Front. For. China (2006) 3: 357–360
DOI 10.1007/s11461-006-0008-6

RESEARCH ARTICLE

WANG Lijuan, LI Jian, LIAN Aizhen

Regeneration and reuse of exhausted solutions of electroless nickel plating wood veneer

Abstract The regeneration of exhausted solutions of electroless nickel plating wood veneer was realized using soluble calcium salt to precipitate and remove phosphite and then using fluoride to remove residual calcium ions from the solution. The effect of the pH value of the solution, treatment temperature and the molar ratio of calcium ions to phosphite ions on the removal efficiency of phosphite was investigated. Wood veneer was electroless plated using regenerated solutions. A coating with better electrical conductivity and electromagnetic shielding was obtained.

Keywords electroless nickel plating, wood, regeneration of exhausted solution, electrical conductivity, electromagnetic shielding

1 Introduction

Some chemical composites such as complex agents, buffering agents and stabilizers in addition to nickel ions, phosphites and hypophosphites occur in exhausted electroless plating solutions. These are pollutants and their disposal is supervised by the Central Government. The consumption of nickel is very large in the world, and this would make nickel insufficient in the future. It is important and necessary to purify and reuse exhausted plating solutions to save resources, protect the environment and decrease costs (Zhang et al., 2002).

In this study, solutions, formed after plating larch veneer, were purified and regenerated by a calcium chloride precipitation process. The regenerated solutions were used to plate larch veneer. Electrical conductivity and electromagnetic shielding were measured.

Translated from *Journal of Northeast Forestry University,* 2005, 33(3): 47–48 [译自:东北林业大学学报, 2005, 33(3): 47–48]

WANG Lijuan (✉), LI Jian, LIAN Aizhen
Key Laboratory of Bio-based Material Science and Technology,
Northeast Forestry University,
Ministry of Education, Harbin 150040, China
E-mail: donglinwlj@sohu.com

2 Theory

When nickel plating solutions are used for a long period, phosphite, sodium and sulphate ions and other accessory substances accumulate to a certain concentration level that affects the deposition of nickel and phosphor.

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+$$

Phosphite and sulphate ions can be removed using calcium chloride as precipitator. Residual calcium ions are removed using NaF; this can avoid pollution of the plating solution.

2.1 Removal of phosphite and sulphate ions

Under acidic conditions: $Ca^{2+} + 2H_2PO_3^- \rightarrow Ca(H_2PO_3)_2 \downarrow$ $K_{sp}^{\phi} = 10^{-3.7}$

Under alkaline conditions: $Ca^{2+} + HPO_3^{2-} \rightarrow CaHPO_3 \downarrow$ $K_{sp}^{\phi}=10^{-4.0}$

Sulphate ion was removed by the reaction: $Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \downarrow$ $K_{sp}^{\phi}=6.3\times10^{-5}$

2.2 Removal of residual calcium ions

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \downarrow$$

Fluoride can be used to control a concentration of calcium ions because the solubility product of calcium fluoride is very low. Calcium fluoride granules are extremely small and can be removed by centrifugal separation. Also, fluoride can enhance the plating rate and improve the hardness of the layer obtained.

3 Materials and methods

3.1 Experimental equipment

The following equipment has been used in our experiment: an H-8 digital display constant temperature water bath, a

portable pH meter, an Agilent E4402B spectrum analyzer, a standard butt coaxial cable line with flange, a YD2511A model intelligent low-resistance measuring instrument and a scanning electron microscope, model of HITACHI-4700A.

3.2 Analytical methods

Nickel ion was measured using the method of GB/T15555.10 (1995). We used the method of testing the content of phosphite as described (Liu, 2001). A precipitation process was used to analyze calcium ions. A small amount of calcium ion in the plating solution was precipitated by NaF and the concentration calculated according to the amount of CaF_2 precipitate.

3.3 Experimental procedures

In the experiment, the alkaline solution in which $NiSO_4$ was used as the main salt and sodium hypophosphite as the reducing agent was used to plate wood veneer four times before it became an exhausted solution.

Plating samples of concentric circles with an outer diameter of 115 mm and an inner diameter of 12 mm were prepared using wood veneers from *Larlix gmelini* with a thickness of 0.6 mm.

To analyze the chemical composition of the exhausted solution, a calcium chloride solution was added to 25 mL of exhausted plating solution; ammonia or glacial acetic can be used to adjust the pH. After that, a certain amount of distilled water was added to the solution until it reached 50 mL. A clear solution was obtained by stirring for 0.5 h, slowly boiling for 14 h and finally filtering the solution. The removal efficiency of phosphite ion was calculated.

The exhausted solution was treated with calcium chloride and further processed with NaF, which made the removal of the residual calcium ions possible by centrifugal separation. A regenerated solution was made by supplying some chemical compounds and adjusting the pH to the same level as the new plating solution.

The pre-treated larch samples were plated by the regenerated solution. The nickel-plated veneer was dried and its electromagnetic shielding and electrical conductivity were measured.

3.4 Measurement of surface resistance

The surface resistance of the metallized wood veneers was evaluated using the method designed according to GJB2604-96 (1996).

3.5 Measurement of electromagnetic shielding effectiveness

The shielding effectiveness of the electro-conductive wood veneers was measured using the method of SJ20524-95 (1995).

4 Results and discussion

4.1 Removal efficiency of phosphite and loss of nickel ions

4.1.1 Effect of pH value

As shown in Fig. 1, given a constant molar ratio, the removal efficiency of phosphite is low when the pH value is low (for example pH = 4); however, the removal efficiency increases noticeably with pH values improving from 4 to 5. The improvement is small when the pH value increases from 6 to 7. This is because the reaction is easier under acidic condition. According to this reaction: $Ca(H_2PO_3)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_3PO_3$, the concentration of H^+ is becoming lower with improved pH so that the trend of dissolution reaction is small. When pH is close to or more than 7, the main reactions to form $Ca(HPO_3)_2$ and $CaHPO_3$ will have very little effect. Thus, the removal efficiency of phosphite is higher under higher pH value when other conditions are kept constant.

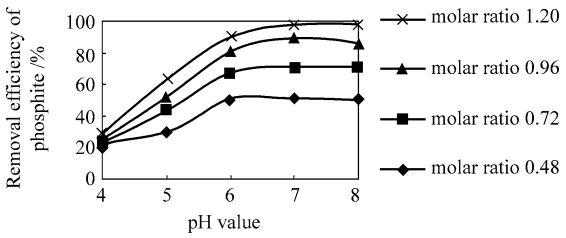

Fig. 1 Effect of pH value on removal efficiency of phosphite

As indicated in Table 1, the loss of nickel ions increases with improved pH values. The reaction that leads to the loss of nickel ions is: $Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \downarrow$. The concentration of hydroxyl increases with rising pH values, which causes more nickel ions to change to nickel hydroxide precipitate, i.e., the loss of nickel ions also increases. Considering prevailing conditions, we think the suitable pH value is 6. The removal efficiency of phosphite can be as high as 90% and under this condition the loss of nickel ions is lower.

Table 1 Effect of pH value on loss of nickel ions

pH value	Concentration of nickel sulfate /(g·L^{-1})	Loss of nickel ion /(g·L^{-1})
4	15.63	0.135
5	15.43	0.335
6	15.33	0.435
7	15.28	0.485

4.1.2 Effect of molar ratio of calcium chloride to phosphite

The effect of the molar ratio of calcium chloride to phosphite on the removal efficiency of phosphite is shown in Fig. 2. An increase in the concentration of calcium chloride can make the chemical equilibrium move to precipitate forming. However, using too much calcium chloride can

lead to more residual calcium ions in the solution when the reaction reaches a chemical equilibrium, which will pollute the plating solution again. Therefore, we take the optimal molar ratio of calcium chloride to phosphite to be 0.72, considering both removal efficiency of phosphite and a solution polluted by calcium ions.

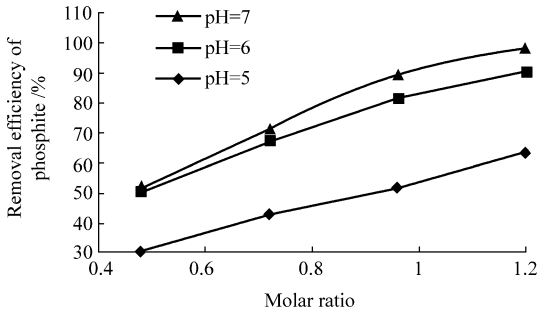

Fig. 2 The effect of molar ratio of calcium chloride to phosphite on the removal efficiency of phosphite

4.1.3 Effect of treatment temperature

Figure 3 shows that the removal efficiency of phosphite increases with rising treatment temperatures. On the one hand, increasing temperatures can cause the chemical equilibrium to move to form precipitate because the precipitation reaction $Ca^{2+} + 2H_2PO_3^- \rightarrow Ca(H_2PO_3)_2 \downarrow$ is an endothermic reaction. On the other hand, increasing temperatures can speed up the reaction and shorten reaction time. However, the removal efficiency of phosphite decreases when the treatment temperature reaches a specified value. The reason is that hypophosphite oxidizes to form phosphite continuously under higher temperatures.

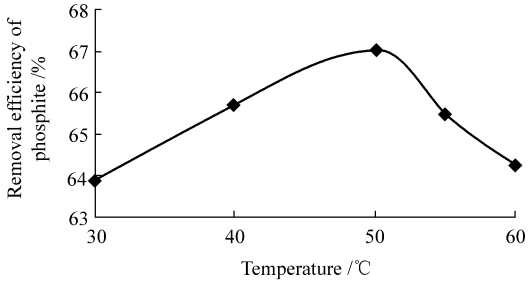

Fig. 3 Effect of treatment temperature on removal efficiency of phosphite

Table 2 Effect of treatment temperature on loss of nickel ions

Temperature /℃	Concentration of nickel sulfate /(g·L^{-1})	Loss of nickel ion /(g·L^{-1})
30	10.83	4.94
40	13.63	2.14
50	15.53	0.24
55	14.48	1.29
60	11.73	4.04

It is indicated in Table 2 that the loss of nickel ions decreases with an increase in temperature when the temperature is below 50ºC; however, it increases under higher temperatures. The suitable treatment temperature is 50ºC.

4.1.4 Effect of treatment time

As shown in Fig. 4, increasing the treatment time has a noticeable effect on the removal efficiency of phosphite when it is less than 8 h. The removal efficiency of phosphite remains almost constant when the treatment time is prolonged beyond 8 h. We found that the plating solution began to decompose after 24 h.

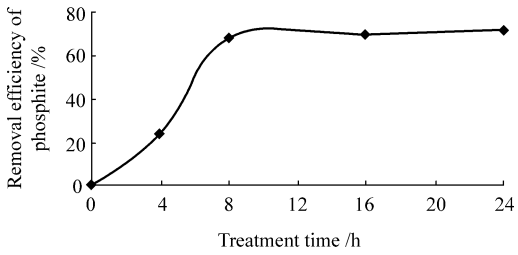

Fig. 4 Effect of treatment time on removal efficiency of phosphite

4.2 Removal of residual calcium ions

Under optimum conditions, residual calcium ions remained in the solution after phosphite was removed. When this solution was supplied to the same concentration as the new plating solution with each composite and used to plate larch wood veneers, it was found that salt crystal with very poor conductivity deposited on the layers, compared with the symmetrical and successive layers obtained from new plating solutions. Through an EDS analysis, we found that the salt crystal was calcium phosphite. The deposition of calcium phosphite crystallization seriously affected the uniformity and continuity of the layers. It is, therefore, necessary to remove residual calcium ions after phosphite is removed, using calcium chloride, which can ensure that we obtain layers with a good performance using regenerated solutions.

To eliminate adverse effects, residual calcium must be removed. The concentration of calcium ions can be controlled on a very small scale using fluoride, because the solubility product constant is small. Fluoride can accelerate the plating rate and a small quantity of fluoride ions will not affect the quality of layers and make the plating process easy. Therefore, sodium fluoride is used to remove residual calcium ions.

4.3 Comparison of regenerated solution with new plating solution

The electrical surface resistance and electromagnetic

shielding effectiveness of layers plated by regenerated and new plating solution are shown in Table 3 and Fig. 5, respectively. The results show that the electrical surface resistance and electromagnetic shielding effectiveness of layers plated by regenerated solutions are close to those obtained by new plating solutions. Its surface resistance ranges from 0.1 to 1 Ω. Its electromagnetic shielding effectiveness is higher than 55 dB with frequencies ranging from 9 kHz to 1.5 GHz, which touches the GJB standard (GJB2604-96, 1996). This indicates that regenerated solutions have a good plating performance.

Table 3 Comparison of electrical conductivity of wood plated by new plating solution and regenerated solution

Test	New plating solution		Regenerated solution	
	Across fiber	Parallel fiber	Across fiber	Parallel fiber
Surface resistance /Ω	0.527,7	0.352,0	0.708,7	0.553,6

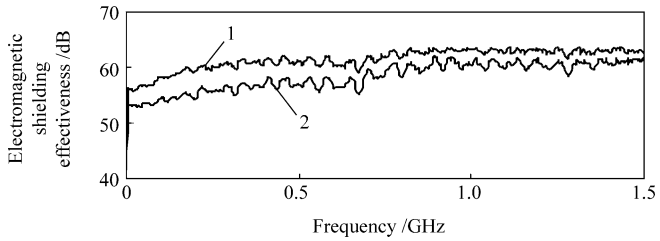

Fig. 5 Comparison of electromagnetic shielding effectiveness of wood plated by new plating solution (1) and regenerated solution (2)

5 Conclusion

1. It is practical to produce regenerated solutions by secondary precipitations. We used soluble calcium salt first and fluoride next.

2. The removal efficiency of phosphite is optimal under the following conditions: a pH value of 6.0, a molar ratio of calcium chloride to phosphite of 0.72, a treatment temperature of 50ºC and an 8 h treatment time.

3. Electrical surface resistance and electromagnetic shielding effectiveness of layers plated by regenerated solution are close to those obtained by new plating solutions. This indicates that purified and regenerated solutions have a good plating performance.

4. Exhausted solutions for nickel plating were successfully purified and regenerated, which established a good foundation for reducing environmental pollution and provided wide applications of nickel plating technology.

References

GB/T15555.10-1995, Solid Waste-determination of nickel- dimethylglyo xime spectrophotometric method, 1995 [GB/T15555.10-1995, 固体废物镍的测定丁二酮肪分光光度法, 1995]

GJB2604-96, Standard regulation of military electromagnetic shielding paint, 1996 [GJB2604-96，军用电磁波屏蔽涂料通用规范，1996]

Liu Z. J., A Study on Stability of Electroless Ni-P Solution [Dissertation], Kunming: Kunming University of Science and Technology, 2001: 25-36 [刘志坚，化学镀镍溶液的稳定性研究[学位论文]，昆明：昆明理工大学，2001: 25–36]

SJ20524-95, Measurement method of shielding effectiveness, 1995 [SJ20524-95, 材料屏蔽效能的测量方法, 1995]

Zhang Y., Zhang J. Y., Fang Y. K., Regeneration and reuse of electroless nickel plating exhausted solution, Plat. Finish., 2002, 24(1): 5–7, 17 [张翼，张婧元，方永奎，化学镀镍液的再生与回用，电镀与精饰，2002, 24(1): 5–7, 17]