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3,096,169

AMMONIACAL AMMONIUM NITRATE SOLUTION OF REDUCED CORROSIVE TENDENCIES

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No Drawing. Filed Feb. 1, 1960, Ser. No. 5,637
16 Claims. (Cl. 71-59)

The present invention relates to the corrosion of ferrous metals. More specifically, the present invention relates to a novel composition having reduced corrosion tendencies toward ferrous metal surfaces.

There is a well recognized corrosion problem in industries concerned with the manufacture, storage, transportation and handling of ammoniacal-ammonium nitrate solutions. In the handling of such solutions it is often necessary to transport and store them in ferrous containers such as drums, tanks and pipelines. In view of the corrosive nature of ammoniacal-ammonium nitrate solutions against ferrous metals, many manufacturers now use storage and transportation facilities constructed of aluminum. Aluminum is used because its oxide film renders the metal inert to attack by the ammoniacal solution. This remedy, however, is a costly one. Corrosion inhibitors of one type or another also have been suggested and attempted with varying degrees of limited success.

One effective method for remedying the problem has been to deactivate the ferrous metal, for instance, by "passivating" the metal surface. "Passivity" is a property exhibited by some metals whereby they become inactive toward certain chemical reagents. When a piece of reactive metal is made passive, its position in the electrochemical series is changed so that it is cathodic to a piece of the same metal which is in the active condition. "Passivation" of ferrous metals employed in a corrosive environment, is generally accomplished by contacting the metal with an oxidizing agent. The oxidizing agent reacts with the ferrous metal forming a thin adherent oxide film on its surface. This protective film shields the ferrous metal from its environment and virtually no corrosion occurs.

Passive films produced by contacting ferrous metal with aqueous solutions of oxidizing agents are found to be very fragile and easily destroyed by mechanical damage, chemical attack or electrolytic reduction. Hence, the addition of a supplementary inhibitor has been necessary to provide protection when the passive film is destroyed. We have found, however, that some proprietary inhibitors, i.e. inhibitors containing reduced sulfur, e.g. NH_4SCN , that are effective inhibitors will frequently destroy the passive film.

Moreover, most passivation procedures require a two-step process, i.e. the ferrous metal must be first immersed in an aqueous solution of the oxidizing agent before it can be exposed to the ammoniacal solution. This is done for two reasons, (1) corrosion of the ferrous metal in the ammonia-ammonium nitrate solutions is extremely rapid resulting in the formation of a gelatinous leposit on the metal's surface preventing access of the oxidizing agent to the surface and (2) the oxidizing agent may be destroyed by reaction with ammonia present in the solution forming nitrogen and its oxides.

It has now been discovered that contacting a ferrous metal with ammoniacal ammonium nitrate solutions containing a soluble copper compound, a soluble trivalent arsenic compound and carbonate ions produces a "tough" passive film on the ferrous metal that offers improved corrosion resistance to the metal. It has also been found that ammoniacal ammonium nitrate solutions containing

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the above components, i.e. copper, trivalent arsenic, and carbonate ions, produce in situ a passive film on ferrous metal that is highly resistant to mechanical damage and electrolytic reduction, as well as chemical attack.

The copper compounds in the present invention are the soluble copper compounds as, for instance, the inorganic compounds such as cupric carbonates, hydroxides, sulfates, nitrates, etc. Of the many carbonate ion-producing compounds, the more particularly suitable are the inorganic compounds, for instance, alkali metal and ammonium carbonates. Preferably, the copper and carbonate components of the present invention are provided by a single compound such as basic copper carbonate.

The quantity of the aforementioned components employed in the present invention can vary considerably but are sufficient to give significant protection against corrosion. Generally, the concentration of the copper component is at least about .01 g. per 100 ml. of ammoniacal solution. The maximum amount of the copper compound is limited only by economic feasibility and is generally not greater than about 0.2 g. per 100 ml. of ammoniacal salt solution. The preferred concentration is about .05 to .15 g. per 100 ml. of ammoniacal solution. The amount of carbonate compound employed is usually that sufficient to provide a carbonate ion concentration of at least about .005, generally about .02 to .1 g. per 100 ml. of ammoniacal solution. When basic cupric carbonate is employed, a concentration of about .01 to 0.2 gram/100 ml. of ammoniacal solution, preferably about .05 to .15, is usually sufficient.

The trivalent arsenic component of the present invention can be provided by a solution of any soluble trivalent arsenic compound, preferably a soluble inorganic trivalent arsenic compound. Inorganic trivalent arsenic compounds that can be employed include, for example, arsenic trioxide, an arsenite such as sodium, potassium or ammonium arsenite and sulfides of trivalent arsenic. Since As_2O_3 dissolves slowly when added to solutions such as ammoniacal ammonium nitrate, it is desirable to first dissolve the compound in alkaline solution such as an aqueous solution of sodium hydroxide, sodium carbonate, ammonia, etc. Like the copper compounds, the arsenic compound may vary in amount, but is sufficient to afford the desired corrosion inhibition. Generally, the concentration of trivalent arsenic compound is at least about 0.01 g./100 ml. of ammoniacal solution, usually less than about 0.5 g./100 ml. and preferably about .05 to .25 g./100 ml. It is preferred that the composition of the present invention also contain small effective amounts of alkali metal, e.g. sodium, hydroxide which can be conveniently provided in the composition as aforementioned, by employing an aqueous solution of the sodium hydroxide to dissolve the trivalent arsenic component. The amount of alkali metal hydroxide employed will usually be as stated before for the arsenic compound. In providing the ammoniacal ammonium nitrate solutions with the components of the present invention, we prefer the absence of significant amounts of halogen ions, e.g. Cl^- , which are known to be passive film destroyers.

Ammoniacal ammonium nitrate solutions may vary considerably in composition. Generally representative of such solutions encountered in industry and which give rise to the corrosion problem discussed hereinbefore, are those having approximately about 1 to 80 percent ammonium nitrate, usually at least about 40 percent, preferably about 60 to 70 percent, about 5 to 35 percent free ammonia, preferably about 10 to 35 percent, and the substantial balance being water, for instance, about 10 to 65 percent water. These percentages are by weight.

It has been noted that the corrosion by ammoniacal solutions is intense in the vapor zone, i.e. the portion of the vessel containing the ammoniacal solution which is in

contact with vapors of the solution. Although the combination of components of the present invention provides good corrosion protection to the portion of the vessel in contact with the ammoniacal solution, adequate protection is not always provided the portion in contact with vapor. This problem can be easily remedied by the addition of vapor phase inhibitors such as urea, NH_4NO_2 , etc. We have also found that the addition of NO_2^- -producing compounds such as an alkali metal nitrite to the ammoniacal solution containing the components of the present invention very effectively reduces vapor phase corrosion and this may be due to the formation of a CuNH_4NO_2 complex. The vapor phase inhibitor is generally present in an amount sufficient to provide adequate corrosion protection, and conveniently is about 0.05 to 0.5 g./100 ml. of ammoniacal solution.

The following examples are included to further illustrate the invention.

EXAMPLE I

As aforementioned when a piece of active metal is made passive, its position in the electrochemical series is changed so that it is more cathodic to a piece of the same metal which is in the active condition. Since the formation of passive films produces a change in the electrical

characteristics of a ferrous metal such as steel, i.e. makes the metal more electropositive, the phenomenon can be effectively studied by observing changes in the single electrode potential of the metal. A series of simple electrolytic cells were set up to achieve this end.

A steel rod was first "activated" (i.e. all surface films were removed) by exposure to 15% HCl at 150° F. until hydrogen bubbles were observed. The rod was then washed in deionized water and placed in an electrolytic test cell filled with an ammoniacal solution consisting of 66.8% NH_4NO_3 , 16.6% NH_3 and 16.6% H_2O . The electrolytic test cell was a large mouth 8-ounce glass jar having a salt bridge comprising a glass tube with agar-agar solution saturated with KCl connected to a calomel cell immersed in saturated KCl. The calomel electrode probe and the "activated" rod were connected by leads to a Sheppard potentiometer by which potential measurements were obtained. Similar tests were conducted on the ammonia-ammonium nitrate solution containing small concentrations of various oxidizing agents and combination of oxidizing agents. The trivalent arsenic compounds where employed were in each case first dissolved with an equal weight of sodium hydroxide in dilute aqueous solution. The results are shown in Table I.

Table I

PASSIVATION OF STEEL IN $\text{NH}_3\text{-NH}_4\text{NO}_3$ SOLUTION USING OXIDIZING AGENTS

Test No.	Oxidizing agent	Concentration g./100 ml. $\text{NH}_3\text{-NH}_4\text{NO}_3$ solution	Observed single electrode potential of steel (volts to calomel)	Observations
1	Blank		-0.74	Steel corroded, appearance of a slimy green ppt. on the steel surface.
2	As_2O_3	0.1	-0.73	Slow corrosion.
3	MnO_2	0.1	-0.73	Rapid corrosion.
4	MnO_2	0.1	-0.73	Do.
	plus As_2O_3	0.1		
5	PbO	0.1	-0.74	Do.
6	PbO	0.1	-0.42 to -0.72 (1 hour.)	Do.
	plus As_2O_3	0.1		
7	PbO_2	0.1	-0.46 to -0.73 (11 minutes)	Do.
	plus As_2O_3	0.1		
8	NaNO_2	0.1	-0.76	Do.
9	NaNO_2	0.1	-0.47 to -0.73 (4 minutes)	Do.
	plus As_2O_3	0.1		
10	$\text{Fe}(\text{NO}_3)_3$	0.1	-0.74	Do.
	plus As_2O_3	0.1		
11	KMnO_4	0.1	-0.76	Rapid corrosion, brown ppt. (due to formation of MnO_2)
12	KIO_3 ; KClO_3	0.1; 0.1	-0.78; -0.77	Rapid corrosion, not too soluble.
13	P_2O_5	0.1	-0.78	Slow corrosion.
	plus As_2O_3	0.1		
14	$(\text{NH}_4)_2\text{CO}_3$	0.2	-0.76	Rapid corrosion.
15	$(\text{NH}_4)_2\text{CO}_3$	1.0	-0.77	
	plus As_2O_3	0.1		
16	Na_2CO_3	1.0	-0.46 to -0.78 (7 minutes)	Slow corrosion. Passive, metal bright and clean.
	plus As_2O_3	0.1		
17	$\text{Na}_2\text{Cr}_2\text{O}_7$	0.1	-0.30 to -0.35	Do.
18	$\text{Na}_2\text{Cr}_2\text{O}_7$	0.1	-0.36 to -0.45	Do.
	plus NH_4SCN	0.1		
19	$\text{Na}_2\text{Cr}_2\text{O}_7$	0.1	-0.40 to -0.44	Passive, metal bright and clean, large white ppt. forms, probably insol. As_2O_3 .
	plus As_2O_3	0.1		
20	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.1	-0.29 to -0.20	Passive, metal bright and clean.
21	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.1	-0.37 to -0.34	Passive, metal bright and clean, large white ppt. forms, probably insol. As_2O_3 .
	plus As_2O_3	0.1		
22	V_2O_5	0.1	-0.36 to -0.74 (15 minutes)	Steel corroded.
23	V_2O_5	0.05	-0.37 to -0.16	Passive.
	plus As_2O_3	0.1		
24	$\text{CuCO}_3\text{-Cu}(\text{OH})_2$	0.1	-0.77	Rapid corrosion.
25	$\text{CuCO}_3\text{-Cu}(\text{OH})_2$	0.1	-0.40 to -0.35	Passive.
	plus As_2O_3	0.1		
26	$\text{CuCO}_3\text{-Cu}(\text{OH})_2$	0.1	-0.77	Rapid corrosion.
	plus NH_4SCN	0.1		
27	CuSO_4	0.1	-0.73	Do.
28	$\text{Cu}(\text{NO}_3)_2$	0.1	-0.73	Do.
29	CuSO_4	0.1	-0.69 to -0.74	Do.
	plus NaAsO_2	0.13=0.1 As_2O_3		
30	$\text{Cu}(\text{NO}_3)_2 + \text{As}_2\text{O}_3$	0.1	-0.50 to -0.71 (20 minutes)	Do.
31	CuSO_4	0.1	-0.76	Do.
	plus $(\text{NH}_4)_2\text{CO}_3$	0.1		
32	CuSO_4	0.1	-0.77	Do.
	plus $(\text{NH}_4)_2\text{CO}_3$	0.1		

Table I—Continued

Test No.	Oxidizing agent	Concentration g./100 ml. NH ₃ -NH ₄ NO ₃ solution	Observed single electrode potential of steel (volts to calomel)	Observations
	CuSO ₄	0.1.....	-0.39 to -0.28.....	Passive.
	plus (NH ₄) ₂ CO ₃	0.1.....		
	plus As ₂ O ₃	0.1.....		
	Cu(NO ₃) ₂	0.1.....	-0.40 to -0.29.....	Do.
	plus (NH ₄) ₂ CO ₃	0.1.....		
	plus As ₂ O ₃	0.1.....		
	PbCO ₃ ·Pb(OH) ₂	0.1.....	-0.75.....	Rapid corrosion.
	2PbCO ₃ ·Pb(OH) ₂	0.1.....	-0.52 to -0.73 (20 minutes).....	Slow corrosion.
	As ₂ O ₃	0.1.....		
	2NiCO ₃ ·3Ni(OH) ₂	0.1.....	-0.76.....	Rapid corrosion.
	2NiCO ₃ ·3Ni(OH) ₂	0.1.....	-0.52 to -0.77 (3 minutes).....	Do.
	As ₂ O ₃	0.1.....		
	2CoCO ₃ ·3Co(OH) ₂	0.1.....	-0.76.....	Do.
	2CoCO ₃ ·3Co(OH) ₂	0.1.....	-0.49 to -0.75 (5 minutes).....	Slow corrosion.
	As ₂ O ₃	0.1.....		

Table I above indicates that most oxidizing agents when added to NH₃-NH₄NO₃ solutions produce untable if any, passive films on exposed steel surfaces, due apparently to their reaction with ammonia. Na₂Cr₂O₇, 25 V₂O₅, (NH₄)₂S₂O₈ and the basic cupric carbonate-trivalent arsenic combination apparently are not too reactive

tact through the external circuit was maintained with the steel. If after five minutes the Flade potential was not exceeded, the copper wire was then brought into physical contact with the steel. Ordinarily this procedure was sufficient to destroy the film. Table II below contains the results of this test.

Table II

EFFECT OF CONTACT WITH A 2", #12 Cu WIRE ON THE SINGLE ELECTRODE POTENTIAL OF STEEL (VOLTS TO CALOMEL)

Test No.	Oxidizing agent	Conc. g./100 ml. NH ₃ -NH ₄ NO ₃ solution	Time exposed, hours	Electrical contact	Time, min.	Physical contact (wire touches rod)	Time, min.
A	(NH ₄) ₂ S ₂ O ₈	0.15	23.0	-0.21 to -0.78..	0.5
B	(NH ₄) ₂ S ₂ O ₈	0.1	26.0	-0.30 to -0.77..	0.75
	plus As ₂ O ₃	0.1					
C	V ₂ O ₅	0.1	26.5	-0.34 to -0.75..	0.5
	As ₂ O ₃	0.1					
D	Na ₂ Cr ₂ O ₇	0.1	25.5	-0.35 to -0.56..	5.0	-0.56 to -0.75..	2.0
E	Na ₂ Cr ₂ O ₇	0.1	26.0	-0.46 to -0.60..	5.0	-0.60 to -0.71..	9.0
	plus NH ₄ SCN.....	0.1					
F	Na ₂ Cr ₂ O ₇	0.1	26.5	-0.44 to -0.59..	5.0	-0.59 to -0.73..	2.0
	plus As ₂ O ₃	0.1					
G	CuCO ₃ ·Cu(OH) ₂	0.1	23.5	-0.28 to -0.58..	5.0	-0.58 ¹
	As ₂ O ₃	0.1					
H	CuSO ₄	0.1	27	-0.28 to -0.59..	-.59 to -0.436 ²
	(NH ₄) ₂ CO ₃	0.1					
	As ₂ O ₃	0.1					

¹ More than 9 days. ² More than 6 days.

with the solution and produce passive films in situ. The same is true in tests 33 and 34 where copper, carbonate and arsenic were supplied in another manner.

The decay of passivity can be observed by recording the decrease in potential when a metal cathodic to the passive steel is brought into electrical contact with it. The potential shift in the more active direction (i.e., more electronegative) is due to the electrolytic reduction of the film by the current that is created by the galvanic couple. When passive steel is activated there is first a steep fall of the potential in the active direction; second, a less steep change lasting for a fraction of a minute to several minutes; and third, by a steep descent to the active value (i.e., complete breakdown of the passive film; -0.71 to -0.77 volts to calomel for NH₃-NH₄NO₃). The value of the potential immediately preceding this last descent is called the Flade potential.

To determine the resistance to electrolytic destruction of the passive films produced by the above reagents, an activated steel rod was first exposed for about a day to NH₃-NH₄NO₃ solution containing the oxidizing agent so that it might become passivated. Then a two-inch piece of No. 12 copper wire was placed in the test solution with the passive steel. Initially only electrical con-

Table II indicates that the basic cupric carbonate-arsenite combination produces a very highly stable and resistant passive film when introduced to ammonia-ammonium nitrate solutions. The combination is also effective in repairing any breaks in the film. A deep scratch was cut on the face of the coupon. The coupon was then reinserted in the ammonia-ammonium nitrate containing the basic cupric carbonate-arsenite combination. The coupon was kept in the ammoniacal salt solution for over 2 weeks with no visible signs of corrosion. A good result was also obtained with another copper, arsenic and carbonate composition in test H.

In summary, the addition of the inhibitor combination of the present invention to corrosive solutions such as ammoniacal salt solutions will inhibit the corrosion of ferrous metal apparatus in which these solutions are handled, stored, etc. This will result in greater product purity and reduce the destruction of shipping and storage facilities which are used commercially such as in the fertilizer business. This advantage can in turn enable manufacturers of these corrosive solutions to use less costly equipment for handling these solutions. Further in many corrosive solutions like ammoniacal salt solutions, the cupric components of the present invention produces a clear solution with an intense blue color,

which color can be used to show that a controlled and adequate concentration of inhibitor is present. In addition, copper is one of the trace elements required for normal growth of many plants. Hence, incorporation of the cupric compounds of the present invention in ammoniacal fertilizer solutions may enhance their value as fertilizers.

We claim:

1. A composition consisting essentially of an aqueous ammoniacal ammonium nitrate solution, about 0.01 gram to less than about 0.5 g./100 ml. of said solution of a trivalent arsenic compound, soluble in said solution, about 0.01 to about 0.2 gram/100 ml. of said solution of a copper compound soluble in said solution, and about .005 to .1 gram/100 ml. of said solution of carbonate ions, the amounts of said compounds and ions being sufficient to substantially reduce the rate of corrosion by said solution to ferrous surfaces.

2. The composition of claim 1 in which there is included a small amount of alkali metal hydroxide.

3. The composition of claim 2 in which the hydroxide is sodium hydroxide.

4. The composition of claim 1 wherein the concentration of the trivalent arsenic compound is about 0.05 to 0.25 gram/100 ml. of said solution, the concentration of the copper compound is about .05 to .15 gram/100 ml. of said solution and the concentration of the carbonate ions is about 0.02 to .1 gram/100 ml. of said solution.

5. The composition of claim 1 where the copper and carbonate ions are supplied by basic copper carbonate.

6. The composition of claim 3 where the copper and carbonate ions are supplied by basic copper carbonate.

7. A composition resistant to corrosion of ferrous surfaces consisting essentially of an aqueous ammoniacal ammonium nitrate solution of about 40 to 80% ammonium nitrate and about 10 to 35% ammonia, having added thereto about 0.05 to 0.25 gram/100 ml. of said solution of As_2O_3 , about 0.01 to 0.2 gram/100 ml. of said solution of basic copper carbonate, and about 0.05 to 0.25 gram/100 ml. of said solution of sodium hydroxide.

8. The composition of claim 7 wherein the amount

of basic copper carbonate is about 0.05 to 0.15 gram/100 ml. of said solution.

9. The composition of claim 7 having added thereto a small, effective amount of sodium nitrite as a vapor phase corrosion inhibitor.

10. A composition consisting essentially of an aqueous ammoniacal ammonium nitrate solution, about 0.01 to less than about 0.5 gram/100 ml. of said solution of an inorganic tri-valent arsenic compound soluble in said solution, about 0.01 to 0.2 gram/100 ml. of said solution of a copper compound soluble in said solution, and about .005 to .1 gram/100 ml. of said solution of carbonate ions, the amounts of said compounds and ions being sufficient to substantially reduce the rate of corrosion by said solution to ferrous surfaces.

11. The composition of claim 10 wherein the copper compound is an inorganic copper compound.

12. The composition of claim 11 wherein the ammoniacal ammonium nitrate solution is of about 1 to 80% ammonium nitrate, about 5 to 35% ammonia with the substantial balance being water and the concentration of the trivalent arsenic compound is about 0.01 to 0.5 gram/100 ml. of said solution, the concentration of the inorganic copper compound is about 0.01 to 0.2 gram/100 ml. of said solution and the concentration of the carbonate ions is about 0.005 to 0.1 gram/100 ml. of said solution.

13. The composition of claim 12 wherein the copper and carbonate ions are supplied by the addition of about 0.01 to 0.2 gram/100 ml. of said solution of basic copper carbonate.

14. The composition of claim 13 in which the trivalent arsenic compound is arsenic trioxide.

15. The composition of claim 12 in which there is included about 0.01 to 0.5 gram/said solution of alkali metal hydroxide.

16. The composition of claim 15 in which the hydroxide is sodium hydroxide.

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