Patented Feb. 22, 1949

2,462,638

UNITED STATES PATENT OFFICE

2,462,638

CORROSION INHIBITING PROCESS

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No Drawing. Application February 15, 1945, Serial No. 573,131

7 Claims. (Cl. 202—57)

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This invention relates to a process for inhibiting corrosion of metals. More particularly, it relates to a method for preventing the corrosive effects of aqueous solutions containing sulfuric acid and certain nitrogen compounds on 18–8 stainless steel (i. e. steel containing 16 to 23% chromium and 7 to 11% nickel), and modified 18–8 stainless steels.

It has been known heretofore that aqueous ammonium sulfate solutions containing 5% of free sulfuric acid attack 18–8 stainless steel (The Book of Stainless Steels, Thum, second edition, The American Society for Metals, 1935, page 386).

In the process for manufacturing hydrogen cyanide by dehydration of formamide (Larson, U. S. Patent 2,086,507) a reaction product is produced which contains in addition to water and hydrogen cyanide, minor amounts of ammonia and formamide. It is the usual practice in carrying out this process to scrub the effluent vapors with sulfuric acid of about 1% to 3% concentration, and thereafter to separate hydrogen cyanide from the resulting solution. The scrubbing operation generally is conducted by contacting the scrubbing liquor counter-currently witn the vapors from the hydrogen cyanide converter, whereby a solution containing about 5% hydrogen cyanide, and about 1% free sulfuric acid is obtained. This solution also contains varying amounts of ammonium sulfate and ammonium formate. Generally, the resulting solution is fed continuously to a stainless steel still, from which the hydrogen cyanide is removed overhead while the remaining acidic solution, containing only a trace of hydrogen cyanide, at a temperature of about 100° C., is withdrawn from the still. Thereafter, it is passed through a cooler, and a portion of the cooled solution is purged from the system. The necessary amount of make-up water and sulfuric acid are added, and the liquor is recycled to the hydrogen cyanide scrubbers. In carrying out this process, considerable difficulty has been encountered due to the corrosion of the stainless steel equipment by the dilute sulfuric acid solution containing the ammonium compounds.

An object of this invention is to provide a method for preventing the corrosion of 18–8 stainless steels and modified 18–8 stainless steels by dilute aqueous sulfuric acid solutions in the above-described process. Other objects of the invention will appear hereinafter.

The objects of the present invention are attained by employing about 0.0005% to 0.10%, preferably 0.0015% to 0.0020%, of copper in an ionizable form as a corrosion inhibitor. It has been discovered in accordance with this invention that, when the aforesaid amount of copper in ionizable form is mixed with a dilute aqueous solution containing sulfuric acid (preferably of 1% to 3% concentration) and ammonium compounds, corrosion of 18–8 and modified 18–8 stainless steels at temperatures within the range of about 20° to 105° C. is almost entirely prevented. By copper in ionizable form is meant copper in a form which is ionized or which forms copper ions in the solution under the conditions employed.

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The invention is illustrated further by means of the following example.

Example.—The effluent vapors from a hydrogen cyanide converter employed in a process such as that described in U. S. Patent 2,086,507 are scrubbed counter currently with an aqueous recycle liquor containing 2.5% of sulfuric acid, in an 18–8 SMO stainless steel (16 to 23% chromium, 7 to 11% nickel, less than 0.17% carbon, molybdenum modified) apparatus, and the resulting solution is stripped of hydrogen cyanide in a continuous still of the same material at a maximum temperature of 100° C. The solution entering the scrubber contains 4 parts per million of iron, and the liquor leaving the still contains 7 to 11 parts per million of iron. About ¼ of the solution leaving the still is purged, and a quantity of water and sulfuric acid sufficient to bring the solution to its initial volume and sulfuric acid content is added. The solution is then recycled to the scrubber. After a limited period of such use, the apparatus is found to be excessively corroded.

The above experiment is repeated exactly, except that copper is added to the recycled solution (to a concentration of 5 to 20 parts per million) in the form of copper sulfate ($CuSO_4 \cdot 5H_2O$), prior to pumping this solution into the scrubber. The iron content of the solution remains constant at 4 parts per million, and even after many months of use there is no noticeable corrosion of either the still or the scrubber.

While in the foregoing example the invention has been illustrated as applied to the prevention of corrosion of molybdenum-modified 18–8 stainless steel by solutions containing sulfuric acid and ammonium compounds, particularly in the scrub liquor employed in the purification of hydrogen cyanide, it will be understood that the invention is not limited thereto but may be uti-

lized in various processes wherein it is desired to prevent the attack of dilute sulfuric acid solutions of the same general nature.

Since the numerous embodiments of the invention may be made without departing from the spirit and scope thereof, it will be understood that I do not limit myself except as set forth in the following claims.

I claim:

1. In a process for preventing corrosion of metals during distillation of hydrogen cyanide from an aqueous solution of hydrogen cyanide, ammonium salts and sulfuric acid, obtained by scrubbing formamide decomposition products with dilute sulfuric acid containing from 1% to 3% by weight of sulfuric acid, the step which comprises contacting a distillation vessel made of steel having a chromium content of 16% to 23%, and a nickel content of 7% to 11%, with the said aqueous solution having dissolved therein from 0.0005% to 0.10% of copper in ionizable form, based on the weight of the said aqueous solution, whereby substantial corrosion of the said steel is prevented.

2. In a process for preventing corrosion of metals during distillation of hydrogen cyanide from an aqueous solution of hydrogen cyanide, ammonium salts and sulfuric acid obtained by scrubbing formamide decomposition products with dilute sulfuric acid containing from 1% to 3% by weight of sulfuric acid, the step which comprises contacting a distillation vessel made of steel having a chromium content of 16% to 23%, and a nickel content of 7% to 11%, with the said aqueous solution, having dissolved therein 0.0005% to 0.10% of copper in ionizable form, based on the weight of the said aqueous solution, at a temperature within the range of 20° to 105° C., whereby substantial corrosion of the said steel is prevented.

3. In a process for preventing corrosion of metals during distillation of hydrogen cyanide from an aqueous solution of hydrogen cyanide, ammonium salts and sulfuric acid obtained by scrubbing formamide decomposition products with dilute sulfuric acid containing from 1% to 3% by weight of sulfuric acid, the step which comprises contacting a distillation vessel made of steel having a chromium content of 16% to 23%, a nickel content of 7% to 11% and a minor proportion of molybdenum with a said aqueous solution having dissolved therein 0.0005% to 0.10% of copper in ionizable form, based on the weight of the said aqueous solution, at a temperature within the range of 20° to 105° C., whereby substantial corrosion of the said steel is prevented.

4. In a process for preventing corrosion of metals during distillation of hydrogen cyanide, from an aqueous solution of hydrogen cyanide, ammonium salts and sulfuric acid obtained by scrubbing formamide decomposition products with dilute sulfuric acid containing from 1% to 3% by weight of sulfuric acid, the step which comprises contacting a distillation vessel made of steel having a chromium content of 16% to 23%, a nickel content of 7% to 11%, and a minor proportion of molybdenum, with the said aqueous solution having dissolved therein 0.0015% to 0.0020% of copper in ionizable form, based on the weight of the said solution, at a temperature within the range of 20° to 105° C., whereby substantial corrosion of the said steel is prevented.

5. In a process for preventing corrosion of metals during distillation of hydrogen cyanide from an aqueous solution of hydrogen cyanide, ammonium salts and sulfuric acid obtained by scrubbing formamide decomposition products with dilute sulfuric acid containing about 2.5% by weight of sulfuric acid, the step which comprises contacting a distillation vessel made of steel having a chromium content of 16% to 23%, a nickel content of 7% to 11% and a minor proportion of molybdenum, with the said aqueous solution having dissolved therein 0.0015% to 0.0020% of copper in ionizable form, based on the weight of the said aqueous solution, at a temperature within the range of 20° to 105° C., whereby a substantial corrosion of the said steel is prevented.

6. In a process for preventing corrosion of metals during distillation of hydrogen cyanide from an aqueous solution of hydrogen cyanide, ammonium salts and sulfuric acid, obtained by scrubbing formamide decomposition products with dilute sulfuric acid containing about 2.5% by weight of sulfuric acid, the step which comprises contacting a distillation vessel made of steel having a chromium content of 16% to 23%, a nickel content of 7% to 11%, and a minor proportion of molybdenum with the said aqueous solution having dissolved therein from 0.0015% to 0.0020% of copper in ionizable form, based on the weight of the said solution, at a temperature within the range of 20° to 105° C., whereby substantial corrosion of the said steel is prevented.

7. In a process for preventing corrosion of metals during distillation of hydrogen cyanide from an aqueous solution of hydrogen cyanide, ammonium salts and sulfuric acid obtained by scrubbing formamide decomposition products with dilute aqueous sulfuric acid containing about 2.5% by weight of sulfuric acid, the steps which comprise contacting a distillation vessel made of steel having a chromium content of 16% to 23%, a nickel content of 7% to 11% and a minor proportion of molybdenum, with the said aqueous solution having dissolved therein 0.0015% to 0.0020% by weight of copper in an ionizable form, based on the weight of the said solution, and distilling hydrogen cyanide continuously from the said solution at a maximum temperature of about 100°, whereby corrosion of the steel in the said distillation vessel is inhibited.

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