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AMMONIACAL AMMONIUM NITRATE SOLUTION WITH HYDROGEN PEROXIDE AS CORROSION INHIBITOR

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My invention relates to the corrosion of ferrous metals. More specifically, my invention relates to a composition consisting essentially of aqueous ammonia, ammonium nitrate and hydrogen peroxide said composition having reduced corrosion tendencies toward metal surfaces.

There is a well recognized corrosion problem in industries concerned with the manufacture, storage, transportation and handling of ammonia-ammonium nitrate aqueous solution. In the handling of this solution it is often necessary to transport and store it in metal containers such as drums, tanks, and pipelines. These containers often have varying amounts of contaminants such as water and the like which tend to increase corrosion to ferrous metal surfaces. Storage and transportation present a favorable situation for contamination of aqueous ammonia-ammonium nitrate solutions with materials such as those containing sulfur. Even slight contamination has been found to cause rapid corrosion and the formation of rust.

This corrosion has resulted in the use of costly aluminum processing, storing and handling equipment and the application of scarce and costly internal coatings to container walls in order to reduce corrosion.

Corrosion inhibitors of one type or another have been suggested and attempted with varying degrees of limited success. An example of such an inhibitor is ammonium thiocyanate which has been found to be relatively unsuccessful and thus generally abandoned. Sodium silicate, another supposed inhibitor, is ineffective and at times has permitted immediate and rapid corrosive attacks.

Other corrosion problems have arisen regarding the use of equipment when contacted with aqueous ammonia-ammonium nitrate solutions in fertilizer plants. The presence of said solutions causes destructive corrosion to the equipment utilized in handling, storage and shipment of fertilizer products. An aqueous ammonia-ammonium nitrate solution in a reasonably pure state is mildly corrosive but in the presence of small amounts of corrosive constituents, i.e. about .05% by weight or more, there is immediate and rapid attack on ferrous metal surfaces. As a practical matter such corrosive constituents are normally found in common commercial plants such as fertilizer plants which produce this solution. The contaminants are in general at least somewhat soluble sulfur constituents either organic or inorganic. Examples of these are sodium sulfide, sodium sulfite, butyl mercaptans and sodium salts of butyl mercaptans.

In my invention I have found a new composition consisting essentially of aqueous ammonia-ammonium nitrate solution having hydrogen peroxide incorporated therein. My composition has reduced corrosion tendencies towards metal surfaces such as steel. The aqueous ammonia-ammonium nitrate solution utilized in my invention can be prepared by the addition of commercial ammonium hydroxide to ammonium nitrate with a subsequent addition of water. The percent of ammonium hydroxide may vary with the desired properties peculiar to each solution. The preferred amount of ammonium hydroxide is about 10 to

35% by weight of the final composition. The amount of ammonium nitrate in my composition may vary from about 1 to 35% by weight of the final composition. Commercial hydrogen peroxide can be utilized in my composition and will usually be about 0.0001 to 3% or more (H_2O_2 basis) of the composition by weight with a preferred amount being about .001 to 0.3% by weight.

I conducted various tests under static conditions at room temperature using mild steel coupons having two-thirds of their length immersed in various solutions. Each test started with 70 ml. of solution in a 4 oz. square jar with the coupon upright therein. The initial series of tests used bright, polished cold-rolled steel coupons. In the later tests hot-rolled steel coupons were used each having a mill-scaled side and edge and the other surfaces polished. In each of the examples there was employed an aqueous solution of 24% ammonium hydroxide, 4% of ammonium nitrate and .14% of varying supposed inhibitor or hydrogen peroxide.

EXAMPLE I

A composition containing aqueous ammonia-ammonium nitrate and sodium silicate was tested according to the above and found to be corrosive with an immediate attack of rust on the steel coupons, and after 3 days of exposure, the rate of corrosion of the coupon was measured at 2270 mdd. which corresponds to a rust penetration of ¼ inch in a nine month period. Mdd. is milligrams weight loss per square decimeter of exposed surface per day of exposure.

EXAMPLE II

A composition containing ammonium thiocyanate and the aqueous ammonia-ammonium nitrate solution was tested according to the above and heavy rust on the immersed steel coupons appeared at the end of a 15 week period.

EXAMPLE III

Using the above testing procedure, an octadecyl amine-aqueous ammonia-ammonium nitrate solution was tested for corrosive tendencies. During an 18 week testing period, heavy rusting occurred thus showing the composition to be ineffective in inhibiting corrosion.

EXAMPLE IV

Similarly a potassium chromate-aqueous ammonia-ammonium nitrate solution was tested and found to be corrosive when in contact with a steel coupon such as described above and medium rust occurred during an 18 week testing period.

EXAMPLE V

Using the above testing procedure, a hydrogen sulfide-aqueous ammonia-ammonium nitrate solution was applied to a steel coupon and a black coating appeared on the metallic surfaces in approximately two weeks.

EXAMPLE VI

Using the above testing procedure a steel coupon was immersed into my aqueous ammonia-ammonium nitrate hydrogen peroxide composition containing by weight 24 percent of NH_4OH, 4 percent of NH_4NO_3 and 1.64 ml. of H_2O_2. This composition exhibited freedom from corrosion during an 8 week testing period.

The hydrogen peroxide is a 31.1 solution and has a specific gravity of 1.147. Table I shows the results of corrosion tests on aqueous ammonia-ammonium nitrate solutions containing varying supposed inhibitors.

Table I

Solution			Static corrosion tests of hot-rolled mild steel (half mill-scaled, half polished)	
Percent NH_4OH	Percent NH_4NO_3	0.14 weight percent	Time exposed, days	Rusting
24	4	Octadecyl amine	127	Heavy rusting.
24	4	$K_2Cr_2O_7$	127	Medium rusting.
24	4	$Na_2SiO_3 \cdot 9H_2O$	127	Heavy rusting.
24	4	$Na_2S \cdot 5H_2O$	10	Do.
24	4	Na_2SO_3	10	Do.
24	4	H_2S	44	Black coating.
24	4	H_2SO_3	13	Slight rust.

Table II shows the results obtained when adding contaminants to aqueous ammonia-ammonium nitrate solutions either with or without hydrogen peroxide incorporated therein.

Table II

[Static corrosion tests of hot-rolled mild steel (half mill-scaled, half-polished)]

Solution		H_2O_2,[a] ml.	Contaminant 0.1 gm.	Time exposed, days	Rusting
Percent NH_4OH	Percent NH_4NO_3				
24	4	2.60	Na_2SO_3	55	No rust, no loss.
24	4	1.64	Na_2S	55	Do.
24	4	.002	Na_2SO_3	55	Do.
24	4	——	Na_2S	10	Heavy rusting (128.3 mdd.).[b]
24	4	——	$NaSO_3$	10	Heavy rusting (1,589 mdd.).[b]

[a] The hydrogen peroxide was a 31.2% solution. Specific gravity is 1.147.
[b] Mdd. is milligrams weight loss per square decimeter of exposed surface per day of exposure.

The data above clearly show that my composition has reduced corrosive tendencies and is effective in overcoming the problem of corrosion in the manufacture, transportation, storage and handling of aqueous ammonia-ammonium nitrate solutions.

I claim:

1. A composition consisting essentially of an ammonia-ammonium nitrate aqueous solution having incorporated therein about 0.0001 to 3% by weight of hydrogen peroxide, said solution having about 10 to 35% by weight of ammonium hydroxide and about 1 to 35% by weight of ammonium nitrate.

2. The composition of claim 1 in which the amount of hydrogen peroxide incorporated is about 0.001 to 0.3%.

3. The composition of claim 1 which includes a small, contaminating amount of a soluble sulfur-containing material sufficient to cause corrosion of ferrous surfaces contacting said compositions.

4. The composition of claim 3 in which the soluble sulfur-containing material is selected from the group consisting of sodium sulfite and sodium sulfide.

5. A container, having internal surfaces of ferrous material having therein an ammoniacal ammonium nitrate composition containing about 0.0001 to 3% by weight of hydrogen peroxide to inhibit corrosion of said ferrous metal surfaces, said solution having about 10 to 35% by weight of ammonium hydroxide and about 1 to 35% by weight of ammonium nitrate.

6. The container of claim 5 wherein is included in the ammoniacal ammonium nitrate composition a small, contaminating amount of a soluble sulfur-containing material selected from the group consisting of sodium sulfite and sodium sulfide sufficient to cause corrosion of ferrous surfaces contacting said composition.

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