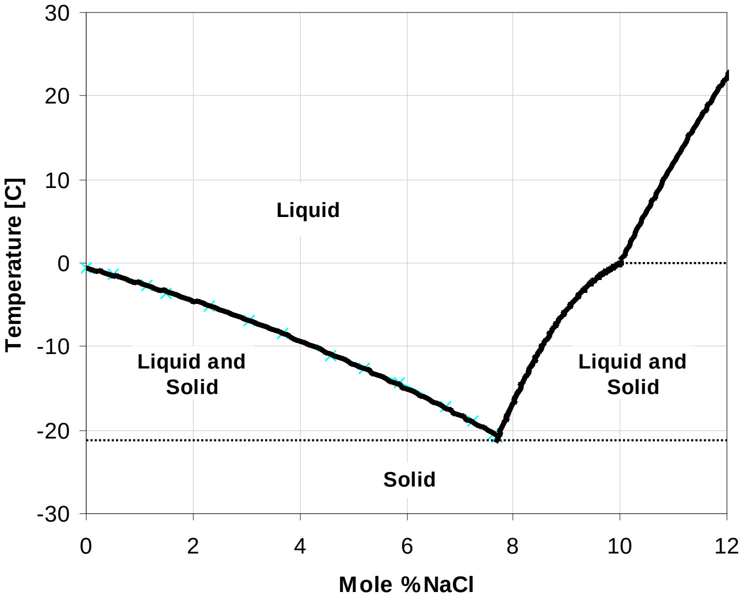
Unlike aircraft deicing chemicals, runway deicers do not need to completely melt accumulated ice and snow. National Research Council publication SHRP-H-332 *(15)* details test procedures for three key properties of runway deicers: 1) the ability to melt ice, 2) the ability to penetrate ice, and 3) the ability to undercut ice. It was not possible to directly relate these properties to specific physical properties, but it is understood that a chemical's freezing point depression is a key factor affecting each property.

Freezing Point Depression

AMS 1431B, the SAE specification for solid runway deicing chemicals, does not specify a required freezing point depression. However, manufacturers do specify a lowest use temperature. Sodium acetate can be used below -18°C. Potassium acetate can be used below -28°C. Sodium chloride should not be used below -10°C.

Although sodium chloride is not used on airfields, it is used here as an example. Figure 2-7 shows the phase diagram for dilute solutions of sodium chloride in water. The figure shows that the recommended minimum use temperature of -10°C is approximately 10°C higher than the eutectic temperature.

Figure 2-7. Phase diagram of aqueous sodium chloride.



This observation was used to set a constraint that candidate FPDs for PDMs must have a eutectic temperature at least 10°C below their lowest use temperature. It was further decided to set the lowest use temperature for candidate runway deicers to a conservative value of -18°C. This results in the constraint that all candidate FPDs must have eutectic temperatures below -28°C.

Because high melting point solids are acceptable runway deicing chemicals, the thermodynamic analysis used previously to screen for eutectic temperatures must be modified. The approximate freezing point depression caused by adding any chemical to water is given by Equation 2-3.

$$\Delta T = 1.86im \tag{2-3}$$

In Equation 2-3, ΔT is the freezing point depression, *i* is the number of species and *m* is the molality of the solution. For a non-ionic compound, *i* is equal to 1. For an ionic compound, *i* is equal to the number of ionic species, assuming the compound is completely dissociated. For example, *i* for calcium chloride is three because it dissociates into one calcium ion and two chloride ions.

Inserting the constraint on the eutectic temperature into Equation 2-4, the following constraint on FPD concentration is obtained.

$$m = \frac{15.05}{i} \tag{2-4}$$

Table 2-9 shows the estimated concentrations needed to meet the use temperature constraint for several candidate FPDs.

TABLE 2-9. Estimated concentrations for limiting eutectic temperature.

Candidate FPD	*i* [ions/mole]	Concentration [mol/kg]	Concentration [g/kg]
Sodium formate	2	7.52	511.5
Potassium formate	2	7.52	632.4
Calcium formate	3	5.02	653.2
Tripotassium citrate	4	3.76	1164.3
Glucose	1	15.05	2711.4

Table 2-9 shows that a minimum of 2,711.4 grams of glucose must be mixed with 1,000 grams of water to produce a solution with an acceptable freezing point. Unfortunately, the solubility of glucose at 20°C is only 910 g/kg of water. Aqueous solutions of glucose cannot be formed that satisfy the limiting eutectic temperature constraint, so glucose would be eliminated from further consideration.

Using this approach, the minimum concentration needed of each candidate to meet the eutectic temperature constraint was calculated. Solubility data were then obtained from *Lange's Handbook (16)* and the HSDB Database *(12)*. If the solubility limit was below the minimum concentration needed, the candidate was rejected. Twenty-four candidates were found to have unacceptable solubility and were rejected. Solubility data for 33 candidates could not be found. These were retained for further screening.

Aquatic Toxicity

The criterion for new runway-deicing formulations was established as a 96-hour LC_{50} in excess of 7,500 mg/L to provide a significant benefit over existing products. This limit would be applicable to both *Ceriodaphnia dubia* and *Pimephales promelas* species. (Although this limit was established for screening purposes, the goal is to develop new products with toxicities as low as possible.)

Aquatic toxicity data were found for 19 of the remaining 47 candidates. Seven of these candidates had LC_{50} values below 7,500 mg/L and were eliminated from further consideration.

Mammalian Health Effects

Health effect data from *Sax's Handbook (11)*, the National Library of Medicine's HSDB website *(12)* and individual MSDSs were examined for each of the remaining 40 candidates. Analysis of these data eliminated seven candidates because of high oral toxicity toward rats and mice.

Carbon-Carbon Brake Oxidation and Runway Corrosion

Many aircraft use carbon composite brake pads in their braking systems. During braking these pads become heated and reach temperatures in excess of 700°C. At these temperatures, carbon exposed to the air will quickly oxidize. To reduce such oxidation, non-wearing brake surfaces are coated with an antioxidant coating.

Stover *(17)* describes an antioxidant coating composed of a zinc-aluminum-phosphate glass. This composition is similar to the generic aluminum-phosphate glass coating proposed by the G-12F Catalytic Oxidation Working Group. Walker et al. *(18)* describe the use of a phosphorus-containing undercoat covered with a boron-containing overcoat. Walker et al. *(19)* further describe a system in which the boron-containing overcoat also contains alkali or alkaline metal silicates, alkali metal hydroxides, boron nitride and boron carbide.

Recent studies *(20-22)* of runway deicing chemicals indicate that sodium- and potassium-based fluids significantly degrade these antioxidant coatings, making carbon composite brakes susceptible to rapid high temperature oxidation. The chemical mechanism by which this degradation takes place is uncertain. Calcium- and magnesium-based fluids cause less degradation than sodium and potassium compounds. Non-ionic compounds do not harm antioxidant coatings.

The current list of candidates contains 12 sodium-based chemicals and 9 potassium-based chemicals. Because considerable research is currently underway into the mechanism of antioxidant coating degradation and into new antioxidant coatings, it was decided to retain these candidates for further evaluation.

Price

Although the price of a chemical is highly dependent upon quantity, grade, and market conditions, the price constraint was tightened to reduce the number of candidate FPDs. Candidates with a price greater than $140 per kilogram were rejected. This constraint eliminated 11 candidates.

Summary of Candidates

Samples of potassium L-lactate could not be purchased. Because of this lack of availability, it was eliminated from further consideration. Table 2-10 lists the 21 candidate FPDs that satisfy the selection constraints for new PDM formulations with improved environmental characteristics. Several of these candidates are used in current runway deicing products.

TABLE 2-10. Candidate freezing point depressants recommended for further evaluation.

Project ID	Formula	Candidate FPD	CAS RN
27.01	$C_3H_4O_3$	Ethylene carbonate	96-49-1
39.03	$C_3H_8O_2$	1,2-Propylene glycol	57-55-6
39.04	$C_3H_8O_2$	1,3-Propylene glycol	504-63-2
40.01	$C_3H_8O_3$	Glycerol	56-81-5
71.04	$C_4H_{10}O_2$	1,3-Butanediol	107-88-0
71.12	$C_4H_{10}O_2$	2-Methyl-1,3-propanediol	2163-42-0
72.01	$C_4H_{10}O_3$	Diethylene glycol	111-46-6
111.01	$C_5H_{12}O_3$	1,1,1-Trimethanolethane	77-85-0
111.02	$C_5H_{12}O_3$	2-(2-Methoxyethoxy)-ethanol	111-77-3
113.01	$C_5H_{12}O_5$	Xylitol	87-99-0
147.03	$C_6H_{10}O_6$	D-Gluconic acid, δ-lactone	90-80-2
151.16	$C_6H_{12}O_3$	2,2-Dimethyl-1,3-dioxolane-4-methanol	100-79-8
157.01	$C_6H_{14}O_3$	2-(2-Ethoxyethoxy)-ethanol	111-90-0
157.03	$C_6H_{14}O_3$	Trimethylolpropane	77-99-6
157.09	$C_6H_{14}O_3$	Dipropylene glycol	25265-71-8
158.01	$C_6H_{14}O_4$	Triethylene glycol	112-27-6
332.01	$C_2H_3NaO_2$	Sodium acetate	127-09-3
749.01	$C_6H_{10}CaO_4$	Calcium propionate	4075-81-4
1509.01	$C_4H_4Na_2O_4$	Disodium succinate	150-90-3
1592.01	$C_4H_4K_2O_6$	L-Tartaric acid dipotassium salt	921-53-9
1829.01	$C_6H_5K_3O_7$	Tripotassium citrate	6100-05-6

The following 12 candidates were also recommended for use in aircraft deicing and anti-icing fluids:

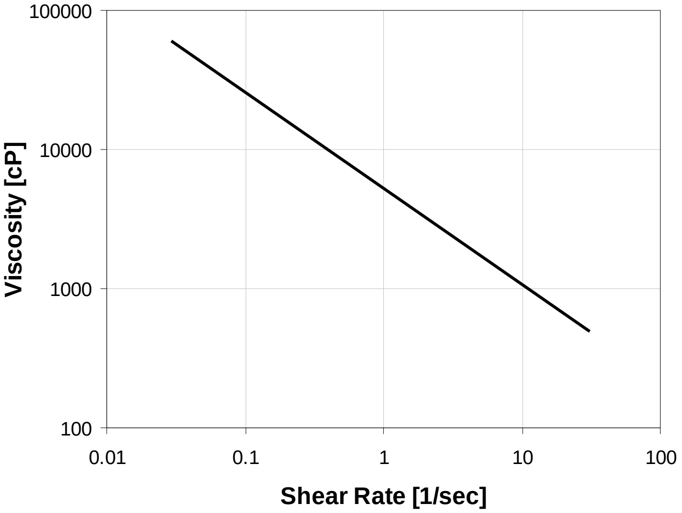
- 2,2-Dimethyl-1,3-dioxolane-4-methanol
- 2-(2-Methoxyethoxy)-ethanol
- 2-(2-Ethoxyethoxy)-ethanol
- 2-Methyl-1,3-propanediol
- 1,2-Propylene glycol
- 1,3-Propylene glycol
- Dipropylene glycol
- Ethylene carbonate
- Triethylene glycol
- Diethylene glycol
- 1,3-Butanediol
- Glycerol

Appendix D details the known information for each of the remaining 9 candidate FPDs.

Thickener Candidates

Figure 2-8 shows the rheological behavior (flow of fluids under strain) of a typical anti-icing fluid. At low shear rates, the fluid has a high viscosity, promoting the formation of a thick coating and slowing drainage. At high shear rates, such as those experienced during takeoff, the fluid has a low viscosity, causing it to readily shed from aerodynamic surfaces.

Figure 2-8. Rheological behavior of typical anti-icing fluid at 0°C.



The shear-thinning behavior required of anti-icing fluids is typically achieved by using associative or particulate thickeners. Typical associative thickeners include polysaccharides such as xanthan gum, welan gum, or carrageenan gum. The most common particulate thickener is lightly cross-linked polyacrylic acid.

Associative thickeners are long-chain, water-soluble polymers. In solution, these polymers are fully extended and randomly oriented. At concentrations greater than what is termed the “overlap concentration,” parts of the polymer chain will associate or entangle. These entanglements produce the high viscosity observed in these polymer solutions. However, these associations also are very weak and can be easily broken by molecular motion. This ease of breakage is why associative thickeners exhibit dramatic shear-thinning behavior.

Polyacrylic acid thickeners typically consist of lightly cross-linked particles having diameters less than 1 micron. When placed in an aqueous solution having a pH in the range of 4 to 10, these particles can swell to 500 times their dry volume. The high viscosity of these solutions is caused by the presence of these large particles and possibly the entanglement of polymeric chains emanating from the particle’s surface. Because these particles are lightly cross-linked, they are easily deformed by fluid motion. This ease of deformation is why particulate thickeners exhibit dramatic shear-thinning behavior.

Thickener Candidates

Four categories of thickening agents that can produce the shear-thinning rheological behavior needed in anti-icing fluids are:

1. Polysaccharides: These agents are long-chain polymers comprising repeat sugar units. They are widely used to thicken food products. Several polysaccharides produce highly shear-thinning aqueous solutions that rapidly recover viscosity after shearing.
2. Synthetic Polymers: Many long-chain polymers will increase the viscosity of aqueous solutions. If this viscosity results from weak inter-molecular bonds or steric hindrance, it is very likely the solution will exhibit shear-thinning behavior.
3. Organoclays: These agents are commonly based on hectorite, a hydrophilic swelling clay composed of silicate sheets that delaminate in water. Organoclays are widely used as rheological modifiers in waterborne coatings, sealants, inks, paper coatings, and ceramics. Organoclay solutions are thixotropic—when a shear is applied the solution's viscosity is greatly reduced; when the shear is removed the solution's viscosity slowly returns to its original high value.
4. Fumed Silica: This agent is composed of small silicon dioxide particles having surface hydroxyl groups. In solution these hydroxyl groups hydrogen bond with groups on other particles, creating a weak network. This network is easily disrupted by applied shear and will reform once the shear is removed.

Organoclays and fumed silica were not considered viable candidates because concern about the effects of adding dispersed solids (potential for settling of solids or residuals) to anti-icing fluids outweighs any possible environmental and performance improvements. Polysaccharide and synthetic polymer candidates were investigated further.

Polysaccharides

Polysaccharides are polymers typically composed of 40 to 3,000 repeat sugar units. Polysaccharides are found in seaweeds, seeds, and plant exudates and are produced by many microorganisms. The most common industrial polysaccharides are *(23)*:

1. Agar: a hydrophilic colloid extracted from marine algae of the class Rhodophyceae. It is insoluble in cold water but soluble in boiling water. Agar gels are used in microbiological research, to stabilize food products, and in many medicinal products. The viscosity of agar solutions is too low for use in anti-icing fluids *(24)*.
2. Alginates: occurs as alginic acid in concentrations ranging from 18 to 40 percent in all brown seaweeds *(23)*. The sodium, potassium, ammonium or propylene glycol salts of alginic acid are typically used as thickening agents. The ester linkages in propylene glycol alginate prohibits it use in alkaline solutions. Although alginate salts can produce aqueous solutions with very high viscosity, their shear-thinning behavior is not large enough for use in anti-icing fluids.
3. Carrageenan: extracted from a number of red seaweeds. It is commonly used as a thickener in toothpastes, shampoos and pharmaceuticals. The viscosity of carrageenan solutions is too low for use in anti-icing fluids *(25)*.
4. Guar Gum: obtained from the seed of the legume *Cyamopsis tetragonolobus*, an annual plant that grows mainly in the arid and semiarid regions of India. Although guar gum can produce high viscosity, shear-thinning solutions, the amount of shear-thinning is not large enough for use in anti-icing fluids *(23)*.

5. Locust Bean Gum: obtained from the seed of the carob tree, which grows in several Mediterranean countries. Used by the ancient Egyptians to bind mummies, locust bean gum is a neutral polysaccharide with a molecular weight reported to be between 300,000 and 360,000 daltons. Locust bean gum solutions are reported to have lower viscosities than carrageenan solutions. Therefore they are not considered as viable candidate thickeners.

6. Pectin: found in all higher plants. Widely used to form food gels. Pectin's solution viscosity is too low for use in anti-icing fluids.

7. Xanthan Gum: an exocellular heteropolysaccharide produced by the *Xanthomonas campestris* bacterium. It is an approved food additive, commonly used in salad dressings and ice creams. Xanthan gum is used in industrial products to thicken fluids, especially as a thickener for drilling fluids. Studies indicate the molecular weight of xanthan gum to be approximately two million daltons *(26)*. Aqueous solutions of xanthan gum have high viscosity and are highly shear-thinning. A 0.5 wt% solution has a viscosity of 8,000 centipoise (cP) at a shear rate of 1 sec^{-1} and a viscosity of 200 cP at a shear rate of 100 sec^{-1} *(23)*. The U.S. Environmental Protection Agency's (EPA's) ECOTOX database reports a 96-hour LC_{50} of 420 mg/L for xanthan gum toward rainbow trout. Xanthan gum is recommended for further investigation.

8. Welan Gum: produced by an *Alcaligenes* species of bacteria in aerobic fermentation. Welan gum solutions have exceptional stability at temperatures of 100°C for extended periods of time *(23)*. Aqueous solutions of welan gum exhibit significant shear-thinning behavior. A 1.0 wt% solution has a viscosity of approximately 10,000 cP at a shear rate of 0.1 sec^{-1} and a viscosity of 1000 cP at a shear rate of 1.7 sec^{-1}. Welan gum is recommended for further investigation.

9. Rhamsan Gum: an anionic, extracellular, microbial polysaccharide produced by a strain of *Alcaligenes* bacteria under aerobic fermentation conditions. Although rhamsan gum can produce high viscosity, shear-thinning solutions, the amount of shear-thinning is not large enough for use in anti-icing fluids *(23)*.

10. Methylcellulose: a methyl ether of cellulose formed from substituting the hydrogen on some of cellulose's hydroxyl groups with methyl groups. Methylcellulose exhibits inverse solubility—it is soluble in cold water but insoluble in warm water. Methylcellulose is available in a wide range of molecular weights, from 10,000 to 250,000 daltons. Although it can produce high viscosity, shear-thinning solutions (a 2 wt% solution of an 86,000 molecular weight methylcellulose has a viscosity of 6,000 cP at a shear rate of 1 sec^{-1} and 1,300 cP at a shear rate of 100 sec^{-1}), the amount of shear-thinning is not large enough for use in anti-icing fluids *(23)*.

11. Hydroxyalkyl Cellulose: a family of non-ionic cellulose ether polymers that are readily soluble in water and are produced in a wide range of molecular weights. Hydroxyethylcellulose is the most widely used member of this family. It is a common thickener for latex paints. A 2 wt% solution has a nominal viscosity of 50,000 cP and is moderately shear-thinning *(23)*. Although hydroxyethylcellulose's properties are not outstanding, it is recommended for further investigation because it is the only non-ionic

thickener with acceptable properties. Experimental evaluation of hydroxyethylcellulose may help determine if ionic nature influences aquatic toxicity.

Synthetic Polymers

Many synthetic polymers are used to thicken cosmetics, paints, coatings, and personal care products. Some of the more common polymers are:

1. Cross-linked Polyacrylic Acid: typically used as a lightly cross-linked polymer in anti-icing fluids, detergents, and surface cleaners. Polyacrylic acid thickeners typically consist of lightly cross-linked particles having diameters less than one micron. When placed in an aqueous solution having a pH in the range of 4 to 10, these particles can swell to 500 times their dry volume. The high viscosity of these solutions is caused by the presence of these large particles and possibly the entanglement of polymeric chains emanating from the particle's surface. Because these particles are lightly cross-linked they are easily deformed by fluid motion. This ease of deformation is why particulate thickeners exhibit dramatic shear-thinning behavior.

2. Polyethylene Oxide: a water soluble, non-toxic, non-ionic polymer used in paints, pharmaceuticals, cleaners, plasticizers, heat transfer fluids, and paper coatings. Also known as polyethylene glycol. Typical molecular weights range from 200 to 7000 daltons. A 50 percent aqueous solution of a 6,000-dalton polyethylene oxide has a viscosity of 100 cP. Polyethylene oxide's solution viscosity is too low for use in anti-icing fluids.

3. Polyvinylpyrrolidone: a water-soluble homopolymer used in the formulation of cosmetics, adhesives and as a plasma extender. A 5 wt% solution of 3,000,000 molecular weight polyvinylpyrollidone was reported to have a viscosity of 350 cP at 25°C. Polyvinylpyrrolidone's solution viscosity is too low for use in anti-icing fluids.

Table 2-11 lists the five thickeners selected for experimental evaluation.

TABLE 2-11. Candidate thickeners.

Project ID	Candidate	Chemical Class
02.001	Kelzan-HP	Polysaccharide
02.002	Kelzan-RD	Polysaccharide
02.003	K1A96	Polysaccharide
02.004	Cellosize DCS HV	Modified Polysaccharide
02.005	Carbopol EZ-4	Synthetic Polymer

Surfactant Candidates

If a mixture of water and propylene glycol was poured onto an aircraft surface, most of the liquid would either bead up into drops or roll right off the surface. This behavior is caused by the mixture's high surface energy—creating a new surface requires considerable energy, so the liquid attempts to minimize its surface area by forming a spherical drop. Surfactants are added to aircraft deicing and anti-icing fluids to reduce their surface energy. With lower surface energy, these fluids will completely spread across aircraft surfaces, thereby ensuring an unbroken liquid coating.

Environmental concerns regarding surfactants are primarily due to aquatic toxicity. The low percentage of surfactant in overall deicer formulations does not pose a significant BOD concern. Most of the surfactants that were examined have LC_{50} values ranging from 1 to 10 mg/L towards fish species. Some have values ranging from 10 to 200 mg/L. Many surfactants lack any experimental values for aquatic toxicity.

Several general observations can be made regarding surfactant toxicity:

- The toxicity of alcohol ethoxylates generally decreases with increasing ethylene oxide chain length.
- Branched alkyl chains are less toxic than linear alkyl chains.
- Secondary alcohols are less toxic than primary alcohols.
- Surfactants containing mixtures of ethylene oxide and propylene oxide are less toxic than those containing only ethylene oxide.

Unfortunately, using these observations to select surfactants with lower aquatic toxicity may decrease performance and biodegradability. Longer ethylene oxide chain lengths increase a surfactant's water solubility, which often causes more foaming. Longer chain lengths also increase surface viscosity, which increases foam stability. Branched alkyl chains degrade slower than linear alkyl chains. Similarly, propylene oxide chains degrade slower than ethylene oxide chains. These potential reductions in performance and biodegradability must be compared against reductions in aquatic toxicity.

Several performance properties were used to select surfactants. The hydrophilic-lipophilic balance (HLB) is a measure of a surfactant's water affinity to its oil affinity. The critical micelle concentration (CMC) is the concentration at which a surfactant saturates water's surface. The cloud point is a measure of surfactant solubility. Of these performance properties, the HLB was the predominant factor used in selection.

Surfactant molecules contain two structural fragments that possess differing solubility. For example, the structure of nonyl ethoxylate is

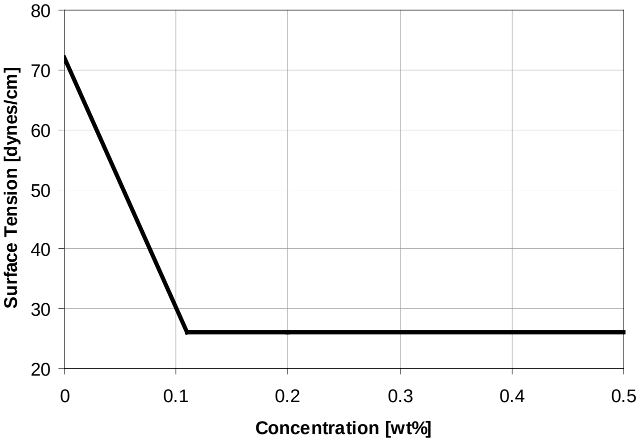
$$CH_3(CH_2)_7CH_2\text{—}O(CH_2CH_2O)_yH$$

The alkyl fragment on the left side of the molecule has high oil solubility, whereas the ethylene oxide fragment on the right side of the molecule has high water solubility.

This binary nature of surfactants can be quantified into a number called the HLB. HLB values depend upon the type and size of each side of the surfactant molecule. Values are typically scaled to fall within the range of 1 to 20. Surfactants with high HLB values are very hydrophilic and promote oil-in-water emulsions. High-HLB surfactants also have a tendency to create stable foams. Surfactants with low HLB values are very lipophilic and promote water-in-oil emulsions. Surfactants with intermediate HLB values can promote either type of emulsion but generally promote oil-in-water emulsions. Surfactants were selected with HLB values in the range of 10 to 15. These should promote wetting of aircraft surfaces while minimizing foaming.

Figure 2-9 shows a graph of surface tension versus surfactant concentration. At zero concentration, the surface tension is equal to that of pure water. As surfactant is added, the surface tension decreases. At a certain concentration, the CMC, adding more surfactant does not cause any further decrease in the surface tension.

Figure 2-9. Determination of critical micelle concentration.



The CMC is a measure of the efficiency of a surfactant. If two surfactants both produce the same minimum surface tension value in water, the surfactant with the lower CMC will be more efficient because it produces the same low surface tension with a lower concentration.

The cloud point is the temperature above which an aqueous solution of a water-soluble surfactant becomes turbid. Storing a surfactant mixture at temperatures significantly higher than its cloud point may result in phase separation. In general, non-ionic surfactants show optimal effectiveness when used near or below their cloud point. Low-foam surfactants should be used at temperatures slightly above their cloud point.

Table 2-12 presents an extensive list of the chemical categories of non-ionic surfactants currently available. For each category, the research team investigated three properties: performance, toxicity, and biodegradability. Performance includes properties such as water solubility, surface tension reduction, HLB, and chemical stability. Table 2-12 indicates which surfactant categories fail to contain acceptable candidates *(27, 28)*. Categories that are believed to contain promising candidates are investigated in more detail.

TABLE 2-12. Non-ionic surfactant categories.

Surfactant Category	Performance	Toxicity	Biodegradability
Acetylenic diols	—	—	—
Alkolamides/alkanolamides	Fail[a]	—	—

TABLE 2-12. Non-ionic surfactant categories.

Surfactant Category	Performance	Toxicity	Biodegradability
Alkoxylated alkyl phenols	—	Fail[b]	Fail[b]
Alkoxylated branched alcohols	—	—	—
Alkoxylated linear alcohols	—	—	—
Alkoxylated secondary alcohols	—	—	—
Alkyl dimethylamine oxides	Fail[a]	—	—
Alkyl glucamides	Fail[c]	—	—
Alkyl polyglucosides	—	—	—
Amine EO-PO copolymers	—	—	—
Dialkyl dimethyl polysiloxanes	—	—	—
EO-PO copolymers	—	—	—
Esterified EO-PO copolymers	Fail[c]	—	—
Ether amine oxides	Fail[a]	—	—
Ethoxylated alkanolamides	—	—	—
Ethoxylated alkyl phenols	—	Fail[b]	Fail[b]
Ethoxylated castor oil	Fail[c]	—	—
Ethoxylated ether amines	—	—	—
Ethoxylated fatty acids	Fail[c]	Fail[d]	Fail[d]
Ethoxylated fatty amines	—	—	—
Ethoxylated phenol	—	Fail[b]	Fail[b]
Ethoxylated sorbitan esters	Fail[c]	—	—
Fatty acid esters	Fail[c]	—	—
Fatty alcohol EO-PO copolymers	Fail[c]	—	—
Fatty amine oxides	Fail[c]	—	—
Fluorinated alkyl alkoxylates	—	—	Fail[e]
Fluorinated alkyl esters	—	—	Fail[e]
Fluorinated alkyl polyoxyethylene ethanols	—	—	Fail[e]
Glycerol esters	Fail[c]	—	—
Sorbitan esters	Fail[c]	—	—

[a] Produce large amounts of stable foam.
[b] Presence of the aromatic ring increases toxicity and reduced biodegradability.
[c] These surfactants hydrolyze in alkaline formulations.
[d] These surfactants readily hydrolyze under acidic or alkaline conditions.
[e] The fluorinated portion of the surfactant does not degrade.

Table 2-12 shows that 10 surfactant categories contain potentially promising candidates. Eighteen surfactants from these categories were selected for experimental testing. Appendix

E lists detailed information on these surfactant candidates. Samples of Pluronic L44 NF could not be obtained and so it was dropped from further consideration.

Certain surfactant-FPD mixtures can produce foam when applied to aircraft surfaces. This foam is very undesirable because it may hinder the “clean wing” decision needed for takeoff. Antifoams are chemicals that can be added to ADFs to facilitate the drainage and breakage of foams. Unfortunately, antifoams are known to have low aquatic toxicity limits and thus should be used sparingly.

It was decided to test antifoams with only two candidate surfactants to assess the need for including them in the final formulated product. Tergitol TMN-10 is an alkoxylated branched alcohol that is reported to have good physical and toxicological properties but may produce too much foam for the test application. Triton CG-110 is an alkyl polyglucoside that is reported to produce a significant quantity of foam. If an antifoam could successfully control foaming with these two surfactants, it should be similarly effective with any of the other surfactants.

Table 2-13 lists the 17 surfactants and two mixtures selected for experimental evaluation.

TABLE 2-13. Candidate surfactants.

Project ID	Trade Name	Description
03.001	Surfynol 465	Acetylenic diol
03.002	Tergitol TMN-6	Alkoxylated branched alcohol
03.003	Tergitol TMN-10	Alkoxylated branched alcohol
03.004	Lutensol XP 50	Alkoxylated branched alcohol
03.005	Lutensol XP 100	Alkoxylated branched alcohol
03.006	Triton DF-16	Alkoxylated linear alcohol
03.007	Bio-Soft N1-5	Alkoxylated linear alcohol
03.008	Bio-Soft N1-7	Alkoxylated linear alcohol
03.009	Merpol SE	Alkoxylated linear alcohol
03.010	Lutensol TDA 10	Alkoxylated linear alcohol
03.011	Plurafac S-405LF	Alkoxylated linear alcohol
03.012	Tergitol 15-S-7	Alkoxylated secondary alcohol
03.013	Tergitol 15-S-12	Alkoxylated secondary alcohol
03.014	Triton CG-110	Alkyl polyglucoside
03.015	Tetronic 904	Amine ethylene-oxide propylene-oxide copolymer
03.016	Tergitol L-64	Ethylene-oxide propylene-oxide copolymer
03.018	Triton CF-32	Ethoxylated alkanolamide
03.019	- mixture -	Tergitol TMN-10 + 10% Ridafoam NS 221.
03.020	- mixture -	Triton CG-110 + 10% Ridafoam NS 221.

Corrosion Inhibitor Candidates

The corrosion of a metal requires oxygen, a conductive solution, and surface areas with differing chemical potential. Because most deicing and anti-icing chemicals contain salts or are mixed with water that contains salts, corrosion of steel and aluminum can readily occur. All deicing and anti-icing chemicals contain one or more corrosion inhibitors. Most corrosion inhibitors function by forming a physical or chemical coating on a metallic surface to prevent contact with oxygen and conductive solutions.

There are many types of corrosion inhibitors for various applications and they can be grouped into two broad categories: organic and inorganic. As a class, organic corrosion inhibitors have less environmental impact than inorganic inhibitors. This observation resulted in a general focus on the selection of organic corrosion inhibitors, although several solid, inorganic inhibitors are recommended for testing in runway deicing chemicals.

Most organic corrosion inhibitors form physical or chemical coatings on metallic surfaces. This surface activity explains why many organic corrosion inhibitors also act as surfactants. The hydrophiles for organic corrosion inhibitors include amines, acids, esters and alcohols. These hydrophiles adsorb onto the metallic surface, leaving their hydrophobic substructures to form a repellant coating.

Corrosion inhibitor packages representative of current deicer products are available from PMC Specialties Group, Inc. under the Cobratec brand. These include:

- Cobratec TT-50-S: an alkaline solution of sodium tolyltriazole dissolved in water
- Cobratec TT-100: solid tolyltriazole available in either prill or powder forms

Candidate corrosion inhibitors were selected primarily based on prior experience. Documentation of corrosion inhibition toward steel and aluminum was the first criterion. Aquatic toxicity was the second criterion. Quantitative data for these criteria were often not available, so qualitative information had to be used for selection.

Appendix F lists 17 candidate corrosion inhibitors that were recommended for further investigation.

Anti-Caking Additive Candidates

Sodium formate is an effective pavement deicing chemical possessing significantly lower BOD than alternative solid FPDs. However, a disadvantage of this compound is that because of its hygroscopic nature, its granules tend to cake, which makes handling and dispersion difficult.

During a period of elevated humidity, sodium formate will form an adsorbed layer of water on particle surfaces. Some of the salt will dissolve into this layer, forming a concentrated solution. When the humidity is reduced or the temperature increased, the adsorbed water evaporates and the dissolved salt recrystallizes. These recrystallized salts often form bridges or welds between particles. This process is called caking and results in the inability of particles to flow freely.

Two additives that have been used or have been proposed for preventing the caking of formate particles are:

- Potassium carbonate: *(29)* describe using less than 5 percent by weight of potassium carbonate to eliminate caking. They also discuss the use of sucrose and mannose as anti-caking additives.
- Tripotassium citrate: *(30)* describes the use of 10 percent by weight tripotassium citrate to eliminate caking.

Both of these additives were evaluated in Tier 2.

SECTION 3

EXPERIMENTAL PLAN

This section describes the rationale, based on laboratory testing, for down-selecting the components of alternative deicing and anti-icing aircraft and airfield formulations selected from literature reviews and computational modeling, as described in Section 2. Tables 3-1 through 3-3 summarize the tiered testing that was conducted to evaluate the components of the alternative deicing and anti-icing formulations. Pure candidates and simple mixtures with water were tested in Tier 1. Candidates that survived Tier 1 testing were subjected to Tier 2 tests involving more-complex mixtures.

TABLE 3-1. Number of components and deicer formulations tested in Tiers 1 and 2.

	Deicer Component				
Tier No.	**FPD**	**Surfactant/ Antifoam**	**Corrosion Inhibitor**	**Thickener**	**Deicer Formulations**
1	26	19	14	6	—
2	2	3	2	3	Type IV AAF
	1[a]				Runway PDM

[a] Evaluated with two anti-caking materials.

TABLE 3-2. Tier 1 deicing/anti-icing formulation tests.

Key Area	Test/Evaluation
Deicing Performance	Freezing point depression, viscosity, contact angle
Environmental Impact	BOD, aquatic toxicity
Safety Properties	Flash point
Cost	Supplier cost estimates

TABLE 3-3. Tier 2 tests for Type IV and runway PDMs.

Key Area	Test/Evaluation
Type IV AAFs	
Deicing Performance	Surface tension (contact angle), viscosity, foaming
Environmental Impact	BOD, aquatic toxicity
Materials Compatibility	Total immersion and sandwich corrosion testing (aluminum clad and anodized aluminum)

TABLE 3-3. Tier 2 tests for Type IV and runway PDMs.

Key Area	Test/Evaluation
Runway Deicer	
Deicing Performance	Water absorption, anti-caking

Upon review of the Tier 1 results, there did not appear to be substantial potential to improve BOD and aquatic toxicity in Type I fluids, nor did there appear to be potential to improve on BOD in PDMs when compared to the current products with the most favorable environmental characteristics. For this reason, the Project Panel directed the research team to focus the Tier 2 tests on Type IV aircraft anti-icing formulations and anti-caking additives for sodium formate runway deicers. The results of the Tier 2 tests yielded a final selection of components for complete Type IV formulation development. Further tests to certify the down-selected formulations, including deicing/anti-icing performance and materials compatibility, are very extensive and were not undertaken as part of this research.

Tier 1 Testing

The objective of Tier 1 testing was to efficiently screen candidate components for applicability. The following tests were conducted for each of the candidate formulation components:

- *Freezing Point Depression*: 1:1 (by weight) mixtures of FPDs with water were prepared. Mixtures were placed in baths maintained at -20°C (requirement for aircraft, AMS 1424) and -14.5°C (requirement for airfields, 1435). FPD mixtures frozen at -20°C were rejected; mixtures not frozen at -20°C but frozen at -14.5°C continued to be evaluated for aircraft deicing applications; and mixtures not frozen at -14.5°C continued to be evaluated for both aircraft and runway deicing applications.

- *Flash Point*: Mixtures were tested for flash point. FPD mixtures having flash points lower than 100°C were rejected.

- *Aquatic Toxicity and Oxygen Demand for FPDs*: Mixtures meeting the requirements for freezing point and flash point were tested for aquatic toxicity, chemical oxygen demand (COD) and five day biochemical oxygen demand (BOD_5). Methods for these tests are presented in the Tier 2 section Environmental Characteristics. FPDs that showed low levels of BOD_5 and/or COD relative to propylene glycol were evaluated further for 28-day BOD. Candidates were ranked first for aquatic toxicity and then for COD (due to uncertainties in BOD testing). Two FPDs were selected for further evaluation as Type IV anti-icers in Tier 2 and one FPD (sodium formate) was selected as a runway deicer in Tier 2.

- *Aquatic Toxicity and Contact Angle for Surfactants:* Neat surfactant solutions were tested and ranked for aquatic toxicity. Each of the eight top ranked surfactants was mixed with water (1:99 by weight), and the contact angle of the mixture was measured in a drop shape analyzer at room temperature (20°C). The contact angle is directly related to the surface tension of the fluid. Three surfactants were down-selected for further testing in Tier 2.

- *Aquatic Toxicity and Viscosity for Thickeners:* Neat solutions of six thickeners were tested for aquatic toxicity. The viscosity of the six thickener:water mixtures, 1:99 and 2:98 (by weight) were determined at two temperatures (0°C and 25°C) and multiple shear rates. At a given concentration and temperature, the viscosity, η, is a function of the shear rate, γ (in sec^{-1}), $\eta = K\,\gamma^n$, where K and n are constants for a specific thickening agent and FPD. The constant K is fairly linear with the thickener concentration, so only two thickener concentrations needed to be tested. The viscosities were compared at room temperature (20°C) and 5°C to examine the effect of temperature. The viscosities of the thickener/water mixtures were also compared to a commercial Type IV anti-icing formulation to evaluate the direction in the changes of the thickener concentrations in the thickener:water mixtures necessary to match the viscosity of the commercial formulation. Three thickeners were down-selected for further evaluation in Tier 2, based on aquatic toxicity and the changes in the direction of the thickener concentrations.
- *Aquatic Toxicity for Corrosion Inhibitors:* Neat solutions were tested and ranked for aquatic toxicity. Two corrosion inhibitors with the lowest toxicity were down-selected for further testing in Tier 2.

At the conclusion of Type I testing, the number of candidate components for the deicer formulations were reduced to the levels indicated in Table 3-1.

Tier 2 Testing

Type IV Aircraft Anti-Icing Formulations

In Tier 2, more complex mixtures of components were tested. The two FPDs selected for Type IV anti-icing formulations were each mixed with an equal amount of water by weight. The two FPD:water mixtures were combined with progressively complex mixtures of additives and evaluated for a range of physical, chemical, and environmental characteristics, as described in the following steps:

- *FPDs and Surfactants:* The FPD:water mixtures were blended separately with the three down-selected surfactants at various concentrations. The control was a commercially available Type IV anti-icing formulation. For each mixture of FPD:water and a surfactant, a surfactant concentration was determined to match the contact angle (surface tension) of the control. The aquatic toxicities of the resulting mixtures were measured and compared to the estimated values based on the neat solution results of Tier 1. The FPD:water:surfactant mixture that had the lowest aquatic toxicity was selected for further Tier 2 testing. The down-selected surfactant also had the lowest cost.
- *FFPDs and Thickeners:* The FPD:water mixtures were blended separately with the three down-selected thickeners at various concentrations. The control was the same commercially available Type IV anti-icing formulation used in the previous tests with the surfactants. For each mixture of FPD:water and a thickener, a thickener concentration was determined to match the viscosity/shear rate of the control at room temperature. The aquatic toxicities of the resulting mixtures were measured and compared to the estimated values based on the neat solution results of Tier 1. The

aquatic toxicity of the FPD/water/thickener formulations was determined primarily by the FPD and not by the thickener itself. The thickener was down-selected based on the cost of the thickener.

- *FPDs, Surfactants and Thickeners:* Each FPD:water mixture was combined with the down-selected thickeners and surfactants at concentrations that were determined to match the characteristics of the commercial Type IV anti-icing formulation. The contact angles and viscosities were measured and compared to the values measured in the previous two tests to determine if there was an interaction between the surfactants and thickeners. Foaming tests were conducted with and without the addition of an anti-foaming additive and compared to the control. The aquatic toxicities of the mixtures were measured and compared to the estimated values based on the neat solution results of Tier 2. One of the two FPD:water:thickener:surfactant mixtures were down-selected.
- *FPDs, Surfactant, Thickener, and Corrosion Inhibitors:* Two corrosion inhibitors were added to the down-selected FPD:water:thickener: surfactant formulation and total immersion and sandwich corrosion tests were carried out with aluminum clad and anodized aluminum coupons. The FPD and corrosion inhibitor mixtures were ranked according to the degree of corrosion on the metal surfaces and compared to the controls to determine if the mixtures would meet the SAE AMS 1428 material compatibility requirements. One corrosion inhibitor was down-selected based on performance and estimated aquatic toxicity of the formulation. BOD, COD, and full aquatic toxicity determinations were conducted on the down-selected formulation.

Runway Deicers

A testing procedure was developed to determine the extent of sodium formate caking under controlled humidity with and without the addition of two anti-caking agents (potassium carbonate and tripotassium citrate). The materials were placed in a humidity chamber set at 50 percent humidity and 30°C, and the amount of water absorbed by each of the materials individually and in combination with each other was measured by weighing the samples over a period of 2 days. A sieve analysis was conducted of the materials before and after they were placed in the humidity chamber to assess the degree of caking.

SECTION 4

TIER 1 RESULTS

The candidate aircraft deicing/anti-icing and airfield deicing formulation components identified for Tier 1 testing included 27 FPDs (5 aircraft, 10 runway, and 12 for both aircraft and runway), 5 thickeners, 20 surfactants, and 17 corrosion inhibitors. Quantities of each component sufficient for Tier 1 testing were ordered from various sources, including chemical distributors (Alfa Aesar, Chemical Marketing Concepts and Sigma-Aldrich) and chemical manufacturers (Air Products, BASF, CP Kelco, Dow, Lubrizol, PMC Specialties, and Stepan). Table 4-1 lists the numbers of components that were ordered, received, and available for testing.

TABLE 4-1. Number of alternative deicing components ordered and available for testing.

Component	Ordered	Not Available	Available for Testing
FPDs	27	1	26
Thickeners	5	0	5
Surfactants	20	1	19
Corrosion Inhibitors	17	3	14

The samples were divided into quantities suitable for aquatic toxicity, BOD and COD profiles, freezing points, flash point, surface tension and viscosity testing. Samples for aquatic toxicity testing, BOD, and COD were sent to the Wisconsin State Laboratory of Hygiene (Madison, WI); flash point samples were sent to Thorstensen Laboratories (Westford, MA); and the remainder to Infoscitex (Waltham, MA) and the University of Massachusetts -Lowell (Lowell, MA) for freezing point, surface tension and viscosity tests.

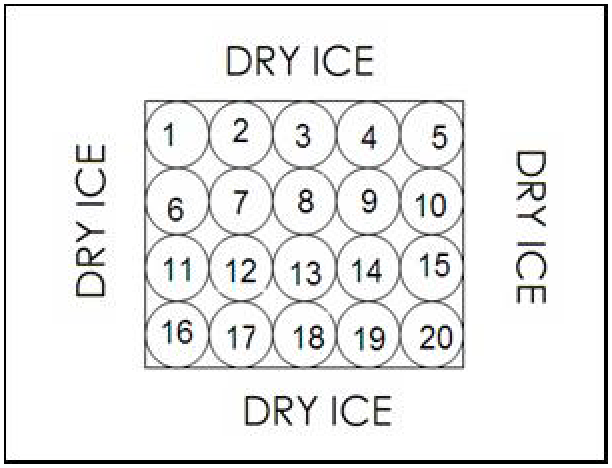
Freezing Point Depression

The following criteria were used in evaluating the freezing point depression performance for the mixtures of FPDs and water:

- FPD mixtures frozen at -14.5°C were rejected from further evaluation
- FPD mixtures not frozen at -14.5°C, but frozen at -20°C were evaluated for runway deicing applications
- FPD mixtures not frozen at -20°C were evaluated for aircraft de-icing applications

A simple freeze test was used to determine whether the FPD:water mixtures met the criteria. The freezing point depression of the candidate FPDs was obtained by dissolving each chemical in a 1:1 ratio with water. Four replicates of each solution were placed in small test tubes mounted in a rack and surrounded by dry ice in a vessel (Figure 4-1). The dry ice was doused with 2-propanol to lower its freezing point.

Figure 4-1. Rack apparatus for freezing point depression tests.



The freezing point of each solution was measured using an alcohol thermometer. First, the solution was allowed to completely freeze. The rack was then removed from the vessel and the melting point for each solution was monitored and recorded. This was repeated for all samples analyzed.

Table 4-2 shows the placement of the test tubes in the rack and the observed results for four FPDs. Measurements were made to determine whether the solutions met the criteria for freezing at -14.5°C and -20°C and the temperatures when they completely froze. Table 4-3 summarizes the results of the freezing point depression tests for all of the FPDs.

TABLE 4-2. Typical results for freezing point depression.

Test Tube Placement (See Location in Figure 4-1)	**Freeze at °C?**		**Completely Freezes (°C)**
	-14.5°C	**-20.0°C**	
1,3-Propylene Glycol: CAS No. 504-63-2			
1	No	No	-50.0 to -52.0
14	No	No	-48 to -48.5
7	No	No	-50
19	No	No	-50
2,3- Butanediol: CAS No. 513-85-9			
5	Yes	Yes	-6.0
12	Yes	Yes	-6.5
13	Yes	Yes	-6.5
20	Yes	Yes	-6.0
2-(2-Methoxyethoxy)-ethanol: CAS No. 111-77-3			
16	Yes	Yes	-55.0

TABLE 4-2. Typical results for freezing point depression.

Test Tube Placement (See Location in Figure 4-1)	**Freeze at °C?**		
	-14.5°C	**-20.0°C**	**Completely Freezes (°C)**
9	Yes	Yes	-57.0
10	Yes	Yes	-55.0
8	Yes	Yes	-56.0
D-Gluconic acid, δ-lactone: CAS No. 90-80-2			
15	Yes	Yes	-22.0
17	Yes	Yes	-22.0
6	Yes	Yes	-22.0
11	Yes	Yes	-24.0

TABLE 4-3. Results of freezing point depression and flash point testing for FPDs.

FPD	CAS Number	Flash Point (°C)		Freeze at °C			State	Aircraft or Runway	Note
		50:50	Neat	-14.5°C	-20°C	Unfreeze			
Frozen at -14°C—Rejected for Further Evaluation									
Ethylene carbonate	96-49-1	>150	160	Yes	Yes	Freezes at 0°C	Solid	A, R	Failed freezing point
Propylene carbonate	108-32-7	135	132	Yes, in slush form	Yes, in slush form	Freezes completely at -30°C and slush forms from -4°C to -30°C	Liquid	A	Failed freezing point
2,3-Butanediol	513-85-9	95	85	Yes	Yes	-4°C	Liquid	A	Failed freeze, BOD/COD
4-Methyl-γ-butyrolactone	108-29-2	>150	96	Yes	Yes	Freezes in slush from -4°C to -20°C	Liquid	A	Failed freeze point
Dimethyl malonate	108-59-8	90	90	Yes	Yes	Freezes as a white solid	Liquid	A	Not miscible; failed freeze
Dimethyl succinate	106-65-0	85	90	Yes	Yes	Frozen solid at 0°C	Liquid	A	Failed; freeze point and not miscible
Sodium acetate	127-09-3	>150	>249	Yes	Yes	Frozen completely at -4°C; freezes at -20°C for 2:1 and 3:1 water:sodium ratios; not frozen at -20°C for 4:1 and 5:1 water:sodium ratios; not frozen at -14.5°C for 2:1 to 5:1 water:sodium ratios at	Solid	R	Failed freezing point at 1:1 (water:sodium) mixture; did not freeze at higher ratios
Calcium propionate	4075-81-4	>150	High	Yes	Yes	-5°C; completely frozen at -6°C	Solid	R	Failed freezing point
Disodium succinate	150-90-3	>150	High	Yes	Yes	-5°C; Completely frozen at -6°C	Solid	R	Failed freezing point

TABLE 4-3. Results of freezing point depression and flash point testing for FPDs.

FPD	CAS Number	Flash Point (°C)		Freeze at °C			State	Aircraft or Runway	Note
		50:50	Neat	-14.5°C	-20°C	Unfreeze			
Not Frozen at -14.5°C but Frozen at -20°C—Further Evaluated for Runway Deicing Applications									
2,2-Dimethyl-1,3-dioxolane-4-methanol	100-79-8	>150	80	No	Yes	-24°C to -19°C; freezes in slush form at -20°C to -25°C	Liquid	A, R	Failed freeze point for aircraft deicer; passed freeze point for runway deicer
Xylitol	87-99-0	>150	High	No	Yes	-21°C; mixes well with water; freezes as a white solid at -22°C; frozen is slush form at -20°C	Solid	R	Passes freezing point test for runway deicer
Not Frozen at -20°C—Further Evaluated for Aircraft and Runway Applications									
1,2-Propylene glycol	57-55-6	100	107	No	No	Freezes at -65°C	Liquid	A, R	—
1,3-Propylene glycol	504-63-2	98	>110	No	No	Freezes at -50°C	Liquid	A, R	—
Glycerol	56-81-5	>150	160	No	No	-25°C; freezes as a white solid at -50°C	Liquid	A, R	—
1,3-Butanediol	107-88-0	110	121	No	No	-29°C to -26°C	Liquid	A, R	—
2-Methyl-1,3-propanediol	2163-42-0	107	>110	No	No	-4.5°C	Liquid	A, R	—
Diethylene glycol	111-46-6	>150	143	No	No	Freezes as a white solid at -50°C; freezes in slush form at -20°C	Liquid	A. R	—
2-(2-Methoxyethoxy)-ethanol	111-77-3	87 <103 >93	84	No	No	-50°C	Liquid	A, R.	—
2-(2-Ethoxyethoxy)-ethanol	111-90-0	84 <103 >93	96	No	No	Not frozen at -50°C	Liquid	A, R	—

TABLE 4-3. Results of freezing point depression and flash point testing for FPDs.

FPD	CAS Number	Flash Point (°C)		Freeze at °C			State	Aircraft or Runway	Note
		50:50	Neat	-14.5°C	-20°C	Unfreeze			
Dipropylene glycol	25265-71-8	139	135	No	No	Did not freeze at -60°C	Liquid	A, R	—
Triethylene glycol	112-27-6	180	165	No	No	-24°C	Liquid	A, R	—
1,1,1-Trimethanolethane	77-85-0	148	160	—	—	Did not mix well with water; crystals do not blend completely with water	Solid	R	Does not mix well with water
D-Gluconic acid,δ-lactone	90-80-2	>150	High	No	No	Solid to slush at -22°C to -21°C; slush to liquid at -15°C to -8°C	Solid	R	—
Trimethylolpropane	77-99-6	>150	172	No	No	Mixes well with water; freezes completely at -22°C; slush forms between -12°C to -21°C	Solid	R	—
L-Tartaric acid dipotassium salt	921-53-9	>150	High	No	No	Mixes well with water; frozen completely as a solid at -35°C; frozen in slush form between -34°C to -16°C	Solid	R	—
Tripotassium citrate	6100-05-6	>150	High	No	No	Completely frozen at -45°C and in slush from at -42°C	Solid	R	—

The costs of the FPDs (on a neat basis) that were further evaluated in Tier 2 are shown in Table 4-4. The costs are based on the Sigma-Aldrich catalog as of August 5, 2008. The costs of large quantities of these chemicals were not readily available. The costs of commercially available current-use aircraft (1.2-propylene glycol) and runway (potassium acetate) deicers are included for comparison.

TABLE 4-4. Cost of FPD on a neat basis (in order of increasing cost).[a]

Application	FPD	Cost, $/kg
Aircraft	Triethylene glycol	14.80
	1,3-Butanediol	17.00
	2-Methyl-1,3-propanediol	18.90
	Trimethylolpropane	23.87
	Dipropylene glycol	26.00
	Glycerol	33.30
	Diethylene glycol	123.20
	1,3-Propylene glycol	154.00
	1,2-Propylene glycol	16.15
Runway	Trimethylopropane	23.90
	Sodium acetate	27.10
	D-Gluconic acid, δ-lactone	35.70
	Tripotassium citrate	41.20
	Xylitol	48.00
	2,2-Dimethyl-1,3-dioxolane-4-methanol	61.50
	L-Tartaric acid dipotassium salt	65.60
	Potassium acetate	15.30

[a] Costs based on Sigma-Aldrich.

Flash Point

The flash point temperature is a measure of the tendency of a material to form a flammable mixture with air. According to the deicing/anti-icing specifications, the flash point of these formulations should not be lower than 100°C as determined by the American Society for Testing and Materials (ASTM) D93 Standard Test Methods for Flash Point by the Pensky-Martens Closed Cup Tester. Table 4-3 presents the flash point temperatures and temperature limits for all of the FPDs with water (1:1 by weight) and as neat solution.

With respect to safety considerations, four FPD mixtures having flash points lower than 100°C were rejected for further evaluation. Two of these FPD mixtures were also rejected because they were frozen at -14.5 °C and two were rejected that were frozen at -20 °C. Table 4-5 summarizes the FPD mixtures that met the requirements for freezing point depression and flash point. Eleven FPDs that did not meet the criteria are also listed.

TABLE 4-5. Summary of FPD mixture aircraft and runway deicing/anti-icing agents meeting performance and safety requirements.

	FPD:Water Mixtures
Further evaluated for aircraft and runway applications	1,3-Butanediol
	Diethylene glycol
	Dipropylene glycol
	D-Gluconic acid, δ-lactone
	Glycerol
	2-Methyl-1,3-propanediol
	1,2-Propylene glycol
	1,3-Propylene glycol
	Sodium acetate
	L-Tartaric acid dipotassium salt
	Triethylene glycol
	Trimethylopropane
	Tripotassium citrate
Further evaluated for runway deicing applications	2,2-Dimethyl-1,3-dioxolane-4-methanol
	Xylitol
Rejected from further evaluation	2,3-Butanediol
	Calcium propionate
	Dimethyl malonate
	Dimethyl succinate
	Disodium succinate
	2-(2-Ethoxyethoxy)-ethanol
	Ethylene carbonate
	4-Methyl-γ-butyrolactone
	2-(2-Methyloxyethoxy)-ethanol
	Propylene carbonate
	1,1,1-Trimethanolethane

The FPDs listed in Table 4-5 that met the criteria for deicing performance and safety criteria were evaluated for their BOD and COD and aquatic toxicity, as described below.

Oxygen Demand

Methods

COD and BOD analyses were conducted on candidate FPDs. COD analyses were performed in triplicate according to ASTM method D1252-88(B). Traditional 5-day BOD analyses were performed in quadruplicate according to *Standard Methods for the Examination of Water and Wastewater*, method 5210B *(31)*. Twenty-eight-day time-series BOD analyses were performed in triplicate using a modification to method 5210B that used 2,120-mL custom BOD bottles rather than the traditional 300-mL bottles. Single dilutions were prepared based on the results of the COD and conventional BOD_5 analyses, and the dissolved oxygen was monitored at 5, 15, and 28 days. As DO concentrations approached 2.0 mg/L, the samples were re-aerated using filtered compressed air and then returned to the incubator. Results were considered valid as long as 2 milligrams or more of oxygen depletion was observed in test vials at each measurement interval during the test. Measurement uncertainty was considered to be too large for accurate reporting with less than 2 mg of oxygen demand exerted over the time interval. COD was used as an estimate of ultimate BOD to compute percent biodegradability of the deicer formulations exerted over time.

The liquid and solid deicer products tested in this study were "neat" products and devoid of ammonia or other combined nitrogen compounds that could contribute to nitrification. Any minimal nitrification that may have occurred during the test periods were eliminated through blank correction. Laboratory blanks were tested along with the samples to correct for the contribution of the "seed" material (i.e., source of microorganisms) and any demand exerted by the reagent water used to prepare the samples. Consequently, only total BOD measurements were made, with the assumption that they would be essentially equivalent to carbonaceous BOD (i.e., oxygen demand for carbon source only). Three replicate glucose-glutamic acid controls were also tested in fresh water at 20°C. Results from these controls showed no indication of method bias.

Results

Testing was conducted for oxygen demand on 24 FPDs (Table 4-6). Results include computed ThOD and COD for all FPDs. One candidate FPD was eliminated before BOD_5 testing was conducted and five candidates were eliminated before the BOD time-series testing was conducted.

COD results ranged from 341,000 to 1,880,000 milligrams per kilogram (mg/kg) and compared well with theoretical oxygen demand for all candidate FPDs. In comparison, COD of propylene glycol was 1,620,000 mg/kg and potassium acetate (K-Ac) deicer was previously determined to be 629,000 mg/kg expressed as K-Ac *(1)*. BOD_5 results could not be obtained for six of the candidate FPDs: 2-methyl-1,3-propanediol, DEG, dimethyl malonate, 1,1,1- trimethanolethane, and triethylene glycol. In four separate attempts, dimethyl malonate, 1,1,1- trimethanolethane, DEG, and triethylene glycol did not degrade during the 5-day test period. Consequently no results could be obtained. BOD_{28} data for these particular compounds show similarly low BOD in the first 10-20 days. This lag period was also observed with some of the deicer formulations examined in similar testing with commercial deicer products *(1)*.

Biodegradability (BOD result expressed as a percent of COD) based on traditional BOD_5 results ranged from 0-76 percent depending on the individual FPDs for which BOD_5 could be determined. Some of the very low values (<5 percent) are suspected to be unreliable because of an inability of seed organisms to acclimate to the FPD as a food source in a test as short as 5-days.

Biodegradability in the 28-day BOD time-series was also widely variable depending on FPD with a range from <1-78 percent at 5-days, <1-87 percent in 15-days, and 11-89 percent in 28-days (Table 4-6). A lag period in BOD exertion for some FPDs is apparent, with low values in 5- and 15-day tests and increased values in 28-day tests. As was the case with the low BOD_5 results, this is likely due to an inability of the seed organisms to acclimate in the short time frame. By 28 days, however, results from most tests indicate that the organisms did acclimate and exhibit substantial BOD. It is uncertain whether an initial acclimation of seed organisms for each individual FPD would ultimately change the final 28-day results.

Because of the uncertainties of the traditional BOD_5 analyses and the 28-day series and the inability to achieve acceptable BOD results for some products, COD was considered a more reliable and consistent parameter for assessing the potential for oxygen demand in the environment. Therefore, COD was ultimately used in the down-selection process to choose FPDs for inclusion in further testing.

TABLE 4-6. Summary of COD and BOD results for candidate FPDs in order of increasing COD.

					BOD Time-Series[d] (g/kg)			**Biodegradation as Percent of COD**			
FPD	**CAS Number**	**ThOD[a] (g/kg)**	**COD[b] (g/kg)**	**BOD_5[c] (g/kg)**	**5 Days**	**15 Days**	**28 Days**	**BOD_5**	**5 Days**	**15 Days**	**28 Days**
L-Tartaric acid dipotassium salt	921-53-9	432	341	231	213	239	242	68	62	70	71
Tripotassium citrate	6100-05-6	345	449	309	262	297	301	69	58	66	67
Disodium succinate	150-90-3	592	684	481	466	533	533	70	68	78	78
Sodium acetate	127-09-3	683	747	552	586	653	667	74	78	87	89
2-(2-Methoxyethoxy)-ethanol	111-77-3	1,730	883	—[e]	24	517	641	—	3	59	73
Ethylene carbonate	96-49-1	908	899	34	5,870	57,600	96,900	4	1	6	11
D-Gluconic acid,δ-lactone	90-80-2	988	976	660	—	—	—	68	—	—	—
Calcium propionate	4075-81-4	1,120	1,090	823	791	913	936	76	73	84	86
Xylitol	87-99-0	1,160	1,170	585	644	915	979	50	55	78	84
Glycerol	56-81-5	1,220	1,190	810	846	985	1	68	71	83	84
Propylene carbonate	108-32-7	1,250	1,200	33,500	—	—	—	3	—	—	—
Diethylene glycol	111-46-6	1,510	1,500	ND[f]	18,500	128	618	—	1	9	41
Triethylene glycol	112-27-6	1,600	1,610	ND[f]	53,600	398	560	—	3	25	35
1,2-Propylene glycol	57-55-6	1,680	1,620	973	1,020	1,270	1,310	60	63	78	81
1,3-Propylene glycol	504-63-2	1,680	1,640	731	814	1,070	1,190	45	50	65	73
1,1,1- Trimethanolethane	77-85-0	1,730	1,680	<1,200[g]	6,310	8,060	406	—	0	0	24
2,2-Dimethyl-1,3-dioxolane-4-methanol	100-79-8	1,820	1,780	10,800	—	—	—	1	—	—	—
Trimethylolpropane	77-99-6	1,910	1,810	<1,200[g]	-17	-21	660	—	-1	-1	36
2,3-Butanediol	513-85-9	1,950	1,820	1,200	—	—	—	66	—	—	—

TABLE 4-6. Summary of COD and BOD results for candidate FPDs in order of increasing COD.

					BOD Time-Series[d] (g/kg)			Biodegradation as Percent of COD			
FPD	**CAS Number**	**ThOD[a] (g/kg)**	**COD[b] (g/kg)**	**BOD$_5$[c] (g/kg)**	**5 Days**	**15 Days**	**28 Days**	**BOD$_5$**	**5 Days**	**15 Days**	**28 Days**
1,3-Butanediol	107-88-0	1,950	1,830	820	843	1,390	1,450	45	46	76	79
2-Methyl-1,3-propanediol	2163-42-0	1,950	1,850	ND[e]	807	1,450	1,480	—	44	78	80
Dipropylene glycol	25265-71-8	1,910	1,860	1,580	12	81	935	0	1	4	50
2-(2-Ethoxyethoxy)-ethanol	111-90-0	1,910	1,880	1,100	399	1,490	1,540	59	21	79	82
4-Methyl-γ-butyrolactone	108-29-2	1,920	1,880	814	—	—	—	43	—	—	—

[a] Theoretical oxygen demand is computed as ThOD = 32 x number of carbons + 8 x number of hydrogens + 16 x number of oxygens.

[b] The percent relative standard deviation from 3 replicates was 5% or less for all COD samples except for 3 samples that had only one replicate due to early elimination of FPD consideration (propylene carbonate, 2,3-butanediol, and D-Gluconic acid,δ-lactone).

[c] The percent relative standard deviation from 4 replicates was 10% or less for all BOD$_5$ samples except 2,2-Dimethyl-1,3-dioxolane-4-methanol, Disodium succinate, Propylene carbonate, and Xylitol.

[d] The percent relative standard deviation from 3 replicates was 10% or less for all BOD time-series samples except 1,1,1- Trimethanolethane, 2-(2-Methoxyethoxy)-ethanol, 2-Methyl-1,3-propanediol, DEG, Dipropylene glycol, and Trimethylolpropane.

[f] — not determined

[f] BOD$_5$ could not be determined due to suspected inability to find optimum sample to organism ratio.

[g] No measurable demand from BOD$_5$ analysis.

Aquatic Toxicity

Methods

Screening toxicity tests were used to approximate toxic endpoints. Procedures to screen a large list of potential deicer components were similar to range-finding toxicity tests, which are used to choose the correct range of concentrations prior to a full definitive acute or chronic bioassay. If toxicity data were available from MSDSs, concentrations were prepared based on those data. A 50 percent dilution series of up to 10 dilutions were prepared for the screening assay for each product tested. Five <24-hour-old *Ceriodaphnia dubia* and two <24-hour-old *Pimephales promelas* larvae were placed in the same test chamber. For several days following hatching, the fish are too young to consume daphnia. Two replicates were prepared for each product concentration. Test duration was 48 hours without renewal. No water quality parameters were measured during or after screening tests. Microtox® assays were performed without replication. If prepared concentrations were found to be out of range for approximating an LC_{50} or half maximal effective concentration (EC_{50}) for any species, a new set of concentrations were prepared and the screening test was repeated for those species. LC_{50}s and EC_{50}s reported for screening tests should only be considered approximations because procedures differ from standard definitive bioassays. Screening toxicity procedures include fewer replicates, non-renewal of test solutions, shorter exposure duration for *Pimephales promelas*, and other procedural variances from definitive toxicity tests. Uncertainty levels cannot be determined due to lack of replication. It is assumed the actual EC or LC50 value lies between the test concentrations which are below and above the calculated EC^{50} or LC^{50}. For this dilution series, the lower and upper limits are one half and double the EC^{50} or LC^{50} respectively.

Results

Results from screening-level bioassays for 24 FPDs (Table 4-7), 19 surfactants (Table 4-8), 14 corrosion inhibitors (Table 4-9), and 6 thickeners (Table 4-10) are presented below. Previous work has identified surfactants and benzotriazole-based corrosion inhibitors as the primary source of toxicity in previous commercial formulations *(1)*. Therefore, FPDs with similar toxicity characteristics, such as 1,2 propylene glycol, would be acceptable alternatives if oxygen demand were less. Considering only aquatic toxicity, several FPDs could be viable candidates, including DEG, xylitol, glycerol, triethylene glycol, and dipropylene glycol. In addition, 2-(2-methoxyethoxy)-ethanol and 1,3 butanediol could be considered if the oxygen demand characteristics were greatly improved over 1,2 propylene glycol.

The evaluation process for candidate surfactants, corrosion inhibitors, and thickeners included consideration of the aquatic toxicity profiles as well as the concentration needed to provide favorable performance. Testing began with aquatic toxicity evaluation, and the results are presented in Tables 4-8, 4-9, and 4-10. These results are only approximations. Compounds are organized by least toxic to most toxic endpoint, determined by the most sensitive species.

Evaluation of performance properties for specific concentrations of these formulation components were conducted in Tier 2 and are discussed in Section 5. Multiple candidates for alternative surfactants, corrosion inhibitors, and thickeners indicate a potential for improved toxicity profiles over these components in previous commercial formulations.

TABLE 4-7. Screening-level toxicity data for candidate FPDs for three species.
The shaded boxes indicate the most sensitive species to each compound.

FPD	Aircraft or Pavement	Microtox® EC$_{50}$[a] (mg/L)	*C. dubia* LC$_{50}$[b] (mg/L)	*P. promelas* LC$_{50}$ (mg/L)
Diethylene glycol	A,P	66,900	53,000	56,900
Xylitol	P	348,000	48,500	52,000
1,2-Propylene glycol	A,P	69,300	46,300	49,600
Glycerol	A,P	130,000	34,900	46,000
Triethylene glycol	A,P	54,000	31,000	59,900
Dipropylene glycol	A,P	25,200	20,600	35,900
2-(2-Methoxyethoxy)-ethanol	A,P	56,700	22,100	18,000
1,3-Butanediol	A,P	17,000	35,900	35,900
2-(2-Ethoxyethoxy)-ethanol	A,P	13,600	16,600	14,400
1,3-Propylene glycol	A,P	29,300	25,300	12,700
1,1,1-Trimethanolethane	P	11,200	26,400	35,800
Ethylene carbonate	P	24,100	8,850	10,500
2-Methyl-1,3-propanediol	A,P	8,530	16,400	32,000
Trimethylolpropane	P	7,550	10,000	29,700
Sodium acetate	P	44,600	7,350	7,350
sodium formate	P	51,800	4,140	7,460
Disodium succinate	P	73,300	3,540	11,300
Propylene carbonate	A	2,880	12,100	4,420
2,2-Dimethyl-1,3-dioxolane-4-methanol	A,P	2,540	8,840	14,900
Calcium propionate	P	39,900	2,260	13,800
L-Tartaric acid dipotassium salt	P	94,100	859	1,020
potassium formate	P	14,700	730	940
Tripotassium citrate	P	34,300	365	433
D-Gluconic acid,δ-lactone	P	408	212	235

[a] The Microtox® EC$_{50}$ is the statistically determined concentration that would result in a 50% reduction in light emission compared to a laboratory control.
[b] The LC$_{50}$ is the statistically determined concentration that would cause death in 50% of the population exposed.

Previous work indicated that alkylphenol and alcohol ethoxylate surfactants approximating those in previous deicer formulations had acute toxicity endpoints between 0.44 and 16 mg/L *(1)*. Eleven of the candidate surfactants evaluated in this study show potential for improved toxicity profiles (Table 4-8). These surfactants include the first eleven candidates in Table 4-8. Considering the minimum endpoint for the three organisms, values range from 20.7 mg/L (moderately less toxic than current surfactants) to 14,900 mg/L (substantially less toxic than current surfactants).

Table 4-8. Screening-level toxicity data for candidate surfactants for three species.
The shaded boxes indicate the most sensitive species to each compound.

Surfactant	Microtox® EC$_{50}$ (mg/L)	*C. dubia* LC$_{50}$ (mg/L)	*P. promelas* LC$_{50}$ (mg/L)
Tergitol L-64	25,000	28,200	14,900
Surfynol 465	1,120	686	437
Tetronic 904	402	25,900	7,210
Triton CF-32	715	361	361
Tergitol TMN-10 + 10% Ridafoam	387	183	105
Tergitol TMN-10	408	160	91.9
Lutensol XP 100	118	54.6	56.5
Tergitol TMN-6	140	65.3	39
Triton CG-110	29.8	163	361
Triton CG-110 + 10% Ridafoam	27.6	298	735
Plurafac S-405LF	94.7	40.7	20.7
Lutensol TDA 10	16.1	14.5	25.3
Triton DF-16	15.6	13.1	15.0
Tergitol 15-S-12	153	12.4	12.4
Lutensol XP 50	25.3	9.34	23.2
Tergitol 15-S-7	13.2	5.30	5.30
Bio Soft N1-7	3.60	3.60	10.2
Ridafoam (anti-foaming product)	3.03	22.8	>780
Merpol SE	2.28	9.33	4.67
Bio-Soft N1-5	1.92	2.47	6.60

Acute toxicity endpoints for benzotriazole-based corrosion inhibitors varied between 4.3 and 81 mg/L in previous testing *(32)*. Nine of the candidate corrosion inhibitors evaluated in this study show potential for improved toxicity profiles (Table 4-9). These corrosion inhibitors include the first nine candidates in Table 4-9. Considering the minimum endpoint for the three organisms, values range from 46.3 mg/L (similar toxicity to current corrosion inhibitors, but other organisms are much less sensitive) to 375 mg/L (substantially less toxic than current corrosion inhibitors).

TABLE 4-9. Screening-level toxicity data for candidate corrosion inhibitors for three species.
The shaded boxes indicate the most sensitive species to each compound.

Corrosion inhibitor	**Microtox® EC$_{50}$ (mg/L)**	***C. dubia* LC$_{50}$ (mg/L)**	***P. promelas* LC$_{50}$ (mg/L)**
Mazon RI 325	375	481	8,840
Triethanolamine	212	1,430	11,500
Sodium silicate	273	223	208
Potassium silicate	164	445	445
Sodium borate decahydrate	150	836	1,780
Potassium phosphate	102	253	311
Korantin SMK	48.0	61.6	119
Potassium carbonate	46.3	310	191
3-Methoxypropylamine	33.5	76.5	101
Cobratec 948	10.4	354	177
Ammonyx CDO Special	35.2	39.2	8.03
DrewPlast 154	3.75	11.1	8.84
Ninol 1301	86.4	3.54	3.54
Ninol 201	38.0	1.06	3.01

Aquatic toxicity endpoints of polyacrilic acid thickeners (Carbopol®) found in commercial products were less (more toxic) than other candidate thickeners. However, given the concentrations used in Type IV formulations, results did not warrant dismissal of any candidate thickeners based solely on toxicity (Table 4-10). Candidates, therefore, must be selected for further testing based upon performance and cost.

TABLE 4-10. Screening-Level Toxicity Data for Candidate Thickeners for Three Species

Thickener	**Microtox® EC$_{50}$ (mg/L)**	**C. dubia LC$_{50}$ (mg/L)**	**P. promelas LC$_{50}$ (mg/L)**
Cellosize DCS HV	7,290	2,770	6,360
Kelzan-HP	2,440	1,310	2,380
Kelzan-RD	2,480	862	2,120
K1A96	2,230	853	3,180
Carbopol EZ-4 (neutralized with KOH)	793	154	177
Carbopol EZ-4 (neutralized with TEA)	375	50.0	265

In addition, tripotassium citrate and potassium carbonate were evaluated as anti-caking agents for sodium formate granular pavement deicer material. Aquatic toxicity was evaluated for tripotassium citrate as a candidate FPD (Table 4-7). Aquatic toxicity endpoints for potassium carbonate were as follows: Microtox® EC_{50}, 48.4; *Ceriodaphnia dubia* LC_{50}, 277 mg/L; *Pimephales promelas* LC_{50}, 277 mg/L. Considering the low concentrations needed as anti-caking agents, neither compound was dismissed because of aquatic toxicity results.

Viscosity

Viscosity measurements of six candidate thickeners for Type IV aircraft anti-icing formulations were made using a Brookfield viscometer. The thickeners were mixed with water at different concentrations, and the viscosity was determined at room temperature (20°C) and at 5°C and compared to a commercially available Type IV anti-icing formulation. The concentration for each thickener in water was based on values obtained in the literature. The test results are presented in Figure 4-2 for each surfactant at the two temperatures. The viscosity curves at both temperatures are virtually parallel to each other; the values are within 20 percent of each other at the two temperatures. Based on this observation, subsequent viscosity measurements were made at room temperature.

A comparison of the viscosities of the surfactant:water mixtures with a commercially available Type IV anti-icing formulation is shown in Figure 4-3. Table 4-11 summarizes the performance testing results of the thickeners and shows the change in thickener concentration to match the viscosity of the commercial Type IV formulation (see each series of curves in Figure 4-3). The viscosity of the Cellulose DCS HV thickener was 37 times lower than the commercial formulation and is not shown in Figures 4-2 and 4-3.

TABLE 4-11. Performance testing results for thickeners.

Thickener	Test Concentration, wt %	Concentration Change[a]
Kelzan HP	0.4	Same
Kelzan RD	0.5	Increase
K1A96	0.75	Decrease
Cellulose DCS HV	1.5	Substantial increase
Carbopol EZ-4 with TEA	0.1	Decrease
Carbopol EZ-4 with KOH	0.1	Decrease

[a] Change in concentration indicates the direction of the test concentration to match the viscosity of the commercially available Type IV runway anti-icer, e.g., the concentration of Kelzan RD must be increased from 0.5 wt% to match the concentration of the commercial Type IV anti-icer.

Figure 4-2. Thickener viscosity/shear rate at 5°C and at room temperature.

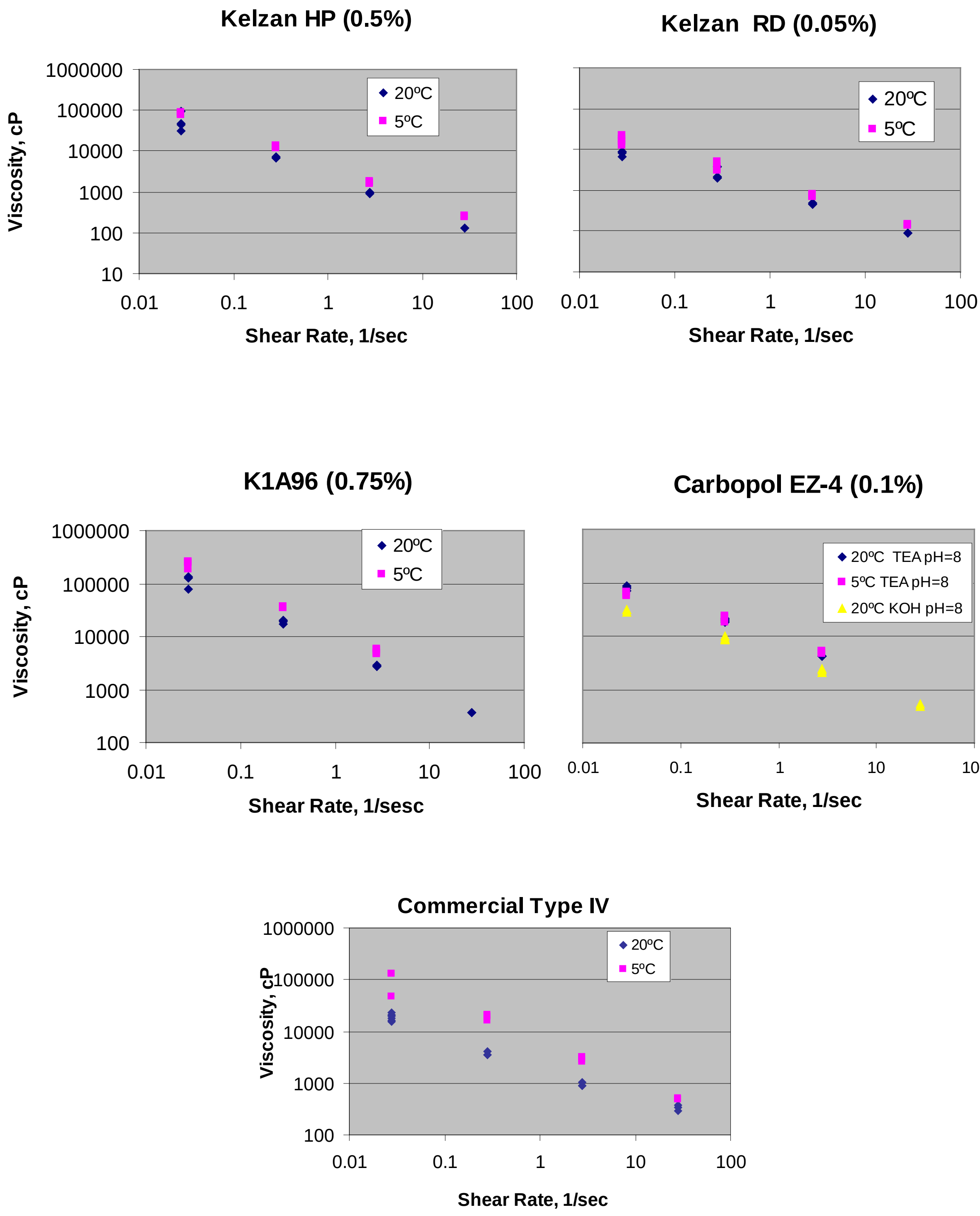
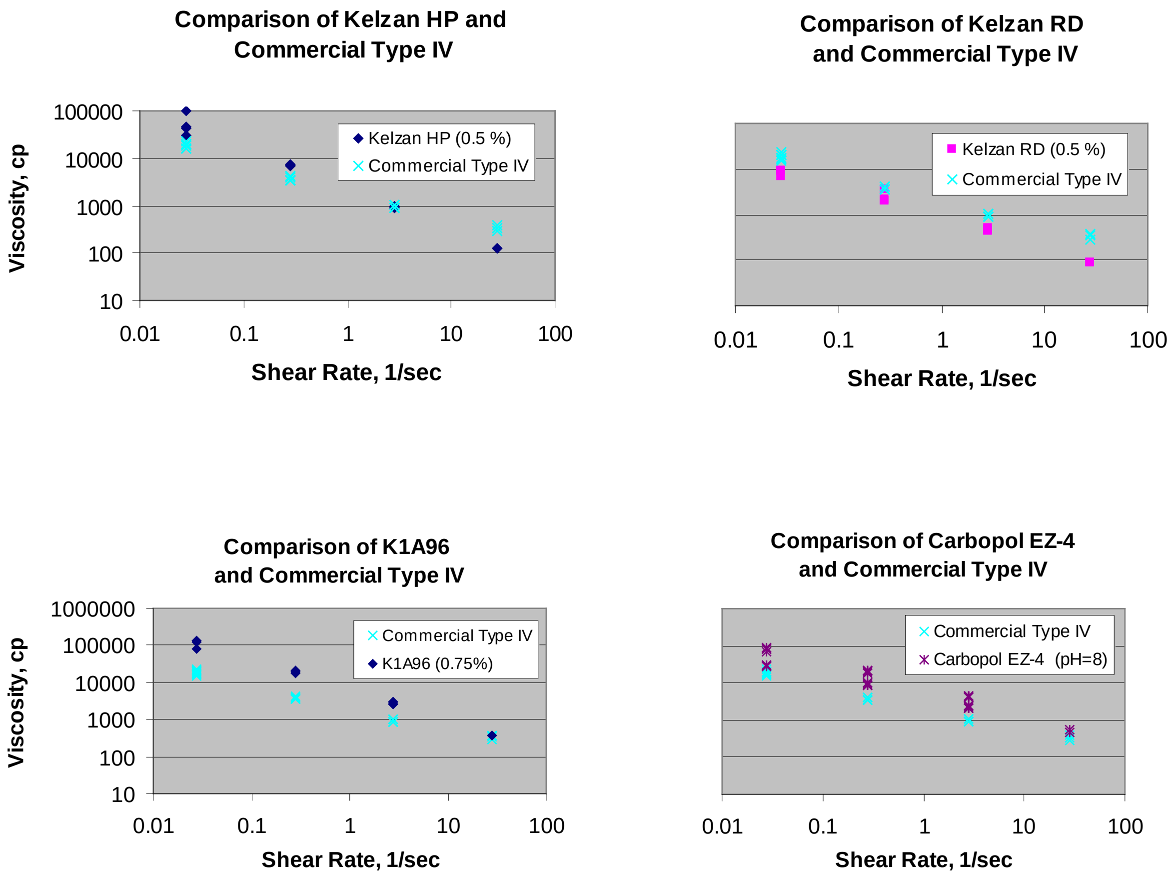


Figure 4-3. Comparison of viscosity for surfactants with commercially available Type IV anti-icing formulation at room temperature.



Contact Angle

The contact angle is a measure of the degree to which the droplet will spread over the surface—the lower the contact angle between the water:surfactant droplet and the surface, the lower the surface tension, and the more the droplet will spread over a wing surface. The contact angle of two concentrations of surfactant:water mixtures (0.5:99.5 and 1:99 percent by weight) was determined using a drop shape analyzer. The measurements were made at the University of Massachusetts-Lowell on a Krüss Drop Shape Analysis System DSA100. Test results are shown in Table 4-12 for the surfactant:water mixtures. The contact angle, a measure of surfactant effectiveness, is generally the same at the two concentrations.

TABLE 4-12. Performance testing results for surfactants.

Surfactant	Contact angle, degrees 0.5:99.5	1:99	Average	Ranking by contact angle
Tergitol L-64	31.5	28.7	30.1	8
Tetronic 904	26.2	23.8	25.0	7
Mixture 2[a]	13.0	13.0	13.0	4
Surfynol 465	13.1	9.5	11.3	3
Triton CF-32	18.4	22.3	20.4	6
Triton CG-110	19.7	14.3	27.0	5
Mixture 1[b]	8.9	11.3	10.1	2
Tergitol TMN-10	7.1	8.5	7.8	1
Distilled water	64.2		64.2	

[a] Mixture 2: Triton CG-110+10% Ridafoam NS 221.
[b] Mixture 1: Tergitol TMN10+10% Ridafoam NS 221.

Down-Selection of Components for Tier 2 Testing

FPDs

Down-selection of FPDs included consideration of results from tests for aquatic toxicity, COD, freezing point, flash point, and a qualitative observation of miscibility (Table 4-13). Aquatic toxicity criteria of 20,000 mg/L for aircraft deicing and anti-icing fluids and 2,000 mg/L for pavement deicer material were used. Because of the uncertainties involved in BOD testing, it was decided that COD would be used in the down-selection process as a more reliable and consistent measure of oxygen demand. COD criteria of 1,600,000 mg/kg (the value for 1,2 propylene glycol) for aircraft deicing and anti-icing fluids and 629,000 mg/kg (the value for potassium acetate) for pavement deicer material were used. The freezing point for FPDs needed to be less than -14.5°C for aircraft deicing and anti-icing fluids and less than -20°C for pavement deicing material to be considered further. FPDs needed a flashpoint of greater than 100°C to be considered further. All FPDs needed to be completely miscible in water in order to be considered further.

These eliminating criteria left only two FPDs for aircraft deicing and anti-icing fluids: glycerol and diethylene glycol. No fluids met test criteria to continue testing for new pavement deicing materials.

TABLE 4-13. Down-selection results for candidate FPDs for potential use as aircraft and pavement deicers and anti-icers.

	Elimination Factors for Selection of Candidate Deicers and Anti-Icers	
Freezing Point Depressants	**Aircraft**	**Pavement**
Liquid		
2,3-Butanediol	Freezing Pt., COD	Aircraft only
4-Methyl-γ-butyrolactone	Freezing Pt., Toxicity	
Dimethyl malonate	Immiscible, Freezing Pt.	
Dimethyl succinate	Immiscible, Freezing Pt.	
Propylene carbonate	Freezing Pt, Toxicity	
1,2-Propylene glycol	Current-use	Current-use
1,3-Butanediol	Toxicity, COD	COD
1,3-Propylene glycol	Toxicity, COD	COD
2-(2-Ethoxyethoxy)-ethanol	Toxicity, COD	COD
2,2-Dimethyl-1,3-dioxolane-4-methanol	Flash pt., Freezing Pt., Toxicity	Flash pt.
2-Methyl-1,3-propanediol	Toxicity, COD	COD
Dipropylene glycol	COD	COD
Glycerol	**Continue testing**	COD
Triethylene glycol	COD	COD
2-(2-Methoxyethoxy)-ethanol	Flash pt., toxicity	Flash pt.
Diethylene glycol	**Continue testing**	COD
Solid		
1,1,1- Trimethanolethane	Pavement only	COD
Calcium propionate		Freezing Pt. COD
D-Gluconic acid,δ-lactone		Toxicity, COD
Disodium succinate		Freezing Pt., COD
Ethylene carbonate		Freezing Pt., COD
L-Tartaric acid dipotassium salt		Toxicity
Potassium L-lactate		Not available
Sodium acetate		Current-use
Sodium formate		Current-use
Trimethylolpropane		COD
Tripotassium citrate		Toxicity
Xylitol		COD

Thickeners

The thickeners were down-selected based on the aquatic toxicity and changes in the test concentration of the thickener necessary to match the viscosity of the commercially available Type IV aircraft deicing formulation. Table 4-14 shows the outcome of the down-selection of the thickeners.

TABLE 4-14. Down-selection rankings for candidate thickeners.

Thickener	Test Concentration, wt%	*Pimephales promelas* LC_{50} (mg/L)	Change in *Pimephales promelas* LC_{50}[a]	Rank
K1A96	0.75	424,000	Increase	1
Kalzan HP	0.5	476,000	Increase	2
Carbopol EZ-4 with TEA	0.1	106,000	Increase	3
Kalzan RD	0.5	424,000	Decrease	4
Carbopol EZ-4 with KOH	0.1	71,000	Increase	5
Cellulosize DCS HV	1.5	424,000	Substantial decrease	6

[a] Resulting from changing thickener concentration from the test concentration to match viscosity of commercially available Type IV aircraft anti-icer. Change in *Pimephales promelas* LC_{50} is in the direction opposite to the concentration change in Table 4-11. For example, increasing the concentration of Kalzan HP from 0.5 wt% to match the concentration of the commercial Type IV anti-icer will reduce the LC_{50} and increase the toxicity of the solution.

Surfactants

The surfactants were ranked on the basis of their aquatic toxicity and effectiveness based on contact angle. Results indicate that toxicity of these surfactants generally increases as surfactant performance improves (Table 4-15).

TABLE 4-15. Performance and aquatic toxicity testing results for surfactants.

Surfactant	*Pimephales promelas* LC_{50} (mg/L)	Contact Angle, degrees			Ranking by Contact Angle
		0.5:99.5	1:99	Average	
Tergitol L-64	14895	31.5	28.7	30.1	8
Tetronic 904	7212	26.2	23.8	25.0	7
Mixture 2[a]	725	13.0	13.0	13.0	4
Surfynol 465	437	13.1	9.5	11.3	3
Triton CF-32	361	18.4	22.3	20.4	6
Triton CG-110	361	19.7	14.3	27.0	5
Mixture 1[b]	105	8.9	11.3	10.1	2
Tergitol TMN-10	92	7.1	8.5	7.8	1
Distilled water		64.2		64.2	

[a] Mixture 2: Triton CG-110+10% Ridafoam NS 221.
[b] Mixture 1: Tergitol TMN10+10% Ridafoam NS 221.

Corrosion Inhibitors

Two corrosion inhibitors, TEA and Mazon RI 235, were down-selected for further evaluation in Tier 2, based on aquatic toxicity (Table 4-13).

SECTION 5

TIER 2 RESULTS

Aircraft Type IV Anti-Icing Fluids

Table 5-1 lists the FPDs, surfactants, thickeners, and corrosion inhibitors that were selected for evaluation during Tier 2 testing of Type IV aircraft anti-icing formulations. Based on the results of Tier 1 testing, the FPDs that were selected showed improvements in COD, BOD and/or aquatic toxicity over propylene glycol. Many surfactants tested in Tier 1 had improvements in toxicity over current-use surfactants. Surfactants were selected to take advantage of these toxicity improvements as much as possible while reducing the contact angle and surface tension to ensure that the formulations completely coat the aircraft surfaces. Thickeners were selected based on their aquatic toxicity and their ability to shear in a manner similar to commercial Type IV anti-icing agents. Corrosion inhibitors were down-selected based on aquatic toxicity.

TABLE 5-1. Candidate components of Type IV aircraft anti-icing fluids evaluated in Tier 2.

FPDs	Surfactants	Thickeners	Corrosion Inhibitors
Glycerol	Tergitol L-64	Kelzan HP	TEA
DEG	Tergitol TMN-10	K1A96	Mazon RI 325
	Triton CG-110 with 10% Ridafoam NS 221	Carbopol EZ-4 with TEA	

Tier 2 experiments involved the testing of more complex mixtures as compared to Tier 1, which focused on mixtures of the components and water:

- FPDs + water + thickeners; FPD:water = 1:1 by weight
- FPDs + water + surfactants; FPD:water = 1:1 by weight
- FPDs + water + thickeners + surfactants; FPD:water = 1:1 by weight
- FPDs + water + thickeners + surfactants + corrosion inhibitors; FPD:water = 1:1 by weight

Tables 5-2 through 5-5 summarize the methodology used to identify Type IV anti-icing formulations with very low aquatic toxicity. The tests shown in Tables 5-2 and 5-3 were done in parallel. For example, in Table 5-2, concentrations were experimentally determined to match the viscosity/shear rate curve of a commercial Type IV anti-icing formulation. The thickener was down-selected for each FPD based on the aquatic toxicity of the formulation and the cost of the thickener. The aquatic toxicity of these mixtures was calculated based on the toxicity of the individual components previously measured in Tier 1.

TABLE 5-2. Method of down-selecting thickeners for selection of FPD and thickener with minimum aquatic toxicity and cost.

FPD	Thickener	Concentration[a] (%)	Aquatic Toxicity	Down Select
DEG	Kelzan HP	A_1	Estimate screening test toxicity based on individual components	A
	K1A96	A_2		
	Carbopol EZ-4 with TEA	A_3		
Glycerol	Kelzan HP	B_1	Estimate screening test toxicity based on individual components	B
	K1A96	B_2		
	Carbopol EZ-4 with TEA	B_3		

[a] Concentrations selected to match commercial Type IV viscosity/shear rate curve.

TABLE 5-3. Method of down-selecting surfactants for selection of FPD and surfactants with minimum aquatic toxicity and cost.

FPD	Surfactant	Concentration[a] (%)	Aquatic Toxicity	Down Select
DEG	Tergitol L-64	C1	Estimate screening test toxicity based on individual components	C
	Triton CG-110 with 10% Ridafoam	C2		
	Tergitol TMN-10	C3		
Glycerol	Tergitol L-64	D1	Estimate screening test toxicity based on individual components	D
	Triton CG-110 with 10% Ridafoam	D2		
	Tergitol TMN-10	D_3		

[a] Concentrations were selected to match commercial Type IV contact angle.

TABLE 5-4. Method of verifying selection of thickeners and surfactants.

FPD	Thickener + Surfactant	Test[a]	Aquatic Toxicity
DEG	A + C	Viscosity/Shear Rate Contact Angle	Measure screening test aquatic toxicity and compare to estimated screening test toxicity based on individual components as measured in Tier 1.
Glycerol	B + D	Viscosity/Shear Rate Contact Angle	Measure screening test aquatic toxicity and compare to estimated screening test toxicity based on individual components as measured in Tier 1.

[a] Compare test results to commercial Type IV formulation; determine if thickening agents absorb surfactants and if surfactants affect viscosity/shear rate behavior.

TABLE 5-5 Method of down-selecting corrosion inhibitors.

FPD	Thickener + Surfactant	Corrosion Inhibitor[a]	Down Select[b]	Aquatic Toxicity
DEG	A + C	TEA Mazon RI 325	E	Perform complete aquatic toxicity tests on down-selected mixture (FPD+A+C+E)
Glycerol	B + D	TEA Mazon RI 325	F	Perform complete aquatic toxicity tests on down-selected mixture (FPD+B+D+F)

[a] Sandwich and immersion corrosion testing with 0.2% by weight of corrosion inhibitors.

[b] If both pass corrosion testing, select corrosion inhibitor with lowest screening test aquatic toxicity. If only one passes corrosion testing, use that corrosion inhibitor.

Similarly, in Table 5-3, the contact angles for the various surfactant concentrations in FPD/water mixtures were measured. For each surfactant, the concentration that matches the contact angle for the commercially available Type IV formulation was selected. The contact angle is related to the surface tension, which should be less than 35 dynes/cm for a Type IV anti-icing formulation *(33)*. The surfactant was down-selected for each FPD based on the aquatic toxicity of the formulation and the cost of the surfactant. The aquatic toxicity of these mixtures was estimated based on the toxicity of the individual components previously measured in Tier 1.

Anti-icing formulations with the thickener and surfactant concentrations found in the tests shown in Tables 5-2 and 5-3 were tested for contact angle and viscosity, as shown in Table 5-4. The primary aim of these tests was to determine if there is any interaction between the thickeners and surfactants that will substantially affect the viscosity and contact angle. Finally, corrosion inhibitors were added to the formulations, and corrosion and full aquatic toxicity testing was carried out to develop a final formulation with minimum aquatic toxicity.

Testing FPDs/Water and Thickeners

The three candidate thickeners were mixed at different concentrations with 1:1 mixtures by weight of the two candidate FPDs and water. A thickener concentration was found for each of the two FPD formulations to match the viscosity/shear rate curve of a commercial Type IV aircraft anti-icing formulation. The viscosities of the candidate FPD/water and thickener solutions were measured at a temperature of 20°C (AMS 1428 Type IV Fluid) and multiple shear rates (0.3 revolution per minute [rpm], 6 rpm and 30 rpm per AMS 1428) on a Brookfield Programmable DV-II+ Viscometer. The measurements were compared to the commercial Type IV AAF.

Procedures for mixing the thickeners (in particulate form) with liquid solutions were followed from the manufacturer’s literature. The following procedures were used:

Kelzan HP and K1A96

- Formulation was done with deionized water at room temperature.
- A mixer or blender was used to ensure adequate dispersion of the thickener particles.
- The FPD/water solution was placed in the mixer and the stirring rate was set to a high value.
- The thickener was slowly added directly into the vortex. Enough thickener was added to produce the desired thickener concentration.
- After all the thickener was added, the mixer was operated for 10 minutes.
- The solution was stored at room temperature.
- The solution was tested after a 24-hour period.
- The appearance of any particles or phases in the solution before use was noted.

Carbopol EZ-4 with TEA

This formulation consists of a mixture of Carbopol EZ-4 in FPD/water neutralized with TEA.

- Formulation was done with warm temperature water. The optimal temperature was between 40 and 50°C.
- A mixer or blender was used to ensure adequate dispersion of the thickener particles.
- The FPD/water solution was placed in the mixer and the stirring rate was set to a medium speed. Setting the mixer to a high speed (greater than 5,000 rpm) could degrade the polymer matrix.
- The thickener was slowly added directly into the vortex. Enough thickener was added to produce the desired thickener concentration.
- After all the thickener was added, the mixer was operated for 10 minutes.
- The initial pH of the solution was measured and recorded.
- Sufficient TEA was added to raise the pH of the solution to 8.0.
- Upon neutralization, the solution had a grainy “applesauce” appearance. This was normal and disappeared within 1 hour.
- The solution was stored at room temperature.
- The solution was tested after a 24-hour period.
- The appearance of any particles or phases was noted before use.

The first set of experiments evaluated the effect of thickener concentration on the viscosity of mixtures of Type IV FPDs and water. Table 5-6 lists the FPDs, thickeners and thickener concentrations that were initially evaluated. The range of thickener concentrations was selected based on the Tier 1 results, in which selected concentrations of the thickeners were mixed with water and the viscosities compared to a commercially available Type IV formulation. The change in concentration of the thickeners to match the viscosity of the commercially available Type IV formulation was evaluated for each thickener.

TABLE 5-6. Test matrix to evaluate the effect of thickener concentration on viscosity.

FPD/Water	Thickener	Thickener Concentration, wt %
Glycerol/water[a] DEG/water[a]	Kelzan HP	0.5
		0.375
		0.25
	K1A96	0.75
		0.563
		0.375
	Carbopol EZ-4 with TEA	0.1
		0.074
		0.05
Commercial Type IV formulation		

[a] 50:50 wt % of FPD/water.

Figures 5-1 and 5-2 show the average viscosities of the three thickeners at different shear rates for each of the FPD/water mixtures. For each thickener concentration, four viscosity measurements were made. For some cases, on the semi-log scale, the data points were not differentiable. In addition, data for water and the commercial Type IV formulation are also shown. A shear rate of 0.084/sec corresponds to 0.3 rpm for a No. 34 Brookfield viscometer spindle; similarly, 1.68/sec and 8.4/sec for 6 and 30 rpm, respectively. Table 5-7 summarizes the concentrations of the thickeners at different shear rates that give the same viscosity as the commercial Type IV formulation.

Figure 5-1. Viscosity of Kelzan HP and K1A96 at different concentrations and shear rates for glycerol/water and diethylene glycol/water mixtures.

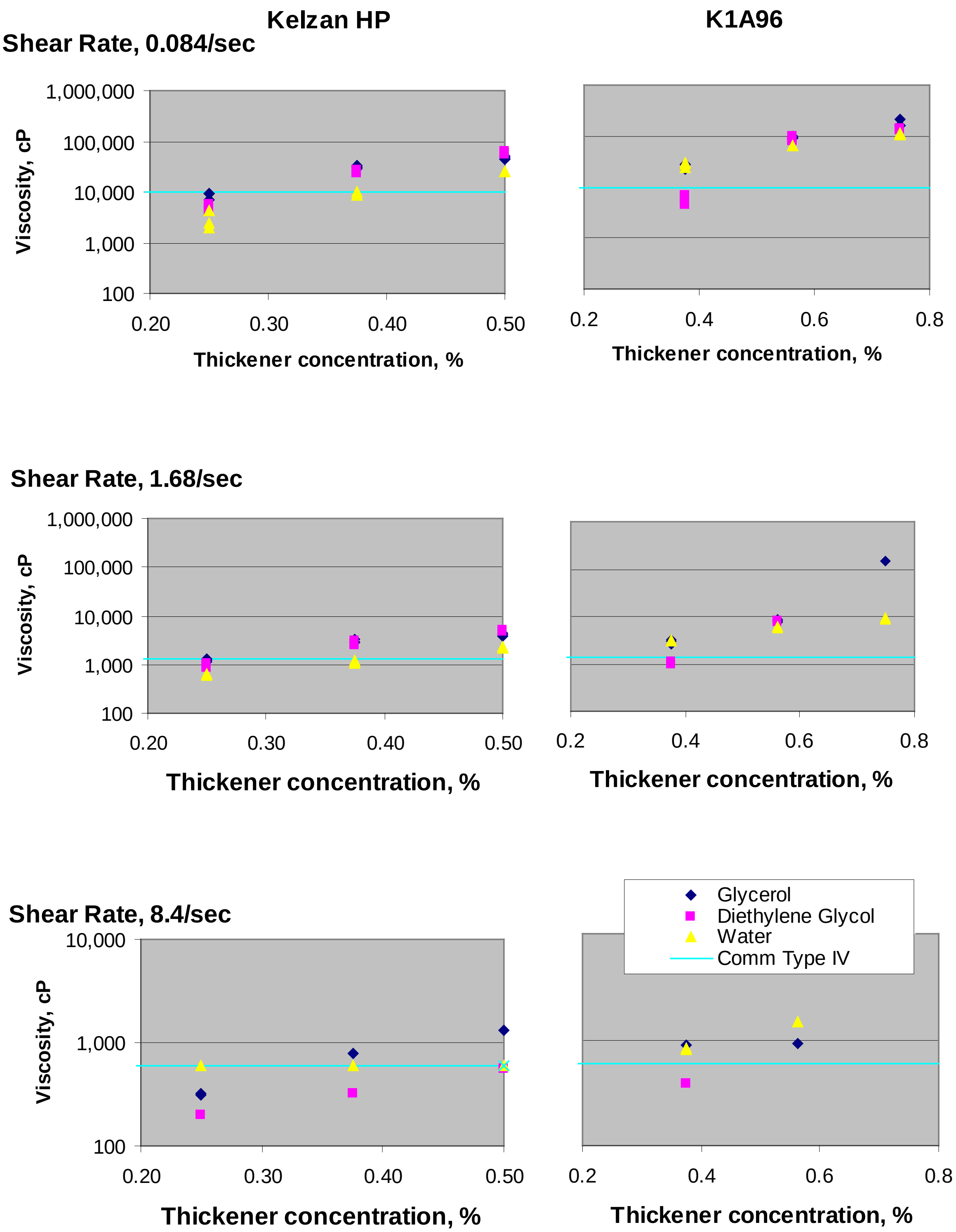


Figure 5-2. Viscosity of Carbopol EZ-4 with TEA at different concentrations and shear rates for glycerol/water and diethylene glycol/water mixtures.

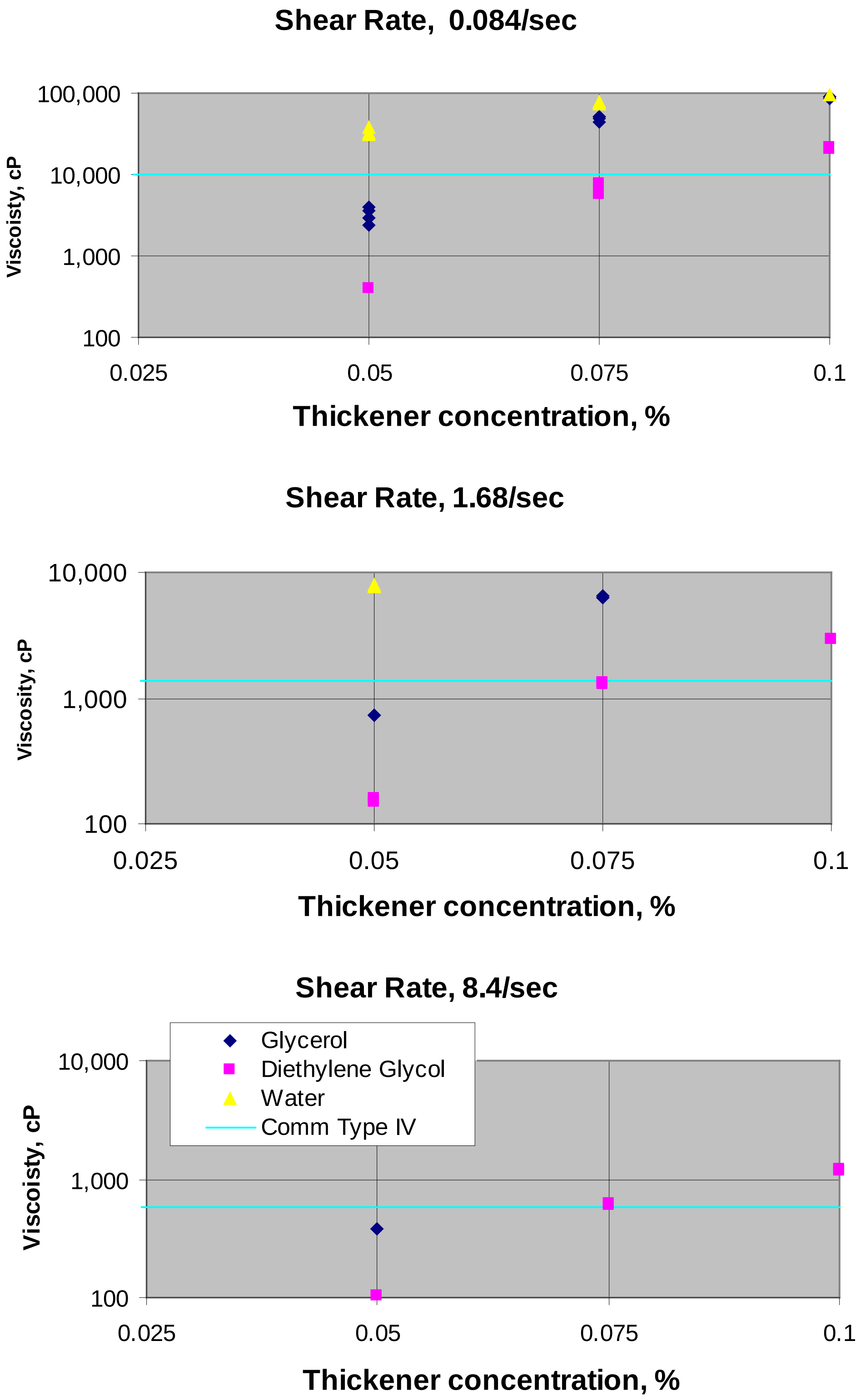


TABLE 5-7. Concentration of thickeners (wt %) for different FPDs to match viscosity of commercial Type IV anti-icing fluid at different shear rates.

		Concentration (%) for Three Different Shear Rates (1/sec)		
FPD/water	**Thickener**	**0.084**	**1.68**	**8.4**
Diethylene glycol[a]	Kelzan HP	0.30	0.30	0.50
	K1A96	0.40	0.40	—[b]
	Carbopol EZ-4/TEA	0.080	0.075	0.075
Glycerol[a]	Kelzan HP	0.25	0.25	0.32
	K1A96	0.30	0.25	—
	Carbopol EZ-4/TEA	0.055	0.055	—
Water	Kelzan HP	0.38	0.40	0.50
	K1A96	0.20	0.20	0.25
	Carbopol EZ-4/TEA	0.025	—	—

[a] 1:1 by weight.
[b] — not determined

Thickener concentrations were selected to match the viscosity/shear rate curve for the commercial Type IV formulation over most of the shear rate range (Table 5-8). Figure 5-3 graphically presents the test results over the entire shear rate range.

TABLE 5-8. Thickener concentrations selected to match viscosity/shear rate curve of commercial Type IV formulation.

FPD	Thickener	Concentration (wt %)
DEG	Kelzan HP	0.25
	K1A96	0.38
	Carbopol EZ-4 with TEA	0.076
Glycerol	Kelzan HP	0.25
	K1A96	0.28
	Carbopol EZ-4 with TEA	0.055

Figure 5-3. Comparison of viscosity/shear rate data for selected thickener concentrations to commercial Type IV formulation.

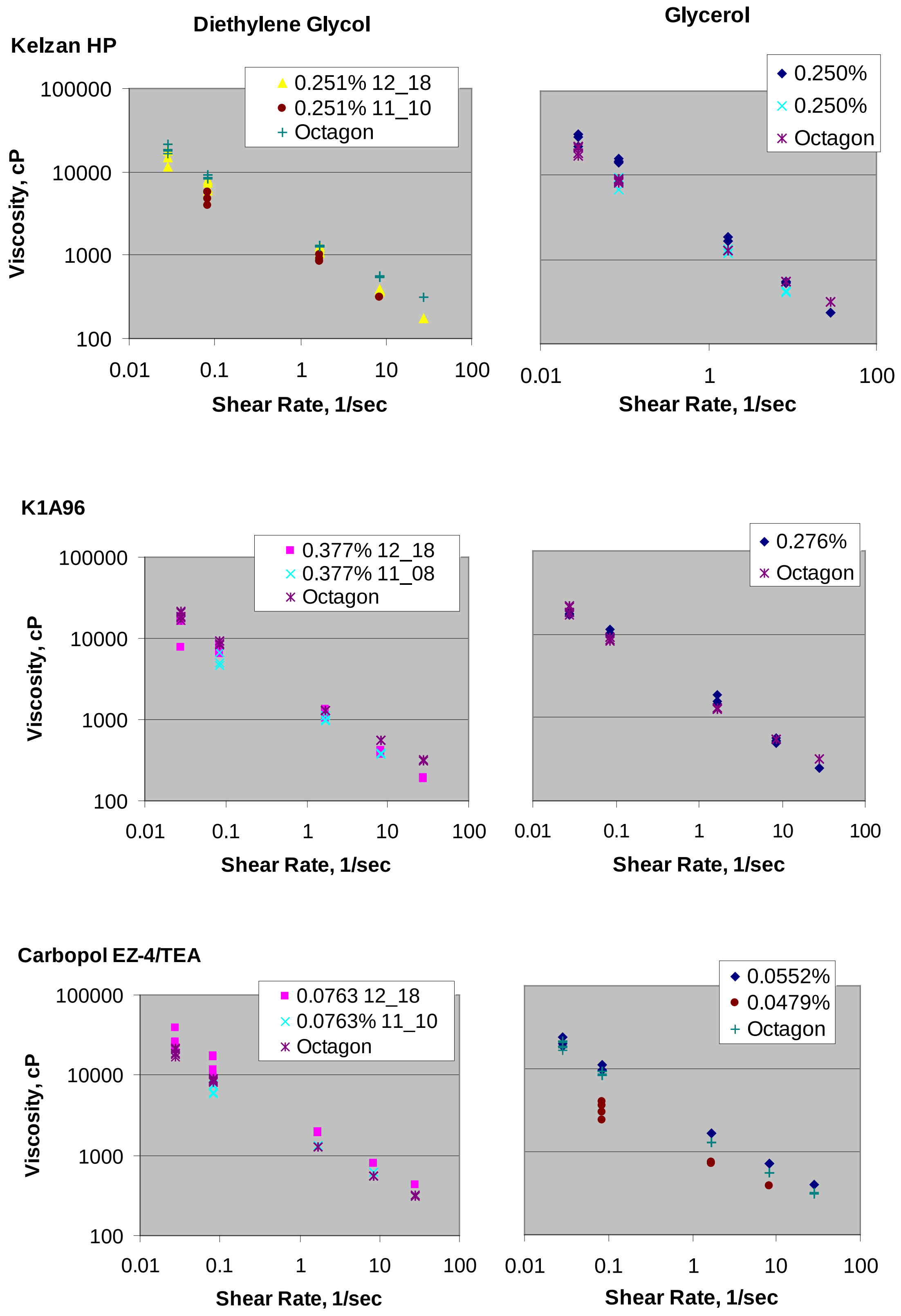


Table 5-9 summarizes the aquatic toxicity and cost of the thickeners at the concentrations shown in Table 5-4 (to match the commercial Type IV formulation). The aquatic toxicity is based on the measured values of the neat components determined in Tier 1. Except for one case (DEG/water/Carbolpol EZ-4), the aquatic toxicity of the FPD/water/thickener formulation was determined primarily by the FPD and not by the thickener itself. An additional consideration used in down-selecting the appropriate thickener was the cost of the thickener in the formulation. The unit costs of the thickeners are given in the sixth column of Table 5-9 for large (bulk) quantities of the thickeners. Although the toxicity of Carbopol EZ-4 (with TEA) is higher than the other two thickeners, the required concentration of Carbopol EZ-4 is much lower. As a result, the cost of the Carbopol EZ-4 thickener in the anti-icing formulation is a factor of two to three lower than Kelzan HP and K1A96 thickeners. Carbopol EZ-4 with TEA was selected as the preferred thickener for the remainder of the Tier 2 test series.

TABLE 5-9. Toxicity and costs of thickeners in FPD/water formulations.

FPD[a]	**Thickener**	**Concentration**[b] **(wt %)**	***P. promelas* LC_{50} for pure product (mg/L)**	**Predicted *P. promelas* LC_{50} in Formulation (mg/L)**	**Unit Cost of Thickener ($/lb)**	**Cost of Thickener in Formulation ($/lb)**
DEG	—	—	56,900	113,800	—	—
	Kelzan HP	0.25	2,400	949,800	6.52	0.0163
	K1A96	0.38	3,200	843,500	10.09	0.0380
	Carbopol EZ-4 with TEA	0.076	270	347,300	10.68	0.0081
Glycerol	—	—	46,000	92,000	—	—
	Kelzan HP	0.25	2,400	950,300	6.52	0.0163
	K1A96	0.28	3,200	1,153,100	10.09	0.0279
	Carbopol EZ-4 with TEA	0.055	270	479,900	10.68	0.0059

[a] Mixture of FPD and water (1:1 by weight).

[b] Concentration selected to match commercial Type IV viscosity vs. shear rate curve.

FPDs/Water and Surfactants

Surfactants evaluated in Tier 1 were down-selected based on pure product toxicity and contact angle. The surfactants selected for testing in Tier 2 were Tergitol L-64, Tergitol TMN-10 and Triton CG-110 mixed with 10 percent (by weight) of Ridafoam NS 22, an anti-foaming agent (Table 5-1). For a given surface, the contact angle is directly related to the liquid surface tension. Surfactants reduce the surface tension of the applied fluids to ensure they completely coat the aircraft and the runway surfaces. In Tier 2, the down-selected surfactants were added to FPD/water mixtures and their concentrations selected such that their contact angle matched the contact angle of the commercial Type IV deicing formulation. As in Tier 1, the contact angle measurements were carried out on a Drop Shape Analysis System DSA 100 (Krüss). Initial experiments were done on a silicon/gold (Si/Au) surface, but the measurements were inconsistent. The experimental procedure was revised for determining an advancing contact angle, in which the contact angle is measured while the drop on a surface is increasing in volume. This volume increase is accomplished by adding liquid to the drop by use of a syringe. This procedure provided more consistent data, especially at low contact angles, enabling the identification of the minimum concentration of candidate surfactant needed to achieve complete wetting of aircraft surfaces.

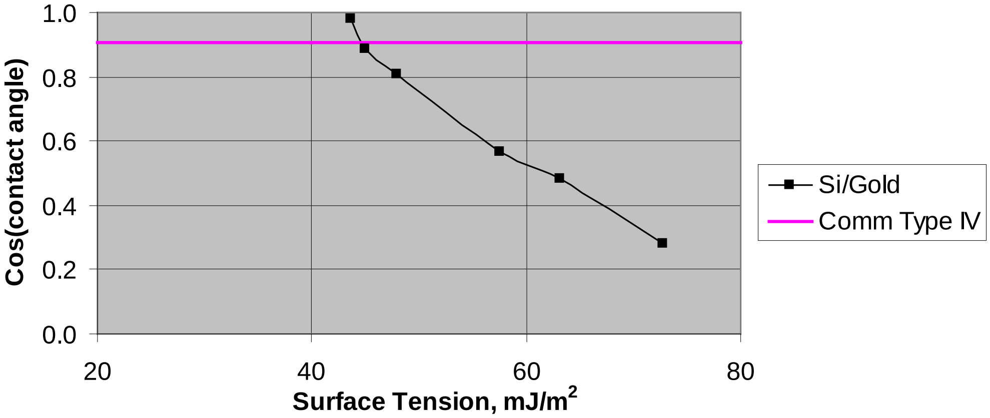
The liquid surface tension is a unique value for a given liquid, independent of the surface and the contact angle. Table 5-10 lists the liquid surface tension for different liquids *(34)*. For a given surface, the liquid surface tension is directly related to the contact angle. The contact angle for the liquids on a Si/Au surface is also given in Table 5-6, together with the measured value of the commercial Type IV formulation. The cosine of the contact angle is shown in Figure 5-4 as a function of the liquid surface tension. For the Si/Au surface, the surface tension for the commercial Type IV formulation is approximately 44 dyne/cm, higher than the reported value of approximately 35 dyne/cm for a Type IV AAF *(33)*.

TABLE 5-10. Liquid surface tension and surface contact angle for neat liquids.

Liquid	Surface Tension, mJ/m^2 (dyne/cm)	Contact Angle[a] (Deg.)
Decane	23.43	—
Hexadecane	27.76	—
Dimethylsulfoxide	43.58	11.83
DEG	45.04	27.53
Ethylene glycol	47.99	36.33
Formamide	57.49	36.43
Glycerol	63.11	47.97
Water	72.75	73.70
Comm Type IV		24.9

[a] For Si/Au surface.

Figure 5-4. Surface tension for Si/Au surface using data from Table 5-10.



The contact angles were measured as a function of surfactant concentration for each FPD/water mixture and matched to the contact angle of a commercial Type IV anti-icing formulation. Each contact angle corresponds to a specific surface tension. Figures 5-5 and 5-6 show the test results for DEG/water (1:1 by weight) glycerol/water (1:1 by weight), respectively. The contact angle for a commercial Type I formulation was also measured and was found to be within 3 degrees of the commercial Type IV formulation.

Figure 5-5. Contact angle measurement results for DEG/water and surfactants.

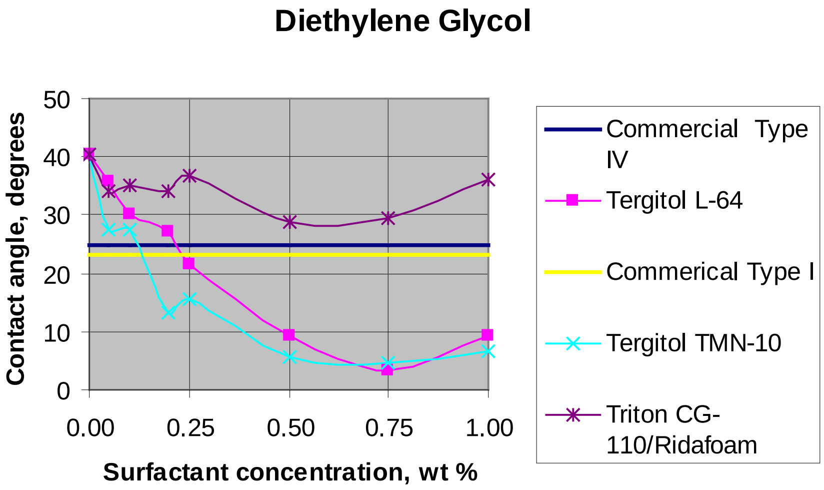


Figure 5-6. Contact angle measurement results for glycerol/water and surfactants.

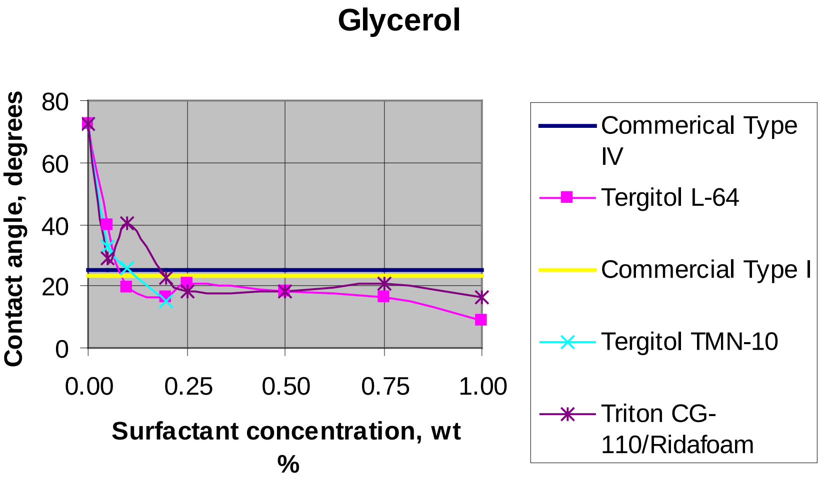


Table 5-11 summarizes the surfactant concentrations for each FPD/water and surfactant combination that results in a contact angle that matches the contact angle for the commercial Type IV anti-icing formulation. The contact angle for the DEG/water/Triton CG-110 formulation was always greater than the commercial Type IV formulation; this formulation was not considered further. Surfactant concentrations shown to have a higher contact angle than the commercially available formulation would need to be increased to reduce the surface tension, thereby increasing aquatic toxicity. Similarly, surfactant concentrations shown to have a lower contact angle than the commercially available formulation would need to be decreased to increase the surface tension, thereby decreasing aquatic toxicity.

TABLE 5-11. Properties of FPD/water/surfactant formulations having the same surface tension as a commercial Type IV formulation.

Formulation	Surfactant Concentration, wt %	*P. promelas* LC_{50} for Pure Product (mg/L)	Predicted P. promelas LC_{50} in Formulation (mg/L)	Price ($/lb)	Relative Price
DEG	50	56,900	113,800	—	—
Tergitol L-64	0.250	14,900	5,960,000	1.5	1.00
Tergitol TMN-10	0.150	90	60,000	2.3	0.92
Triton CG-110 + 10% Ridafoam	—	740	—	2.1	—
Glycerol	50	46,000	92,000	—	—
Tergitol L-64	0.100	14,900	14,900,000	1.5	1.00
Tergitol TMN-10	0.150	90	60,000	2.3	2.30
Triton CG-110 + 10% Ridafoam	0.200	740	370,000	2.1	2.79

Table 5-11 also shows the *Pimephales promelas* LC_{50} for the pure solutions as obtained from the Tier 1 results and the expected LC_{50} for the concentrations in the formulation. Tergitol L-

64 has a significantly lower toxicity than the two other surfactants. The LC_{50} for the rest of the surfactants was close to those of the FPD. Based on these data, Tergitol L-64 was tentatively down-selected for further testing.

Another criterion for down-selection was the relative cost of the surfactants. Table 5-11 shows the market price of the surfactants and the price of the surfactants in the formulation (concentration x price) relative to Tergitol L-64. For the DEG formulation, the price of Tergitol TMN-10 is slightly lower than that of Tergitol L-64, but Tergitol L-64 is the final choice because of the difference in aquatic toxicity. For glycerol, the price of Tergitol L-64 in the formulation is lower than the other two surfactants, so Tergitol L-64 is still the final choice.

FPDs/Water, Thickeners and Surfactants

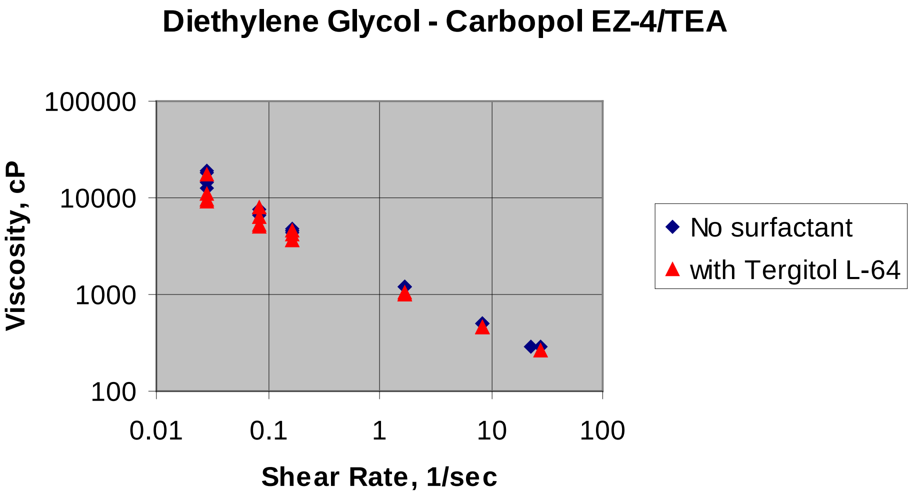
Surfactants were added to the FPD, water, and thickener mixtures at the concentrations found in the previous section, and the resultant mixtures were subjected to viscosity/shear rate and contact angle tests. The primary aim of these tests was to determine if there was any interaction between the thickeners and surfactants that will substantially affect the viscosity and surface tension of the formulations. Foaming tests were also carried out for the formulations.

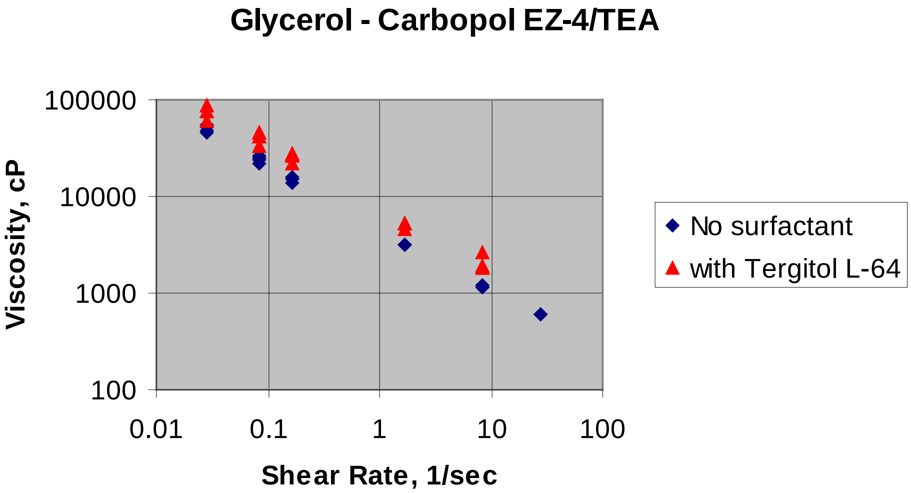
One concern was the effect of the surfactant on the viscosity/shear rate characteristics. DEG/ and glycerol/water formulations were prepared with the Carbopol EZ-4/TEA thickener at the concentrations shown in Table 5-12. The samples were split into two portions and Tergitol L-64 was added to the samples at the concentration shown in Table 5-12. Viscosity was measured for both samples at the same shear rates. The viscosity of the DEG/water formulation without the Tergitol L-64 surfactant was 10 to 15 percent higher than with the surfactant (Figure 5-7), but for glycerol, the viscosity with the surfactant was 60 to 72 percent higher than without the surfactant. There is an uncertainty in the measurements of about 20 percent, so that there is very little effect of the surfactant on the DEG formulation, but there is a measured increase in the viscosity of the glycerol formulation with the addition of the surfactant.

TABLE 5-12. Type IV anti-icing formulations containing a thickener and a surfactant.

Formulation Components	Concentration (wt %)
DEG	50.0
Thickener: Carbopol EZ-4 with TEA	0.076
Surfactant: Tergitol L-64	0.25
DEG	50.0
Thickener: Carbopol EZ-4 with TEA	0.076
Surfactant: Tergitol TMN-10	0.15
Glycerol	50.0
Thickener: Carbopol EZ-4 with TEA	0.055
Surfactant: Tergitol L-64	0.10
Glycerol	50.0
Thickener: Carbopol EZ-4 with TEA	0.055
Surfactant: Tergitol TMN-10	0.15

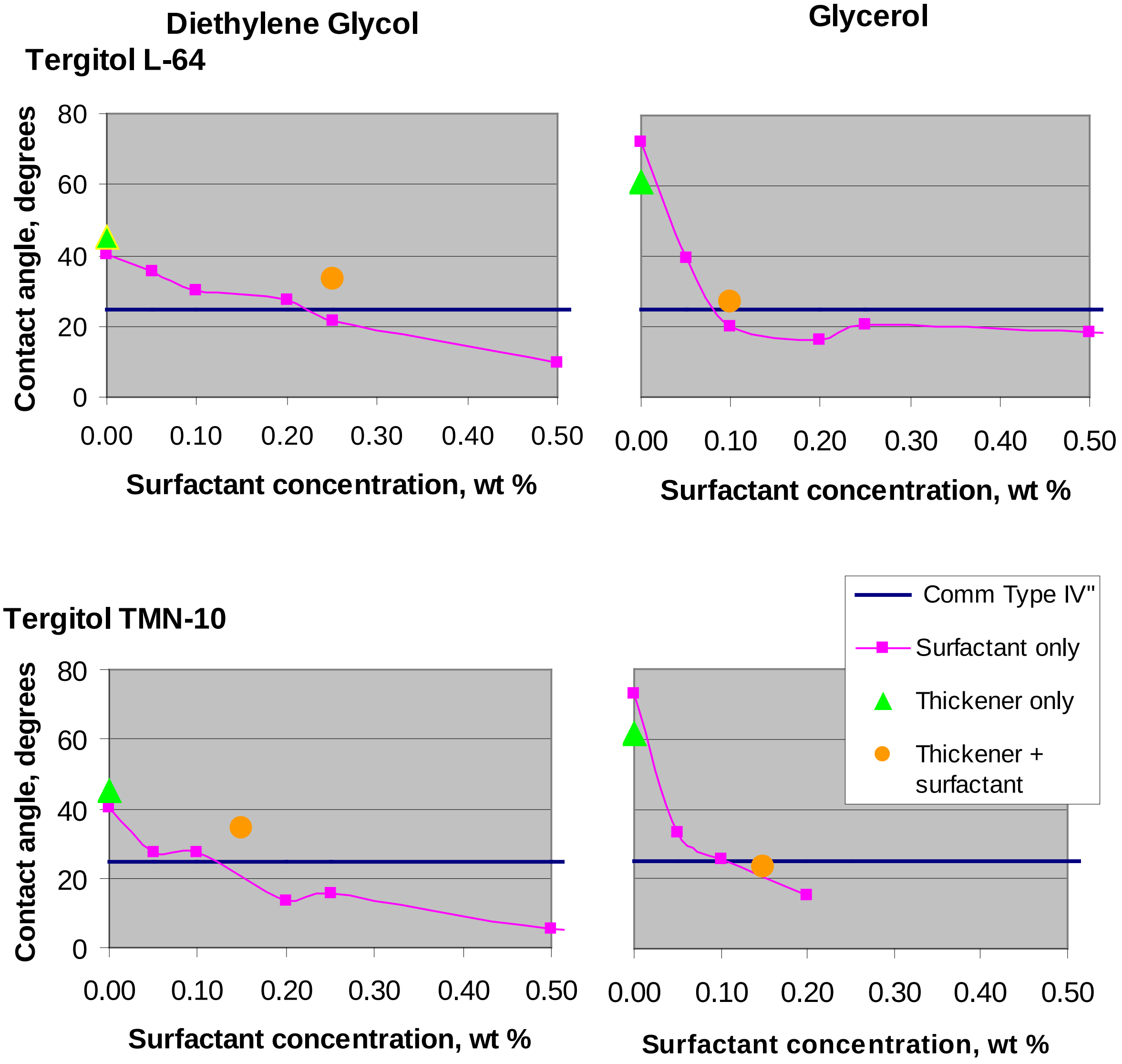
Figure 5-7. Comparison of Viscosity of DEG/ and glycerol/water/thickener (Carbopol EZ-4/TEA formulations with and without the addition of surfactant.





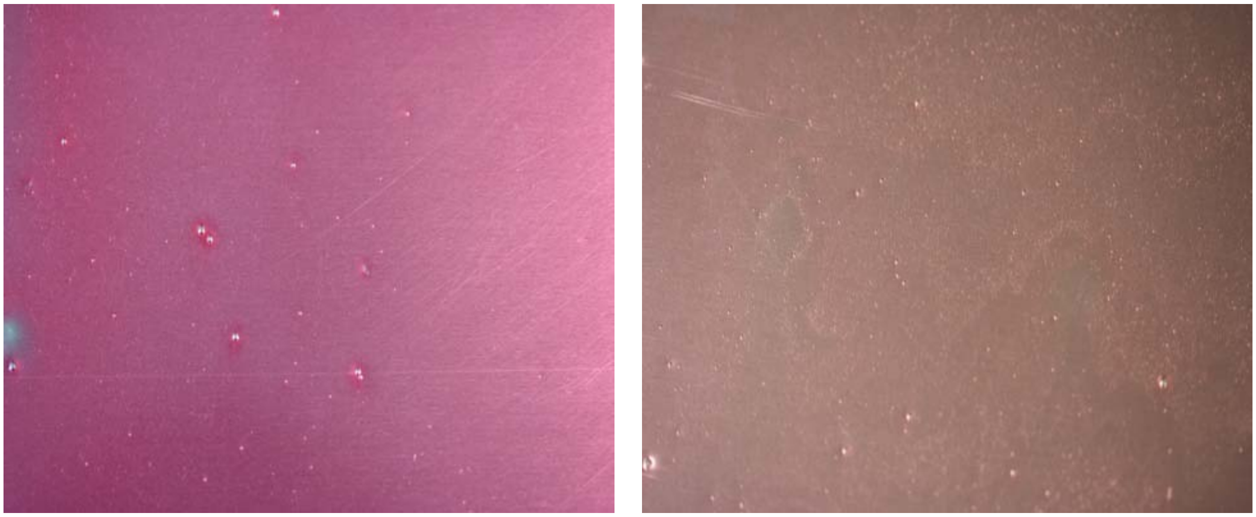
There is also concern that the thickener in the formulation may absorb some of the surfactant, essentially decreasing the effective surfactant concentration, increasing the surface tension, and inhibiting the spreading of the fluid over the aircraft. Surface angle measurements were made on the DEG/water and glycerol/water formulations containing the thickener with and without the surfactants at the concentrations shown in Table 5-12 and compared to the FPD/water formulations containing just the surfactant (see Figure 5-8). The thickener concentration for both formulations matched the viscosity/shear rate curve for the commercial Type IV anti-icing formulation. Figure 5-8 graphically shows the results. For DEG/water/thickener mixtures containing either Tergitol L-64 or Tergitol TMN-10, the thickener tends to increase the contact angle (and surface tension) over mixtures containing the surfactant, while there seems to be very little effect of the thickener for the glycerol mixtures. This result suggests that for the DEG/water formulations containing both a thickener and surfactant, the surfactant concentration should be increased to match the contact angle for the commercial Type IV formulation. The contact angle for the DEG/water mixture with only the thickener as an additive is 5 degrees higher than without the thickener, whereas for glycerol/water mixtures the contact angle is about 10 degrees less. There is an uncertainty in the contact angle measurements of about 3 degrees. The results indicate for the DEG formulations, the surfactant appears to be absorbed by the thickener, essentially increasing the contact angle and surface tension. There does not appear to be an effect of the thickener on the contact angle for the glycerol formulations.

Figure 5-8. Effect of thickener on contact angle for FPD/water/surfactant mixtures.



Foaming is a potential problem for deicing aircraft because the deicing formulation may cover the windows and impair visibility for the pilot. Foaming tests have been included in AMS 1424H for SAE Type I deicing/anti-icing fluids but have not been included in the requirements for Type IV anti-icing fluids. However, because of the safety implications, foam testing with the down-selected DEG and glycerol formulations with Tergitol L-64 (see Table 5-12) was conducted. The test procedures for quantifying foaming characteristics were modified from those of AMS 1424H. An aluminum plate was placed in a dry ice chamber and reached a temperature of -10°C. The anti-icing formulation was heated to 60°C and placed in a blender for 15 seconds. The plate was then taken out of the dry ice and placed in a plastic container at an angle of 10 degrees with the horizontal. The heated fluid was then poured on the plate and observed for 15 minutes. Photographs of the film were taken throughout the test period. The photographs shown in Figure 5-9 (top row) were taken of the middle of the film. A control test was done with a commercially available Type IV fluid. For all three formulations, less than 5 percent of the surface layer had foam initially; the foam then dissipated within 15 minutes. Foam persisted at the edges of the film.

Figure 5-9. Photographs of foaming tests.



DEG without Ridafoam ***Glycerol formulation without Ridafoam***

DEG with Ridafoam ***Glycerol formulation with Ridafoam***

Ridafoam, an anti-foaming agent, was placed in the two formulations containing Carbopol EZ-4/TEA and Tergitol L-64 at 10 percent of the surfactant concentration (Table 5-12). Foaming tests were performed on the two formulations. No foam formed initially and throughout the test run. Photographs taken at the edge of the film containing Ridafoam are shown in Figure 5-9 and indicate the absence of foam at the edge of the film, unlike the films not containing Ridafoam. The anti-icing formulations with Tergitol L-64 performed as well as the commercially available anti-icer with respect to foaming; less foam was present with the addition of Ridafoam.

At this point in experiments, diethylene glycol (DEG) and glycerol were considered to be equally promising freezing point depressant candidates. The key screening data used to differentiate these two candidates shows that the properties of the two freezing point depressants are very similar (Table 5-13). The melting point, normal boiling point, and flash point for both FPDs are all acceptable. Glycerol's theoretical oxygen demand and aquatic toxicity, as measured by microtox testing, are lower than DEG's. DEG's aquatic toxicity toward ceriodaphnia dubia and pimephales promelas is lower than glycerol's. The mammalian toxicity, as measured by rat oral LD_{50}, is nearly identical for both candidates.

TABLE 5-13. Key freezing point depressant properties.

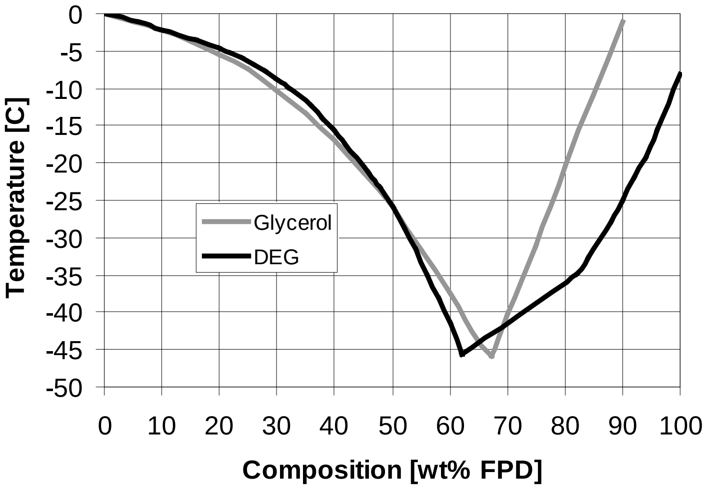
	Property	DEG	Glycerol
1	CAS Number	111-46-6	56-81-5
2	Melting Point, [C]	-10[a]	170[a]
3	Normal Boiling Point [C]	246[a]	287[a]
3	Flash Point [F]	290[b]	320[b]
4	Theoretical Oxygen Demand [g O_2/g FPD]	1.508	1.216
5	Aquatic Toxicity, Microtox [mg/l]	66,896[c]	129,617[c]
6	Aquatic Toxicity, *C. Dubia* [mg/l]	53,044[c]	34,865[c]
7	Aquatic Toxicity, *P. Promelas* [mg/l]	56,851[c]	46,004[c]
8	Rat Oral LD_{50} [mg/kg]	12,565[d]	12,600[d]

a) NIST Chemistry WebBook.
b) Aldrich Chemical Catalog.
c) ACRP, 2008.
d) Lewis, 2000.

Figure 5-10 shows the freezing point curves for mixtures of each candidate with water. The black curve represents values for DEG *(8)*. The gray curve represents values for glycerol *(35)*. To the left of the eutectic point, the curves are nearly identical, indicating very little difference in each chemical's ability to depress the freezing point of water. However, to the right of the eutectic point, glycerol's curve rises much faster than DEG's. This rapid increase is attributable to glycerol's higher melting point.

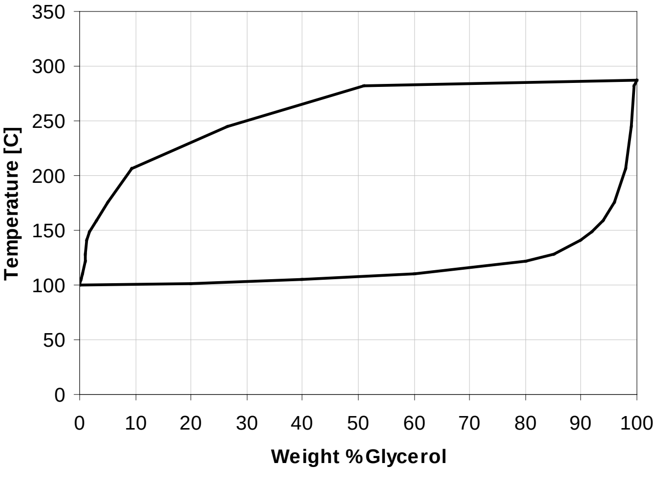
This rapid increase in the melting point of glycerol solutions could cause operational problems. For example, Figure 5-10 shows that at -20°C a 90 wt% glycerol solution would partially freeze into a slurry, whereas a 90 wt% DEG solution would still be completely liquid. Because glycerol solutions are known to supercool (remain a liquid below its freezing point), it is likely that the solution will not form an actual slurry but just a highly viscous solution.

Figure 5-10. Freezing point curves for final candidates.



Even though deicing fluids are not applied with more than 60 wt% freezing point depressant, asymmetric evaporation would cause the fluids to concentrate freezing point depressants. Figure 5-11 shows the vapor-liquid equilibrium curves for glycerol-water mixtures at atmospheric pressure *(36)*. The experimental temperatures are significantly higher than those encountered during deicing operations, but the low temperature curves will have a form similar to the one shown.

Figure 5-11. Glycerol-water vapor liquid equilibrium.



For example, Figure 5-11 shows that a 50 wt% mixture at 200°C would separate into a vapor fraction containing 8 wt% glycerol and a liquid fraction containing 98 wt% glycerol. While data could not be located, it is likely that the curves would behave in a similar fashion at lower temperatures. As a result, DEG was considered a more promising FPD for the final formulation than glycerol.

FPDs/Water, Thickeners, Surfactants, and Corrosion Inhibitors

Corrosion tests using sandwich and total immersion were conducted with the two most promising DEG formulations shown in Table 5-14 according to the specifications in SAE AMS 1428 Type IV Fluid. Sandwich corrosion testing was conducted in accordance with ASTM F 1110, Standard Test Method for Sandwich Corrosion Test. Filter papers saturated with concentrated and diluted anti-icing fluids were placed between a sandwich of aluminum alloy panels. Corrosion was evaluated by comparison with control panels using ASTM D 1193, Type IV water. The sandwich panels were placed for 8 hours in an oven with forced air circulation capable of maintaining 37.7°C and for 16 hours in a humidity test chamber capable of maintaining 95 to 100 percent relative humidity at 37.7°C. The pattern was repeated for 5 days. On the sixth and seventh days, the panels were kept in the humidity test chamber for 48 hours. The total test time was 168 hours. Table 5-15 shows the sandwich corrosion test results for 2024-T3 bare anodized (with sulfuric acid instead of chromic acid for environmental reasons) and 2024-T3 Alclad panels. After testing, the panels did not show corrosion worse than the control panels.

TABLE 5-14. Formulations used in corrosion testing.

Formulation component	Weight percent
FPD: DEG/water	50:50
Thickener: Carbopol EZ-4 with TEA	0.076
Surfactant: Tergitol L-64	0.250
Corrosion inhibitors:	
TEA or	0.2
Mazon RI-325	0.2

TABLE 5-15. Sandwich corrosion test results.

Test Solution	2024-T3 Bare Aluminum	2024-T3 Alclad
Corrosion inhibitor - TEA		
DEG—concentrated	1*	1
DEG—diluted with water (1:1 wt)	1	1
Corrosion inhibitor—Mazon RI 325		
DEG—concentrated	1	1
DEG—diluted with water (1:1 wt)	1	1
Control (ASTM D 1193, Type IV water)	1	1

* 1 denotes very slight corrosion or very slight discoloration, and/or up to 5% of area under filter paper corroded

Total immersion testing was carried out in accordance with ASTM F 483, Standard Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals. The method involves immersing three test coupons of the same alloy in concentrated and diluted anti-icing solutions for 168 hours at an oven test temperature of 38°C. The coupons were weighed before, during (end of 24 hours) and after the tests and observed for visible changes in comparison to a control (virgin) coupon. Table 5-16 shows the test results and indicates that the coupons do not have a weight change greater than the allowed weight change.

TABLE 5-16. Total immersion corrosion test results.

Test Panel	Weight Change Allowed, mg/cm^2 per 24 hrs	Weight Change mg/cm^2 per 24 hrs			
		TEA		Mazon RI 325	
		Concen	Dilute (1:1)	Concen	Dilute (1:1)
AMS 4037 Aluminum alloy, anodized	0.3	0.02	0.01	0.02	0.03
AMS 4041 Aluminum alloy	0.3	<0.01	0.01	0.01	0.01

Environmental Characteristics

Aquatic toxicity was tested through the entire formulation process, and the final formulations were tested for COD and BOD. A synthesis of these results and changes as additional components were added are discussed in this section.

Aquatic Toxicity

Methods

Alternative deicer formulations were evaluated for toxicity in a step-wise fashion after each additional component was added (Table 5-17). Screening toxicity tests were followed by definitive toxicity tests on the final formulations. Definitive toxicity tests were conducted following EPA guidelines. Briefly, each definitive acute test consisted of a 50 percent dilution series with five treatments plus a laboratory control. Moderately hard reconstituted water was used as the laboratory control and product dilution water. Each treatment consisted of four replicates with 5 *C. dubia* or 10 *Pimephales promelas* per replicate. The acute assays were conducted in an environmental chamber at 20°C with a 16-/8-hour light/dark cycle. Test treatments were renewed daily with freshly prepared solutions, and water quality parameters including dissolved oxygen, pH and conductivity were monitored daily. At 48 hours for *C. dubia* and 96 hours for *Pimephales promelas*, the survival per replicate was recorded for calculation of an LC_{50} using Probit or Spearman-Karber analysis, as appropriate *(37)*.

Definitive chronic tests were used to evaluate sublethal endpoints with *Pimephales promelas* (weight) and *C. dubia* (young produced). Like the definitive acute tests, chronic assays consisted of a 50 percent dilution series of five treatments and a laboratory control. Laboratory control and dilution water was moderately hard water. Each treatment was replicated 10 times with one *C. dubia* or two fish per replicate. Organisms were <24 hours old at the start of the tests. Tests were maintained in an environmental chamber at 25°C with a 16-/8-hour light/dark cycle. Treatments were renewed with freshly prepared solutions daily. Water quality parameters were monitored daily. The number of young in the *C. dubia* test replicates were recorded and removed daily. The *C. dubia* chronic test was terminated when at least 80 percent of lab control individuals released their third brood (day 6 or 7). The *Pimephales promelas* chronic tests were terminated on day 7 when the fish from each replicate were removed for weighing. Three-brood totals and fish dry weight were used to calculate inhibition concentrations (IC_{25}) using the EPA IC_p program *(38)*.

In addition to the species used in regulatory requirements, the luminescent marine bacterium, *Vibrio fischeri* , also known as Microtox® (Azure Environmental, Carlsbad, CA, USA), were included in the battery of toxicity test species. While not used as a regulatory tool, the rapid results can be very useful, especially when evaluating many treatments during toxicity characterization. In this assay, freeze-dried bacteria were re-hydrated in a saline solution. A measured aliquot of re-hydrated bacteria were added to the test treatments and controls. The luminescence endpoint was determined spectrophotometrically after 15 minutes at a test temperature of 15°C. EC_{50}s were calculated using the Microtox® software.

Results

Results from the stepwise toxicity testing showed how toxicity changed as each additional component was included in the formulation (Table 5-17). These results were compared to theoretical results based on toxicity of the individual components. The theoretical values were determined under the assumption that there were no synergistic or antagonistic toxicity interactions among chemicals when they were included in the mixture. Using this assumption, the theoretical toxicity endpoint was the most toxic endpoint (lowest value) of the components, given that component's concentration in the formulation. Addition of most components resulted in toxicity endpoints similar to theoretical values. However, addition of the anti-foaming agent to the first formulation indicated a synergistic interaction for all three organisms (the formulation was more toxic than the theoretical value).). Similarly, synergistic interactions in the Microtox® and *P. promelas* tests were observed from addition of TEA in the final formulation. For the second formulation, addition of the thickener resulted in toxicity endpoints similar to theoretical values for *C. dubia* and *Pimephales promelas*, but results from the Microtox® test indicate synergistic interactions with addition of the thickener and the surfactant.

In most cases, it was valid to assume that individual component toxicity could be used to determine formulation toxicity. The instances where this was not true toxicity evaluation was more complicated, requiring empirical observations to understand which components were responsible for final formulation toxicity. In addition, different interactions were observed depending on the FPD. Of particular interest was the difference between addition of the thickener to DEG as opposed to that for glycerol. In the DEG formulation, results were similar to theoretical values, but a synergistic interaction for toxicity was present in this step for the glycerol formulation. This indicated that synergistic interactions for the same component were different depending on the composition of the rest of the formulation. In this case, it was only a difference in FPD that caused a difference in the synergistic interaction.

TABLE 5-17. Comparison of theoretical values with measured test results for step-wise Type IV anti-icer formulation construction

		Theoretical Values			Test Results		
Added Component	**Percent of Mixture**	**Microtox® EC_{50}[a] (mg/L)**	***C. dubia* LC_{50}[b] (mg/L)**	***P. promelas* LC50 (mg/L)**	**Microtox® EC_{50}** (mg/L)**	***C. dubia* LC_{50}*** (mg/L)**	***P. promelas* LC_{50} (mg/L)**
DEG formulation							
Water	50	—	—	—	—	—	—
DEG	50	130,000	110,000	110,000	130,000	110,000	110,000
Carbopol EZ4 with TEA[c] (thickener)	0.0763	130,000	66,000	110,000	140,000	71,000	120,000
Tergitol L-64 (surfactant)	0.25	130,000	66,000	110,000	110,000	57,000	140,000
Ridafoam (anti-foaming agent)	0.025	12,000	66,000	110,000	25,000	25,000	59,000
TEA (corrosion inhibitor, does not include Ridafoam) -***final formulation***	0.2	110,000	66,000	110,000	43,000	53,000	89,000
Glycerol formulation							
Water	50	—	—	—	—	—	—
Glycerol	50	260,000	70,000	92,000	260,000	70,000	92,000
Carbopol EZ4 with TEA (thickener)	0.0552	260,000	70,000	92,000	43,000	66,000	71,000
Tergitol L-64 (surfactant)	0.1	260,000	70,000	92,000	18,000	75,000	63,000
Ridafoam (anti-foaming agent)	0.01	12,000	70,000	92,000	18,000	53,000	63,000

Screening toxicity results are only approximations. Screening toxicity procedures include fewer replicates, non-renewal of test solutions, shorter exposure duration for *Pimephales promelas*, and other procedural variances from definitive toxicity tests. Compounds are organized by least toxic to most toxic endpoint, determined by the most sensitive species.

[a] The Microtox® EC_{50} is the statistically determined concentration that would result in a 50% reduction in light emission compared to a laboratory control.

[b] The LC_{50} is the statistically determined concentration that would cause death in 50% of the population exposed.

[c] TEA.

Results of definitive aquatic toxicity tests on the final formulation indicate that acute and chronic toxicity endpoints were substantially greater (lower toxicity) than results previously published for current-use formulations (Table 5-18, *(1)*). Acute toxicity endpoints ranged from 219 to 13,800 mg/L in tests with current-use formulations with each of the four tested products having one or more of the three endpoints at least as low as 528 mg/L. The lowest of the acute toxicity endpoints in the final DEG formulation in this research was 32,700 mg/L in the final DEG formulation.

Chronic toxicity endpoints ranged from 79.4 to 1,350 mg/L in tests with current-use formulations with each of the four tested products having one or more of the three endpoints at least as low as 130 mg/L *(1)*. The lowest of the chronic toxicity endpoints in the final DEG formulation from this research was 8,970 mg/L in the final DEG formulation (Table 5-18).

In current-use formulations, surfactants were identified as the component with the greatest influence on toxicity *(1)*. In the final formulation developed from this research, toxicity results indicate that the chosen surfactant had little or no influence on toxicity. The primary components influencing toxicity in the final formulation were the FPD, the thickener, and the corrosion inhibitor. Even with these influences, the test results indicate that toxicity endpoints were one to three orders of magnitude greater (less toxic) than those from current-use formulations.

Table 5-18. Results from definitive aquatic toxicity testing of final Type IV DEG formulation (95% confidence interval).

	Acute toxicity		***Chronic toxicity***		
Microtox® EC_{50}[a] (mg/L)	***C. dubia*** **LC_{50}[b] (mg/L)**	***P. promelas*** **LC_{50} (mg/L)**	***C. dubia*** **IC_{25}[c] (mg/L)**	***P. promelas*** **IC_{25} (mg/L)**	***S. Capricorutum*** **IC_{25} (mg/L)**
54,900	*32,700*	*126,000*	8,970	60,200	42,100
(53,700–56,100)	*(28,600–37,400)*	*(116,000–136,000)*	(4,730–13,800)	(56,600–62,500)	(40,100–44,000)

[a] The Microtox® EC_{50} is the statistically determined concentration that would result in a 50% reduction in light emission compared to a laboratory control.
[b] The LC_{50} is the statistically determined concentration that would cause death in 50% of the population exposed.
[c] The C_{25} is the statistically determined concentration that would cause a 25% inhibition in growth (*P. promelas*) or reproduction (*C. dubia*).

Biochemical Oxygen Demand

Methods

BOD_5 and COD were tested on the final formulation. Tests were run in triplicate and results were reported as the average and percent relative standard deviation. Analytical methods are identical to Tier 1 methods as reported from Tier 1 testing in section 4.

Results

The concentration of COD in the final formulation was 752 g/Kg with a relative standard deviation of 0.96%. These results are consistent with Tier 1 testing results on neat DEG (COD = 1,500 g/Kg) considering that the final formulation contains 50% DEG. The concentration of BOD_5 could not be determined. Difficulties with seed acclimation to DEG as described in Tier 1 testing remained in tests with the final formulation. The original Tier 1 testing on neat DEG was characterized by inadequate DO depletion at low DEG concentrations (up to 333 mg/L) and too much DO depletion at higher DEG concentrations (above 581 mg/L). DEG dilutions between these concentrations were attempted for neat DEG and for formulations with various components added. Depletion of DO was always too little or too much to determine reliable BOD_5 concentrations. Results from the BOD_{28} tests indicated that the microorganism population eventually acclimated to DEG with accelerated biodegradation occurring approximately halfway through the 28-day test period. These results suggest that microorganism populations in receiving streams would likely acclimate to this FPD if used regularly for anti-icing purposes.

Runway Deicers

The effectiveness of potassium carbonate and tripotassium citrate to prevent the caking of sodium formate granules was experimentally tested. Tripotassium citrate was identified in Tier 1 as a candidate FPD having a lower oxygen demand and a lower toxicity potential than current products. Potassium carbonate was identified in Tier 1 as a potential corrosion inhibitor having a greater toxicity potential, but if used in low enough concentrations with a low toxicity FPD, the blend would likely still meet toxicity goals. It also serves as an FPD. The candidate components of the runway deicers evaluated in Tier 2 are given in Table 5-19, together with their properties. Anti-caking data on these additives for sodium formate were not found.

TABLE 5-19. Candidate components and properties of runway deicers to be evaluated.

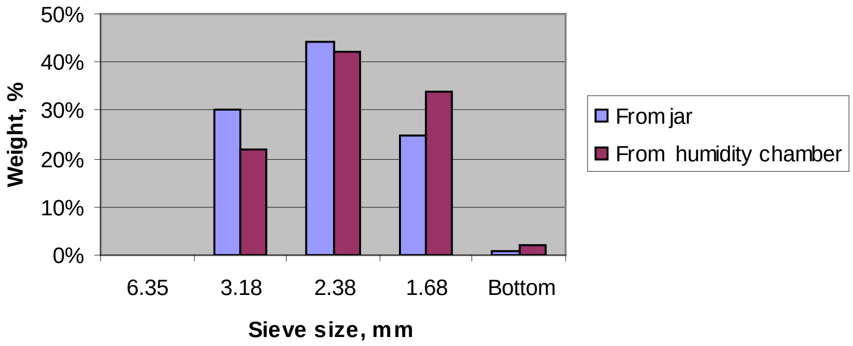
Property	FPD: Sodium Formate	Anti-Caking Additive	
		Tripotassium Citrate	Potassium Carbonate
CAS Number	141-53-7	6100-05-6	584-08-7
Formula	CHO2Na	C6H5O7K3·H2O	CO3K2
ThOD	0.118 g O2/g	0.392 g O2/g	-0.116 g O2/g[a]
Solubility Limit in Water	46.8 wt% [1]	60.6 wt%	52.8 wt%
Eutectic Temperature	-23°C [1]	—	—

[a] Potassium carbonate is an inorganic compound and may not exert any BOD.

A testing procedure was developed to evaluate the use of additives to prevent caking for sodium formate runway deicers. The chemicals were obtained from Sigma-Aldrich. The procedure started with drying the components and mixtures of the components in a desiccator), sieving the sodium formate in an automatic sieve shaker, and weighing the individual components/mixtures. Approximately 7.5 percent by weight of the anti-caking powders were added to the sodium formate. The powders were placed in two sets of sample dishes and kept at constant temperature (30°C) and humidity (50 percent) in an environmental chamber for a period of time. After one day, one complete set of the powders were removed, weighed, desiccated, sieved and then weighed again. The second set of powders remained in the environmental chamber for another day (a total of 2 days), and the procedure was repeated as for the first day. The percentage of powder passing through the sieve was the metric used to evaluate additive effectiveness.

In the first set of experiments, aluminum boats of sodium formate, sodium formate and potassium carbonate, and sodium formate and tripotassium citrate were prepared and passed though sieves to obtain their size distribution. Figure 5-12 shows the sieved weight analysis of the sodium formate (taken from the storage jar and desiccated). The anti-caking additives were fine powder and passed through the smallest sieve (2.38 millimeters). Approximately 7.3 to 7.5 percent of the anti-caking agents were added to sodium formate. The boats were then placed in an environmental chamber at a temperature of 30°C and 50 percent relative humidity for 2 days. One set of boats was removed after 1 day and the second set after 2 days. The particles were agglomerated after 1 day and 2 days. After 1 day, the boat containing just the sodium formate gained 1.3 percent moisture, while the boats containing sodium formate + potassium carbonate and sodium formate + tripotassium citrate gained 8.9 percent and 3.9 percent (relative to the weight of sodium formate), moisture, respectively. After two days, the boats gained 1.4 percent, 11.7 percent and 3.0 percent, respectively; all of the materials were dissolved in water. *These results were not consistent because the mixtures with the anti-caking agents gained more moisture than the sodium formate alone.* After removing the boats from the humidity chamber, the boats were placed in a dessicator for 4 days until all of the moisture was removed from each boat; all of the materials were agglomerated. The sieve analysis of the sodium formate taken from the humidity chamber after 1 day, desiccated for 4 days, and then gently separated, is shown in Figure 5-12.

Figure 5-12. Sieve analysis of sodium formate.



Next, the moisture pickup of individual components was determined by placing the components in the environmental chamber (30°C, 50 percent relative humidity). Table 5-20 shows the moisture pickup for each component after 1 and 2 days. After the first day, the aluminum boats containing the potassium carbonate were corroded and were partially dissolved after the second day. Further anti-caking experiments with potassium carbonate were discontinued. Tripotassium citrate was not desiccated prior to testing and lost moisture during the tests.

TABLE 5-20. Moisture pickup of individual components of sodium formate and anti-caking agents.

	Moisture Pickup[a] (wt %)	
Component	**After 1 Day**	**After 2 Days**
Sodium formate	1.47	3.03
Potassium carbonate	40.24	—
Tripotassium citrate	-1.52	-2.59

---

[a] Relative to individual component.

Further experiments with sodium formate and mixtures of sodium formate and tripotassium citrate were continued. Table 5-21 shows the composition of the mixtures that were tested. Boats 1 and 2 contained only sodium formate and tripotassium citrate, respectively. Boats 3 and 4 contained 12.5 percent and 11.2 percent of tripotassium citrate relative to sodium formate. After one day in the humidity chamber (relative humidity 50 percent; temperature, 30°C), sodium formate picked up 1.3 percent water and tripotassium citrate picked up only 0.023 percent. However, the mixtures of tripotassium citrate and sodium formate picked up from 4.5 to 7,1 percent water. Although tripotassium citrate picked up a negligible amount of water, the mixtures of tripotassium citrate and sodium formate picked up more water than the sodium formate by itself, indicating that the tripotassium citrate produces a synergistic water absorption effect. After two days, sodium formate picked up 2.5 percent of water and tripotassium citrate lost some mass, the mixtures of sodium formate and tripotassium citrate picked up about 13-14 percent water.

It was hypothesized that the aluminum in the boats was contributing some exchange of the sodium or potassium ions in the FPD and anti-caking agents, enhancing the absorption of moisture. However, the experiments were replicated with plastic boats, and the moisture absorption results were similar to those found with the aluminum boats. There is no ready explanation for these observations. Further testing was discontinued. No satisfactory anti-caking solution to sodium formate was found.

TABLE 5-21. Anti-caking experiments with sodium formate and potassium citrate.

	Boat			
	1, Sodium Formate	**2, Tripotassium Citrate**	**3, KCitrate/ NaFormate**	**4, KCitrate/ NaFormate**
Potassium citrate/sodium formate, wt %	0	—	12.5	11.2
Water pickup//NaFormate + KCitrate) after one day, wt %	1.3	0.023	7.1	4.5
Water pickup/(NaFormate + KCitrate) after two days, wt %	2.5	-2.2	14.4	13.2
Incremental water pickup between first and second days, H20/NaFormate, wt %	1.1	—	8.1	9.7

SECTION 6

DEGRADATION PATHWAYS FOR DOWN-SELECTED DEICER COMPONENTS

Although each candidate component was carefully screened for environmental impact, it is possible that their degradation products could have significant effects. For example, nonylphenol ethoxylate surfactants have a much lower environmental impact than does nonylphenol, one of their degradation products. Possible degradation pathways and degradation products for the down-selected components of the final Type IV formulation were examined to evaluate the potential for significant environmental effects.

DEG

DEG is the proposed FPD. As such, its mixture with water will constitute more than 90 percent of the weight of the final deicing or anti-icing product. The molecular structure of DEG is:

$$HO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$$

Pearce and Heydman *(39)* examined the biodegradation of DEG by various strains of the *Psedomonas* bacteria species. They proposed that the biodegradation of DEG by Acinetobacter S8 begins with a dehydration reaction that forms ethylene glycol monovinyl ether:

$$HO\text{-}CH2\text{-}CH2\text{-}O\text{-}CH{=}CH2 + H2O \qquad (6\text{-}1)$$

This glycol ether product further degrades to ethylene glycol and vinyl alcohol:

$$HO\text{-}CH_2\text{-}CH_2\text{-}OH + HO\text{-}CH{=}CH_2$$

The ethylene glycol product undergoes an additional dehydration reaction, similar to Equation 1, to yield water plus another vinyl alcohol molecule. These vinyl alcohol molecules then react to form acetaldehyde:

$$O{=}CH\text{-}CH_3$$

Acetaldehyde degrades into ethanol and acetic acid:

$$CH_3\text{-}CH_2\text{-}OH + CH_3\text{-}C(O)\text{-}OH$$

Both of these products are consumed by common bacterial metabolism and are thus not expected to persist in the environment. The other intermediate degradation products are fairly reactive and are thus also not expected to persist in the environment.

The University of Minnesota Biocatalysis/Biodegradation Database (UM-BBD) *(40)* does not contain a degradation pathway for DEG. However, its rule-based expert system was able to suggest the following possible pathway:

In the first step, one of DEG’s primary alcohols is converted by dehydrogenation to an aldehyde:

$$HO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH{=}O$$

The aldehyde is then converted to a carboxylate:

$$HO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}C(O^-)=O$$

These two reaction steps are repeated for DEG's remaining hydroxide to produce a dicarboxylate:

$$O=(^-O)C\text{-}CH_2\text{-}O\text{-}CH_2\text{-}C(O^-)=O$$

This dicarboxylate degrades at the ether linkage into an alcohol and an aldehyde, specifically a glycolate and a glyoxylate:

$$O=(^-O)C\text{-}CH_2\text{-}OH + O=CH\text{-}C(O^-)=O$$

Both of these products are consumed by common bacterial metabolism and are thus not expected to persist in the environment. The other intermediate degradation products are fairly reactive and are thus also not expected to persist in the environment.

Tergitol L-64

Surfactant biodegradation is typically classified into primary degradation and ultimate degradation. Primary degradation occurs when the surfactant's molecular structure has been sufficiently changed such that it no longer exhibits surface activity. Ultimate biodegradation occurs when the surfactant's molecular structure has been changed into carbon dioxide, water, mineral salts, and biomass. The focus in this section is on the reaction pathways that lead to the ultimate biodegradation of Tergitol L-64.

Tergitol L-64 is a non-ionic ethylene oxide/propylene oxide copolymeric surfactant. It is marketed by Dow Chemical as being readily biodegradable. An example structure is shown in Equation 6-2:

$$[(\text{-}CH_2\text{-}CH_2\text{-}O)_n\text{-}(CH(CH_3)\text{-}CH_2\text{-}O\text{-})_m] \qquad (6\text{-}2)$$

The values of n and m are proprietary but probably range from 6 to 20.

The ethylene oxide portion of the surfactant degrades by forming shorter glycol ethers, including ethylene glycol and DEG [5]. The degradation pathways and products should thus be the same as those described previously for the degradation of DEG.

The degradation mechanism for the propylene oxide portion of the surfactant's molecular structure is less certain. There is general agreement that the branching of this portion inhibits biodegradation [5]. One possible mechanism is the oxidation of an end group to propionaldehyde [6]:

$$CH_3\text{-}CH_2\text{-}CHO$$

Propionaldehyde is then further oxidized to propanoic acid [6]:

$$CH_3\text{-}CH_2\text{-}CO\text{-}OH$$

An alternative mechanism would result in the production of acetone [6]:

$$CH_3\text{-}CO\text{-}CH_3$$

Table 6-1 lists the aquatic toxicities for these possible degradation products to the rainbow trout (*oncorhynchus mykiss)*.

TABLE 6-1. Toxicity of Tergitol L-64 degradation products.

	Compound	96-hour LD_{50} Rainbow Trout
1	Propionaldehyde	5 mg/L [a]
2	Propanoic Acid	51 mg/L
3	Acetone	4.4 mg/L

[a] This value is for 24 hours.

Table 6-1 indicates that the degradation products are fairly toxic to rainbow trout. It is also possible that these products are toxic to bacteria, which could partly account for the reported poor biodegradation.

TEA

TEA is the proposed corrosion inhibitor. It would typically be used in formulations at less than 2 percent by weight. TEA's molecular structure is:

$$N(CH_2\text{-}CH_2\text{-}OH)_3$$

Frings et al. showed that TEA can be completely degraded to acetate and ammonia under anaerobic conditions *(41)*. UM-BBD also lists a degradation pathway for TEA *(40)*. The product of the first degradation step is the unstable hemiaminal intermediate:

$$(HO\text{-}CH_2\text{-}CH_2)_2N(CH(OH)\text{-}CH_3)$$

This intermediate will degrade into diethanolamine and acetaldehyde:

$$(HO\text{-}CH_2\text{-}CH_2)_2NH + O{=}CH\text{-}CH_3$$

Diethanolamine will undergo the same degradation steps to produce ethanolamine and acetaldehyde:

$$HO\text{-}CH_2\text{-}CH_2NH_2 + O{=}CH\text{-}CH_3$$

UM-BBD reports that both of these products are consumed by common bacterial metabolism and are thus not expected to persist in the environment.

Table 6-2 shows the aquatic toxicity of TEA and its degradation products to *Pimephales promelas*. The data indicate that the aquatic toxicity of the degradation products is much higher than that of TEA.

Carbopol EZ-4

Carbopol, the proposed thickener, is a lightly crosslinked poly(acrylic acid) polymer. Studies conducted by Lubrizol found that Carbopol does not biodegrade *(42)*. These studies also showed that Carbopol does not pass through municipal waste water treatment facilities into lakes and rivers but adsorbs onto biomass and is therefore removed with the biomass during treatment.

TABLE 6-2. Toxicity of TEA and its degradation products.

	Compound	96-hour LD_{50} *Pimephales Promelas*
1	TEA	11,800 mg/L
2	Diethanolamine	1,370 mg/L
3	Ethanolamine	2,070 mg/L
4	Acetaldehyde	36.8 mg/L

SECTION 7
CONCLUSIONS

This section presents the significant conclusions drawn from the findings of this research, organized by topic.

General Conclusions

A candidate alternative Type IV formulation was identified with significantly reduced toxicity compared to current use products. The final candidate formulation has aquatic toxicity values that are an order of magnitude or more improved over the least toxic commercial Type IV products tested. This formulation would need addition of a dye and additional certification testing that my warrant formulation modification.

Toxicity identification techniques were successful in helping to improve the toxicity profile of alternative fluids. The Toxicity Identification Evaluation (TIE) approach used in evaluation of current-use products identified surfactants as the primary contributor to aquatic toxicity. Using this information to choose alternative surfactants resulted in a candidate Type IV formulation with substantially lower aquatic toxicity.

The physical properties of the candidate alternative Type IV formulations were affected by interactions between the surfactants and thickeners. For diethylene glycol/water formulations containing the surfactant and thickener, the viscosity was only slightly lower than mixtures without the surfactant, while the thickener tends to increase the contact angle (or surface tension) over mixtures containing just the surfactant. For glycol/water formulations containing the surfactant and thickener, the viscosity was about 60-70 percent higher than without the surfactant, while there didn't appear to be an effect of the thickener on the contact angle.

Numerous potential alternative components were identified. This research resulted in one candidate alternative Type IV formulations using several alternative components; however, numerous potentially viable alternative components were identified that have potential to improve environmental performance. Empirical testing with all possible alternatives was beyond the scope of this research, but this information could be used in future work attempting to formulate alternative deicers.

The techniques used in identifying a less-toxic Type IV formulation have potential applicability to developing Type I formulations with reduced toxicity. The focus of the research was directed towards the identification of alternative Type IV formulations with significantly less toxicity than currently available products. The final candidate Type IV formulation is less toxic than the least toxic Type I commercial product currently in use, indicating that there is a potential for applying the same methods which led to substantial improvement in toxicity for Type IV formulations to reformulating Type I products.

There is no current evidence to suggest that either the alternative FPD or thickener present significant concerns relative to degradation pathways and degradation products.

The evidence in the literature suggests that the biodegradation by-products of the alternative surfactant and corrosion inhibitor may be have greater aquatic toxicity than the parent

products. Both of these additives are used in a wide range of products. Further investigation of concentrations resulting from degradation would be needed to fully evaluate this.

The use of molecular modeling can significantly improve efficiency of the chemical product development process. The search for an improved formulation necessitated the evaluation of thousands of candidate components. Experimentally evaluating each of these candidates would have been costly and highly unproductive—the large majority of these candidates were not viable. Physical property estimation techniques were able to quickly and inexpensively evaluate these candidates computationally, selecting only the most promising compounds for experimental evaluation.

Oxygen Demand

ThOD is a good screening criterion for oxygen demand of freezing point depressants. The COD results for FPDs compared well with ThOD.

Conventional BOD tests produced unreliable results for some of the FPDs. The success of BOD testing was highly variable and dependent on how well microorganisms acclimated to FPDs.

COD was the most useful metric in down-selecting FPDs for oxygen demand. The reliance on COD was necessary because of the uncertainties encountered with BOD tests.

FPDs are the predominant source of oxygen demand in all deicer formulations. The relative concentrations of all other components are so small that any contribution to oxygen demand is insignificant.

No candidate FPD was found with potential for improvement of BOD characteristics compared to the least toxic current-use Type I fluids and pavement deicer formulations. Of the candidate FPDs with improved aquatic toxicity compared to Type I fluids and pavement deicers, BOD and COD were not improved compared to current-use products.

DEG and glycerol were identified as promising alternative FPDs for Type IV fluid formulations. Of the FPDs with favorable performance characteristics, DEG and glycerol were the most promising candidates to provide improvements in aquatic toxicity and BOD characteristics as compared to current-use products. Concerns regarding the potential for glycerol to dry out and form residuals after application led to the selection of DEG as the preferred FPD.

Parameters such as molecular weight, freezing point depression, application rates, and transport phenomena would need to be considered to gain a comprehensive understanding of the potential impact of PDMs on dissolved oxygen in receiving waters. These characteristics were recognized as potentially significant factors in the actual oxygen demand load from deicer applications, but further investigation of these properties was beyond the scope of this research.

Aquatic Toxicity

Screening-level toxicity testing identified potentially viable alternative components in each of the categories of FPDs, surfactants, corrosion inhibitors, and thickeners. Identified candidates included 7 FPDs, 11 surfactants, 9 corrosion inhibitors, and 6 thickeners.

a reliable predictor of formulation toxicity. However, in several instances this was not the case, demonstrating the importance of laboratory confirmation of predictions based on theoretical values.

Pavement Deicers

There were apparent synergistic interactions between sodium formate and tripotassium citrate that increased absorption of water and cannot be readily explained. Resolution of the counter-intuitive results is beyond the scope of this investigation.

SECTION 8

SUGGESTED FUTURE RESEARCH TOPICS

This section presents issues and activities that were identified during the research as being suitable subjects of future research and development by ACRP or others.

Further development of the alternative Type IV formulation could be conducted. The purpose of the Tier 1 and Tier 2 tests was to screen and evaluate candidate components for anti-icing performance (freezing point depression, viscosity, surface tension, foaming), environmental impact (biochemical oxygen demand, chemical oxygen demand, aquatic toxicity), materials compatibility (total immersion and sandwich corrosion on aluminum alloys) and safety properties (flash point). The results of these tests showed that formulations with significantly improved toxicity and lower oxygen demand compared to current products, and acceptable performance properties were developed. Some of these key tests, such as aquatic toxicity and corrosion testing, could be replicated by an independent laboratory to validate these results.

The tests conducted in Tier 2 demonstrated that the concentration chosen for the corrosion inhibitor, triethanolamine, in the final formulation was acceptable, but can possibly be reduced and still be acceptable. It is recommended that the sandwich and corrosion tests be replicated at lower corrosion inhibitor concentrations to determine the lowest acceptable concentration.

The final formulation could then be subjected to a water spray endurance test (WSET) to verify it has a sufficient holdover time (HOT) to perform as a Type IV anti-icing fluid. If the fluid's HOT is acceptable an aerodynamic acceptance test should then be conducted to ensure the final formulation's rheological performance is acceptable.

The formulations would then need the addition of a dye and require further testing to achieve certification by the Anti-icing Materials International Laboratory (AMIL), Université du Québec à Chicoutimi (UQAC) (Quebec, Canada) and Scientific Material International (SMI) (Miami. FL) under AMS 1428F. Specifically, the program would need to include tests on fluid stability, anti-icing performance, aerodynamic acceptance, and the effect on aircraft materials (sandwich and total immersion testing on other alloys, low-embrittling cadmium plate, stress-corrosion resistance, hydrogen embrittlement and transparent plastics).

Examination of low toxicity formulation components. The formulation's surfactant, and corrosion inhibitor have lower toxicities than other chemicals in their respective product classes. The use of low toxicity chemicals such as these could be considered as alternative components in other products.

A standard metric is needed for expressing the potential oxygen demand loading from PDMs. Specifically, the following conceptual metric is proposed for consideration:

> Grams of oxygen needed to oxidize the chemicals needed to achieve and maintain one square meter of runway free of ice for one hour.

Improved methods are needed to minimize the effect of microorganism acclimation on variability of BOD measurements. BOD—Exploration of microorganism acclimation for FPDs would be needed to better understand potential oxygen demand for several of the candidate FPDs including the final choice of DEG.

Investigation of degradation by-products of certain candidate additives is needed. Although certain candidate surfactants, corrosion inhibitors, and thickeners are extensively used in a wide range of products, the increased toxicity of their possible degradation products would warrant further investigation. Specifically, by-products from bio-degradation in waterways receiving airport runoff would need to be identified.

Further work would be needed to find suitable anti-caking agents for sodium formate. A more extensive list of anti-caking materials and coatings would need to be formulated, together with extensive testing with mixtures of sodium formate. Alternatively, techniques for pelletizing sodium formate could be investigated for improving handling characteristics.

The caking behavior of sodium formate would need to be investigated further. Some operators claim sodium formate’s caking tendency makes it unusable. Others reported that a simple mechanical shock was sufficient to eliminate any caking problems. Variables such as time of storage and humidity during storage would need to be quantified to determine when a caking problem may occur.

Once the conditions promoting sodium formate’s caking behavior have been determined and particulate agglomerates repeatedly produced, the microscopic nature of these agglomerates would need to be examined. The theory explained in this report, the formation of salt bridge between particles, can be verified by microscopic examination. The effect anti-caking additives have on the formation and strength of these salt bridges may also be able to be evaluated by microscopic examination.

A more scientifically based process for selected anti-caking additives would need to be developed. The solubility of anti-caking additives into the adsorbed sodium formate-water mixture as well as the phase behavior of the resulting ternary solution would provide guidance in the selection process.

It is believed that the experimental procedure used to evaluate the effect of anti-caking additives in this research is sound and can produce quantitative results. However, the method for distributing anti-caking additives among the sodium formate particles would need to be modified.

SECTION 9

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Appendix A
Potential ADF FPDs Identified in Search

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
001.01	$C_2H_2O_2$	Ethanedial	107-22-2
008.01	$C_2H_4O_2$	Methyl formate	107-31-3
008.02	$C_2H_4O_2$	Hydroxy acetaldehyde	141-46-8
014.01	$C_2H_6O_2$	Ethylene glycol	107-21-1
026.01	$C_3H_4O_2$	β-Propiolactone	57-57-8
026.02	$C_3H_4O_2$	Methylglyoxal	78-98-8
026.03	$C_3H_4O_2$	Propanedial	542-78-9
026.04	$C_3H_4O_2$	Glycidaldehyde	765-34-4
027.01	$C_3H_4O_3$	Ethylene carbonate	96-49-1
027.02	$C_3H_4O_3$	Methyl glyoxylate	922-68-9
033.01	$C_3H_6O_2$	Methyl acetate	79-20-9
033.02	$C_3H_6O_2$	Ethyl formate	109-94-4
033.03	$C_3H_6O_2$	1,3-Dioxolane	646-06-0
033.04	$C_3H_6O_2$	1-Hydroxy-2-propanone	116-09-6
033.05	$C_3H_6O_2$	Glycidol	556-52-5
033.06	$C_3H_6O_2$	Methoxyacetaldehyde	10312-83-1
033.07	$C_3H_6O_2$	3-Hydroxy-propanal	2134-29-4
034.01	$C_3H_6O_3$	1,3,5-Trioxane	110-88-3
034.02	$C_3H_6O_3$	Dimethyl carbonate	616-38-6
034.03	$C_3H_6O_3$	Methyl glycolate	96-35-5
034.04	$C_3H_6O_3$	2,3-Dihydroxypropanal	367-47-5
034.05	$C_3H_6O_3$	Dihydroxyacetone	96-26-4
034.06	$C_3H_6O_3$	DL-Glyceraldehyde	56-82-6
034.07	$C_3H_6O_3$	Methylene glycol monoacetate	86011-33-8
034.08	$C_3H_6O_3$	2-Hydroxyethyl formate	628-35-3
039.01	$C_3H_8O_2$	2-Methoxy ethanol	109-86-4
039.02	$C_3H_8O_2$	Dimethoxymethane	109-87-5
039.03	$C_3H_8O_2$	1,2-Propylene glycol	57-55-6
039.04	$C_3H_8O_2$	1,3-Propylene glycol	504-63-2
040.01	$C_3H_8O_3$	Glycerol	56-81-5
051.01	$C_4H_4O_3$	Succinic anhydride	108-30-5
052.01	$C_4H_4O_4$	1,4-Dioxane-2,5-dione	502-97-6
052.02	$C_4H_4O_4$	Ethylene oxalate	3524-70-7
052.03	$C_4H_4O_4$	1,4-Dioxane-2,6-dione	4480-83-5
058.01	$C_4H_6O_2$	2,3-Butanedione	431-03-8
058.02	$C_4H_6O_2$	γ-Butyrolactone	96-48-0
058.03	$C_4H_6O_2$	4-Methyl-2-oxetanone	3068-88-0

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
058.04	$C_4H_6O_2$	1,2,3,4-Diepoxybutane	1464-53-5
059.01	$C_4H_6O_3$	Acetic anhydride	108-24-7
059.02	$C_4H_6O_3$	Propylene carbonate	108-32-7
059.03	$C_4H_6O_3$	Methyl pyruvate	600-22-6
059.04	$C_4H_6O_3$	p-Dioxanone	3041-16-5
060.01	$C_4H_6O_4$	Dimethyl oxalate	553-90-2
065.01	$C_4H_8O_2$	Ethyl acetate	141-78-6
065.02	$C_4H_8O_2$	1,4-Dioxane	123-91-1
065.03	$C_4H_8O_2$	3-Hydroxy-2-butanone	513-86-0
065.04	$C_4H_8O_2$	Methyl propionate	554-12-1
065.05	$C_4H_8O_2$	Propyl formate	110-74-7
065.06	$C_4H_8O_2$	1,3-Dioxane	505-22-6
065.07	$C_4H_8O_2$	Isopropyl formate	625-55-8
065.08	$C_4H_8O_2$	2-Methyl-1,3-dioxolane	497-26-7
065.09	$C_4H_8O_2$	Glycidyl methyl ether	930-37-0
065.10	$C_4H_8O_2$	4-Methyl-1,3-dioxolane	1072-47-5
065.11	$C_4H_8O_2$	1-Hydroxy-2-butanone	5077-67-8
065.12	$C_4H_8O_2$	4-Hydroxy-2-butanone	590-90-9
065.13	$C_4H_8O_2$	Methoxyacetone	5878-19-3
065.14	$C_4H_8O_2$	3-Hydroxy tetrahydrofuran	453-20-3
065.15	$C_4H_8O_2$	3-Methoxy propanal	2806-84-0
065.16	$C_4H_8O_2$	3-Hydroxy-2-butanone	52217-02-4
065.17	$C_4H_8O_2$	β-Hydroxybutyraldehyde	107-89-1
066.01	$C_4H_8O_3$	Methyl lactate	547-64-8
066.02	$C_4H_8O_3$	2-Methoxy-1,3-dioxolane	19693-75-5
066.03	$C_4H_8O_3$	Methyl methoxyacetate	6290-49-9
066.04	$C_4H_8O_3$	1,3,5-Trioxepane	5981-06-6
066.05	$C_4H_8O_3$	Ethyl glycolate	623-50-7
066.06	$C_4H_8O_3$	Ethylene glycol monoacetate	542-59-6
066.07	$C_4H_8O_3$	Methyl 3-hydroxypropanoate	6149-41-3
066.08	$C_4H_8O_3$	2-Methoxy ethyl formate	628-82-0
066.09	$C_4H_8O_3$	trans-Tetrahydro-3,4-furandiol	22554-74-1
066.10	$C_4H_8O_3$	1,3-Dioxan-5-ol	4740-78-7
067.01	$C_4H_8O_4$	1,3,5,7-Tetroxane	293-30-1
067.02	$C_4H_8O_4$	Methyl-2,3-dihydroxy propanoate	15909-76-9
071.01	$C_4H_{10}O_2$	1,4-Butanediol	110-63-4
071.02	$C_4H_{10}O_2$	2,3-Butanediol	513-85-9

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
071.03	$C_4H_{10}O_2$	1,2-Dimethoxyethane	110-71-4
071.04	$C_4H_{10}O_2$	1,3-Butanediol	107-88-0
071.05	$C_4H_{10}O_2$	2-Ethoxyethanol	110-80-5
071.06	$C_4H_{10}O_2$	1,1-Dimethoxyethane	534-15-6
071.07	$C_4H_{10}O_2$	1-Methoxy-2-propanol	107-98-2
071.08	$C_4H_{10}O_2$	1,2-Butanediol	584-03-2
071.09	$C_4H_{10}O_2$	2-Methyl-1,2-propanediol	558-43-0
071.10	$C_4H_{10}O_2$	1,1-Dimethoxyethane	25154-53-4
071.11	$C_4H_{10}O_2$	2-Methoxy-1-propanol	1589-47-5
071.12	$C_4H_{10}O_2$	2-Methyl-1,3-propanediol	2163-42-0
071.13	$C_4H_{10}O_2$	3-Methoxy-1-propanol	1589-49-7
072.01	$C_4H_{10}O_3$	DEG	111-46-6
072.02	$C_4H_{10}O_3$	Trimethoxymethane	149-73-5
072.03	$C_4H_{10}O_3$	1,2,4-Butanetriol	3068-00-6
072.04	$C_4H_{10}O_3$	1,2,3-Butanetriol	4435-50-1
072.05	$C_4H_{10}O_3$	2-Hydroxymethyl-1,3-propanediol	4704-94-3
073.01	$C_4H_{10}O_4$	meso-Erythritol	149-32-6
090.01	$C_5H_6O_3$	Glutaric anhydride	108-55-4
090.02	$C_5H_6O_3$	Methyl succinic anhydride	4100-80-5
090.03	$C_5H_6O_3$	2,3,4-Pentanetrione	921-11-9
097.01	$C_5H_8O_2$	2,3-Pentadione	600-14-6
097.02	$C_5H_8O_2$	δ-Valerolactone	542-28-9
097.03	$C_5H_8O_2$	2,4-Pentadione	123-54-6
097.04	$C_5H_8O_2$	2-Methyltetrahydrofuran-3-one	3188-00-9
097.05	$C_5H_8O_2$	4-Methyl-γ-butyrolactone	108-29-2
097.06	$C_5H_8O_2$	Methyl cyclopropanecarboxylate	2868-37-3
097.07	$C_5H_8O_2$	β-Methyl-γ-butyrolactone	1679-49-8
097.08	$C_5H_8O_2$	3,3-Dimethyl-2-oxetanone	1955-45-9
097.09	$C_5H_8O_2$	α-Methyl-γ-butyrolactone	1679-47-6
097.10	$C_5H_8O_2$	4,5-Dihydro-5-methyl 3(2H)furanone	34003-72-0
097.11	$C_5H_8O_2$	1,5-Pentanedial	111-30-8
097.12	$C_5H_8O_2$	Dihydro-5-methyl-2(3H)furanone	57129-69-8
097.13	$C_5H_8O_2$	2-Oxopentanal	7332-93-6
097.14	$C_5H_8O_2$	Tetrahydro-4H-pyran-4-one	29943-42-8
097.15	$C_5H_8O_2$	Tetrahydrofuran-2-carbaldehyde	79710-86-4
097.16	$C_5H_8O_2$	Tetrahydrofuran-3-carbaldehyde	7681-84-7
097.17	$C_5H_8O_2$	Dimethylpropanedial	1185-34-8

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
098.01	$C_5H_8O_3$	Methyl acetoacetate	105-45-3
098.02	$C_5H_8O_3$	Acetoxyacetone	592-20-1
098.03	$C_5H_8O_3$	Ethyl pyruvate	617-35-6
098.04	$C_5H_8O_3$	5-(Hydroxymethyl)dihydro-2(3H)furanone	32780-06-6
098.05	$C_5H_8O_3$	2-Acetoxypropanal	22094-23-1
098.06	$C_5H_8O_3$	Succinaldehydic acid, methyl ester	13865-19-5
099.01	$C_5H_8O_4$	Dimethyl malonate	108-59-8
099.02	$C_5H_8O_4$	Methylene diacetate	628-51-3
099.03	$C_5H_8O_4$	1,2-Propanediol diformate	53818-14-7
100.01	$C_5H_8O_5$	D-(+)-Ribonic acid gamma-lactone	5336-08-3
104.01	$C_5H_{10}O_2$	Ethyl propanoate	105-37-3
104.02	$C_5H_{10}O_2$	Methyl butyrate	623-42-7
104.03	$C_5H_{10}O_2$	Propyl acetate	109-60-4
104.04	$C_5H_{10}O_2$	1-Methylethyl acetate	108-21-4
104.05	$C_5H_{10}O_2$	Methyl isobutyrate	547-63-7
104.06	$C_5H_{10}O_2$	Butyl formate	592-84-7
104.07	$C_5H_{10}O_2$	2-Methylpropyl formate	542-55-2
104.08	$C_5H_{10}O_2$	1,3-Dioxepane	505-65-7
104.09	$C_5H_{10}O_2$	4-Methyl-1,3-dioxane	1120-97-4
104.10	$C_5H_{10}O_2$	Tetrahydro-2-furanmethanol	97-99-4
104.11	$C_5H_{10}O_2$	2,4-Dimethyl-1,3-dioxolane	3390-12-3
104.12	$C_5H_{10}O_2$	3-Hydroxy-3-methyl-2-butanone	115-22-0
104.13	$C_5H_{10}O_2$	cis-1,2-Cyclopentanediol	5057-98-7
104.14	$C_5H_{10}O_2$	tert-Butyl formate	762-75-4
104.15	$C_5H_{10}O_2$	2-Ethyl-1,3-dioxolane	2568-96-9
104.16	$C_5H_{10}O_2$	2-Methyl-1,3-dioxane	626-68-6
104.17	$C_5H_{10}O_2$	sec-Butyl formate	589-40-2
104.18	$C_5H_{10}O_2$	trans-1,2-Cyclopentanediol	5057-99-8
104.19	$C_5H_{10}O_2$	4-Hydroxy-3-methyl-2-butanone	3393-64-4
104.20	$C_5H_{10}O_2$	2,2-Dimethyl-1,3-dioxolane	2916-31-6
104.21	$C_5H_{10}O_2$	3-Hydroxy-2-pentanone	3142-66-3
104.22	$C_5H_{10}O_2$	2-Hydroxy-3-pentanone	5704-20-1
104.23	$C_5H_{10}O_2$	5-Hydroxy-2-pentanone	1071-73-4
104.24	$C_5H_{10}O_2$	3-Methyl-3-oxetanemethanol	3143-02-0
104.25	$C_5H_{10}O_2$	4-Hydroxy-2-pentanone	4161-60-8
104.26	$C_5H_{10}O_2$	1-Hydroxy-2-pentanone	64502-89-2
104.27	$C_5H_{10}O_2$	4-Methoxy-2-butanone	6975-85-5

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
104.28	$C_5H_{10}O_2$	cis-1,3-Cyclopentanediol	16326-97-9
104.29	$C_5H_{10}O_2$	3-Hydroxy-2,2-dimethylpropanal	597-31-9
104.30	$C_5H_{10}O_2$	Ethyl glycidyl ether	4016-11-9
104.31	$C_5H_{10}O_2$	Tetrahydro-3-furanylmethanol	15833-61-1
104.32	$C_5H_{10}O_2$	Tetrahydro-4H-pyran-4-ol	2081-44-9
104.33	$C_5H_{10}O_2$	3-Methoxy-2,2-dimethyloxirane	26196-04-3
104.34	$C_5H_{10}O_2$	2-Methyltetrahydro-2-furanol	7326-46-7
104.35	$C_5H_{10}O_2$	Tetrahydro-2-hydroxy-2H-pyran	694-54-2
104.36	$C_5H_{10}O_2$	4-Hydroxy-3-methyl-2-butanone	9006-26-2
105.01	$C_5H_{10}O_3$	Ethyl carbonate	105-58-8
105.02	$C_5H_{10}O_3$	Ethyl lactate	97-64-3
105.03	$C_5H_{10}O_3$	1,3,6-Trioxocane	1779-19-7
105.04	$C_5H_{10}O_3$	2-Methoxyethanol acetate	110-49-6
105.05	$C_5H_{10}O_3$	Methyl-3-hydroxybutanoate	1487-49-6
105.06	$C_5H_{10}O_3$	2-Hydroxymethyl-1,3-dioxane	39239-93-5
105.07	$C_5H_{10}O_3$	Methyl 2-hydroxy-2-methylpropionate	2110-78-3
105.08	$C_5H_{10}O_3$	2-Hydroxyethyl propionate	24567-27-9
105.09	$C_5H_{10}O_3$	Methyl 3-hydroxy-2-methylpropanoate	42998-03-8
105.10	$C_5H_{10}O_3$	Methyl 2-hydroxybutanoate	29674-47-3
105.11	$C_5H_{10}O_3$	Ethyl methoxyacetate	3938-96-3
105.12	$C_5H_{10}O_3$	1,1-Dimethoxy-2-propanone	6342-56-9
105.13	$C_5H_{10}O_3$	Propyl glycolate	90357-58-7
105.14	$C_5H_{10}O_3$	Methoxyethanol acetate	32718-56-2
106.01	$C_5H_{10}O_4$	Monoacetine	26446-35-5
106.02	$C_5H_{10}O_4$	D-2-Deoxyribose	533-67-5
106.03	$C_5H_{10}O_4$	Methyl dimethoxyacetate	89-91-8
106.04	$C_5H_{10}O_4$	1-Monoacetin	106-61-6
107.01	$C_5H_{10}O_5$	D-Ribose	50-69-1
107.02	$C_5H_{10}O_5$	1,3,5,7,9-Pentaoxecane	16528-92-0
107.03	$C_5H_{10}O_5$	D-Arabinose	10323-20-3
107.04	$C_5H_{10}O_5$	D-Xylose	58-86-6
107.05	$C_5H_{10}O_5$	α-D-Xylose	31178-70-8
107.06	$C_5H_{10}O_5$	Arabinose	147-81-9
107.07	$C_5H_{10}O_5$	D-Ribulose	488-84-6
110.01	$C_5H_{12}O_2$	1,5-Pentanediol	111-29-5
110.02	$C_5H_{12}O_2$	2,2-Dimentyl-1,3-pentanediol	126-30-7
110.03	$C_5H_{12}O_2$	Diethoxymethane	462-95-3

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
110.04	$C_5H_{12}O_2$	2,2-Dimethoxypropane	77-76-9
110.05	$C_5H_{12}O_2$	2-Propoxyethanol	2807-30-9
110.06	$C_5H_{12}O_2$	2,4-Pentanediol	625-69-4
110.07	$C_5H_{12}O_2$	1,2-Pentanediol	5343-92-0
110.08	$C_5H_{12}O_2$	3-Ethoxy-1-propanol	111-35-3
110.09	$C_5H_{12}O_2$	1,3-Dimethoxypropane	17081-21-9
110.10	$C_5H_{12}O_2$	1-Ethoxy-2-methoxyethane	5137-45-1
110.11	$C_5H_{12}O_2$	2-Isopropoxy ethanol	109-59-1
110.12	$C_5H_{12}O_2$	3-Methoxy-1-butanol	2517-43-3
110.13	$C_5H_{12}O_2$	1,1-Dimethoxypropane	4744-10-9
110.14	$C_5H_{12}O_2$	2-Ethoxy-1-propanol	19089-47-5
110.15	$C_5H_{12}O_2$	2-Methyl-2,3-butanediol	5396-58-7
110.16	$C_5H_{12}O_2$	2-Methyl-1,4-butanediol	2938-98-9
110.17	$C_5H_{12}O_2$	1,2-Dimethoxypropane	7778-85-0
110.18	$C_5H_{12}O_2$	2,3-Pentanediol	42027-23-6
110.19	$C_5H_{12}O_2$	3-Methyl-1,2-butanediol	50468-22-9
110.20	$C_5H_{12}O_2$	1,3-Pentanediol	3174-67-2
110.21	$C_5H_{12}O_2$	1,4-Pentanediol	626-95-9
110.22	$C_5H_{12}O_2$	3-Methyl-1,3-butanediol	2568-33-4
110.23	$C_5H_{12}O_2$	2-Methyl-1,3-Butanediol	684-84-4
110.24	$C_5H_{12}O_2$	4-Methoxy-1-butanol	111-32-0
111.01	$C_5H_{12}O_3$	1,1,1-Trimethanolethane	77-85-0
111.02	$C_5H_{12}O_3$	2-(2-Methoxyethoxy)-ethanol	111-77-3
111.03	$C_5H_{12}O_3$	1,1,1-Trimethoxyethane	1445-45-0
111.04	$C_5H_{12}O_3$	2,3,4-Pentanetriol	14642-48-9
111.05	$C_5H_{12}O_3$	1,3-Dimethoxy-2-propanol	623-69-8
111.06	$C_5H_{12}O_3$	1,1,2-Trimethoxyethane	24332-20-5
111.07	$C_5H_{12}O_3$	3-Ethoxy-1,2-propanediol	1874-62-0
112.01	$C_5H_{12}O_4$	Pentaerythritol	115-77-5
112.02	$C_5H_{12}O_4$	Tetramethoxymethane	1850-14-2
112.03	$C_5H_{12}O_4$	3-(2-Hydroxyethoxy)-1,2-propanediol	14641-24-8
113.01	$C_5H_{12}O_5$	Xylitol	87-99-0
113.02	$C_5H_{12}O_5$	Adonitol	488-81-3
113.03	$C_5H_{12}O_5$	D-Arabitol	488-82-4
131.01	$C_6H_6O_6$	D-Mannaric acid, 1,4:3,6-dilactone	2900-01-8
136.01	$C_6H_8O_3$	trans-3,4-Dihydro-3,4-dimethyl-2,5-furandione	35392-94-0
136.02	$C_6H_8O_3$	cis-3,4-Dihydro-3,4-dimethyl-2,5-furandione	16844-07-8

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
136.03	$C_6H_8O_3$	Dihydro-3,3-dimethyl-2,5-furandione	17347-61-4
136.04	$C_6H_8O_3$	3-Acetyldihydro-2(3H)-furanone	517-23-7
136.05	$C_6H_8O_3$	Dihydro-3-ethyl-2,5-furandione	14035-81-5
136.06	$C_6H_8O_3$	3-Methylglutaric anhydride	4166-53-4
137.01	$C_6H_8O_4$	DL-Lactide	615-9-2
137.02	$C_6H_8O_4$	3,6-Dimethyl-1,4-dioxane-2,5-dione	95-96-5
137.03	$C_6H_8O_4$	2,5-Dimethyl-2,4-dihydroxy-3(2H)-furanone	10230-62-3
137.04	$C_6H_8O_4$	Methyl 2,4-dioxopentanoate	20577-61-1
137.05	$C_6H_8O_4$	2,2-Dimethyl-1,3-dioxane-4,6-dione	2033-24-1
143.01	$C_6H_{10}O_2$	5-Ethyldihydro-2(3H)-furanone	695-06-7
143.02	$C_6H_{10}O_2$	2,5-Hexadione	110-13-4
143.03	$C_6H_{10}O_2$	2-Oxepanone	502-44-3
143.04	$C_6H_{10}O_2$	2,3-Hexanedione	3848-24-6
143.05	$C_6H_{10}O_2$	3-Methyl-2,4-pentanedione	815-57-6
143.06	$C_6H_{10}O_2$	2,4-Hexanedione	3002-24-2
143.07	$C_6H_{10}O_2$	δ-Hexalactone	823-22-3
143.08	$C_6H_{10}O_2$	3,4-Hexanedione	4437-51-8
143.09	$C_6H_{10}O_2$	Cyclobutanecarboxylic acid methyl ester	765-85-5
143.10	$C_6H_{10}O_2$	2-Hydroxycyclohexanone	533-60-8
143.11	$C_6H_{10}O_2$	Dihydro-4,5-dimethyl-2(3H)-furanone	6971-63-7
143.12	$C_6H_{10}O_2$	β-Isopropyl-β-propiolactone	10359-02-1
143.13	$C_6H_{10}O_2$	β-Propyl-β-propiolactone	15964-17-7
143.14	$C_6H_{10}O_2$	Isocaprolactone	3123-97-5
143.15	$C_6H_{10}O_2$	Ethyl cyclopropanecarboxylate	4606-07-9
143.16	$C_6H_{10}O_2$	4-Methyl-2,3-pentanedione	7493-58-5
143.17	$C_6H_{10}O_2$	Tetrahydro-4-methyl-2H-pyran-2-one	1121-84-2
143.18	$C_6H_{10}O_2$	3,3-Dimethyldihydro-2(3H)-furanone	3709-08-8
144.01	$C_6H_{10}O_3$	Ethyl acetoacetate	141-97-9
144.02	$C_6H_{10}O_3$	Propanoic anhydride	123-62-6
144.03	$C_6H_{10}O_3$	Methyl levulate	624-45-3
144.04	$C_6H_{10}O_3$	3-Acetoxy-2-butanone	4906-24-5
144.05	$C_6H_{10}O_3$	5,5-Dimethyl-1,3-dioxan-2-one	3592-12-9
144.06	$C_6H_{10}O_3$	Pantolactone	599-04-2
144.07	$C_6H_{10}O_3$	Acetone D-glyceraldehyde	15186-48-8
144.08	$C_6H_{10}O_3$	4-Acetoxy-2-butanone	10150-87-5
144.09	$C_6H_{10}O_3$	Butanoic acid, 2-oxo-, ethyl ester	15933-07-0
144.10	$C_6H_{10}O_3$	Methyl propionylacetate	30414-53-0

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
144.11	$C_6H_{10}O_3$	2-Hydroxyhexanedial	141-31-1
144.12	$C_6H_{10}O_3$	DL-Mevalonic acid lactone	674-26-0
144.13	$C_6H_{10}O_3$	Butyl glyoxylate	6295-06-3
145.01	$C_6H_{10}O_4$	Dimethyl succinate	106-65-0
145.02	$C_6H_{10}O_4$	1,2-Diacetoxyethane	111-55-7
145.03	$C_6H_{10}O_4$	Diethyl oxalate	95-92-1
145.04	$C_6H_{10}O_4$	1,1-Diacetoxyethane	542-10-9
145.05	$C_6H_{10}O_4$	Dimethyl methylmalonate	609-02-9
145.06	$C_6H_{10}O_4$	Hexahydro-[1,4]dioxino[2,3-b]-1,4-dioxin	4362-05-4
145.07	$C_6H_{10}O_4$	Methyl 4-methoxyacetoacetate	41051-15-4
145.08	$C_6H_{10}O_4$	1,2:5,6-Dianhydrogalactitol	23261-20-3
146.01	$C_6H_{10}O_5$	Diethyl pyrocarbonate	1609-47-8
146.02	$C_6H_{10}O_5$	Methoxyacetic anhydride	19500-95-9
147.01	$C_6H_{10}O_6$	DL-Dimethyl tartarate	608-69-5
147.02	$C_6H_{10}O_6$	D-Galactonic acid, γ-lactone	2782-07-2
147.03	$C_6H_{10}O_6$	D-Gluconic acid, δ-lactone	90-80-2
150.01	$C_6H_{12}O_2$	Ethyl butanoate	105-54-4
150.02	$C_6H_{12}O_2$	Butyl acetate	123-86-4
150.03	$C_6H_{12}O_2$	Isobutyl acetate	110-19-0
150.04	$C_6H_{12}O_2$	Ethyl isobutyrate	97-62-1
150.05	$C_6H_{12}O_2$	Methyl pentanoate	624-24-8
150.06	$C_6H_{12}O_2$	Methyl 2-methylbutanoate	868-57-5
150.07	$C_6H_{12}O_2$	Propyl propanoate	106-36-5
150.08	$C_6H_{12}O_2$	4-Hydroxy-4-methylpentan-2-one	123-42-2
150.09	$C_6H_{12}O_2$	Methyl isopentanoate	556-24-1
150.10	$C_6H_{12}O_2$	Isopropyl propionate	637-78-5
150.11	$C_6H_{12}O_2$	Pentyl formate	638-49-3
150.12	$C_6H_{12}O_2$	tert-Butyl acetate	540-88-5
150.13	$C_6H_{12}O_2$	sec-Butyl acetate	105-46-4
150.14	$C_6H_{12}O_2$	Isopentyl formate	110-45-2
150.15	$C_6H_{12}O_2$	Methyl pivalate	598-98-1
150.16	$C_6H_{12}O_2$	2-Methoxytetrahydropyran	6581-66-4
150.17	$C_6H_{12}O_2$	1,3-Dioxocane	6572-90-3
150.18	$C_6H_{12}O_2$	2,2-Dimethyl-1,3-dioxane	695-30-7
150.19	$C_6H_{12}O_2$	cis-1,2-Cyclohexanediol	1792-81-0
150.20	$C_6H_{12}O_2$	cis-2,4-Dimethyl-1,3-dioxane	15042-59-8
150.21	$C_6H_{12}O_2$	2-Isopropyl-1,3-Dioxolane	822-83-3

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
150.22	$C_6H_{12}O_2$	2-Propyl-1,3-dioxolane	3390-13-4
150.23	$C_6H_{12}O_2$	2,3-Epoxypropyl isopropyl ether	4016-14-2
150.24	$C_6H_{12}O_2$	5,5-Dimethyl-1,3-dioxane	872-98-0
150.25	$C_6H_{12}O_2$	2-Ethyl-2-methyl-1,3-dioxolane	126-39-6
150.26	$C_6H_{12}O_2$	trans-1,2-Cyclohexanediol	1460-57-7
150.27	$C_6H_{12}O_2$	cis-2-Ethyl-4-methyl-1,3-dioxolane	4359-46-0
150.28	$C_6H_{12}O_2$	cis-4,6-Dimethyl-1,3-dioxane	3390-18-9
150.29	$C_6H_{12}O_2$	4,4-Dimethyl-1,3-dioxane	766-15-4
150.30	$C_6H_{12}O_2$	trans-4,5-Dimethyl-1,3-dioxane	1121-20-6
150.31	$C_6H_{12}O_2$	trans-4,6-Dimethyl-1,3-dioxane	1121-87-5
150.32	$C_6H_{12}O_2$	4-Hydroxy-3-hexanone	4984-85-4
150.33	$C_6H_{12}O_2$	2-Ethoxytetrahydrofuran	13436-46-9
150.34	$C_6H_{12}O_2$	cis-1,3-Cyclohexandiol	823-18-7
150.35	$C_6H_{12}O_2$	1,3-Cyclohexanediol	504-01-8
150.36	$C_6H_{12}O_2$	1,2-Cyclohexanediol	931-17-9
150.37	$C_6H_{12}O_2$	2,4-Dimethyl-1,3-dioxane	766-20-1
150.38	$C_6H_{12}O_2$	Ethyl ethoxymethyl ketone	76086-05-0
150.39	$C_6H_{12}O_2$	1-Methylbutyl formate	58368-66-4
150.40	$C_6H_{12}O_2$	Glycidyl propyl ether	3126-95-2
150.41	$C_6H_{12}O_2$	Tetrahydropyran-2-methanol	100-72-1
150.42	$C_6H_{12}O_2$	trans-1-Methyl-1,2-cylcopentanediol	20557-45-3
150.43	$C_6H_{12}O_2$	2.6-Dimethyl-1,4-dioxane	10138-17-7
150.44	$C_6H_{12}O_2$	trans-1,3-Cyclohexanediol	5515-64-0
150.45	$C_6H_{12}O_2$	Tetrahydro-5-methyl-2-furanmethanol	6126-49-4
150.46	$C_6H_{12}O_2$	1,4-Cyclohexanediol	556-48-9
150.47	$C_6H_{12}O_2$	6-Hydroxy-2-hexanone	21856-89-3
150.48	$C_6H_{12}O_2$	tert-Amyl methanoate	757-88-0
150.49	$C_6H_{12}O_2$	trans-1,4-Cyclohexanediol	6995-79-5
150.50	$C_6H_{12}O_2$	cis-1,4-Cyclohexanediol	931-71-5
150.51	$C_6H_{12}O_2$	Methyl 2-methylbutanoate	53955-81-0
150.52	$C_6H_{12}O_2$	Methyl tetrahydrofurfuryl ether	19354-27-9
150.53	$C_6H_{12}O_2$	trans-2,4-Dimethyl-1,3-dioxane	15042-60-1
150.54	$C_6H_{12}O_2$	3-Methyl-1,2-cyclopentanediol	27583-37-5
150.55	$C_6H_{12}O_2$	trans-2-Methoxy-cyclopentanol	7429-45-0
150.56	$C_6H_{12}O_2$	cis-2-Methoxy-cyclopentanol	13051-91-7
150.57	$C_6H_{12}O_2$	2,2,4-Trimethyldioxolane	1193-11-9
150.58	$C_6H_{12}O_2$	3-Ethyl-3-hydroxymethyl oxetane	3047-32-3

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
150.59	$C_6H_{12}O_2$	trans-1,2-Cyclobutanedimethanol	55659-54-6
151.01	$C_6H_{12}O_3$	Paraldehyde	123-63-7
151.02	$C_6H_{12}O_3$	Ethyl 3-hydroxybutanoate	5405-41-4
151.03	$C_6H_{12}O_3$	2-Ethoxyethyl acetate	111-15-9
151.04	$C_6H_{12}O_3$	1-Methoxy-2-propyl acetate	108-65-6
151.05	$C_6H_{12}O_3$	Methyl 3-hydroxy-3-methylbutanoate	6149-45-7
151.06	$C_6H_{12}O_3$	Ethoxymethyl propionate	54078-53-4
151.07	$C_6H_{12}O_3$	Ethyl ethoxyacetate	817-95-8
151.08	$C_6H_{12}O_3$	4,4-Dimethoxy-2-butanone	5436-21-5
151.09	$C_6H_{12}O_3$	cis-2,4,6-Trimethyl-1,3,5-trioxane	1499-02-1
151.10	$C_6H_{12}O_3$	L-Acetone glycerol	22323-82-6
151.11	$C_6H_{12}O_3$	Ethyl 2-hydroxybitanoate	52089-54-0
151.12	$C_6H_{12}O_3$	D-Acetone glycerol	14347-78-5
151.13	$C_6H_{12}O_3$	2,3-Butanediol monoacetate	56255-48-2
151.14	$C_6H_{12}O_3$	Methyl 2-hydroxy-3-methylbutanoate	17417-00-4
151.15	$C_6H_{12}O_3$	Methyl 2-hydroxy-2-methylbutanoate	32793-34-3
151.16	$C_6H_{12}O_3$	2,2-Dimethyl-1,3-dioxolane-4-methanol	100-79-8
151.17	$C_6H_{12}O_3$	Ethyl 2-hydroxy-2-methylpropionate	80-55-7
151.18	$C_6H_{12}O_3$	Propyl lactate	616-09-1
151.19	$C_6H_{12}O_3$	1,2,3-Cyclohexanetriol	6286-43-7
151.20	$C_6H_{12}O_3$	Tetrahydro-2,5-dimethoxy-furan	696-59-3
151.21	$C_6H_{12}O_3$	3,3-Dimethoxy-2-butanone	21983-72-2
151.22	$C_6H_{12}O_3$	Butyl glycolate	7397-62-8
152.01	$C_6H_{12}O_4$	Methyl 3,3-dimethoxypropionate	7424-91-1
152.02	$C_6H_{12}O_4$	DEG monoacetate	2093-20-1
152.03	$C_6H_{12}O_4$	2,3-Dihydroxypropyl propionate	624-47-5
153.01	$C_6H_{12}O_5$	6-Deoxy-L-mannose	3615-41-6
154.01	$C_6H_{12}O_6$	Glucose	50-99-7
154.02	$C_6H_{12}O_6$	L-Sorbose	87-79-6
154.03	$C_6H_{12}O_6$	Hexahydroxycyclohexane	87-89-8
154.04	$C_6H_{12}O_6$	D-Mannose	3458-28-4
154.05	$C_6H_{12}O_6$	Galactose	26566-61-0
154.06	$C_6H_{12}O_6$	Fructose	7660-25-5
154.07	$C_6H_{12}O_6$	Muco-inositol	488-55-1
154.08	$C_6H_{12}O_6$	D-Gulose	4205-23-6
156.01	$C_6H_{14}O_2$	1,1-Diethoxyethane	105-57-7
156.02	$C_6H_{14}O_2$	2-Butoxy-1-ethanol	111-76-2

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
156.03	$C_6H_{14}O_2$	1,6-Hexanediol	629-11-8
156.04	$C_6H_{14}O_2$	1,2-Diethoxyethane	629-14-1
156.05	$C_6H_{14}O_2$	1,2-Hexanediol	6920-22-5
156.06	$C_6H_{14}O_2$	2,3-Dimethyl-2,3-butanediol	76-09-5
156.07	$C_6H_{14}O_2$	2-Methyl-2,4-pentanediol	107-41-5
156.08	$C_6H_{14}O_2$	2,5-Hexanediol	2935-44-6
156.09	$C_6H_{14}O_2$	1-Propoxy-2-propanol	1569-01-3
156.10	$C_6H_{14}O_2$	2-Isobutoxyethanol	4439-24-1
156.11	$C_6H_{14}O_2$	1,1-Dimethoxy-butane	4461-87-4
156.12	$C_6H_{14}O_2$	1,4-Dimethoxybutane	13179-96-9
156.13	$C_6H_{14}O_2$	1,1-Dimethoxy-2-methyl-propane	41632-89-7
156.14	$C_6H_{14}O_2$	2-Methyl-1,3-pentanediol	149-31-5
156.15	$C_6H_{14}O_2$	3-Methyl-1,5-pentanediol	4457-71-0
156.16	$C_6H_{14}O_2$	3-Methyl-2,4-pentanediol	5683-44-3
156.17	$C_6H_{14}O_2$	2-Ethyl-2-methyl-1,3-propanediol	77-84-9
156.18	$C_6H_{14}O_2$	3,3-Dimethyl-1,2-butanediol	59562-82-2
156.19	$C_6H_{14}O_2$	2,3-Dimethyl-1,3-butanediol	24893-35-4
156.20	$C_6H_{14}O_2$	1,3-Hexanediol	21531-91-9
156.21	$C_6H_{14}O_2$	2,4-Hexanediol	19780-90-6
156.22	$C_6H_{14}O_2$	2-Methyl-2,3-pentanediol	7795-80-4
156.23	$C_6H_{14}O_2$	meso-3,4-Hexanediol	22520-39-4
156.24	$C_6H_{14}O_2$	3-Methoxy-2,2-dimethyl-1-propanol	57021-67-7
156.25	$C_6H_{14}O_2$	1,5-Hexanediol	928-40-5
156.26	$C_6H_{14}O_2$	2-Ethyl-1,2-butanediol	66553-16-0
156.27	$C_6H_{14}O_2$	4-Methyl-1,4-pentanediol	1462-10-8
156.28	$C_6H_{14}O_2$	4-Methoxy-1-pentanol	818-56-4
156.29	$C_6H_{14}O_2$	1-Methoxy-2-propoxyethane	77078-18-3
156.30	$C_6H_{14}O_2$	3,4-Hexanediol	922-17-8
156.31	$C_6H_{14}O_2$	2,3-Hexanediol	617-30-1
156.32	$C_6H_{14}O_2$	2,2-Dimethyl-1,3-butanediol	76-35-7
156.33	$C_6H_{14}O_2$	1-Isopropoxy-2-propanol	3944-36-3
156.34	$C_6H_{14}O_2$	2,5-Dioxaoctane	500005-28-7
156.35	$C_6H_{14}O_2$	2,2-Dimethoxybutane	3453-99-4
157.01	$C_6H_{14}O_3$	2-(2-Ethoxyethoxy)-ethanol	111-90-0
157.02	$C_6H_{14}O_3$	Di(2-methoxyethyl) ether	111-96-6
157.03	$C_6H_{14}O_3$	Trimethylolpropane	77-99-6
157.04	$C_6H_{14}O_3$	Di(2-hydroxypropyl) ether	110-98-5

Table A-1. Initial list of candidate FPDs.

ID	Formula	Candidate	CAS RN
157.05	$C_6H_{14}O_3$	3,5,7-Trioxanonane	5648-29-3
157.06	$C_6H_{14}O_3$	1,2,6-Hexanetriol	106-69-4
157.07	$C_6H_{14}O_3$	1,1,1-Trimethoxypropane	24823-81-2
157.08	$C_6H_{14}O_3$	1,1,3-Trimethoxypropane	14315-97-0
157.09	$C_6H_{14}O_3$	Dipropylene glycol	25265-71-8
157.10	$C_6H_{14}O_3$	3-Methyl-2,3,4-pentanetriol	1185-10-0
158.01	$C_6H_{14}O_4$	Triethylene glycol	112-27-6
158.02	$C_6H_{14}O_4$	1,1,1,2-Tetramethoxyethane	34359-77-8
160.01	$C_6H_{14}O_6$	D-Mannitol	69-65-8
160.02	$C_6H_{14}O_6$	Galactitol	608-66-2
160.03	$C_6H_{14}O_6$	Sorbitol	50-70-4
160.04	$C_6H_{14}O_6$	L-Mannitol	643-01-6

Appendix B
Details on Candidate ADF FPDs Recommended for Further Evaluation

FINAL CANDIDATE FPDS FOR ADFS AND AAFS

The following paragraphs detail information for each candidate FPD selected for experimental evaluation:

Ethylene Carbonate: Candidate 027.01. This candidate's CAS number is 96-49-1. Its chemical formula is C3H4O3. Ethylene carbonate is used as a safe, environmentally friendly solvent. Its melting point is 36.8°C *(5)*. Its flash point is 160°C *(6)*. Its Aldrich catalog price is $10.68 per kilogram. Its theoretical oxygen demand is 0.908 g oxygen per g chemical. Quantitative values could not be found for its aquatic toxicity. Its rat oral LD50 is 10,000 mg/kg *(11)*.

1,2-Propylene glycol: Candidate 039.03. This candidate's CAS number is 57-55-6. Its chemical formula is $C_3H_8O_2$. 1,2-Propylene glycol is widely used in deicing fluids and other antifreeze products. It is also used as a humectant in foods, an emollient in cosmetics, a solvent for food colors, and as an industrial heat transfer fluid. Its melting point is -60°C *(5)*. Its flash point is 225°F *(6)*. Its Aldrich catalog price is $15.41 per kilogram. Its theoretical oxygen demand is 1.682 g oxygen per g chemical. Its 96 hour LC50 for fathead minnow is 55,700 mg/L *(10)*. Its rat oral LD50 is 20,000 mg/kg *(11)*. Although noninjurious, a drop applied to the human eye causes immediate stinging *(12)*. A composition of 39% by weight 1,2-propylene glycol in water would have an initial freezing point of -20°C *(8)*. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) biological oxygen demand.

1,3-Propylene glycol: Candidate 039.04. This candidate's CAS number is 504-63-2. Its chemical formula is $C_3H_8O_2$. Its melting point is -27°C *(5)*. Its flash point is greater than 230°F *(6)*. Its Aldrich catalog price is $139.00 per kilogram. Its theoretical oxygen demand is 1.682 g oxygen per g of chemical. Its 24 hour LC50 for goldfish is greater than 5,000 mg/L *(10)*. Its mouse oral LD50 is 4,773 mg/kg *(11)*. No information on human health effects was found for this candidate. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) freezing point depression with water; 4) biological oxygen demand.

Glycerol: Candidate 040.01. This candidate's CAS number is 56-81-5. Its chemical formula is $C_3H_8O_3$. Glycerol is used as a solvent, humectant, emollient, sweetener, and plasticizer. Its freezing point is 20°C *(5)* although its high liquid viscosity promotes significant subcooling. Its flash point is 320°F *(6)*. Its Aldrich catalog price is $14.04 per kilogram. Its theoretical oxygen demand is 1.216 g oxygen per g chemical. Its 96 hour LC50 for rainbow trout is 54 ml/L *(10)*. Its rat oral LD50 is 12,600 mg/kg *(11)*. Glycerol dropped onto the human eye causes a strong stinging and burning sensation but no obvious injury *(12)*. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) freezing point depression with water; 4) biological oxygen demand.

Propylene carbonate: Candidate 059.02. This candidate's CAS number is 108-32-7. Its chemical formula is $C_4H_6O_3$. Propylene carbonate is used as a solvent in lithium batteries, a plasticizer and as an extraction solvent. Its melting point is -55°C *(5)*. Its flash point is 270°F *(6)*. Its Aldrich catalog price is $13.80 per kilogram. Its theoretical oxygen demand is 1.254 g oxygen per g chemical. No data was found on aquatic toxicity. Its mouse oral LD50 is 20,700 mg/kg *(11)*. No information on human health effects was found for this candidate. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) freezing point depression with water; 4) biological oxygen demand.

2,3-Butanediol: Candidate 071.02. This candidate's CAS number is 513-85-9. Its chemical formula is $C_4H_{10}O_2$. 2,3-Butanediol is used as a solvent for dyes, a humectant, plasticizer and a cross-linker. Its melting point is 25°C *(5)*. Its flash point is 185°F *(6)*. Its Aldrich catalog price is $499.00 per kilogram. Its theoretical oxygen demand is 1.953 g oxygen per g chemical. No data was found on aquatic toxicity. Its mouse LD50 is 5,462 mg/kg *(11)*. No information on human health effects was found for this candidate. We recommend that additional pricing information first be obtained. Only if a significantly lower price is found would we then recommend the following experiments: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) freezing point depression with water; 4) biological oxygen demand.

1,3-Butanediol: Candidate 071.04. This candidate's CAS number is 107-88-0. Its chemical formula is $C_4H_{10}O_2$. 1,3-Butanediol is used in deicing fluids, in the cosmetic and pharmaceutical industry as a glycerin substitute, and as a plasticizer. It is an efficient antimicrobial agent, inhibiting gram-negative and gram-positive microorganisms, molds and yeasts *(12)*. Its melting point is -77°C {{415 Daubert, T. E. 1989}}. Its flash point is 250°F *(6)*. Its Aldrich catalog price is $16.17 per kilogram. Its theoretical oxygen demand is 1.953 g oxygen per g chemical. No data was found on aquatic toxicity. Its rat oral LD50 is 18,610 mg/kg *(11)*. It is considered to be slightly toxic with the probable oral lethal dose in humans between 5 and 15 g/kg *(12)*. A small drop applied to the eye will cause immediate severe stinging but irrigation with water brings rapid and complete relief. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) freezing point depression with water; 4) biological oxygen demand.

2-Methyl-1,3-propanediol: Candidate 071.12. This candidate's CAS number is 2163-42-0. Its chemical formula is C4H10O2. Used as an emulsifier and humectant in personal care products. Its melting point is reported to be below -50°C *(6)*. Its flash point is greater than 110°C. Its Aldrich catalog price is $16.17 per kilogram. Its theoretical oxygen demand is 1.953 g oxygen per g chemical. Quantitative values could not be found for its aquatic toxicity. Its rat oral LD50 is greater than 5,000 mg/kg *(11)* .

Diethylene glycol: Candidate 072.01. This candidate's CAS number is 111-46-6. Its chemical formula is $C_4H_{10}O_3$. Diethylene glycol (DEG) is used as a deicing fluid, humectant, solvent, mold release agent, and lubricant additive. Its melting point is -10°C *(5)*. Its flash point is 290°F *(6)*. Its Aldrich catalog price is $14.28 per kilogram. Its theoretical oxygen demand is 1.508 g oxygen per g of chemical. Its 96 hour LC50 for fathead minnow is 75,200 mg/L *(10)*. Its rat oral LD50 is 12,565 mg/kg *(11)*. The major hazard to humans from DEG is from the ingestion of a single large dose *(12)*. The lethal dose for humans is approximately 1 ml/kg. It is not irritating to the eyes or skin. A composition of 45% by weight DEG in water would have an initial freezing point of -20°C *(8)*. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) biological oxygen demand.

4-Methyl-γ-butyrolactone: Candidate 097.05. This candidate's CAS number is 108-29-2. Its chemical formula is $C_5H_8O_2$. Its melting point is -31°C *(5)*. Its flash point is 204.8°F *(6)*. Its Aldrich catalog price is $367.00 per kilogram. Its theoretical oxygen demand is 1.918 g oxygen per g chemical. No data was found on aquatic toxicity. Its rat oral LD50 is 8,800 mg/kg *(11)*. No information on human health effects was found for this candidate. We recommend that additional pricing information first be obtained. Only if a significantly lower price is found would we then recommend the following experiments: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) freezing point depression with water; 4) biological oxygen demand.

Dimethyl malonate: Candidate 099.01. This candidate's CAS number is 108-59-8. Its chemical formula is $C_5H_8O_4$. Its melting point is -62°C *(5)*. Its flash point is 194°F *(6)*. Its theoretical oxygen demand is 1.211 g oxygen per g chemical. No data was found on aquatic toxicity. Its rat oral LD50 is 5,331 mg/kg *(11)*. No information on human health effects was found for this candidate. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) freezing point depression with water; 4) biological oxygen demand.

2-(2-Methoxyethoxy)-ethanol: Candidate 111.02. This candidate's CAS number is 111-77-3. Its chemical formula is C5H12O3. Its melting point is -70°C *(6)*. Its flash point is 84°C. Aldrich catalog price is $12.61 per kilogram. Its theoretical oxygen demand is 1.731 g oxygen per g chemical. Its 96 hr LC50 for bluegill is 7,500 mg/L *(10)*. Its rat oral LD50 is 5,500 mg/kg *(11)*.

Dimethyl succinate: Candidate 145.01. This candidate's CAS number is 106-65-0. Its chemical formula is $C_6H_{10}O_4$. Dimethyl succinate is used as a solvent for fruit flavors and as a flavoring compound. Its melting point is 17°C *(5)*. Its flash point is 194°F *(6)*. Its Aldrich catalog price is $128.02 per kilogram. Its theoretical oxygen demand is 1.423 g oxygen per g chemical. No data was found on aquatic toxicity. Its rat oral LD50 is greater than 5,000 mg/kg *(11)*. No information on human health effects was found for this candidate. A solubility limit in water of 29% was reported *(12)*. This limit may be too low to produce the freezing point depression needed to meet our requirements. We thus recommend the following experiments to further evaluate this candidate: 1) solubility limit in water at room temperature; 2) 96 hour LC50 for ceriodaphnia dubia; 3) 96 hour LC50 for fathead minnow; 4) freezing point depression with water; 5) biological oxygen demand.

2,2-Dimethyl-1,3-dioxolane-4-methanol: Candidate 059.02. This candidate's CAS number is 100-79-8. Its chemical formula is $C_6H_{12}O_3$. An experimental value for the melting point was not found. The melting point was estimated to be 28.3°C by Joback's method *(9)*. Its flash point is 176°F *(6)* although another source *(11)* reported a much lower flash point of 99°F. Its Aldrich catalog price is $58.83 per kilogram. Its theoretical oxygen demand is 1.816 g oxygen per g of chemical. Its 96 hour LC50 for fathead minnow is 16,700 mg/L *(10)*. Its rat oral LD50 is 7,000 mg/kg *(11)*. No information on human health effects was found for this candidate. We recommend the following experiments to further evaluate this candidate: 1) pure melting point determination; 2) pure flash point determination; 3) 96 hour LC50 for ceriodaphnia dubia; 4) freezing point depression with water; 5) biological oxygen demand.

2-(2-Ethoxyethoxy)-ethanol: Candidate 157.01. This candidate's CAS number is 111-90-0. Its chemical formula is $C_6H_{14}O_3$. A common synonym is diethylene glycol monoethyl ether. It is used as a solvent in coatings and a diluent in brake fluid. Its melting point is -78°C*(34)*. Its flash point is 205°F *(6)*. Its Aldrich catalog price is $12.81 per kilogram. Its theoretical oxygen demand is 1.908 g oxygen per g chemical. Its 96 hour LC50 for fathead minnow is 9,650 mg/L *(10)*. Its rat oral LD50 is 5,500 mg/kg *(11)*. This candidate probably does not pose a serious hazard from eye contact *(12)*. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) freezing point depression with water; 3) biological oxygen demand.

Dipropylene glycol: Candidate 157.09. This candidate's CAS number is 25265-71-8. Its chemical formula is $C_6H_{14}O_3$. Dipropylene glycol is used as an antifreeze, plasticizer, solvent, and cosmetic additive. Its melting point is -40.2°C {{415 Daubert, T. E. 1989}}. Its flash point is 280°F *(6)*. Its Aldrich catalog price is $25.97 per kilogram. Its theoretical oxygen demand is 1.908 g oxygen per g of chemical. Its 24 hour LC50 for goldfish is greater than 5,000 mg/L *(10)*. Its rat oral LD50 is 14,850 mg/kg *(11)*. Industrial handling and use of dipropylene glycol should present no significant problems from ingestion, skin contact, or vapor inhalation *(12)*. A composition of 48% by weight dipropylene glycol in water would have an initial freezing point of -20°C *(8)*. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) 96 hour LC50 for fathead minnow; 3) biological oxygen demand.

Triethylene glycol: Candidate 158.01. This candidate's CAS number is 112-27-6. Its chemical formula is $C_6H_{14}O_4$. Triethylene glycol is used as a deicing fluid, humectant, solvent, lubricant, and plasticizer. Its melting point is -7°C *(5)*. Its flash point is 330°F *(6)*. Its Aldrich catalog price is $12.95 per kilogram. Its theoretical oxygen demand is 1.598 g oxygen per g of chemical. Its 96 hour LC50 for fathead minnow is 59,900 mg/L *(10)*. Its rat oral LD50 is 17,000 mg/kg *(11)*. Triethylene glycol may be considered safe for many applications where intake is limited *(12)*. Essentially no hazard exists with respect to skin and eye contact or even prolonged inhalation. A composition of 48% by weight triethylene glycol in water would have an initial freezing point of -20°C *(8)*. We recommend the following experiments to further evaluate this candidate: 1) 96 hour LC50 for ceriodaphnia dubia; 2) biological oxygen demand.

Appendix C
Potential PDM FPDs Identified in Search

Table C-1. Initial candidate FPDs.

ID	Formula	Candidate	CAS RN
0161.01	$CHKO_2$	Potassium formate	590-29-4
0162.01	$CHNaO_2$	Sodium formate	141-53-7
0165.01	$C_2H_2CaO_4$	Calcium formate	544-17-2
0167.01	C_2HNaO_3	Sodium glyoxylate	2706-75-4
0168.01	$C_2H_2MgO_4$	Magnesium formate	6150-82-9
0331.01	$C_2H_3KO_2$	Potassium acetate	127-08-2
0332.01	$C_2H_3NaO_2$	Sodium acetate	127-09-3
0335.01	$C_3H_3NaO_3$	Sodium pyruvate	113-24-6
0359.01	$C_3H_3KO_4$	Potassium beta-hydroxypyruvate	—
0360.01	$C_3H_3NaO_4$	Sodium beta-hydroxypyruvate	3431-81-0
0496.01	$C_2H_6CaO_2$	Calcium methoxide	2556-53-8
0497.01	$C_3H_5NaO_2$	Sodium propionate	137-40-6
0501.01	$C_4H_6CaO_4$	Calcium acetate	114460-21-8
0502.01	$C_4H_6MgO_4$	Magnesium acetate	16674-78-5
0504.01	$C_4H_5NaO_3$	Sodium-2-oxobutyrate	2013-26-5
0509.01	$C_6H_6CaO_6$	Calcium pyruvate	52009-14-0
0517.01	$C_3H_5NaO_3$	Sodium DL-lactate	72-17-3
0518.01	$C_3H_5KO_3$	Potassium L-lactate	85895-78-9
0521.01	$C_4H_5KO_4$	Methyl potassium malonate	38330-80-2
0636.01	$C_4H_7NaO_2$	Sodium butyrate	156-54-7
0640.01	$C_5H_7NaO_3$	3-Methyl-2-oxobutanoic acid sodium salt	3715-29-5
0651.01	$C_4H_7NaO_3$	Sodium 2-hydroxybutyrate	5094-24-6
0651.02	$C_4H_7NaO_3$	(+/-) Sodium 3-hydroxybutyrate	150-83-4
0655.01	$C_5H_7KO_4$	Ethyl potassium malonate	6148-64-7
0693.01	$C_6H_8CaO_8$	Calcium glucarate	87-73-0
0693.02	$C_6H_8CaO_8$	Calcium D-glucarate	5793-88-4
0743.01	$C_4H_{10}MgO_2$	Magnesium ethoxide	2414-98-4
0746.01	$C_5H_9NaO_2$	Sodium trimethylacetate	143174-36-1
0749.01	$C_6H_{10}CaO_4$	Calcium propionate	4075-81-4
0751.01	$C_6H_9NaO_3$	alpha-Ketohexanoic acid sodium salt	13022-85-0
0751.02	$C_6H_9NaO_3$	3-Methyl-2-oxopentanoic acid sodium salt	3715-31-9
0751.03	$C_6H_9NaO_3$	4-Methyl-2-oxopentanoic acid sodium salt	4502-00-5
0773.01	$C_6H_{10}MgO_6$	Magnesium L-lactate	18917-93-6

Table C-1. Initial candidate FPDs.

ID	Formula	Candidate	CAS RN
0776.01	$C_6H_{10}CaO_6$	Calcium L-lactate	41372-22-9
0797.01	$C_6H_{10}CaO_8$	Calcium DL-glycerate	67525-74-0
0798.01	$C_6H_9KO_7$	5-Keto-D-gluconic acid potassium salt	91446-96-7
0799.01	$C_6H_9NaO_7$	D-Galacturonic acid sodium salt	14984-39-5
0799.02	$C_6H_9NaO_7$	Sodium D-glucuronate	207300-70-7
0828.01	$C_6H_{11}NaO_2$	Sodium hexanoate	10051-44-2
0867.01	$C_6H_{11}KO_7$	Potassium D-gluconate	299-27-4
0868.01	$C_6H_{11}NaO_7$	Sodium D-gluconate	527-07-1
0879.01	$C_6H_{14}CaO_2$	Calcium isopropoxide	15571-51-4
0905.01	CK_2O_3	Potassium carbonate	584-08-7
0906.01	CNa_2O_3	Sodium carbonate	497-19-8
0911.01	$C_2K_2O_4$	Potassium oxalate	6487-48-5
0912.01	$C_2Na_2O_4$	Sodium oxalate	62-76-0
0922.01	$C_3Na_2O_5$	Sodium mesoxalate	7346-13-6
1174.01	$C_3H_2Na_2O_4$	Sodium malonate dibasic	141-95-7
1270.01	$C_3H_2Na_2O_6$	Sodium mesoxalate monohydrate	31635-99-1
1509.01	$C_4H_4Na_2O_4$	Disodium succinate	150-90-3
1520.01	$C_5H_4Na_2O_5$	alpha-Ketoglutaric acid disodium salt	305-72-6
1552.01	$C_4H_4Na_2O_5$	DL-Malic acid disodium salt	676-46-0
1566.01	$C_6H_3Na_3O_8$	Oxalomalic acid trisodium salt	89304-26-7
1589.01	$C_4H_4Na_2O_6$	L-Tartaric acid disodium salt	6106-24-7
1592.01	$C_4H_4K_2O_6$	L-Tartaric acid dipotassium salt	921-53-9
1823.01	$C_5H_6K_2O_5$	(+/-)-Potassium citramalate	—
1824.01	$C_5H_6Na_2O_5$	(+/-)-Citramalic acid sodium salt	102601-31-0
1829.01	$C_6H_5K_3O_7$	Tripotassium citrate	6100-05-6
1830.01	$C_6H_5Na_3O_7$	Trisodium citrate	6132-04-3

Appendix D

Details on Candidate PDM FPDs Recommended for Further Evaluation

FINAL CANDIDATE FPDS FOR PDMS

The following paragraphs detail information for each candidate FPD selected for experimental evaluation:

1,1,1-Trimethanolethane: Candidate 111.01. This candidate's CAS number is 77-85-0. Its chemical formula is $C_5H_{12}O_3$. Its melting point is 200.5°C *(5)*. Its flash point is 320°F *(6)*. Its Aldrich catalog price is $19.50 per kilogram. Its theoretical oxygen demand is 1.731 g oxygen per g chemical. Quantitative values could not be found for its aquatic or mammalian toxicity.

Xylitol: Candidate 113.01. This candidate's CAS number is 87-99-0. Its chemical formula is $C_5H_{12}O_5$. Xylitol is used as an artificial sweetener. Its melting point is 92.6°C *(5)*. Because it is a room temperature solid, its flash point is considered to be high. Its Aldrich catalog price is $90.40 per kilogram *(6)*. Its theoretical oxygen demand is 1.157 g oxygen per g chemical. Quantitative values could not be found for its aquatic toxicity. Its rat oral LD50 is 16,500 mg/kg *(11)*.

D-Gluconic acid, δ-lactone: Candidate 147.03. This candidate's CAS number is 90-80-2. Its chemical formula is $C_6H_{10}O_6$. It decomposes at 160°C *(6)*. Because it is a room temperature solid, its flash point is considered to be high. Its Aldrich catalog price is $93.70 per kilogram *(6)*. Its theoretical oxygen demand is 0.988 g oxygen per g chemical. Quantitative values could not be found for its aquatic or mammalian toxicity.

Trimethylolpropane: Candidate 157.03. This candidate's CAS number is 77-99-6. Its chemical formula is $C_6H_{14}O_3$. Its melting point is 60.3°C *(5)*. Its flash point is 341.6°F *(6)*. Its Aldrich catalog price is $22.83 per kilogram *(6)*. Its theoretical oxygen demand is 1.908 g oxygen per g chemical. Its 96 hr LC50 for sheepshead minnow is 14,400 mg/L *(10)*. Its rat oral LD50 is 14,100 mg/kg *(11)*.

Sodium acetate: Candidate 332.01. This candidate's CAS number is 127-09-3. Its chemical formula is $C_2H_3NaO_2$. It is a room temperature solid. Its flash point is greater than 480°F *(6)*. Its Aldrich catalog price is $72.50 *(6)*. Its theoretical oxygen demand is 0.683 g oxygen per g chemical. Its 120 hr LC50 for fathead minnow is 13,330 mg/L *(10)*. Its rat oral LD50 is 3,530 mg/kg *(11)*.

Calcium propionate: Candidate 749.01. This candidate's CAS number is 4075-81-4. Its chemical formula is $C_6H_{10}CaO_4$. Because it is a room temperature solid, its flash point is considered to be high. Its Aldrich catalog price is $26.50 per kilogram *(6)*. Its theoretical oxygen demand is 1.117 g oxygen per g chemical. Quantitative values could not be found for its aquatic toxicity. Its rat oral LD50 is 3,920 mg/kg *(11)*.

Disodium succinate: Candidate 1509.01. This candidate's CAS number is 150-90-3. Its chemical formula is $C_4H_4Na_2O_4$. Because it is a room temperature solid, its flash point is considered to be high. Its Aldrich catalog price is $58.50 per kilogram *(6)*. Its theoretical oxygen demand is 0.592 g oxygen per g chemical. Quantitative values could not be found for its aquatic or mammalian toxicity.

L-Tartaric acid dipotassium salt: Candidate 1592.01. This candidate's CAS number is 921-53-9. Its chemical formula is $C_4H_4K_2O_6$. Because it is a room temperature solid, its flash point is considered to be high. Its Aldrich catalog price is $105.20 per kilogram *(6)*. Its theoretical oxygen demand is 0.283 g oxygen per g chemical. Quantitative values could not be found for its aquatic or mammalian toxicity.

Tripotassium citrate: Candidate 1829.01. This candidate's CAS number is 6100-05-6. Its chemical formula is $C_6H_5K_3O_7$. Because it is a room temperature solid, its flash point is considered to be high. Its Aldrich catalog price is $133.50 per kilogram *(6)*. The theoretical oxygen demand is 0.392 g oxygen per g chemical. Quantitative values could not be found for its aquatic or mammalian toxicity.

Appendix E
Details on Candidate Surfactants Recommended for Further Evaluation

CANDIDATE SURFACTANTS

Detailed information of candidates from promising surfactant categories is presented.

Acetylenic diols

These surfactants are often called Gemini surfactants because they contain two symmetric hydrophobic substructures. They are reported to provide good surface tension reduction and low foaming.

- Surfynol 465: Product of Air Products and Chemicals. Reported to give good wetting. The surfactant is formed by reacting ethylene oxide oligomers with 2,4,7,9-tetramethyl-5-decyne-4,7-diol. On average there are 10 moles of ethylene oxide per mole of surfactant. The surface tension of a 1% solution with water is 25.8 dynes/cm. The surfactant's HLB is 13. The cloud point of a 5% solution is 63°C. The 72 hr EC50 for Skeletonema costatum is 93 mg/L. The rat oral LD50 is 6,300 mg/kg.

Alkoxylated branched alcohols

In this class of surfactants the hydrophobe is a branched hydrocarbon and the lipophobe is a chain of ethylene oxide and/or propylene oxide repeat units.

- Tergitol TMN-6: Product of the Dow Chemical Company. A branched secondary alcohol ethoxylate. Reported to provide superior wetting. The critical micelle concentration in water at 25°C is 800 ppm. The surface tension of a 1% solution with water is 27 dynes/cm at 25°C. The surfactant's HLB was reported to be 13.1. On average there are 8 moles of ethylene oxide per molecule. The hydrophobe is 2,6,8-trimethyl-4-nonanol. The Ross-Miles foam height for a 0.1% solution at 25°C was 150 mm initially and then 24 mm after five minutes. The cloud point of a 1% by weight aqueous solution is 36°C. The BOD was reported as 36% on day 20. The 96 hr LC50 for Pimephales promelas is 39 mg/L. The 48 hr LC50 for Daphnia is 81.2 mg/L. The rat oral LD50 is 3,260 mg/kg.

- Tergitol TMN-10: Product of the Dow Chemical Company. A branched secondary alcohol ethoxylate. The critical micelle concentration in water at 25°C is 1,313 ppm. The surface tension of a 1% solution with water is 30 dynes/cm at 25°C. The surfactant's HLB was reported to be 14.4. On average there are 11 moles of ethylene oxide per molecule. The hydrophobe is 2,6,8-trimethyl-4-nonanol. The Ross-Miles foam height for a 0.1% solution at 25°C was 118 mm initially and then 28 mm at five minutes. The cloud point of a 1% by weight aqueous solution is 76°C. The BOD was reported as 33% on day 20. The 96 hr LC50 for Pimephales promelas is 103 mg/L. The 48 hr LC50 for Daphnia is 164.9 mg/L. The rat oral LD50 is 5.65 ml/kg.

- Lutensol XP 50: Product of the BASF Corporation. An ethoxylated branched C10 alcohol. The surface tension of a 0.1% solution with water is 26 dynes/cm at 23°C. The surfactant's HLB is 10.0. On average there are 5 moles of ethylene oxide per mole of surfactant. The hydrophobe is a 2-propylheptyl group. Predicted to be readily biodegradable.

- Lutensol XP 100: Product of the BASF Corporation. An ethoxylated branched C10 alcohol. The surface tension of a 0.1% solution with water is 30 dynes/cm at 23°C. The surfactant's HLB is 14.5. On average there are 10 moles of ethylene oxide per mole of surfactant. The hydrophobe is a 2-propylheptyl group. Estimated to have an LC50 for daphnia magna between 10 and 100 mg/L. Predicted to be readily biodegradable.

Alkoxylated linear alcohols

In this class of surfactants the hydrophobe is a linear hydrocarbon and the lipophobe is a chain of ethylene oxide and/or propylene oxide repeat units. At least five moles of ethoxylation is needed for aqueous applications.

- Triton DF-16: Product of the Dow Chemical Company. The MSDS reports the product's main ingredient to be alkoxylated (ethoxylated and propoxylated) primary C8-C10 alcohols. It is reported to be readily biodegradable and a good low foaming wetting agent. The critical micelle concentration in water at 25°C is 530 ppm. The surface tension of a 1% solution with water is 30 dynes/cm at 25°C. The surfactant's HLB is 11.6. The cloud point of a 1% aqueous solution is 36°C. Eighty-two percent of the product will biodegrade in 20 days. The male rat oral LD50 is 500 mg/kg. The 96 hr LC50 for Pimephales promelas is 13.3 mg/L. The female rat oral LD50 is 616 mg/kg.

- Bio-Soft N1-5: Product of Stephan Company. Comprised of ethoxylated C11 alcohol. Reported to give moderate foam production and promote excellent wetting. The surfactant's HLB is 11.2. On average there are 5 moles of ethylene oxide per mole of surfactant. The cloud point of a 1% aqueous solution is 18°C. It is expected that 97% of this surfactant be primarily degraded in five to seven days and 84% ultimately degraded in 28 days. The 96 hr LC50 for Pimephales promelas ranges from 0.48 to 13 mg/L. The 48 hr LC50 for Daphnia magna ranges from 0.29 to 72 mg/L. The rat oral LD50 ranges from 2,000 to 3,340 mg/kg.

- Bio-Soft N1-7: Product of Stepan Company. Comprised of ethoxylated C11 alcohol. Reported to give moderate foam production and promote excellent wetting. The surfactant's HLB is 12.9. On average there are 7 moles of ethylene oxide per mole of surfactant. The cloud point of a 1% aqueous solution is 58°C. It is expected that 97% of this surfactant be primarily degraded in five to seven days and 84% ultimately degraded in 28 days. The 96 hr LC50 for Pimephales promelas ranges from 0.48 to 13 mg/L. The 48 hr LC50 for Daphnia magna ranges from 0.29 to 72 mg/L. The rat oral LD50 ranges from 2,000 to 3,340 mg/kg.

- Merpol SE: Product of the Stepan Company. Reported to be a low foaming surfactant with excellent wetting properties. Use levels typically range from 0.01 to 0.1 wt%. The surface tension of a 0.01 wt% aqueous solution is 28 dynes/cm, a 0.1 wt% aqueous solution is 27 dynes/cm, and a 1.0 wt% aqueous solution is 27 dynes/cm. The solubility limit in water is 0.1 wt%. The surfactant's HLB is calculated to be 10.5. The Ross-Miles foam height for a 0.1% solution at 40°C was 40 mm initially and 20 mm after ten minutes when conducted with soft water. The cloud point of a 1% aqueous solution is less than 3°C.

- Lutensol TDA 10: Product of the BASF Corporation. Also known as Iconol TDA-10. Comprised of ethoxylated tridecyl alcohol. Reported to have excellent rapid wetting properties and produce relatively low amounts of foam. The surface tension of a 0.1% aqueous solution is 31 dynes/cm at 25°C. The surfactant's HLB is 14.0. On average there are 10 moles of ethylene oxide per mole of surfactant.
- Plurafac S-405LF: Product of the BASF Corporation. Comprised of alkoxylated C6 to C10 linear alcohols. At 25°C the surface tension of a 0.1 wt% aqueous solution is 32 dynes/cm, a 0.01 wt% aqueous solution is 31 dynes/cm and a 0.001 wt% aqueous solution is 73 dynes/cm. The Ross-Miles foam height for a 0.1 wt% solution is 20 mm initially and 0 mm after five minutes. The cloud point of a 1% aqueous solution is 28°C. Reported to be readily biodegradable. The rat oral LD50 is estimated to be between 2,380 and 2,745 mg/kg.

Alkoxylated secondary alcohols

In this class of surfactants the hydrophobe is a secondary hydrocarbon and the lipophobe is a chain of ethylene and/or propylene oxide repeat units.

- Tergitol 15-S-7: Product of the Dow Chemical Company. Secondary alcohol ethoxylate. Reported to provide superior wetting. The critical micelle concentration in water at 25°C is 38 ppm. The surface tension of a 1% solution with water is 30 dynes/cm at 25°C. The surfactant's HLB was reported to be 12.1. On average there are 7 moles of ethylene oxide per mole of surfactant. The Ross-Miles foam height for a 0.1% solution at 25°C was 117 mm initially and then 28 mm after five minutes. The cloud point of a 1% by weight aqueous solution is 37°C. In 28 days the surfactant was more than 60% degraded. The 96 hr LC50 for this family of surfactants ranges from 3.4 to 4.9 mg/L. The 48 hr EC50 (immobilization) to Daphnia magna for this family of surfactants is 4.01 mg/L. The typical rat oral LD50 for this family of surfactants is estimated to be greater than 3,000 mg/kg.
- Tergitol 15-S-12: Product of the Dow Chemical Company. Secondary alcohol ethoxylate. The critical micelle concentration in water at 25°C is 104 ppm. The surface tension of a 1% solution with water is 33 dynes/cm at 25°C. The surfactant's HLB is reported to be 14.5. On average there are 12 moles of ethylene oxide per molecule. The Ross-Miles foam height for a 0.1% solution at 25°C is 124 mm initially and 43 mm after five minutes. The cloud point of a 1% by weight aqueous solution is 89°C. Calculated molecular weight is 728 g/mol. Chemical oxygen demand 2.15 mg/mg. Theoretical oxygen demand 2.18 mg/mg. 96 hr LC50 for Pimephales promelas ranges from 6.9 to 10.9 mg/L. 48 hr LC50 for Daphnia magna is 8.7 mg/L. The rat oral LD50 is 2,909 mg/kg.

Alkyl polyglucosides

These surfactants are reported to have low toxicity and be highly biodegradable. Unfortunately they are also noted to produce stable foams. It is most likely that these will be used in conjunction with an anti-foam.

- Triton CG-110: Product of the Dow Chemical Company. The MSDS reports the product's main ingredients are 60.0% D-glucopyranose, oligomeric, decyl octyl glycoside (CAS 68515-73-1), less than 2% decanol and less than 2% octanol. Reported to provide good wetting, be soluble in highly alkaline solutions and readily biodegradable. Also reported to produce moderately to highly stable foam. The critical micelle concentration in water at 25°C is 1748 ppm. The surface tension of a 1% solution with water is 27 dynes/cm at 25°C. The Ross-Miles foam height for a 0.1% solution at 25°C was 105 mm initially and then 100 mm after five minutes. The cloud point of a 1% by weight aqueous solution is greater than 100°C. The BOD values indicate 100% degradation on day 20. The 96 hr LC50 for Pimephales promelas is 190 mg/L. The 48 hr EC50 for Daphnia magna is 294 mg/L.

Amine EO-PO copolymers

Only a single candidate was found for this surfactant category. In general this category of surfactant is reported to provide good wetting and very low foaming.

- Tetronic 904: Product of the BASF Corporation. The surface tension of a 0.1% solution with water is 35 dynes/cm at 25°C. The surfactant's HLB is between 12 and 18. The cloud point of a 1% aqueous solution is 74°C.

EO-PO copolymers

These surfactants are known to have low aquatic toxicity and be very low foaming. Unfortunately the presence of the propylene oxide chain inhibits biodegradation. Candidates from this category must be carefully evaluated to ensure they are not persistent in the environment. The surface tension of these surfactants is also higher than desirable. It is very likely they will need to be used in combination with a co-surfactant.

- Tergitol L-64: Product of the Dow Chemical Company. Reported to give good wetting, high thermal and chemical stability, and provide efficient foam control. The surface tension of a 1% solution with water is 44 dynes/cm at 25°C. The surfactant's HLB was reported to be 15. The Ross-Miles foam height for a 0.1% solution at 25°C was 48 mm initially and then 18 mm after five minutes. The cloud point of a 1% by weight aqueous solution is 62°C. Biodegradation is greater than 60% after 28 days. LC50 for aquatic organisms is greater than 100 mg/L in the most sensitive species tested.
- Pluronic L44 NF: Product of the BASF Corporation. The surface tension of a 0.1% solution with water is 45 dynes/cm at 25°C. The surfactant's HLB is between 12 and 18. The cloud point of a 1% aqueous solution is 65°C. Biodegradation is report to be between 0 and 10% at 28 days. The 96 hr LC50 for rainbow trout is estimated to be greater than 46.4 mg/L. The 48 hr EC50 for daphnia magna is estimated to be greater than 100 mg/L.

Ethoxylated alkanolamides

These surfactants have similar properties to ethoxylated alcohols. They are also more expensive than ethoxylated alcohols.

- Triton CF-32: Product of the Dow Chemical Company. The hydrophobe is an oligomer of propylene oxide. Reported to have exceptionally low foaming. The surface tension of a 1% solution with water is 37 dynes/cm at 25°C. The surfactant's HLB was reported to be 11. The cloud point of a 1% by weight aqueous solution is 25°C. Only 34% is biodegraded after 20 days. The 96 hr LC50 for Pimephales promelas is 412 mg/L. The 96 hr LC50 for rainbow trout is 186 mg/L. The 48 hr EC50 for Daphnia is 660 mg/L. The male rat LD50 is 1,414 mg/kg.

Other Surfactants

Although three additional classes of surfactants were considered, specifically dialkyl dimethyl polysiloxanes, ethoxylated ether amines and ethoxylated fatty amines, no candidates were found with satisfactory properties.

Antifoams

These chemicals destabilize the liquid-air interface causing foam coalescence and breakage. Some of these products are dispersible but not soluble in water. Anti-foam dispersions may give a cloudy appearance to deicing and anti-icing fluids. Typically anti-foams are used in concentrations ranging from 0.02 to 0.05 wt%.

- Pluriol P1000: Product of the BASF Corporation. This anti-foam is a polypropylene glycol with an average molecular weight of 1000. Its solubility in water at 25°C is 0.22 wt%. The 96 hr LC50 for golden orfe is estimated to be greater than 100 mg/L. The rat oral LD50 is estimated to be greater than 2,000 mg/kg.

- Pluronic L101: Product of the BASF Corporation. This anti-foam is an EO-PO block copolymer. It has an HLB ranging from 1 to 7. It is not soluble in water. The 96 hr LC50 for golden orfe is estimated to be greater than 100 mg/L.

- Ridafoam NS 221: Product of the BASF Corporation. This anti-foam is non-silicone based. It is comprised of at least 80 wt% paraffin oils and petroleum distillates. The 96 hr LC50 for rainbow trout is reported to be greater than 1,000 mg/L. The 48 hr LC50 for daphnia magna is reported to be greater than 1,000 mg/L. The rat oral LD50 is reported to be greater than 5,000 mg/kg.

Appendix F
Candidate Corrosion Inhibitors Recommended for Further Investigation

INITIAL CANDIDATE CORROSION INHIBITORS

Mazon RI 325: Candidate 04.001—a product of the BASF Corporation. Unknown composition. Free of nitrites, nitrates, chromates and phenolics. Protects aluminum and steel. No information on toxicity or biodegradability was found.

Ammonyx CDO Special: Candidate 04.002—a product of the Stepan Company. Cocoamido-propylamine oxide. No information on aquatic toxicity or biodegradability was found. The rat oral LD50 is between 500 and 5,000 mg/kg.

Ninol 1301: Candidate 04.003—a product of the Stepan Company. A PEG-6 cocamide. No information on aquatic toxicity or biodegradability was found. The mouse oral LD50 is 3,300 mg/kg.

Ninol 201: Candidate 04.004—a product of the Stepan Company. Produced by condensing one mole of oleic acid with two moles of diethanolamine. No information on aquatic toxicity or biodegradability was found. The mouse oral LD50 is 3,300 mg/kg.

Ninol SR-100: Candidate 04.005—oleic diethanolamine produced by the Stepan Company. No information on aquatic toxicity or biodegradability was found.

Korantin SMK: Candidate 04.006—a product of the BASF Corporation. Reported to provide superior corrosion protection for aluminum in alkaline media. An organophosphate based corrosion inhibitor. No information on aquatic toxicity or biodegradability was found.

DrewPlast 154: Candidate 04.007—a product of the Stepan Company. Lauryl diethanolamide. No information on aquatic toxicity or biodegradability was found. The rat oral LD50 is 2.700 mg/kg.

Cobratec 948: Candidate 04.008—a product of PMC Specialties Group, Inc. Unknown composition. Recommended for use in aircraft and runway deicing fluids. Sold as a liquid containing 85% of a proprietary multi-metal corrosion inhibitor. Will need to be checked for the presence of triazoles. No information on aquatic toxicity or biodegradability was found.

3-Methoxypropylamine: Candidate 04.009—the 96 hr LC50 for golden orfe is between 100 and 220 mg/L. The rat oral LD50 is 690 mg/kg.

Triethanolamine: Candidate 04.010—the 96 hr LC50 for lepomis macrochirus ranges from 450 to 1000 mg/L. The rat oral LD50 is 4,920 mg/kg. This chemical is expected to readily biodegrade.

Potassium phosphate: Candidate 04.011—reported as a possible corrosion inhibitor in runway deicing chemicals.

Potassium silicate: Candidate 04.012—reported as a possible corrosion inhibitor in runway deicing chemicals.

Potassium carbonate: Candidate 04.013—reported as a possible corrosion inhibitor in runway deicing chemicals.

Potassium laurate: Candidate 04.014—reported as a possible corrosion inhibitor in runway deicing chemicals.

Potassium stearate: Candidate 04.015—reported as a possible corrosion inhibitor in runway deicing chemicals.

Sodium silicate: Candidate 04.016—reported as a possible corrosion inhibitor in runway deicing chemicals.

Sodium borate decahydrate: Candidate 04.017—reported as a possible corrosion inhibitor in runway deicing chemicals.