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ENVIRONMENTALLY BENIGN DEICING/ANTI-ICING TECHNOLOGY

Richard S. Sapienza
Kenneth J. Heater

METSS Corporation
720 G. Lakeview Plaza Blvd
Columbus, OH 43085

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MATERIALS & MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7734

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THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

Jaime S. Tiley
JAIMIE S. TILEY
Pollution Prevention R&D
Materials Engineering Branch

William E Berner
WILLIAM E. BERNER
Assistant Chief
Systems Support Division

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Richard S. Sapienza
Kenneth J. Heater

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METSS Corporation
720 G. Lakeview Plaza Blvd
Columbus, OH 43085

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MATERIALS & MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
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Under a Phase I SBIR program, METSS has demonstrated the technical feasibility of developing environmentally benign deicing/anti-icing fluids based on glucose, lactates, and their salts. Models developed by METSS to identify potential replacement materials for the current glycol-based systems governed the selection of these materials. These simple models take into account a number of physical, chemical, and structural attributes determined to be important to materials that exhibit good deicing/anti-icing behavior. Known structural attributes for biodegradability governed the selection of materials that would address environmental concerns. The formulations developed by METSS were subjected to tests derived from SAE AMS 1424. BOD and COD tests were performed to assess environmental impact. The results of the Phase I program clearly indicate the technical feasibility of developing *direct replacement* deicing/anti-icing fluids based on glucose and lactate systems that address environmental impact issues without compromising performance. Near term commercialization of the proposed systems is assured by the abundant supply of these low cost agricultural products, low processing costs, and a number of parties who have a vested interest in expanding markets for these materials. Further development of the proposed technologies should emphasize performance optimization, materials compatibility testing and formulation optimization efforts needed to support full qualification testing against AMS 1424 and 1428 specifications.

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TABLE OF CONTENTS

1.0 PROGRAM OBJECTIVES

The objectives of the SBIR program as defined by the Air Force are presented in this section along with the primary objectives METSS set forth in its Phase I program plan to achieve the goals of the program.

1.1 SBIR Program as Defined by the Air Force

OBJECTIVE: Develop an environmentally benign aircraft deicing/anti-icing agent.

DESCRIPTION: The use of glycols as aircraft deicers has come under scrutiny due to the Clean Water Act. Ethylene glycol is toxic and is no longer purchased by the Airforce for the purpose of deicing, while propylene glycol based deicers have a significant adverse environmental impact in surface and groundwater from airfield runoff due to the high biological oxygen demand (BOD) of glycol degradation. Alternative materials are being sought to replace glycol-based aircraft deicers. The USAF is seeking to develop an environmentally benign deicing/anti-icing agent that eliminates or significantly reduces the BOD of airfield runoff, is nontoxic, noncorrosive, to aircraft components, and cost-effective. Life Cycle Cost Assessment shall be included in each phase. This assessment will represent the systematic process in the life cycle by identifying environmental consequences and assigning monetary value.

PHASE I: Phase I research should require the development and testing of a alternative deicing material that demonstrates acceptable deicing/anti-icing performance (using SAW AMS 1424 and/or 1428 as a performance guideline), is noncorrosive to common aerospace materials, nontoxic, and environmentally acceptable. Included with this phase will be life cycle analysis for the alternatives. The approach to selection will be a rational design that includes computational prediction of properties i.e. toxicity and partition coefficient, understanding of icing mechanism as well as syntheses and testing of candidate materials.

PHASE II: Phase II should include the identification of a few candidates, further testing and development to support the performance and environmental acceptability of the deicing/anti-icing agent(s), as well as the fabrication and demonstration of a prototype delivery system to apply the material(s) developed for the purpose of deicing an aircraft. Included with this phase will be life cycle analysis of alternate agent(s), processes, system, or facility.

POTENTIAL COMMERCIAL MARKET: The proposed deicing technology would have broad applications in the civil aviation community as well as potential for cross-over into runway and roadway deicing applications.

1.2 Major Phase I Objectives

When the SBIR program was initiated, METSS set forth the following specific objectives to develop direct replacement deicer/anti-icing fluids:

1. Identify candidate materials and industrial suppliers to support the program development efforts using a rational approach to design and chemical selection based on theoretical models and computational methods of prediction.
2. Devise a sound strategy for screening candidate materials and directing the formulation development effort that includes a tiered approach to testing (saving the more expensive and time consuming tests for the best qualified materials), utilizes models and predictive techniques to screen and evaluate the performance of candidate materials, provides the data needed to direct formulation development and optimization efforts, and sets a solid foundation for Phase II development efforts.
3. Identify at least three formulations that merit subsequent evaluation and development under a Phase II program, i.e., candidates which are economically sound, environmentally friendly, biodegradable, and have the physical properties to serve as direct replacement deicing/anti-icing fluids for DoD and commercial aircraft applications.
4. Consider cost-of-ownership issues in the selection of new candidate formulations and ensure the technologies considered are commercially viable alternative to the existing glycol systems.
5. Cultivate a working relationship with the industrial program participants to optimize program success and establish a solid foundation for subsequent commercialization efforts.

2.0 PROGRAM SIGNIFICANCE

Exposure to weather conditions on the ground that are conducive to ice formation can cause accumulation of frost, snow, slush, or ice on aircraft surfaces or components of the aircraft that are critical to safe flight. The air worthiness of the aircraft can be restored if the frozen deposits are removed with deicing agents. Aircraft deicing fluids typically contain at least 50% glycol, with the balance being water, corrosion inhibitors, viscosity modifiers, wetting agents and dyes. Corrosion inhibitors are necessary to protect the materials used in the construction of the aircraft, while wetting agents ensure complete coverage of the surfaces being treated. Viscosity modifiers are used to tailor the performance properties of the fluids to ensure adequate protection against ice formation during short (Type I fluids) and long (Type II fluids) hold-over periods prior to take-off.

It has been estimated that between 49 and 80% falls to the apron when deicing solutions are applied to aircraft unless the fluid is captured for recycling. The deicing solution flows away to be further diluted and possibly mixed with runway runoff and other local sources of storm water. Ethylene glycol and propylene glycol are currently used in aircraft deicing but both of these materials have come under scrutiny due to the Clean Water Act. Ethylene glycol-based fluids are toxic and require expensive treatment and disposal. Propylene glycol, although non-toxic, biodegrades too rapidly imposing excess oxygen demand on the environment or the waste treatment facility. As a consequence of these factors, new and more environmentally benign deicing/anti-icing compounds are needed to replace the large quantities of glycol-based runway and wing deicers used at military and civilian airports. The size of this market is significant at over 25 million gallons per year with a material cost of about $.60/pound.

Environmentally friendly deicing/anti-icing materials developed should meet or exceed the performance of the existing glycol systems, providing a *direct replacement* alternative to existing MIL-A-8243D materials. Emphasis should be placed on materials and system compatibility issues to ensure an easy transition into the field. New materials should be cost effective and readily available, providing a near term solution to the existing Air Force need. Total *cost-of-ownership* issues should be addressed at each stage of the development process that include material costs, usage, and disposal costs.

3.0 BACKGROUND

3.1 Deicing/Anti-icing Procedures

Deicing is a procedure by which frost, ice or snow is removed from the aircraft to provide clean surface. *Anti-icing* implies the application of a fluid that provides protection against the formation of frost and ice, or the accumulation of snow on the surfaces of an aircraft for a limited period of time. These steps can be performed sequentially or together.

Deicing may be accomplished by the use of chemicals, heat, or mechanical means. In practice all three methods are usually combined since:

- the use of chemicals alone would be too costly for melting accumulations of snow or ice
- heat alone would require a special building to prevent heat losses
- pure mechanical methods may damage the aircraft (although new ultrasonic techniques are currently being developed by NASA Lewis that may make pure mechanical methods possible).

Typically, frozen accumulations are removed by deicing fluids that are applied at high temperatures (approximately 70 to 80°C) and pressures. The synergistic action melts the ice, snow, or frost and breaks the adhesion of the ice to the surface of the aircraft. The deicing procedure leaves the surface of the aircraft wet, so in order to guard against re-freezing the deicing fluid must contain a sufficient amount of freezing point depressant to lower the freezing point of the residual fluid on the aircraft below ambient or surface temperatures. The FAA Advisory Circular 20-117 recommends that “the freeze point of the residual fluids should not be greater than 11°C (20°F) below ambient or surface temperature, whichever is less”. The use of neat deicing fluids for anti-icing provides some limited protection against re-freezing during light precipitation conditions. At low volume airports where taxi times are low, neat deicing fluids work effectively to retard re-freezing during taxiing and takeoff under light precipitation and frost-forming conditions, and thus allow airport operations to proceed uninterrupted.

Deicing fluids cannot be used for anti-icing purposes during heavy precipitation or freezing rain conditions. During precipitation or frost-forming conditions, deicing fluids only offer time-limited protection against re-freezing and ice or snow buildup. Precipitation will dilute the residual fluid, raising its freezing point, and freezing on the surface of the aircraft may occur. Additionally, dilution of the residual fluid by ensuing precipitation lowers the viscosity of the fluid, reducing the film thickness of the fluid remaining on the aircraft, and eventually flushing the fluid from the aircraft surfaces. For these reasons, the FAA recommends that a close inspection of the aircraft be performed immediately prior to takeoff to ensure that it is aerodynamically clean and free of ice, snow, or frost accumulations. Frozen deposits, if left untreated, can significantly affect the aerodynamic performance of the aircraft by reducing lift and altering thrust and drag characteristics. Additionally, severe damage to the engines may occur if ice buildup on the wings dislodges during the takeoff run and strikes the turbine fan blades. Thus, removal of frozen accumulations from aircraft surfaces prior to takeoff is required by the FAA's clean aircraft concept which states that "flight, following ground operations conducive to aircraft icing, should not be attempted unless it is ascertained that the aircraft is free of any ice formations that may degrade the aircraft's performance or change its flight characteristics".

During precipitation or frost-forming conditions, several techniques may be used to maintain an aerodynamically clean aircraft following deicing, through rotation and takeoff. Most desirably, the deicing operation should be performed as close to the takeoff point as possible. End of the runway deicing is practiced at several airports in the United States. This procedure eliminates the possibility of re-freezing prior to takeoff, since takeoff commences immediately following the deicing procedure. End of the runway deicing is considered remote deicing since the deicing operation is removed from the gate and terminal area. Remote deicing can be performed by either using a mobile facility which includes several deicing trucks working in tandem, or by using a fixed facility, usually a "drive through" station. One type of fixed facility, referred to as a "car wash" system, is a large structure that surrounds the aircraft and deices using multiple spray nozzles fixed to the structure at adjustable angles. Both systems, mobile and fixed, have distinct advantages. Mobile facilities lend flexibility for reconfiguring depending on storm conditions; and fixed facilities enable collection of spent deicing fluid and thus ease the management of storm water runoff.

Although end of the runway deicing is the only reliable method for ensuring that an aircraft is aerodynamically clean at takeoff during precipitation conditions, many airports are configured such that they do not permit end of runway deicing. At these facilities, anti-icing techniques must be employed if takeoff during precipitation is to be permitted and long taxi times and delays are expected. Anti-icing fluids must only be applied to aerodynamically clean surfaces (their application therefore following deicing procedures). Anti-icing fluids serve to protect the clean surfaces of the aircraft from further accumulations of frozen deposits for a finite period of time.

3.2 Conventional Fluids

Aircraft *deicing* fluids typically contain at least 90% glycol, with the balance being water, corrosion inhibitors, wetting agents, and an orange dye (blue dyes may be used for runway deicers). The corrosion inhibitors (e.g., phosphates, nitrates, borates and silicates) are necessary to protect the materials used in the construction of the aircraft. Military formulations (MIL-A-8243B Amendment 4, 8/75) may also contain a triazole compound (0.5% benzotriazol or tolyltriazole) to reduce the hazard of fluid decomposition on noble metal electrodes. Wetting agents (nonionic and anionic surfactants are typically used due to their superior performance on metal surfaces) ensure complete coverage of the surfaces being deiced. A small amount of water may be used to solubilize the additives and raise the flash point of the fluid. In practice, deicing fluids are typically diluted prior to use, to achieve maximum freeze point depression.

Traditionally, in North America, anti-icing has been performed using cold, undiluted deicing fluids. The freezing point of these fluids decreases when diluted with precipitation and the residual fluid provides the needed protection against re-freezing. However, during certain weather conditions, because of the low film thickness and low viscosity of these fluids, the fluids can run off the surface of the aircraft before its freeze protection is depleted. Because of the time-limited protection that deicing fluids provide, and because of the rapidly increasing air traffic and subsequent longer taxi times, thickened, non-Newtonian anti-icing fluids are being investigated for use at several of the larger airports in North America. These "Type II fluids" (with the conventional, non-thickened fluids being Type I) contain a pseudo-plastic thickening agent that increases the fluid's viscosity and allows the fluid to adhere to aircraft surfaces. The thick protective film provides a longer holdover time, especially in conditions of freezing precipitation.

The current aircraft *anti-icing* fluids (AAFs) contain glycols for freeze point depression, with added water, corrosion inhibitors, wetting agents, and stabilizers. Thickening agents may be used in Type II fluids to increase the fluid's viscosity and allow the fluid to adhere to the aircraft surfaces. Current AAFs contain a minimum of glycol (usually 50 - 60%), and enough water to solubilize the thickening agent. Because of the water added to solubilize the thickener, the neat anti-icing fluid has already achieved its minimum freezing point. Further dilution of the fluid increases the freezing point and reduces its protection against re-freezing. Anti-icing fluids are typically colorless.

The thickening agents used in the Type II fluids give the fluid its non-Newtonian behavior, and enhance its anti-icing protection. Non Newtonian fluids are defined as fluids with a viscosity dependent on shear, i.e. the fluid has a higher viscosity at low shear rates and a lower viscosity at higher shear rates. The non-Newtonian design is critical to the performance of AAFs. When the aircraft is stationary or taking off, the fluid is at low shear, the fluid's viscosity is high, and its high viscosity prevents flow, thus enabling it to adhere to the aircraft surface. During the takeoff run, the fluid experiences high shear, its viscosity is reduced, and the fluid flows from the aircraft. Early non-Newtonian fluids had high viscosities which were found to have adverse effects on the aerodynamic performance of the aircraft, reducing the lift coefficient at takeoff by greater than 12%. Current non-Newtonian fluids have substantially lower viscosities and lower lift losses of 2-7%, as compared to Type I ethylene glycol-based deicing fluids, which have lift losses of 1-3%.[1] The anti-icing fluids, when applied to a clean aircraft, form a high viscosity, protective layer on the surface of the aircraft and block the adhesion of frozen deposits. However, the protection provided by these fluids is time limited. The amount of anti-icing protection they provide (defined as the holdover time) varies tremendously with weather conditions (temperature, type, and rate of precipitation), type of fluid used, and type of aircraft anti-iced. Because of these varied and ever-changing conditions, the holdover times for anti-icing fluids cannot be predicted. Inspection of the aircraft immediately prior to takeoff is necessary at all times to ascertain that all aerodynamic surfaces are free of adhering ice, snow, or frost.

3.3 The Need for New Deicing/Anti-icing Fluid Technology

Aircraft deicing and anti-icing fluids based on glycol chemistries (ethylene glycol and propylene glycol) are currently used by military and commercial operations. However, these materials have come under scrutiny due to the Clean Water Act. Ethylene glycol-based fluids create a hazardous waste, requiring expensive disposal. Propylene glycol, although non-toxic, biodegrades too rapidly imposing a large oxygen demand on the environment or the waste treatment facility. This can lead to environmental problems, including *fish kill* in natural waterways. To compensate for this, airports using propylene glycol-based deicing fluids must reduce the rate at which they feed the runoff to the waste treatment facility. *Accordingly, new biodegradable and environmentally benign deicing/anti-icing compounds must be developed for aircraft and runways with performance equal to or better than current compounds.*

4.0 PHASE I PROGRAM

METSS developed a Phase I program plan that was divided into three major thrust areas. Each of the thrust areas was then divided up into a number of specific tasks that were discussed in detail in the original proposal. Actual efforts performed to support the Phase I development efforts were defined through continued interaction with the program sponsors and largely dictated by the successes encountered as a results of model development, formulation, testing and evaluation efforts. A review of the Phase I program development efforts is presented in this section.

4.1 Model Development Efforts

A critical technical evaluation was performed on available candidate deicing/anti-icing materials (including propylene glycols) to identify the physical, chemical, and/or structural characteristics that make these deicing/anti-icing materials effective. These elements

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[1] Ethylene Glycol Product Information Bulletin, Union Carbide Chemicals and Plastics Co., Danbury, Conn., 1990.

formed the basis for models developed by METSS to screen and select additional materials that could potentially demonstrate favorable deicing/anti-icing behavior.

Some of the models developed and used by METSS to support the Phase I program efforts were mathematical in nature. For instance, freezing point depression follows Raoult's law, i.e., the performance of a given compound as a freezing point depressant is proportional to the number of molecules (or ions) of solute per unit solvent (water). This would imply that high solubility, lower molecular weight materials are most desired. For example, only 46 g (1 mole) of methanol will depress the freezing point of 1 kg water the same extent (1.86°C) as will 342 g (1 mole) of sugar. However, mathematical models are limited in their application to estimating colligative properties and rarely take into account the structural/physical characteristics that can dominate molecular interactions and ultimately dictate physical behavior. For example, based solely on colligative properties, one would estimate the freezing point depression of propylene glycol in water (50/50 solution) to be -12.2 °C, while in actuality it is -32 °C. Thus, METSS placed significant emphasis on identifying structural characteristics that would favor good deicing/anti-icing performance.

Other rationale for the model development efforts included a simple evaluation of ice formation and melting processes and consideration of factors affecting chemical solution processes. Melting is generally carried out by application of heat, requiring approximately 80 calories per gram mole of water. Heat can be provided by direct heating, radiation absorption processes, or chemical methods including heat of solution. Heat of solution is the net energy generated during solvent-solute interactions. When a salt or chemical is dissolved in water, it destroys some of the hydrogen bonding or ionic bonding inherent to the chemicals (water or deicing fluid) followed by establishing new bonds (hydrogen bonding) with water. If the energy associated in the second step is greater than the energy required in the first step, then the system becomes exothermic. In other words, the system releases heat which is essential for melting the ice as well as dissolving water in large scale. For example, the solution of a salt in water is a two step process, namely (1) breaking of ionic bonds to create free salt ions and (2) hydration of the salt ions.

Hydration of the ions is a strong exothermic process and the energy released exceeds the heat required for the ionization process. The steps involved in the solubility of liquid in water are similar in nature, but may involve the loss of associative bond interactions of the liquid solute with its own neighbors and the formation of associative bonds with water. In water, associative bond formation involves hydrogen bonding. If the number of bonds are greater and stronger than the bonds destroyed in step 1, then an exothermic reaction takes place creating a solution with water. A largely exothermic process can produce enough excess heat to lead to melting. In other words, solvents which are largely soluble in water and the ones which can dissolve salts or other solute atoms with large water of hydration would be good deicing fluids. Further, since the depression of freezing point is proportional to the total number of moles of ions in the solution, strong electrolytes containing multivalent cations and/or anions in fluids with high dielectric constant should be ideal for deicing. The ideal liquid for deicing should be: (1) a good solvent for water and (2) a good solvent for easily ionizable salts with more than two ions.

Solubility parameters will end up playing a large role in defining these potential interactions. The smaller the difference in the solubility parameters or two liquids, the greater the probability mutual solubility will occur. In case of hydrogen bonded liquids such as water, it will largely depend on the difference in the hydrogen bonding component of the solubility parameter. Since water is highly polar, the oxygen to hydrogen ratio in a molecule gives a rough approximation of its polar interaction and hydrogen bonding capacity. In addition, for ionic species, the capacity of a liquid to ionize a salt depends on its dielectric constant. The higher the dielectric constant, the greater the degree of ionization. Dielectric constant is directly proportional to polarizability and can be used as a measure of polar bonding capacity, along with the ratio of oxygen atoms to hydrogen atoms in the molecular unit. Table 4.1 provides a list of selected solvents, their Hildebrand solubility parameter (δ_t), the hydrogen bonding component (δ_h) of the solubility parameter (as defined by Hansen), and dielectric constant (K). This table is provided for illustrative purposes only.

Table 4.1. Candidate Deicing Materials

Liquid	δ_t	δ_h	K
Water	23.4	16.7	0.5
Methyl alcohol	14.5	10.9	0.25
Ethylene glycol	14.6	12.7	0.33
Propylene glycol	14.6	11.4	0.22
Glycerol	16.5	8.5	0.25
Ethylene Carbonate	14.7	5.5	0.33
Propylene Carbonate	13.3	2.0	0.22
Formamide Acetamide	19.2	9.3	0.33
Methyl Formamide	16.3	8.5	0.20
Ethyl Formamide	13.9	8.5	0.15
Methyl Acetamide	14.6	8.5	0.33
Pyrrolidone	14.1	8.5	0.15
N Methyl L Pyrrolidone	11.3	5.5	0.11
Propiolactone	13.3	5.5	0.50
Butyrolactone	12.6	5.5	0.33
Furfural alcohol	12.5	8.5	0.25
Ethyl Lactate	10.0	5.5	0.38
Caprolactan	12.7	5.5	
Piperidone	13.6	8.5	
Methyl Ethyl Sulfone	13.4	5.5	

A combination of solvents can also be used in formulation development efforts to achieve a balance of properties that might not be achievable using single component additions to water. In these formulations, one solvent may be good for solubilizing water and the other may be very good for dissolving salts.

4.2 Literature and Commercial Review

At the onset of the program, a literature and market survey was conducted to establish a background and framework to compare various state-of-the-art deicing agents and to identify available technologies that could serve as alternatives to the glycol systems currently used by the Air Force. The intent of the literature search was to identify materials currently being used or being developed for deicing/anti-icing applications, and to investigate the properties of other materials METSS identified as having specific deicing/anti-icing potential. Potential material suppliers were identified as part of this review. Technologies identified as having specific merit were incorporated into the METSS materials evaluation program. The following guidelines were followed during the initial literature survey:

Materials Wanted:

- known glycol substitutes
- existing roadway or other deicer/anti-icing materials
- readily available materials

Materials Avoided:

- known environmental toxins, e.g., ammonium/amine containing compounds
- known corrosive materials, e.g., chloride, nitrates, sulfates, phosphate salts
- low molecular weight alcohols and glycols
- materials lacking near-term commercial potential
- high cost specialty materials (e.g., cosmetic humecants).

4.3 Industry Participation

After selecting the Phase I candidate materials, METSS contacted industry suppliers to solicit industry participation in the SBIR program and obtain samples to support the Phase I program efforts. Interested parties worked interactively with METSS to formulate and reformulate candidate materials at their own expense, thus augmenting the Phase I efforts undertaken by METSS with additional lab support and technical expertise. Continued industry involvement in the Phase II program will establish a solid foundation for product commercialization, facilitating technology transfer and decreasing the time it takes to get the final product formulations to market. A summary of the industry participants in the Phase I program is provided in Table 4.2, along with a description of the product support provided.

Table 4.2. Phase I Program Participants

Supplier	Product Description
Ajinomoto Co, Inc.	lactic acid-based humectant
Alzo,Inc.	sugar-based additive
Horizon Products	glucoside chemicals
UBE Industries	glycerin carbonate
SPI Polyols	sorbitol chemicals
Cryotech	CMA, KAc acetates
Purac America, Inc.	lactates
Minnesota Corn Processors	corn stillage and steepwater
IceBan America	fermentation waste
KMCO	acetate and formates
Great Lakes Chemical	furfuryl chemicals
Octagon Processing	MIL-A-8243D control and formate

4.4 Formulation Development

The formulation development efforts followed a strict regiment outlined as follows:

- Initial Screening - Properties of candidate materials were screened to establish baseline properties.
- Initial Formulation - Initial formulations of the best candidate materials were prepared based on the best available data.
- Formulation Optimization - Initial formulations were optimized through an iterative process of formulation, testing and evaluation and reformulation.
- Down-Selection - The field of potential candidate deicing/anti-icing formulations was narrowed through the course of the optimization efforts.
- Final Selection – The best performing formulations were selected for further development under a well defined Phase II program plan.

A number of different materials were identified as potential formulation candidates to support the Phase I materials development efforts. Under ideal circumstances a single base-stock material would be used and formulation development efforts would be limited to maximizing such factors as water miscibility, wetting, corrosion protection, viscosity, etc., and determining the exact amount of base-stock material needed to maximize freezing point depression. However, based on the models developed by METSS, we fully expected our best performers would be mixtures of one or more of these components. Thus, formulation development efforts were quite extensive as consideration had to be given to a number of additional factors including component ratios, molar volumes, chemical stability, and low temperature miscibility. Furthermore, since METSS was trying to identify and maximize synergistic effects between two or more of these materials, which are not easily modeled, an Edisonian approach was required to identify these relationships and maximize their effect through repeated formulation, testing and evaluation efforts.

METSS typically used the models developed to determine which materials were likely to exhibit favorable synergistic behavior, and then prepared and tested a series of formulations to identify starting points for performance optimization (including single component testing). Freezing point depression experiments were used as the primary means of screening materials candidates. Once favorable formulations were developed (i.e., formulations meeting the freezing point depression requirements of AMS 1424), further formulation modifications were limited to adjusting such factors as pH and viscosity. METSS endeavored to develop formulations with a pH in the range of 4-8 to minimize potential problems with materials compatibility. Methods were identified to modify the viscosity of the optimized formulations to match that of the MIL-A-8243D glycol control (50% water).

4.5 Phase I Testing and Evaluation Efforts

The major challenge of any *Testing and Evaluation* program is to define a set of criteria that can be used to develop and qualify candidate materials for further development and eventual qualification as replacement fluids. A tiered approach to testing and evaluation is preferred. The first tier of testing and evaluation is defined so that a large number of materials or formulations can be screened efficiently and effectively. The results of the materials screening studies (first tier) can then be used to:

1. eliminate candidate materials that demonstrate no potential for further development
2. provide the information needed to direct subsequent formulation, reformulation, and optimization efforts.

The second tier of testing and evaluation is more extensive, designed to evaluate some of the more critical performance characteristics of the best candidate formulations. The results of the second tier of testing and evaluation can be used to:

1. perform the final down-selection of candidate materials for further development under the Phase II program effort
2. provide the information needed to direct initial Phase II optimization efforts.

The final tier of testing and evaluation will be the battery of tests and evaluation procedures that need to be completed to fully qualify the new materials prior to commercialization. Most of these tests will be performed under the Phase II program.

The Phase I materials were evaluated according to a test protocol developed by METSS and the Air Force. The performance criteria for deicing fluids have traditionally been governed by specifications of the Aerospace Division of Society of Automotive Engineers (SAE), specifically SAE AMS 1424 and/or 1428. As such, SAE AMS 1424 (Type I fluids) and 1428 (Type II fluids) were used as guidelines for evaluating the candidate materials. Emphasis was placed on developing Type I fluids under the Phase I program. The test protocol developed was established to provide a metric by which the Phase I candidate materials could be screened and evaluated for their potential as direct replacement deicing/anti-icing fluids. Simple and fast screening tests were used to evaluate large numbers a candidate materials and formulations, followed by more expensive and time consuming tests after the candidate field was narrowed to the most promising materials. This type of "tiered testing" approach allowed METSS to place an emphasis on materials development and demonstrate the *technical feasibility* of using the candidate fluids for deicing/anti-icing applications under the Phase I program without prematurely addressing other qualification issues.

Testing and evaluation efforts performed under the Phase I program included:

- **BOD/COD Testing** - BOD testing provided a measure of environmental impact relative to existing glycol-based formulations (BOD: biological oxygen demand; COD: chemical oxygen demand, often referred to as TOD: total oxygen demand).
- **Toxicology Assessment -** For each of the material candidates, available chemical information was gathered to support a toxicological assessment.
- **H_2O Solubility Limits** - As the formulations developed need to be miscible with water across a broad range of concentrations and temperatures, so experiments were performed to determine the extent of miscibility with water, i.e. the concentration range over which a single miscible phase existed.
- **Heat of Solution Experiments** - A heat of solution less than or equal to zero (more exothermic) ensures solution readily mixes with water; in addition, more exothermic reactions may indicate better deicing potential. Thus, experiments were performed to determine which materials not only formed miscible solutions, but how much heat was generated as the liquids forming the solution were mixed.
- **Differential Scanning Calorimetry Experiments (DSC)** - DSC experiments were used as an initial measure of T_m and the change in T_m with H_20 concentration. The DSC traces also provided some valuable insight with regard to phase behavior and provided valuable insight into the crystalline nature of a number of the candidate materials. The appearance and disappearance of crystallinity with water content may be linked to molecular level behavior favoring freezing point depression.
- **ASTM D1177 - Freezing Point of Aqueous Engine Coolants** - ASTM D1177 was used as a final measure of performance for the deicing/anti-icing fluids developed, providing standardized freezing point depression data in accord with the AMS specifications.

- **Viscosity** - Viscosity measurements were performed to determine the relative potential of formulating the candidate replacement materials with a viscosity in the range of conventional MIL-A-8249D compliant deicing fluids. Similar viscosity profiles will help ensure deicing/anti-icing performance and ensure the replacement materials can be applied using existing delivery systems.
- **Modified WSET Testing** - METSS constructed a modified WSET chamber with test conditions identical t those spelled out in AMS 1424, however test are run for set period of time and compared to glycol control instead of timing the progression of ice formation. This apparatus will be used to support Phase II testing and evaluation efforts, saving time and dollars by allowing METSS to perform quick in-house testing to verify and optimize fluid performance before going to more expensive AMS qualification testing.
- **pH** – The pH of each of the formulations was determined to provide some assurance of materials compatibility.
- **Materials Compatibility** – Materials compatibility is a critical element of the program development efforts, as the replacement fluids developed must be compatible with existing aircraft materials and delivery systems. Screening tests were performed under Phase I in accord with ASTM F483 (Standard Test Method for Total Immersion Corrosion Test for Aircraft Chemicals) to determine how aggressive the initial formulations developed by METSS were to the aircraft materials specified in AMS 1424. Individual component testing was also performed to determine the corrosive nature of each of the chemicals used in the Phase I formulation development efforts.

5.0 PHASE I RESULTS

A summary of the Phase I results is presented in this section. An emphasis is placed on presenting the *positive* results of the Phase I efforts that have set the foundation for the Phase II program.

5.1 Model Development Efforts

METSS developed a number of screening criteria for the selection of potential as deicing/anti-icing materials based on a number of physical and chemical considerations. The following elements were deemed the most important in developing an appropriate model for selecting candidate deicing/anti-icing materials (consideration was also given to structures that were known to favor biodegradability):

- solubility parameter modeling
- hydrogen bonding capacity and potential for dipole-dipole interaction
- heat of solution and heat capacity

- solubility limits in water
- potential for ionization or solubilization of electrolytes
- ionic behavior lending itself to higher water of hydration
- potential for forming molecular structures which can accommodate water molecules in closed spaces.

In addition, emphasis was placed on identifying material candidates that were known to be non-toxic and biodegradable.

Consideration of all of the model elements, indicated that freezing point depression would be larger for a mixture of an organic liquid and electrolyte, than a mixture of organic liquids alone. However, most electrolytes are not highly soluble in organic liquids, particularly in non-polar liquids. Hence the ideal organic liquid for deicing/anti-icing fluid technologies should be highly polar so that it has the capacity to dissolve both water and the electrolyte. For an organic liquid to be highly soluble in water, it has to have a solubility parameter close to that of water and should have high hydrogen bonding capability. Electrolytes, which may be soluble in water and the deicing fluid, should be soluble in water and produce ions that have a high number of water hydration. Furthermore, the number of ions provided by a molecule of the electrolyte should be large. However, the electrolyte should not cause corrosion to the airframe or be environmentally toxic.

Balancing these factors eliminated a large number of potential chemistries. For example ammonium/amine containing compounds chloride, nitrates, sulfates, and phosphate salts can be eliminated due to their corrosive nature. The models pointed to simple molecules like lactic acid, lactides, and lactates, indicating these materials may offer great potential for deicing Lactic acid is very similar the ethylene glycol in chemical structure, except one of the hydroxyl group is replaced by carboxyl group on one hand and the carbon atom is substituted by methyl group. The presence of the carboxyl group enhances the potential for ionizing and solubilizing electrolytes. Furthermore, both -OH and -COOH groups have great potential for hydrogen bonding with water. The presence of OH group in the #2 position enhances the potential for ionization, leading to a higher ionization constant and greater degree of dissociation. A very subtle aspect of this molecular architecture is the presence of CH3 group in the 2 position which prevents intermolecular interaction and molecular packing as present in ethylene glycol. Instead, the breakdown of symmetry allows lactic acid to have greater potential for intermolecular interaction such as with water and hence greater deicing potential. Propylene glycol, which has the CH3 group at the #2 position to the OH group, has similar capacity for breaking down the symmetry and enhance intermolecular interaction.

Another close parallel to ethylene glycol are mono and disacharides such as glucose, fructose, and sucrose. They exist as cyclic structures in which five of the carbon atoms are attached to OH groups and one carbon atom having an aldehyde or ketone group gives and oxide bond. Its potential as an efficient deicing fluid arise from its solubility parameter, strong hydrogen bonding capacity and potential and breakdown of cyclic structure in presence of water, with formation of aldehyde or ketonic groups. However, like ethylene glycol, the hexoses are very symmetrical and are more prone to intramolecular interaction, instead of intermolecular interaction with water. The presence of CH3 can be helpful in facilitating intermolecular interaction by breaking down the molecular symmetry. In other words, a methylglucoside will be a better deicing fluid that glucose, galactose or fructose. This is indicative of the greater power of the glycoproteins for deicing. The glycoproteins have methyl glucoside as chelating partner. Further methyl glucosides may form molecular assembly in space with greater distance between the layers of hexose rings, which facilitates the accommodation of H2O within the intramolecular assembly in space.

5.2 Results of Literature Review

There were several chemistries emphasized in the literature that are currently being developed or used as deicing/anti-icing materials, especially in roadway and runway applications, including:

- potassium acetate (K-Ac)
- calcium magnesium acetate (CMA)
- sodium acetate and sodium formate.

Potassium acetate is currently being developed as a roadway/runway deicing/anti-icing fluid, offering substantially less potential environmental impact than glycol-based fluids. Potassium acetate deicers are cited as having several significant operational advantages over glycol deicers, including melting at lower temperatures, providing a longer residual effect and being less slippery. From an environmental perspective, potassium acetate has a lower BOD (biological oxygen demand) and decomposes at lower temperatures. The latter may be a disadvantage where storm water discharges are regulated by permits with numerical limits for BOD. The price of potassium acetate is comparable to that of propylene glycol. Cyrotech has developed a runway deicing fluid based on potassium acetate which has passed AMS 1435, including all materials compatibility requirements. However, concerns remain over materials compatibility issues with existing aircraft materials, and the aircraft industry is reluctant to consider the use of fluids based on this type of chemistry on its aircraft. While METSS has not emphasized the development of new deicing/anti-icing fluids based on potassium acetate, it does exhibit some very favorable properties that are worth investigating and potentially mimicking with less aggressive chemistries. For instance, recent developments concerning mixed acetate/propionate salts may demonstrate better materials compatibility. The use of these materials as *additives* in other fluid formulations could provide some synergistic benefits while limiting the risk of corrosive attack.

Sodium formate, which is perhaps the most benign of these materials, has a significantly lower oxygen demand than any of the currently used deicing/anti-icing fluids and a freezing point curve similar to sodium chloride down to about -14 ^{o}C. However, sodium formate also has the following disadvantage relative to other available technologies and was therefore not carried forward as a potential candidate for development:

- low water solubility limit (tendency to precipitate out at low temperatures)
- potential materials compatibility problems
- questionable availability.

Another class of materials identified through the literature search included **antifreeze glycoproteins** (AFGP). AFGPs, with molecular weights of 30,000, can depress the freezing point of water as much as an equivalent weight of sodium chloride. This is an incredible 500 times its apparent colligative effect. It has also been found that smaller proline containing AFGPs, while having very limited antifreeze capability themselves, have a synergistic function with the larger more active AFGP molecules, possibly making them effective additives in appropriate deicing/anti-icing systems. However, these materials are only in the initial stages of development and were not considered under the program as they do not provide a near-term alternative for the Air Force.

These materials, were not emphasized in the METSS Phase I program, primarily because of issues related to materials compatibility, i.e., these materials or natural by-products of these materials (generated through hydrolysis) are considerably corrosive in nature and could pose significant materials compatibility problems with existing aircraft materials.

5.3 Identification and Selection of Best Candidate Technologies

Based on the results of the literature search and modeling efforts, METSS elected to focus its Phase I development efforts on the following classes of materials:

- **glucose materials** and their **salts**
- **lactates** and their **salts**.

The basis for selecting these materials included:

- these materials conformed to the models developed
  - ⇒ very favorable structural attributes (similar to propylene glycol)
  - ⇒ lower BOD than propylene glycol
  - ⇒ exothermic heat of solution
  - ⇒ they are highly soluble in water
- they are known to be non-toxic
- they are readily biodegradable
- they are cost effective to produce
- feed-stock materials are readily available agricultural products
- as a consequence of the large surplus of starches and sugars in the US (the basis for the synthesis of these materials), there is a large amount of interest in commercialization these materials as deicing/anti-icing fluids.

Metylglucoside is a known chemical enhancer of deicing chemicals having an exothermic heat of solution of -3 cal/mol (potentially enhancing its deicing abilities). It is readily available (made for oil drilling mud) and cost approximately $0.35-.40/lb. METSS believes that the structure of methyl glucoside may help it mechanically remove ice from the airframe surface. The structure of methyl glucoside is closely related to the glucose-based non-ionic detergents which have hydrophilic and hydrophobic moieties; the hydrophilic moiety being the glucose and the hydrophobic moiety being the alkyl chain. The hydrophilic moiety will make it compatible with water. The hydrophobic moiety sticking to the airframe surface will make it slick and allow broken ice to detach and remove easily. A variety of glucoside surfactant agents are available commercially that may enhance this action.

METSS has filed a patent based upon the use of **lactate** chemistries for a deicing agent which is environmentally benign and can be produced from a relatively inexpensive feed-stock material, lactic acid or 2-propanoic acid. This material is a natural and abundant organic acid with structural similarities to propylene glycol. Both of its optical isomers (L and D forms) occur in nature. Derivatives of this material (lactates) will biodegrade more slowly than glycol-based systems and more uniformly. The deicing agents can be prepared from pure components, or, more preferably, are prepared from any of a number of industrial waste streams. Typically these waste streams include components such as lactic acid fractions and low molecular weight sugars such as sorbitols, maltoses and glucoses. New developments in lactic acid based biodegradable polymers are driving new advancements in lactic acid production technology and will promote the introduction of other lactic acid products into consumer markets.

5.4 Phase I Testing and Evaluation

Phase I testing and evaluation results are presented in this section. Emphasis is placed on the freezing point depression data and BOD/COD test results, as these are considered the primary measures of Phase I success. The results of the materials compatibility testing are also presented, but are not emphasized at this point in time as METSS has not incorporated any measure of corrosion protection into the Phase I formulations. The development of formulations containing appropriate corrosion inhibitors will be pursued under Phase II. Other testing and evaluations are addressed as needed to demonstrate the potential of developing deicing/anti-icing formulations which are compliant with AMS 1424 and 1428.

5.4.1 Freezing Point Depression

The Air Force has set a goal for the environmentally friendly glycol replacement fluids to meet or exceed the freezing point depression requirements set forth in ASM 1424. For Type I fluids, the lowest operational use temperature is established at +5 ^{O}F (-15 ^{O}C). This value is determined by taking +23 ^{O}F (the outside air temperature established for WSET test conditions) and subtracting a buffer of 18 ^{O}F. Thus, new fluids do not necessarily have to match the performance of the existing glycol materials. However, the glycols do provide a good metric which can be used to assess the technical merit of the new materials. In accord with AMS 1424, any material that can provide freezing point depression to -15 °C and meet the hold-over time requirements may be a suitable replacement candidate.

METSS established a goal of developing formulations that exceeded the AMS 1424 requirement of -15 °C by at least 10 °C, for an internal metric for freezing point depression goal of -25 °C at 50% water. This will help ensure the formulations developed can be appreciably diluted without freezing, thus meeting hold-over time requirements.

The freezing point depression data is perhaps the most critical data for demonstrating the potential of developing replacement deicing/anti-icing fluids. Freezing point depression data, measured in accord with ASTM D1177, is presented in Table 5.1. Reported values for a MIL-A-8243D glycol-based deicer provided by Octagon and a potassium acetate solution provided by Cryotech are included for comparative purposes. All formulations were normalized to 50% water for relative comparison since the MIL-A-8243D solution was provided at 50% water.

It is clear from the results presented in Table 5.1 that the methods used by METSS to develop new deicing/anti-icing fluid formulations were successful. The METSS lactate formulations are improvements on Ice Ban's commercially available lactate-based formulation. While the methods applied to developed the METSS formulations can be applied to improve Ice Ban's material, none of the METSS formulations currently contain Ice Ban's material as a component. The METSS glucoside formulation is also an improvement on commercially available methyl glucoside products. However, in this instance, the METSS formulation contains the commercial product as a base-stock material.

Table 5.1. Freezing Point Depression Data - Best Phase I Formulations

Sample/Formulation	Freezing Point (°C)
MIL-A-8243D	-32
Potassium Acetate	-62
Methyl Glucoside	-17
Ice Ban (lactate solution)	-14
METSS Glucoside 1	-26
METSS Lactate 1	-28
METSS Lactate 2	-38
METSS Lactate 3	-37
METSS Lactate 4	-41

During the initial formulation efforts, many of the materials developed demonstrated a fairly constant melting point (as determined by DSC) across a broad range of water concentrations. This behavior indicates the formulations developed will be able to absorb significant quantities of water prior to freezing (favorable for long hold-over times) and may be able to be used at lower concentrations. Additional D1177 measurements were also performed using more conventional methods to determine the freeing point depression characteristics of the best performers as a function of water concentration. These results are presented in Table 5.2 for some of the best performing deicing fluid formulations.

Table 5.2. Freezing Point Depression Data vs. Water Concentration

Sample/ Formulation	Freezing Point (^oC)						
	% H_2O						
	25	30	40	50	60	70	80
METSS Lactate 1	-26.7	-32.2	-28.9	-28	ND	-17.2	-7.8
METSS Lactate 2	ND	ND	ND	-38	ND	ND	ND
METSS Lactate 3	ND	-18.9[a]	-22.2	-37	ND	-17.2	-9.4
METSS Lactate 4	-24.4[b]	ND	ND	-41	ND	ND	-8.9
METSS Glucoside 1	ND	-5	-9	-26	-18.9	ND	ND

a: 32% water
b: 26% water
ND: Not Determined

Factors dictating the initial water content of the final formulations will include:

- freezing point depression requirements
- desired hold over times (freezing point depression requirements must be maintained as solution is diluted by precipitation)
- solution viscosity/rheological behavior
- material costs.

5.4.2 Environmental Compatibility

BOD/COD testing was performed to determine the environmental impact of the candidate deicing/anti-icing formulations relative to the glycol-based systems. COD or TOD tests provide a measure of the total amount of oxygen needed to fully biodegrade a given material. BOD5 tests (five day BOD tests) were performed to determine the amount of material degraded after 5 days. A ratio of BOD5 to TOD provides a measure of how much of the material biodegrades in a 5 day period (rate of biodegradation). The major requirement is that the new deicing/anti-icing materials biodegrade at a rate less than that of propylene glycol. A ratio between 0.4 and 0.7 indicates a readily and rapidly degradable compound while values below 0.4 indicate slowly degradable materials.

A summary of the environmental impact data collected under Phase I is reported in Table 5.3. *All of the candidate materials tested exert significantly less total demand on oxygen than the glycol-based systems and biodegrade slower than propylene glycol.* Both of these factors demonstrate the potential of developing more environmentally friendly deicing/anti-icing formulations. BOD/COD data were not been determined for METSS Lactate 3 and 4, however these materials are expected to exhibit better biodegradability characteristics than the METSS Lactate 1.

Table 5.3. Phase I Biodegradability Data

Sample	TOD or COD	BOD5	BOD/TOD
Propylene glycol	1.68 g/g	1.14 g/g	0.68
Ethylene glycol	1.29 g/g	0.70 g/g	0.54
Potassium Acetate	0.32 g/g	0.28g/g	0.87
Lactic Acid	1.07 g/g	0.64 g/g	0.60
Glucose	1.07 g/g	0.65 g/g	0.61
Ice Ban	0.53 g/g	0.51 g/g	0.96
METSS Glucoside 1	0.78 g/g	0.26 g/g	0.33
METSS Lactate 1	0.56 g/g	0.36g/g	0.64
METSS Lactate 2	0.53 g/g	0.26 g/g	0.49

5.4.3 Materials Compatibility

With the issues of freezing point depression and environmental impact addressed, materials compatibility becomes the next major driver in the formulation development efforts. The development of a fully formulated system with corrosion control additives is outside of the scope of the Phase I program. However, as a general rule, formulation efforts should be driven toward neutral pH values to limit corrosive behavior. Thus, as a supplemental means of optimizing formulations for materials compatibility, METSS made an effort to formulate candidate deicing/anti-icing fluids with a pH in the range of 4 to 8. In the absence of aggressive corrosive ions, this is typically considered a safe range of pH for most of the metals of interest to deicing/anti-icing fluids. pH data is presented in Table 5.4 for the best candidate materials.

Table 5.4. pH of Candidate Formulations

Sample	pH	Sample	pH
MIL-A-8243D	7	METSS Lactate 1	4*
Methyl Glucoside	11	METSS Lactate 2	7-8
Ice Ban (lactate solution)	3.5	METSS Lactate 3	7
METSS Glucoside 1	4*	METSS Lactate 4	7

The corrosive potential of the candidate deicing fluid formulations was investigated using methods outlined in ASTM F483 - *Standard Test Method for Total Immersion Corrosion Test for Aircraft Chemicals*. Candidate test materials were specified in AMS 1424. A full battery of tests was performed on METSS Glucoside I and METSS Lactate 4. Test results are presented in Tables 5.5 and 5.6. Both of the METSS formulations tested were found to be generally corrosive to steel and magnesium, with little or no effect on the other materials testes. METSS would like to emphasize that materials compatibility testing performed with the Phase I formulations may be of limited practical value since the formulations developed to date have only been optimized with regard to freezing point depression performance. *No additional additives have been included to these formulations, including additive packages typically used for corrosion control.* Thus, Phase I materials compatibility testing only demonstrates which technologies have a greater propensity for materials compatibility in the un-modified (no additives) state.

Table 5.5 - Total Immersion Corrosion Data – METSS Glucoside I

Test Metal	Weight Change (mg/cm^2)		Observations
	24 h	168 h	
2024-T3 anodic	-0.0449	-0.1631	Slight discoloration
2024-T3 1.5% Alclad	-0.0213	-0.1147	Slight dulling
7076-T6 Alclad	-0.0201	-0.0993	Very slight dulling
Mg/Dichromate Treated	-21.103	-33.2796	White scale, significant pitting
6Al-4V Titanium	0.0012	0.0071	Brown, transparent discoloration
1025 Carbon Steel	-0.7558	-4.000	Uniform dull gray-brown discoloration

Table 5.6 - Total Immersion Corrosion Data – METSS Lactate 4

Test Metal	Weight Change (mg/cm²)		Observations
	24 h	168 h	
2024-T3 anodic	-0.0496	-0.2612	Slightly duller than control
2024-T3 1.5% Alclad	-0.0496	-0.2589	Slight dulling with darkened polish lines
7076-T6 Alclad	-0.0260	-0.2045	Slight dulling with darkened polish lines
Mg/Dichromate Treated	-7.3753	-26.9054	Frosted appearance
6Al-4V Titanium	0.0035	-0.0024	No change
1025 Carbon Steel	-0.4972	-2.2766	Dull gray color

An extensive investigation of materials compatibility will be performed under the Phase II program using the fully formulated products. However, in an effort to develop some insight into the corrosion potential of some of the materials used to support the Phase I formulation development efforts, METSS performed some screening tests against carbon steel and magnesium (the two materials most susceptible to corrosion). The results of the screening experiments are presented in Table 5.7. Products from Cryotech (KAc) and Octogon (glycol) were used as controls. The screening tests clearly indicate potential problems with using lactic acid in new product formulations without further neutralization of its corrosive potential. Ethyl lactate was found to be non-corrosive and the results of the sodium lactate experiments demonstrate the addition sodium hydroxide (or another strong base) may control the corrosive behavior of lactic acid. This also raises the question of whether conventional salt-based inhibitor systems might be used in final product formulations to obtain the level of corrosion control required for aircraft application. The methyl glucoside sample tested was determined to be non-corrosive to steel and magnesium, which bodes favorably for Phase II development efforts.

5.4.4 Viscosity

The viscosity of the deicing/anti-icing fluids is important for two reasons:

- consistent viscosity's will ensure the replacement materials can be applied using the same procedures as the existing glycol solutions
- rheological properties of deicing/anti-icing fluids significantly impact performance, particularly with regard to hold-over time and aerodynamic performance (e.g., sufficient viscosity is needed to prevent the fluid film from flowing and thinning).

Table 5.7 Total Immersion Corrosion Test Results - Screening Tests

Fluid	Test Metal	Weight Change (mg/cm^2)		Comments
		24 h	168 h	
Cryotec	Steel	0.0035	0.0106	No change
	Mg	4.0921	-2.1028	Mottled white deposits
Octogon	Steel	0.0035	-0.0035	No change
	Mg	0.0035	0.0142	Slight brownish dulling
Ice Ban	Steel	-0.45	-1.0993	Slight dulling
	Mg	-0.8645	0.2979	Thick, white scale covering
Lactic Acid	Steel	-0.4322	-2.1525	Dull grey color
	Mg	-1.318	-60.6667	Coupon shiny, drastically thinned
Sodium Lactate	Steel	-0.0071	-0.5106	Dull brown color
	Mg	-1.1763	-2.8014	Soln orange, light frosting on coupon
Ethyl Lactate	Steel	0.0248	0.0248	Dull brownish color
	Mg	-0.0035	-0.0071	Slight discoloration
Methyl Glucoside*	Steel	0.0283	-0.0035	Brown staining from solution
	Mg	0.0035	-0.1170	Brown deposits near edges

*Methyl Glucoside sample was 70/30 Methyl Glucoside/H_2O

The viscosity (Brookfield) of each of the candidate formulations was determined at 18 °C and -5 °C, and compared to that of the MIL-A-8243D control. Results are reported in Table 5.8. All formulations are 50% water. Other test results (not reported) indicate the low viscosity formulations can be readily thickened with small amounts of silicates (< 3%). Polymeric thickeners were not tested to eliminate possible film formation problems. Furthermore, silicates have been known to have a favorable effect on freezing point depression.

5.4.5 Other Phase I Test Results

A number of other experiments were performed that impacted the Phase I development efforts that were not deemed critical to demonstrating the technical feasibility of the Phase I program efforts. Brief comments are made on these efforts for completeness:

- Solubility limits of candidate tests materials were determined in the early stages of the program. This is one of the reasons sodium formate was removed from the Phase I development program. The remaining Phase I candidates exhibit high water solubility even at very low temperatures.

- Heat of solutions experiments were performed to verify that all of the formulations (50% water) exhibited an exothermic heat of solution when additional water (70% total water) was added. METSS Lactate 1 demonstrated the highest temperature rise, potentially making it the better *deicing* candidate.

5.8. Formulation Viscosity Measurements

Sample	**18 °C (cPs)**				**-5 °C (cPs)**			
	6 rpm	12 rpm	30 rpm	60 rpm	6 rpm	12 rpm	30 rpm	60 rpm
MIL-A-8243D	30	30	28	28.5	275	287	290	293
METSS Glucoside 1	17.5	13.6	12	13.3	113	100	100	97.5
METSS Lactate 1	15	10	10	11.5	100	100	85	85
METSS Lactate 2	ND	ND	ND	ND	ND	ND	ND	ND
METSS Lactate 3	17.5	15	14	16	188	175	175	176
METSS Lactate 4	15	11.3	11	11.5	113	100	97.5	97.5

ND: not determined

6.0 PHASE I SUMMARY

The technical feasibility of developing environmentally benign aircraft deicing materials was demonstrated under the Phase I program. Further formulation development, testing and evaluation efforts will be needed to fully develop the concepts demonstrated under the Phase I program and to support product commercialization efforts.

The following is a brief summary of the Phase I program results:

- METSS identified five potential candidates that could serve as alternative environmentally benign aircraft deicing materials.
- METSS demonstrated that these materials exhibit freezing point depression behavior that exceeds the requirements of AMS 1424 by at least 10 ^{o}C.
- METSS demonstrated that these materials are more environmentally friendly than current glycol-based deicing/anti-icing fluids.
- The formulations developed under the Phase I program are comprised of chemistries that fit the models developed by METSS to identify favorable candidates for deicing/anti-icing applications. These models will be used to support subsequent program development efforts.
- The formulations developed are void of known corrosive or otherwise aggressive ions.
- The formulations developed can be formulated to neutral pH to assist materials compatibility issues.
- The results of the total immersion corrosion tests indicate that deicing/anti-icing fluids based on some of the Phase I chemistries will have to be formulated with appropriate corrosion inhibitors to prevent corrosive attack of some aircraft alloys. The results of these tests also indicate the potential to do so.
- The formulations developed by METSS are based on readily available materials in abundant supply. Materials and production costs are very reasonable - *new formulations should be a fraction of the cost of existing glycol systems.*