

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 August 2011 (25.08.2011)

(10) International Publication Number
WO 2011/103295 A1

PCT

(51) International Patent Classification:
C09K 3/18 (2006.01)

(21) International Application Number:
PCT/US2011/025253

(22) International Filing Date:
17 February 2011 (17.02.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/305,312 17 February 2010 (17.02.2010) US

(71) Applicant (for all designated States except US): **BATTELLE MEMORIAL INSTITUTE** [US/US]; 505 King Avenue, Columbus, OH 43201 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CHAUHAN, Satya P.** [US/US]; 1073 Bluffpoint Drive, Columbus, OH 43235 (US). **ROSHON, Melissa S.** [US/US]; 4100 Saturn Road, Hilliard, OH 43026 (US). **SAMUELS, William D.** [US/US]; 2300 Hood Avenue, Apt. R., Richland, WA 99354 (US).

(74) Agent: **SUTTER, Gary M.**; MacMillan, Sobanski & Todd, LLC, One Maritime Plaza; 5th Floor, 720 Water Street, Toledo, OH 43604 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: COMPOSITIONS FOR DEICING/ANTI-ICING

(57) Abstract: A non-toxic deicing/anti-icing fluid includes at least 20% by weight of a freeze point depressant selected from short chain polyols having 3 to 5 carbon atoms. The fluid further includes at least 10% by weight of water, a thickener, a surfactant, and a pH moderator. The fluid meets the requirements of SAE/ AMS 1428 or its revisions for a non-Newtonian, Type II, III, or IV aircraft deicing/anti-icing fluid.



WO 2011/103295 A1

TITLE

COMPOSITIONS FOR DEICING/ANTI-ICING

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of United States Provisional Application No. 61/305,312, filed February 17, 2010, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] This invention relates in general to improved, thickened, fluid compositions to remove ice, frost, and snow from surfaces and/or to prevent ice from forming on surfaces. More specifically, in certain embodiments, this invention relates to formulation of environmentally-friendly, non-Newtonian fluids, primarily for aircraft deicing/anti-icing, as required per Society of Automotive Engineers Aerospace Material Specification (SAE/AMS) 1428. However, other applications of deicing/anti-icing, such as wind-turbine blades and third-rail where the rail is for making electrical contact, are also possible.

[0003] Several types of aircraft deicing/anti-icing fluids (ADFs/AAFs) are used to remove deposits of ice, frost and snow from aerodynamically-critical surfaces before an aircraft can safely lift off the runway. Additionally, the film of such a liquid, left on the aircraft, provides some protection from refreezing of water due to freezing precipitation. The anti-icing property of these fluids can be quantified by the Water Spray Endurance Test (WSET), which is fully described in SAE/AMS 1428 Specification. Four different types of ADF/AAFs, namely Types I, II, III, or IV, can be qualified for use on an aircraft, depending on how the fluid is used and the anti-icing protection achieved. The anti-icing protection requirement for Type I fluids is only 3 minutes, with Types II and IV being 30 and 80 minutes, respectively. To achieve the much longer WSET times for Types II and IV fluids, the fluids are thickened and these exhibit non-Newtonian (pseudoplastic) behaviors, also referred to

as shear-thinning behavior. The shear thinning behavior allows for maximum anti-icing protection due to the uniform coverage by a high viscosity fluid when the aircraft is stationary (zero shear). This fluid greatly thins out during an aircraft take-off roll as the shear rate rapidly increases, which allows the aircraft to shed the majority of the fluid, thus restoring the aerodynamics of the airfoil.

[0004] The primary difference between Type II and Type IV fluids is that a Type II can be used both for deicing and anti-icing while Type IV is used just for anti-icing after a deicing step is completed. In either case, such fluids typically contain a mixture of a glycol, such as ethylene glycol (EG) or diethylene glycol (DEG) or propylene glycol (PG) with water, the glycol plus water typically adding up to more than 95% by weight (wt%). These fluids also contain additives such as thickeners, surfactants, anti-foamers, corrosion inhibitors, anti-precipitants, and dyes to meet the specifications. All of these chemicals are of potential concern to airports as they are required to obtain storm water discharge permits under the applicable environmental protection agencies. The concerns are: (a) high levels of oxygen demand due to natural biodegradation of glycols; (b) mammalian toxicity of some glycols, such as EG (which is also a hazardous air pollutant) and DEG; (c) toxicity of degradation products of commonly-used surfactants; (d) toxicity and non-biodegradability of commonly used corrosion inhibitors and other additives.

[0005] The vast majority of Type II and IV fluids use PG as a freeze-point depressant but it has a high chemical oxygen demand (COD) and biological oxygen demand (BOD). The thickened fluids typically use alkylphenol ethoxylate (APE) surfactants, the biodegradation products of which have been shown to be endocrine disruptors, and as such these are banned in Europe and are under EPA scrutiny in the U.S. A number of fluids also use benzyltriazole or tolytriazole corrosion inhibitors, which are toxic and non-biodegradable and thus persist in the environment.

[0006] The thickened fluids of prior art typically use large molecules (polymers) that typically thicken by molecular entanglement or gelation due to pH adjustment. These polymers often have performance deficiencies as they leave gel-forming residues on aircraft surfaces. The quantity of residue is typically proportional to the

amount of thickener (polymer) used as that is the primary controller of viscosity and rheology. Additionally, these thickeners typically have relatively flat viscosity vs. temperature curve in the 20° C to -30° C range. If a certain, high viscosity is targeted for the 0 to -10° C, which is the majority of operating range, one gets undesirably high viscosities at 20° C which makes fluid preparation and handling harder as well as at temperature below -10° C which makes aerodynamic performance poorer and the gel residue problem worse.

[0007] Various patents are known that describe some of the approaches, partial solutions, and inherent problems for addressing the requirements for aircraft anti-icing. However, the thickened aircraft fluids described in the patents have functional and/or environmental deficiencies. The functionally superior formulations rely on use of components that were recently recognized as environmentally unfriendly and are in various phases of being banned. A high performance, environmentally friendly, thickened aircraft fluid is therefore desired. Such fluids may also be useful for other applications, such as (a) deicing/anti-icing of wind-turbine blades and (b) stationary surfaces such as the third rail for electric trains.

SUMMARY OF THE INVENTION

[0008] This invention relates to improved compositions for deicing/anti-icing. In certain embodiments, the composition is an environmentally-friendly deicing/anti-icing fluid, which includes short chain polyols having 3 to 5 carbon atoms, and mixtures thereof, a thickener, nonionic surfactant(s), and other additives, which is functionally superior to prior-art fluids with respect to its anti-icing properties. This fluid in certain embodiments is non-toxic to mammals and can typically have at least a 25 lower aquatic toxicity.

[0009] Also, in certain embodiments, the deicing/anti-icing fluids meet or exceed the requirements of SAE/AMS 1428, especially Type IV anti-icing fluids with a freeze point below -32°C and a WSET of over 80 minutes in an undiluted form. The fluids may also be used as a Type II fluid for deicing and anti-icing with a WSET above 30 minutes for undiluted fluid.

[0010] In certain embodiments, the compositions include bio-based C₃-C₅ polyols, such as PG, glycerol, and xylitol, to substantially reduce the carbon footprint of the fluid.

[0011] In certain particular embodiments, the compositions eliminate the use of toxic surfactants such as alkylphenol ethoxylates (APEs) and/or toxic corrosion inhibitors such as triazoles (e.g., benzyltriazoles) used in prior-art fluids, thus lowering the aquatic toxicity with LC₅₀ (lethal concentration above which 50% of species such as fathead minnows or daphnia magna die, at conditions described in AMS 1428) values of at least 1,000 mg/L (the higher the value, the lower the toxicity).

[0012] In other embodiments, the compositions include associative polymers, such as cross-linked polyacrylic acid copolymers, in combination with non-NPE surfactants that strongly associate (interact) with the polymers to achieve desired thickening at freezing temperatures with substantially reduced polymer usage, and thus improved preparation and handling of the fluid due to a lower viscosity at warmer temperatures.

[0013] In certain embodiments, the compositions include mixtures of glycerol and other petroleum-based or bio-based C₃-C₅ polyols to reduce the COD/BOD of the fluid as well as to achieve desired thickening with a reduced quantity of thickener, which minimizes the formation of gel-forming residues on aircraft surfaces.

[0014] In other embodiments, the compositions include environmentally friendly anti-precipitants or chelating agents to give protection from hardness ions, such as calcium, if the fluid is to be diluted, while reducing the requirement for corrosion inhibitors and thus reduce the toxicity of the fluid.

[0015] Also, in certain embodiments, the compositions include non-foaming or low-foaming, nonionic surfactants that associate with the polymeric thickener to reduce or eliminate the use of anti-foamers, further reducing the toxicity of the fluid.

[0016] Various additional aspects of the compositions will become apparent to those skilled in the art from the following detailed description of the preferred embodiments and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Figure 1 is a plot showing viscosity at different temperatures of anti-icing fluids.

[0018] Figure 2 is a plot showing the effect of associating anti-precipitant concentration on viscosity at different temperatures of deicing/anti-icing fluids.

[0019] Figure 3 is a plot showing the effect of a pH modifier on viscosity at different temperatures of deicing/anti-icing fluids.

[0020] Figure 4 is a plot showing the effect of associating surfactant and glycerol on viscosity at different temperatures of deicing/anti-icing fluids.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] As previously mentioned, a fluid with strong anti-icing properties meeting the specifications in SAE/AMS 1428 contains, as a minimum, a freeze point depressant (FPD), water, a thickener, and a surfactant. Other additives to manage dilution by hard water, foaming on spraying, inhibit corrosion, and to give the required color to the formulation, may be added. All ingredients except water can potentially degrade the environment on discharges after application. We have discovered compositions that, in certain embodiments, eliminate the toxic components while maintaining or exceeding the functional requirements of aircraft deicing/anti-icing.

[0022] The viscosity, rheology, and surface activity of an anti-icing formulation are significant for achieving anti-icing properties. A typical prior-art, anti-icing fluid uses a shear thinning thickener, so as to easily shed off an aircraft on takeoff due to application of shear, which produces a relatively flat viscosity curve on chilling, as shown in Figure 1. The curves (A) and (B) are based on use of natural thickener, xanthan gum (Ref.: U.S. Pat. No. 5,772,912). As shown, up to about 0.5% thickener is needed to reach a viscosity of 60,000 cP at -5° C, but this makes the 20° C viscosity about 55,000 cP, which is thick for fluid preparation and handling. Also, a viscosity of 65,000 cP at -20° C is unlikely to pass aerodynamic acceptance test. Curves (C)

and (D) are examples of formulations we have made that show rapid viscosity rise on chilling from 20° C down to freezing temperature, using only about 0.2% or less thickener and especially, non-NPE associating surfactants. Among these two latter curves, the formulation (D) is more attractive as it shows a decline in viscosity after about -5° C to -10° C, which allows the fluid to have excellent anti-icing behavior while not being too thick to pass aerodynamic acceptance test (SAE/AMS 1428) at temperatures below -20° C. Rapidly rising and then falling viscosity on chilling is desired over flat curves in some applications. As described in more detail below, these special effects on viscosity are in some embodiments based on using special surfactants and potentially a special FPD blend. In some embodiments, these viscosity properties are provided by the interaction between surfactant(s) and polymeric thickener(s).

[0023] In certain embodiments, the present compositions are useful as an environmentally friendly and functionally superior deicer/anti-icer, primarily for use on aircrafts, that contains a mixture of C₃-C₅ polyols and water, the total weight of which is about 95-99%. Some examples of FPDs are glycerol; 1, 2 propanediol (a C₃ polyol, commonly referred to as propylene glycol (PG)); 1, 3 propanediol (C₃, PDO); DEG (C₄); and xylitol (C₅), among others. The COD of PG, which is the most widely used FPD in Type II and IV fluids, is 1.68 kg O₂/kg fluid. The COD values of glycerol and xylitol, on the other hand, are 1.22 and 1.16 kg O₂/kg respectively. Therefore, glycerol and xylitol are preferred for lower-COD fluids. In certain embodiments, to optimize certain physical properties, these are used in combination with other C₃-C₅ polyols. The relative proportions of the FPD and water can be varied to obtain a freeze point below -32°C. The FPDs can be biobased (e.g., derived from plants) or non-biobased (e.g., derived from petroleum or other materials).

[0024] In certain embodiments, the fluid composition includes a thickener which associates with surfactant(s) and some FPDs to achieve optimum viscosity and rheology, allowing viscosity at temperature of formulation to be low, viscosity at typical operating temperatures to be high enough to obtain a high WSET value, and providing a medium viscosity at very low temperatures. This thickener-surfactant

association may provide a synergistic effect on thickening, thereby reducing the amount of thickener needed. The associative polymers are water-soluble. Examples of thickeners are synthetic polymers of carboxylic acid group, such as polyacrylic acid (PAA). The polymers may be lightly cross-linked (co-polymerized) with hydrophobic monomers/ macromonomers to allow association with hydrophobic portions of surfactants. The typical concentration of the polymers thickener is 50 ppm to 0.5 wt%, preferably 0.1 to 0.2 wt %. These polymers are typically partially neutralized with an alkali such as potassium or sodium hydroxides or an alkylamine, to achieve a pH value of 6.5 to 8.5, with a preferred value being 6.9 to 7.5. A particular alkali is potassium hydroxide. Other thickeners could also be useful.

[0025] In certain embodiments, the surfactant has a synergistic effect on thickening, thereby reducing the amount of thickener needed.

[0026] In certain embodiments, the compositions are useful as aircraft anti-icing fluids (AAF's). These fluids can be more difficult to formulate than aircraft deicing fluids (ADF's).

[0027] The rheology of an AAF or ADF can depend on several ingredients that are used for functions other than thickening: surfactant for improved wetting, alkali for pH modification, the freezing point depressant(s), and chelating agent for anti-precipitation.

[0028] In certain embodiments, fluid composition includes one or more non-ionic surfactants to not only provide for a reduction in the surface tension of the FPD to obtain uniform coverage of the aircraft surfaces, but to also enhance the thickening effect of the polymeric thickener. While a wide variety of nonionic surfactants are available, many are unsuitable due to toxicity, lack of biodegradability, and functional performance reasons. As mentioned earlier, unlike a majority of the prior-art formulations, APEs, which are functionally excellent, are to be excluded in certain embodiments. In other embodiments, surfactants that fall out of the formulation at any temperature on dilution are excluded. Typically useful surfactants are alkoxyated branched alcohol and alkoxyated linear or secondary alcohols, with branched alcohols being preferred. These surfactants can have an association with the thickener

as described above. These surfactants typically have a formula, $\text{CH}_3\text{C}_n\text{H}_{2n}\text{O}(\text{C}_2\text{H}_4\text{O})_y\text{H}$, which can be simplified as $\text{C}_{n+1}\text{C}_{2n+3}\text{O}(\text{EO})_y\text{H}$. The surfactants of use typically have “n” values ranging from about 6 to 18 and “y” values ranging from about 2 to 20. The hydrophilic lipophilic balance (HLB) values of these surfactants typically vary from about 6 to 18. The surfactant(s) are to be selected to balance their hydrophobic character, as represented by the hydrocarbon ($\text{CH}_3\text{C}_n\text{H}_{2n}$) chain and the hydrophilic character, as represented by the ethylene oxide ($\text{C}_2\text{H}_4\text{O}$) or EO units. The preferred values of “n”, “y”, and HLB are 8-12, 3-14, and 6-12, respectively. In some compositions, non-foaming or low-foaming surfactants are used, for example, surfactants having an HLB less than 10. Other types of surfactants could also be useful.

[0029] In certain embodiments, the fluid composition includes an anti-precipitant to manage dilution with water containing hardness ions. A variety of chelating agents, such as EDTA (sodium ethylenediaminetetraacetate) or HEDTA (sodium hydroxyethylethylenediaminetriacetate) are used in prior art. However, EDTA or HEDTA cause excessive corrosion of certain aircraft components, which leads to the requirement of corrosion inhibitors, and which are typically toxic; these are also inadequately biodegradable. Therefore, in certain embodiments, non-EDTA, non-HEDTA chelating agents, such as polymeric dispersants or aminopoly-carboxylates are used. The preferred anti-precipitant helps control the viscosity of the fluid as well, as shown in Figure 2.

[0030] The compositions may also include a pH moderator, which can be any material(s) suitable for modifying or maintaining the pH of the composition within a certain range. Some nonlimiting examples include basic materials such as alkali metal hydroxides (e.g., potassium hydroxide or KOH) or triethanolamine (TEA). The pH modification can have a significant effect on the rheology of the fluid as shown in Figure 3.

[0031] The fluid may include a defoamer if one or more of the surfactants have a high HLB value. Also, a food grade dye may be added to meet specifications.

[0032] An unexpected observation was the beneficial thickening effect of glycerol when combined with a thickener and surfactant. For example, on substituting PG with some glycerol, not only did the COD of the fluid decline, but also the amount of polymer and surfactant needed to achieve the viscosity behavior decreased. This is illustrated in Figure 4. The baseline (lowest viscosity) curve is for the case where no surfactant is added along with the thickening polymer and the freeze point depressant is PG. When an associating surfactant is added, the viscosity increases significantly. Further, when a surfactant is added and some PG is substituted by glycerol, the viscosity increases substantially. In certain embodiments, this synergy of effect allows one to make the fluid more environmentally friendly and also to reduce the formation of gel-foaming residues on aircraft surfaces. A similar synergistic effect may also be found with mixtures of glycerol and other petroleum or bio-based C₃-C₅ polyols (e.g., PG, PDO and/or xylitol).

[0033] In certain embodiments, the compositions include a non-triazole compound to serve as a corrosion inhibitor, if needed to meet the materials compatibility specifications for aluminum, steel, and cadmium. This excludes triazole compounds such as benzotriazole and tolytriazole. Examples of less toxic corrosion inhibitors are: carboxylates, silicates, phosphonates, sulfonates, amines, and amides.

[0034] Also, in certain embodiments, a deicing/anti-icing formulation is provided based on C₃-C₅ polyols which is partly or entirely bio-based, thus reducing the carbon footprint of the fluid. Examples of bio-based polyols of this invention are glycerol, PG, PDO, and xylitol, all of which have been successfully utilized in our formulations.

[0035] The use of multi-function components in the compositions can minimize the number of additives used in the compositions, thereby improving the environmental friendliness of the compositions by reducing corrosivity and toxicity. For example, in certain embodiments, the compositions contain the following components: freezing point depressant(s), thickener(s), surfactant(s), pH moderator(s) and water.

[0036] The following Tables 1 and 2 show some examples of deicing/anti-icing fluids of this invention.

Table 1 -- Examples of Compositions of Deicing/Anti-Icing Fluids

Component Composition	Wt% Range	Wt% Preferred for Type IV Fluid
C3-C5 Polyol	20-90	45-65
Non-NPE Nonionic Surfactant #1	0.003-0.40	0.05-0.20
Non-NPE Nonionic Surfactant #2	0.002-0.20	0.01-0.10
Water	10-80	35-45
Polycarboxylic Acid Thickener	0.005-0.50	0.05-0.20
Potassium Hydroxide	To achieve pH of 6.5 to 8.5	To achieve pH of 6.9 to 7.5
Chelating Agent	0.005-0.50	0.03-0.20
Antifoamer	0-0.20	0.05-0.10
Non-triazole Corrosion Inhibitor	0-0.50	0.01-0.20

Table 2 -- Further Examples of Compositions of Deicing/Anti-Icing Fluids

Propylene Glycol	20	85	50	50	30	0	0	0	0
Glycerol	0	0	0	0	30	0	30	40	0
PDO	0	0	0	0	0	50	30	0	30
Xylitol	0	0	0	0	0	0	0	20	30
Non-NPE Nonionic Surfactant #1	0.025	0.10	0.20	0.14	0.20	0.40	0.15	0.25	0.30
Non-NPE Nonionic Surfactant #2	0.005	0.05	0.10	0	0.03	0.002	0.01	0.05	0.06
Water (Balance)	~79.5	~14.5	~49.0	~49.5	~39.0	~51.0	~39.5	~39.0	~39.0
Polycarboxylic Acid Thickener	0.03	0.15	0.30	0.14	0.23	0.40	0.15	0.30	0.35
Potassium Hydroxide (pH)	(6.8)	(7.0)	(8.5)	(7.2)	(7.5)	(7.2)	(7.5)	(7.3)	(7.2)
Chelating Agent	0.025	0.05	0.10	0.08	0.20	0.10	0.05	0.05	0.10
Antifoamer	0.20	0	0.10	0	0.05	0.05	0.10	0	0
Non-triazole Corrosion Inhibitor	0	0	0.20	0.08	0.10	0.10	0.05	0.20	0.10

CLAIMS

1. A non-toxic deicing/anti-icing fluid comprising:
at least about 20% by weight of a freeze point depressant selected from the group consisting of short chain polyols having 3 to 5 carbon atoms, and mixtures thereof;
at least about 10% by weight of water;
a thickener;
a surfactant; and
a pH moderator;
the fluid meeting the requirements of SAE/AMS 1428 or its revisions for a non-Newtonian, Type II, III, or IV aircraft deicing/anti-icing fluid.
2. A fluid according to claim 1, wherein the freeze point depressant is selected from the group consisting of glycerol, 1,2 propanediol, 1,3 propanediol, erythritol, diethylene glycol, xylitol, and mixtures thereof.
3. A fluid according to claim 2, wherein the freeze point depressant is a mixture of at least 10% glycerol and another of the short chain polyols.
4. A fluid according to claim 2, wherein all or a portion of the freeze point depressant is bio-based.
5. A fluid according to claim 1, wherein the amount of freeze point depressant is about 45-65% by weight to meet the requirements of a Type IV fluid.
6. A fluid according to claim 1, wherein the thickener associates with the surfactant to more efficiently thicken the fluid.

7. A fluid according to claim 1, wherein the thickener is a cross-linked polymer of carboxylic acids and hydrophonic-character cross-linking monomers.
8. A fluid according to claim 8, wherein the thickener is polyacrylic acid based polymer present in the range of 50 ppm to 0.4 percent by weight.
9. A fluid according to claim 1, wherein the surfactant is nonionic and contains one or more ethoxylated alcohols containing a hydrophobic backbone of at least 6 carbons and a hydrophilic group of at least 2 ethoxylates.
10. A fluid according to claim 9, wherein the surfactant has a branched hydrophobic backbone.
11. A fluid according to claim 10, wherein the surfactant is present in the range of 50 ppm to 0.4 percent by weight.
12. A fluid according to claim 1, wherein the surfactant does not include an alkylphenol ethoxylate.
13. A fluid according to claim 1, wherein the pH of the fluid is between 6.5-8.5 and the pH modifier is selected from the group consisting of sodium hydroxide, potassium hydroxide, an alkylamine, and mixtures thereof.
14. A fluid according to claim 13, wherein the pH of the fluid is between 6.9 and 7.5 and the pH control modifier is potassium hydroxide.
15. A fluid according to claim 1, further comprising an anti-precipitant.
16. A fluid according to claim 15, wherein the concentration of the anti-precipitant is in the range of 50 ppm to 0.2% by weight.

17. A fluid according to claim 16, wherein the anti-precipitant is selected from the group consisting of polymeric dispersants, aminocarboxylates, other biodegradable non-EDTA chelating agents, and mixtures thereof.

18. A fluid according to claim 1, further comprising 50 ppm to 0.2% by weight of a corrosion inhibitor.

19. A fluid according to claim 18, wherein the corrosion inhibitor is selected from the group consisting of carboxylates, phosphonates, sulfonates, amines, silicates, amides, and mixtures thereof.

20. A fluid according to claim 18, wherein the corrosion inhibitor does not include compounds containing triazoles.

21. A fluid according to claim 1, further comprising an anti-foaming agent, present in the range of 50 ppm to 0.2% by weight.

22. A non-toxic fluid comprising:
at least about 20% by weight of a freeze point depressant selected from the group consisting of short chain polyols having 3 to 5 carbon atoms, and mixtures thereof;
at least about 10% by weight of water;
a thickener; and
a surfactant;
the freeze point depressant providing a synergistic thickening effect combined with the thickener and surfactant.

23. A fluid according to claim 22, wherein the freeze point depressant comprises glycerol.

24. A fluid according to claim 22, wherein the thickener comprises a polymeric thickener.

25. A non-toxic fluid comprising:
at least about 20% by weight of a freeze point depressant selected from the group consisting of short chain polyols having 3 to 5 carbon atoms, and mixtures thereof;
at least about 10% by weight of water;
a polymeric thickener; and
a surfactant;
a surfactant that functions as both a wetting agent and thickener.

26. A non-toxic fluid comprising:
at least about 20% by weight of a freeze point depressant selected from the group consisting of short chain polyols having 3 to 5 carbon atoms, and mixtures thereof;
at least about 10% by weight of water;
a thickener; and
a surfactant;
the fluid having a viscosity at 0.06 sec⁻¹ shear rate and at 0°C to -10°C of at least 10,000 cP.

27. A fluid according to claim 27, wherein the viscosity is at least 20,000 cP.

28. A non-toxic fluid comprising:
- at least about 20% by weight of a freeze point depressant selected from the group consisting of short chain polyols having 3 to 5 carbon atoms, and mixtures thereof;
 - at least about 10% by weight of water;
 - a thickener;
 - a surfactant; and
 - an anti-precipitant that serves a second function of helping to control the viscosity of the fluid.
29. A fluid according to claim 28, wherein the anti-precipitant helps to reduce the viscosity.

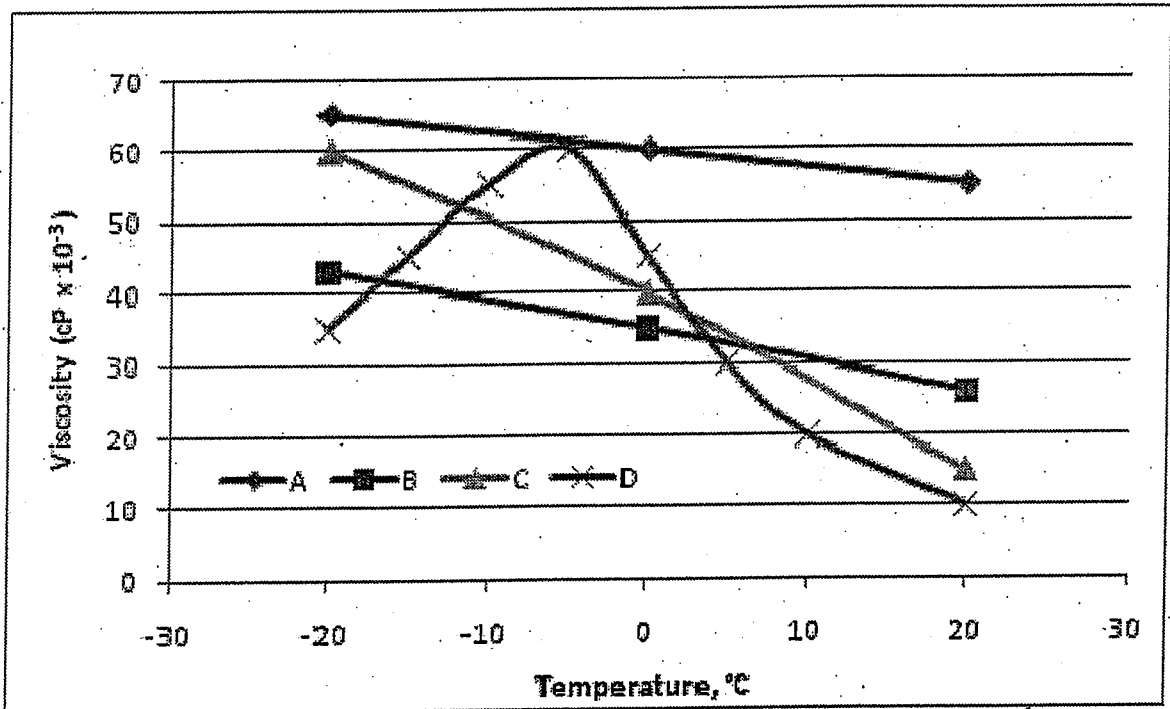


Figure 1. Viscosity for Various Fluids at a Shear Rate of 0.06 sec^{-1} .

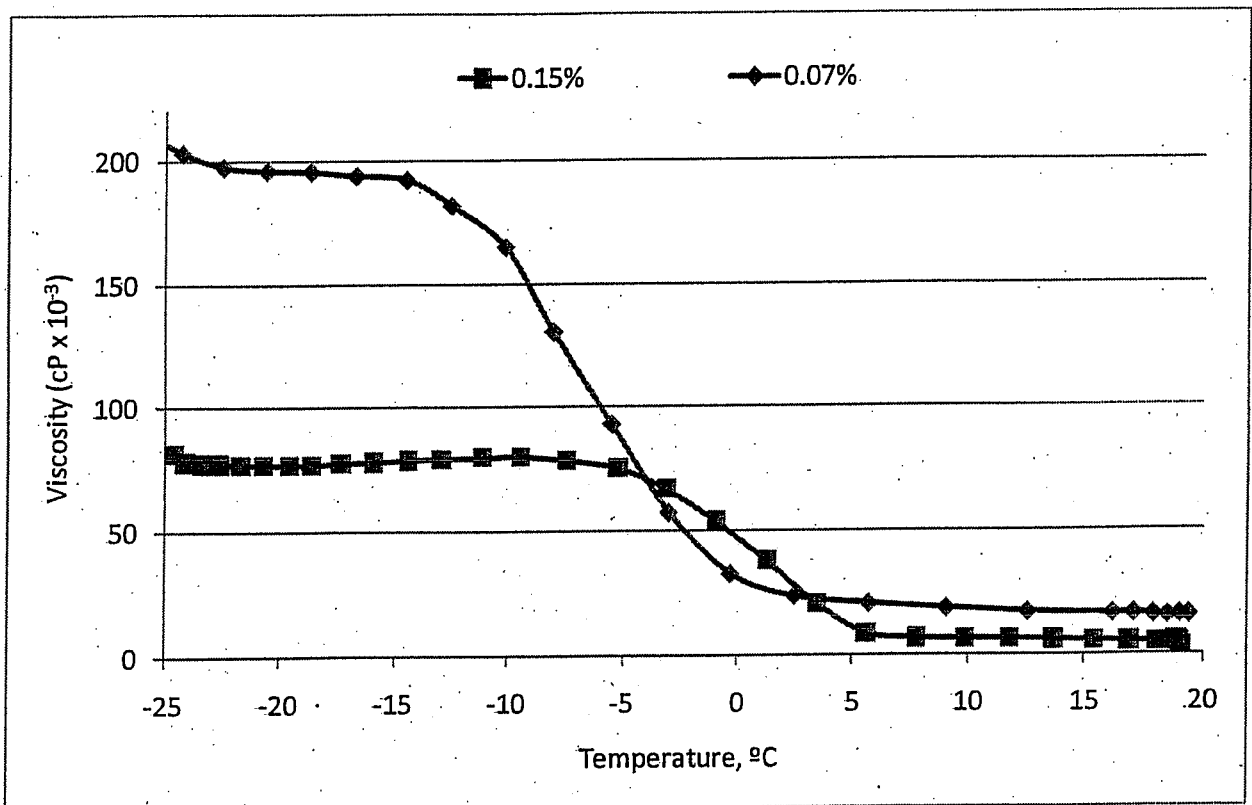


Figure 2. Effect of Associating Anti-precipitant Concentration on Viscosity at a Shear Rate of 0.06 sec^{-1} .

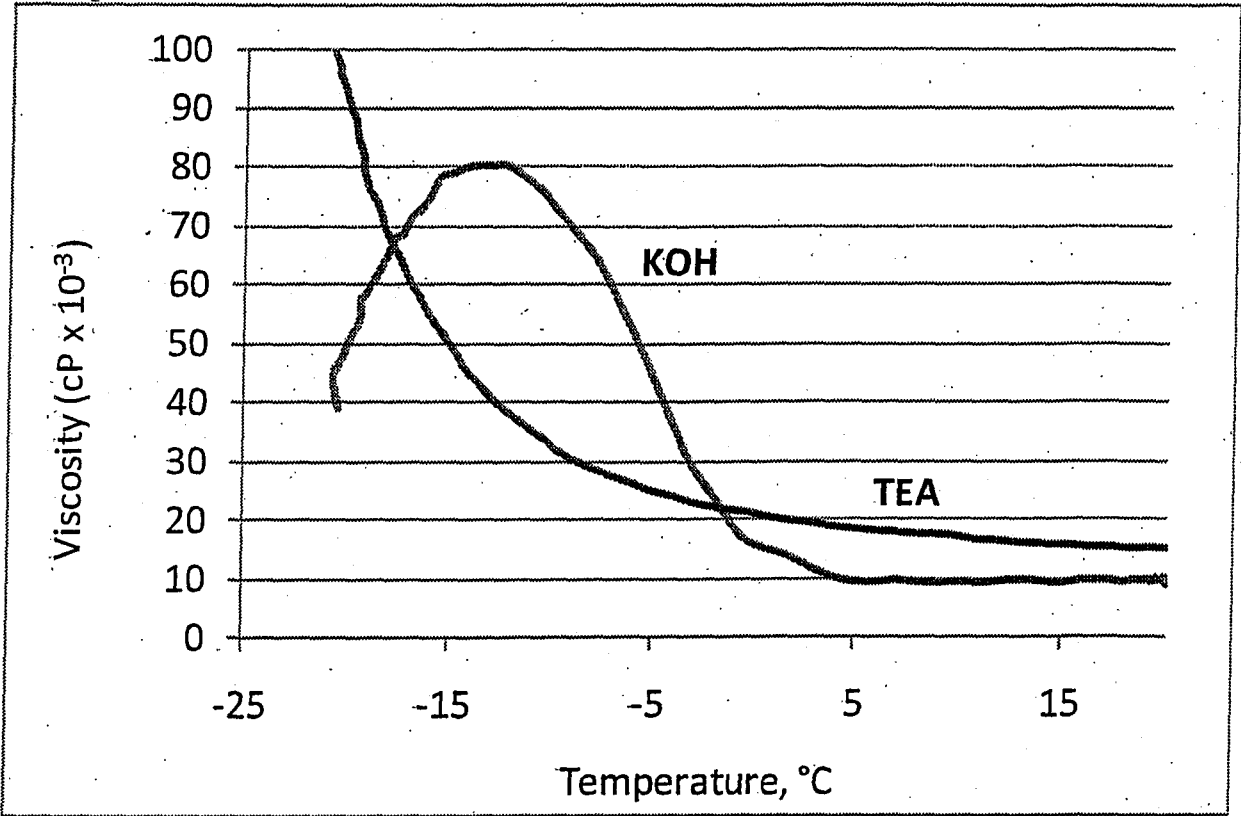
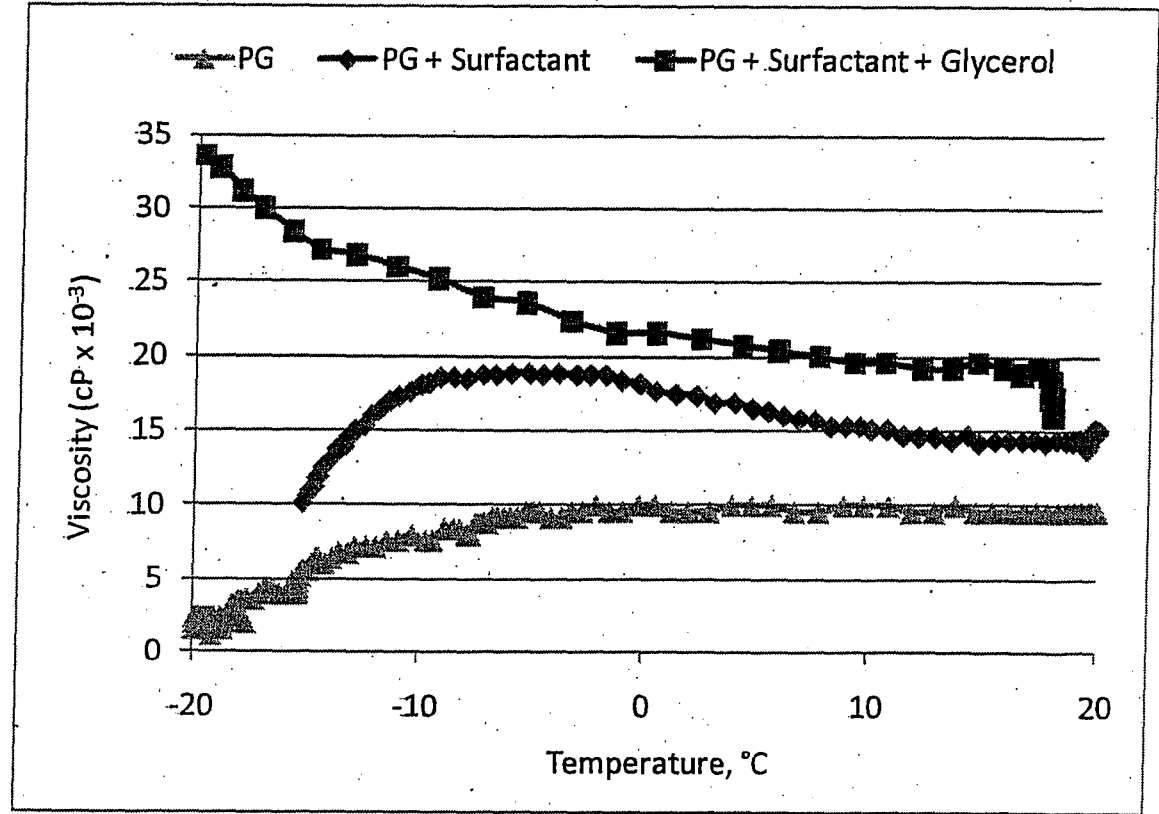


Figure 3. Effect of pH Modifier at a Shear Rate of 0.06 sec⁻¹.



Effect of Associating Surfactant and Glycerol on Viscosity at a Shear Rate of 0.06 sec⁻¹.

Figure 4.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2011/025253

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K3/18

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/200087 A1 (WEHNER ANN [US] ET AL) 30 August 2007 (2007-08-30)	1-21
A	paragraphs [0075], [0076], [0079] - [0081], [0083], [0085], [0086], [0096], [0100]	22-29
X	----- US 4 954 279 A (MA FRANK [CA] ET AL) 4 September 1990 (1990-09-04)	1-21
A	claims 1,8 column 5, line 23 - line 55 column 6, line 21 - line 38 examples 3,5,6,7	22-29
A	----- WO 2005/105945 A2 (BATTELLE MEMORIAL INSTITUTE [US]; SAMUELS WILLIAM D [US]; CONKLE NICH0) 10 November 2005 (2005-11-10) page 11 ----- -/-	1-21

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

25 July 2011

Date of mailing of the international search report

01/08/2011

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Domínguez Gutiérrez

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/025253

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/29146 A1 (FOSTER MILLER INC [US]; WESTMARK CAROLYN S [US]; JOBACK KEVIN G [US];) 26 April 2001 (2001-04-26) the whole document -----	1-21
X	US 2006/038159 A1 (FUKUTANI YASUO [JP] ET AL) 23 February 2006 (2006-02-23)	22-24
A	claims 13,16,19,20,23,32 paragraphs [0071], [0093], [0101] -----	25,28,29
X	US 5 273 673 A (ASHRAWI SAMIR S [US] ET AL) 28 December 1993 (1993-12-28)	25
A	claims 1-4,10,11,14,21 -----	1-14,26
X	US 5 708 068 A (CARDER CHARLES HOBERT [US] ET AL) 13 January 1998 (1998-01-13)	26,27
A	claims 1,3,8,10 column 22, line 44 - line 48 column 19, line 41 - line 48 -----	1-14
X	US 5 750 047 A (LEMMA SOLOMON [US]) 12 May 1998 (1998-05-12) claims 1,5,12,23,26 column 7, line 6 - line 9 examples 12-25 -----	28,29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/025253

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-21

A non-toxic deicing/anti-icing fluid composition with a polyol component, water, a thickener, a surfactant and a pH moderator; wherein the fluid meeting the requirements of SAE/AMS 1428 or its revisions for a non-Newtonian, Type II, III, or IV aircraft deicing/anti-icing fluid.

2. claims: 22-24

A non-toxic fluid composition with a polyol component, water, a thickener, and a surfactant; wherein the polyol component provide a synergistic thickening effect combined with the thickener and surfactant.

3. claim: 25

A non-toxic fluid composition with a polyol component, water, a thickener, and a surfactant; the surfactant acting as both a wetting agent and a thickener.

4. claims: 26, 27

A non-toxic fluid composition with a polyol component, water, a thickener, and a surfactant; wherein the fluid has a viscosity at 0.06 sec⁻¹ shear rate and at 0°C to -10°C of at least 10,000 cP.

5. claims: 28, 29

A non-toxic fluid composition with a polyol component, water, a thickener, a surfactant and an anti-precipitant.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/025253

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007200087 A1	30-08-2007	US 2009218541 A1	03-09-2009
US 4954279 A	04-09-1990	AT 70078 T	15-12-1991
		AU 594187 B2	01-03-1990
		AU 7762387 A	03-03-1988
		CN 87106033 A	23-03-1988
		DE 3774966 D1	16-01-1992
		DK 447987 A	29-02-1988
		EP 0257720 A2	02-03-1988
		ES 2026900 T3	16-05-1992
		FI 873716 A	29-02-1988
		GR 3003947 T3	16-03-1993
		IS 3254 A7	30-11-1987
		JP 6074408 B	21-09-1994
		JP 63099284 A	30-04-1988
		NO 873622 A	29-02-1988
		NZ 221595 A	28-05-1990
		PT 85614 A	01-09-1987
WO 2005105945 A2	10-11-2005	CA 2563638 A1	10-11-2005
		EP 1743009 A2	17-01-2007
		EP 2261295 A1	15-12-2010
WO 0129146 A1	26-04-2001	CA 2387718 A1	28-06-2001
		CA 2387923 A1	26-04-2001
		EP 1238038 A1	11-09-2002
		EP 1240269 A1	18-09-2002
		WO 0146334 A1	28-06-2001
US 2006038159 A1	23-02-2006	WO 2004074397 A1	02-09-2004
		KR 20060030011 A	07-04-2006
US 5273673 A	28-12-1993	CA 2086037 A1	01-03-1994
		EP 0586127 A1	09-03-1994
		JP 6158034 A	07-06-1994
US 5708068 A	13-01-1998	AT 274561 T	15-09-2004
		CA 2198296 A1	24-08-1998
		CN 1191882 A	02-09-1998
		CZ 9700554 A3	16-09-1998
		DE 69730408 D1	30-09-2004
		DE 69730408 T2	08-09-2005
		EP 0860490 A1	26-08-1998
		JP 10237428 A	08-09-1998
US 5750047 A	12-05-1998	AT 246235 T	15-08-2003
US 5750047 A		CA 2231805 A1	13-09-1998
		CN 1198462 A	11-11-1998
		CZ 9800724 A3	16-09-1998
		DE 69816684 D1	04-09-2003
		DE 69816684 T2	15-04-2004
		DK 864626 T3	03-11-2003
		EP 0864626 A1	16-09-1998
		HU 9800571 A2	29-03-1999
		JP 10298541 A	10-11-1998
		PL 325303 A1	14-09-1998