

1

3,297,577

CHEMICAL DEICER

Norman W. Standish, Cleveland, and Walter R. Tuuri, Chesterland, Ohio, assignors to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio
No Drawing. Filed Dec. 12, 1963, Ser. No. 329,966
8 Claims. (Cl. 252-70)

The present invention relates to an improved chemical deicer composition and more particularly relates to an ammonium nitrate-urea deicing composition which is essentially non-corrosive to cadmium or cadmium-containing alloys.

The present invention is an improvement over that disclosed and claimed in the copending U.S. patent application of Norman W. Standish and Gordon G. Cross, Serial No. 224,821, filed September 19, 1962.

The aforementioned copending U.S. patent application discloses a substantially chloride free chemical deicer which causes little or no corrosion of iron, steel, aluminum and aluminum alloys and the deicer is composed of an intimate mixture of from 10 to 45% by weight of urea and from 90 to 55% by weight of ammonium nitrate, said mixture having a deicing temperature no greater than 0° F. The more highly preferred deicer composition, having a deicing temperature of less than about -5° F., comprises from 22 to 29% by weight of urea and from 78 to 71% by weight of ammonium nitrate. The deicer compositions of the copending patent application may contain corrosion inhibitors such as the alkali metal salts of the various phosphoric acids such as sodium phosphate, sodium pyrophosphate, sodium polyphosphates, potassium phosphates, potassium pyrophosphate, potassium polyphosphates, 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 and others.

The deicer compositions of this invention are useful in the melting of ice and snow on driveways, walkways, streets, airport runways, bus and truck loading areas, etc., where most of the equipment is constructed of metals including cadmium, cadmium alloys and cadmium plated steels.

The deicer compositions of the present invention embody those of the said copending U.S. patent application but in addition include certain proportions of certain compounds which have been found to prevent corrosion of surfaces composed of cadmium, cadmium plated steel and cadmium alloys such as cadmium alloy with lead, zinc, tin, etc. Cadmium plated steel usually gives the greatest corrosion because it is actually an electrolytic couple where cadmium is the anode and tends to dissolve.

The compounds which inhibit corrosion of surfaces composed of cadmium, cadmium plated metals and cadmium alloys when said surfaces are in contact with the deicer include ammonium and alkali metal sulfides, sulfur containing compounds which produce sulfide ions by decomposition or by reaction with cadmium metal, and other salts and compounds containing sulfur in the anion wherein sulfur is below its maximum oxidation state, and alkali metal carbonates and bicarbonates. Specific examples of the corrosion inhibitors of this invention include ammonium sulfide, sodium sulfide, potassium sulfide, sodium dithionate, potassium sulfite, sodium bisulfite, ammonium bicarbonate, ammonium carbonate, potassium bicarbonate, potassium carbonate, sodium bicarbonate, sodium carbonate, thiourea, thioacetamide, dithiobiuret, and the like.

It is preferred that the deicer of the present invention contain from 0.001 to about 10 parts by weight and most preferred 0.01 to about 5 parts by weight of at least one of the aforementioned cadmium corrosion inhibitors per

2

100 parts by weight of combined urea and ammonium nitrate.

The deicer compositions of the present invention containing ammonium or alkali metal carbonates or bicarbonates do not contribute to the breakdown of concrete in roads, bridges, curbs, etc., and moreover, these inhibitors also serve as fire extinguishers or retardants in the deicer compositions. The carbonates are exceptionally good on concrete and actually reduce greatly the attack normally found with nitrate solutions.

The deicer composition embodied herein may be prepared in any convenient manner provided an intimate mixture of the urea and ammonium nitrate components is made. The components may be dry mixed in a pebble or ball mill, for instance, until an intimately mixed powder results. When the urea and ammonium nitrate are fused, cooled and granulated or when the urea-ammonium nitrate mixture in water solution is spray dried or just dried and ground, it is preferred that the cadmium corrosion inhibitor be added to the dry solid urea-ammonium nitrate mixture thus avoiding any chemical reaction which might occur between the inhibitor and the urea or ammonium nitrate components either in the molten state or in warm solution. In other words, any method which produces an intimate mixture of solid urea, ammonium nitrate and one or more of the cadmium corrosion inhibitors may be used.

The following examples will further illustrate our invention.

Example I

In each case a plate of 1020 carbon steel having the dimensions of 2" x 1" which was cadmium plated (electrolytically) to a depth of 5 mils as defined by Class I cadmium plate for military specification was placed in 25 cc. of a 10% by weight solution of deicer in water. The dry deicer was made up of a fused particulate mixture of 73 parts by weight of ammonium nitrate, 26 parts by weight of urea and 0.95 part of a sodium phosphate. 0.5 part by weight of the corrosion inhibitor to be tested was added in finely divided solid form to this deicer and was intimately mixed therewith. The corrosion rate in each case was determined by measuring weight loss of the plate after 24 hours in the deicer solution. The results are given in the following table:

Material tested as corrosion inhibitor:	Weight loss in grams after 24 hours
Non (control) -----	¹ 0.1405
Anthranilic acid -----	¹ 0.1335
Ammonium oxalate -----	¹ 0.1425
8-hydroxy quinoline -----	¹ 0.1378
Mercaptobenzothiazole -----	¹ 0.1380
Sodium arsenate -----	0.0263
Ammonium carbonate -----	0.0009
Ammonium thiocyanate -----	0.0982
Lead nitrate -----	¹ 0.1404
Zinc nitrate -----	¹ 0.1330
Aluminum nitrate -----	¹ 0.1349
Ammonium sulfide -----	0.0004
Ammonium bicarbonate -----	0.0082
Potassium cyanide -----	¹ 0.1336
Sodium dithionate -----	0.0092
Potassium bicarbonate -----	0.0052
Sodium bisulfite -----	0.0063
Sodium sulfide -----	0.0003
Ammonium persulfate -----	¹ 0.1349
Ammonium fluoride -----	¹ 0.1336
Sodium bicarbonate -----	0.0045
Thiourea -----	0.0672

¹ Cadmium layer was completely removed.

The deicing temperature for a deicer of any of the foregoing compositions was determined by adding 100 g. of the deicer to 200 g. of crushed ice. The resulting mixture was then stirred and the deicing temperature attained was found to be -15° F. The deicing temperature is the lowest temperature observed while the above mixture of ice, water and deicer mixture was being stirred.

Deicing temperatures ranging from about 0° F. to about -15° F. were obtained when compositions containing from 10 to 45% by weight of urea, 90 to 55% by weight of ammonium nitrate and from 0.01 to about 5 parts by weight of one or more of the foregoing cadmium corrosion inhibitors per 100 parts by weight of combined urea-ammonium nitrate were used.

Example II

Example I was repeated using a 10% solution of deicer in water. The deicer was made up of 74 parts by weight of ammonium nitrate, 26 parts by weight of urea and the indicated parts by weight of sodium bicarbonate. The weight loss of cadmium from a cadmium coated steel plate was determined after the plates had been immersed for 24 hours in the deicer solution.

Parts by wt. of sodium bicarbonate per 100 parts of deicer:	weight loss in grams after 24 hrs.
0.5 -----	0.0000
1.0 -----	0.0000

Example III

A concrete slab which has been weathered for six months was cut into 2" x 2" x 2½" pieces. This provided specimens with four freshly cut sides and two cured sides. These specimens were totally immersed and saturated in a 4% aqueous solution of deicer composed of 74 parts by weight of ammonium nitrate and 26 parts by weight of urea as the control and another deicer solution containing in addition to the deicer a small amount of ammonium carbonate expressed as parts by weight per 100 parts by weight of combined ammonium nitrate-urea. Each of the concrete specimens in the test solutions was then subjected to nine freeze-thaw cycles (-40° to +78° F.) over a period of 21 days. The weight loss of the specimen was then determined.

Deicer:	Percent weight loss
Ammonium nitrate-urea -----	6.5
Ammonium nitrate-urea plus 0.04 part by weight of ammonium carbonate -----	1.5
Ammonium nitrate-urea plus 0.4 part by weight of ammonium carbonate -----	1.5

We claim:

1. A deicer composition substantially free of chloride ions comprising an intimate mixture of from 10 to 45% by weight of urea, from 90 to 55% by weight of ammonium nitrate and from 0.001 to about 10 parts by weight

per 100 parts by weight of combined urea and ammonium nitrate of a corrosion inhibitor for surfaces containing cadmium selected from the group consisting of ammonium and alkali metal sulfides, sodium dithionate, potassium sulfite, sodium bisulfite, thiourea, thioacetamide, dithiobiuret, alkali metal and ammonium carbonates and alkali metal and ammonium bicarbonates.

2. A solid deicer composition substantially free of chloride ions comprising an intimate mixture of from 22 to 29% by weight of urea, from 78 to 71% by weight of ammonium nitrate and from 0.01 to about 5 parts by weight per 100 parts by weight of combined urea and ammonium nitrate of a corrosion inhibitor for surface containing cadmium selected from the group consisting of ammonium and alkali metal sulfides, sodium dithionate, potassium sulfite, sodium bisulfite, thiourea, thioacetamide, dithiobiuret, alkali metal and ammonium carbonates and alkali metal and ammonium bicarbonates.

3. The deicer composition of claim 2 wherein the corrosion inhibitor is sodium bicarbonate.

4. The deicer composition of claim 2 wherein the corrosion inhibitor is potassium bicarbonate.

5. The deicer composition of claim 2 wherein the corrosion inhibitor is sodium sulfide.

6. The deicer composition of claim 2 wherein the corrosion inhibitor is thiourea.

7. The deicer composition of claim 2 wherein the corrosion inhibitor is ammonium carbonate.

8. The method for melting ice comprising adding to ice a mixture comprising an intimate mixture of from 10 to 45% by weight of urea, from 90 to 55% by weight of ammonium nitrate and from 0.001 to about 10 parts by weight per 100 parts by weight of combined urea and ammonium nitrate of a corrosion inhibitor for surfaces containing cadmium selected from the group consisting of ammonium and alkali metal sulfides, sodium dithionate, potassium sulfite, sodium bisulfite, thiourea, thioacetamide, dithiobiuret, alkali metal and ammonium carbonates and alkali metal and ammonium bicarbonates.

References Cited by the Examiner

UNITED STATES PATENTS

2,474,603	6/1949	Vites et al. -----	252—8.55
2,980,620	4/1961	Hatch -----	252—70
3,185,648	10/1964	Standish et al. -----	252—70

FOREIGN PATENTS

Corrosion, vol. 11, #4, April 1955, pp. 65-67, Chemical Engineering, December 1964, 1954, pp. 230 and 232,

SAMUEL H. BLECH, Primary Examiner.

JULIUS GREENWALD, ALBERT T. MEYERS,
Examiners.

J. D. WELSH, Assistant Examiner.