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NITROGEN SOLUTIONS WITH CORROSION INHIBITOR

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This invention relates to corrosion inhibition of metals, and especially ferrous metals, and in particular is concerned with the corrosion inhibition of ferrous metals by solutions of nitrogen compounds such as ammonium nitrate.

Aqueous solutions of nitrogen compounds find wide application in agriculture as fertilizers. They may be applied to the ground by the farmer without any further treatment or may be reacted with other compounds, such as phosphorous compounds, by the commercial fertilizer mixer to provide fertilizer solutions or solid fertilizer mixes. Examples of such nitrogen solutions are aqueous solutions of ammonium nitrate which may also contain added free ammonia. Other nitrogen compounds such as urea may also be added. Examples of additional possible constituents of nitrogen solutions would include ammonium sulfate, sodium nitrate, ammonium carbamate, ammonium carbonate and ammonium phosphates.

It is well known that aqueous solutions of ammonium nitrate are very corrosive to ferrous metals used in apparatus such as tanks, vessels and pipes for the production, transportation, or storage of these solutions. Aqueous solutions of ammonium nitrate which contain free ammonia and/or urea also exhibit this corrosive effect. There have been numerous suggestions for the reduction or inhibition of corrosion of ferrous metals by aqueous solutions of such nitrogen compounds. Some investigators have suggested the use of the noble metals, expensive alloys, or lined equipment. Others have suggested the use of various additives such as thiourea, various alkyl mercaptans, ethyl sulfide, thioacetic acid and sodium dichromate. One of the more successful additives disclosed in the prior art for reducing corrosion is ammonium thiocyanate, as taught by Beekhuis et al. in U.S. Patent No. 2,215,077. However, corrosion continues to be a serious problem as evidenced by some commercial use of expensive aluminum tank cars in an effort to partially circumvent the problem. What is needed, therefore, is an additive which will more effectively inhibit the corrosive effects of solutions of ammonium compounds on ferrous metals than the additives now conventionally employed.

An object of this invention is to provide an effective corrosion inhibitor for nitrogen solutions. A further object of this invention is to provide a method of inhibiting the corrosion of ferrous metals by nitrogen solutions. A further object of this invention is to provide compositions and methods for reducing the corrosive effects of aqueous solutions of ammonium nitrate which may also contain added nitrogen compounds such as ammonia and/or urea. A still further object is to provide compositions of aqueous ammonium nitrate and possibly other nitrogen compounds such as urea and/or ammonia and also containing an additive which will effectively inhibit the corrosive effects of said solutions on ferrous metals used in apparatus for the production, transportation or storage of said solutions.

According to the present invention, we have found that a combination of ammonium thiocyanate or an alkali metal thiocyanate and lignin derivatives such as found in lignin waste sulfite liquor or sulfate "black liquor" are highly effective for the inhibition of corrosion of ferrous metals by nitrogen solutions such as aqueous solutions of ammonium nitrate which may also contain free ammonia and/or urea. We have found that the novel combination

of this invention exhibits a synergistic activity since the additive combination is more effective in reducing corrosion of ferrous metals by such aqueous ammonium solutions than either an ammonium or alkali metal thiocyanate, or the lignin derivatives, added without the other.

As used herein the term "lignin derivatives" refers broadly to one or more of the water soluble derivatives, generally salts, formed in any one or more of the wood pulping processes.

In the pulp and paper industry, in which raw wood or other cellulosic material is converted to paper, the raw wood or cellulosic material must first be converted to pulp by removing the lignin, which accounts for about 50% of its composition, from the fibrous pulp. This is accomplished by one of three chemical processes; the sulfate process, the sulfite process and the soda process. All involve cooking the raw wood or cellulosic material with the "cooking liquor" to convert the lignin to soluble derivatives, facilitating its removal from the pulp. There is also the semi-chemical process, in which only part of the lignin is removed, which usually uses a more mild or neutral cooking liquor. In each process there results a large amount of waste or spent liquor containing the soluble lignin derivatives, other wood extractives and the cooking chemicals. These are now recovered to the extent that it is economically feasible. The nature of the liquor varies according to the material pulped, whether it be hard or soft wood, grasses or woody stem plants, seed hair or leaves. The spent liquor will also vary according to the type of chemical pulping process used to free the cellulose fiber, whether the pulping operation is full or semi-chemical and whether the chemical process is acid, alkaline or neutral.

In the sulfate process, the raw wood is cooked with a solution containing sodium hydroxide, sodium sulfide and usually sodium carbonate, thereby converting the lignin to its alcohol and acid derivatives. Appreciable amounts of organic sulfur compounds are also present in the sulfate liquor which is known as "black liquor" as well as the inorganic cooking chemicals. The lignins are obtained from the waste sulfate liquor by partial neutralization of the highly alkaline liquor to precipitate them as alkali lignins.

The soda process is very similar to the sulfate process, both being alkaline processes. The cooking chemicals are the same except that the soda process does not employ sodium sulfide. The lignins obtained from the soda liquor are also known as the alkali lignins.

In the sulfite process, the wood is treated, or cooked, with an aqueous solution of a bisulfite such as calcium, magnesium, sodium or ammonium bisulfite, containing sulfur dioxide, in order to break down the lignin and convert it to the sulfonic acid derivatives. The sulfite solution is then neutralized with lime or soda to give the dilute liquor. It can also be evaporated to dryness after neutralization to give a brown granular solid. The lignin sulfonates present are the sulfonate salts derived from the sulfonic acid derivatives of lignin in the sulfite liquor. These are also commercially available as the salts of most metals such as calcium, sodium, etc., as well as ammonium. The waste sulfite liquor contains, in addition to the sulfonic acid derivatives of lignin, various hexosans and pentosans, organic acids, and other complex organic matter plus any residual inorganic cooking chemicals. The lignin sulfonates are believed to be polymers with molecular weights of about 2,000–15,000 and 2–4 monomer units per atom of sulfoxyl sulfur.

The waste liquors containing the lignin derivatives are effective in our invention when used as the dilute liquor or concentrated liquor or they may be reduced to a dried powder and added as such to the nitrogen solutions. Examples of commercial products containing lignin waste

liquor derivatives which may be used are Marasperse, Maratan, Nalco 889, Binderine, Glutrin, Meadol and Indulin. Nalco 889 contains primarily sodium lignin sulfonates and sodium sulfite and small amounts of sodium nitrate and sodium carbonate.

Although alkali metal thiocyanates such as sodium thiocyanate may be used in the additive combination, it is preferred to employ ammonium thiocyanate.

The additive combination may be incorporated in the aqueous nitrogen solution by adding the lignin derivatives separately before or after addition of the thiocyanate additive. However, it is advisable to first prepare a solid mixture or aqueous solution containing predetermined amounts of both additives and to then add a calculated amount of the resulting premix to the nitrogen solution.

The quantity of additive combination which need be incorporated in an aqueous nitrogen solution to effectively inhibit corrosion is not narrowly critical. In general, however, there should be at least about 0.01% by weight on a dry basis of the additive combination in a nitrogen solution. The recommended amount, however, of the additive combination which should be incorporated in a nitrogen solution is from about 0.08 to about 0.16% by weight on a dry basis. Larger amounts of the additive combination may be employed if desired and may be warranted in special situations, but in general they are not needed.

The constituents of the inhibitor combination are usually employed in a 1:1 ratio by weight to each other. One very effective corrosion resistant nitrogen solution contains about 0.05% by weight of ammonium thiocyanate and about 0.05% by weight of lignin sulfate liquor (70% solids).

The percentages by weight of lignin derivatives in the nitrogen solutions are based herein on the lignin derivatives in a dry form, unless otherwise specified. Since lignin waste liquors may contain from about 10 to 70% solids the percentages given above for the lignin derivatives on a dry basis would obviously be greater if calculated on a waste liquor solution basis or concentrates thereof. It should be understood, however, that because of the complexity and variability of the composition of the lignin waste liquors obtained from the various pulping processes, some differences should be expected, but these are readily compensated for by those skilled in the art.

Other materials may also be advantageously incorporated in the nitrogen solutions and/or additive combination premixes. For example, we have found that the addition of sodium tetraborate to an ammonium thiocyanate-sulfate liquor additive combination also provides a particularly effective corrosion inhibitor.

The new additive compositions of this invention are especially useful in aqueous solutions which contain ammonium nitrate in concentrations of about 35–75% by weight with or without free ammonia in concentrations of about 8–50% by weight. These solutions may also contain as much as about 15% by weight of urea.

In order to more fully illustrate the utility of the novel compositions of this invention, the following examples are set out, wherein all percentages are by weight. In Examples 4, 5 and 8 the solution contained 56% ammonium nitrate and 26% ammonia.

EXAMPLE 1

Forty welded mild carbon steel coupons were sand blasted to clean them of all mill scale. The coupons were then washed with carbon tetrachloride to remove oil, washed with soap and water, rinsed with water and then washed with methanol. When dry, they were placed in an oven at 105° C. for 4 hours and then transferred to a desiccator until a constant weight was attained. Each coupon was weighed on a micro balance. The forty clean, dry coupons were then divided into 4 sets of 10 coupons. One set of 10 coupons was immersed in aqueous solutions containing about 60–74% ammonium nitrate and about 19–34% free ammonia. A second set of 10 was immersed in aqueous ammonium nitrate-ammonia solutions which also contained 0.1% NH_4SCN. A third set of 10 was immersed in aqueous ammonium nitrate-ammonia solutions which contained 0.1% Nalco 889. A fourth set of 10 coupons was immersed in aqueous ammonium nitrate-ammonia solutions which contained 0.05% NH_4SCN and 0.05% Nalco 889. After an immersion period of seven days the coupons were removed, washed with water, washed with inhibited muriatic acid to remove the corrosion products, washed with soap and water and then with methanol. The coupons were dried in an oven at 105° C. for 4 hours and then kept in a desiccator until a constant temperature was reached. They were again weighed on a micro balance and the rate of corrosion determined from the loss in weight and recorded in inches per year. As was expected, the most corrosion was present in the area of welding. The following results were obtained at room temperature as the average corrosion rate of the 10 coupons in each set as recorded in inches per year.

Table I

Additive:	Rate of Corrosion (in./year)
NH_4SCN	0.017
Nalco 889	0.204
NH_4SCN+Nalco 889	0.011
Control (no additive)	0.348

The results clearly show that the additive combination is much superior as a corrosion inhibitor to either of the constituents of the combination when used as a single additive. The additive combination gave a corrosion rate which is 36% less than that obtained when only NH_4SCN was used as a corrosion inhibitor. The additive combination gave a corrosion rate which was 95% less than that obtained when the Nalco 889 was used as a single additive. Thus, the results clearly illustrate that the additive combination is surprisingly superior to either NH_4SCN or Nalco 889 as a single additive for the inhibition of corrosion by aqueous solutions of ammonium nitrate containing free ammonia.

EXAMPLE 2

Five coupons were cleaned as described in Example 1, weighed and then immersed in an aqueous solution which contained about 55% ammonium nitrate, 25% ammonia, and 10% urea, and also 0.05% NH_4SCN and 0.05% Nalco 889 as a corrosion inhibitor combination. After an immersion period of seven days, the coupons were removed and cleaned as described in Example 1 and then weighed and the loss in weight recorded. An average corrosion rate of 0.011 inch per year was obtained.

EXAMPLE 3

The procedure described in Example 2 was followed except that the ammonium nitrate-ammonia-urea solution contained 0.05% NH_4SCN and 0.05% of sulfate "black liquor" concentrated to about 30% water by weight. An average corrosion rate of 0.010 inch per year was obtained.

EXAMPLE 4

In a test similar to Example 1 with an aqueous ammonium nitrate-ammonia solution containing 0.05% NH_4SCN and 0.05% of sulfate "black liquor" concentrated to about 30% water by weight, an average corrosion rate of 0.012 inch per year was obtained. A similar ammonioum nitrate-ammonia solution to which was added 0.1% of the sulfate liquor had an average corrosion rate of 0.022 inch per year. The additive combination thus had a corrosion rate about 45% less than that obtained with the sulfate liquor alone.

EXAMPLE 5

In another test similar to Example 1, with an aqueous

ammonium nitrate-ammonia solution containing 0.05% NH_4SCN and 0.05% of dried powdered sulfate "black liquor," an average corrosion rate of 0.012 inch per year was obtained.

EXAMPLE 6

In another test similar to Example 1, with an aqueous ammonium nitrate-ammonium solution containing about 64% ammonium nitrate and 30% ammonia and an additive combination of 0.037% NH_4SCN, 0.037% sulfate "black liquor" concentrated to about 30% water by weight, and 0.037% sodium tetraborate, a corrosion rate of 0.007 inch per year was obtained.

EXAMPLE 7

To an aqueous 83% ammonium nitrate solution was added 0.05% by weight of ammonium thiocyanate and 0.05% by weight of spent sulfate liquor. At 170° F. this solution had a corrosion rate of 0.0031 inch per year as compared to an identical control solution containing no inhibitor which had a corrosion rate of 0.0038 inch per year. The uninhibited solution thus had a corrosion rate about 23% higher than the inhibited solution. The test temperature of 170° F. was used to maintain all of the ammonium nitrate in solution.

EXAMPLE 8

In a test with an aqueous ammonium nitrate-ammonia solution containing 0.1% of spent sulfite liquor as the single additive, corrosion rates of 0.353 and 0.324 (average=0.339) inch per year were obtained. In a similar test with the ammonium nitrate-ammonia solution containing 0.05% NH_4SCN and 0.05% of the sulfite liquor, an average corrosion rate of 0.012 inch per year was obtained. The additive combination thus gave a much lower corrosion rate than the sulfite liquor when used as a single additive.

The spent sulfite liquor used in this test had the following analysis:

Specific gravity	1.267
Total solids, g./l.	665.5
Sulfated ash, g./l.	108.6
Calcium oxide, g./l.	43.1
Magnesium oxide, g./l.	1.78
Total sulfur, g./l.	40.7
Sulfur trioxide, g./l.	5.05
Free sulfur dioxide, g./l.	1.14
Loosely combined SO_3, g./l.	12.1
Sulfone SO_2, g./l.	64.1
Volatile acids—	
Acetic, g./l.	16.4
Formic, g./l.	0.49
Alcohols and acetone—	
Methyl alcohol, mg./l.	10.5
Ethyl alcohol, mg./l.	989
Acetone, mg./l.	408.3
Furfural, g./l.	0.32
Pentoses, g./l.	37.0
Lignin, g./l.	280
Total sugars, g./l.	146.1
pH	4.0

Various changes and modifications of the invention can be made and, to the extent that such variations incorporate the spirit of this invention, they are intended to be included within the scope of the appended claims.

What is claimed is:

1. A solution comprising aqueous ammonium nitrate, a member of the group consisting of ammonium thiocyanate and alkali metal thiocyanates and a water soluble inorganic salt of the lignin containing material present in chemical and semichemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes.

2. A solution containing water, ammonium nitrate, ammonia, a member of the group consisting of ammonium thiocyanate and alkali metal thiocyanates and a water soluble inorganic salt of the lignin containing material present in chemical and semichemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes.

3. A solution containing water, ammonium nitrate, ammonia, and a corrosion inhibitor comprising ammonium thiocyanate and a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes.

4. A solution containing water, ammonium nitrate, ammonia and urea and as a corrosion inhibitor an additive combination comprising a member of the group consisting of ammonium thiocyanate and alkali metal thiocyanates and a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes.

5. The process of reducing corrosion of ferrous metals by an aqueous solution of ammonium nitrate which comprises adding ammonium thiocyanate and a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes to said solution.

6. A process of reducing corrosion of ferrous metals by an aqueous solution of ammonium nitrate containing free ammonia which comprises adding ammonium thiocyanate and a water soluble inorganic salt of the lignin containing material present in chemical and semichemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes to said solution.

7. A process of reducing corrosion of ferrous metals by a solution of ammonium nitrate containing free ammonia which comprises adding ammonium thiocyanate, sodium tetraborate and a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes, to said solution.

8. The process of reducing corrosion of ferrous metals by an aqueous solution of ammonium nitrate containing free ammonia and urea which comprises adding ammonium thiocyanate and a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes to said solution.

9. The process of reducing corrosion of ferrous metals by an aqueous solution of ammonium nitrate which comprises adding a member of the group consisting of ammonium thiocyanate and alkali metal thiocyanates and a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes to said solution.

10. A solution comprising aqueous ammonium nitrate, and 0.08 to 0.16% by weight on a dry basis of an additive combination comprising (1) a member of the group consisting of ammonium thiocyanate and alkali metal thiocyanates, and (2) a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes.

11. A solution containing water, ammonium nitrate, ammonia, and a corrosion inhibitor comprising 0.08 to 0.16% by weight on a dry basis of an additive combina-

tion comprising (1) ammonium thiocyanate and (2) a water soluble inorganic salt of the lignin containing material present in chemical and semi-chemical pulping waste liquor from the pulping of raw cellulosic material by the processes consisting of sulfite, sulfate and soda processes.

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