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(54) Titre : FLUIDES ANTIGEL OU DE DEGIVRAGE SANS DANGER POUR L'ENVIRONNEMENT QUI UTILISENT DES SOUS-PRODUITS DE TRAITEMENT DE TRIGLYCERIDES

(54) Title: ENVIRONMENTALLY BENIGN ANTI-ICING OR DEICING FLUIDS EMPLOYING TRIGLYCERIDE PROCESSING BY-PRODUCTS

(57) Abrégé/Abstract:
Deicing composition comprised of glycerol-containing by-products of triglyceride processing processes are disclosed.

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(54) Title: ENVIRONMENTALLY BENIGN ANTI-ICING OR DEICING FLUIDS EMPLOYING TRIGLYCERIDE PROCESSING BY-PRODUCTS

(57) Abstract: Deicing composition comprised of glycerol-containing by-products of triglyceride processing processes are disclosed.

ENVIRONMENTALLY BENIGN ANTI-ICING OR DEICING FLUIDS EMPLOYING TRIGLYCERIDE PROCESSING BY-PRODUCTS

FIELD OF THE INVENTION

The present invention relates to deicing fluid compositions and methods for deicing surfaces and for preventing ice formation (anti-icing) on surfaces or within fluids. More particularly the present invention relates to deicing/anti-icing fluid compositions comprising components obtained as glyercol-containing by-products of processing triglycerides for the purpose of manufacturing products such as biodiesel, soaps and fatty acids and salts thereof.

BACKGROUND OF THE INVENTION

Freezing point lowering compositions are in widespread use for a variety of purposes, especially to reduce the freezing point of an aqueous system so that ice cannot be formed or to melt formed ice. Generally, freezing point lowering compositions depend for their effectiveness upon the molar freezing point lowering effect, the number of ionic species that are made available and the degree to which the compositions can be dispersed in the liquid phase in which the formation of ice is to be precluded and/or ice is to be melted.

The most pervasive of the commonly used products for deicing are common salt, calcium chloride, magnesium chloride and urea, with common salt (sodium chloride) being the least expensive and most commonly used. Common salt is widely used to melt ice on road surfaces and the like. In this manner the salt forms a solution with the available liquid in contact with the ice and thereby forms a solution with a lower freezing point than the ice itself so that the ice is melted. Chloride salts, however, suffer from relatively severe drawbacks, such as the harmful effects on surrounding vegetation by preventing water absorption in the root systems, the corrosive effects on animal skin such as the feet of animals, clothing, roadways and motor vehicles, and the deleterious effects on surface and ground water. Thus, any new method of deicing or new deicing composition that can reduce the amount of

chloride salts, or eliminate chloride salts entirely, would solve a long felt need in the art.

Other inorganic salts also are known to be useful as freezing point lowering agents such as, potassium phosphates, sodium phosphates, ammonium phosphates, ammonium nitrates, alkaline earth nitrates, magnesium nitrate, ammonium sulfate and alkali sulfates

Another drawback of certain prior art deicing fluids is their high chemical and biological oxygen demands, which make them environmentally unfavorable. The glycols are exemplary of deicing fluids that particularly suffer from this type of environmental drawback. Thus, any new method of deicing or new deicing composition that can reduce the chemical or short term biological oxygen demands would also solve a long felt need in the art.

Typical solutions of low freezing point deicing and anti-icing agents include chloride salt brines, ethylene glycol and propylene glycol solutions. The use of chloride brines in anti-icing compounds can reduce, although not eliminate, the impacts of chlorides when applied as solids for deicing. Brines and glycol solutions also are employed as components of fluids used to transfer heat in applications where the fluid may be exposed to temperatures below the normal freezing point of water. Ethylene glycol solutions are well known for use as coolants for automobiles and the like in regions where the temperature may fall below the normal freezing point of water. Ethylene and propylene glycols are used in relatively large quantities at major airports in northern climates in order to keep air traffic flowing during inclement weather. The fluids generally are applied to the wings, fuselage and tail of aircraft and in some instances to the runways to remove ice. However, as mentioned above, these glycol compounds likewise have environmental drawbacks and can be detrimental to aquatic life and to sewage treatment processes.

Other prior art deicing fluids, such as alcohols, have toxic effects and high volatility particularly in the low molecular weight range. Further, some of these may

be the cause of offensive smell and fire danger. Furthermore, mono- and polyhydric alcohols oxidize in the presence of atmospheric oxygen to form acids, which can increase corrosion of materials.

Due to the problems associated with deicing agents as described above there have been attempts to discover even more deicing agents. For, example, Kaes, United States Patent No. 4,448,702 discloses the use of a freezing-point lowering composition and method that calls for the addition of a water soluble salt of at least one dicarboxylic acid having at least three carbon atoms, such as a sodium, potassium, ammonium or organoamine salt of adipic, glutaric, succinic or malonic acid.

Peel, United States Patent No. 4,746,449, teaches the preparation of a deicing agent comprising 12-75% acetate salts, trace-36% carbonate salts, 1-24% formate salts and 1-32% pseudolactate salts that is prepared from a pulp mill black liquor by fractionating the black liquor into a low molecular weight fraction and concentrating the collected low molecular weight fraction to produce the deicing agent.

United States Patent No. 4,960,531 teaches that small amounts of methyl glucosides, i.e., less than 10%, can be employed as a trigger to conventional salt deicers.

Back, et al., United States Patent Number 5,993,684, teaches the use of polyhydric alcohols including glycerol in anti-icing or deicing applications, but does not teach the use of by-product streams from triglyceride processing comprising glycerol. Further, Back teaches against the inclusion of potassium and halide salts or the use of glycol in formulations.

Parks, et al., United State Patent Number 4,501,775, teaches the use of low concentrations of polyhydroxyalkanes including glycerol, for the specific purpose of application to coal and mineral ores to insure that any ice formed is physically weak and will not deter the unloading of the coal or mineral ores. Further, Parks does not teach the use of by-product streams from triglyceride processing comprising glycerol.

Roe., United States Patent Number 4,426,409, teaches the use of polyhydric alcohols, including glycerol, in formulations for the purpose, as in Parks above, of reducing the cohesive strength of particles when frozen. Further, Roe does not teach the use of by-product steams from triglyceride processing comprising glycerol.

Special mention is also made of Sapienza, United States Patent. Nos. 5,876,621, 5,980,774, 6,129,857 and 6,506,318, which disclose especially useful deicing and anti-icing compositions.

Mention is also made of a number of other patents that employ industrial process streams in preparing deicing and/or anti-icing compositions. Examples of such patents are Bloomer, United States Patent No. 6,080,330 (desugared sugar beet molasses); Toth et al., United States Patent No. 4,676,918 (alcohol distilling waste); Janke et al., United States Patent No. 5,709,812 (whey); Janke et al., United States Patent No. 5,709,813 (vintner's condensed solubles); Janke et al., United States Patent No. 5,635,101 (corn wet milling process by-products); Bytnar, United States Patent No. 6,468,442 (corn syrup); and Hartley et al., United States Patent No. 6,299,793 (corn syrup).

However, there still exists in the art a need for further improved deicing and/or anti-icing compositions and methods that are environmentally benign and relatively inexpensive to obtain. Preferably, these new and improved compositions are free or significantly reduce the use of inorganic salts, are more environmentally benign and are prepared from relatively inexpensive raw materials while still possessing desirable freezing point depression properties. Likewise, there also exists a need in the art for new deicing and/or anti-icing agents that can be used in combination with prior art deicing agents such as inorganic salts or glycols, to substantially reduce the amount of inorganic salts or glycols needed to accomplish the deicing/anti-icing objectives, and thereby concomitantly reduce the environmental effects of the salts and/or glycols. Surprisingly, it has been found that compositions disclosed herein meet these needs while facilitating by-product disposition from production of soaps, fatty acids and bio-

diesel. Production of biodiesel is an important strategy to reduce dependence on fossil hydrocarbons for transportation fuel, and providing a means for achieving economic value from the by-product stream is an important element in achieving the reasonable production economics.

SUMMARY OF THE INVENTION

The present inventors have found that excellent deicing compositions can be obtained from the by-product of reactions with triglycerides to produce products such as biodiesel, soaps and fatty acids. Triglycerides, the principal components of animal fats and of vegetable oils, are esters of glycerol (glycerine), a trihydric alcohol, with fatty acids of varying molecular weight. Triglyceride reactions of interest include, but are not limited to (1) saponification to produce soap, (2) hydrolysis to produce fatty acids which have various industrial applications including conversion to soaps and (3) transesterification to produce monoesters that can be employed as deisel engine fuel (bio-diesel). The latter reaction, production of biodiesel, is of growing importance as part of the efforts to reduce dependence on fossil fuels, and one impediment in this field is finding a profitable use for the glycerol containing by-product of the reaction.

It is therefore a preferred embodiment of the present invention to provide deicing and/or anti-icing compositions comprising by-products of reactions with triglycerides to produce products such as soaps, fatty acids and monoesters, said by-products comprising glycerol.

In a further preferred embodiment of the present invention the triglyceride processing by-product deicing and/or anti-icing composition is combined with an effective freezing point lowering amount of (a) a hydroxyl-containing organic compound selected from the group consisting of hydrocarbyl aldosides; sorbitol and other hydrogenation products of sugars, monosaccharides, maltodextrins and sucrose; maltitol; glycols; monosaccharides and mixtures thereof, and/or (b) an organic acid

salt selected from the group consisting of a carbonic acid salt, a carboxylic acid salt, a hydroxycarboxylic acid salt, a dicarboxylic acid salt and mixtures thereof.

The present invention still further provides a method for reducing the amount of inorganic salt necessary to achieve effective deicing and/or anti-icing, comprising adding to the inorganic salt, an effective freezing point reducing amount of the triglyceride processing by-product deicing and/or anti-icing composition alone, or in combination with an effective freezing point lowering amount of (a) a hydroxyl-containing organic compound selected from the group consisting of hydrocarbyl aldosides; sorbitol and other hydrogenation products of sugars, monosaccharides, maltodextrins and sucrose; maltitol; glycols; monosaccharides and mixtures thereof, and/or (b) an organic acid salt selected from the group consisting of a carbonic acid salt, a carboxylic acid salt, a hydroxycarboxylic acid salt, a dicarboxylic acid salt and mixtures thereof.

The compositions of the present invention further may comprise a variety of other materials to enhance the deicing and anti-icing performance, such as, but not limited to, coarse solids to improve vehicle traction, corrosion inhibitors to prevent or reduce vehicular and infrastructure corrosion and buffers to control the pH of the compositions.

The compositions and methods of the present invention can be applied to a wide variety of surfaces, including both metallic and non-metallic surfaces of aircraft, which prevents icing, removes frozen water from the surface and prevents its reformation. The invention provides for a deicing composition that can be used on airport runways, bridges, streets, other structures including power lines and industrial equipment and the like. Further, the compositions can be used in heat transfer applications such as, but not limited to, automobile radiator coolants, air conditioner fluids and process heat transfer fluids, and in other applications in which it is vital or desired to maintain a liquid in the unfrozen state, e.g., as in a fire extinguisher or in well drilling fluids, such as those used in drilling for oil and gas. Additionally, the

present invention provides for an anti-icing composition that can be applied to a surface, such as bridges, prior to the onset of icing conditions in order to prevent icing from occurring.

Still further, the compositions of the present invention can be used as a deicer and/or anti-icer for pre-harvest fruit and vegetable crops or other vegetation, such as, but not limited to, golf course greens.

DETAILED DESCRIPTION OF THE PREFFERED EMBODIMENT

The present invention provides novel compositions useful as deicing agents and/or anti-icing agents. The novel compositions of the present invention comprise a by-product from one or more of saponification, hydrolysis and transesterification reactions with triglycerides for the purpose of producing products such as soaps and fatty acids and bio-diesel. Considering these reactions in turn;

Saponification

Saponification, an alkaline hydrolysis of fats and oils with caustic, is the traditional method for manufacture of soap. In this method fats and/or oils are mixed with caustic (such as sodium hydroxide) and boiled. After cooling, salt (NaCl) is added causing the mixture to separate into two layers with the "neat" soap on top and "spent lye" on the bottom. The "spent lye" is the primary by-product and comprises a mixture of glycerol, salt and unreacted caustic together with small quantities of unseparated soap. Typically this spent lye will contain 5-15% glycerol and 8-20% salt. Processing of the spent lye to recover glycerol can proceed through the following steps:

a. Skimming off most or all of the free soap and then boiling the spent lye with fatty acid to remove free caustic and . This is followed by cooling and further skimming.

b. Removal of impurities by coagulation with alum or ferric chloride (purified spent lye).
c. Neutralization with an acid such as HCl (neutralized spent lye).
d. Addition of caustic to raise the pH range to 8.5-9.0 (pH adjusted spent lye).
e. The crude glycerol resulting from the above is then concentrated in two stages of evaporation. During this process the salt crystallizes and is removed as a glycerol-containing solid (glycerol remnant) and the water is removed as vapor. The result of this operation is partially refined glycerol containing up to about 80% glycerol.

In this invention it is envisioned that the glycerol-salt solution obtained at any point in the above sequence could be employed directly, or with minimum evaporation for water removal, as a component of a deicing or anti-icing formulation. For example, in some applications the untreated spent lye could be employed following minimal skimming and neutralization of spent caustic. The small amount of soap remaining could be a useful component in certain deicing or anti-icing applications where efficient surface wetting and/or corrosion resistance is important.

Treatment of rock salt, coal and ores to prevent freezing fall within this category as well as application to surfaces for pedestrian and vehicular use. In many applications, a desirable component of deicing and anti-icing formulations can be made while omitting the coagulation step (b) and completely or partially omitting the evaporation step (e).

Hydrolysis

While saponification was the predominant method of soap manufacture in the US prior to World War II, since the 1940's this method has been partially supplanted by direct hydrolysis of animal fats and vegatable oils to fatty acids

and glycerol (fat splitting). In 1998 world-wide glycerol production from saponification was 200,000 tons and from fatty acid production was 315,000 tons. This hydrolysis typically takes place at high temperature and pressure (ca 500F and 600 psi) in a vertical counter-flow reactor with the fat/oil phase flowing upward and the hot water phase flowing downward. Reactor overheads contain the fatty acid product and the bottoms stream is a water/glycerol stream containing about 12% glycerol. While some of the fatty acid production goes to other applications, the bulk of the recovered fatty acids separately are reacted with caustic to produce soap. In this process the fatty acids/glycerol containing by-product is not separated by salt addition and the resulting 88-90% product, after concentration by evaporation, contains about 5% of other material such as ash (catalyst residue), and heavier organic materials.

In this invention it is envisioned that the bottoms product from the hydrolysis reactor, containing about 12% glycerol can be employed directly as a component of a deicing or anti-icing formulation. Alternatively, this material may be partially concentrated by evaporation.

Transesterification

Tranesterification in this instance involves the splitting of the triglyceride ester in the presence of a monohydroxy alcohol (e.g., methanol or ethanol) so as to produce monoesters of the fatty acids comprising the original triglycerides. It has been found that esters produced in this fashion can be injected as fuels into diesel engines either pure or blended with fossil diesel. This product has become known as biodiesel.

The presently claimed invention employs the glycerol-containing by-product from transesterification reactions, such as biodiesel production, as a valuable component of several deicing and anti-icing formulations. A factor delaying broader use of bio-diesel fuels is the need to find markets for the by-product

glycerol to provide income to offset the otherwise high cost of biodiesel fuels. Preferably this market should lie outside the traditional uses for glycerol, and should not require purification to the standards required for the traditional applications. The present inventors unexpectedly have found an economically viable use of triglyceride processing by-products as a de-icing agent and/or anti-icing agent.

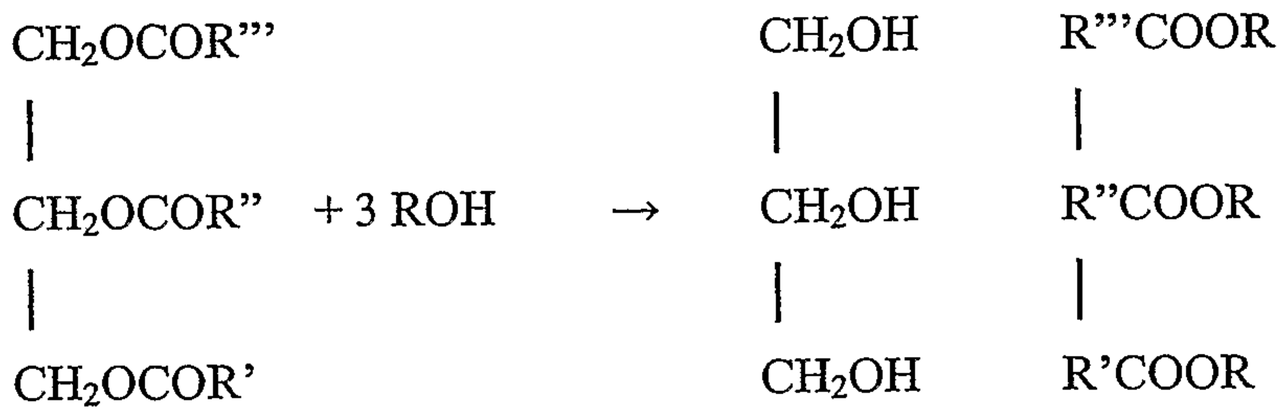
There are three basic routes to production of biodiesel:

- Base catalyzed transesterification of the oil
- Acid catalyzed transesterification of the oil
- Conversion of the oil to fatty acids (hydrolysis per above) and subsequent esterification to biodiesel.

The base catalyzed route is the most popular because of the reaction efficiency, mild operating conditions and requiring only simple materials of construction.

In general, the catalyst used for transesterification of the oil to produce biodiesel commercially is typically any base, most preferably sodium hydroxide or potassium hydroxide. The catalyst is dissolved in the alcohol using a standard agitator mixer. The alcohol/catalyst mix is then charged into a closed reaction vessel and the oil or fat is added. The system from here is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol, around 160°F, to speed up the reaction. Reaction time varies from about 1 to about 8 hours, and some systems recommend that the reaction take place at room temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may

cause problems with soap formation and the separation of the glycerin/glycerol by-product downstream. The general biodiesel reaction is shown below:



wherein R', R" and R"' independently are the same or different fatty acid chains associated with the oil or fat, typically palmitic, stearic, oleic and linolelic acids for naturally occurring oils and fats. R is any hydrocarbyl compound, generally an alkyl group, such as methyl and/or ethyl.

Once the reaction is complete, two major products exit: a glycerol-containing by-product and biodiesel (or soap). Each has a substantial amount of the excess methanol that was used in the reaction. The reaction catalyst is sometimes neutralized at this step if needed. The glycerol phase is much more dense than the biodiesel phase and the two can be gravity separated with glycerol simply drawn off the bottom of the settling vessel. In some cases, a centrifuge may be employed to speed the separation of the two phases.

Once the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed via flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerol and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used.

In some cases the crude glycerol is recovered by a distillation or evaporation step wherein the remaining liquid has a high glycerol, perhaps

80% ,or higher. At atmospheric pressure glycerol boils at 290C. Operation at such a high temperatures can lead to a dark, discolored product due to degradation or reaction with any remaining fatty acids. For the purposes of the present invention, it may be desirable to remove the alcohol by distillation while still retaining the bulk of the water in the glycerol containing bottoms product. By this procedure, high temperature distillation is avoided that would be the case if the bottoms product were a glycerol concentrate.

The glycerol-containing by-product may further contain catalyst, unreacted fatty acids, unseparated biodiesel and soaps. In accordance with the present invention this glycerol-containing by-product can be used directly as a deicing and/or anti-icing agent of the present invention.

In preferred embodiments, the base catalyst that is employed in the transesterification reaction is neutralized prior to use of the biodiesel by-product as a de-icing and/or anti-icing agent. The base catalyst may be neutralized with any acid, although, generally in commercial reactions with triglycerides to produce products such a biodiesel, soaps and/or fatty acids, the catalyst is neutralized by addition of hydrochloric acid. In the practice of the present invention, the present inventors have found that it is preferred to neutralize the base catalyst with an organic acid, such as, but not limited to acetic and/or lactic acid. Of course, other organic acids such as, but not limited to carbonic, hydroxycarboxylic, carboxylic and/or dicarboxylic acids can be employed as neutralizing agents in accordance with the present invention.

It is also contemplated within the scope of the present invention that prior to employing the biodiesel by-product as the deicing or anti-icing composition, one or more of the catalyst, the unreacted fatty acids, the unseparated biodiesel or other impurities can be removed by conventional separation techniques known to those skilled in the art to provide a substantially pure glycerol-containing by-product stream.

It is also envisioned that the compositions of the invention can be prepared for use in either a liquid or a solid format. For instance, the compositions can be prepared as a liquid by mixing with water and sprayed or spread on surfaces. Alternatively it can be prepared in a solid form. Optionally the solid may be further processed using methods well known in the art such as, for example, pelletizing, prilling, flaking, or macerating to provide the formulation in a final useable solid form. Any of the binders known to those skilled in the art optionally may be present and may either be inert or may be comprised of components that actively help lower the freezing point and/or provide improved traction, for example, cinders, sawdust, sand, gravel, sugars, maltodextrins, naturally occurring minerals such as magnesium chloride, trona and mixtures thereof can be used.

It is further envisioned that the compositions of the present invention may also comprise corrosion inhibitors. Such corrosion inhibitors may include, but are not limited to, inhibitors comprising salts of gluconic acid or inhibitors comprising salts of monocarboxylic acids.

The amount of triglyceride processing by-product deicing or anti-icing composition of the present invention that is required to be effective in the total deicing or anti-icing agent can vary over a considerable range. For example we have found that addition of as little as 3% glycerol to a 27% magnesium chloride solution can reduce the eutectic freezing point from –35C to –46C. In other cases, the formulation may consist entirely of the by-product material. For example a composition of 32% glycerol, 22% NaCl in water (typical of a saponification by-product) has a freezing point of - 32C which is substantially below the –21C eutectic of NaCl. In solid formulations, the triglyceride processing by-product deicing and/or anti-icing composition may comprise as much as 100% of the final formulation to be added to the solid carrier material.

It is further contemplated within the scope of the present invention, that in addition to the triglyceride processing by-product, the deicing or anti-icing composition can be combined with an effective freezing point lowering amount of an additive comprising (a) a hydroxyl-containing organic compound selected from the group consisting of hydrocarbyl aldosides; sorbitol and other hydrogenation products of sugars, monosaccharides, maltodextrins and sucrose; maltitol; glycols glycerol; monosaccharides and mixtures thereof, and/or (b) an organic acid salt selected from the group consisting of a carbonic acid salt, a carboxylic acid salt, a hydroxycarboxylic acid salt, a dicarboxylic acid salt and mixtures thereof. The amount of additive generally ranges from about 0.5 to about 95 weight percent based on the weight of the additive and by-product.

Certain of the hydrocarbyl aldosides useful in the practice of the present invention are known to those of ordinary skill in the art such as the di- and polysaccharides. Examples of hydrocarbyl aldosides useful in the practice of the present invention is the glucofuranoside sucrose (table sugar), and maltose and higher polyglucosides.

The hydrocarbyl aldosides also comprise alkyl aldosides. Alkyl aldosides can be prepared, for example, as described in U.S. Pat. Nos. 4,223,129 and 4,329,449, which are incorporated herein by reference. Typical of the alkyl aldosides useful in the practice of the present invention are alkyl glucosides, alkyl furanosides, alkyl maltosides, alkyl maltotriosides, alkylglucopyranosides, mixtures thereof and the like.

Other hydroxyl-containing compounds useful in the practice of the present invention are sorbitol and other hydrogenation products of sugars, monosaccharides, maltodextrins and sucrose such as maltitol, xylitol and mannitol; glycols such as ethylene glycol and propylene glycol; glycerols; and monosaccharides. These materials are available commercially and are well known to those of ordinary skill in the art.

The organic salt components useful in the practice of the present invention include the carboxylic acid salts, the hydroxycarboxylic acid salts, dicarboxylic acid salts.

The carboxylic acid salts that are useful in the practice of the present invention are likewise available commercially and are known to those skilled in the art. Carboxylic acid salts preferred for use in the practice of the present invention comprise the sodium or potassium salts of formates, acetates, propionates, butyrates and mixtures thereof. Also preferred are potassium acetate and/or potassium formate.

The hydroxycarboxylic acid salts that are useful in accordance with the present invention are available commercially and are known to those skilled in the art. Preferred hydroxycarboxylic acid salts comprise the salts of lactic acid such as sodium lactate and potassium lactate. However, any of the cesium, sodium, potassium, calcium and/or magnesium salts of hydroxycarboxylic acids may be employed such as sodium gluconate.

The dicarboxylic acid salts that are useful in accordance with the present invention are available commercially and are known to those skilled in the art. Preferred dicarboxylic acid salts comprise sodium and potassium salts of oxalates, malonates, succinates, glutarates, adipates, maleates, fumarates and mixtures of any of the foregoing.

Also useful as a deicing component in certain of the compositions of the present invention are the high solubility carbonic acid salts. Preferred carbonate salts for use in the practice of the present invention are potassium carbonate, potassium bicarbonate, sodium carbonate and cesium carbonate. Potassium carbonate is especially preferred.

Also useful as deicing components in certain compositions of the present invention are the highly soluble salt forms of sodium formate, potassium acetate and sodium lactate. In many applications, the addition of these salts has been found to provide synergistically unexpected reductions in freezing points.

The following table presents some examples of the combination of glycerol with other deicing components:

Example	1	2	3	4	5	6	7	8
Composition, wt%								
Glycerol	50	25		25			25	
Potassium Carbonate		25	47					
Sodium Formate								
Potassium Acetate				25	25	50		
Sodium lactate							25	50
Water	50	50	53	50		50	50	50
Freezing point, C	-23	-37	-20	-41	-18	-60	-39	-32

Comparing examples 1, 2 and 3, it is noteworthy that the freezing point of a 50% mixture of glycerol and potassium carbonate is lower that a 50% solution of glycerol or a 47% solution of potassium carbonate. A comparison of examples 1, 7 and 8 show the same phenomenon with sodium lactate. In the case of potassium acetate (examples 1, 4, 5 and 6), the 25/25 mixture has a freezing point one would expect by a linear

interpolation of the freezing point of the components at 50%. In this case, the effect of glycerol substitution is to provide a deicing/anti-icing formulation having a low freezing point, substantially below the freezing point of 25% potassium acetate. This improvement is coupled with the other characteristics provided by glycerol and the other constituents that may be present in a by-product glycerol-containing material. These other characteristics may include, better viscosity and wetting capabilities, and/or corrosion inhibition properties.

In certain instances, where the use of the organic acid components of the present invention causes the pH of the total composition to be too high to meet regulatory or industry specifications, it is contemplated herein to use a buffering agent to lower the pH to acceptable levels. Suitable buffering agents may be selected from any of the known buffering agents. Especially preferred is boric acid. For example in certain highway applications, compositions including potassium carbonate and/or potassium bicarbonate in combination with the triglyceride processing by-product of the present invention, may have a pH above 12 depending on the exact formulation, and most state highway departments prefer deicers having a pH below 12. An effective amount of boric acid or other buffering agent may be added to reduce the pH of the deicing compounds to less than 12, i.e., to from about 11.5 to about 11.8 or lower, to meet the specifications. Alternatively, during the preparation of the carbonate the pH can be adjusted by continued reaction to bicarbonate or separate addition of same.

The present invention still further contemplates combining the triglyceride processing by-product deicing composition with other industrial process streams useful in deicing and/or anti-icing products. For example, the other industrial process streams may be selected from any such streams containing the hydroxyl or oganic acid compounds enumerated above including, but not limited to, those selected from the group consisting of a grain stillage, grain steepwaters, wood stillage, corn syrups,

products of agricultural or milk fermentation processes, products of sugar extraction processes such a desugared sugar beet molasses and/or desugared sugar cane molasses, hydrogenation products of sugars, monosaccharides, maltodextrins and sucrose and mixtures of any of the foregoing. These industrial streams may be employed directly, or may be treated, such as by alcoholysis to convert the hydroxyl containing compounds to esters, or by reacting convert the organic acids to anionic organic acid salts, such as with a caustic.

Generally the triglyceride processing by-product deicing and/or anti-icing agents useful in the practice of the present invention may be used in solid form, liquid form or liquid form mixed with water.

In addition to (a) the certain hydroxyl-containing organic compounds and (b) the certain organic acid salts, it is contemplated by the present invention that other organic components may be included in the deicing and/or anti-icing compositions of the present invention. Exemplary of such materials are citrate salts such as sodium citrate; amino acids and their salts such as lysine glutamate, sodium pyrrolidone carboxylate and sodium glucoheptonate; lignin components such as lignin sulfonate; boric acid and its salts; sodium gluconate and other gluconic acid salts; and mixtures of any of the foregoing.

In the methods of the present invention, the deicing and/or anti-icing compositions of the present invention are applied, such as by spraying for liquid forms, or spreading for solid forms, onto the surface desired to be treated. In the case of deicing, the surface already has ice formed thereon, and the deicing compositions of the present invention melt the ice already formed and are further effective in preventing additional ice formation. In the case of anti-icing, upon learning of a weather forecast that predicts possible dangerous icing conditions, the roads, bridges, airplanes, runways, growing produce or other surfaces can be pretreated with the anti-

icing compositions of the present invention in similar manner in order to prevent ice formation on the treated surfaces.

In situations where some inorganic salts such as sodium chloride, magnesium chloride and calcium chloride, can be tolerated, the present invention provides an improved method for reducing the amount of salt to be added to achieve an equivalent or better deicing and/or anti-icing effect, and thereby reduce the detriment to the environment. Further, we have found that addition of the glycerol-containing by-products is effective in lowering the effective use of these chlorides into temperature regions substantially below the eutectic points of the simple chloride solutions. For example, we made a mixture of 90% of a crude glycerol stream obtained from soap production, containing glycerol, sodium chloride and some remaining soap and 10% of additional sodium chloride and determined that the resulting liquid did not encounter ice formation until a temperature of –35C, considerably below the sodium chloride eutectic of –21C. The addition of salt separated some of the dissolved soap, but a small amount of soap remained providing for good wetting characteristics of the resulting formulation.

Many variations of the present invention will suggest themselves to those skilled in the art in light of the above-detailed description. For example, the triglyceride processing by-product can be combined with any industrial process stream that contains carboxylic acid salts, hydroxycarboxylic acid salts and/or dicarboxylic acid salts in preparing compositions of the present invention. Additionally, a wide variety of glucosides, carbonates, hydrocarbyl aldosides, and a variety of combinations of the components of the present invention may be employed as additives to the triglyceride processing by-product in the compositions of the present invention. All such obvious modifications are within the full-intended scope of the appended claims.

The above-referenced patents, test methods, and publications are hereby incorporated by reference.

What is claimed is:

1. A deicing and/or anti icing composition comprising one or more glycerol-containing by-products of triglyceride reactions selected from the group consisting of (1) glycerol containing by-products of triglyceride saponification reactions, (2) glycerol containing by products of triglyceride hydrolysis reactions glycerol, (3) glycerol containing by-products of tranesterification reactionsand (4) mixtures thereof.

2. A deicing and/or anti-icing composition as defined in Claim 1 wherein said glycerol-containing by-product further comprises unreacted fatty acid, unseparated reactants, unseparated product and mixtures thereof.

3. A deicing and/or anti-icing composition as defined in Claim 1 wherein said saponification by-product is selected from the group consisting of spent lye, skimmed spent lye, purified spent lye, neutralized crude glycerol, pH adjusted crude glycerol, desalted crude glycerol, glycerol remnant, partially refined glycerol and mixtures thereof.

4. A deicing or anti-icing composition as defined in Claim 1 wherein said by-product of a triglyceride hydrolysis reaction comprises a reactor bottoms stream from a hydrolysis reactor.

5. A deicing and/or anti-icing composition as defined in Claim 4 wherein said reactor bottoms further is processed through an evaporation step to remove at least part of the water contained therein.

6. A deicing and/or anti-icing composition as defined in Claim 1 wherein said triglyceride processing by-product comprises a glycerol containing by-product of a catalyzed transesterification reaction employing a monoalcohol to produce monoesters from fats and oils.

7. A deicing and/or anti-icing composition as defined in Claim 6 wherein said monoesters are produced for use in diesel fuel.

8. A deicing and/or anti-icing composition as defined in Claim 6 wherein said monoalcohols are selected from the group consisting of methanol, ethanol and mixtures thereof.

9. A deicing and/or anti-icing composition as defined in Claim 6 wherein said glycerol containing by-product comprises the transesterification reactor effluent from which unconverted monoalcohol has been at least partially stripped for recovery and/or recycling.

10. A deicing and/or anti-icing composition as defined in Claim 9 wherein said reactor effluent further is processed to remove at least part of the contained water.

11. A deicing and/or anti-icing composition as defined in Claim 6 wherein a base is used as a catalyst in said transesterification reaction.

12. A deicing and/or anti-icing composition as defined in Claim 11 wherein said base is selected from the group consisting of sodium hydroxide, potassium hydroxide and mixtures thereof.

13. A deicing and/or anti-icing composition as defined in Claim 11 wherein said base catalyst is neutralized with an acid neutralizer.

14. A deicing and/or anti-icing composition as defined in Claim 13 wherein said acid neutralizer is selected from the group consisting of inorganic acids carbonic acids, hydroxycarboxylic acids, carboxylic acids, dicarboxylic acids and mixtures thereof.

15. A deicing and/or anti-icing composition as defined in Claim 14 wherein said acid neutralizer comprises acetic acid, lactic acid or mixtures thereof.

16. A deicing and/or anti-icing composition as defined in Claim 9 wherein said triglyceride processing by-product is processed further to remove substantially all of said base catalyst, unreacted fatty acid and unseparated product.

17. A deicing and/or anti icing composition as defined in Claim 1 wherein said glycerol-containing triglyceride processing by-product is present in an amount ranging from about 2 to about 100 weight percent of the total composition.

18. A deicing and/or anti-icing composition as defined in Claim 1 wherein said composition further comprises an effective freezing point lowering amount of an additive comprising (a) a hydroxyl-containing organic compound selected from the group consisting of hydrocarbyl aldosides; sorbitol and other hydrogenation products of sugars, monosaccharides, maltodextrins and sucrose; maltitol; glycols; monosaccharides and mixtures thereof, and/or (b) an acid salt selected from the group consisting of a carbonic acid salt, a carboxylic acid salt, a hydroxycarboxylic acid salt, a dicarboxylic acid salt and mixtures thereof.

19. A deicing and/or anti-icing composition as defined in Claim 18 wherein said additive is present in an amount ranging from about 0.5 to about 95 weight percent based on the weight of the hydroxyl-containing triglyceride processing by-product and additive combined.

20. A deicing and/or anti-icing composition as defined in Claim 18 wherein said hydrocarbyl aldoside comprises an alkyl aldoside.

21. A deicing and/or anti-icing composition as defined in Claim 20 wherein said alkyl aldoside is selected from the group consisting of alkyl glucosides, an alkyl furanosides, alkyl maltosides, alkyl maltotriosides, alkylglucopyranosides and mixtures thereof.

22. A deicing and/or anti-icing composition as defined in Claim 18 wherein said hydrocarbyl aldoside comprises a disaccharide, a polysaccharide or mixtures thereof.

23. A deicing and/or anti-icing composition as defined in Claim 18 wherein said hydrogenation product of sugars comprises sorbitol, maltitol, xylitol, mannitol or mixtures thereof.

24. A deicing and/or anti-icing composition as defined in Claim 18 wherein said glycols comprise ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol or mixtures thereof.

25. A deicing and/or anti-icing composition as defined in Claim 18 wherein said monosaccharide is selected from the group consisting of glucose, fructose and mixtures thereof.

26. A deicing and/or anti-icing composition as defined in Claim 18 wherein said carboxylic acid salts are selected from the group consisting of potassium or sodium salts of formates, acetates, propionates, butyrates and mixtures thereof.

27. A deicing and/or anti-icing composition as defined in Claim 18 wherein said hydroxycarboxylic acid salt is selected from the group consisting of the sodium and potassium salts of lactic acid, gluconic acid and mixtures thereof.

28. A deicing and/or anti-icing composition as defined in Claim 18 wherein said dicarboxylic acid is selected from the group consisting of the potassium or sodium salts of oxalates, malonates, succinates, glutarates, adipates, maleates, fumarates and mixtures of any of the foregoing.

29. A deicing and/or anti-icing composition as defined in Claim 1 wherein said carbonic acid is selected from the group consisting of the potassium carbonate, potassium bicarbonate, sodium carbonate, sodium bicarbonate and mixtures of any of the foregoing.

30. A deicing and/or anti-icing composition as defined in Claim 1 wherein said hydroxyl-containing triglyceride processing by-product is combined with an effective freezing point reducing amount of a hydroxyl-containing organic industrial process stream.

31. A deicing and/or anti-icing composition as defined in Claim 30 wherein said industrial process stream is selected from the group of grain stillage, wood stillage, grain steepwaters, products of agricultural or milk fermentation processes, cane or beet sugar extraction processes and mixtures thereof.

32. A deicing and/or anti-icing composition as defined in Claim 1 wherein said hydroxyl-containing triglyceride processing by-product stream is combined with an effective freezing point reducing amount of an organic component selected from the group consisting of citrate salts, amino acids, amino acid salts, lignin components, boric acid, boric acid salts sodium citrate, lysine glutamate, sodium pyrrolidone carboxylate, sodium glucoheptonate, lignin sulfonate and mixtures thereof.

33. A deicing and/or anti-icing composition as defined in Claim 1 wherein said hydroxyl-containing triglyceride processing by-product stream is combined with an effective freezing point reducing amount of an inorganic salt.

34. A deicing and/or anti-icing composition as defined in Claim 27 wherein said inorganic salt is selected from the group consisting of sodium chloride, calcium chloride, magnesium chloride, potassium phosphates, sodium phosphates, ammonium phosphates, ammonium nitrates, alkaline earth nitrates, magnesium nitrate, ammonium sulfate, alkali sulfates and mixtures thereof.

35. A method of deicing and/or anti-icing a surface, said method comprising adding to said surface a composition as defined in Claim 1.

36. A method as in Claim 35 wherein said surface is a pedestrian walkway or a vehicular roadway, highway, bridge or parking facility.

37. A method as in Claim 35 wherein said surface is an aircraft surface comprising wings, fuselage or tail surfaces.

38. A method as in claim 35 wherein said surface is an airport runway or taxiway.

39. A method as in Claim 35 wherein said surface comprises the deck or portion of a superstructure of a ship.

40. A method as in Claim 35 wherein said surface comprises weather exposed industrial equipment.

41. A method as in Claim 40 wherein said industrial equipment is selected from the group consisting of conveyor systems; storage facilities; support systems and lines for transmission of electric power or electronic signals; or exposed machinery or processing equipment.

42. A method as in Claim 35 wherein said surface comprises the surfaces of particles selected from the group consisting of coal, ores, sand and gravel.

43. A liquid material for use at temperatures below the freezing point of water, said liquid comprising the anti-icing composition as defined in Claim1.

44. A method as defined in Claim 43 wherein said liquid material is used as a fire extinguisher fluid.

45. A liquid material as defined in Claim 43 wherein said liquid material is used as a heat transfer agent.

46. A liquid material as defined in Claim 45 wherein said heat transfer agent is employed in an application selected from the group consisting of vehicular

radiator systems, air conditioning systems, systems for transferring process heat and systems for recovery of heat from process or power generation systems.

47. A liquid material as defined in Claim 43 wherein said liquid material is used as a component of fluids used in drilling oil and gas wells.

48. A method for deicing and/or anti-icing comprising of applying the deicing or anti-icing composition defined in Claim 1 in a solid format to an area in need of deicing or anti-icing.

49. A method as in Claim 48 wherein said solid format is achieved be absorbing or adsorbing said deicing or anti-icing composition on an inert solid or binder.

50. A method as in Claim 49 wherein said inert solid or binder is selected from the group consisting of cinders, sand, sawdust, gravel and mixtures thereof.

51. A method as in Claim 48 wherein said solid format is achieved by absorbing or adsorbing said deicing or anti-icing composition on a solid deicing material.

52. A method as in Claim 51 wherein said solid deicing material is selected from the group consisting of sugars, maltodextrins, inorganic salts, organic salts or mixtures thereof.

53. A method as in Claim 52 wherein said inorganic salts are selected from the group consisting of sodium chloride, magnesium chloride, calcium chloride, trona and mixtures thereof.

54. A method as in Claim 52 wherein said organic salts are selected from the group consisting of sodium or potassium salts of formic acid, acetic acid, lactic acid, calcium magnesium acetate, or mixtures thereof.

55. A method as in Claim 48 wherein the solid format is achieved by processing said composition employing a procedure for converting a liquid to a solid.

56. A method as in Claim 55 wherein said procedure is selected from the group consisting of pelletizing, prilling, flaking, macerating and combinations thereof.

57. A deicing or anti-icing composition as in Claim 1 further comprising a corrosion inhibitor.

58. A deicing or anti-icing composition as in Claim 57 wherein said corrosion inhibitor is selected from the group consisting of inhibitors comprising salts of gluconic acid, inhibitors comprising monocarboxylic acid salts and mixtures thereof.

59. A deicing or anti-icing composition as in Claim 1 further comprising solid materials to provide traction for vehicular traffic.

60. A deicing /andor anti-icing composition as in Claim 59 wherin said solid materials are selected from the group consisting of sand, gravel, abrasives, salt and mixtures thereof.

61. A method for preventing frost damage to vegetation, said method comprising applying the deicing and/or anti-icing compositon as in Claim 1 to said vegetation.

62. A method as in Claim 61 wherein said vegetation comprises pre-harvest fruits and vegetables, buds of fruit trees, recreational surfaces or golf greens.

63. A process for preparing the glycerol-containing by product as defined in Claim 9 wherein the major portion of unconverted monoalcohol is removed from said reactor effluent prior to removing a major amount of the water contained therein.

64. A process as described in Claim 63 wherein the process is a fractional distillation process conducted at low pressure, or under a vacuum.