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METHOD OF PROTECTING METAL
STRUCTURES

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This invention relates to the protection of metal structures, such as bridges, trestles, railway tracks, and the like, from corrosion.

The invention is particularly concerned with the elimination of the corrosive action upon steel structures due to brine drippings and the like from railway refrigerator cars. The corrosion of the steel undercarriages of cars, bridges and similar structures at a relatively rapid rate, due to the action of brine drippings, has long presented a serious problem to the railroads. It has been necessary to repair and replace steel structures, subjected to this corrosive action, at frequent intervals and at consequent great expense, or, alternatively, attempts have been made to protect these structures by frequent applications of suitable coatings of paint or the like, at considerable expense.

In accordance with the present invention, however, the corrosive action of brine drippings is effectively offset by simply counter-acting or inhibiting the activity of the salts deposited by the drippings, wherever and whenever they happen to fall. The invention, likewise, contemplates the application of a protective coating, capable of resisting the action of brine drippings and the like, in the course of use of ordinary iced refrigerator cars so that bridge structures and the like may be protected, in this way, not only against the ordinary ice drip but against the action of subsequent brine drippings and without the expense of painting the entire structure.

It has been recognized that various chromium salts, such as sodium chromate, and various permanganates and silicates are useful as inhibitors of corrosion. These substances added in small quantities to a circulatory brine system, for example, may effectively prevent the corrosive action of the brine. However, the corrosive action of brine drippings cannot, in a commercially practicable and effective manner, be inhibited or offset by the addition of sodium chromate, for example, to the brine mixture. This is due to the relatively high solubility of sodium chromate. The quantity of this which is sufficient as an inhibitor in a closed, circulatory system and which, from the standpoint of commercial practicability, could not be greatly exceeded in a brine dripping system, is only a small fraction of that required to provide a saturated solution. On the other hand, the brine itself is a substantially saturated solution of salt, i. e., sodium chloride, calcium chloride, magnesium chloride, or mixtures of two or more of these. Accordingly, when brine drippings are deposited on a steel structure and exposed to

the air, evaporation of the water, which will quickly set in, will cause salt to be deposited. Now if sodium chromate is present in the amount indicated in such a brine, it will remain in solution until substantially all of the water has evaporated and it will therefore not be deposited but will be carried off in the brine which drips away from the structure. Accordingly, the salt deposited as the result of the initial evaporation of the water will be without the protecting influence of a corresponding deposit of chromate.

Now, a feature of applicant's invention is in the employment of a corrosion inhibitor of a type which when used in commercially practicable quantities and such as required for the desired effect, will create a substantially saturated solution of the inhibitor. It will be understood that if a brine mixture, in the form of a substantially saturated salt solution and a substantially saturated solution of an appropriate inhibitor is allowed to drip upon an open surface, the tendency to deposit the corrosive salt will be no greater than the tendency to deposit the corrosion inhibitor and accordingly the corrosive action of the salt will be offset. Moreover, if the brine solution is not quite saturated, insofar as the corrosive salt is concerned but is thoroughly saturated insofar as the corrosion inhibitor is concerned, there will be a tendency to first deposit the inhibitor and subsequently deposit the salt so that all danger of corrosive action is avoided.

I have discovered that strontium chromate satisfies excellently the requirements of an inhibitor of the type specified. Its solubility in a saturated, common salt solution at the usual temperature of the brine drippings is approximately .2 of 1%. This quantity of strontium chromate is ample, and, in fact, just about right, in a saturated brine solution to offset the corrosive action of the brine. It will be apparent, therefore, that a brine solution which is substantially saturated with respect to the corrosive salt and is also substantially saturated with strontium chromate will, upon the evaporation of the liquid from the brine drippings on a steel structure, simultaneously deposit the corrosion inhibitor along with the corrosive salt so that the effect of the latter will be effectively offset. If the brine mixture is not a fully saturated salt solution, a correspondingly smaller amount of strontium chromate may be used, although it is preferable, if possible, to have the solution more nearly saturated with respect to the inhibitor than with respect to the corrosive salt.

In lieu of strontium chromate, calcium chromate may be employed. This has a somewhat higher solubility than the strontium chromate but due to its greater availability, a somewhat larger quantity may be added to the brine solution without rendering the mixture prohibitively expensive for railway car refrigeration purposes. Accordingly, a satisfactory brine mixture, which will be free from corrosive action upon railway bridge structures, and the like, may be produced by the addition to a substantially saturated sodium or calcium chloride brine solution of sufficient calcium chromate to form a substantially saturated solution of the chromate. Other chromates may undoubtedly be employed in lieu of the strontium or calcium chromate or in admixture with one, or both, of these chromates so long as the solution will be substantially saturated by a relatively small quantity of the chromate or chromates, say, not exceeding about a 4% solution, and so long as the chromates are not prohibitively expensive. Certain forms of zinc chromate, for example, may be found to have satisfactory solubility and other characteristics, although in some forms zinc chromate is too highly soluble to be usable for the purposes of this invention. A form having the formula $K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$, commonly known as zinc yellow, is of a satisfactory character.

The invention may be practiced in a variety of different ways. If desired, sufficient strontium chromate or calcium chromate or a mixture of these, or any other suitable corrosion inhibitor of the type desired, may be added to the refrigerating mixture in a refrigerator car to provide a substantially saturated solution of the inhibitor. This will insure the presence of sufficient of the inhibitor in the brine drippings to accomplish the desired effect. If this method is employed, the appropriate amount of the inhibitor must be added each time that the refrigerating mixture is replenished.

In lieu of adding directly an inhibitor of the type specified, several reagents, capable of producing this inhibitor in the brine solution, may be added in appropriate quantities. Thus, there may be added a soluble chromate, such as sodium chromate, and strontium or calcium chloride in sufficient quantity to react with the chromate to produce the desired amount of strontium or calcium chromate.

It is also possible to prepare a dry mixture of the brine-producing salt, such as sodium chloride, calcium chloride, magnesium chloride, or the like, or a mixture of these, and an appropriate quantity of the inhibitor, such as strontium or calcium chromate, or there may be added to the dry brine salt or mixture of salts a mixture of a soluble chromate, such as sodium chromate and strontium or calcium chloride in the dry state. The quantity of the inhibitor added or formed should be in correct proportion to the brine-producing salt so that the resulting brine will be as nearly saturated with the inhibitor as with the salt. This dry mixture, then, of appropriate character, when applied to the ice in the compartment of a refrigerating car will produce brine having in solution an appropriate inhibitor substantially to the saturation point or to as high a degree of saturation as the brine-producing salt itself. The brine drippings, therefore, resulting from this mixture will carry protection against their normal corrosive action.

A still further method of practicing the invention is to simply provide a pot or receptacle or other container having a quantity of the selected inhibitor beneath the brine dripping outlet or outlets of the refrigerator compartment. The brine itself will then contain no inhibitor but in passing through the inhibitor in the pot, will absorb a sufficient quantity to produce a substantially saturated solution of the inhibitor in the drippings. The pot, in this case, should be so constructed that the drippings will be forced to pass through a sufficient quantity of the inhibitor to insure picking up enough to substantially saturate the brine solution and the latter may then pass out through a suitable orifice in the bottom or side or other portion of the pot and be discharged upon the railway tracks or bridge structure without danger of corrosive action. Suitable means may be provided for preventing solid portions of the inhibitor from being washed out of the pot.

In lieu of providing a separate pot beneath the brine compartment means may be employed within the compartment for retaining the refrigerating mixture above the bottom of the compartment. With this arrangement the brine produced upon the melting of the ice may descend toward the bottom of the compartment and there or in transit come in contact with and dissolve a suitable quantity of the inhibitor.

As previously indicated, the invention may be used to advantage in connection with ordinary ice meltings not containing brine. The drippings in this case, after passing through a pot of the type mentioned, for example, and containing a substantially saturated solution of the inhibitor, will deposit a coating upon the steel structure of bridges and the like and will offset the corrosive action not only of the ice water but also of brine drippings later deposited on the same portions from refrigerator cars.

By way of demonstrating the corrosion inhibiting efficacy of strontium and calcium chromate, the results of certain laboratory tests may be cited. In these tests samples of structural steel in the form of angle irons were cleaned and placed in an intermittent dipping apparatus so that they were alternately suspended for fifteen minutes in a brine solution and then for fifteen minutes in air above the brine solution over a period of five days. This treatment is equivalent to relatively severe, actual working conditions over a considerably longer period. The tests were made with respect to brine solutions of different characters. In one test the brine was simply a solution of sodium chloride containing 120 grams of the salt to 280 c. c. of water. In the second test a solution of 120 grams of sodium chloride, 240 gram of calcium chromate and 280 c. c. of water was used. The samples of structural steel were weighed prior and subsequent to the five-day treatment periods and the loss of weight, due to corrosion, noted. The samples from the first test, involving no inhibitor, showed a loss of 0.33%. Samples from the second test showed a loss of 0.06%. These tests, therefore, demonstrated the corrosion inhibiting value of the small quantity of calcium chromate as an inhibitor.

In a further test conducted in the same manner, a brine solution was used containing 159 grams of sodium chloride, .68 gram of calcium chromate and 140 c. c. of water. As the result of intermittent dipping of samples of structural steel in this solution over a period of five days, it was found that the samples protected by calcium

chromate showed a loss in weight of only 0.034%.

Still another test was run in the same manner to demonstrate the efficacy of strontium chromate, the brine solution in this case contained 159 grams of sodium chloride, .55 gram of strontium chromate and 440 c. c. of water. The samples of steel subjected to intermittent dipping in this solution showed a loss of weight of 0.054%.

In connection with the foregoing tests and the disclosure of the invention in general, it may be stated that the solubility of calcium chromate ($\text{CaCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) in a saturated sodium chloride brine at 0° C. has been found to be 3.14 grams per 100 c. c. of the brine. Under similar conditions the brine will become saturated with 0.11 gram of strontium chromate per 100 c. c. of the brine. Accordingly, it will be noted that in the foregoing tests the various brine solutions, particularly those containing the calcium chromate, were not saturated from the standpoint of the chromate. Due to the availability of the calcium chromate, however, it will be possible, commercially, to employ a more nearly saturated calcium chromate solution than those involved in the tests. It may be further stated that calcium chromate forms three different types of crystals, known as anhydrous and hemihydrate and mono-hydrate. The anhydrous salt is less soluble than the others and, therefore, will be most desirable from the standpoint of this invention in that a smaller quantity will produce a substantially saturated metastable solution.

While the nature of the invention has been set forth in considerable detail, it will be understood that numerous variations may be made in the procedure as well as in the composition of the brine solution or mixture and the character of the corrosion inhibitor without departing from the principles and scope of the invention. The terms and expressions used herein are to be regarded as terms of description and not of limitation.

What I claim is:

1. A method of preventing corrosion of metal structures from the action of brine drip which comprises adding to the brine before it strikes such structures a sufficient quantity of a chromate, soluble only to the extent of between .1 and 4 per cent, to substantially saturate the brine drip solution.

2. A method of preventing corrosion of metal structures from the action of brine drip which comprises adding to the brine before it strikes such structures a sufficient quantity of at least

one of the group consisting of strontium, zinc and calcium chromates to substantially saturate the brine drip solution.

3. A method of preventing corrosion of metal structures from the action of brine drip which comprises passing the brine drip through a mass comprising a sparingly soluble chromate under conditions causing the brine drip to become substantially saturated with said chromate before being deposited upon the metal structure under evaporating conditions.

4. A method of preventing corrosion of metal structures from the action of brine drip which comprises passing the brine drip through a mass of at least one of the group consisting of strontium, zinc, and calcium chromates under conditions causing the brine drip to become substantially saturated with the chromate before being deposited upon the metal structure under evaporating conditions.

5. A method of protecting a metal structure from corrosion which comprises causing a substantially saturated solution of at least one of the group consisting of strontium, zinc and calcium chromates to be deposited upon said structure in such manner and under such conditions that it may evaporate.

6. A method of protecting a steel railway structure from corrosion which comprises causing the drip from a refrigerating compartment to pass through a sufficient quantity of chromate of at least one of the group consisting of strontium, zinc and calcium chromates and under such conditions as to cause said drip to become saturated with said chromate before permitting said drip to be deposited upon said structure.

7. A method of protecting a steel railway structure from corrosion which comprises causing the drip from a refrigerating compartment to pass through a sufficient quantity of a chromate salt, capable of forming not more than a 4% solution, under such conditions as to cause said drip to become substantially saturated with said agent, before permitting said drip to be deposited on said structure.

8. A method of preventing corrosion of metal structures from the action of brine drip which comprises providing in the brine before it strikes such structures a sufficient quantity of a chromate, soluble only to the extent of between 0.1 to 4 per cent, to substantially saturate the brine drip solution.

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