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Selective removal of nickel from iron substrate by non-cyanide strippers①

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Abstract: A novel nickel stripper using ammonia as the key component was developed to substitute cyanide for removing nickel film from iron substrates. Its compositions are: ammonia 150 g/L, hydrogen peroxide 50 g/L, ammonium chloride 100 g/L, EDTA 7.5 g/L, copper chloride 15 g/L and glucopyrone 1.2 g/L. The optimum operating conditions are: pH 9.5-11, temperature 40-50 ℃ and stripping time 1 h. It shows many advantages over the traditional cyanide stripper including no toxicity, mild operation, lower cost, larger holding capacity, faster stripping rate and good protection for the base metal, and can meet the technical requirements in industry.

Key words: nickel stripping; non-cyanide composition; environment-friendly technology
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1 INTRODUCTION

Many different types of fabricated articles and parts are plated with nickel or a nickel alloy[1]. However, many of these types of parts may be rejected by prescribed quality standards in the production because they contain slight or gross imperfections. Consequently, it becomes necessary to remove the nickel or nickel alloy coating, reclaim the base substrate, and then recoat the substrate with a nickel containing material. In general, nickel metals can be removed from a substrate by immersing the article in a stripper containing preferably at least an oxidizing agent and a strong ligand, and their combination is designed to remove the nickel metal without harming the underlying substrate. The stripper compositions can be explained by the following equation from the point of chemistry[2]:

$$S(\text{stripper}) = Lig + Ox + Ad_1 + Ad_2 \quad (1)$$

where Lig represents ligands for metals(Ni/Sn) and its function is to form stable complexes with the target metals in aqueous solution, such as $Ni(CN)_4^{2-}$; Ox means oxidants to transform metals to higher oxidation states(i. e. Ni/Sn → Ni(Ⅱ)/Sn(Ⅳ)), such as hydrogen peroxide; Ad_1 is the substrate corrosion inhibitor and designed to protect the base metals during the finishing process, and Ad_2 represents the other additives in the stripper including accelerator, pH adjuster and surfactant, etc. Traditionally the cyanide-type stripper has been wildly used in industry because its convenient operation and good protection of the substrates. However the treatment of the spent cyanide solution is a nightmare. In the past, various processes have been proposed for stripping defective nickel coatings from substrates. In Ref. [3], a nickel strip formulation is disclosed for stripping nickel and nickel alloys from metallic and non-metallic substrates. Herein, the nickel strip formulation includes a single nitro compound as the oxidizing agent, a sulfide ion as accelerator and a zwitterion. The zwitterion acts as both ligand for the metal being dissolved and buffer to control the pH of the stripper. Bastenbeck[4] and Lash[5] reported an acid composition which contains sulfamate, nitrate, chloride, and preferably an oxidant such as hydrogen peroxide, a complexing agent such as ethylene diamine tetraacetrate. It showed many advantages such as fast stripping rate, complete removal of nickel coatings and excellent color remained after finishing. However it has disadvantages such as significant attack on the substrate and serious exothermal reaction, which leads it difficult to be accepted by the industry. Rao[6] and Li[7] reported an effective ligand for extraction of nickel in alkaline media, but the direct cost seems a challenge unless using recycling process to recover it. Another nickel stripper is invented by Lash[8] which is an alkaline solution comprising a nitro-substituted aromatic compound, elemental sulfur, and especially alkali phos-

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phate as the corrosion attack inhibitor, but it results in slow-down of the stripping process and new environmental trouble of phosphorus. Maybe the copper etching is a inspiring process for us to seek new methods to selectively dissolve nickel at lower costs, in which the copper is etched by ammonia with Cu(Ⅱ) salt as accelerator and air as oxidant[9, 10].

A novel stripper with lower cost, fast rate, good protection of the base metal and mild operation is directed to remove nickel from iron substrate in the present paper, in which ammonia-ammonium chloride buffer, cuperous chloride, hydrogen peroxide, sodium ethylene diamine tetraacetrate (EDTA) and glucopyrone functions as nickel ligand(Lig) and pH adjuster, stripping accelerator, oxidant, oxidant stabilizer and ferrous corrosion inhibitor, respectively. The stripping process can be explained as the following reactions:

$$Ni + 6NH_3 + H_2O_2 \rightarrow Ni(NH_3)_6^{2+} + 2OH^- \quad (2)$$

$$Ni + 6NH_3 + 2Cu(NH_3)_4^{2+} \rightarrow Ni(NH_3)_6^{2+} + 2Cu(NH_3)_4^{+} \quad (3)$$

$$H_2O_2 + 2Cu(NH_3)_4^{+} \rightarrow 2OH^- + 2Cu(NH_3)_4^{2+} \quad (4)$$

Batch tests were conducted to establish the optimum conditions such as operation temperature, pH, concentration of the ingredients, etc.

2 EXPERIMENTAL

Reagents of ammonia, ammonium chloride, cupric chloride, hydrogen peroxide, hydrochloric acid, sodium ethylene diamine tetraacetrate (EDTA) and glucopyrone were AR grade and purchased from Aldrich-Sigma Company. Electroplated nickel plates with 12 μm nickel film on the iron base were provided by Inco Corp and shaped in 3 cm × 5 cm size as the samples. A working solution simulated to copper etchant[11-13] was prepared by containing 50 g/L H_2O_2, 150 g/L $NH_3 \cdot H_2O$, 100 g/L NH_4Cl and 7.5 g/L EDTA, and was used as a basis to seek the optimum operating parameters. All stripping tests were finished in a water-bath device at fixed time(1-2 h) corresponding to that in industry and at fixed solid-liquid ratio of 1 cm^2 Ni plate/mL stripper except for capacity tests. In all tests the operation temperature was fixed (±1 ℃) and one or several sampling plates were placed in a 100 mL beaker poured with different compositions. The stripped plates were rinsed with 1% HCl solution to remove possible sludge on their surface and cleaned by distilled water before drying at (100 ±5) ℃. The nickel lost(specifically the relative Ni stripped) in each test was calculated by the plate mass difference before and after stripping process, and this index was used to estimate the stripping properties of the composition such as speed, holding capacity. Iron attack under different conditions were calculated from the Fe concentration measured by AAS(atomic adsorption spectroscopy) in the residual solution. A compromised results from the above two was used to assess the stripper compositions. Generally a comprehensive index of nickel stripping rate ≥20 mg/($cm^2 \cdot h$), nickel holding capacity ≥ 30 g/L(stripper) and iron attack ≤0.2 mg/($cm^2 \cdot h$) can be accepted by industry[1].

3 RESULTS AND DISCUSSION

3.1 Optimum stripping pH

Fig. 1 shows the relationship between pH and the nickel removal in the working solution at ambient temperature((30 ±1) ℃). The solution pH was adjusted by hydrochloric acid or ammonia and the stripping time maintained the same(2 h).

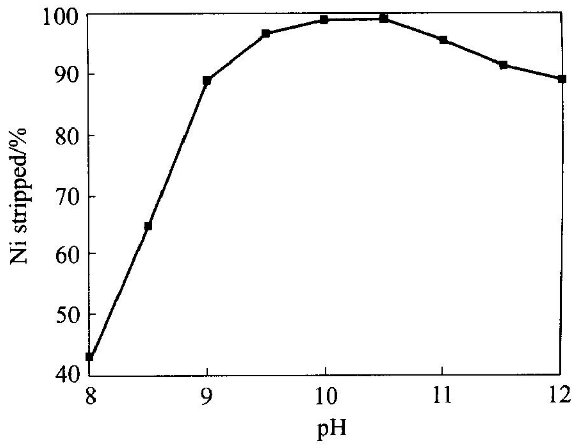

Fig. 1 Effect of pH on Ni stripping

Evidently the nickel dissolving process is very sensitive to pH of the stripper and the preferred pH is 9.5-11. Because at lower pH the free ammonia concentration is low, but at higher pH the possible side-reaction of Ni(Ⅱ) precipitation may become serious and results in some films on nickel surface[7].

3.2 Operation temperature

Fig. 2 shows the nickel removal at different operation temperature. In each test the pH of the working solution was fixed at 10 ±0.1 and the stripping time maintained the same (2 h).

Obviously the nickel stripping process rely closely on the operation temperature and the optimum temperature is 40-50 ℃. It is easy to understand that the stripping rate is slow at low temperature, and it also goes down when temperature becomes too high because of the significant evaporation of ammonia and the possible precipitation such as $Ni(OH)_2$, $Ni(OH)Cl$. One advantage of this stripper is the mild

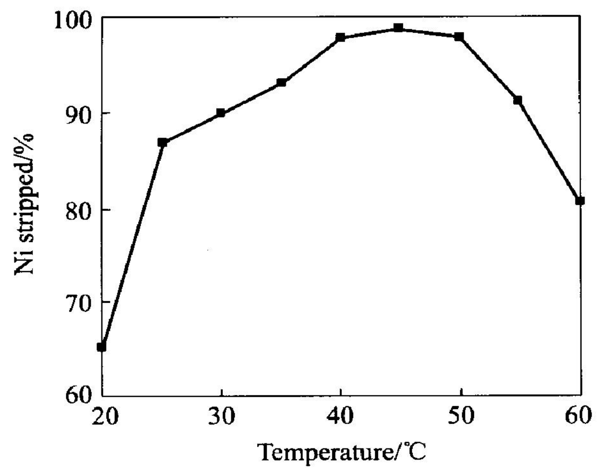

Fig. 2 Effect of temperature on Ni stripping

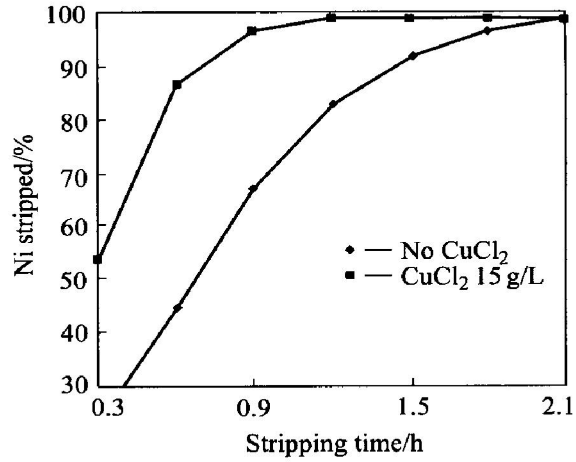

Fig. 4 Kinetics comparison

operation compared to cyanide-type, in which temperature should be maintained at 85 ~ 90 ℃, so it results in serious air pollution because of the evaporative cyanide besides its notorious wastewater problem.

3.3 Stripping accelerator

$Cu(NH_3)_4Cl_2$ (transformed from $CuCl_2$ in ammonia media) is one of the cheapest accelerators used in alkaline media to promote oxidation-reduction process, and is widely applied in metal corrosion, etching, and surface finishing[10, 12]. The promotion of Cu(II) on nickel stripping can be seen from Fig. 3 (1 h) and Fig. 4, where pH and temperature are controlled at (10 ±0.1) and (45 ±1) ℃, respectively.

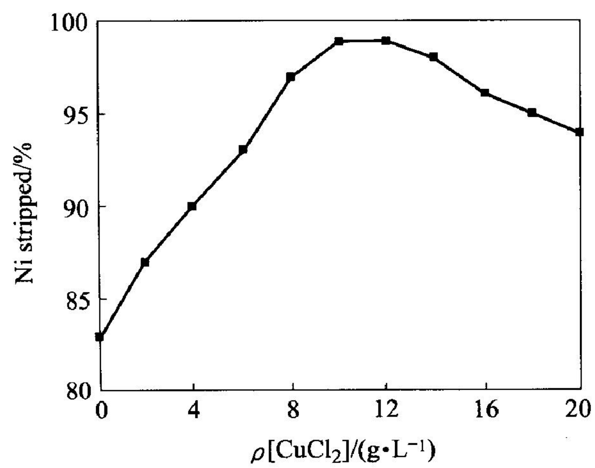

Fig. 3 Cu(II) promotion on Ni stripping

It is clear that $CuCl_2$ dosage should be 8 ~ 16 g/L and preferably 10 ~ 15 g/L, as shown in Fig. 3. A possible explanation for the negative effect of higher $CuCl_2$ concentration (≥16 g/L) on nickel dissolution is that a thin copper film may be partially formed on the nickel surface and isolates some nickel surface from solution, especially at the late stage when H_2O_2 concentration goes down sharply. Fig. 4 reflects more clearly the kinetic difference of strippers containing or without accelerator, and 12 μm nickel film can be effectively removed in 1 h when using 15 g/L $CuCl_2$ as accelerator.

3.4 Iron protection

Glucopyrone is a very useful iron-corrosion inhibitor[14, 15] with higher selectivity and lower dosage in alkaline media. Fig. 5 and Fig. 6 show the effects of glucopyrone on both nickel stripping process and iron protection, respectively. The operating parameters of the working solution are: temperature (45 ± 1) ℃, stripping time 1 h, pH 10 ±0.1 and 15 g/L $CuCl_2$.

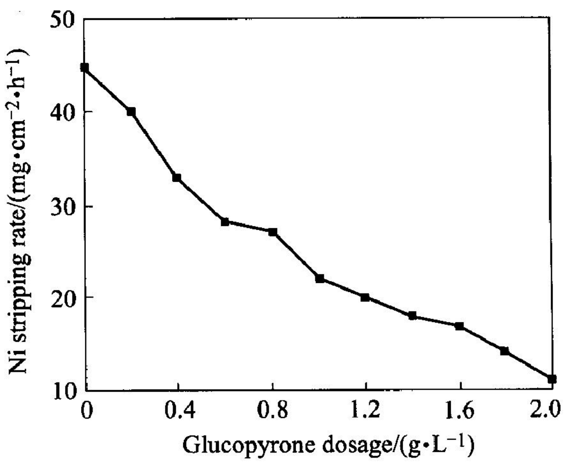

Fig. 5 Glucopyrone retarding on Ni stripping

Fig. 5 and Fig. 6 indicate that the concentration of glucopyrone should be controlled below 1.4 g/L to maintain the nickel stripping rate at a practical scale (≥20 mg/(cm^2·h)) and higher than 1.0 g/L to keep iron corrosion at lower rate (≤0.2 mg/(cm^2·h)), respectively. As a compromised result the glucopyrone dosage is selected at (1.0 ~ 1.4) g/L.

3.5 Holding capacity and comparison with cyanide

A series of capacity tests (150 g/L $NH_3·H_2O$,

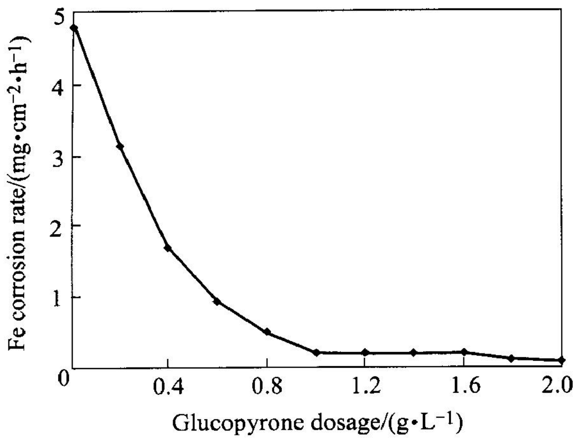

Fig. 6 Glucopyrone inhibition on Fe corrosion

100 g/L NH_4Cl, 7.5 g/L EDTA, 50 g/L H_2O_2, 15 g/L $CuCl_2$, 1.2 g/L glucopyrone, temperature 40 − 50 ℃, stripping time 1 h, pH = 10 − 11) including comparison with cyanide (90 g/L NaCN, 35 g/L NaOH, 100 g/L NBS, temperature 85 − 90 ℃, stripping time 1 h, pH = 10 − 11) were finished and the average results were listed in Table 1.

Table 1 Technical index review

Method	Ni stripping rate/(mg·cm^{-2}·h^{-1})	Fe attack/(mg·cm^{-2}·h^{-1})	Capacity(Ni)/(g·L^{-1})
Non-cyanide	25.3	0.15	41.3
Cyanide	21.7	0.15	32.5

A comprehensive estimation about this ammonia-type stripper can be got clearly from Table 1. Its advantages over the traditional cyanide stripper are without toxicity, mild operation temperature, good protection of the base metal, faster nickel-stripping rate and larger holding capacity.

4 CONCLUSIONS

The newly developed ammonia-type nickel stripper can selectively remove nickel from iron base. Its compositions are: ammonia 150 g/L, hydrogen peroxide 50 g/L, ammonium chloride 100 g/L, EDTA 7.5 g/L, copper chloride 15 g/L and glucopyrone 1.2 g/L. The optimum operating conditions are: pH9.5 − 11, temperature 40 − 50 ℃ and stripping time 1 h. The application index are: nickel holding capacity 41.3 g/L, stripping rate 25.3 mg/(cm^2·h) and iron attack 0.15 mg/(cm^2·h), which can meet the present technical requirements in industry. It shows better technical index than that of the traditional cyanide and is a prospective substitute for cyanide-type stripper.

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