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3,185,648

DEICER COMPOSITION

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This invention relates to a chemical deicer composition and more particularly pertains to a composition comprising a mixture of urea and ammonium nitrate and to a method for melting ice and removing ice from surfaces by treatment with said composition.

The use as chemical deicers of freezing point depressants such as sodium chloride and calcium chloride is well known. Both compounds are relatively inexpensive, they are quite effective in melting ice and snow at subfreezing temperatures, and they are used extensively as deicers.

In recent years, because of the tremendous increase in motor vehicle traffic, these ice-melting chloride salts have found widespread use in the melting of ice and snow on driveways, streets, roads, bridges and other vehicular roadways. Such materials are soluble in water so that no disposal problem exists as in the case of cinders, slag, sand, or other purely abrasive materials. These latter materials are water-insoluble, and during melting and thawing periods, are washed off the roadways and clog catch basins, sewer lines, etc. The ice-melting salts, on the contrary, create no such problem and although their initial cost per pound is higher than cinders or related abrasive type materials, the over-all costs of these deicing salts frequently are lower as there are fewer maintenance problems encountered.

It is well known that chlorides of sodium and calcium are extremely corrosive to steel, particularly in the dilute solutions encountered on roadways where these deicing salts are diluted by melting snow, ice or rain. Several inhibitors have been developed for use with the chlorides such as the alkali metal chromates and the like. These inhibiting salts have reduced somewhat the corrosion of the underbodies of trucks, passenger cars, etc., although the localized pitting type of corrosion which chlorides produce upon aluminum and its alloys still takes place and is a very serious problem.

Although the protection against the corrosion of steel by the alkali metal chlorides can be minimized by the use of additives, certain other metals which are used in vehicle construction, such as aluminum and its alloys, are still highly susceptible to chloride corrosion. Aluminum alloys and alloys of ferrous metals are components of aircraft, railroad cars, buses, trucks, and other vehicles; and it is one object of our invention to minimize corrosion of these metals which are subject to contact with the deicing salt solution resulting from the melted ice and snow. Aluminum and its alloys, and particularly highly stressed aluminum and its alloys such as auto parts constructed by stamping techniques, are attacked in such a local manner by the chloride ion that these salts cannot be safely used where they will be splashed upon the aluminum or aluminum alloy surface. The inhibiting salts, such as chromates, seem to have no effect on reducing the pitting-type of corrosion which the chlorides cause on aluminum alloys.

Aqueous solutions containing urea and ammonium nitrate have been, and are presently, used as plant fertilizers. Aqueous urea-ammonium nitrate fertilizer solutions are mentioned in U.S. Patents, Nos. 2,022,672; 2,549,430; 2,855,286; and 3,029,139. Urea is described as an ice-melting salt in U.S. Patent No. 2,980,620. An aqueous solution of a eutectic mixture of urea and ammonium nitrate is disclosed as a useful refrigerating com-

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position in U.S. Patent No. 2,136,385. The latter patent discloses that a ternary composition of 100 parts by weight of water, 75 parts by weight of urea and 75 parts by weight of ammonium nitrate constitutes a mixture having an eutectic freezing point of -19.3°F .

It is quite well known to those skilled in the art that the term "eutectic" denotes a minimum in the freezing point versus composition curve of a system and that the particular mixture which exists as liquid or solid at this minimum temperature is known as the "eutectic mixture." Thus, U.S. Patents No. 2,136,385 teaches those skilled in the art that the aqueous eutectic mixture of urea and ammonium nitrate consists of about equal-weight proportions of urea and ammonium nitrate. It is also well known by those skilled in the art that the temperature at which a solid changes to a liquid is called its melting point and that the freezing point is the temperature at which a liquid changes to a solid so that both points are the same for a given substance. It is apparent, then, that the "freezing" points or temperatures mentioned herein also mean the "melting" points or temperatures of the particular systems described and, of course, the converse is also true.

As was mentioned earlier, a number of salt mixtures, including mixtures of urea, ammonium nitrate and water, have been used as refrigerants or hold-overs. As a refrigerant composition, the mixture must remain liquid at all temperatures of the particular application so that it can be circulated throughout the cooling system. A hold-over composition is frozen during the operation of the refrigerating apparatus forming a cryohydrate which, in turn, melts during idle refrigeration periods and withdraws its latent heat of fusion from the chamber to be cooled, thus, maintaining the desired temperature. In the case of a refrigerant, the lowest possible freezing point is desirable. This will result from using the highest concentration of salt or salts which can be obtained in the solutions. In the case of a hold-over composition, a very high negative heat of fusion is also desirable. With both the refrigerant and the hold-over, the composition of the useful mixture is always constant.

On the other hand, a chemical deicer functions in a manner which is completely different from that of a refrigerant or hold-over. In the deicing process, there is initially a limited supply of liquid water available on the surface of the ice and a large excess of deicer. As melting proceeds and water forms, the composition of the solution changes, the temperature of the composition varies, the area of the deicer exposed changes, and the solution temperature either increases or decreases depending on a negative or positive heat of solution of the deicer. Thus, at no time are the composition or physical characteristics of the mixture constant. A measure of the temperature of a mixture of deicer and ice is a measure of the composite effect of all these changing factors which generally gives a higher temperature than the freezing point. For a given salt, the "deicing temperature" and the "freezing temperature eutectic" are different and what type and the degree of difference is not predictable. Sodium chloride, for instance, has a freezing temperature eutectic of -22.4°F . and it has a deicing temperature of -6°F . Ammonium nitrate alone has a freezing temperature eutectic of -17.5°F . and a deicing temperature of $+5^{\circ}\text{F}$. Similarly, urea alone has a deicing temperature of $+11^{\circ}\text{F}$. The freezing temperature eutectic of the mixture of 53% by weight ammonium nitrate and 47% by weight urea is -19.3°F . but the deicing temperature of this mixture is above 0°F . Similarly, the freezing temperature eutectic of a 50:50 by weight mixture of ammonium nitrate and urea is in the range of $+5^{\circ}\text{F}$.

It is the object of the present invention to provide a chemical deicer composition which, even at sub-freezing

temperatures, rapidly wets and melts ice when applied thereto. It is another object to provide a chemical deicer which is not injurious to the soil or plant life but, on the contrary, is composed entirely of plant nutrients. It is another object to provide a chemical deicer which will not cause corrosion or discoloration of surfaces, and particularly stressed aluminum and aluminum alloy surfaces with which it may come in contact. That these and other objects have been accomplished by the present invention will become apparent from the following description and illustrative examples.

We have discovered a novel deicing composition having a deicing temperature no greater than 0° F. comprising an intimate mixture of from 10 to 45% by weight of urea and from 90 to 55% by weight of ammonium nitrate. More highly preferred in the present invention is the deicing composition possessing a deicing temperature of less than about -5° F. comprising from 22 to 29% by weight of urea and from 78 to 71% by weight of ammonium nitrate.

The composition of the present invention is a chloride-free deicer composition which has a marked depressing action on the melting point of ice and which is essentially harmless to most surfaces it may contact, including aluminum and its alloys. Moreover, the deicer composition of our invention is comparable as an ice melter on a weight basis with the alkali metal chlorides. In addition, our composition has the advantage of being comprised entirely of plant nutrients.

Our discovery is particularly useful in conjunction with the melting of ice and snow in driveways and walkways adjacent to lawns, shrubs, flowers and trees. The composition embodied in this invention is useful also in the melting of ice and snow on airport runways, bus and truck loading areas, etc. where most of the equipment is constructed of various metals, including both steel and aluminum.

The composition embodied herein may be prepared in any convenient manner providing an intimate mixture of the two essential components results. In a least preferred but operable procedure the individual components may be dry-mixed in a pebble or ball-mill, for instance, until an intimately mixed powder results. It is more preferred, however, that the desired amounts of urea and ammonium nitrate may be mixed and heated until molten and the melt then can be cooled and granulated or pulverized. Similarly, in another highly preferred manner, an aqueous solution of the desired proportions of urea and ammonium nitrate may be prepared followed by removal of the water by evaporation and granulation or grinding of the solid. For instance, a fairly concentrated aqueous solution of the desired proportions of urea and ammonium nitrate may be added to a continuous drum drier to produce flakes, or the aqueous solution, or the molten mixture, may be subjected to treatment in a prilling tower which results in a prilled product of granular form. In any event, the method whereby the deicing composition embodied herein is prepared is not critical and is without the scope of the present invention. Any method which produces an intimate mixture of solid urea and ammonium nitrate in particulate form may be used.

If it is so desired, a corrosion inhibitor (primarily for additional corrosion protection for ferrous metals) may be included in the deicer composition of this invention. The deicer compositions embodied herein are useful without inhibitors, particularly when they are maintained at a pH of 7 or above. Corrosion inhibitors, which are preferred, include the water-soluble salts of the phosphoric acids, water-soluble salts of chromic acid, water-soluble dichromate salts, sodium nitrite, borax, and such proprietary mixtures as Banox, a material sold by Calgon, Inc., which is a mixture of phosphates. Other useful corrosion inhibitors include the water-soluble ammine complexes described in U.S. Patent No. 2,957,762.

The most preferred corrosion inhibitors for use in the

present invention are the water-soluble phosphate salts, such as trisodium phosphate, and the sodium polyphosphates, such as sodium hexametaphosphate. The phosphate inhibitors are particularly useful in conjunction with the deicer compositions even when the pH of the system is below 7.

It is also indeed unobvious and unexpected that a mixture of from 22 to 29% by weight of urea, from 77.99 to 70.99% by weight of ammonium nitrate and from 0.01 to 2% by weight of a water-soluble phosphate salt has been found to have a deicing temperature of no greater than -10° F.

The deicer composition of the present invention is applied to an ice-covered surface, such as a roadway, by broadcasting. The deicer is not blown from the ice surface by the wind because rapid melting follows at points where the deicer contacts the ice and the liquid area spreads rapidly as the melting process continues.

In the following illustrative examples, the amounts of the various ingredients are expressed as parts by weight unless otherwise indicated.

Example I

A blend of 26 parts of urea and 74 parts of ammonium nitrate was fused with heat and the melt was thoroughly mixed. The mixture was then allowed to cool to room temperature and the solid cake was granulated to form a coarse granular material. To 200 g. of crushed ice were added 100 g. of the aforementioned granular mixture and the resulting ice-salt mixture was stirred and the deicing temperature attained was found to be -8° F. The deicing temperature is the lowest temperature observed while the above mixture of ice, water and urea-ammonium nitrate was being stirred. A deicing temperature of -8° F. was again observed when the foregoing procedure was repeated.

When the foregoing procedure was repeated, starting with a 50:50 by weight mixture of urea and ammonium nitrate, a deicing temperature of +2° F. was observed.

When the foregoing procedure was repeated, starting with urea alone in place of the urea-ammonium nitrate mixture, a deicing temperature of +11° F. was observed.

When the foregoing procedure was repeated using ammonium nitrate alone in place of urea, a deicing temperature of +5° F. was observed.

Example II

The procedure of Example I was repeated, starting with a 22:78 by weight mixture of urea:ammonium nitrate. A deicing temperature of -6° F. was observed.

When the foregoing procedure was repeated using a 10:90 by weight mixture of urea:ammonium nitrate, a deicing temperature of 0° F. was observed.

Example III

The procedure of Example I was repeated, starting with a 29:71 by weight mixture of urea-ammonium nitrate. A deicing temperature of -7° F. was observed.

When the foregoing procedure was repeated using a 45:55 by weight mixture of urea-ammonium nitrate, a deicing temperature of 0° F. was found.

When the foregoing procedure was repeated using sodium chloride in place of the urea-ammonium nitrate mixture, a deicing temperature of -6° F. was observed.

Example IV

An aqueous solution of 26 parts of urea, 73 parts of ammonium nitrate and 1 part of trisodium phosphate was prepared and the water was then removed from the solution by evaporation with heat. The residual solid mixture was granulated and 100 g. of this granulated mixture was added to 200 g. of crushed ice, and the procedure outlined in Example I was followed. A deicing temperature of -15° F. was observed.

The surface of metal panels completely coated with acrylic paint, lacquer, and enamel was coated with a 10%

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by weight aqueous solution of the above deicer and the water was allowed to evaporate at room temperature. The panel surface was then wiped and buffed. No apparent change in the surface appearance, gloss, etc. was observed. When the 10% aqueous solution of the above deicer was applied to nylon and to wool carpeting and allowed to dry, a fluffy residue was left which disappeared upon slight brushing of the carpet. The above deicer was superior to sodium chloride and calcium chloride in this respect.

We claim:

1. A solid deicer composition having a deicing temperature of no higher than about -5° F. consisting of from 22 to 29% by weight of urea, from 78 to 71% by weight of ammonium nitrate, and from 0 to 2% by weight of a corrosion inhibitor selected from the group consisting of trisodium phosphate and the sodium polyphosphates.

2. The composition of claim 1 wherein the corrosion inhibitor is trisodium phosphate.

3. A solid deicer composition having a deicing temperature no higher than about -8° F. consisting of 26% by weight of urea and 74% by weight of ammonium nitrate.

4. A solid deicer composition having a deicing temperature no higher than about -6° F. consisting of 22% by weight of urea and 78% by weight of ammonium nitrate.

5. A solid deicer composition having a deicing temperature no higher than about -7° F. consisting of 29% by weight of urea and 71% by weight of ammonium nitrate.

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6. A solid deicer composition having a deicing temperature no higher than about -15° F. consisting of 26% by weight of urea, 73% by weight of ammonium nitrate, and 1% by weight of trisodium phosphate.

7. The method for melting ice comprising adding to ice a particulate, intimate mixture of a solid substantially free of chloride ions consisting essentially of from 10 to 45% by weight of urea and from 90 to 55% by weight of ammonium nitrate.

8. The method for melting ice comprising adding to ice a granular, intimate mixture of a solid substantially free of a chloride ions consisting essentially of from 22 to 29% by weight of urea and from 78 to 71% by weight of ammonium nitrate and from 0 to 2% by weight of a corrosion inhibitor selected from the group consisting of trisodium phosphate and the sodium polyphosphates.

9. A solid deicing composition having a deicing temperature of no higher than about -5° F. consisting of from 22 to 29% by weight of urea, 77.99 to 70.99% by weight of ammonium nitrate, and from 0.01 to 2% by weight of a corrosion inhibitor selected from the group consisting of trisodium phosphate and sodium polyphosphates.

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