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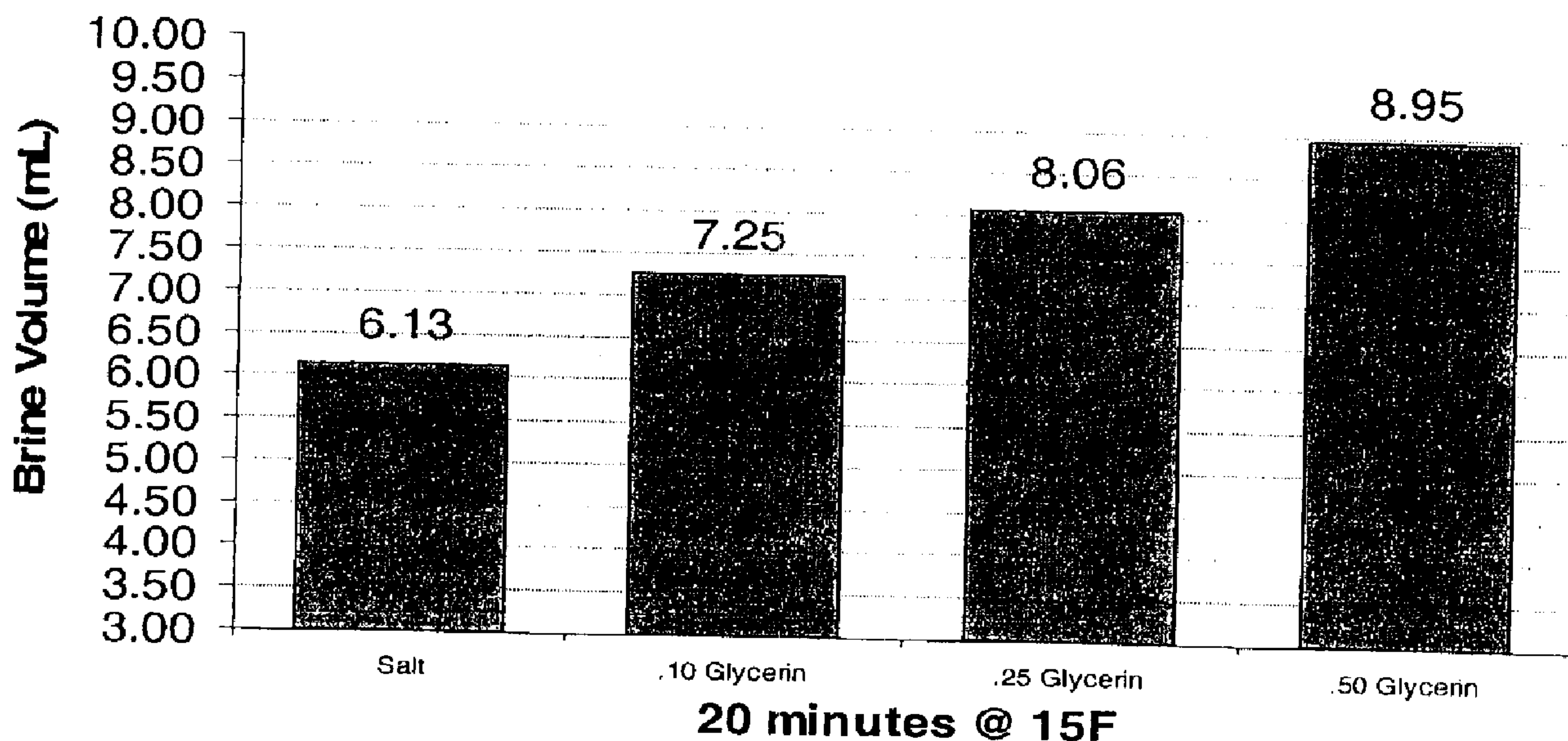
(71) Demandeur/Applicant:
OSSIAN, INC., US

(72) Inventeur/Inventor:
OSSIAN, KENNETH C., US

(74) Agent: OYEN WIGGS GREEN & MUTALA LLP

(54) Titre : SEL DE DEGLACAGE ENDUIT DE GLYCERINE

(54) Title: GLYCERIN COATED ICE MELTER



(57) Abrégé/Abstract:

Solid ice melters are improved with a small exterior coating of glycerin which prevents caking and bridging and enhances melt value.

ABSTRACT OF THE DISCLOSURE

Solid ice melters are improved with a small exterior coating of glycerin which prevents caking and bridging and enhances melt value.

TITLE: GLYCERIN COATED ICE MELTER**FIELD OF THE INVENTION**

5 This invention relates to de-icing and ice melting compositions for use in reducing ice and snow accumulation on surfaces.

BACKGROUND OF THE INVENTION

De-icing compositions are widely used in northern areas of the country, particularly
10 in the northern climates subject to heavy ice and snow conditions in the winter months. One of the inventors of the present composition has numerous patents on ice melters. See, for example, U.S. Patent No. 7,122,127, which relates to liquid ice melters, and U.S. Patent No. 5,683,619 which relates to solid ice melting compositions which are environmentally friendly. The disclosure of these patents is incorporated herein by reference.

15 A good ice melter for roads, sidewalks, parking lots, etc. is inexpensive, easy to manufacture, effective in melting snow and ice, and easy to apply. The best ones also provide reduced corrosion to application equipment while also having beneficial effects to vegetation. All of these advantages in one ice melter has been a goal of the ice melting industry for some time.

20 Effective in melting means a product capable of melting below zero F. Ease of application is also important because labor cost is one of the largest components of melting snow and ice. Liquid melters bring ease to the application process.

In Ossian, Inc.'s earlier U.S. Pat. No. 5,683,619 (Ossian & Steinhauser), we created a product that melted below zero and could have a positive effect on vegetation. The major
25 disadvantages to this earlier invention were the high cost to produce the product and cost of application. It used calcium chloride and urea in a dry melter composition. When calcium chloride is manufactured for industrial use it starts out as a liquid. The water is then evaporated to form a flake or pellet. This manufacturing process uses considerable energy adding to the cost of manufacture for the raw material. Some of this cost could be avoided
30 if the ice melter were liquid as finished.

The solid ice melter of U.S. Pat. No. 5,683,619 is advantageous in that it is an effective melter, and it brings a positive effect on vegetation. It is in content a combination

of urea and calcium chloride in a solid particle format. In recent times it has been of interest to develop liquid ice melters. In some environments, liquid ice melters are preferred to solid ice melters in that they give better coverage, they are much quicker acting melters, and they are more economical to prepare.

5 The liquid ice melter of U. S. Patent No. 7,122,127 is a product that is less expensive to manufacture, easy to use, melts below zero and can have a positive effect on vegetation. In that invention, we used liquid calcium chloride solution combined with either dry or liquid urea, in critical ratios to achieve an effective liquid ice melter.

10 The present inventor has invented both solid ice melters of the type described above and liquid ice melters of the type described above. Both have their useful approaches depending on the use, climate and conditions. One particularly preferred ice melter is the solid type ice melter of U. S. Patent No. 6,039,890 which relates to a quick acting ice melter, its melt value enhanced by the addition of an ice melter compatible surface active agent. The present invention represents yet a further improvement on the invention of U.
15 S. Patent No. 6,039,890 of March 21, 2000 entitled "QUICK ACTING ICE MELTING COMPOSITION", Ossian et al. The disclosure of this patent is incorporated herein by reference.

20 In the most general sense, the above-identified U. S. Patent No. 6,039,890 uses a variety of different surfactant surface active agents as coatings of solid ice melters to achieve enhanced melt values and provide quicker melt action. The application of the present Applicant, Ossian, along with another joint inventor, U. S. Serial No. 11/566,390 filed December 4, 2006 and entitled "PROCESSED RAFFINATE MATERIAL FOR ENHANCING MELT VALUE OF DE-ICERS" involves addition of the product known as raffinate to conventional liquid or solid ice-melters in order to further enhance melt value.
25 The present invention may be used with the system of the previously incorporated by reference '890 patent or with the system of Serial No. 11/566,390 to the extent it describes solid melters with raffinate additives. The disclosure of Serial No. 11/566,390 is also incorporated by reference.

30 The most common and therefore least expensive solid ice melters are those based upon chemical salts that gradually dissolve and form a salt solution (brine) which lowers freezing point. Salts used are chloride or acetates salts of Group I or Group II metals, such

as sodium, potassium, calcium and magnesium. These salts can then be combined with environmentally friendly organic materials to enhance their melt value such as urea.

In instances where chemical salts are used, these are generally white in color which blend completely in color with the snow. It is at times desirable to add dyes to these so that
5 the person apply the de-icer can easily distinguish areas where the icer has been spread and areas where it has not. Typically used are environmentally friendly water soluble, visible dyes of distinctly different colors than white.

The dye material must not be introduced into the de-icer with water because the chemical salts as above described tend to be hygroscopic and the contact with moisture will
10 cause them to bridge or cake in the packages. This is of course undesirable. It affects their ability to spread, the amount of surface upon which they can effectively be used, and make them difficult to handle.

It has further been found and, indeed, my previous Patent No. 6,039,890 addresses the speed of melting as a critical component for an effective de-icer. The reason for this is
15 quite simple. Ice on surfaces represents a risk and the quicker the ice is removed, the more effective the ice melter and thus the higher the value it has to the consumer.

Accordingly, it is a primary objective of the present invention to enhance melt value of conventional chemical salt de-icers.

It is another objective of the present invention to enhance melt value using an
20 environmentally friendly, water soluble material which will dissolve water soluble dyes.

Yet a further objective of the present invention is to provide a coating material on conventional chemical salt de-icers which can apply not only ice melt value enhancement but also anti-caking and anti-bridging properties to allow for easier packaging and spreading of the de-icer.

25 A further objective of the present invention is to find an effective uses for industrial waste stream glycerin which is currently a glut on the market due to the high popularity of bio-diesel fuel.

A method and means for accomplishing each of the above objectives as well as others will become apparent from the detailed description of the invention which follows
30 hereinafter.

BRIEF SUMMARY OF THE INVENTION

Solid ice melters are improved with a small exterior coating of glycerin which prevents caking and bridging and enhances melt value.

5 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing melt value increase with addition of glycerin as a coating on the solid ice melt composition surface.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

10 It goes without saying that the ice melters of the present invention may be used alone or in combination with abrasives and absorbents, for example as described in the earlier incorporated by reference U. S. Patent No. 6,039,890.

The de-icer composition of the present invention is normally solid and is formed from a mixture by way of example of metal salts of alkaline and alkaline earth metals.
15 Preferably with metal chloride salts and most preferably, the alkaline and alkaline earth metals, such as sodium chloride, potassium chloride, magnesium chloride and calcium chloride. Acetate salts may also be employed.

In its broadest process sense, these materials are mixed, then ground, screened for size and blended with any coating material, mixed and are then discharged into a packaging
20 bin.

Ice melters attract moisture from the surrounding environment, and then creates a liquid brine. This brine lowers the freezing point of water, and effectively dissolves ice and snow on contact until it becomes so diluted to a concentration where its freezing point is raised nearly to that of water. At this point in time, its effectiveness is gone. As is well
25 known, ice melters work because the ice melting composition or brine lowers the temperature at which water will freeze. In ice melter compositions that do not contain surface active agents at the interface of the ice melter brine and the packed snow or ice, the molecules are attracted inward in accordance with natural principles of adhesion. However, it has now been discovered that with the addition of surface active molecules as
30 hereinafter described, the adhesion attraction of like molecules of a liquid substance is equalized, the surface tension reduced, and as a result the ice melting brine penetrates more

quickly into the ice or packed snow, increasing significantly its melting speed. This is the invention of the '890 patent.

The critical component in the '890 patent ice melter invention is the surface active agent that reduces the surface tension in the melting brine produced by the various ice melting salts. This surface active agent must be able to reduce surface tension in high salt solution concentrations at temperatures below the freezing point of water. This is referred to as being ice melter compatible.

The complexity of measuring surface active agent's effects on surface tension when used with ice melting agents to increase melting volume and melting speed can be overwhelming at best. The surface tension will change with each salt, the concentration of that salt in the solution, and the temperature of the solution. In the melting process, the concentration of the salt is constantly changing because the melting process is one of constant dilution. Also, temperature could and often changes with each application. The colder the temperature, the greater the surface tension becomes. It becomes even more complex when combinations of various ice melting salts are used.

There are several agents that can be used to reduce surface tension. Some of the various possibilities include nonionic, anionic, cationic and amphoteric surfactants. For these surface active agents to be successful, they would exhibit superior wetting properties in a high salt solution of sodium chloride, calcium chloride, magnesium chloride, potassium chloride or urea, either individually or in combination.

The overall objective is to reduce the surface tension in a high salt brine solution. This will allow the dry salt to convert to a liquid melting brine faster to increase the melting volume and the melting speed of the ice melting salt.

In the past, chemical salt based solid de-icers often incorporated a dye for visibility. This was done by adding it to propylene glycol which was mixed with the other materials. Propylene glycol was used because one would normally not want to add water to a chemical salt based de-icers, since the water would accentuate and accelerate caking and bridging. It has now been discovered that if very low levels of glycerin are used to dissolve the dye, then the dye and glycerin mixture or even glycerin alone can be used as coating on the solid mix with surprising results. First, it is cheaper than propylene glycol.

Second, contrary to propylene glycol, it has the advantage of being an anti-caking agent and surprisingly it also enhances melt value.

Ice melting salts such as sodium chloride or blends of sodium chloride, calcium chloride, and magnesium chloride by their nature will congeal and cake. This is a major safety issue with salt storage in large storage areas. The salt may bridge, only to give away later potentially causing injury or even death to someone who could be buried by the landslide effect of the salt pile. Such salt piles are common at city storage areas.

Caking and congealing of salt or salt blends is also a major problem in packaged containers. Over time the material packs from the pressure of being piled on top of other bags. Add to this that salt is slightly hygroscopic and this drawing moisture action will lead to caking and bridging not only in bulk storage but as well in bag storage, such as at stores.

Glycerin added in a small percentage as an exterior coating will decrease the caking of salt in either bulk storage or bag storage and will increase melt value.

Increasing melt value of salt is a goal of users in the field. Increasing the melt value of salt will reduce the quantity of salt being used. Reducing the amount of salt usage has long been a goal of users in the industry. In Patent No. 6,039,890, we introduced the concept of coating salt with surfactants to increase melt value. This has been very effective and millions of pounds of product have been used employing this technique. This low level glycerin coating improves it further.

Glycerin may be coated alone or coated on top of a surfactant coated material and may be coated as glycerin in pure form or by product glycerin and may be mixed with visible dye or not mixed with visible dye, as the applicator wishes. An important feature is that a low level addition of glycerin is used. Generally speaking, the amount of glycerin can be from about 0.05% by weight to about 1.0% by weight of the total weight of the ice melt composition. Most preferably, it is from about 0.05% by weight to about 0.5% by weight of the total weight of the ice melt composition. The mentioned lower level of glycerin is needed in order to achieve anti-caking and anti-bridging and melt value enhancement; the upper level is the amount to get the most efficient melt value enhancement. Beyond the upper level, economies of the increased amounts are not justified for the slight additional benefit, and run-off of product becomes an issue.

The following are typical industrial specifications for preparing a product which is both the '890 patent and the present improvement all in the same ice melter.

Production Specifications - Procedures for Blue Dye plus Surfactant mixes:

- 5 1. Begin with an empty tank;
2. Add 100 gallons of glycerin;
3. Add 4500 grams of blue polymeric colorant;
4. Mix with mixer blades;
5. Add 100 gallons 8 mol nonionic surfactant;
- 10 6. Mix with mixer blades;
7. Mix with prop prior to adding to the blender/mixer.

One gallon of dye will weight approximately 9.5 lbs per gallon.

The above mix could be repeated using just the glycerin. The ratio would be 4500
15 grams of polymeric colorant to 200 gallons of glycerin.

The dye mixture is added to salt as a coating process in a blender/mixer. The dye mixture ratio may vary per product. The glycerin and nonionic surfactant may vary per product. A typical production example follows:

20 **Production Specifications - Procedures for dye coating**

1. Begin with an empty and clean blender;
2. Add 5000 lbs of screened salt;
3. Add 2 gallons Blue Dye Surfactant mix;
4. Add additional 5000 lbs of screened salt;
- 25 5. Add additional 2 gallons of Blue Dye Surfactant mix;
6. Let mixer run approximately two minutes, discharge into packaging bin.

The small weight percentages of the glycerin, surfactant and dye coating used in the above 10,000 pound batch are as follows:

30 Glycerin content: .00206
 Nonionic surfactant: .00175

Polymeric colorant: .000002

The typical ranges of the above will vary depending on the specific product, but for the most part will fall into the following ranges:

- 5 Glycerin content: from .001 to .006
 Nonionic surfactant: from .001 to .002
 Polymeric colorant: from .000001 to .000002

10 The polymeric colorant can be any suitable water soluble environmentally friendly dye. It can for example be Liquitint® Brilliant Orange, Liquitint® Pink AL, Liquitint® Green HMC, and Liquitint® Patent Blue. The dyes can be purchased from Milliken Chemical, 1440 Campton Road, Inman, South Carolina 29349.

The following example and tests are offered to further illustrate but not limit the process and product of the present invention.

15

EXAMPLE

To test the value of glycerin, glycerin from bio-diesel production was tested, as below described:

20 Salt (NaCl) was screened through a #4 US screen to eliminate large particles everything was kept on a #10 screen to eliminate the fines since fines are a big contributor to salt caking.

Four samples were weighed out to 1000 grams each and water was added to equal ½ percent. Sodium chloride can pick up ½ percent moisture in storage. Various levels of glycerin were added to the samples as shown below:

25 Sample A sodium chloride plus 5 grams of water

Sample B sodium chloride plus 5 grams of water plus 1 gram of Glycerin

Sample C sodium chloride plus 5 grams of water plus 2.5 grams of Glycerin

Sample D sodium chloride plus 5 grams of water plus 5 grams of Glycerin

30 All samples were placed in a lab oven at 120 degrees F for seven days to accelerate caking issues from summer heat. The results were:

Sample A – hard cake

Sample B – slight caking

Sample C – limited caking – extremely friable

Sample D – free flowing

From the results above observed, we concluded small percentages of glycerin either
 5 pure or from bio-diesel fuel production waste stream can significantly reducing caking of
 sodium chloride in storage. This knowledge was then used to set up melt value tests.

Using the Strategic Highway Research Program (SHRP) H-205.1 standards for
 testing ice melt value for ice melters the following samples were placed in a laboratory
 controlled freezer and melt values established for 20 minutes at 15 degrees F. The test was
 10 repeated four times and averages plotted on the graph of Figure 1.

All samples were screened through #4 US Screen and on #10 screen – no fines were
 present in the samples tested. One sample was not treated as a control and the other three
 samples were coated with different levels of glycerin.

Sample # 1 – sodium chloride

15 Sample # 2 – sodium chloride coated with .10 per cent glycerin

Sample # 3 – sodium chloride coated with .25 per cent glycerin

Sample # 4 – sodium chloride coated with .50 per cent glycerin

From the above example, it is seen that the present invention has demonstrated that
 20 glycerin derived from bio-diesel production and used in small percentages will reduce
 caking and bridging in storage of sodium chloride. The ice melting tests (Figure 1) have
 shown glycerin coated onto sodium chloride or blends of sodium chloride with additional
 ice melting agents in small percentages will increase melt value. In addition, glycerin can
 enhance the dye mix process commonly used in ice melters without causing caking and
 25 bridging. Glycerin replaces the water and/or propylene glycol that are added as the carrier
 for dye mixes that are used to coat ice melting salts. Glycerin dye mixes may also be
 blended with surfactants prior to coating the ice melting salts, as discussed above.

What is claimed:

1. A solid ice melt composition, comprising:
a solid ice melter; and
5 a small but anti-caking and melt value enhancing effective amount of an exterior ice
melting surface coating of glycerin.
2. The solid ice melt composition of claim 1 wherein the coating is a mixture of
glycerin and a water soluble environmentally friendly visible dye.
- 10 3. The solid ice melt composition of claim 1 wherein the glycerin is agricultural grade
glycerin derived from an industrial waste stream.
4. The solid ice melt composition of claim 1 wherein the industrial waste stream
15 source of glycerin is selected from the group consisting of transesterification,
saponification and hydrolysis.
5. The solid ice melt composition of claim 4 wherein the industrial waste source of
glycerin is from biodiesel fuel production.
- 20 6. The solid ice melt composition of claim 2 wherein the glycerin and water soluble
environmentally friendly dye is selected from the group consisting of selected from the
group consisting of biodegradable polymeric colorants.
- 25 7. The solid ice melt composition of claim 1 wherein the amount of glycerin is from
about .05% to about 1.0% of the total weight of the ice melt composition.
8. The solid ice melt composition of claim 1 wherein the amount of glycerin is from
about 0.5% to about 0.2% of the weight of the total weight of the ice melt composition.
- 30 9. The solid ice melt composition of claim 1 which is a salt based ice melt.

10. The solid ice melt composition of claim 1 wherein the salts are selected from the group consisting of chloride and acetate salts.

11. The solid ice melt composition of claim 10 wherein the salts are selected from the
5 group consisting of sodium chloride, potassium chloride, magnesium chloride, calcium acetate, magnesium acetate, potassium acetate and sodium acetate.

12. The solid ice melt composition of claim 1 which includes sugar derived agriculture by products of cane, beat and corn sugar production.

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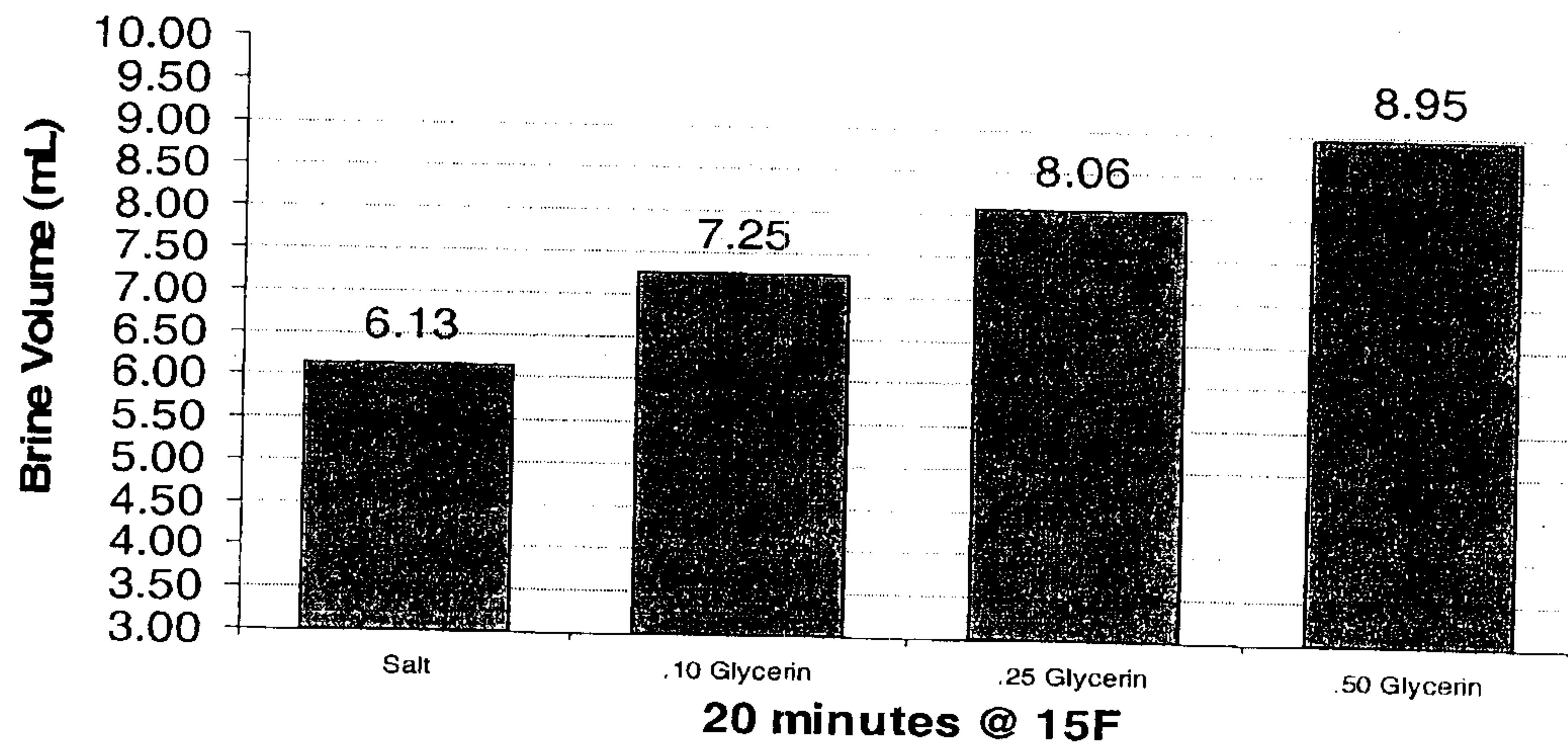


Figure 1

Brine Volume (mL)

