

Preparation of salt-based colloid palladium of high concentration^①

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Abstract: A kind of salt-based colloid palladium of high concentration was prepared, with concentration up to 3.6 g/L on amount of PdCl₂. The optimal preparation conditions of the salt-based colloid palladium were that the PdCl₂ and NaCl concentrations were respectively 3.6 g/L and 175 g/L, mole ratio of Sn to Pd was 50:1, reaction temperature was 20~35 °C, with urea, ascorbic acid and vanillin added in a proper amount. The test results of optimal condition show that the time of starting hydrogen-deposition is 9 s, the time of completely coating copper on a test substrate is 2 min, the stability time of colloid palladium is 98 h after it is diluted into 0.1 g/L (on amount of PdCl₂) when the solution temperature is 20 °C, the backlight lever of electroless copper plating layer is 10th grade of 10-grade system, the adhesion force of the copper layer is up to GB5270-85 of China, and the average particle size of the colloid palladium is 81 nm measured by Master Sizer.

Key words: salt-based colloid palladium; preparation; activation; stability

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1 INTRODUCTION

Electroless plating is one of the most important surface treatment technologies. An amount of activation particles must be adsorbed on substrate before electroless plating. The activator used in electroless plating influences directly on the uniformity, adhesion force of the layer and the time of starting hydrogen-deposition. Therefore, activator is most important to electroless plating^[1, 2]. Two-step activation, colloid palladium, copper-tin colloid and ion palladium are applied in electroless plating^[3]. The two-step activation is rarely applied in automatic production because of the complicated process. The copper-tin colloid is rarely applied because of little activation. Though the activation and stability is nice, the ion palladium has a high cost because unstable and expensive NaBH₄ is used to reduce Pd²⁺. The colloid palladium is widely applied in electroless plating, especially the electroless copper plating in printed circuit board (PCB) due to the better activation, less dosage, simple technique and reliable quality.

There are two kinds of colloid palladium, which are an acid-based colloid palladium and a salt-based colloid palladium. The acidity of acid-based colloid palladium is so high that "pink ring"

is produced on the hole wall after depositing copper^[4-6]. In addition, the acid mist pollutes environment badly during production and application^[7, 8]. In contrast to acid-based colloid palladium, salt-based colloid palladium can overcome the above disadvantages. As present, reports on salt-based colloid palladium are mostly the introductions of its components^[2, 3, 9-13]. In these reports, the concentration of colloid palladium is in the range of 0.1 to 0.25 g/L (on amount of PdCl₂), while the reports on high concentration colloid palladium are few. In this paper, the palladium chloride concentration was up to 3.6 g/L, while the concentration was diluted to 0.1 g/L in application. Obviously, the salt-based colloid palladium has advantages such as low cost and convenient transport.

2 EXPERIMENTAL

2.1 Preparation of salt-based colloid palladium

An amount of stannous chloride was dissolved into some water. According to mole ratio of Sn to Pd (2:1), the SnCl₂ solution was gauged and added into PdCl₂ solution with slow agitation and at constant temperature. After several minutes, the surplus SnCl₂ solution was added into the above mixed solution of SnCl₂ and PdCl₂ when the color

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of blended solution turned brown dark. After agitating for 10 min, the total mixed solution was dispersed into the stabilization solution which contained NaCl, SnCl_2 , urea, ascorbic acid and vanillin. After maturing 4 h in a water bath heater, the salt-based colloid palladium was obtained.

2.2 Activation test of salt-based colloid palladium

In this paper, a PCB was used as the substrate of electroless plating. A piece of PCB was cut into many test pieces with size of $4\text{ cm} \times 4\text{ cm}$. A test piece was first washed in alkali cleaner solution at $70 - 80\text{ }^\circ\text{C}$ before etching the test piece in $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ solution. After etching, the test piece was dipped in the $\text{NaCl}/(\text{NH}_2)_2\text{CO}$ solution, then the test piece was put in a activation solution of salt-based colloid palladium for about 5 min at $20 - 30\text{ }^\circ\text{C}$. The concentration of an activation solution was 0.1 g/L (on amount of PdCl_2). After activation, the test piece was dipped in HBF_4 solution.

After the above pretreatment, copper was electrolessly plated on the test piece at $30\text{ }^\circ\text{C}$. Cu^{2+} concentration was 2.3 g/L in a bath solution. The time of starting hydrogen-deposition and the time of completely coating copper on a substrate are adopted to measure the activation of colloid palladium in the test. The time of starting hydrogen-deposition is the time when hydrogen bubbles occur in the bath since the test piece is dipped into a bath. The time of completely coating copper on a substrate is the time when the surface of test piece is coated with copper completely since the test piece is dipped into a bath. The activation solution was the colloid palladium diluted by the solution of NaCl and NH_2CONH_2 , and the concentration of the activation solution was 0.1 g/L (on amount of PdCl_2). The test time was measured by a stopwatch.

2.3 Stability time of salt-based colloid palladium

50 mL activation solution was filled in a tube with volume capacity of 50 mL . Air was flowed from the bottom by a small glass pipe when the temperature of activation solution was $20\text{ }^\circ\text{C}$ and airflow was 20 L/h (WM-2H gas compressor). In this paper, a stability time is used to measure the stability of salt-based colloid palladium. The stability time is the time when the brown dark solution disappears completely and becomes transparent since air flows^[16].

2.4 Backlight lever test

According to above-mentioned steps, copper was deposited on a piece of PCB by electroless plating for 10 min. The test piece was cut along the center of holes according to Fig. 1. Then the hole side of the cut piece was polished by sand papers.

Backlight levers were determined according to the picture of 10-lever system.

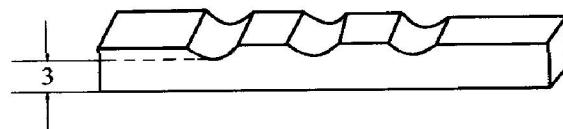


Fig. 1 Picture of backlight test (mm)

2.5 Granularity analysis of salt-based colloid palladium

After adding 3 mL salt-based colloid palladium solution into 400 mL methanol, the particle size of the colloid palladium was measured by Master Sizer2000 Particle Meter (Malvern, English).

2.6 Adhesion force test of electroless copper plating layer

Adhesion force was measured according to GB5270—85 of China standard.

3 RESULTS AND DISCUSSION

3.1 Impact of mole ration of Sn to Pd on activation and stability of salt-based colloid palladium

Salt-based colloid palladium was prepared according to experiment step 2.1. The impacts of $n(\text{Sn})/n(\text{Pd})$ on the activation and stability of the colloid palladium are shown in Figs. 2 and 3 when PdCl_2 concentration was 1.6 g/L , NaCl concentration was 200 g/L and other components were fixed.

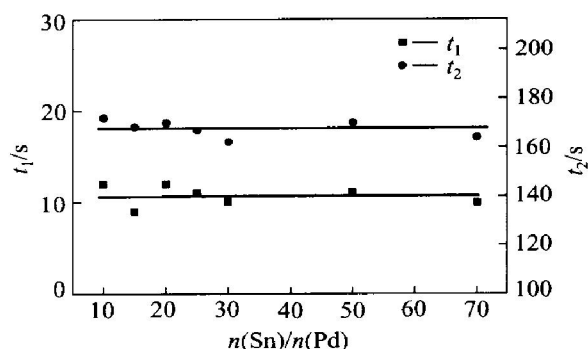


Fig. 2 Impact of $n(\text{Sn})/n(\text{Pd})$ on activation of salt-based colloid palladium

In this paper, t_1 stands for the time of starting hydrogen-deposition, t_2 stands for the time of completely coating copper on a substrate, t_3 stands for the stability time. It is presented in Figs. 2 and 3 that the time of starting hydrogen-deposition 12, 9, 12, 11, 10, 11, 10 s, the time of completely coating copper on a substrate was 172, 168, 170, 167, 162, 170, 164 s, the stability time of salt-based colloid palladium was 10, 15, 25, 35, 50, 54, 70 h when $n(\text{Sn})/n(\text{Pd})$ was 10, 15, 20, 25, 30, 50, 70 respectively. It was testified that $n(\text{Sn})/n(\text{Pd})$ had less effect on the activation of

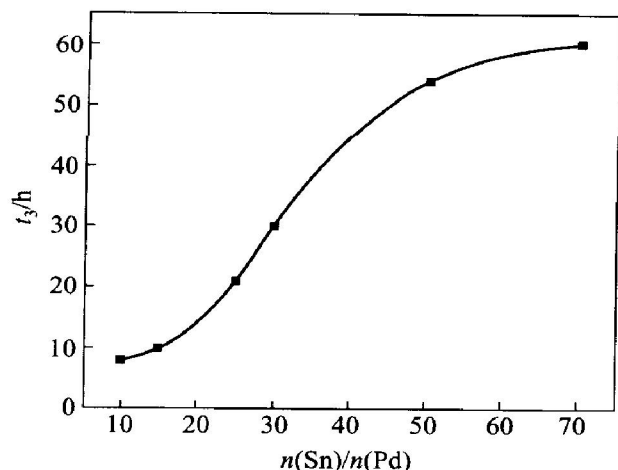
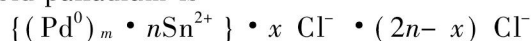


Fig. 3 Impact of $n(\text{Sn})/n(\text{Pd})$ on stability of salt-based colloid palladium

salt-based colloid palladium, but the stability of salt-based colloid palladium increased with the increases of $n(\text{Sn})/n(\text{Pd})$.

Because the concentration of activation solution was 0.1 g/L (PdCl_2), the concentration of colloid palladium particles was almost the same and the quantity of Pd particle deposited on a unit area of a substrate was nearly uniform after activation. Therefore, the time of starting hydrogen-deposition and the time of completely coating copper on a substrate were almost equal. The structure of colloid palladium is



Sn^{2+} in colloid palladium particles and in the solution are oxidized into Sn^{4+} when air is aerated into the colloid solution, and colloid palladium loses stability to precipitate. When palladium concentration in a solution was fixed, Sn^{2+} concentration increased with the increases of $n(\text{Sn})/n(\text{Pd})$. The more the concentration of Sn^{2+} , the more stable the colloid palladium. The stability time of salt-based colloid palladium was 54 h when $n(\text{Sn})/n(\text{Pd})$ was 50:1, which was equal to that of acid-based colloid palladium ZL-14 prepared by the author and applied in industry widely. Therefore, it can satisfy the requirement of industry application when $n(\text{Sn})/n(\text{Pd})$ is 50:1 in the preparation of salt-based colloid palladium.

3.2 Impact of NaCl concentration on activation and stability of salt-based colloid palladium

The impacts of NaCl concentration on the activation and stability of the colloid palladium are shown in Figs. 4 and 5 when PdCl_2 concentration was 1.6 g/L, $n(\text{Sn})/n(\text{Pd})$ was 50:1 and other components were fixed.

In Fig. 4, the time of starting hydrogen-deposition is about 10 s and the time of completely coating copper on a substrate is 170 s approximately

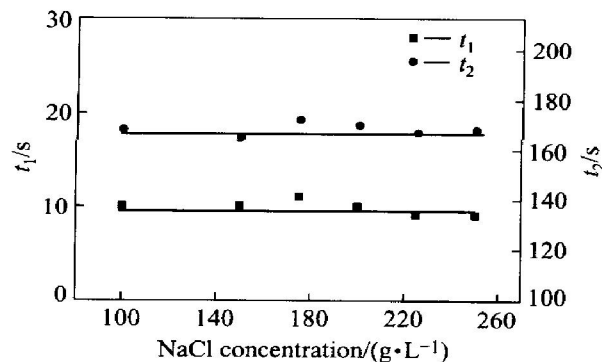


Fig. 4 Impact of NaCl concentration on activation of salt-based colloid palladium

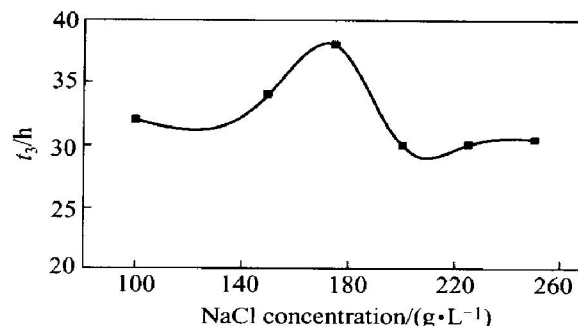


Fig. 5 Impact of NaCl concentration on stability of salt-based colloid palladium

when NaCl concentration is in the range of 100 – 250 g/L. Obviously, the impact of NaCl concentration on salt-based colloid palladium is little. There are some impacts of NaCl concentration on the stability time according to Fig. 5. When NaCl concentration is 175 g/L, the stability time is up to 38 h.

Because the concentration of activation solution is 0.1 g/L (PdCl_2), the concentration of colloid palladium particle was almost same and the nearly same quantity of Pd was deposited on a test piece after activation. So the time of starting hydrogen-deposition and the time of completely coating copper on a substrate are almost invariable. From the structure of colloid palladium, Cl^- can increase the stability of colloid palladium. The stability of salt-based colloid palladium increases with the increases of sodium chloride concentration. However, when NaCl concentration is more than 175 g/L, the stability time of salt-based colloid palladium decreased with the increases of sodium chloride concentration. Because NaCl is a strong electrolyte, the double-charge-layer of colloid is compressed by Cl^- when NaCl concentration is more than 175 g/L, ζ voltage of a colloid palladium decreases. As a result, the stability of salt-based colloid palladium falls down.

3.3 Impact of PdCl_2 concentration on activation and stability of salt-based colloid palladium

The impacts of PdCl_2 concentration on the activation and the stability of the colloid palladium are respectively shown in Figs. 6 and 7 when NaCl concentration is 175 g/L, $n(\text{Sn})/n(\text{Pd})$ is 50 : 1 and other components are fixed.

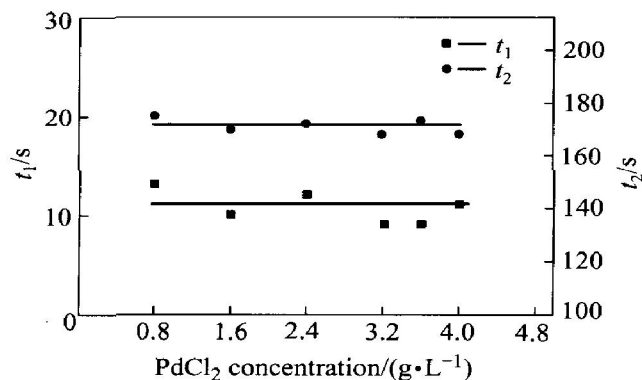


Fig. 6 Impact of PdCl_2 concentration on activation of salt-based colloid palladium

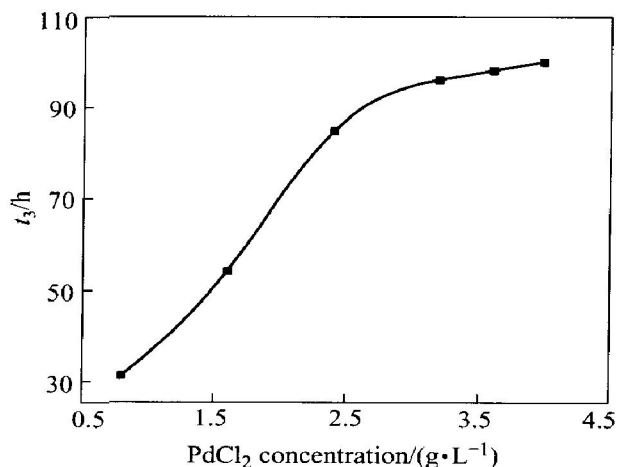


Fig. 7 Impact of PdCl_2 concentration on stability of salt-based colloid palladium

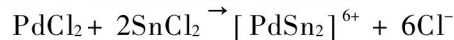
In Fig. 7, the stability time of salt-based colloid palladium is 31, 54, 85, 96, 98, 100 h when palladium chloride concentration is 0.8, 1.6, 2.4, 3.2, 3.6, 4.0 g/L respectively. It turns out that PdCl_2 concentration has less effect on the activation of salt-based colloid palladium, but the stability of salt-based colloid palladium increases as PdCl_2 concentration increases.

Because the palladium chloride concentration in an activation solution is 0.1 g/L (PdCl_2), the concentration of colloid palladium particles is almost the same, the quantity of Pd deposited on test piece after activation is nearly uniform. As a result, the time of starting hydrogen-deposition and the time of completely coating copper on a substrate are almost the same.

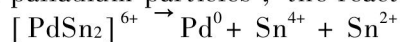
The higher the concentration of PdCl_2 is, the faster the colloid palladium cores form. In this way, colloid palladium particles are very fine and colloid particles contain more Sn^{2+} . So the stability of colloid palladium increases with the increases

of PdCl_2 concentration. But Pd separates directly out of the solution because colloid palladium cores forms too fast when the PdCl_2 concentration was equal to or more than 4.0 g/L.

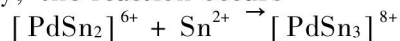
In experiment, it is found that the grass green solution with little activation was produced when the surplus SnCl_2 solution was added too early or too late in a PdCl_2 solution. The reaction occurs as follows in the solution at first.



$[\text{PdSn}_2]^{6+}$ is unstable and it decomposes to fine palladium particles, the reaction is



If the surplus SnCl_2 solution was added too early, the reaction occurs



$[\text{PdSn}_3]^{8+}$ is a grass green ion in a solution, its activation is very little. Therefore, the activation of colloid palladium is bad. When the surplus SnCl_2 solution is added too late, colloid particles become too large, so the activation and stability is also bad. Therefore the surplus SnCl_2 solution should be added into the solution in a proper time in the preparation of salt-based colloid palladium.

3.4 Impact of reaction temperature on activation of salt-based colloid palladium

Impact of reaction temperature on the activation of salt-based colloid palladium is described in Fig. 8 when PdCl_2 concentration is 1.6 g/L, $n(\text{Sn})/n(\text{Pd})$ is 50 : 1, NaCl concentration is 175 g/L and other components are fixed.

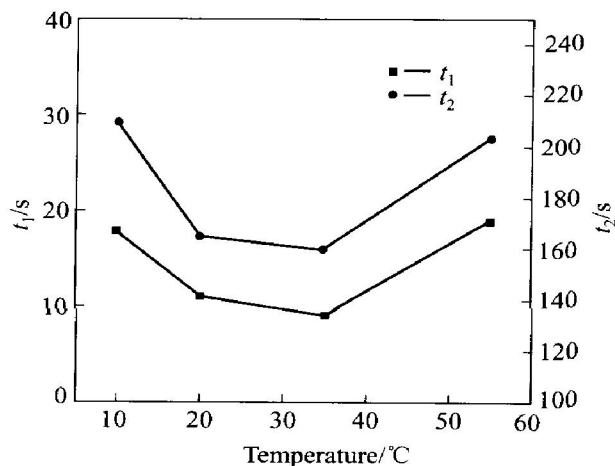


Fig. 8 Impact of reaction temperature on activation of salt-based colloid palladium

In Fig. 8, the time of starting hydrogen-deposition is 18, 11, 9, 19 s and the time of completely coating copper on a substrate is 210, 165, 163, 208 s when the reaction temperature is 10, 20, 35, 55 °C respectively. Obviously, the activation of salt-colloid palladium is the best when the reaction temperature is in the range of 20–35 °C.

The speed of forming colloid particles was slow

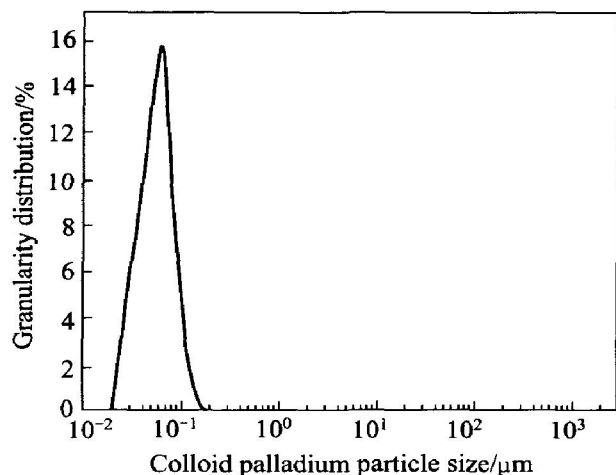


Fig. 9 Granularity distribution of salt-based colloid palladium

wer when the reaction temperature was lower. When the reaction temperature was too high, colloid particle formed would congregate and become large because of faster reaction and heat movement. Therefore, a colloid palladium with good activation could be only obtained when the reaction temperature is 20–35 °C.

4 CONCLUSIONS

1) When $n(\text{Sn})/n(\text{Pd})$ is fixed, the stability of salt-based colloid palladium increased as PdCl_2 concentration increases. When PdCl_2 concentration is constant, the stability of salt-based colloid palladium increases as $n(\text{Sn})/n(\text{Pd})$ increases. The stability of salt-based colloid palladium increases as NaCl concentration increases when NaCl concentration is 100–175 g/L.

2) The salt-based colloid palladium has a high activation when reaction temperature is 20–35 °C.

3) The optimal preparation conditions of the salt-based colloid palladium are that PdCl_2 concentration is 3.6 g/L, $n(\text{Sn})/n(\text{Pd})$ is 50:1, NaCl concentration is 175 g/L, the reaction temperature is 20–35 °C and urea, ascorbic acid and vanillin are added in a proper amount.

4) Salt-based colloid palladium is prepared. The time of starting hydrogen-deposition is 9 s, the time of completely coating on a substrate is 2 min. The stability time of activation solution (0.1 g/L PdCl_2) is 98 h when solution temperature is 20 °C, the particle sizes of salt-colloid palladium is 81 nm, the backlight lever of electroless copper plating layer is 10th grade and the adhesion force of the copper layer is up to GB5270–85 of China stand-

ard after electroless copper plating for 10 min.

REFERENCES

- [1] JIN Hong, CHEN Sen. Printed circuit technology [M]. Beijing: Chemical Industry Publishing Company, 2003. 12–20.
- [2] ZHANG Yong-feng, MA Ling-jun, GUO Wei-min. Activation technology of nonmetal electroless plating [J]. Material Exploitation and Utility, 2004, 15(2): 30–34.
- [3] LI Bing, WEI Xi-wen, ZHANG Zhao-yang. Study on activation technique of electroless nickel plating on nonmetal material [J]. Material Protect, 2001. 2, (34) 2: 17–18.
- [4] JIANG Xiao-xia, SHEN Wei. Electroless Plating Theory and Practice [M]. Beijing: National Defence Industry Publishing Company, 2000. 6.
- [5] ZHENG Ya-jie, GONG Zhu-qing, CHEN Ba-zhen. Hole metalization of printed circuit board and path of technology improvement [J]. Material Report, 2003, 17(4): 11–13.
- [6] Gulla M, Conlan W. Catalyst Solution for Electroless Deposition of Metal on Substrate [P]. US 3874882, 1975.
- [7] Hidber P C, Helbig W, Kim E. Microcontact printing of palladium colloids: Micro-scale patterning by electroless deposition of copper [J]. Langmuir, 1996, 12 (5): 1375–1380.
- [8] Gulla M, Conlan W Jr. Catalyst Solution for Electroless Metal Deposition on a Substrate [P]. US 3904792, 1975.
- [9] GONG Fan, WANG Bi-rsheng. Development of the activation technology of electroless plating [J]. Application Science, 2002, (29) 3: 59–60.
- [10] CHEN Da-hong. Printed circuit hole metalization [J]. Electro Technology, 2001. 5, (22) 3: 102–105.
- [11] Brandow S, Chen M S, Wang T. Size-controlled colloidal Pd(II) catalysts for electroless Ni deposition in nanolithography applications [J]. Electrochem Soc, 1997, 12, (144) 10: 3425–3433.
- [12] Gulla M, Dutkewych O B, Blandon J J. Catalyst Metal of Reduced Particle Size [P]. US 4634468, 1987.
- [13] YU Wei-yong, LIU Ma-hong, LIU Hai-fan. Preparation of polymer-stabilized noble metal colloids [J]. Journal of Colloid and Interface Science, 1999, (210): 218–221.
- [14] Cohen R L, Meek R L. Process for Electroless Plating Using Colloid Sensitization and Acid Rinse [P]. US 4008343, 1977.
- [15] Kanoh O, Yoshida Y, Ogiso Y. Activating Catalytic Solution for Electroless Plating and Method for Electroless Plating [P]. US 5989787, 1999.
- [16] ZHENG Fu-yang, MA Yan-chun. Impact of several chloride on stability and activation of salt-based colloid palladium [J]. Plating and Finishing, 1990, 12 (3): 9–12.

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