FINAL REPORT

Pretreated Starch Solutions for Low Environmental Impact Aircraft Deicing

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14. ABSTRACT

Objectives. Deicers currently used for aircraft deicing, including ethylene glycol and propylene glycol, pose significant threats to surface waters. Oxidized starch may provide a less toxic deicer with lower biochemical oxygen demand. The objectives of this research were to 1) evaluate freezing point depression of different starch formulations, 2) determine the biological oxygen demand and aquatic toxicity of the most effective formulation, and 3) to provide a preliminary evaluation of compatibility of oxidized starch solutions with aircraft materials. Technical Approach. Starch solutions were oxidized using hydrogen peroxide and catalysts. The oxidized starch solutions were evaluated for freezing point depression and post-treated to reduce viscosity. The most effective formulation was then evaluated for oxidation products corrosivity, aquatic toxicity, and biochemical oxygen demand. Results. Freezing point depression of oxidized starch formulations ranged from 19.7 to 28?C viscosities similar to those of commercially available deicers were after post-treatment with granular activated carbon. Oxidized starch exerted a BOD5 up to six times lower than glycol deicers; toxicity was greater than pure propylene glycol but lower than propylene glycol deicer formulations. Corrosion testing indicated compatibility with aerospace materials in most cases. Organic acids were identified by gas chromatography/mass spectrometry as the primary constituents in the oxidized starch solution and their sodium salts are likely responsible for freezing point depression. Benefits. The proposed deicing system would provide effective aircraft deicing while exerting minimal environmental effects (e.g., lower toxicity to aquatic organisms and lower biochemical oxygen demand). Furthermore, these deicers could be made from waste starch, promoting sustainability within DoD.

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List of Acronyms

ASTM	American Society for Testing and Materials
BOD	Biochemical oxygen demand
BOD_5	BOD at 5 days
BOD_U	ultimate BOD
BSTFA	bis(trimethyl)triflouroacetamide
CHP	Catalyzed H_2O_2 propagations
COD	Chemical oxygen demand
DO	Dissolved oxygen
DoD	Department of Defense
EDTA	Ethylenediaminetetraacetic acid
FID	Flame ionization detector
GAC	Granular activated carbon
GC	Gas chromatograph
GC/MS	Gas chromatography/mass spectroscopy
HPLC	High performance liquid chromatography
ISCO	In situ chemical oxidation
LAS	Linear alkyl benzene sulfonate
LC_{50}	Median lethal dose
MBAS	Methylene blue active substances
SAE	Society of Automotive Engineers
TDS	Total dissolved solids
ThOD	Theoretical oxygen demand

Keywords

Deicer, Fenton’s reagent, Catalyzed hydrogen peroxide propagations, starch, sustainability, green chemistry

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ABSTRACT

Objectives. Deicers currently used for aircraft deicing, including ethylene glycol and propylene glycol, pose significant threats to surface waters. Oxidized starch may provide a less toxic deicer with lower biochemical oxygen demand. The objectives of this research were to 1) evaluate freezing point depression of different starch formulations, 2) determine the biological oxygen demand and aquatic toxicity of the most effective formulation, and 3) to provide a preliminary evaluation of compatibility of oxidized starch solutions with aircraft materials.

Technical Approach. Starch solutions were oxidized using hydrogen peroxide and catalysts. The oxidized starch solutions were evaluated for freezing point depression and post-treated to reduce viscosity. The most effective formulation was then evaluated for oxidation products, corrosivity, aquatic toxicity, and biochemical oxygen demand.

Results. Freezing point depression of oxidized starch formulations ranged from 19.7 to 28˚C; viscosities similar to those of commercially available deicers were after post-treatment with granular activated carbon. Oxidized starch exerted a BOD_5 up to six times lower than glycol deicers; toxicity was greater than pure propylene glycol but lower than propylene glycol deicer formulations. Corrosion testing indicated compatibility with aerospace materials in most cases. Organic acids were identified by gas chromatography/mass spectrometry as the primary constituents in the oxidized starch solution and their sodium salts are likely responsible for freezing point depression.

Benefits. The proposed deicing system would provide effective aircraft deicing while exerting minimal environmental effects (e.g., lower toxicity to aquatic organisms and lower biochemical oxygen demand). Furthermore, these deicers could be made from waste starch, promoting sustainability within DoD.

OBJECTIVE

Aircraft deicing and anti-icing operations are crucial to successful flight operations. Icing of aircraft during takeoff can result in severe consequences; even small amounts of ice present on wings or tail components can interfere with the aerodynamic properties necessary for flight (Berktold and Werners, 1993). The military specification for aircraft deicing fluids is Society of Automotive Engineers (SAE) Specification 1424. Under this specification, Type I deicers are low viscosity fluids that are shed from the aircraft during take off. Type IV deicers are higher viscosity fluids that provide continued protection during extended freezing precipitation.

Deicer formulations are based on the principle that the addition of a nonvolatile solute to water lowers the freezing point of the resulting solution. Ethylene glycol and propylene glycol are currently the most commonly used aircraft deicers. Although they are highly effective deicing agents, these synthetic chemicals have significant detrimental effects on the environment (Corsi et al., 2006). Ethylene glycol exerts a theoretical oxygen demand (ThOD) of 1.1 g O_2/g, and the ThOD of propylene glycol is even higher, at 1.7 g O_2/g. Propylene glycol is more widely used than ethylene glycol because of its greater freezing point depression (Castro et al., 2005) and lower aquatic toxicity. However, propylene glycol does exhibit significant toxicity to terrestrial and aquatic animals; the 48 hr LC_{50} of propylene glycol to *Daphnia magna* is 8,500 mg/L, and the 96 hr LC_{50} to fathead minnows is 17,700 mg/L (Verschueren, 1983).

Alternative deicer formulations, such as aqueous solutions composed of modified monomeric organic molecules, have been the focus of recent study. Several organic acids and keto acids, such as succinate and acetate, have been shown to lower the freezing point of water (Dunuwila and Berglund, 2005). Yang and Montgomery (2003, 2007) produced organic acids from molasses and corn steep water by promoting alkaline sugar degradation. They reported freezing point depression of up to 28˚C for solutions containing the sodium salts of sugar acids obtained by alkaline hydrolysis of glucose and subsequent neutralization with sodium hydroxide (NaOH). Dairy waste conversion to calcium magnesium acetates and propionates (Fu and Mathews, 2005; Huang and Yang, 1998; Yang et al., 1992) utilized microbiological methods that are not currently optimized for commercial use. Wood derived pyrolysis liquors yielded calcium-formate, acetate and propionate (Oehr and Barrass, 1992), but the authors noted low economic feasibility without additional recovered products. Ganjyal et al. (2007) produced levulinate, a keto acid, from grain sorghum, but freezing point depression was not sufficient for aircraft applications. Despite extensive research into organic acids as deicers, no glycol replacements have been identified for the airline industry. Ethylene glycol and propylene glycol remain the most common aircraft deicing compounds used by the military, and alternatives are needed to reduce environmental impacts of aircraft deicing.

A potential environmentally friendly deicer may be derived from starch. Starch has been used previously for pavement deicing (Bytnar, 2006). However, those starch formulations required the addition of sodium chloride due to the low water solubility of starch, and are not compatible with aircraft materials due to the presence of corrosive sodium chloride. Starch may be made more soluble by oxidation into smaller molecules. Parovuori et al. (1995) described the effects of oxidation using very dilute Fenton's reagent on potato starch. They found that the molecular weight of the starch decreased, and that the smaller polymers contained increased numbers of carbonyl groups. Their results were similar to those reported by Zhu and Bertoft (1997) and Zhu et al. (1998), who documented increased hydroxylation and carbonyl groups after starch oxidation. Oxidized starches have also been used as food additives and as a complexing agent in detergents (Mathew and Adlercreutz, 2009). An advantage of using oxidized starch as a deicing formulation is that numerous sources of starch are available as waste products. Many food processing operations produce waste starches, which could be pretreated and used as deicing materials.

Catalyzed H_2O_2 propagations (CHP; modified Fenton's reagent) is a process that provides efficient production of reactive oxygen species for starch oxidation. The use of CHP has become increasingly popular for industrial waste treatment and the remediation of soils and groundwater. The process is based on the catalyzed decomposition of hydrogen peroxide by soluble iron, iron chelates, or iron minerals to generate the strong oxidant hydroxyl radical (OH•), as well as other reactive oxygen species. It is based on Fenton's reagent, a laboratory procedure in which dilute hydrogen peroxide is slowly added to a solution of excess iron (II) to generate hydroxyl radical in near-stoichiometric yield (Walling, 1975):

$$H_2O_2 + Fe^{2+} \rightarrow OH\bullet + OH^- + Fe^{3+} \quad k = 76\ M^{-1}\ s^{-1} \qquad (1)$$

Hydroxyl radical is one of the strongest oxidants found in nature. The most common reactions of hydroxyl radical are electrophilic substitution to aromatic compounds and addition to alkenes. Another class of hydroxyl radical reactions is hydrogen abstraction from saturated compounds such as alkanes, a pathway that proceeds at a slower rate relative to electrophilic substitution and addition. Chemicals that react very rapidly with hydroxyl radical are limited by the rate of diffusion of hydroxyl radical in water, which is $\approx 10^{10}\ M^{-1}\ s^{-1}$, rather than the rate at which it attacks the chemical. Therefore, the rate at which hydroxyl radical attacks highly reactive contaminants in aqueous systems is referred to as diffusion-controlled. Some general rules have been established for the reactivity of hydroxyl radical with organic contaminants. Rate constants $>10^9\ M^{-1}\ s^{-1}$ are considered high enough to be effective for in situ chemical oxidation (ISCO) treatments, while rate constants $<10^8\ M^{-1}\ s^{-1}$ are considered too low to be effective. Almost all aromatic compounds, even those with a high degree of halogenation, react rapidly with hydroxyl radical. In contrast, alkanes exhibit relatively low reactivity with hydroxyl radical; in particular, chlorinated and fluorinated alkanes such as carbon tetrachloride, chloroform, hexachloroethane, and freons (e.g., 1,1,2-trichloro-2,2,1-trifluoroethane), are effectively non-reactive.

Compared to traditional Fenton's reagent, relatively high concentrations of hydrogen peroxide are used for CHP (i.e. 2–20% [0.6–3.6 M]). At these hydrogen peroxide concentrations, the hydroxyl radical generated in the Fenton's initiation reaction (equation 2) reacts with hydrogen peroxide to promote a series of propagation reactions:

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad k = 2.7\ x10^7\ M^{-1}s^{-1} \qquad (2)$$

$$HO_2\bullet \leftrightarrow O_2\bullet^- + H^+ \qquad pK_a = 4.8 \qquad (3)$$

$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \qquad k = 10^6\text{-}10^8\ M^{-1}s^{-1} \tag{4}$$

$$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \qquad k = 1.2 \times 10^6\ M^{-1}s^{-1} \tag{5}$$

Although the rate constant for reaction (2) is relatively low, these reactions become important when the concentration of hydrogen peroxide is high (e.g., > 1%). Therefore, the rates of generation of perhydroxyl radical ($HO_2\bullet$), superoxide radical anion ($O_2\bullet^-$), and hydroperoxide anion (HO_2^-) become significantly greater at higher hydrogen peroxide concentrations. Perhydroxyl radical is a relatively weak oxidant; superoxide is a weak reductant and nucleophile in aqueous systems, and hydroperoxide anion is a strong nucleophile. Although some of these species (e.g., superoxide) are not very reactive in deionized water, their reactivity is significantly increased in systems that have solutes such as hydrogen peroxide or starch, which provides a solvent effect, increasing the reactivity of superoxide (Smith et al. 2004).

CHP reactions that generate hydroxyl radicals, superoxide, and hydroperoxide provide a mixture of oxidants, reductants, and nucleophiles that can degrade almost all organic contaminants. For example, carbon tetrachloride and hexachloroethane, which are unreactive with hydroxyl radical, are rapidly degraded in CHP systems through reactions with superoxide in the presence of sufficient hydrogen peroxide to provide a solvent effect (Watts et al. 1999; Teel and Watts 2002; Smith et al. 2004). Therefore, these reactive oxygen species increase the range of reactivity, making CHP a near-universal system for the transformation of organic compounds in starch solutions. While it is not known what mechanism would be responsible for the oxidative modification of starch by CHP, hydrolytic cleavage of glycosidic bonds, followed by subsequent oxidation of the monomer and oligomer products is one likely mechanism.

The objectives of the proposed research were to 1) evaluate freezing point depression of different pretreated starch formulations, 2) determine the BOD and aquatic toxicity of the most effective freezing point depression formulation, and 3) to provide a preliminary evaluation of compatibility of pretreated starch solutions with aircraft materials. Starch solutions were treated with hydrogen peroxide and catalysts to partially oxidize the starch. The pretreated starch solutions were then evaluated for freezing point depression. The formulation that promoted the largest freezing point depression was evaluated for starch oxidation products, corrosivity, aquatic toxicity, and biochemical oxygen demand.

Starches are a common constituent in food processing wastes and have the potential to provide an alternative feedstock for deicer and anti-icer production. If successful, pretreated starch could provide an effective deicing/anti-icing agent for DoD that is characterized by lower aquatic toxicity and BOD than ethylene glycol or propylene glycol. Furthermore, the cost of the deicer may be less than that of glycols if waste materials can be used as sources for starch, and the beneficial use of waste materials would also promote sustainability within DoD.

TECHNICAL APPROACH

Materials

Chloroform, sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), iron(III) EDTA, and pyridine were purchased from JT Baker (Phillipsburg, NJ). Corn starch was obtained from ACH Foods (Memphis, TN), and potato starch was purchased from EM Science (Gibbstown, NJ). Hydrogen peroxide (50% mass/mass), bis(trimethyl)triflouroacetamide (BSTFA) and DARCO activated carbon were purchased from Sigma Aldrich (St. Louis, MO). F-200 and F-300 activated carbon were provided *gratis* by Calgon Carbon (Pittsburgh, PA). A freezing tube was obtained from Lab Glass (Kingsport, TN); the dimensions were 260 mm × 54 mm (outside diameter), and the volume was approximately 200 mL. Seed microorganisms for Biological Oxygen Demand (BOD) were obtained from Polyseed (The Woodlands, TX). Reagents for nitrate measurement were purchased from Hach (Loveland, CO). Linear alkyl benzene sulfonate stock solution was purchased from Ricca Chemical Company (Arlington, TX). Dialysis tubing was purchased from Spectrapore (Rancho Dominguez, CA). Metal coupons of a given alloy were taken from a single stock sheet and finished per ASTM standards by Metal Finishing Company (Wichita, KS). All reagent water (>17 MΩ•cm) was collected from a Barnstead Nanopure II ultrapure deionizing system.

Summary of Experimental Procedures

Evaluation of pretreated starch solutions for aircraft deicing followed five specific steps:

1. Evaluation of the starch and oxidant dose that provided the greatest freezing point depression
2. Optimization of the oxidation pretreatment procedure
3. Optimization of post-treatment procedure
4. Determination of the chemical oxygen demand, biochemical oxygen demand, and toxicity of the optimal pre-treated starch solution
5. Evaluation of the corrosivity of the optimized oxidized starch solution

Freezing Point Determination

The freezing point of all oxidized starch solutions was determined using ASTM Method D 1177. Each sample was immersed in a cooling bath prepared by adding dry ice to acetone in a 2 L Dewar flask. Agitation was conducted using a 1.6 mm diameter stainless steel rod with five coils at its end with a diameter such that coils touched the wall of the freezing tube. The stirrer was reciprocated by a windshield wiper motor connected through mechanical linkages; a photograph of the test apparatus is shown in Figure A1. The temperature of the oxidized starch solutions was monitored with a 100 Ω calibrated platinum resistance thermometer (Omega Engineering, Stamford, CT) connected through an Omega Model HH804U digital temperature indicator to a Dell Inspiron 5500 computer. The output from the probe was plotted as a function of time at 1 sec intervals. Freezing point was determined from the slope changes on the temperature vs. time curves by identifying the temperature peak following release of the heat of fusion from the test solution.

An aliquot of the oxidized starch solution was placed in the sample tube and immersed in the cooling bath so that the sample level in the freezing tube was below the bath level. A minimum sample volume of 50 mL was used to ensure adequate agitation by the mechanical stirrer and immersion of the resistance thermometer. When the temperature of the sample approached the expected freezing point, a wire loop containing a frozen droplet of deionized water was inserted into the bottom of the freezing tube to initiate freezing with minimal sub-cooling of the bulk solution. The increase in temperature preceding crystallization of the bulk solution was usually less than 1˚C.

Initial Evaluation of Substrates and Oxidant Dose

The experimental matrix for investigating freezing point depression by oxidized starch was a central composite rotatable experimental design using the concept of response surfaces (Cochran and Cox, 1992). Central composite rotatable designs are multivariable, multilevel experimental procedures that analyze the interactions between variables and produce response equations. These procedures have the potential to show statistically significant interactions between variables, unlike a one-variable-at-a-time strategy, and can also lower the ultimate number of experiments conducted while maintaining a high degree of statistical significance in the results. In central composite designs, experimental parameters are chosen to achieve complete rotatability around the central point of a two-level matrix. Using such matrix designs, all of the vertices within the experimental boundaries are tested, and interpolation anywhere within the three-dimensional space is valid (Diamond, 1989).

The central composite design used in this research was characterized by two variables at five levels with five center points for statistical validity (Box and Draper, 1987; Hogg and Ledolter, 1992; Cochran and Cox, 1992). The central composite matrix was characterized by 5 center points and 4 star points set at a factor of 1.4142 on the far end of the coded scale to achieve complete rotatability (Box et al., 1978). The two variables investigated to determine the effect of starch to oxidant (H_2O_2) ratios on freezing point depression of the oxidized starch solution were the initial mass of potato or corn starch (5.0 g–50 g) and the concentration of hydrogen peroxide (15%–27.8%). The specific masses and concentrations used in each trial are listed in Table 1. Trials 1 through 8 quantified freezing point response across the range of experimental values while trials 9 through 13 represented replicates (center points) used to quantify precision. The experimental data were analyzed by linear regression through least squares analysis to develop regression equations to describe the systems and to provide graphical representations of the data in the form of response surfaces (Box and Draper, 1987). Each term of the regression equation was validated by quantifying its standard error to ensure that it was within the 90% interval of a single sided t-distribution. In addition, the entire regression equation was evaluated based on the R^2 fit. The response surfaces that graphically illustrate the regression equations were created using the SYSTAT® software package.

Reactions were conducted in 1 L Erlenmeyer flasks with agitation on a shaker table at 175 rpm until all of the hydrogen peroxide was consumed. The volume of reaction solution (water and H_2O_2) was held constant at 100 mL, and 0.18 g iron (III)-EDTA for a final concentration of 5 mM iron (III). (Iron-EDTA was used as the catalyst in order to maintain a neutral pH regime during the CHP oxidation reactions.)

Chemical Oxidation Pre-treatment

Based on the results of the initial evaluation of oxidized starch solutions a hydrogen peroxide concentration of 25% and a starch mass of 50 g/100 mL hydrogen peroxide solution were selected for further evaluation. Starch was pretreated in 2 L Erlenmeyer flasks containing 100 g starch and 200 mL of reaction solution containing 5 mM iron (III)-EDTA and 25% (vol/vol) hydrogen peroxide at pH 7. The reactions proceeded for 24 hr with agitation at 175 rpm. Oxidation of the starch solutions promoted acidic conditions (likely due to the formation of organic acids); therefore, the flasks were dosed after 24 hr with 12.5 mL of 12 M sodium hydroxide (NaOH) to maintain a neutral pH, and the reaction was allowed to proceed until the hydrogen peroxide concentrations were undetectable (< 10 mg/L). After the reaction was complete, the reaction pH was adjusted from 5 to 7.5 by a second addition of NaOH. To increase freezing point depression, samples were concentrated by placing in an oven at 55˚C and evaporated until a final volume equal to 120 mL/100 g of starch treated was attained.

Post-treatment of Pre-treated Starch Solutions

Two post-treatment conditions were evaluated to reduce the viscosity of the pretreated starch solutions through selective removal of higher molecular weight oxidation products: granular activated carbon (GAC) and diffusion through dialysis tubing.

GAC post-treatment was conducted by adding 10 g of GAC to 120 mL of the oxidized starch solution in a 1 L Erlenmeyer flask. The flask was agitated on a shaker table at 175 rpm for 48 hr, and the slurry was then passed through a No. 28 screen under vacuum to provide coarse particle separation. Finer particles were removed by centrifugation at 4000 rpm for 10 min. The supernatant was decanted and adjusted to pH 7.5 using 5 N NaOH prior to viscosity and freezing point determination.

Dialysis post-treatment was performed by suspending cellulose ester dialysis tubing (molecular weight cutoff 500 Daltons) in 19 L of continuously stirred deionized water. Dialysis post-treatment was conducted for 168 hr followed by evaporation of the dialysate to 120 mL in a convection oven at 40˚C. The evaporated dialysate was adjusted to pH 7.5 using 5 N NaOH prior to freezing point determinations.

Subsequent evaluations of foaming, BOD, COD, toxicity, corrosivity, and chemical constituents by GC/MS were conducted using GAC post-treated oxidized corn starch.

Viscosity Determination

Viscosity of the starch solutions was determined using Oswald viscometer tubes, maintained at a constant temperature of 0˚C by suspension of the viscometer tubes in an ice water bath. The viscometer tubes were filled with the test solution and placed in the ice water bath for 10 min before measuring the viscosity to ensure that the solution was in temperature equilibrium.

Foaming Properties

The oxidized starch solutions were assayed for the presence of surfactants that may cause foaming using ASTM Standard D 2330 (2008). A standard curve was prepared using a linear alkyl benzene sulfonate (LAS) stock solution. Preliminary pH measurement was performed conductively (rather than colorimetrically, as specified in ASTM D 2330) due to the opacity of the starch solution. A 100 mL aliquot of the solution was adjusted to pH 8.2 in a 250 mL separatory funnel followed by addition of 25 mL 1,000 mg/L methylene blue. Chloroform (25 mL) was then added and the contents vigorously shaken for 30 sec. The chloroform layer that formed at the bottom of the separatory funnel was then drained into another 250 mL separatory funnel. Two additional 25 mL chloroform extractions were conducted. Following the third chloroform extraction, phosphate buffer (prepared per ASTM D 2330) was added to the second separatory funnel and the contents mixed for an additional 30 sec. The chloroform layer was drawn out of the funnel through a fiberglass mat into a 100 mL volumetric flask. Sufficient chloroform was added to increase the volume to 100 mL. The absorbance of the resulting solution was then measured at 650 nm on a Spectronic 20 Genesys spectrophotometer.

Chemical and Biochemical Oxygen Demand

COD was measured using Standard Method 5220 B (APHA, 2005). A glucose standard curve was prepared with standards of 20, 100, 300, 600, and 900 mg/L as O_2. Each sample was digested with acidic dichromate reagent and refluxed at 103˚C for 2 hr. Sample absorbance was measured on a Spectronic 20 Genesys spectrophotometer at 600 nm.

BOD at 5 days (BOD_5) and ultimate BOD (BOD_U) were determined for the pretreated starch solution using Standard Method 5210 (APHA, 2005). To determine the 5-day BOD, three dilutions of the pretreated starch solution were prepared in triplicate 300 mL BOD bottles. Each sample was then seeded with microorganisms and incubated for 5 d at 20˚C. Dissolved oxygen (DO) was measured before and after incubation using a YSI model 52 DO meter.

BOD_U was computed from triplicate samples of diluted pretreated starch solution and duplicate dilution water controls. Samples were incubated in 300 mL BOD bottles at 20˚C and DO was monitored every 5 days for 60 days. Samples were reaerated as the DO approached 2 mg/L. To correct for nitrogenous oxygen demand, nitrate was measured colorimetrically at each 5-day monitoring period. BOD_U and the first order decay rate (k) were calculated based on the DO concentration vs. time assuming first order kinetics:

$$BOD(t) = BOD_U(1-e^{-kt}) \tag{6}$$

Toxicity Testing

Toxicity testing was conducted on *Ceriodaphnia dubia* using Standard Method 8712 (APHA, 2005) with the oxidized starch solution. Toxicity testing was performed using *Ceriodaphnia* <24 hr old. Several dilutions of the post-treated starch solution were prepared (10%–100% vol/vol). The testing was conducted in 125 mL wide mouth flint-glass bottles using 100 mL volumes of the diluted post-treated starch solutions. *Ceriodaphnia* motility was observed at 1 hr, 4 hr, 24 hr, and 48 hr (Stephen, 1977). Non-motile organisms were quantified and used to determine the LC_{50} for the post-treated starch solution.

Corrosion Testing

Corrosion testing was conducted using ASTM standard procedures on a number of aerospace materials prepared as coupons including aluminum alloys, titanium alloy, and coated steel. Each set of test coupons was cut from the same piece of stock using an abrasive water jet. In each case, test coupons were prepared and treated with post-treated starch solutions as prescribed in the applicable ASTM standards.

Assessment of corrosive effects under conditions of total immersion was evaluated using ASTM Standard F 483 (2008). The evaluation included mass changes and visual changes to the test coupons resulting from treatment with the oxidized starch solution. Prior to treatment, the specimens were weighed and visually inspected. The oxidized starch solution was heated to 38˚C in a water bath for the duration of the immersion test. Following immersion of the test coupon in the oxidized starch solution for periods of 24 and 168 hr, the coupons were weighed and inspected for dulling, etching, accretions, and pitting.

Assessment of corrosive effects to unpainted aircraft surfaces were evaluated using ASTM Standard F 485 (2008). Specimens of clad aluminum and titanium alloy were treated by immersion with the post-treated starch solution so that 50% of the coupon area was covered. Following a 30 min drying period at 45˚ to the horizontal in a mechanical convection oven at 150˚C, the coupons were allowed to cool to room temperature and rinsed under tap water for 1 min. The coupons were then rinsed for 15 sec under deionized water and allowed to air dry for 30 min before examination of the panels for residues or stains.

Assessment of damaging effects to coated aircraft surfaces was evaluated using ASTM Standard F 502 (2008). Clad 7075-T6 aluminum test coupons were coated with a chemical conversion coating conforming to MIL-DTL-81706, Class 1A and given an epoxy polyamide primer coating (thickness equal to 0.6 to 0.8 mil) conforming to MIL-PRF-23377. A top coat (thickness equal to1.2 to 1.8 mil) conforming to MIL-PRF-85285 was subsequently applied. The oxidized starch solution was applied to approximately 50% of the panel area and the panel was placed in an oven at 38˚C for 30 min. The coupons were subsequently rinsed with deionized water, and allowed to air dry for 24 hr. The coupons were visually inspected prior to determination of coating durability (hardness). Coating hardness was determined by pushing drawing pencils (hardness equal to 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H 4H, 5H, and 6H) of increasing hardness at an angle of 45˚ to the horizontal along treated and untreated areas of the coupon with uniform pressure until a pencil was found that cut through the coating. Prior to each hardness determination, the pencil lead was squared by abrading with 320 grit sandpaper. Coating hardness was characterized by the pencil that left a black mark but did not cut the coating, with the next hardest pencil cutting the coating.

Assessment of corrosive effects to faying surfaces was evaluated using ASTM Standard F 1110 (2008). Coupon sandwiches consisting of two layers of 50 mm x 100 mm by 1 mm clad and anodized 2024-T3 and 7075-T6 aluminum coupons (anodized according to MIL-A-8625-Type 1 with a hot water seal) were constructed. Each sandwich consisted of one pair of coupons of each alloy separated by filter paper saturated with the test solution. A separate set of sandwiches was prepared and treated with deionized water as a control. Following the regime of exposure to the oxidized starch solution as outlined in ASTM Method F 1110, the panels were visually inspected according to a qualitative rating system:

0 – No visible corrosion and no discoloration present

1 – Very slight corrosion or discoloration and/or up to 5% of area corroded

2 – Discoloration and/or up to 10% of area corroded

3 – Discoloration and/or up to 25% of area corroded

4 – Discoloration and/or more than 25% of area corroded, and/or pitting present

Assessment of corrosive effects to cadmium plated surfaces was evaluated using ASTM Method F 1111 (2008). Test coupons with dimensions of 25.4 mm x 50.8 mm x 1.27 mm were prepared from 4130 steel and cadmium plated to a thickness of 0.013 mm. The coupons were evaluated by a procedure similar to total immersion testing. Initially coupons were immersed in methyl *n*-propyl ketone, the excess solvent was removed, and the coupons allowed to dry in an oven at 110˚C for 1 hr. Following removal from the oven, the coupons were placed in a desiccator for 1 hr and then weighed. The coupons were placed in a starch solution maintained at 38˚C in a water bath for 24 hr; the coupons were then removed and rinsed in a 1 L jar with constant flow of clean tap water. Following this immersion, the coupons were sequentially rinsed with deionized water and acetone and placed in an oven at 110˚C for 1 hr, and cooled to ambient temperature in a desiccator. The coupons were weighed and inspected for dulling, etching, accretions, and pitting.

Qualitative Chemical Analysis

To determine the chemical consituents of the oxidized starch solution, chemical analysis was conducted using gas chromatography/mass spectrometry (GC/MS). Samples were silylated using BSTFA with 1% trimethyl-chorosilane (vol/vol) in pyridine as described by Bartolozzi et al. (1997). Samples of the oxidized starch solution were dried at 105˚C and 10 mg of the resulting material was added to a 2 mL target vial. Pyridine (1 mL) and 400 µL of BSTFA were added, and the vial was capped. The vial was vortexed for 1 min and then placed in an oven at 60˚C. After 2 hr, the vial was removed and vortexed again for 1 min. All suspended particles were allowed to settle prior to removing the supernatant. The extracted liquid was then discharged into another target vial and analyzed by gas chromatography on an HP 5890 Series II gas chromatograph with a Supelco (St. Louis, MO) SPB-5 (15 m x 0.53 mm x 1.5 µm) column and flame ionization detector (FID) to determine an appropriate temperature program. The GC conditions were: injector temperature of 300˚C, detector temperature of 320˚C, initial oven temperature of 60˚C, program rate of 10˚C/min, and final oven temperature of 280˚C.

RESULTS

Initial Evaluation of Substrates and Oxidant Dose

A comparison of freezing point depression data for oxidized corn starch and oxidized potato starch is shown in Table 1. This evaluation of freezing point depression indicates that oxidized corn starch promoted greater freezing point depression than potato starch over the entire range of oxidation conditions evaluated. Potato starch contains significantly greater masses of phosphate that corn starch, which likely results in precipitate formation; phosphate also scavenges hydroxyl radical. Therefore, all subsequent experiments were conducted with corn starch.

Table 1. Central composite rotatable design matrix parameters and data for determination of freezing point depression.

Trial	Coded Values		Actual Values		Freezing Point (˚C)		Difference (˚C)
	Starch Mass (g)	[H_2O_2] (% vol.)	Starch Mass (g)	[H_2O_2] (% vol.)	Potato Starch	Corn Starch	
1	-1	-1	11.6	17.2	-2	-3.7	1.7
2	1	-1	43.4	17.2	NA*	-9.6	NA
3	-1	1	11.6	27.8	-2.5	-3.5	1
4	1	1	43.4	27.8	-7.8	-10.6	2.8
5	-1.4142	0	5.0	22.5	-2.2	-1.9	0.3
6	1.4142	0	50.0	22.5	NA*	-12.6	NA
7	0	-1.4142	27.5	15.0	NA*	-7.3	NA
8	0	1.4142	27.5	30.0	-5	-7.5	2.5
9	0	0	27.5	22.5	-4.7	-7.3	2.6
10	0	0	27.5	22.5	-4.4	-7.5	3.1
11	0	0	27.5	22.5	-4.8	-7.4	2.6
12	0	0	27.5	22.5	-4.6	-7.3	2.7
13	0	0	27.5	22.5	-4.7	-7.6	2.9

* Potato starch did not completely dissolve and formed precipitates.

The experimental data from the central composite design experiments were used to develop regression equations to quantitatively describe the oxidation condition–freezing point relationship using least squares analysis. The regression equation for corn starch is represented graphically in the form of a response surface contour plot in Figure 1. A maximum freezing point depression of 12˚C for oxidized corn starch was observed with 50 g starch/100 mL and 22.5% hydrogen peroxide, which is approximately half the freezing point depression of ethylene glycol and propylene glycol formulations. Based on the response surface plot for corn starch (Figure 1), oxidation conditions of 50 g starch per 100 mL oxidant solution and 25% hydrogen peroxide were selected for post-treatment evaluation. These conditions were chosen because they provided near optimum freezing point depression while providing a practical mass of starch and volume of hydrogen peroxide if the process is scaled to a larger level.

Concentration and Post-treatment of Oxidized Starch Solutions

A complete process diagram indicating the post treatments employed for each experimental procedure is shown in Appendix A (Figure A2). Evaporation of the oxidized starch solutions resulted in freezing point depression of up to 28˚C. However, the evaporated solutions had viscosities greater than 140 cP at 0˚C, which would be difficult to apply to aircraft surfaces. High molecular weight compounds are likely responsible for the high viscosity of the oxidized starch solutions; therefore, GAC and dialysis post-treatment were employed to lower the viscosity of the oxidized starch solutions. The properties of the oxidized starch solutions after post-treatment with different GACs are summarized in Table 2. The viscosity of the oxidized starch solution decreased with increasing masses of GAC used for post-treatment. However, the freezing point increased slightly with increasing GAC treatment. These findings indicate that higher molecular weight oxidation products were not only responsible for increased viscosity but also for a small degree of increased freezing point depression. These results were confirmed when the freezing point was normalized to total dissolved solids (TDS) to yield the same theoretical TDS concentration as the control containing no GAC. In each case, the freezing point depression normalized for TDS was less for samples treated with GAC. When the sample treated with 50 g DARCO GAC was evaporated by a factor equal to the TDS concentration of the control over sample TDS, the freezing point decreased to -26.2˚C while the actual TDS concentration increased less than 2% to 543 g/L and the viscosity rose from 11 to 33 cP. Freezing point depression of 26.2˚C is in the same range as commercial deicing formulations, which depress the freezing point by 25˚C to 30˚C.

Different GAC varieties were not equally effective in lowering the viscosity of oxidized starch solutions. DARCO GAC (12-20 mesh) provided the greatest viscosity reduction, followed by Calgon F-200 (12-40 mesh) and Calgon F-300 (9-30 mesh). However, the viscosity corresponding to a given freezing point was similar in all three GAC treatments. DARCO GAC required approximately 10% of the GAC compared to Calgon F-300 to achieve the same viscosity and freezing point (when normalized for TDS). Similarly, significantly more Calgon F-200 GAC was required to achieve the same viscosity reduction. Post-treatment with 50 g DARCO GAC provided a viscosity similar to commercially available deicers in application ready dilutions (Dow, 2009).

Dialysis was also investigated as a method for lowering the viscosity of the oxidized starch solutions. Diffusion of the oxidized starch solutions through dialysis tubing also resulted in decreased viscosity in the dialysate. A TDS-normalized freezing point of –28˚C was achieved with dialysis post-treatment. However, the dialyzed sample was significantly more viscous than the GAC-treated oxidized starch solutions. Furthermore, dialysis post-treatment requires significantly more time, and does not offer an operational advantage over GAC treated samples. Therefore, GAC was used for post-treatment of all oxidized starch solutions in subsequent experiments.

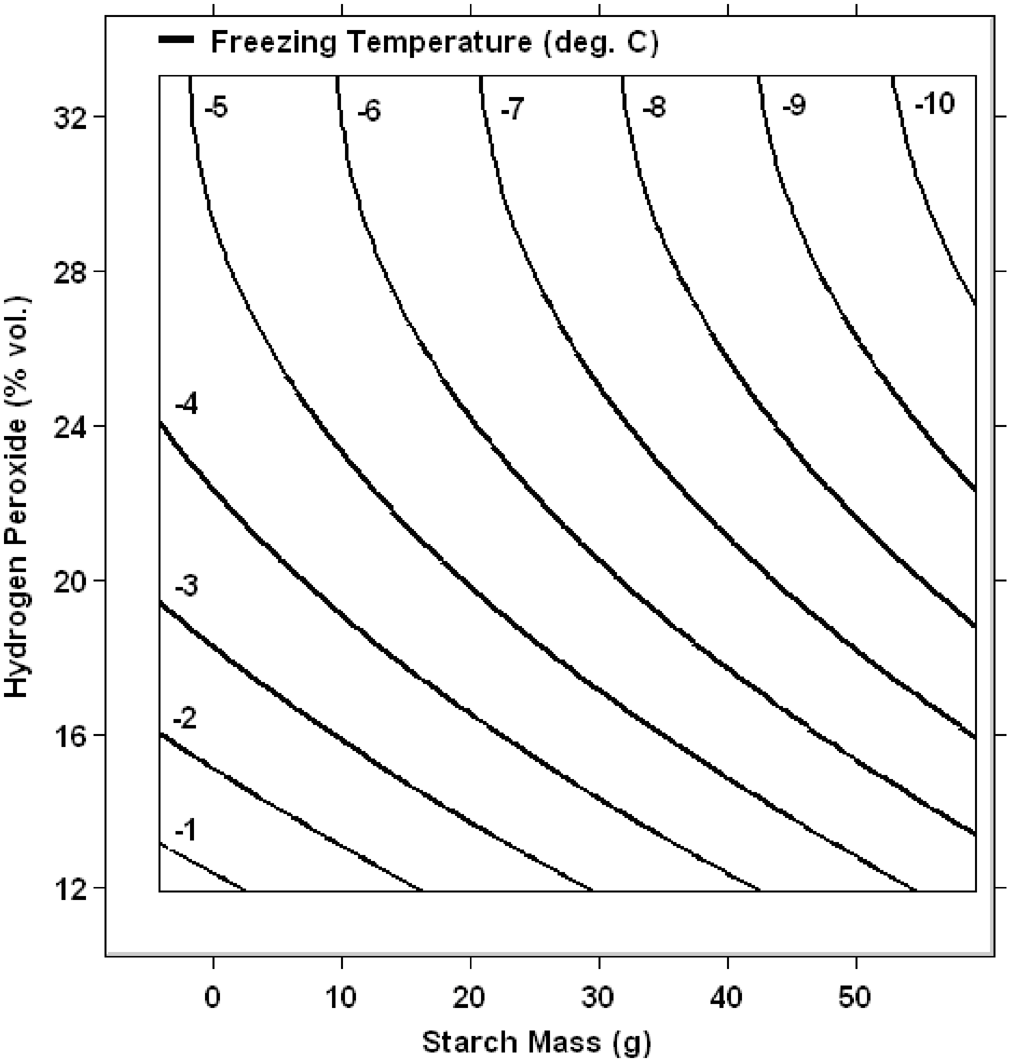

Figure 1. Response surface plot of oxidized corn starch solution freezing temperature as a function of hydrogen peroxide concentration and starch mass.

Table 2. Properties of evaporated oxidized starch solutions after different GAC post-treatments.

Granular Activated Carbon Type	Carbon Mass (g/100 mL)	Freezing Point (˚C)	Kinematic Viscosity at 0˚C (cP)	Total Dissolved Solids (g/L)	TDS Normalized Freezing Point (˚C)*
Sigma Aldrich DARCO 12-20 Mesh	50	-19.7	11	534	-23.4
	25	-22.7	52	569	-25.3
	5	-25.8	104	585	-28.0
	0	-28.0	143	634	-28.0
Calgon F-300 9-30 Mesh	50	-26.2	100	626	-27.4
	0	-28.0	221	655	-28.0
Calgon F-200 12-40 Mesh	50	-22.8	70	557	-26.0

* The TDS normalized freezing point assumes that there is a linear relationship between TDS and freezing point. In other words, if the TDS constituency present in the solution was increased to an amount equal to the TDS of the control, the freezing point of this solution would be approximated by the TDS normalized freezing point. TDS normalized freezing point equals the observed freezing point multiplied by the ratio of TDS in the control to TDS in the sample.

Foaming Properties

Foaming of deicer solutions can interfere with their application to aircraft surfaces, so potential foaming of oxidized starch solutions was quantified by measuring methylene blue active substances (MBAS) (APHA, 2005). Lin et. al. (1999) described the effect of LAS on foaming in domestic wastewater; MBAS concentrations >10 mg/L promote foaming. MBAS was found to be relatively low in the oxidized starch solutions. MBAS was 150 µg/L as linear alkyl benzene sulfonate (LAS), molecular weight = 340, which is relatively low compared to other industrial waters. Because the measured MBAS in the oxidized starch solution was nearly two orders of magnitude less than the concentration reported by Lin et. al. (1999), foaming of the pretreated starch solutions during application would likely be minimal.

Chemical and Biochemical Oxygen Demand

Deicers in common use, such as ethylene glycol and propylene glycol, exhibit high chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Therefore, discharge of these deicers to surface waters can result in oxygen depletion with significant detrimental effects on aquatic biota. The oxidized starch solution treated with 50 g of DARCO activated carbon was evaluated for BOD and COD because it exhibited a similar rheology to commercially available deicer formulations. Results of COD and BOD analysis of the oxidized starch solution are listed in Table 3. The COD of the oxidized starch solution was 340 g/L, which is significantly lower than for the glycols. Normalized to the TDS concentration, the COD of the oxidized starch deicer was 0.637 g O_2/g, lower than the ThOD of ethylene glycol (1.11 g O_2/g) and the ThOD of propylene glycol, 1.68 g O_2/g. The five-day biochemical oxygen demand (BOD_5) of the oxidized starch solution was 103 g/L. Normalized to the TDS concentration, the BOD_5 was 193 g/L, which was significantly lower than that of ethylene glycol and propylene glycol.

BOD_U, based on the BOD exerted after 60 days, was 229 g/L (Table 4). Based on a BOD_U of 229 g/L, the predicted BOD was computed at five day intervals using Equation 6. A summary of BOD results is listed in Table 4 and the actual and predicted oxygen depletion as a function of time is shown in Figure 2. Because the ultimate BOD is only 67% of the COD, 33% of the oxidized starch solutions are likely comprised of a slowly- or non-biodegradable fraction. Although chemical composition and physical properties may vary between GAC treated solutions (solutions with higher TDS will also likely exhibit a greater proportion of higher molecular weight constituents), oxygen demand will likely vary in proportion to the TDS concentration.

Table 3. Comparison of COD and BOD for an oxidized starch solution with GAC post-treatment with ethylene glycol and propylene glycol.

Product	COD (g O_2/L)	TDS Normalized COD (g O_2/g)	BOD_5 (g O_2/L)	TDS Normalized BOD_5 (g O_2/g)
Ethylene Glycol	1230	1.11*	1000**	1110
Propylene Glycol	1860	1.68*	400 – 800**	414 - 829
GAC Treated Oxidized Starch	340	0.637	103	193

* COD was estimated as ThOD.

** BOD_5 estimates reported by Switzenbaum et. al. (2001).

Table 4. Biochemical oxygen demand for an oxidized starch solution treated with 50 grams DARCO activated carbon.

COD (g/L)	BOD_5 (g/L)	BOD_5 Standard Error	BOD_{60} (g/L)	BOD_{60} Standard Error	BOD_{60} % of COD	Oxygen depletion rate constant (1/d)
340	103	3.16	229	10.21	67%	0.097

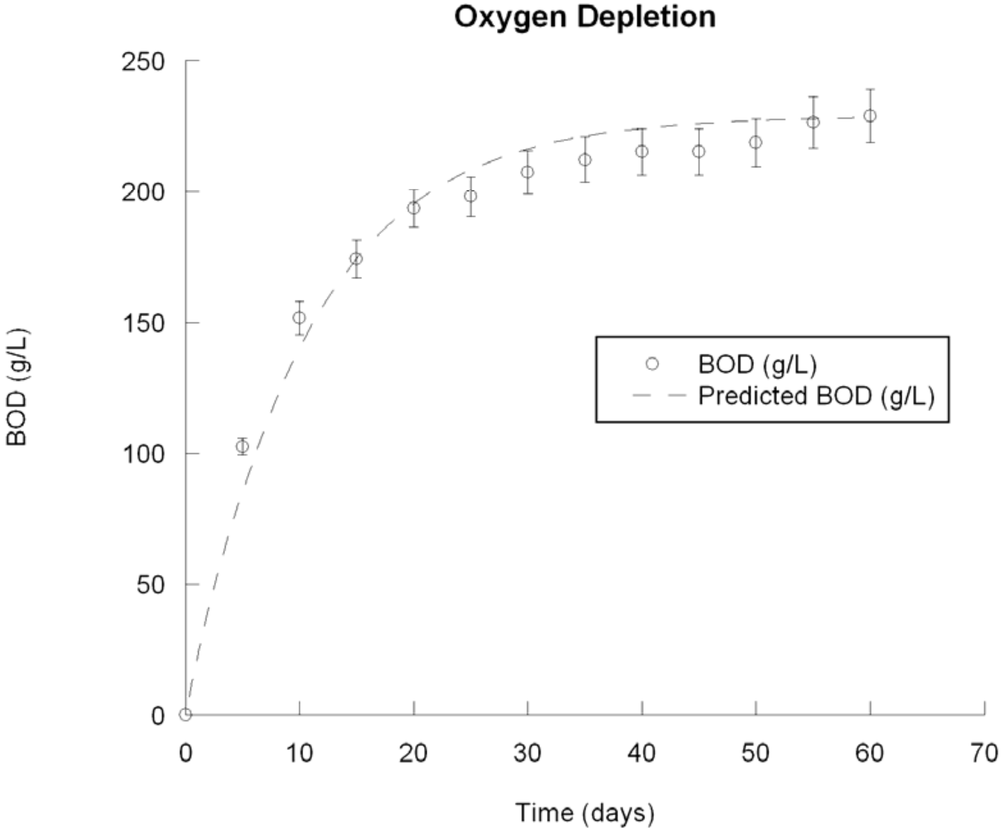

Figure 2. Observed and predicted biochemical oxygen demand with time for samples treated with 50 g DARCO activated carbon. Error bars equal the standard error of six replicates.

Toxicity Testing

In addition to the potential effects of COD and BOD on surface waters, deicers released to surface waters can potentially be toxic to aquatic organisms. A comparison of the lethal aqueous concentrations after 48 hr exposure (48-hr LC_{50}) to *Ceriodaphnia dubia* is listed in Table 5. The 48-hr LC_{50} to *Ceriodaphnia dubia* was 3.52 mL/L (2.73 g/L) for the oxidized starch solution. This toxicity is greater than that of pure propylene glycol; however, it is lower than propylene glycol formulations. Glycols formulated for aircraft deicing exhibit greater toxicity than pure glycols due to the presence of corrosion inhibitors and other additives (Corsi et al., 2006). Future work may include identifying toxic compounds and the selective removal of these constituents.

Table 5. Comparison of 48-hr LC_{50} to *Ceriodaphnia dubia* for an oxidized starch solution given GAC post-treatment with both pure and deicer formulated ethylene glycol and propylene glycol.

Product	LC_{50} (g/L)
Ethylene Glycol (Pure)	34.4*
Propylene Glycol (Pure)	18.3*
Ethylene Glycol (Formulated)	13.1*
Propylene Glycol (Formulated)	1.02*
Oxidized Starch Solution	2.73

* LC_{50} reported by Pillard (1995)

Corrosion Testing

Corrosion testing was conducted based on ASTM standards using a number of aerospace materials prepared as coupons including aluminum alloys, titanium alloy, and coated steel. Test coupons were prepared and treated with the oxidized starch solution as prescribed in the applicable ASTM standards.

The results of corrosive effects under conditions of total immersion of 7075-T6 alclad aluminum (ASTM F 483) and effects on cadmium plated 4130 steel (ASTM F 1111) are listed in Table 6. No corrosion of these metals by the oxidized starch solutions was evident. The effect of oxidized starch solutions on unpainted and painted surfaces (ASTM F 485 and F 502) is shown in Table 7. Exposure of 7075-T6 alclad aluminum, 6Al-4V titanium, and 7075-T6 coated alclad aluminum to the oxidized starch solutions showed no detectable staining, streaking, blistering, or discoloration. However, the sandwich corrosion test (ASTM F 1110, listed in Table 8) showed some corrosivity to 2024-T3 anodized aluminum, 2024-T3 alclad aluminum, 7075-T6 anodized aluminum, and 7075-T6 alclad aluminum, suggesting that the oxidized starch solutions may not be acceptable for use on exposed faying surfaces. Corrosion between faying surfaces may be the result of organic acid salts giving the solution a strong electrolytic effect. Furthermore, the potential to corrode between faying surfaces may prove problematic if adequate sealing of faying surfaces is not conducted prior to deicer application. However, in general, corrosion testing indicated minimal effect of the pretreated starch solution on the aerospace substrates tested.

The absence of visible corrosion under conditions of total immersion (ASTM F 483) in conjunction with low coupon mass loss suggests that treated starch solutions are suitable for application to aircraft materials. Furthermore, application of pretreated starch solutions to painted and unpainted surfaces (ASTM F 485) indicates acceptability as a deicer for aircraft exteriors. However, the sandwich corrosion test (ASTM F 1110) showed significant damage to samples. Corrosion between faying surfaces may be the result of organic acid salts that gave the solution a strong electrolytic effect. The potential to corrode between faying surfaces may prove problematic if adequate sealing of faying surfaces is not done prior to deicer application. In general, corrosion testing indicated little effect of the pretreated starch solution on the aerospace substrates tested.

Table 6. Mass loss due to corrosion and qualitative comparison of samples tested in accordance with ASTM F 483 and F 1111.

ASTM Test Method	Alloy	Average Mass Loss ($mg/cm^2/24hrs$)		Comments
		24 hours	168 hours	
F483	7075-T6 Alclad Aluminum	0.03 ± 0.003	0.16 ± 0.016	No visible corrosion
F1111	4130 Steel (Cadmium Plated)	0.28 ± 0.016	NA	No visible corrosion

Table 7. Qualitative evaluation of unpainted and painted surfaces according to ASTM F 485 and F 502.

ASTM Test Method	Alloy	Results
F485	7075-T6 Alclad Aluminum	No evidence of residue or stain
	6Al-4V Titanium	No evidence of residue or stain
F502	7075-T6 Alclad Aluminum (Coated*)	Both exposed and unexposed panels were abraded at a minimum pencil hardness of 4H. No streaking, discoloration or blistering of the finish was evident

Table 8. Qualitative evaluation of sandwich corrosion effects per ASTM F 1110.

Replicate	2024-T3 Anodized Aluminum	2024-T3 Alclad Aluminum	7075-T6 Anodized Aluminum	7075-T6 Alclad Aluminum
1	4	3	4	4
2	4	3	4	4
3	4	3	4	4
4	4	4	4	4

0 – No visible corrosion and no discoloration present.
1 – Very slight corrosion or discoloration and/or up to 5% of area corroded.
2 – Discoloration and/or up to 10% of area corroded.
3 – Discoloration and/or up to 25% of area corroded.
4 – Discoloration and/or more than 25% of area corroded, and/or pitting present.

Qualitative Chemical Analysis

A chromatogram of the oxidized starch solution is shown in Figure 3, and the compounds identified in the extract via mass spectrometry are listed in Table 9 with their relative proportions. These results indicate that carboxylic acids comprise the majority of the pretreated starch solutions; acetic, propanoic, and butanedioic acids are the predominant organic acid constituents. These acids may have been responsible for the corrosive effects on faying surfaces. Furancarboxylic acid was detected in small amounts (0.4% of the total extract) and may be partially responsible for the higher aquatic toxicity relative to ethylene glycol.

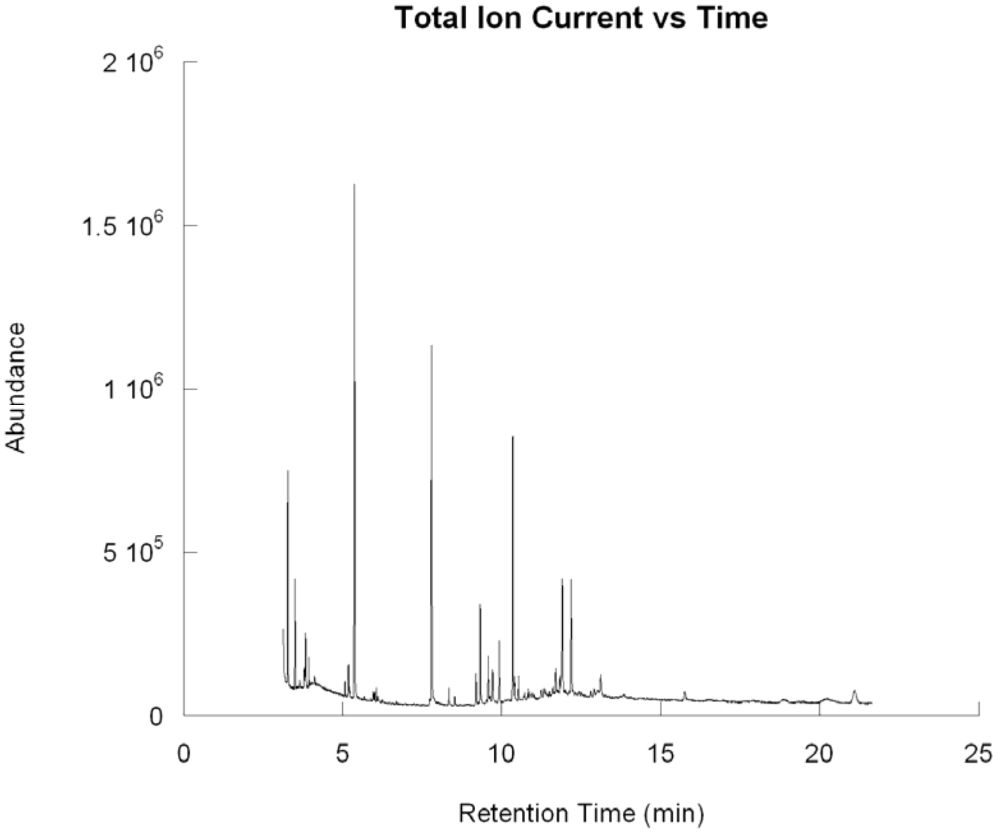

Figure 3. Total ion current as a functions of time for a sample of pretreated starch derivatized with BSTFA.

Table 9. Compound identification from GC/MS analysis for the ten most abundant constituents (excluding derivatization artifacts).

Compound Identification	Retention Time (min)	Percent of Total
Acetic acid	5.38	29.2%
Propanoic acid	7.80	21.2%
Butanedioic acid	10.35	16.3%
D-Glucopyranose	12.19	7.49%
2-Butenedioic acid	11.91	7.46%
Pentenoic acid,	9.33	4.79%
Butanedioic acid	9.93	2.59%
L-Threonic acid	9.59	1.60%
Maltose	21.11	1.44%
DL-Malic acid	9.20	0.98%

The results of research represent proof of concept for the use of oxidized starch solutions for deicing operations and demonstrates a potential ecological advantage to receiving waters. In addition, use of starch-based waste products could potentially be used as feedstock for deicer preparations, perhaps providing an economic advantage over existing products.

Conclusions

Aqueous solutions of modified corn and potato starch were oxidized using CHP (modified Fenton's reagent) as a basis for lowering the freezing point for aircraft deicing. Oxidized corn starch formulations provided greater freezing point depression than oxidized potato starch formulations. Freezing point depression of oxidized starch solutions was as high as 28˚C, which approaches that of commercially available glycol deicers. However, oxidized starch solutions were highly viscous (>140 cP); therefore, high viscosity compounds were removed with GAC. Oxidized starch solutions exerted a BOD_5 up to six times lower than glycol deicers but have a 48-hr LC_{50} to *Ceriodaphnia dubia* greater than pure propylene glycol but lower than propylene glycol deicer formulations. Aircraft materials compatibility was demonstrated for ASTM tests F 483, F 485, F 502, and F 1111; however, application to faying surfaces using ASTM test F 1110 showed some corrosion. Carboxylic acids were identified as the primary constituents of oxidized starch solutions. The results of this proof of concept study demonstrate that oxidized starch solutions have benefits over glycol deicers with the exception sandwich corrosion. In addition to use as aircraft deicers, oxidized starch formulations may also have applications as environmentally friendly runway deicers.

BENEFITS

The results of this research demonstrate that oxidized starch solutions have potential in aircraft deicing operations. In meeting the objectives of the proposed research, results under WP-1677 showed that 1) freezing point depression of up to 28˚C could be achieved using oxidized starch solutions, 2) the BOD and COD of oxidized starch solutions was significantly less than that of ethylene glycol and propylene glycol, 3) the toxicity of the oxidized starch solutions to *Ceriodaphnia* was greater than that of ethylene glycol but less than that of propylene glycol formulations, and 4) the corrosion potential of oxidized starch solutions was minimal, except for faying surfaces. Because this was a limited-scope study, further research is needed before demonstration studies are conducted under ESTCP. Subsequent research could potentially focus on identifying and isolating the deicing potential of each of the carboxylic acids that are present in oxidized starch solutions and the use of solar irradiation to oxidize the starch, which could make the process more economical. One of these components may potentially have excellent deicer characteristics while posing a minimal threat to aquatic life and minimal corrosivity. In summary, the results of this proof of concept research show strong potential for oxidized starch as an environmentally friendly deicer formulation, and the topic is worthy of future study.

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ASTM Standard F 502, 2008. Standard test method for effects of cleaning and chemical maintenance materials on painted aircraft surfaces. ASTM International, West Conshohocken, PA, DOI: 10.1520/F0502-08

ASTM Standard F 1110, 2008. Standard test method for sandwich corrosion test. ASTM International, West Conshohocken, PA, DOI: 10.1520/F1110-08

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APPENDICES

Appendix A. Supporting Information

Figure A1. Photograph of freezing point apparatus built in accordance with ASTM D 1177.

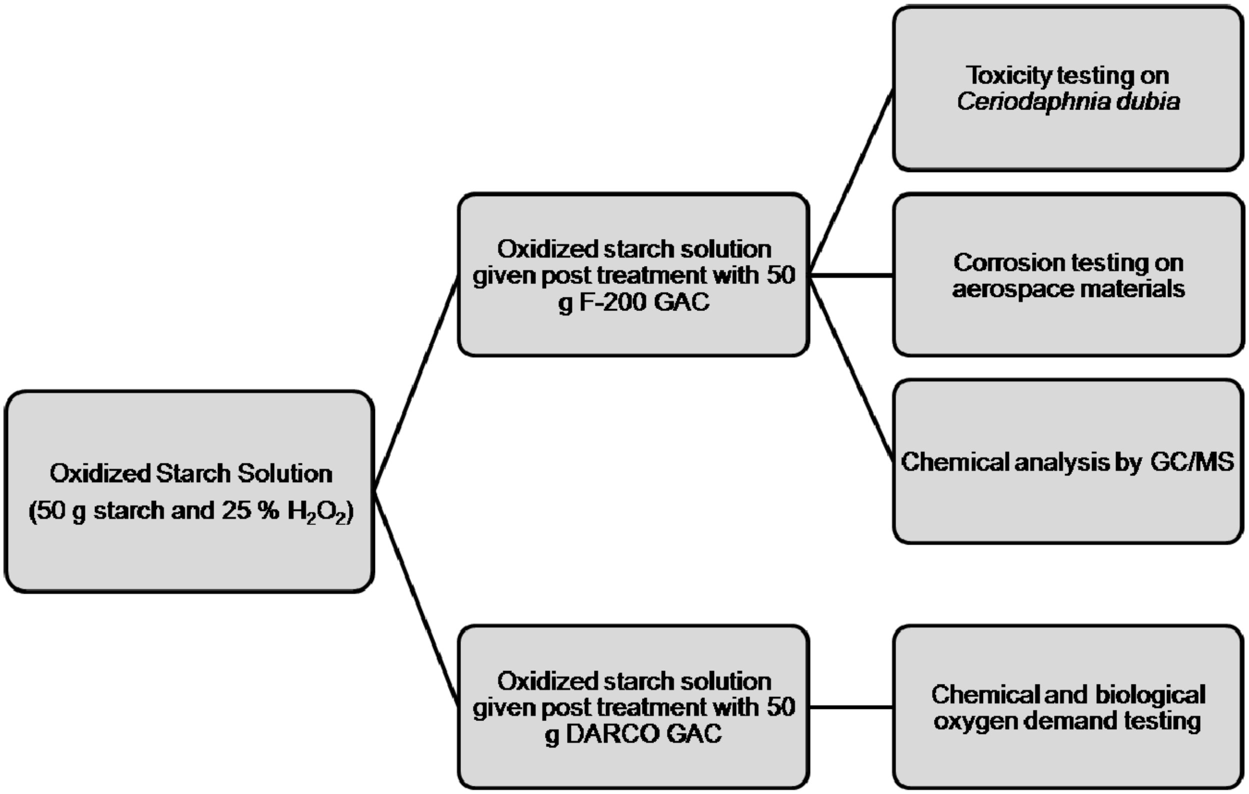

Figure A2. Flow chart depicting experimental sequence

Appendix B. List of Technical Publications.

Conference/symposium proceedings

Use of Oxidized Starch Formulations for Aircraft Deicing. 2009. Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C. December 1-3, 2009. (Watts, R.J, J. Plahuta, A.L. Teel)