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(54) Titre : LIQUIDE POUR LA PREVENTION DU GEL DES AERONEFS ET DES PISTES D'ENVOL ET
D'ATERRISSAGE
(54) Title: LIQUID FOR THE PREVENTION OF FREEZING OF AIRCRAFTS AND RUNWAYS

(57) **Abrégé/Abstract:**

The present invention relates to an environmentally friendly liquid for the prevention of freezing of aircrafts and runways, said liquid being particularly suitable to various spraying equipments. The vapor pressure of the said liquid is less than 5 Pa, and the acute oral toxicity, LD₅₀, is more than 10 000 mg/kg. This anti-freezing liquid comprises 10-60 wt.% trimethyl glycine or derivatives thereof, and 40-90 wt.% water, and optionally additives known for anti-freezing liquids.



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(21) International Application Number: PCT/FI98/00663 (22) International Filing Date: 26 August 1998 (26.08.98) (30) Priority Data: 973552 29 August 1997 (29.08.97) FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): ILVES, Antti [FI/FI]; Viertotie 12 A 35, FIN-06400 Porvoo (FI). REIJONEN, Heikki [FI/FI]; Kevättie 1 C, FIN-02200 Espoo (FI). NIEMINEN, Jukka-Pekka [FI/FI]; Viertokuja 1 G 27, FIN-06400 Porvoo (FI). (74) Agent: FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN-00100 Helsinki (FI).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LIQUID FOR THE PREVENTION OF FREEZING OF AIRCRAFTS AND RUNWAYS (57) Abstract The present invention relates to an environmentally friendly liquid for the prevention of freezing of aircrafts and runways, said liquid being particularly suitable to various spraying equipments. The vapor pressure of the said liquid is less than 5 Pa, and the acute oral toxicity, LD₅₀, is more than 10 000 mg/kg. This anti-freezing liquid comprises 10–60 wt.% trimethyl glycine or derivatives thereof, and 40–90 wt.% water, and optionally additives known for anti-freezing liquids.		

Liquid for the prevention of freezing of aircrafts and runways

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The present invention relates to an environmentally friendly liquid for the prevention of freezing of aircrafts and runways, said liquid being particularly suitable to various spraying equipments.

- 10 The prevention of formation of ice onto aircrafts and runways, as well as ice removal is commonly accomplished with several anti-freezing chemicals to ensure a safe take-off, landing, and flight, particularly in wintertime. These anti-freezing agents are generally ethylene or propylene glycol based sprayable solutions or foams, if necessary mixed with thickening agents to increase the viscosity, water, surface active agents, and
- 15 corrosion inhibitors. Such ethylene or propylene glycol based anti-freezing agents are toxic, polluting the environment as they are flushed into the earth. Further, an unpleasant odor is released therefrom into and carried by air currents. Such anti-freezing agents may also cause corrosion problems. The anti-freezing agents commonly sprayed onto aircrafts generally contain at least 60% glycol, normally
- 20 ethylene glycol, or a mixture of other glycols.

- The function of the anti-freezing agent is to remove snow, ice and hoarfrost from the surface of the aircraft that have formed as the aircraft stays at the airport. The snow, ice and hoarfrost freezed on the aircraft significantly influence the aerodynamic
- 25 properties, and the performance of the engines thereof, eventually leading to dangerous situations, for instance during the take-off of the machine. For this reason the machines are always checked before the departure to make sure they are free from ice, snow and hoarfrost.

- 30 The prevention of freezing of the runways and ice removal therefrom include the use of anti-freezing chemicals. The main function of these chemicals is to diffuse through the snow and ice already formed to weaken the bonding therein, allowing

them to be much more easily removed by mechanical means. In addition, anti-freezing chemicals are used in conditions where water and snow may freeze on the runway.

5 The *SU patent publication No 1664808* discloses a composition useful for the prevention of freezing, and for thawing powdered or granular materials like flour, sand, or any of the kind. This composition comprises magnesium or calcium chloride, ammonia, carbohydrates, glycerin, lactic acid, volatile acids, betaine, amino acids, fatty compounds, as well as water. The purpose of this composition is
10 to prevent the freezing of the powdered material, particularly during transport thereof, on the walls and bottom of the container, and the aggregation thereof, as well as to thaw the material already frozen.

The *US patent publication No 5079036* describes an anti-freezing composition for the
15 prevention of freezing and aggregation of a solid granular material like mineral coal or ore during handling and transport thereof at a temperature below 0°C. This composition forms a foam onto the solid particles. It comprises a solution suitable as an anti-freezing agent, such as of salts like sodium chloride, potassium chloride, magnesium chloride, calcium chloride, or of polyhydroxy compounds or monoalkyl
20 ethers or dialkyl ethers, such as ethylene and propylene glycols, glycerol, sugar and mixtures thereof. Further, cellulose derivatives, for instance sodium carboxymethyl cellulose and ethyl hydroxyethyl cellulose are mentioned as suitable anti-freezing agents. Besides this anti-freezing agent the composition includes an anionic or amphoteric surface active agent allowing the formation of a stable foam. For this
25 purpose suitable compounds are such anionic surface active agents as sulphonates, and such amphoteric surface active agents as the derivatives of betaine, among others. In addition, the composition contains water.

The *European patent publication 743305* discloses a anti-freezing composition,
30 particularly for the prevention of freezing of aircrafts and the wings thereof. This publication presents a novel surface active agent, namely a polyether amide, that may be used in combination with alkylen glycol based anti-freezing agents, using

polyacryl acids as thickeners. Moreover, said compositions typically comprise a corrosion inhibitor, optionally an amine, potassium hydroxide or alkalimetal hydroxide, and water.

- 5 Most common water based anti-freezing liquids are typically aqueous mixtures of ethylene and propylene glycols, and water. Particularly, ethylene glycol is used in various applications of the automobile industry. Disadvantages of ethylene glycol are, however, the toxicity, and the polluting character thereof. Accordingly, propylene glycol is often used instead of ethylene glycol in applications where a
10 lower toxicity is required. Although propylene glycol is relatively nontoxic, it is, however, also environmentally questionable. Another drawback of propylene glycol is that the viscosity thereof increases significantly at low temperatures, making a higher pumping power necessary.
- 15 Compared to ethylene glycol, the lower toxicity of ethanol makes its use more attractive. The use of ethanol is, however, limited by the high volatility, and as a consequence the liability thereof to catch fire, as well as by the great viscosity increase at low temperatures, this viscosity increase being, however, less significant than with propylene glycols. For this reason, ethanol is widely used as a cooling
20 liquid in laboratories and in situations where nontoxicity is required.

Corrosion, particularly when using glycols, makes the search for expensive and effective corrosion inhibitors indispensable. The compositions and concentrations of corrosion inhibitors are difficult to control. Generally, as a result of an effective
25 inhibitor a liquid with a very low toxicity becomes toxic. Normally, complex solutions make the final liquid more expensive.

An object of the present invention is to provide an anti-freezing liquid particularly useful for the prevention of freezing of aircrafts and runways, and the equipment
30 therefor, and by means of which it is possible to solve the problems associated with the state of the art, and to eliminate the disadvantages thereof.

Further, an object of the invention is to provide an anti-freezing liquid suitable for aircrafts and runways, the use thereof being environmentally safe and economical, as well as without any risk to the health.

- 5 The anti-freezing liquid for aircrafts and runways of the invention is characterized in the appended claims.

According to the invention the preferable compound useful as a component of the said anti-freezing liquid for aircrafts and runways is trimethyl glycine, or the salts
10 of trimethyl glycine hydrate. Trimethyl glycine, or betaine, is particularly preferable. Betaine may for instance be prepared by extracting from natural products such as from sugar beets, or by a biochemical process thus allowing the production of a biological anti-freezing liquid with a favorable life cycle.

- 15 The liquid used for the prevention of freezing of the aircrafts and runways according to the invention contains 10—60% trimethyl glycine or a derivative thereof, and 40—90% water; preferably 40—55% trimethyl glycine or a derivative thereof, and 45—60% water, all percentages being by weight.

- 20 According to one aspect of the invention there is provided use of a liquid for the prevention of freezing of aircrafts and runways, wherein the liquid comprises 10-60 wt-% trimethyl glycine, or a salt of trimethyl glycine hydrate, and 40-90 wt-% water.

Among the advantages of this anti-freezing liquid are the nontoxicity and safety thereof, and the lack of odor. Several of its physical properties are the same as with
25 glycol solutions, and it may be used at temperatures between -50 and +100°C. It is preferably used at temperatures ranging from -40°C to +80°C. A characteristic of the anti-freezing chemicals is that they lower the freezing temperature. This freezing temperature should be no higher than -20°C, with betaine a freezing temperature as low as -50°C may even be attained.

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If necessary or desired, the anti-freezing liquid of the invention may be combined with conventional corrosion inhibitors, stabilizing and marker agents, thickeners, surface active agents, other anti-freezes like glycols and salts, as well as compounds
5 for controlling the acidity, all of them well known in the art.

The anti-freezing liquid of the present invention is less toxic and less polluting than the anti-freezing liquids already known in the art. Said liquid is not classified as a hazardous waste, and it may be disposed of easily, thus lowering the costs. The waste liquid may be handled without any special measures, it may be absorbed into the earth, or drained into the sewer, whereas ethylene and propylene glycols, as well as ethanol commonly used in the state of the art must be disposed of in a special way as hazardous wastes.

The anti-freezing liquid according to the present invention is suitable for various applications for the prevention of freezing of, or for ice removal from aircrafts, runways, and the like, particularly at low temperatures and in situations where the liquid must be environmentally friendly and nontoxic.

The evaluation of the toxicity of the compounds is based on the LD₅₀ values from the literature. The LD₅₀ values used are tested orally in rats. The results are shown below in Table I.

Table I

Compound	LD ₅₀ /mg/kg
Ethylene glycol	4 700
Propylene glycol	20 000
Ethanol	7 060
Trimethyl glycine	11 179

In table II the kinematic viscosities of the liquids are compared at the concentration of 50%.

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Table II

Solution	Concentration % by weight	Kinematic viscosity, mm ² /s			
		20°C	0°C	-10°C	-20°C
Ethylene glycol	50	3.48	7.40	11.7	19.6
Propylene glycol	50	6.44	18.70	38	87
Ethanol	50	3.10	7.22	12.20	23
Trimethyl glycine	50	5.90	12.80	21.50	38

Table III illustrates how different compounds decrease the freezing point of a 50% solution.

Table III

Liquid	Freezing point of a 50% solution, °C
Ethylene glycol	-35
Propylene glycol	-34
Ethanol	-38
Trimethyl glycine	-42

The following Table IV shows the effect of trimethyl glycine on the freezing point of aqueous solutions.

Table IV

Concentration of trimethyl glycine % by weight	Freezing point, °C
10	-2,1
20	-5,1
25	-7,2
30	-10,7
35	-15
50	-42

The surface tensions of typical anti-freezing agents are presented below in Table V. The surface tension of trimethyl glycine is comparable to that of water, and higher than with glycols.

Table V

Solution	Surface tension, mN/m
Water	72
Ethylene glycol (50 wt-%)	55
Propylene glycol (50 wt-%)	45
Trimethyl glycine solution (50 wt-%)	76

Table VI shows the vapor pressures of several anti-freezing liquids at 37.8°C. Since the vapor pressure of the trimethyl glycine solution is lower than with other solutions, it is not evaporated/volatilized so easily by an air stream.

Table VI

Solution	Vapor pressure, Pa (T=37,8°C)
Water	6.1
Ethylene glycol (50 wt-%)	5.5
Propylene glycol (50 wt-%)	5.2
Trimethyl glycine solution (50 wt-%)	4.1

The liquid according to the present invention containing 10-60% trimethyl glycine or derivatives thereof, and 40—90% water, by weight, is applicable in the anti-freezing systems for aircrafts and runways, particularly for spraying onto the surface desired.

The vapor pressure of the liquid of the invention is below 5 Pa. LD₅₀ value is more than 10 000 mg/kg (orally in rats), and the flash point thereof is above 100°C.

Further, the freezing point of a 50% solution is less than -38°C, the surface tension thereof being more than 55 dyn/cm. Its storage life in standardized conditions, at room temperature, is more than 2 years. The viscosity, an important characteristic of an anti-freezing liquid, may be stably adjusted to a desired range.

Trimethyl glycine is a nontoxic and odorless raw material from the nature that biodegrades in the nature to 80% in 20 days. The slow biodegradation is a problem associated for instance with propylene glycols used formerly. Trimethyl glycine lowers the freezing point of water, the heat transfer properties thereof are excellent, unpleasant odors are not released from it, and it may be used without any corrosion inhibitors to prevent corrosion since it is as such only weakly corrosive. For

example the corrosion of copper alloys is clearly below 1 $\mu\text{m}/\text{year}$ when the liquids according to this invention are used. Further, they do not corrode polycarbonate, acryl, or painted surfaces.

- 5 The glycols previously used as anti-freezes are harmful to the sealing materials present in aircraft structures, whereas anti-freezing liquids based on trimethyl glycine are free of such negative effects. The recovery of the anti-freezing liquids containing glycols from the airports for the disposal, or reuse thereof is very complicated, the complete recovery being anyway impossible. The trimethyl glycine solutions need
10 not to be recovered since they degrade quickly in the nature. The handling of the trimethyl glycol solutions is safe because of the low vapor pressures, and accordingly the low volatilities thereof. On the contrary, for instance for ethylene glycol a limiting vapor pressure of 50 ppm (TVL) is determined for safety reasons. The safety to the environment is to mentioned as one of the major advantages of
15 using trimethyl glycinee solution as a liquid for the prevention of freezing of aircrafts and runways.

- The invention is described above with reference only to some preferable examples thereof, the details of which should not, however, be considered as narrowly limiting
20 the invention. Many modifications and variations are possible within the scope and spirit of the invention defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Use of a liquid for the prevention of freezing of aircrafts and runways, wherein the liquid comprises 10-60 wt-% trimethyl glycine, or a salt of trimethyl glycine hydrate, and 40-90 wt-% water.
2. The use according to claim 1, wherein the liquid comprises 40-55 wt-% trimethyl glycine, or a salt of trimethyl glycine hydrate, and 45-60 wt-% water.
3. The use according to claim 1 or 2, wherein the liquid comprises trimethyl glycine, or a salt of trimethyl glycine hydrate, from a biological source.
4. The use according to any one of claims 1 to 3, wherein the liquid is used at a temperature ranging between -50 and +100°C.
5. The use according to any one of claims 1 to 4, wherein the liquid is used at a temperature ranging between -40 and +80°C.
6. The use according to any one of claims 1 to 5, wherein the liquid further comprises a corrosion inhibitor, a stabilizer, a marker, a thickener, a surface active agent, another anti-freeze, or a compound for controlling acidity, or any combination thereof.
7. The use according to any one of claims 1 to 6, wherein the liquid comprises 50 wt-% of trimethyl glycine and 50 wt-% of water, has a vapour pressure at 37.5°C less than 5 Pa, an acute oral toxicity, LD₅₀, in rats more than 10 000 mg/kg, a freezing point below - 38°C and a surface tension more than 55 dyn/cm.
8. A method of preventing freezing of aircrafts and runways comprising the step of applying a liquid to said aircraft or said runway, wherein the liquid comprises 10-60 wt-% trimethyl glycine, or salts of trimethyl glycine hydrate, and 40-90 wt-% water.

9. A method of preventing freezing of aircrafts and runways according to claim 8, by applying a liquid to said aircraft or said runway wherein the liquid comprises 40-55 wt- % trimethyl glycine, or a salt of trimethyl glycine hydrate, and 45-60 wt- % water.
10. A method of preventing freezing of aircrafts and runways according to claim 8 or 9, by applying a liquid to said aircraft or said runway wherein the liquid comprises trimethyl glycine, or a salt of trimethyl glycine hydrate, from a biological source.
11. A method of preventing freezing of aircrafts and runways according to any one of claims 8 to 10, by applying a liquid to said aircraft or said runway wherein said anti-freezing liquid is used at a temperature ranging between -50° and +100°C.
12. A method of preventing freezing of aircrafts and runways according to any one of claims 8 to 10, by applying a liquid to said aircraft or said runway wherein said anti-freezing liquid is used at a temperature ranging between -40° and +80°C.
13. A method of preventing freezing of aircrafts and runways according to any one of claims 8 to 12, by applying a liquid to said aircraft or said runway wherein the liquid further comprises a corrosion inhibitor, a stablizer, a marker, a thickener, a surface active agent, another anti-freeze, or a compound for controlling acidity, or any combination thereof.