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CORROSION INHIBITING SALT COMPOSITIONS CONTAINING SODIUM TRIPOLYPHOSPHATE, ALUMINUM SULFATE, AND A SOLUBLE FERROCYANIDE

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ABSTRACT OF THE DISCLOSURE

A crushed rock salt composition for snow and ice control having reduced corrosion characteristics comprising at least about 96.5% of crude crushed rock salt, from about 0.05 to 3% sodium tripolyphosphate, from about 0.05 to 3% of a sulfate selected from the group consisting of zinc and aluminum sulfate and a small amount of a soluble ferrocyanide.

BACKGROUND OF THE INVENTION

This invention relates to corrosion inhibitor compositions and more particularly to compositions which, when admixed with crude crushed rock salt for snow control purposes, will reduce the normally associated enhanced corrosive effect of salt upon metal, and particularly steel of automotive vehicles.

The use of crude crushed rock salt or halite in snow and ice control of streets and highways is an accepted and well established practice. It is also well known that the use of salt to remove snow and ice produces conditions which favor and accelerate corrosion of steel fabricated vehicles such as automobiles, trucks, road maintenance vehicles, buses or the like, which travel on the thus salted highways. The corrosion usually is most severe on the inside of the fenders and on the underside and frames of cars and other vehicles which are subjected to an almost constant spray of salt, salt water or brine, snow, water and perhaps sand and other abrasive debris which is present on the highway surface. The customary undercoating of cars and special paint treatment is useful only to a limited extent since imperfections in the protective coatings either are present naturally or occur due to nicks, scratches and the like from abrasive particles which strike the undersurface during ordinary driving. Such imperfections or lack of protective coating result in areas of potential oxidation of the steel undersurface. The normal oxidation or rusting of steel is apparently enhanced in the presence of salt, as indicated above. The end result of such salt enhanced corrosion is the rapid rusting out of fenders, bodies, rocker panels, bumpers, grills and the like, which effectively reduces the value and useful life of the vehicle or at the least requires costly repaint or repair of the vehicle. Because of this corrosion problem associated with salt treatment of highway snow control, an effort has been made by state, municipal and other government bodies to use a corrosion inhibitor in conjunction with highway salt treatment which will hopefully reduce the corrosion expense but permit the safety benefit of the snow control program. It is especially important to consider the cost aspects of any additive so that maximum protection from corrosion is achieved at a cost which is sufficiently within practical or economic limits.

Therefore, it would be desirable to provide a crude crushed rock salt composition with reduced corrosion properties which is useful for highway snow and ice control. The composition should be low in cost, effective and relatively nontoxic. A further desideratum is the provision of a method of treating a crude crushed rock salt to be used in snow and ice control to reduce the corrosion properties of the salt to vehicles which utilize highways to which it is applied.

SUMMARY OF THE INVENTION

Accordingly, in one broad form, the present invention comprises a crude crushed rock salt composition of reduced corrosion properties comprising from about 94 to about 99.8 percent of crushed rock salt, from about 0.05 to 3 percent of sodium tripolyphosphate, from about .05 to 3 percent of a sulfate selected from the group consisting of zinc and aluminum sulfates and from .005 to about .1 percent of a ferrocyanide. In the most preferred form the rock salt is present in amounts of from about 98.5 to 99.5 percent, the sodium tripolyphosphate from about 0.1 to 1.5 percent, the sulfate from about 0.1 to 1.5 percent, and the ferrocyanide from about 0.005 to .015 percent. The sulfate can be in the form of the anhydrous salt or as the hydrate. The ferrocyanide is a soluble or dispersible ferrocyanide such as sodium, potassium, ammonium, calcium and ferric ammonium ferrocyanide (Prussian blue-A) or ferric ferrocyanide (Prussian blue-B).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples will illustrate various compositions which are employed in the present invention and the test procedure for ascertaining the effectiveness of the aforesaid compositions in retarding or reducing the accelerated corrosion rate of steel due to the presence of salt. This in turn simulates conditions which are encountered by steel vehicles traveling over roads treated with salt for snow control purposes. The first series of tests involve contact of steel panels with brine solutions which contain the anticorrosive salt compositions of this invention. The second series of tests involve a simulated actual running operation for a motor vehicle whereby brine spray from automobile wheels splashes against a series of steel test plates.

TEST SERIES

Test procedure

Cold rolled steel panels 2 inches square were bent into a V-shape to permit insertion into a standard laboratory widemouthed 8 oz. bottle. The panels were polished with fine emery paper, degreased and weighed for testing. The various test compositions were mixed with 200 ml. of a 10% brine solution and placed in the 8 oz. jars containing the 2" x 2" steel specimen. The jars were capped, shaken for about 30 seconds and allowed to stand for 24 hours. At the end of 24 hours the jars and contents were shaken, all but 25 ml. of the brine discarded, and the jar recapped. At 24 hour intervals each jar was uncapped to admit air, recapped and shaken. At the end of the fourth day 25 ml. of distilled water was added to each test jar. At the end of seven days the steel test panel was cleaned by the method given in Corrosion Handbook by Uhlig and weighed. Corrosion results were determined by the following procedure.

The corrosion rate: Given in terms of MDD (milligram loss per square decimeter per day).

Percent effective against corrosion:

Percent effective (total)

$$= \frac{100 \times \left[\begin{pmatrix}\text{wt. loss}\\ \text{from salt}\end{pmatrix} - \begin{pmatrix}\text{wt. loss with}\\ \text{additive}\end{pmatrix}\right]}{\text{Wt. loss from salt}}$$

Percent effective in reducing corrosion due to salt=

$$100 \times \frac{\left[\begin{pmatrix}\text{wt. loss}\\ \text{from salt}\end{pmatrix} - \begin{pmatrix}\text{wt. loss}\\ \text{in } H_2O\end{pmatrix}\right] - \left[\begin{pmatrix}\text{wt. loss}\\ \text{with additive}\end{pmatrix} - \begin{pmatrix}\text{wt. loss}\\ \text{in } H_2O\end{pmatrix}\right]}{(\text{Wt. loss from salt}) - (\text{wt. loss in } H_2O)}$$

TABLE I

Ex.	Salt [3]	STPP, percent [1]	$ZnSO_4$ percent $\cdot 7 H_2O$	Corrosion rate, MDD [2]	Percent effective Total	Salt
A	None	None (distilled water).		10		
B	CC [3]	Blank (salt only).		46		
C	CC	1.0	0.1	36	22	

See footnotes at end of Table VI.

TABLE II

Ex.	Salt [3]	STPP, percent [1]	$ZnSO_4$ percent $\cdot 7 H_2O$	Corrosion rate, MDD [2]	Percent effective Total	Salt
A	CC [4]			48		
B	CC	0.5	0.05	34	29	
C	CC	0.5	0.1	32	33	
D	CC	0.5	0.2	35	27	
E	CC	1.0	0.05	33	31	
F	CC	1.0	0.1	36	25	
G	CC	1.0	0.2	29	40	

See footnotes at end of Table VI.

TABLE III

Ex.	Salt [3]	STPP, percent [1]	$ZnSO_4$ percent $\cdot 7 H_2O$	Corrosion rate, MDD [2]	Percent effective Total	Salt
A	CC [4]			47		
B	CC	0.2		36		
C	CC	1.0		40		
D	CC	0.5	0.005	39		

See footnotes at end of Table VI.

TABLE IV

Ex.	Salt [3]	STPP, percent [1]	$ZnSO_4$ percent $\cdot 7 H_2O$	Corrosion rate, MDD [2]	Percent effective Total	Sal
A	CC	0.1	0.1	28		
B	CC	0.2	0.2	23		
C	CC	0.5	0.5	24		

See footnotes at end of Table VI.

TABLE V

Ex.	Salt [3]	STPP, percent [1]	$ZnSO_4$ percent $\cdot 7 H_2O$	Corrosion rate, MDD [2]	Percent effective Total	Salt
A	CC			40		
B	CC	1.0	1.0	14		
C	CC	0.2	0.2	18		
D	CC	0.2	0.1	18		
E	CC	0.2	0.05	21		
F	CC	0.2	0.02	28		
G	CC	0.1	0.2	16		
H	CC	2.0	2.0	17		

See footnotes at end of Table VI.

TABLE VI

Ex.	Salt [3]	STPP, percent [1]	$ZnSO_4$ percent $\cdot 7 H_2O$	Corrosion rate, MDD [2]	Percent effective Total	Salt
A	CC			40		
B	CC	0.1		34		
C	CC	0.1	0.02	30		
D	CC	0.1	0.05	32		
E	CC	0.1	0.1	27		
F	CC	0.1	0.15	24		
G	CC	0.1	0.2	25		
H	CC	0.2		24		
I	CC	0.2	0.1	21		
J	CC	0.2	0.15	22		
K	CC	0.2	0.2	21		
L	CC	0.2	0.3	20		
M	CC	0.3		28		
N	CC	0.3	0.1	20		
O	CC	0.3	0.2	21		
P	CC	0.3	0.3	21		

[1] STPP=Sodium tripolyphosphate.
[2] MDD=Milligram loss per square decimeter per day.
[3] CC=Northern crude crushed rock salt treated with 75 p.p.m. ferric ferrocyanide, except where otherwise noted.
[4] CC=Pure salt, no ferrocyanide added.

TABLE VII

Ex.	Salt [1]	STPP, percent	$Al_2(SO_4)_3 \cdot 18 H_2O$	Corrosion rate, MDD	Percent effective Total	Salt
A	CC			40		
B	CC	0.5		29	28	43
C	CC	0.4	0.1	23	43	57
D	CC	0.3	0.2	11	72	97
E	CC	0.3	[2] 0.1	20	50	67
F	CC	0.45	0.05	28	30	40
G	CC	0.44	[3] 0.05	19	52	70
H	CC [4]			67		
I	CC [4]	1.0		38	43	
J	CC [4]	0.9	0.1	36	46	
K	CC [4]	0.8	0.2	40	40	
L	CC [4]	0.7	0.3	41	39	
M	CC [4]	0.6	0.4	37	45	
N	CC [4]	0.5	0.5	29	54	

[1] Crushed rock salt with 100 p.p.m. or 0.01% ferric ferrocyanide.
[2] 0.1% $ZnSO_4 \cdot 7H_2O$ added.
[3] 0.05% $ZnSO_4 \cdot H_2O$ added.
[4] Pure salt, no ferrocyanide added.

TABLE VIII

Ex.	Salt	STPP, percent	Additive(s) in percent	Corrosion rate, MDD	Percent effective Total	Salt corrosion
A	CC [1]			39		
B	CC [1]		0.01% ferric ferrocyanide	39	0	
C	CC [1]	0.5		26	36	
D	CC [1]	0.3	0.2% $Al_2(SO_4)_3 \cdot 18H_2O$	19.5	50	
E	CC [1]	0.3	0.2% $ZnSO_4 \cdot 8H_2O$	23.0	41	
F	CC [1]	0.3	0.1% $Al_2(SO_4)_3 \cdot 18H_2O$ +0.1% $ZnSO_4 \cdot 7H_2O$.	22.8	42	
G	CC [1]	0.3	0.01% $Fe(NH_4)Fe(CN)_6$ +0.2% $Al_2(SO_4)_3 \cdot 14H_2O$.	8	79	100
H	CC [2]	0.3	0.2% $Al_2(SO_4)_3 \cdot 18H_2O$	15.5	60	81
I	CC [2]	0.3	0.2% $ZnSO_4 \cdot 7H_2O$	23.5	40	
J	CC [2]	0.3	0.1% $Al_2(SO_4)_3 \cdot 18H_2O$ +0.1% $ZnSO_4 \cdot 7H_2O$.	20.5	47	
K	CC [2]	0.3	0.2% $Al_2(SO_4)_3 \cdot 18H_2O$	10	74	100
L	CC [2]	0.3	0.17% $Al_2(SO_4)_3 \cdot 14H_2O$	10	74	100
M	CC [2]	0.3	0.1% $Al_2(SO_4)_3 \cdot 14H_2O$	24	38	
N	CC [2]	0.3	0.15% $Al_2(SO_4)_3 \cdot 14H_2O$	22	44	
O	CC [2]	0.3	0.17% $Al_2(SO_4)_3 \cdot 14H_2O$	10	74	100
P	CC [2]	0.3	0.2% $Al_2(SO_4)_3 \cdot 14H_2O$	15	61	

[1] Northern crude crushed rock salt.
[2] Northern crude crushed rock salt treated with 0.01% ferric ferrocyanide.

Additional tests were performed under conditions which closely approximate winter road field testing after application of salt for snow control. The test involved the placing of 2 x 4 inch coupons of S.A.E. No. 1010 cold rolled steel (20 gauge) in a plexiglass rack inclined at a 45° angle and spaced about ¼ inch apart. The rack of coupons was suspended inside and under a fender housing of a car which was raised to elevate the same off the ground. The test solution was placed in pans under each wheel which was rotated with a rubber 1½ inch diameter ring placed in the shaft of a 1750 r.p.m. motor. The rubber ring was applied to the metal rim of each wheel for driving the wheel at about 150 r.p.m. The spray from the tires was concentrated at the center of the tread and the coupon rack arranged so that the radial or peripheral stream from the tire struck the leading edges of the coupons arranged therein. Splash guards conserved the solutions dripping from the fender underside, tire and rack. The coupons were cleaned and weighed before the test and after rust was removed by immersion in 10% NaOH with 10% zinc dust. Loss in weight in milligrams per square decimeter was reported as the corrision rate.

The following results were obtained, using the following formula dissolved in water to make a 5 or 10% salt solution:

Formula:	Percent
Northern Crude Crushed Rock Salt	99.04
Sodium tripolyphosphate	.60
Aluminum Sulfate·$14H_2O$	.34
Ferric ferrocyanide	.01

The control was alternate 5 and 10% salt solutions prepared from Northern Crude Crushed Rock Salt, which had been treated with 0.01% Prussian Blue.

The wheels were rotated for periods of 30 minutes four times daily for twelve days in alternate 5 and 10% salt solutions. The following results were obtained:

	Corrosion in Mg./square decimeter	Percent Effective (Total)
Control	973	
Test Composition	232	76

While several particular embodiments of this invention are shown above, it will be understood, of course, that the invention is not to be limited thereto, since many modifications may be made, and it is contemplated, therefore, by the appended claims, to cover any such modifications as fall within the true spirit and scope of this invention.

I claim:

1. A crushed rock salt composition for snow and ice control having reduced corrosion properties consisting essentially of crude rock salt in an amount of at least 96.5%, from about 0.05 to 3% sodium tripolyphosphate, from about 0.05 to 3% of aluminum sulfate and from .005 to .1% of soluble ferrocyanide.

2. A composition according to claim 1 wherein the sodium tripolyphosphate is present in an amount of from 0.1 to 1.5%.

3. A composition according to claim 1 wherein the sulfate is present in an amount of from 0.1 to 1.5%.

4. A composition according to claim 1 wherein the ferrocyanide is present in an amount of from 0.005 to 0.015%.

5. A composition according to claim 1 wherein the rock salt constitutes at least 98.5% of the composition.

6. A composition according to claim 1 wherein the components are rock salt, sodium tripolyphosphate, aluminum sulfate and ferric ferrocyanide.

7. A crushed rock salt composition for snow and ice control having reduced corrosion properties consisting essentially of about 99% crushed rock salt, about ⅔ sodium tripolyphosphate, about ⅓% $AL_2(SO_4)_3 \cdot 14H_2O$ and about 0.0075% ferric ferrocyanide.

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