



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

|  |           |  |
|--|-----------|--|
| <b>(51) International Patent Classification<sup>4</sup> :</b><br><br><b>C23F 11/08</b>   | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 90/04046</b><br><br><b>(43) International Publication Date:</b> 19 April 1990 (19.04.90) |
| <b>(21) International Application Number:</b> PCT/US88/03557<br><b>(22) International Filing Date:</b> 12 October 1988 (12.10.88)<br><br><b>(71)(72) Applicant and Inventor:</b> MURRAY, W., Bruce [US/US]; 28 Willow Grove, Irvine, CA 92714 (US).<br><br><b>(74) Agent:</b> STRAUSS, Robert, E.; Plante, Strauss & Vanderburgh, 1020 N. Broadway, Suite 305, Santa Ana, CA 92706 (US).<br><br><b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), NO, SE (European patent), SU, US.   |           | <b>Published</b><br><i>With international search report.</i>   |
| <b>(54) Title:</b> CORROSION INHIBITION OF SODIUM AND CALCIUM CHLORIDE<br><br><b>(57) Abstract</b><br><br><p>There is disclosed a corrosion inhibited sodium and calcium chloride composition preferably in granular form, which is uniformly coated with a minute to minor quantity of an inhibitor comprising chiefly superphosphate and a minor amount of magnesium oxide or hydroxide. There is also disclosed a method for inhibiting corrosion of sodium and calcium chloride which comprises supplying to the metal surface which is exposed to corrosive attack by sodium and calcium chloride, a minute quantity of an inhibitor comprising chiefly superphosphate and a minor amount of magnesium oxide or hydroxide. The magnesium oxide or hydroxide functions to cement the inhibitor as a tenacious coating on the salt granules, and also to enhance the effectiveness of the phosphate corrosion inhibition.</p> |           |  |

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

|    |                              |    |  |    |                          |
|----|------------------------------|----|--|----|--------------------------|
| AT | Austria                      | ES | Spain                                    | MG | Madagascar               |
| AU | Australia                    | FI | Finland                                  | ML | Mali                     |
| BB | Barbados                     | FR | France                                   | MR | Mauritania               |
| BE | Belgium                      | GA | Gabon                                    | MW | Malawi                   |
| BF | Burkina Fasso                | GB | United Kingdom                           | NL | Netherlands              |
| BG | Bulgaria                     | HU | Hungary                                  | NO | Norway                   |
| BJ | Benin                        | IT | Italy                                    | RO | Romania                  |
| BR | Brazil                       | JP | Japan                                    | SD | Sudan                    |
| CA | Canada                       | KP | Democratic People's Republic<br>of Korea | SE | Sweden                   |
| CF | Central African Republic     | KR | Republic of Korea                        | SN | Senegal                  |
| CG | Congo                        | LI | Liechtenstein                            | SU | Soviet Union             |
| CH | Switzerland                  | LK | Sri Lanka                                | TD | Chad                     |
| CM | Cameroon                     | LU | Luxembourg                               | TG | Togo                     |
| DE | Germany, Federal Republic of | MC | Monaco                                   | US | United States of America |
| DK | Denmark                      |    |  |    |                          |

CORROSION INHIBITION OF SODIUM AND CALCIUM CHLORIDE  
TECHNICAL FIELD OF THE INVENTION

This invention relates to a corrosion inhibitor for sodium and calcium chloride brines, and in particular to a corrosion inhibitor which can be added to granular sodium and calcium chloride.

5

## BACKGROUND ART

Sodium and calcium chloride are widely used industrial chemicals. Perhaps the most commonly observed application of sodium and calcium chlorides is the use of these salts as a road cover in freezing climates, where their high solubility depresses the freezing point of water, thereby melting ice and snow on the surfaces to which it is applied. Other applications of significant volume are the use of calcium chloride as a curing accelerator in concrete, as an additive in drilling muds to control density and clay flocculation, as a drainage aid in paper mills, as a high density liquid used as ballast in tractor tires, and as a desiccant in refrigeration plants.

10

15

A common problem experienced in the various applications of sodium and calcium chloride is that the salts promote corrosive attack on metal surfaces. The corrosiveness of sodium and calcium chloride brines is particularly troublesome in the road cover applications where the brine which is splashed on the undersurfaces of cars can cause rapid corrosion and deterioration of the under panels and rocker panels of a car. Since modern car manufacturing techniques have almost universally adopted unitized construction for weight and manufacturing efficiencies, any corrosive attack of brines on the undersurfaces of automobiles is particularly troublesome as the deterioration of such surfaces by corrosion is often not economically repairable. Furthermore, the salts added to roads adversely affects roadside vegetation and has been observed to have killed roadside trees. These salts are frequently transported as saturated brine solutions in pipeline, and their corrosiveness to steel presents a

25

30

significant problem to such handling.

The use of calcium chloride brines in other applications such as concrete curing accelerators or as additives to drilling muds also creates serious corrosion problems. Most construction concrete is reinforced with steel bars which are embedded in the concrete and the presence of calcium chloride in the concrete accelerates corrosive attack of the reinforcing steel. The calcium chloride in drilling muds causes an accelerated corrosion of well tubing and equipment used in oil drilling applications. The use of calcium chloride as a drainage aid in the paper industry has been limited by the corrosive nature of its solutions.

The problem of accelerated corrosion by sodium and calcium chloride brines is thus a problem which has not, heretofore, been adequately addressed by the prior art. Some solutions to the problem have included the substitution of other salts such as calcium or magnesium acetates or chromates for the road cover applications. These substitutions are not satisfactory because of a prohibitively high cost and because of potentially adverse effects on the environment.

Ideally, any corrosion inhibitor used with sodium and calcium chlorides should be effective at extremely low concentrations to minimize environmental problems and should be colorless to avoid staining or discoloring of metal surfaces, wearing apparel and the like which come in contact with brine solutions of sodium or calcium chloride. The inhibitor should be effective over a very wide range of concentrations, particularly when applied for inhibiting corrosion of brines used in road covers since the brines which are formed by melting of ice and snow in the presence of sodium and calcium chloride can be expected to have an extremely wide range of concentration of the sodium and calcium chloride. The inhibitor should also be soluble over the wide range of concentrations anticipated in its application. Finally, the inhibitor should be compatible with the sodium and calcium

chloride manufacturing process and permit the manufacture of granular and corrosion inhibited sodium and calcium chloride without any significant effect on the granulation process.

BRIEF STATEMENT OF THE INVENTION

5 This invention comprises a composition of sodium and calcium chloride which contains an effective and minor content of a corrosion inhibitor. Preferably the composition comprises a mixture of sodium or calcium chloride and the inhibitor in proportions from one part inhibitor to between about 15 and  
10 100 parts sodium or calcium chloride. The inhibitor is a mixture of superphosphate, and magnesium oxide or magnesium hydroxide, with the magnesium oxide or hydroxide present in an amount from 0.1 to about 0.35 parts, expressed as magnesium oxide per part of superphosphate (typically 18-20%  $P_2O_5$ ).

15 The invention also comprises a method of manufacture of granular sodium or calcium chloride in which an effective and minor content of a slightly soluble corrosion inhibiting mixture of superphosphate and magnesium oxide or magnesium hydroxide is incorporated as a coating on sodium or calcium  
20 chloride granules. In the preferred method, the granules of salt, either sodium or calcium chloride, or mixtures thereof, are moistened with the addition of from 0.5 to 3 weight percent of a saturated brine, i.e., a saturated solution of sodium or calcium chloride. Thereafter the finely subdivided  
25 inhibitor mixture is added in the aforementioned proportions. The inhibitor mixture contains magnesium oxide and granules of superphosphate in the aforementioned proportions. This method is effective to coat the salt granules.

## BEST MODE OF PRACTICE

This invention comprises a corrosion inhibited composition of sodium or calcium chloride, or mixtures thereof, preferably in granular form, which contains a corrosion inhibitor at a weight ratio of inhibitor to sodium or calcium chloride from one part per 15 to 100 parts of the sodium or calcium chloride. Preferably, the weight ratio of the inhibitor to the sodium and calcium chloride is one part per 17 to about 75 parts sodium or calcium chloride, and, most preferably, is one part inhibitor per 15-50 parts of sodium or calcium chloride.

The invention can be applied to inhibition of corrosion by sodium and calcium chloride brines, by the direct addition of the inhibitor to those brines, or by the addition of the inhibitor to the dry salts, so that the inhibitor becomes available when the salts are dissolved in water. In an application for the inhibition of corrosion of metal parts of cars, trucks and other vehicles which are contacted by road salt and brine, the inhibitor is preferably applied to the dry salts prior to the application of the salts to the road or street. In typical road and street applications, approximately 400 to 800 pounds of salt, either sodium chloride or calcium chloride or mixtures thereof, are applied per mile of a road or street which is about 20 feet wide. This is usually sufficient to meet most ice and snow conditions, e.g., up to about 0.1 inch of ice or 1 inch of snow at temperatures of about 10° to about 25° F. The salt settles to the pavement and forms brine which prevents bonding of the ice or snow to the pavement. In heavy traffic, the loose snow and ice is melted by frictional heat from traffic, or is removed by snow plows and blowers.

In other applications, such as prevention of corrosion of metal surfaces contacted by concentrated brine solutions, e.g., pipelines in which the brines are transported, the inhibitor of the invention is directly added to the brine at the aforementioned percentage of the dry weight of salt in the brine.

The inhibitor is a mixture of superphosphate and magnesium oxide or hydroxide in weight proportions of 0.1 to 0.35 parts magnesium oxide or hydroxide<sup>1</sup> per part of superphosphate (18-20% P<sub>2</sub>O<sub>5</sub>). As will be explained hereinafter, it is believed that the compositions of the invention form a passivating film which consists of an insoluble sodium and calcium phosphate, most probably an insoluble calcium orthophosphate. The magnesium oxide or hydroxide controls the pH and ensures optimum conditions for the formation of the protective, insoluble calcium phosphate film.

Superphosphate is a source of phosphate that is commonly used in the fertilizer industry. It is acidulated phosphate rock which is prepared by the addition of either sulfuric acid or phosphoric acid to ground phosphate rock. It commonly contains from 18 to 48 weight percent available (water soluble) phosphate, expressed as P<sub>2</sub>O<sub>5</sub>. It has an acid pH value, typically from 2.5 to about 3.5, and contains insoluble calcium sulfate and calcium hydrogen phosphate.

The sodium and calcium chlorides employed in the invention can be obtained from any suitable commercial source. A convenient source of calcium chloride is the brine obtained by the neutralization of hydrochloric acid with limestone. Such brines are available with salt concentrations from about 15 to about 40 weight percent, usually from 25 to about 35 weight percent. The sodium chloride can be commercially produced salt, usually obtained by solar evaporation from salt ponds. These sodium and calcium chloride brines are preferably pre-concentrated to obtain a saturated brine, e.g., about 26 and about 38 weight percent salt content, respectively, to which the inhibitor composition can be added.

When the inhibitor is added to aqueous solutions of the salt, it is added in the aforesaid weight proportions, based on the dry weight of the salt in the solution.

---

<sup>1</sup> As used herein, the proportions and quantities of magnesium oxide or hydroxide are expressed on a MgO basis.

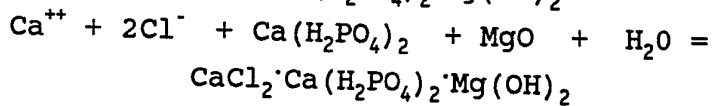
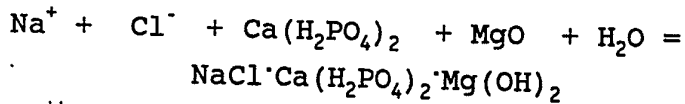
The brines as previously described, can contain a congeneric content of calcium carbonate. Since calcium carbonate can cause subsequent processing problems and inefficient utilization of the phosphate, it is preferred that these  
5 brines also be pretreated, prior to the granulation of the calcium chloride, to reduce, or eliminate entirely, the carbonates. This can be accomplished by acidification of the brine with a strong mineral acid, preferably hydrochloric acid, reducing the pH of the brine to approximately 3.5 which  
10 decomposes the carbonates and liberates carbon dioxide. Thereafter, the brines can be processed to prepare granules of sodium or calcium chloride, e.g., by evaporative concentration and crystallization.

In the preferred method, as applied to granular sodium or  
15 calcium chloride, the granular salts are premoistened by the application of from about 1 to 3 weight percent of a saturated solution of the salt which is being treated. Thereafter, or simultaneously, the corrosion inhibitor is added as a dry mixture to the premoistened sodium or calcium chloride  
20 granules by dry blending the inhibitor with granules of sodium and calcium chloride in conventional mixing equipment, such as double cone mixers, rotating drum mixers, etc. Alternatively, the inhibitor can be added as a dry premixed composition of the superphosphate and magnesium oxide or  
25 hydroxide, in the proportions previously stated, to the salt. In applications where the salt is spread on roads and highways, the inhibitor can be added dry to the mixture of salt and sand which is used in the road spreader. Usually, a mixture of 90 percent sand and 10 percent salt is spread on  
30 roads. The dry inhibitor mixture can be added to the sand and salt mixture prior to application, or can be added to the sand and salt mixture in the road spread as it is being applied to the road.

The inhibitor is added in quantities sufficient to achieve the aforementioned weight proportion of inhibitor to sodium and calcium chloride.



The anhydrous sodium and calcium chloride is commonly produced in granular condition with particle size from about 3/16 to about 1/4 inch. Preferably, the inhibitor is employed as a finely subdivided powder with a particle size passing a screen of 100, preferably of 250, and most preferably of 325 mesh. It has been observed that the magnesium oxide very favorably affects the distribution and stability of the inhibitor throughout the salt granules. The magnesium oxide and hydroxide apparently react with moisture of the granules and binds the inhibitor composition as a very uniform and tenacious coating on the salt granules. It is believed that these reactions proceed as follows:

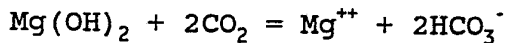
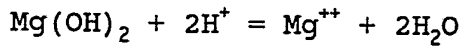


The product of this reaction forms as a very tenacious coating on the surface of the granules and resists separation from the granules during storing and handling of the inhibited product.

If desired, a physical mixture of powdered sodium or calcium chloride and the inhibitor mixture of superphosphate and magnesium oxide or magnesium hydroxide in the aforementioned weight proportions can also be extruded to compact the inhibitor in the anhydrous sodium and calcium chloride particles. In this application, the sodium and calcium chloride and from 1 to 3 weight percent brine, and the aforementioned proportions of the inhibitor are blended in a powdered condition, e.g., as powders having size ranges passing a 10 mesh, preferably passing a 100 mesh U.S. Standard screen, and are then compacted in a dry powder extruder into extrudates having sizes, typically from 3/16 to about 3/8 inch.

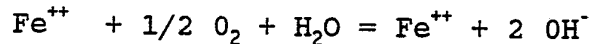
The corrosion inhibition of brines obtained from the sodium and calcium chloride compositions of the invention is achieved by the mechanisms set forth in the following paragraphs:

Dissolution of the inhibitor in the brine essentially liberates calcium dihydrogen phosphate and magnesium hydroxide. The magnesium hydroxide reacts with the free acid in the brine and neutralizes (buffers) its free carbon dioxide content up to 8.3:

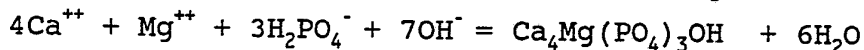


Thus, the inhibitor importantly furnishes the cations  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  and the anion  $\text{H}_2\text{PO}_4^-$ .

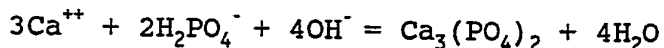
The corrosion of a metal surface such as iron with an aerated brine solution typically proceeds in accordance with the following reaction:



As apparent from the preceding equation, the corrosive attack results in solution of the metal, liberating ferrous ions and forming hydroxyl ions. Typically, the pH of the brine surrounding the cathodic area of the metal surface (where the hydroxyl ions are produced) rises significantly, from neutrality to a value of approximately 9.5. This rise in the pH, in the presence of an excess quantity of calcium, magnesium and dihydrogen phosphate ions furnished by the inhibitor, results in one of the following reactions:



or



The resultant orthophosphate precipitate is very insoluble and forms a passivating film over the cathodic surface of the metal (iron), isolating it from further corrosive attack since it prevents oxygen reduction. The reaction could be quite complex and other insoluble phosphate complexes could also be present. The precipitation of the insoluble phosphate film is controlled by the solubility constant of the above reactions. At an alkaline pH, and in the presence of an excess quantity of calcium cations, even a trace of orthophosphate is converted to the insoluble phosphate film.

The protective films are apparent from their colors, e.g., the film formed by the calcium magnesium phosphate is a blue-yellow film which forms on steel immersed in the inhibited sodium chloride brines. The tricalcium phosphate film appears as a thin grey precipitate on steel immersed in inhibited calcium chloride brines. In either case, corrosion is effectively inhibited.

The following experiments describe the corrosion inhibition which is achieved with the sodium and calcium chloride and soluble phosphate solutions of the invention.

#### Example 1

In this experiment, precorroded, mild steel coupons, one inch by three inches, 1/16 inch thick were cleaned, dried and weighed, and each of the coupons were placed in a beaker, partially filled with an aqueous solution of the salt. The coupons were rotated in the aqueous solutions at 20 rpm. throughout the test.

The salts were used at a concentration of 10 grams per liter, with and without the inhibitor. The inhibitor, when present, was at a concentration of 0.48 grams per liter, and comprised a mixture of one part magnesium oxide per four parts (by weight) of superphosphate (18-20%  $P_2O_5$ ). The coupons were removed, dried and weighed after 1, 2 and 4 days immersion in the test solutions, and the results which were obtained for sodium and calcium chloride salt solutions were as follows:

TABLE 1  
Weight Loss Rate (MDD)\*

| <u>Days Of Exposure</u>          | <u>One Day</u> | <u>Two Days</u> | <u>Four Days</u> |
|----------------------------------|----------------|-----------------|------------------|
| 1. NaCl (control)                | -41.3          | -35.5           | -31.3            |
| 2. NaCl + inhibitor              | 0.0            | + 0.9           | + 0.2            |
| 3. CaCl <sub>2</sub> (control)   | -42.2          | -37.6           | -33.4            |
| 4. CaCl <sub>2</sub> + inhibitor | +1.8           | +2.5            | +1.5             |

\* Values reported as milligrams loss per square decimeter per day

The preceding data show evidence of a very high degree of corrosion inhibition in that the very aggressive corrosion rates of the sodium chloride and calcium chloride were effectively eliminated and the coupons were entirely passive to the solutions.

In a similar test, conducted at solution concentrations of 100 grams per liter with only twice the concentration of the inhibitor (0.96 grams/liter), the coupons exhibited no weight loss after one day of exposure.

Similar results were obtained when aluminum test coupons, magnesium test coupons and zinc test coupons were substituted for the mild steel coupons in the reported experiment.

#### Example 2

In this experiment, varied concentrations of magnesium oxide were included with superphosphate as the inhibitor for sodium chloride solutions. The same general procedure used in Example 1 was also used in this experiment. The sodium chloride brine had a salt concentration of 30 grams and 0.5 grams superphosphate per liter. The magnesium oxide was used in increasing increments of concentration in five test solutions. The pH values, and the corrosion results are reported in the following table:

TABLE 2

|                         |         |         |         |         |         |
|-------------------------|---------|---------|---------|---------|---------|
| MgO <sub>2</sub> (gms.) | 0       | 0.05    | 0.10    | 0.25    | 0.50    |
| pH*                     | 3.76    | 5.74    | 6.20    | 7.27    | 8.10    |
| Loss**                  | -0.0009 | +0.0007 | +0.0015 | +0.0019 | +0.0017 |

\* (after 15 min)

\*\* Total weight change after 24 hours for test coupons weighing 10.5 to 10.9 grams

The test data show evidence that magnesium oxide functions to enhance the corrosion inhibition of superphosphate, as the weight loss of the coupons responded remarkably to the presence of the magnesium oxide, and the net weight gain of the samples in which magnesium oxide was included evidenced

the formation of a deposit on the steel coupons.

### Example 3

In a similar experiment, the inhibitor mixture of 5 weight parts of superphosphate and 1 weight part of magnesium oxide was used in varied amounts in a brine solution containing 30 grams salt per liter. Cleaned, precorroded mild steel coupons with net weights of 10.5 to 10.9 grams were tested in separate beakers of the brine contained varied concentrations of the inhibitor mixture, and the one-day weight losses were determined for each solution. The following results were obtained:

TABLE 3

|                 |        |        |         |         |         |         |
|-----------------|--------|--------|---------|---------|---------|---------|
| Inhibitor (gms) | 0      | 0.12   | 0.24    | 0.36    | 0.48    | 0.60    |
| Loss*           | -.0061 | -.0035 | +0.0002 | +0.0006 | +0.0011 | +0.0014 |

\* Total weight change after 24 hours for test coupons weighing 10.5 to 10.9 grams

The data evidence a very high degree of effectiveness of the inhibitor, which very rapidly decreased the corrosiveness of the brine solution, until the corrosion was eliminated at an inhibitor concentration of about 0.2 grams per liter.

### Example 4

A large number of steel coupons were immersed in inhibited brine solutions for a period of 24 hours. The coupons were then removed, dried and treated with 0.1 N sulfamic acid to dissolve any film or surface deposits. The resultant solutions were analyzed for calcium, magnesium and phosphate contents, and the results were as follows, for each of the test solutions reported in Example 3:

TABLE 4

|                              |       |      |      |      |      |      |
|------------------------------|-------|------|------|------|------|------|
| Inhibitor (gms)              | 0     | 0.12 | 0.24 | 0.36 | 0.48 | 0.60 |
| Calcium (ppm)                | trace | 3    | 7    | 10   | 13   | 15   |
| Magnesium (ppm)              | 0     | 2    | 2    | 3    | 3    | 4    |
| Phosphate (PO <sub>4</sub> ) | 07    | 74   | 140  | 210  | 280  | 340  |

The data indicate that the deposit on the steel coupons was a phosphate which contained increasingly greater amounts of

calcium and magnesium, as the inhibitor concentration increased. The deposit is also readily visible, as it appears as a blue-yellow uniform coating on steel coupons after one day immersion in the inhibited sodium chloride brines, and as  
5 an uniform grey coating on steel coupons after one day immersion in inhibited calcium chloride brines.

#### Example 5

The ease with which salt granules can be uniformly coated with the inhibitor can be demonstrated in a laboratory  
10 experiment in which 75 grams of calcium chloride granules and 75 grams of sodium chloride granules are placed in separate beakers, and 3.2 grams of a saturated calcium chloride and saturated sodium chloride brine, respectively, are added to  
15 each beaker to premoisten the granules. After briefly stirring the granules, five grams of the dry mixture of 1 part magnesium oxide to 4 parts superphosphate are added. The resultant mixture is agitated by stirring for a brief period, about 2 minutes, and it is observed that the granules in the  
20 beakers acquire a uniform coloration, with the sodium chloride granules appearing slightly off-white, and the calcium chloride granules appearing grey. The inhibitor powder disappears entirely, and all the granules in each beaker acquire a very uniform color and appearance.

The invention has been described with reference to the  
25 illustrated and presently preferred embodiment. It is not intended that the invention be unduly limited by this disclosure of the presently preferred embodiment. Instead, it is intended that the invention be defined, by the reagents, and steps, and their obvious equivalents, set forth in the  
30 following claims:

What is claimed is:

1. A dry granular composition comprising:
  - a. a salt selected from the group consisting of sodium and calcium chloride;
  - b. an inhibitor mixture of magnesium oxide or hydroxide and superphosphate in weight proportions from 0.1 to 0.35 part magnesium oxide or hydroxide per part superphosphate, present in the granular composition in a weight amount of 1 part inhibitor mixture per 15 to 100 parts salt, sufficient to inhibit the corrosion of brines of said salt on metal surfaces.
2. The composition of claim 1 wherein said inhibitor is present in an amount from one part per 17 to about 75 parts of said salt.
3. The composition of claim 1 wherein said inhibitor is present in an amount from one part per 50 parts of said salt.
4. The composition of claim 1 wherein said composition is a homogeneous mixture of granules of calcium chloride uniformly coated with said inhibitor.
5. The composition of claim 1 wherein said composition is a homogeneous mixture of granules of sodium chloride uniformly coated with said inhibitor.
6. The composition of claim 1 which is prepared by the addition of a dry powder mixture of magnesium oxide or hydroxide and superphosphate to moist granules of said salt.

7. The method of inhibiting the corrosion of metal surfaces by brines of salts selected from the group of sodium and calcium chlorides which comprises:  
incorporating in said brines an inhibitor mixture of magnesium  
oxide and superphosphate in weight proportions from 0.1 part  
5 magnesium oxide per part superphosphate, in a weight amount  
of 1 part inhibitor mixture per 100 to 400 parts salt,  
sufficient to inhibit the corrosion of said brines on metal  
surfaces.
8. The method of claim 7 wherein said inhibitor is present in an amount from one part per 175 to about 250 parts of said salt.
9. The method of claim 7 wherein said inhibitor is present in an amount from one part per 200 parts of said salt.
10. The method of claim 7 including the step of dispersing said inhibitor composition in said brines in a sufficient quantity to provide sufficient phosphate at the corrosion sites to form a passivating film on said metal  
5 surface.
11. The method of claim 10 as applied to the prevention of corrosion wherein said metal surfaces are the metal surfaces of vehicles exposed to brines formed from calcium or sodium chloride applied to road surfaces as a  
5 cover.



12. The method of preparing corrosion inhibited salts which comprises adding a dry powder mixture of an inhibitor mixture of magnesium oxide and superphosphate in weight proportions from 0.1 to 0.35 part magnesium oxide or hydroxide per part superphosphate, to a granular salt composition containing from 0.5 to about 3 weight percent water, at a weight amount of 1 part inhibitor mixture per 15 to 100 parts salt, and uniformly mixing the resultant mixture until said inhibitor mixture is dispersed as a uniform coating over said salt granules.

13. The method of claim 12 wherein said inhibitor is added in an amount from one part per 17 to about 100 parts of said salt.

14. The composition of claim 12 wherein said inhibitor is added in an amount from one part per 50 parts of said salt.

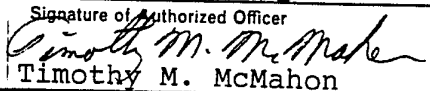
15. The method of claim 12 wherein said salt is calcium chloride.

16. The method of claim 12 wherein said salt is sodium chloride.

17. The method of claim 12 as applied to dry granules of said salt and including the step of moistening the salt by the addition thereto of water sufficient to form from 0.5 to about 3 weight percent of a saturated solution of said salt on the surface of said salt.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 88/03557

|   |  |                                     |
|---|--|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>   |  |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC   |  |                                     |
| IPC (4): C23F 11/08   |  |                                     |
| US. Cl. 422/7 252/387   |  |                                     |
| <b>II. FIELDS SEARCHED</b>  |  |                                     |
| Minimum Documentation Searched <sup>7</sup>   |  |                                     |
| Classification System   | Classification Symbols   |                                     |
| U.S.  | 422/7, 12, 13, 18, 252/387, 389.2, 397, 400.2  |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>   |  |                                     |
|   |  |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>9</sup>  |  |                                     |
| Category <sup>*</sup>   | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup> | Relevant to Claim No. <sup>13</sup> |
| A   | US, A, 3,598,858 (RALSTON) 29 June, 1971.<br>See entire document.  |                                     |
| A   | US, A, 3,542,686 (MILLER) 24 November 1970.<br>See entire document.  |                                     |
| A   | US, A, 3,432,428 (WIRTH et al.) 11 March 1969. See entire document.  |                                     |
| A   | US, A, 3,215,637 (CLERBOIS) 02 November 1965. See entire document.   |                                     |
| <p><sup>*</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&amp;" document member of the same patent family</p> |  |                                     |
| <b>IV. CERTIFICATION</b>  |  |                                     |
| Date of the Actual Completion of the International Search   | Date of Mailing of this International Search Report  |                                     |
| 10 July 1989  | 31 JUL 1989  |                                     |
| International Searching Authority   | Signature of Authorized Officer  |                                     |
| ISA/US  | <br>Timothy M. McMahon     |                                     |