United States Patent Office

3,015,630

Patented Jan. 2, 1962

3,015,630

AQUEOUS SOLUTION FOR STRIPPING NICKEL

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No Drawing. Filed Aug. 24, 1959, Ser. No. 835,426

9 Claims. (Cl. 252—101)

This invention relates to stripping solutions and more particularly, to stripping solutions for removing platings of nickel or nickel alloys.

Coatings of nickel are well known as corrosion inhibitors on the surface of articles subject to corrosive atmospheres. The deposition of such a coating through normal production procedures may produce in some situations a faulty coating which must be completely removed so that a new coating of nickel may be applied. Some nickel stripping solutions and compounds have been reported. However, in the case of complex assemblies such as, for example, steel coolant passages in heat exchangers having copper fins silver brazed to the steel, it has been found that prior available compositions for removing a nickel coating have not proven satisfactory. In many cases the stripping solutions pit, etch or otherwise injure the under surfaces of the copper, the silver braze or the steel. Although some of the commercial chemical stripping agents may satisfactorily strip nickel from individual materials, such solutions have been found to be relatively slow acting as well as unsuitable for removing nickel platings from such complex assemblies as copper-silver braze-steel assemblies.

It is a principal object of this invention to provide a class of stripping solutions which will remove defective nickel or nickel alloy coatings from simple as well as complex assemblies in such a manner that the surfaces underlying the nickel or nickel coating are not adversely affected or significantly dissolved.

It is another object of this invention to provide a stripping solution which removes nickel coatings from complex copper-silver brazed-steel assemblies within practical time limits.

It has been discovered that the foregoing and other objects of our invention can be obtained by the use of an aqueous stripping solution comprising nitric acid, sulfuric acid, water and an inhibitor in the form of at least one of the nitrates of silver, magnesium, cobalt, aluminum and nickel.

Initial studies indicated that inorganic acids were best suited as strippers of nickel coatings. Since both nitric and sulfuric acids are highly oxidizing inorganic acids it was considered that these be studied as a basis for a stripping solution.

To provide a suitable composition for stripping nickel from complex assemblies including copper base, silver base and iron base alloys and still avoid the objections to presently available commercial stripping solutions, it was found necessary to inhibit base metal acid attack through a judicious balance of acids and inhibitors while removing the nickel coating at a reasonable rate.

It was found that in solutions of nitric acid, steel is rapidly attacked with the reduction of the nitric acid. The iron in the steel is oxidized apparently to soluble ferrous nitrate, thus to allow the reaction to proceed readily. In concentrated solutions, however, the steel is passivated and suffers little attack due to the formation of an insoluble adherent film on the metal surface.

Copper, on the other hand, is readily attacked by nitric

acid. Unlike steel, it does not become passive at the higher acid concentrations.

Nitric acid, however, was selected as the principal reactant or stripping agent. A series of aqueous solutions were prepared containing HNO_3 in the range of 10–69% to enable selection of a useful HNO_3 range. (All percentages mentioned herein are percent by weight unless specifically designated otherwise.)

Although it was found that nickel was removed at a suitable rate within the 20–70% HNO_3 range, 35–60% HNO_3 was most attractive. Nevertheless, copper, iron or silver based metals were attacked by the acid at an undesirable rate.

It was found that an addition of as little as 1% H_2SO_4 in the presence of silver nitrate showed considerable reduction in iron base material attack rate over the above listed aqueous nitric acid solutions. However, copper and silver were still rapidly attacked. A solution of 38.5% HNO_3, 19.8% H_2SO_4 and 2.4% $AgNO_3$ completely inhibited all action on steel after immersion for one hour at 80° F. and greatly reduced attack on the copper and silver.

By increasing the H_2SO_4 to about 31% and reducing the HNO_3 to about 33% in a saturated silver nitrate solution, it was found that attack was suitably inhibited on copper and silver as well as on the iron in a complex copper-silver braze-steel assembly.

In order to establish a useful range for nickel removal from materials based on copper, iron or silver or their combinations in complex assemblies, a large number of solutions were prepared some of which are listed in the following Table I:

TABLE I

Useful aqueous stripping solutions (80° F.) percent by weight)

Ex.	HNO_3	H_2SO_4	Inhibitor	Remarks
2A	66.3	1.25	0.7 $AgNO_3$	Fe O.K.; slow attack on Ag and Cu.
5A	38.5	19.8	2.4 $AgNO_3$	Do.
5C	33.1	31.1	1.7 $AgNO_3$	Cu and Fe O.K.; slow attack on Ag.
7B	25.1	47.3	1.2 $AgNO_3$	Cu, Fe, Ag O.K.
11A	26.2	49.3	1.2 $AgNO_3$	Do.
13A	23.9	45.0	6.0 $Mg(NO_3)_2$	Do.
13F	23.9	45.0	6.0 $Ni(NO_3)_2$	Do.

At this point it was established that a satisfactory stripping solution for steel alone comprised of 20–70% HNO_3 with at least 1% H_2SO_4 in the presence of a nitrate inhibitor. However, it was found that at least 20% H_2SO_4 was required and preferably 45–50% H_2SO_4 should be included along with the nitrate inhibitor to prevent the HNO_3 from attacking copper during the nickel stripping period.

Regarding the combination of steel, copper and silver braze, it was established that a range of 23–28% HNO_3 and 45–50% H_2SO_4 with a nitrate inhibitor gave superior results.

Since a weak link in a copper-silver braze-steel composite was the silver braze, a series of tests was conducted to study the effective range and type of nitrate inhibitor on the action of nitric acid and to study the degree of cooperation of such inhibitors with sulfuric acid to prevent etching of silver braze. Nitrates of cobalt, magnesium, aluminum and nickel were found to be most effective in addition to silver nitrate shown in Table I. Some of the solutions which were prepared in this series of tests are listed in Table II.

TABLE II

Useful aqueous stripping solutions tested on silver braze: 50Ag–18Cd–16.5Zn 15.5 Cu. at 80° F. (percent by weight)

Example	HNO_3	H_2SO_4	Inhibitor	Corrosion rate (inches per year)
15A	33.6	31.7	None	0.822
15B	33.6	31.7	1.7 $AgNO_3$	0.416
15D	32.0	30.1	5.0 $Mg(NO_3)_2$	0.115
15C	32.0	30.1	5.0 $Ni(NO_3)_2$	0.072
I-1	25.1	47.9	None	0.410
I-2	25.1	47.3	1.2 $AgNO_3$	0.259
I-4	24.7	46.5	2.9 $Cr(NO_3)_2$	0.598
I-5	24.7	46.5	2.9 $Cu(NO_3)_2$	0.561
I-6	24.7	46.5	2.9 KNO_3	0.599
I-8	24.7	46.5	2.9 $Al(NO_3)_3.9H_2O$	0.156
I-10	24.7	46.5	2.9 $Mg(NO_3)_2.6H_2O$	0.0015
I-12	24.7	46.5	2.9 $Ni(NO_3)_2.6H_2O$	.005
I-13	24.7	46.5	2.9 $Ba(NO_3)_2$	[1] 0.369
I-14	24.7	46.5	2.9 $Pb(NO_3)_2$	[1] 0.326
I-15	24.7	46.5	2.9 $Co(NO_3)_2$	0.175
I-17	24.0	45.1	5.7 $Fe(NO_3)_3.9H_2O$	0.666

[1] Severe pitting.

A method which can be used to make the stripping solution of this invention involves first dissolving the nitrate inhibitor in the water before adding the acids. If aqueous solutions of HNO_3 (for example 70% HNO_3) or of H_2SO_4 (for example 95%) are used, allowance should be made for the water they contain.

The acids are then added slowly to the water-nitrate solution to prevent excessive heat formation. The solution is then allowed to cool to the desired operating temperature.

When silver nitrate is used as an inhibitor, a white precipitate of Ag_2SO_4 may form upon cooling to room temperature. However, this precipitate will not affect the solution or its stripping properties.

The stripping rate of the solution is somewhat dependent upon its temperature. Although increased rates can be obtained at 100° F. over those at 80° F., it is preferred that the temperature be maintained below about 105° F. to avoid base metal pitting under certain instances noted at about 110° F. in some cases.

Although this invention has been described in connection with specific examples, those skilled in the art of electroplating, cleaning and stripping will readily recognize the modifications and variations of which this invention is capable.

What we claim is:

1. An aqueous solution for stripping nickel consisting essentially of in percent by weight 20–70 HNO_3; at least 1 H_2SO_4; at least 0.5 of a metal nitrate, the metal of said metal nitrate being selected from the group consisting of silver, magnesium, cobalt, aluminum and nickel; with the balance water.

2. An aqueous solution for stripping nickel consisting essentially of in percent by weight 20–70 HNO_3; 20–50 H_2SO_4; 0.5–6 of a metal nitrate, the metal of said metal nitrate being selected from the group consisting of silver, magnesium, cobalt, aluminum and nickel, with the balance water.

3. An aqueous solution for stripping nickel consisting essentially of in percent by weight 35–60 HNO_3; 30–50 H_2SO_4; 0.5–6 of a metal nitrate, the metal of said metal nitrate being selected from the group consisting of silver, magnesium, cobalt, aluminum and nickel, with the balance water.

4. An aqueous solution for stripping nickel consisting essentially of in percent by weight 23–28 HNO_3; 45–50 H_2SO_4; 0.5–2.4 of a nitrate of silver; with the balance water.

5. An aqueous solution for stripping nickel consisting essentially of in percent by weight 23–28 HNO_3; 45–50 H_2SO_4; 2–6 of a nitrate of magnesium; with the balance water.

6. An aqueous solution for stripping nickel consisting essentially of in percent by weight 23–28 HNO_3; 45–50 H_2SO_4; 2–6 of a nitrate of cobalt; with the balance water.

7. An aqueous solution for stripping nickel consisting essentially of in percent by weight 23–28 HNO_3; 45–50 H_2SO_4; 2–6 of a nitrate of nickel; with the balance water.

8. An aqueous solution for stripping nickel consisting essentially of in percent by weight 23–28 HNO_3; 45–50 H_2SO_4; 2–6 of a nitrate of aluminum; with the balance water.

9. An aqueous solution for stripping nickel consisting essentially of, in percent by weight, 23–28 HNO_3; 45–50 H_2SO_4; 0.5–6 of a metal nitrate, the metal of said metal nitrate being selected from the group consisting of silver, magnesium, cobalt, aluminum and nickel, with the balance water.

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