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(54) Titre : COMPOSITION DE DEGIVRAGE A BASE D'ORTHOPHOSPHATE MONOACIDE
(54) Title: MONOHYDROGEN ORTHOPHOSPHATE DEICING COMPOSITION

(57) Abrégé/Abstract:
A deicing composition which includes NaCl and an orthophosphate selected from the group consisting of $MgHPO_4$, Na_2HPO_4, K_2HPO_4, $(NH_4)_2HPO_4$, hydrated forms thereof and mixtures thereof. When the monohydrogen orthophosphate has the alkali metal ions or ammonium cation, the deicing composition includes a water soluble magnesium salt. A method of deicing using the deicing composition also is described.

ABSTRACT OF THE INVENTION

A deicing composition which includes NaCl and an orthophosphate selected from the group consisting of $MgHPO_4$, Na_2HPO_4, K_2HPO_4, $(NH_4)_2HPO_4$, hydrated forms thereof and mixtures thereof. When the monohydrogen orthophosphate has the alkali metal ions or ammonium cation, the deicing composition includes a water soluble magnesium salt. A method of deicing using the deicing composition also is described.

A MONOHYDROGEN ORTHOPHOSPHATE DEICING COMPOSITION

Field of the Invention

The present invention is directed to a deicing composition and a method for utilizing the deicing composition. More particularly, the present invention is directed to a deicing composition which comprises the deicer salt NaCl and a corrosion inhibitor which includes magnesium, sodium, potassium or ammonium monohydrogen orthophosphate ($MgHPO_4$, Na_2HPO_4, K_2HPO_4 or $(NH_4)_2HPO_4$), and if the alkali metal or ammonium orthophosphate is used, the composition includes a water soluble magnesium salt.

Background of the Invention

Calcium chloride and alkali metal salts, such as sodium chloride, are extensively used in very large quantities on the roads of many countries for snow and ice removal. The use of calcium chloride or sodium chloride has, however, met with some resistance due to their corrosive effect on ferrous metal and deleterious effect on concrete. Indeed data has been released suggesting that the cost of the damage associated with the widespread application of salt is approximately fourteen times the direct cost associated with the application of the salt; D. M. Murray, et al., An Economic Analysis of the Environmental Impact of Highway Deicing, U.S. Environmental Protection Agency, Cincinnati, Ohio, EPA-600/A-76-105 (May 1976). Accordingly, it would be highly desirable to provide a deicing composition which deices rapidly, has a reduced level of concrete damage such as by scaling the surface of the concrete, and reduces corrosion of ferrous metallic objects.

Various additives have been proposed for mixing with salt to aid in inhibiting corrosion caused by the salt. British Patent No. 1328509 to Bishop et al. describes a composition suitable for use in the inhibition of corrosion caused by salt, which includes a water soluble polyphosphate and a surface active agent. The surface active agent is various amine compounds. In an article by E. E. Steed, Road Research Laboratory, Ministry of Transport, UK Report LR268-1969, polymetaphosphate inhibitors which require the presence of calcium ions are described to be effective as a corrosion inhibitor for brine solutions.

There is a serious need to provide a low cost deicing composition which reduces oxidative corrosion caused by aqueous solutions of NaCl. Depending on cost, a deicing composition which reduces such corrosion or rust would be highly desirable for use on roadways where large quantities of the deicing composition are required. The present invention is directed to providing a corrosion resistant, low cost, deicing composition which is suitable for highway and sidewalk use.

Accordingly, one of the principle objects of the invention is to provide a deicing composition which deices rapidly. Another object of this invention is to provide a deicing composition which causes a reduced level of corrosion to ferrous metal. Yet another important object of this invention is to provide a deicing composition which utilizes NaCl as a cost effective deicer, but reduce the highly corrosive effect of NaCl on ferrous metal.

These and other objects of the invention will become apparent from the following description.

Summary of the Invention

Orthophosphates tend to form slightly soluble compounds with magnesium salts and may not be expected to perform well together as corrosion inhibiting compositions. Surprisingly, this invention combines NaCl and the orthophosphates selected from the group consisting of $MgHPO_4$, Na_2HPO_4, K_2HPO_4, or $(NH_4)_2HPO_4$ which may be in the hydrated form, to produce an effective anticorrosive/antiscaling deicer composition which provides new and unexpected anticorrosive activity over other deicing compositions.

The present invention is directed to a non liquid or dry deicing composition comprising NaCl as a deicer salt in an amount effective for deicing a surface with frozen water there-on, and an amount of orthophosphate selected from the group consisting of $MgHPO_4$, Na_2HPO_4, K_2HPO_4, $(NH_4)_2HPO_4$, hydrated forms thereof and mixtures thereof effective for the reduction of corrosion of ferrous metal by aqueous solutions of NaCl. When the monohydrogen salt has the alkali metal ions sodium or potassium or the ammonium cation, the deicing composition includes a water soluble salt of magnesium, such as $MgCl_2$ or $MgSO_4$, in an amount effective to aid the ammonium or alkali metal monohy-drogen phosphate in reducing the corrosion of ferrous metal by aqueous solutions of NaCl. In this aspect of the invention, the water soluble magnesium salt provides for reduced corrosion of ferrous metal and except in the case of the ammonium cation, reduces the scaling that NaCl causes on concrete. However, additional metals such as zinc or other additives such as amines are not required to provide a composition which has effective anticorrosive properties.

The present invention is also directed to a method for deicing a surface having frozen water thereon

by applying the deicing composition of the invention onto the surface of the ice.

Detailed Description of the Invention

As used herein "monohydrogen orthophosphate" means orthophosphates selected from the group consisting of $MgHPO_4$, Na_2HPO_4 K_2HPO_4, $(NH_4)_2HPO_4$ and mixtures thereof. These orthophosphates may be in their hydrated form, such as $MgHPO_4 \cdot 3H_2O$, where there generally will be from about 1 to about 3 waters of hydration, or sodium hydrogen phosphate which has up to 12 waters of hydration.

As used herein "ferrous metal" means iron or alloys of iron including steel which undergo corrosion or oxidation under ambient conditions.

As used herein water soluble salt means a water solubility of at least about 10 g/l at 30° C.

According to the invention, the alkali metal or ammonium monohydrogen orthophosphate used in combination with a water soluble magnesium salt reduces the corrosive effect on ferrous metal that is usually associated with aqueous solutions of NaCl or, magnesium monohydrogen orthophosphate reduces the corrosive effect on ferrous metal that is usually associated with aqueous solutions of NaCl.

The deicing composition comprises NaCl and a corrosion inhibitor selected from the group consisting of $MgHPO_4$, an alkali metal or ammonium monohydrogen orthophosphate in combination with a water soluble magnesium salt and mixtures thereof, where the corrosion inhibitor is in an amount effective to reduce the corrosive effect on metal of aqueous solutions of NaCl.

The effective ratio of the orthophosphate to NaCl can vary widely. The deicing composition of the invention contains at least about 1.0 weight %, and preferably from about 2 to about 10 weight %, based upon

the weight of the deicing composition on a dry basis, of monohydrogen orthophosphate in combination with about 90 weight percent and preferably from about 90% to about 98 weight %, based upon the weight of the composition on a dry basis, of NaCl. Due to its low cost, sodium chloride is in the major amount of the deicing composition, such as about 95 weight percent of the deicing composition, with the monohydrogen orthophosphate being present in an amount effective to reduce the rate of corrosion of ferrous metal and/or scaling of concrete by aqueous solutions of deicer salts.

The monohydrogen orthophosphate may be made by the neutralization of phosphoric or superphosphoric acid and water with a base or base precursor such as NaOH, Na_2CO_3, $Mg(OH)_2$, $MgCO_3$ or MgO to a pH of about 7. In this aspect the acid is neutralized with the base to a pH in the range of from about 5 to about 9 yielding the water soluble orthophosphate salt and water. Water soluble magnesium salts such as magnesium sulfate ($MgSO_4 \cdot 7H_2O$) or magnesium chloride may be combined with the alkali metal or ammonium monohydrogen orthophosphate such as disodium phosphate (Na_2HPO_4) with large excesses of NaCl to provide the deicing composition of the invention, which in this aspect of the invention is $MgHPO_4 \cdot 3H_2O + Na_2SO_4 + NaCl$.

One or more water soluble magnesium salts such as $MgCl_2 \cdot XH_2O$ and $MgSO_4 \cdot YH_2O$ where X = 0 to 6 and Y = 0 to 7 are added to the corrision inhibitor which includes the alkali metal or ammonium monohydrogen orthophosphate in an amount effective to aid the orthophosphate to reduce corrosion of the highly corrosive NaCl. These magnesium salts may be used alone or in combination, but their total amount should not exceed about 9 weight percent of the deicing composition and should not replace the orthophosphate such that it goes below 1.0 weight percent or NaCl such that it goes below about 90 weight percent.

For best results the amount of magnesium ion should be in a molar amount that is about equal to the amount of phosphate ion provided by aqueous solutions of the deicing compositions. The deicing composition of the invention is provided by blending the NaCl and water soluble monohydrogen orthophosphate and other additives in the desired weight ratio and blending them until a substantially homogeneous solid mixture is obtained.

The deicing composition of the invention is applied to a structure coated with ice or snow by any suitable means, such as by mechanical spreading. The deicing composition of the invention melts ice at about the rate of pure NaCl, but protects ferrous metal from the corrosive effects of NaCl. The deicing composition of the present invention can also be combined with conventional materials intended to increase traction, such as sand, gravel, and the like.

The following examples further illustrate various features of the present invention but are intended to in no way limit the scope of the invention which is set forth in the appended claims.

EXAMPLE I

The corrosivity of various deicers was measured by an alternate immersion corrosion test involving the use of 2" x 3" S.A.E. 1010 carbon steel panels which were degreased in hexane and dried after a methanol rinse. The steel panels had a 1/4" diameter hole drilled in the center and near the top of the 2" side. The panels had numbers stamped in each of them. All panels were weighed to the nearest tenth of a milligram after drying. Three percent by dry weight basis of deicer solutions were prepared in all cases except for plain water. Four panels were suspended by a rod pushed through the 1/4" holes and separated by segments of

rubber tubing. Each assembly was suspended in the water or 3% deicer solutions such that the panels were 1/2 immersed. During two 1 hour periods each work day the panels were suspended in air to achieve good contact with oxygen. The other 22 hours of each work day the panels were 1/2 immersed. Over weekends, panels were 1/2 immersed. At the end of each week, old solution was removed and replaced with new solution of the same type. At the end of one month the panels were removed and the solutions cleaned with 1820 g hot water, 180 g of concentrated hydrochloric acid and 2 g of Rodine 213. The panels were weighed and the percent protection against salt induced corrosion was calculated as follows:

% Protection Against Salt* Induced Corrosion = 100 x

1- $\frac{\text{Avg Wt Loss in Test Sol'n-Avg Wt Loss in Water-Avg Cleaning Wt Loss}}{\text{Avg Wt Loss in Salt Sol'n-Avg Wt Loss in Water-Avg Cleaning Wt Loss}}$

3% Solution	Average Weight Loss	Percent Protection Against Salt Induced Corrosion
Water	0.4744	100.0
3% solution of sodium chloride	0.9567	0.0
3% solution of 98.0% NaCl 2.0% $MgHPO_4 \cdot 3H_2O$	0.0174	194.8
3% solution of 95.6% NaCl 2.8% $MgSO_4 \cdot 7H_2O$ 1.6% Na_2HPO4	0.0182	194.6
3% solution of 93.77% NaCl 3.23% $MgCl_2 \cdot 2H_2O$ 3.00% Na_2HPO_4	0.4093	15.6

3% solution of 96.1% NaCL 2.0% Na_2HPO_4 1.9% $MgCl_2 \cdot H_2O$	0.0145	195.4
3% solution of 94.8% NaCl 5.2% $MgHPO_4 \cdot 3H_2O$	0.0116	196.0
3% solution of 96.1% NaCl 2.0% Na_2HPO_4 1.97% $MgCl_2 \cdot 2H_2O$	0.0145	195.4

* As used in the samples "salt" means sodium chloride.

CLAIMS:

1. A non-liquid deicing composition comprising at least about 90 weight percent NaCl; from about 1 to about 10 weight percent of a monohydrogen orthophosphate corrosion inhibitor to reduce the corrosion of ferrous metal by an aqueous solution of NaCl; and a water soluble magnesium salt, wherein the monohydrogen orthophosphate corrosion inhibitor is selected from the group consisting of Na_2HPO_4 or hydrated forms thereof, K_2HPO_4 or hydrated forms thereof, $(NH_4)_2HPO_4$ or hydrated forms thereof and mixtures thereof and wherein the water soluble magnesium salt is in an amount effective to aid the sodium, potassium or ammonium monohydrogen orthophosphate in reducing corrosion by NaCl.

2. A deicing composition as recited in claim 1 wherein the orthophosphate is phosphoric acid neutralized with a base to a pH in the range of from about 5 to about 9.

3. A deicing composition as recited in claim 1 wherein the water soluble magnesium salt comprises not more than about 9 weight percent of the deicing composition.

4. A deicing composition as recited in claim 2 wherein the salt of phosphoric acid is neutralized with a base selected from the group consisting of NaOH, Na_2CO_3 and mixtures thereof.

5. A deicing composition as recited in claim 3

wherein the water soluble magnesium salt is present in an amount to provide magnesium ion in a molar amount which is about equal to the amount of phosphate ion provided by aqueous solutions of the deicing composition.

6. A deicing composition as recited in claims 1, 3 or 5 wherein the water soluble magnesium salt is selected from the group consisting of $MgCl_2 \cdot XH_2O$, $MgSO_4 \cdot YH_2O$ and mixtures thereof wherein X = 0 to 6 and Y = 0 to 7.

7. A method for deicing a surface having frozen water thereon, said method comprising applying the deicing composition recited in claims 1, 3 or 5 to a surface with frozen water thereon.

8. A method for deicing a surface having frozen water thereon, said method comprising applying the deicing composition recited in claim 2, to a surface with frozen water thereon.

9. A method for deicing a surface having frozen water thereon, said method comprising applying the deicing composition recited in claim 6 to a surface with frozen water thereon.

10. A non-liquid deicing composition comprising at least about 90 weight percent NaCl and from about 1 to about 10 weight percent of $MgHPO_4$ or hydrated forms thereof to reduce the corrosion of ferrous metal by an aqueous solution of NaCl.

11. A deicing composition as recited in claim 10

wherein the NaCl comprises from about 90 to 98 weight percent of the deicing composition and the $MgHPO_4$ comprises about 2 to about 10 weight percent of the deicing composition.

12. A method for deicing a surface having frozen water thereon, said method comprising applying the deicing composition recited in claims 10, 11 or 12 to a surface with frozen water thereon.

13. A non-liquid deicing composition consisting essentially of NaCl in an amount effective for deicing; a water soluble magnesium salt; and a monohydrogen orthophosphate corrosion inhibitor in an amount effective for the reduction of corrosion of ferrous metal by an aqueous solution of NaCl, wherein the monohydrogen orthophosphate corrosion inhibitor is selected from the group consisting of Na_2HPO_4 or hydrated forms thereof, K_2HPO_4 or hydrated forms thereof, $(NH_4)_2HPO_4$ or hydrated forms thereof, and mixtures thereof and wherein the water soluble magnesium salt is in an amount effective to aid the sodium, potassium or ammonium monohydrogen orthophosphate in reducing corrosion by NaCl.

14. A deicing composition as recited in claim 13 wherein the orthophosphate is phosphoric acid neutralized with a base to a pH in the range of from about 5 to about 9.

15. A deicing composition as recited in claim 13 wherein the water soluble magnesium salt comprises not more than about 9 weight percent of the

deicing composition.

16. A deicing composition as recited in claim 14 wherein the salt or phosphoric acid is neutralized with a base selected from the group consisting of NaOH and mixtures thereof.

17. A deicing composition as recited in claim 15 wherein the water soluble magnesium salt is present in an amount to provide magnesium ion in a molar amount which is about equal to the amount of phosphate ion provided by aqueous solutions of the deicing composition.

18. A deicing composition as recited in claim 13 wherein the NaCl comprises from about 90 to about 98 weight percent of the deicing composition and the orthophosphate comprises about 2 to about 10 weight percent of the deicing composition.

19. A method for deicing a surface having frozen water thereon, said method comprising applying the deicing composition recited in claims 13, 14 or 15 to a surface with frozen water thereon.

20. A non-liquid deicing composition consisting essentially of NaCl in an amount effective for deicing and $MgHPO_4$ or hydrated forms thereof in an amount effective for the reduction of corrosion of ferrous metal by an aqueous solution of NaCl.

21. A deicing composition as recited in claim 20

wherein the sodium chloride comprises at least about 90 weight percent of the deicing composition and the $MgHPO_4$ comprises about 1 to about 10 weight percent of the deicing composition.

22. A deicing composition as recited in claim 20 wherein the NaCl comprises from about 90 to about 98 weight percent of the deicing composition and the orthophosphate comprises about 2 to about 10 weight percent of the deicing composition.

23. A method for deicing a surface having frozen water thereon, said method comprising applying the deicing composition recited in claims 20, 21 or 22 to a surface with frozen water thereon.

24. A deicing composition as recited in claims 13 or 20 wherein the water soluble magnesium salt is selected from the group consisting of $MgCl_2 \cdot XH_2O$, $MgSO_4 \cdot YH_2O$ and mixtures thereof wherein X = 0 to 6 and Y = 0 to 7.

25. A method for deicing a surface having frozen water thereon, said method comprising applying the deicing composition recited in claim 24 to a surface with frozen water thereon.