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PREVENTING CORROSION OF FERROUS METALS

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The present invention relates to methods of reducing corrosion of ferrous metals by ammonium nitrate solutions containing free ammonia.

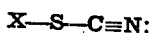
In recent processes for the ammoniation of superphosphates, use is made of solutions containing large percentages of ammonium nitrate and also free ammonia. The provision of methods which reduce or prevent the corrosion of apparatus in which these solutions are handled constitutes a major problem in the commercial use of these solutions, since, when ammonium nitrate-ammonia solutions of the concentrations used are shipped in tank cars of the usual construction, rapid corrosion occurs, and the tank soon is not usable. Also corrosion occurs in apparatus constructed of ferrous metals in which the solutions are handled.

It is an object of this invention to provide a method for reducing the rate of corrosion of ferrous metals by corrosive solutions of ammonium nitrate containing free ammonia, so that it is commercially practicable to employ apparatus of these metals for the storage and transportation of such solutions.

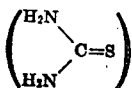
It is a further object of this invention to provide solutions of ammonium nitrate containing free ammonia which but slowly corrode ferrous metals.

According to the present invention, the apparatus which may be a storage tank, tank car, conveying pipe, measuring tank or the like, is constructed of the ferrous metals commonly used for this purpose, such as cast iron, wrought iron and low carbon steels, for example structural steel, which are subject to severe corrosion by ammoniacal solutions of ammonium nitrate.

We have found that particularly good results are obtained in minimizing the corrosive effect on such ferrous metals of ammonium nitrate-ammonia solutions by incorporating in the solution a compound of the group consisting of the thiocyanates and thiourea. These materials are compounds containing divalent sulfur linked to an atom of carbon with the remaining valences of the carbon atom being satisfied by nitrogen. Thus, the thiocyanates, also called sulfocyanates and sulfocyanides, have the formula



and thiourea has the formula



When a thiocyanate is the material employed, we prefer alkali metal (including ammonium) thiocyanates. However, we may employ alternatively other inorganic thiocyanates, which incorporate the thiocyanate ion in the solution. For example, ferric thiocyanate may be added to the solution although the cation of this material is relatively insoluble. By reaction with the solution, a ferric compound is precipitated, but the thiocyanate ion is thereby incorporated in the solution. By the addition of a compound containing divalent sulfur linked to an atom of carbon and the remaining valences of the carbon atom being satisfied by nitrogen the rate of corrosion of ferrous metals by ammoniacal ammonium nitrate solutions is reduced to a very low rate.

The quantity of the thiocyanate or thiourea which may be added to reduce the rate of corrosion may vary from a very small percentage upward. It is preferred, however, that the solution contains 0.01% to 2% of these materials. More than 2% may be present although the presence in the solution of a high proportion of the thiocyanate or thiourea is not necessary to accomplish the purposes of the invention. For example, solutions made up of 60 parts ammonium nitrate, 20 parts ammonia and 20 parts water to which 0.05% ammonium thiocyanate or thiourea was added, corroded an assembly of low carbon steel and cast iron at only a small fraction of the rate of corrosion of these metals by a solution of the same composition except that it contained no thiocyanate or thiourea. Accordingly, it is desirable to incorporate in the solution an amount of the thiocyanate or thiourea which is a minor proportion of the amount of ammonium nitrate in the solution.

This invention has specific application to aqueous solutions of ammonium nitrate containing free ammonia in which the ammonium nitrate constitutes about 50% or more of the solution (for example, 40% to 80%) and in which the ammonium nitrate is dissolved in 5% or stronger aqua ammonia, preferably in an aqua ammonia of about 25% or greater strength, due to the relatively high rates of corrosion exhibited by these solutions.

This invention also has specific application to contacting, at temperatures below about 50° C., ferrous metals with solutions containing ammonium nitrate and free ammonia in which the thiocyanate or thiourea has been incorporated.

In order that this invention may be more clearly understood, the following examples typical of

preferred methods of procedure are given by way of illustration:

Example I.—To a solution containing 60 parts ammonium nitrate, 20 parts ammonia and 20 parts water, 0.1% of sodium thiocyanate is added. The solution is then introduced into a container made of low carbon steel or cast iron and stored in such a container at room temperature.

Very little corrosion of the carbon steel or cast iron occurs during long periods of contact with the solution. For example, the rate of corrosion of a specimen of low carbon steel in the above solutions containing 0.1% sodium thiocyanate was less than 2% of the rate of corrosion of the same steel in the ammonium nitrate-ammonia-water solution without thiocyanate being added. With thiocyanate added the rate of corrosion of cast iron by the solution was but 2% of the rate without thiocyanate.

In place of the sodium thiocyanate used in this example, another alkali metal thiocyanate (including ammonium thiocyanate) may be added to the ammonium nitrate-ammonia-water solution.

Example II.—To a solution containing 60 parts ammonium nitrate, 20 parts ammonia and 20 parts water, 1% of thiourea is added. The solution is then introduced into apparatus constructed of cast iron and low carbon steel at room temperature.

Very little corrosion of the cast iron and steel by the solution occurs. It has been found the rates of corrosion of the cast iron and steel are reduced to but 3% and 1%, respectively, of the rates of corrosion of these materials by a solution of the same composition but containing no thiourea.

The following theory is offered as a possible explanation of the effectiveness of the above processes for inhibiting corrosion of ferrous metals by ammoniacal ammonium nitrate solutions. It appears from our observations of the action of numerous salt solutions on ferrous metal that the chemical reaction which causes rapid corrosion of ferrous metals by ammoniacal ammonium nitrate solutions is peculiar to nitrate solutions and ferrous metals. Further, in the case of the nitrate solutions, rapid corrosion of the metal as a result of this reaction occurs only with the ammoniacal solutions. Thus, in the case of acid and neutral solutions of ammonium nitrate, hydrogen is evolved by the corrosion of ferrous metal by the solutions. In the case of corrosion by ammoniacal ammonium nitrate solutions, instead of detecting the evolution of hydrogen, we have observed that ammonia is formed by reactions taking place during corrosion of the metal

by the solution. Under the conditions encountered in the corrosion of ferrous metals by ammoniacal ammonium nitrate, the presence in the solution of even a small amount of a sulfur compound of the type described appears to inhibit the particular type of corrosion there involved.

In our copending application Serial No. 116,711, filed December 19, 1936, we are claiming the process of reducing corrosion of a ferrous metal by solutions of ammonium nitrate containing free ammonia by dissolving in the solution a compound containing divalent sulfur linked to carbon, of which class of compounds the thiocyanates and thiourea disclosed and claimed herein are examples.

This application is in part a continuation of our copending application Serial No. 726,734, filed May 21, 1934.

We claim:

1. The process of reducing corrosion of ferrous metals by a solution of ammonium nitrate containing free ammonia which corrodes ferrous metals, which comprises dissolving in said solution a thiocyanate in amount sufficient to materially decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

2. The process of reducing corrosion of ferrous metals by a solution of ammonium nitrate containing free ammonia which corrodes said ferrous metals, which comprises dissolving an alkali metal thiocyanate in said solution in amount sufficient to materially decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

3. The process of reducing corrosion of ferrous metals by a solution containing about 50% or more ammonium nitrate dissolved in about 25% or stronger aqua ammonia, which comprises dissolving 0.01% to 2% of an alkali metal thiocyanate in said solution, and contacting said solution with said ferrous metal.

4. As a new composition of matter suitable for storage, transportation and use in contact with ferrous metals, a solution containing free ammonia, ammonium nitrate and a thiocyanate in amount sufficient to materially decrease the rate of corrosion of a ferrous metal by said solution.

5. As a new composition of matter suitable for storage, transportation and use in contact with ferrous metals a solution containing about 50% or more ammonium nitrate in solution in about 25% or stronger aqua ammonia, in which is dissolved 0.01% to 2% of a thiocyanate.

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