

UNITED STATES PATENT OFFICE

2,220,059

PROCESS FOR REDUCING CORROSION BY
AMMONIACAL SOLUTIONS OF INORGANIC
SALTS AND NEW COMPOSITION OF RE-
DUCED CORROSIVENESS

Herman A. Beekhuis, Jr., Petersburg, Va., and
Charles K. Lawrence, Baldwinsville, N. Y., as-
signors to The Solvay Process Company, New
York, N. Y., a corporation of New York

No Drawing. Application June 13, 1938,
Serial No. 213,452

14 Claims. (Cl. 23—239)

The present invention relates to methods of reducing corrosion of ferrous metals by solutions of inorganic salts in ammoniacal liquors.

In recently developed processes for the ammoniation of superphosphates use is made of solutions containing large percentages of inorganic salts and also free ammonia. Such solutions are in general quite corrosive in their action on ferrous metals. The provision of methods which reduce or prevent the corrosion of apparatus constructed of ferrous metals in which these solutions are handled constitutes a major problem in the commercial use of these solutions, since, when they 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, therefore, an object of the present invention to provide a method for reducing the rate of corrosion of ferrous metals by solutions of inorganic salts in ammoniacal liquors to an extremely low rate.

It is a further object of this invention to provide solutions of inorganic salts in ammoniacal liquors which corrode ferrous metals only extremely slowly.

It is a further object of this invention to provide a method for rendering solutions of inorganic salts, in ammoniacal liquors, which normally corrode ferrous metals rapidly, much less corrosive in their action on said ferrous metals.

In general, ammoniacal solutions of inorganic salts are corrosive with respect to ferrous metals and the process of this invention may be employed to reduce the rate of corrosion of ferrous metals by such solutions. The invention is particularly applicable to ammoniacal solutions of those nitrogenous salts which are employed in the production of fertilizers; for example, solutions of ammonium salts, such as ammonium nitrate and ammonium chloride, or nitrates, such as sodium nitrate and ammonium nitrate; or solutions containing ammonium carbonate or carbamate, particularly solutions of urea in ammoniacal liquors which also contain compounds of ammonia and carbon dioxide. Ammoniacal solutions of thiocyanates, such as ammonium thiocyanate, may be treated in accordance with

this invention to reduce the corrosion of ferrous metals contacted therewith.

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 low carbon steels, for example structural steel, cast iron and wrought iron.

In employing this invention a compound of 10 trivalent arsenic is incorporated in a solution of an inorganic salt in an ammoniacal liquor, such as aqua or anhydrous liquid ammonia, particularly an ammoniacal liquor of 5% or greater strength. The trivalent arsenic compound added to the ammoniacal solution (i. e. prior to incorporation in the solution) may be, for example, arsenic trioxide (As_2O_3), or a sulfide of trivalent arsenic, for instance, As_2S_2 (realgar) or As_2S_3 , such as precipitated arsenic trisulfide or orpiment, or an arsenite, for instance sodium or ammonium arsenite. In case arsenic trioxide is used, it may be in any of its forms, for instance white arsenic, either crystalline, as octahedral crystals or amorphous, or vitreous arsenic trioxide. The incorporation of a trivalent arsenic compound in a solution of an inorganic salt in an ammoniacal liquor reduces the rate of corrosion of ferrous metals in contact with the solution to an extremely low rate.

Compounds of trivalent arsenic dissolve but slowly when added directly to the ammoniacal salt solutions except at elevated temperatures which, if employed, would necessitate the use of high pressure equipment and the consumption 35 of large quantities of heat. Accordingly, the arsenic compounds are preferably first dissolved in an alkaline solution, such as an aqueous solution of soda ash, caustic soda, ammonia, or the like. Small quantities of the alkaline solution 40 containing arsenic may then be added to the ammoniacal salt solution.

The quantity of arsenic compound added may vary from a very small percentage upward, and may vary with the composition of the salt solution. In general, it is preferred to add the arsenic compound in the amount of about 0.05% or more (calculated as As_2O_3). The objects of the invention may be obtained by adding large amounts 50 of the arsenic compounds, although the arsenic

compound in solution will constitute a minor proportion by weight of the total composition and no added advantage is obtained by adding the arsenic compound in excess of the solubility thereof in the particular solution employed. Less than 0.05% may be added, though the protection afforded is not as great as with the preferred amounts.

Our invention has specific application to ammoniacal solutions of the nitrates, particularly of ammonium nitrate. 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 to 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 trivalent arsenic compound appears to inhibit the particular type of corrosion involved.

The preferred ammoniacal solutions of nitrate to which our invention has specific application are 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, particularly in an aqua ammonia of about 25% or greater strength due to the relatively high rates of corrosion exhibited by these solutions.

Our invention further has specific application to the prevention of corrosion by ammoniacal urea-carbonate solutions; that is, ammoniacal solutions of mixtures of urea, ammonium carbonate and ammonium carbamate such as may be produced in conjunction with the synthesis of urea. Our preferred urea-carbonate solutions, to which the invention relates, may contain between about 25% and about 50% urea, between about 5% and about 30% of combined ammonia and carbon dioxide, in the form of ammonium carbonate and ammonium carbamate, and the remainder an ammoniacal liquor of 5% or greater strength. We have found the addition of a trivalent arsenic compound, as above indicated, is very effective in reducing the rate of corrosion of ferrous metals by these solutions.

In order to protect the ferrous metals even further, we have found it desirable also to add to the solution a compound of the general class of compounds which contain divalent sulfur linked to carbon and preferably linked to an atom of carbon with the remaining valences of the carbon atom linking the carbon to nitrogen. As illustrative of these compounds which further reduce the rate of corrosion, the following are noted:

(a) Carbon disulfide ($S=C=S$);

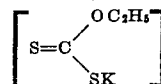
(b) The thio alcohols, such as ethyl mercaptan (C_2H_5SH), and benzyl mercaptan ($C_6H_5CH_2SH$);

(c) The thio ethers, such as diethyl sulfide [$(C_2H_5)_2S$];

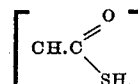
(d) The organic thio acids, their salts and esters, such as:

(1) Thiocyanates ($X-S-C\equiv N$), e. g., ethyl thiocyanate, alkali metal thiocyanate, ammonium thiocyanate, etc.

(2) Derivatives of the thio analogues of carbonic acid, such as potassium xanthate

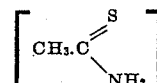


(3) Thiocarboxylic acids, such as thioacetic acid

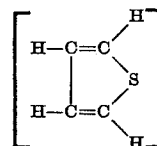


(4) Thiophenols, such as thiophenol (C_6H_5SH), and thio beta naphthol ($C_{10}H_7SH$);

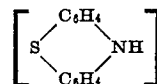
(e) Thioamides such as thiourea [$(NH_2)_2C=S$] and thioacetamide



(f) Heterocyclic compounds containing divalent sulfur in the ring such as thiophene



and thiodiphenyl amine



Compounds containing divalent sulfur linked to carbon are suitable for use in carrying out this invention, but it is preferred to use compounds in which the remaining valences of the carbon atom linked to divalent sulfur are satisfied by one or more atoms of nitrogen such as the thiocyanates and thiourea.

The quantity of organic sulfur compound which may be incorporated to reduce the rate of corrosion may vary from a very small percentage upward. It is preferred, however, that the solution contain 0.004% to 0.8% of these materials (calculated as sulfur). More than 0.8% (calculated as sulfur) may be present although the presence in the solution of a high proportion of the sulfur compounds is not necessary to accomplish the purposes of the invention and the amount of the sulfur compound is, in general a minor proportion by weight of the amount of the total inorganic salt content of the solution. For example, any of the materials listed in the preceding paragraph may be added, to a solution containing 60 parts of ammonium nitrate, 20 parts ammonia, 20 parts water and 0.1% arsenic trioxide (As_2O_3), in amount corresponding to 0.04% sulfur.

The rate of corrosion of ferrous metals by ammoniacal salt solutions varies with the varying conditions under which the solutions and metals are in contact with each other. The protection afforded the metal under some conditions en-

countered in commercial shipment and use of the solutions may be materially increased by the addition of the above described sulfur compounds to the solution. Further, the addition of these sulfur compounds serves to protect the arsenic compounds in the solution. Thus, while under most conditions the presence of the arsenic compound alone affords a lasting protection against corrosion, when corrosion does occur a product of the reaction of ferrous metals with ammoniacal solutions of inorganic salts appears to be a ferrous compound which is soluble in the solution but is oxidized by the air to an insoluble ferric compound. This ferric compound is precipitated from the solution and appears to adsorb arsenic compounds. By incorporating in the solution a divalent sulfur compound, removal from the solution of arsenic compound, with a consequent loss in the protective action of the arsenic compound in the solution against corrosion of the metal, may be prevented. Accordingly, the divalent sulfur compounds perform, in conjunction with the arsenic compounds, the double function of protecting the metal against corrosion under varying conditions and of guarding against loss of the protective action of the trivalent arsenic compounds.

Example 1.—An alkaline arsenite solution is prepared by dissolving 10 parts octahedral crystalline arsenic trioxide in 90 parts of a 15% aqueous solution of sodium hydroxide at room temperature. One part of the arsenite solution so prepared is added to 100 parts of a solution containing 60% ammonium nitrate, 20% ammonia, and the remainder chiefly water. The solution so produced contains 0.1% arsenite (calculated as As_2O_3). The thus treated solution is then contacted with apparatus made of ferrous metal. It has been found that the rates of corrosion of low carbon steel and cast iron contacted with such a solution are extremely low; thus, low carbon steel submerged in the solution was corroded at a rate equivalent to a penetration of only 0.002 inch per year; cast iron at 0.003 inch per year. In a similar solution but containing 0.05% As_2O_3 , low carbon steel is corroded at a rate equivalent to a penetration of 0.003 inch per year.

Example 2.—Vitreous arsenic trioxide, commercial white arsenic, orpiment and realgar are individually dissolved in caustic solutions. These solutions are added to ammoniacal solutions of ammonium nitrate as in Example 1. Upon contacting the solutions with low carbon steel apparatus, similar results are obtained as in the above example.

Example 3.—To 100 parts of a solution containing 60% ammonium nitrate, 20% ammonia, and 20% water are added 0.1 part ammonium thiocyanate and 0.5 part of an arsenite solution prepared as in Example 1. The solution, which then contains 0.04% ammonium thiocyanate (calculated as sulfur) and 0.05% arsenite (calculated as As_2O_3), is then contacted with low carbon steel. Steel contacted with a solution so treated has been found to be corroded at a rate equivalent to an average penetration of less than 0.001 inch per year.

Example 4.—50 pounds of commercial white arsenic and 75 pounds soda ash are dissolved in 50 gallons of water at about 95° C. with agitation. The solution so prepared and about 300 pounds of a crude aqueous 33% ammonium thiocyanate solution are added to 45 tons of a solution containing 60% ammonium nitrate, 20%

ammonia, and the remainder chiefly water. The ammoniacal ammonium nitrate solution is then placed in a conventional type tank car for shipment.

Example 5.—1 part of an alkaline arsenite solution prepared as in Example 1 is added to 100 parts of a solution containing 33% urea, 17.7% combined carbon dioxide and ammonia, 27.8% free ammonia and the remainder chiefly water. The solution so prepared contains 0.1% arsenite (calculated as As_2O_3). This solution is then contacted with low carbon steel which has been found to be corroded thereby at a rate equivalent to a penetration of less than 0.001 inch per year.

Example 6.—1 part of an alkaline arsenite solution, prepared as in Example 1, is added to 100 parts of a solution containing 58% ammonium nitrate, 16% urea, 13% ammonia and the remainder chiefly water. This solution is then contacted with low carbon steel which has been found to be corroded thereby at a rate equivalent to a penetration less than 0.001 inch per year.

We claim:

1. The process of reducing corrosion of a ferrous metal by an ammoniacal solution of an inorganic salt, which comprises incorporating in said solution a trivalent arsenic compound in amount sufficient to 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 a ferrous metal by an ammoniacal solution of an inorganic salt, which comprises incorporating an arsenite in said solution in amount sufficient to 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 a ferrous metal by an ammoniacal solution of an inorganic salt, which comprises incorporating a sulfide of trivalent arsenic in said solution in amount sufficient to decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

4. The process of reducing corrosion of a ferrous metal by an ammoniacal solution of an inorganic salt, which comprises incorporating in said solution both a trivalent arsenic compound and a compound containing divalent sulfur linked to carbon in amounts sufficient to decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

5. The process of reducing corrosion of a ferrous metal by an ammoniacal solution of an inorganic salt, which comprises incorporating in said solution both a trivalent arsenic compound and an alkali metal thiocyanate in amounts sufficient to decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

6. The process of reducing corrosion of a ferrous metal by a solution of ammonium nitrate containing free ammonia, which comprises incorporating in said solution a trivalent arsenic compound in amount sufficient to decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

7. The process of reducing corrosion of a ferrous metal by a solution of ammonium nitrate containing free ammonia, which comprises incorporating in said solution both a trivalent arsenic compound and a compound containing divalent sulfur linked to carbon in amounts suffi-

cient to decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

5 8. The process of reducing corrosion of a ferrous metal by a solution of ammonium nitrate containing free ammonia, which comprises incorporating in said solution both a trivalent arsenic compound and an alkali metal thiocyanate in amounts sufficient to decrease the rate of corrosion of a ferrous metal by said solution, and
10 contacting said solution with said ferrous metal.

9. The process of reducing corrosion of a ferrous metal by an ammoniacal solution of urea and a compound of carbon dioxide and ammonia, which comprises incorporating in said solution a
15 trivalent arsenic compound in amount sufficient to decrease the rate of corrosion of a ferrous metal by said solution, and contacting said solution with said ferrous metal.

20 10. As a new composition of matter of reduced corrosiveness with respect to ferrous metals, an ammoniacal solution of an inorganic salt containing a trivalent arsenic compound in amount sufficient to decrease the rate of corrosion of a ferrous
25 metal by said solution.

11. As a new composition of matter, an ammoniacal solution of an inorganic salt containing a trivalent arsenic compound and a compound containing divalent sulfur linked to carbon in amounts sufficient to decrease the rate of corrosion of a ferrous metal by said solution. 5

12. As a new composition of matter, an ammoniacal solution of ammonium nitrate containing a trivalent arsenic compound in amount sufficient to decrease the rate of corrosion of a ferrous metal by said solution. 10

13. As a new composition of matter, an ammoniacal solution of ammonium nitrate containing a trivalent arsenic compound and a compound containing divalent sulfur linked to carbon in
15 amounts sufficient to decrease the rate of corrosion of a ferrous metal by said solution.

14. As a new composition of matter, an ammoniacal solution of urea and a compound of ammonia and carbon dioxide containing a trivalent arsenic compound in amount sufficient to decrease the rate of corrosion of a ferrous metal by said solution. 20

HERMAN A. BEEKHUIS, JR.
CHARLES K. LAWRENCE. 25