A Study on Conductive Polymer in PCB Manufacturing

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Abstract. Making Hole Conductive is one of the key technologies in Printed Circuit Board manufacture. For a long time, electroless copper was the unique technology of hole metallization process. However, it’s long process, high water consumption and the resulting huge amount of waste water. A large number of toxic and harmful chemicals are also discharged into the environment, causing great harm to the health of workers and the environment. In this paper, the environmentally materialization technology-selective organic conductive coating (SOC) technology was studied. The resource consumption, product quality, and environmental and economic benefits of the traditional PTH and new SOC technology applied in the making hole conductive were compared and analyzed in detail through the investigation of long-term operation examples. The necessity, advantages and practicality of SOC technology were revealed.

1. Introduction
With the increasing demand for electronic products, the structure of PCB is becoming complex, resulting in high-density interconnect technology, commonly known as HDI (High Density Interconnect). HDI embodies the most advanced technology of contemporary PCB manufacturing, bringing the fine wire of PCB and the miniaturization of the aperture. With the high density and high performance of electronic equipment, the through holes and blind vias on the PCB are widely used, and the requirements for hole metallization are getting higher and higher. The hole metallization technology determines the reliability of the metallization performance between the layers of electronic products. It is one of the key process of PCB manufacturing. However, the traditional plating through hole (PTH) generates hydrogen gas during the process of reducing copper[1], which is not conducive to the manufacture of micro-blind holes, and it is necessary to find a new and reliable alternative process. On the other hand, the traditional hole metallization process is complicated. Whether it is from the manufacturing technology or from the cost, Making Hole Conductive (MHC) is one of the key process in the PCB manufacturing, and its technological progress is very important to improve PCB quality and reduce production costs. In addition, serious negative environmental impacts are also the main problems that traditional PTH urgently needs to solve[2]. At present, the hole metallization process is transitioning from the traditional electroless copper plating to the new technology direction, especially the selective organic conductive coating (SOC). SOC is an ideal hole metallization process[3]. In this paper, through theoretical analysis and specific examples, the technical, economic and environmental benefits of traditional methods and new conductive polymers used in the conductance of holes are...
studied in detail, and the necessity, advancement and feasibility of traditional electroless copper plating techniques are replaced by selective organic conductive polymers.

2. Research Methods
On the basis of analyzing the development of hole metallization technology, this paper firstly defines the traditional PTH and SOC process design parameters, and compares the material consumption, energy consumption, emissions and cost on a case-by-case basis to explore their respective characteristics. Then, through the company's five years operation data of these two types of large-scale production, long-running actual data statistics, through case comparison, analysis and discussion of the advanced performance and feasibility of SOC process.

3. Results and Discussion

3.1. Hole Metallization Principle, Application and Technical Analysis

(1) The core technology of circuit board production
No matter what kinds of printed circuit boards, the formation of line graphics is the first priority, so far, the mainstream method of forming line graphics is the graphics transfer method. For traditional two-layer or more boards, the line between the layers is conducted through the metal through holes, and the HDI board adds the micro-blind hole metallization technology. All the via holes must be metallized to achieve electrical conductivity. In order to metallize the interlayer insulating material, it is necessary to first conduct the conductors for subsequent copper plating deposition. Currently, the industrial metallization process is still based on traditional electroless copper.

(2) Analysis of the Principles and Technical Features of Traditional PTH and SOC Process
The traditional PTH process is to form a layer of conductive copper on the wall of the insulating hole \(^4\). The principle is to first adsorb a layer of palladium on the hole wall, and then under strong alkaline conditions, using the palladium as catalyst, the \(\text{Cu}^{2+}\) is reduced to \(\text{Cu}\) by formaldehyde, and deposited on the wall of the insulating hole to conduct a metallization function for the subsequent thick copper plating. The strong complexing agent EDTA is used to stabilize the copper-containing material ion plating solution. The reaction mechanism is as follows:

\[
\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \xrightarrow{\text{P}\text{d}} \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 \uparrow
\]

The process is long and generally requires 6 steps, as follows: Conditioner → Microetch → Predip → Activator → Acceleration / Reduction → Electroless copper. The water and electricity resources and energy used in the PTH process are numerous, and the process control is complicated, which also brings many uncertainties to the stability of the process production. In order to solve this problem, the most effective method is to simplify the process and not use or use less pollutants that affect the environment. Through the unremitting efforts of the industry, different alternative technologies have been introduced, ATOTECH has successfully developed the use of sodium potassium tartrate \(^5\) to replace EDTA complexing agent used in PTH process. Waste water treatment is relatively easy, and it has been widely used in PCB manufacturing; Shipley integrated sensitization and activation for the first time in one step \(^6\), later, RohmHaas developed a low palladium, low formaldehyde and non-accelerated PTH process, which can also save energy. Improvements in consumption and wastewater treatment \(^7\); Macdermid invented the Phoenix process, using sodium hypophosphite as a reducing agent to replace formaldehyde \(^8\); Guangdong Guanghua has studied glyoxylate as a reducing agent to replace formaldehyde \(^9\). However, these technologies have been improved in the original process, the process has not been shortened, the process is still complicated, and the problem cannot be solved fundamentally. In latest and simpler energy-saving and environmentally friendly processes, such as palladium \(^10\), Carbon \(^11\), Graphite \(^12\), Graphene/Graphene Oxide \(^13\), Pyrrole \(^14\)/ Thiophene \(^15\) conductive polymer, etc. are used, and a series of direct metallization processes have been developed, and the development prospects of conductive polymer processes are promising.

In the 1970s, Japanese scientist Hideki Shirakawa, American scientist Heeger AJ and Macdiarmid AG jointly invented conductive polymers and won the 2000 Nobel Prize in Chemistry. The invention of conductive polymers laid a new process for PCB hole metallization. The theoretical basis. In the 1990s,
Blasberg Oberflächentechnik GmbH introduced a direct metallization process using conductive polymers as conductive layer\cite{16} and named DMS-E. Initially they chose polypyrrole as conductive polymer\cite{17}, but polypyrrole monomer has a very high vapor pressure at room temperature, affecting the health of operators; Zhang Peng et al. studied the technology of pyrrole film formation after secondary oxidation and find the process is complicated\cite{18}, while Poly(3, 4-ethylenedioxythiophene) (PEDOT) has better conductivity. Under the same conditions, the monomer vapor pressure is small, and the process only requires three steps \cite{19}. Polytetraphene replaces polypyrrole as conductive polymer for new generation of printed circuit boards since then.

The selective organic conductive coating (SOC) \cite{20} process deposition of initiator on resin and glass fiber. The 3,4-ethylenedioxythiophene (EDOT) monomer is polymerized into poly 3,4-Ethylenedioxythiophene (PEDOT), which forms a layer of conductive polymer on an insulating substrate, it’s a simple MHC process. The reaction mechanism of this process as follows:

\[
\begin{align*}
3\text{MnO}_2 + 2 \text{EDOT} + 2\text{nH}^+ & \rightarrow \left( \text{Mn}^{2+} \right)_{\text{n}} + \text{2nH}_2\text{O} \\
\end{align*}
\]

**3.2. Analysis of Material Consumption, Energy Consumption and Cost of PTH and SOC Technology**

Table 1 and Table 2 respectively show the control parameters of PTH and SOC process design of Guangdong Toneset Sci-Tech Co., Ltd.

| Table 1. PTH process control parameters and main pollutants |
|------------------------------------------------------------|
| Process               | Material  | Cont. | Consumption* | Time/min | Temp./ ºC | Main Pollutant |
| Conditioner          | Cleaner 2613A | 45 g/L | 0.3 kg   | 5-8     | 45~55   | Alkaline Surfactant |
|                      | Cleaner 2613B | 2.5%   | 0.2 kg   |         |         | Oxidant Acid |
| Micro-etch           | \(\text{Na}_2\text{S}_2\text{O}_8\) | 45 g/L | 3.0 kg   | 1-2     | 20~30   | Inorganic Salt Acid |
|                      | \(\text{H}_2\text{SO}_4 (98\%)\) | 2% (v/v) | 2.7 kg |         |         | Inorganic Salt Acid |
| Pre-dip              | Pre-dip 2624 | 200 g/L | 2.0 kg  | 1-3     | R.T.    | Pd\(^{2+}\), Sn\(^{2+}\) Acid |
|                      | HCl (37%) | 1.0% | 0.1 kg |         |         | Inorganic Salt Acid |
| Pre-dip              | Pre-dip 2624 | 200 g/L | 0.1 kg | 5-8     | 35~45   | Pd\(^{2+}\), Sn\(^{2+}\) Acid |
| Activator            | Activator 2616B | 1.0% | 0.5 kg |         |         | Reducing Agent Cu\(^{2+}\) Chelator |
|                      | HCl (37%) | 1.0% | / |         |         | Chelator |
| Acceleration         | Accelerator 2627 | 8% | 2.0 kg | 2-3     | 25~35   | HCHO Alkaline |
|                      | PTH 2638A | 5.2% | 8.0 kg |         |         | Alkaline |
|                      | PTH 2638B | 6% | 3.5 kg |         |         | Alkaline |
|                      | PTH 2638E | 0.2% | 0.1 kg |         |         | Alkaline |
| Electroless Copper   | HCHO (37%) | 1.3% | 4.0 kg | 18-25   | 28~34   | HCHO Alkaline |
|                      | PTH 2638C | ----- | 14.0 kg |         |         | Alkaline |
|                      | PTH 2638D | 3.0% | 0.1 kg |         |         | Alkaline |

*Consumption indicates the needed amount of the materials for the production of 100 m² printed circuit boards.
Table 2. SOC process control parameters and main pollutants

| Process   | Material        | Consumption* | Time/min | Temp./℃ | Main Pollutant     |
|-----------|-----------------|--------------|----------|---------|-------------------|
| Conditioner | Conditioner 2301A | 5%           | 0.5 kg   | 0.9-1.2 | 48~52 | Surfactant         |
| Conditioner | Conditioner 2301B | 2%           | 0.2 kg   |          |       | Surfactant         |
| Initiator | Initiator 2302 | 120 mL/L | 1.2 kg   | 1.0-1.5 | 86~90 | NaMnO₄, Boric Acid |
| Initiator | Boric Acid      | 10 g/L      | 0.1 kg   |          |       |                   |
| Initiator | Polymerizer 2303A | 20 mL/L | 0.5 kg   | 1.5-2.0 | 16~22 | EDOT               |
| Initiator | Polymerizer 2303B | 40 mL/L | 0.5 kg   |          |       | Polysulfonate      |
| Initiator | Regulator 2303C | pH 1.9~2.1  | 0.1 kg   |          |       | Inorganic Salt     |
| Polymerization | Phosphoric Acid | 4 g/L     | 0.1 kg   |          |       | Phosphoric Acid    |

*Consumption indicates the needed amount of the materials for the production of 100 m² printed circuit boards

It can be found that: (1) PTH chemical treatment process requires 6 steps and 14 materials, and the production of 100m² printed circuit board requires about 42.65 kg of chemicals; water consumption is 50 L/min, and treatment time is at least 1h. (2) The SOC process requires only 3 steps and 8 materials. The production of 100 m² printed circuit board requires about 3.2 kg of chemicals; the water consumption is 24 L/min, and the processing time is within 10 min. Therefore, the traditional PTH has a long process, requires a lot of chemical, consumes a large amount of water, and has a long time. The SOC process has made great progress in reducing material consumption and reducing resource use, and the production cycle is significantly shortened, product delivery is accelerated and efficiency is improved.

3.3. Analysis of the Types and Quantities of PTH and SOC Process Waste

According to the monthly production capacity of 30,000 square meters per line, based on the amount of chemical used in Table 1, Table 2 and the water consumption of the process, it is assumed that all chemical will not be affected by other factors such as bringing in, bringing out, evaporating, etc. The amount of waste bath and waste water discharged can be calculated as in Table 3.

Table 3. Theoretical Waste Liquid and Wastewater Discharge*

| Process | Waste Solution (kg) | Waste Water (L) |
|---------|---------------------|-----------------|
| PTH     | 12,795 = 42.65/100*30000 | 1,716,000 = 10*5*34320 |
| SOC     | 9600 = 3.2/100*30000   | 823,680 = 8*3*34320 |

*Calculated according to effective working hours per month (34320 min = 26 days/month*22 h/day*60 min/h)

It can be seen that the SOC emissions are greatly reduced compared to the traditional PTH process, in which the waste liquid discharge is only 3/4 of the PTH, and the wastewater discharge is reduced to half. On the point of the main material components, PTH needs to use copper, palladium, tin and other metal materials, as well as formaldehyde, complexing agents and other materials, so there are corresponding emissions of these substances, copper bath waste also needs to be dealt with, the process is complicated and processing cost is high; while the SOC not only has a small amount of waste liquid discharge, but the processing is relatively simple, the corresponding processing cost is low, and the amount of harmful substances is greatly reduced. Correspondingly, cost comparison accounting for two processes shows that PTH requires 10 kinds of special materials, while SOC only needs 6 kinds. From the cost of raw materials and usage, the cost of SOC special materials is only half of PTH. Other acid and alkali and other auxiliary materials are also used less frequently; in terms of labor, PTH requires manual upload and download plates, while SOC can use automatic discharge and closing machine, all the chemical can be automatically added which greatly saves labor costs; In terms of cost of water, electricity and wastewater treatment, the cost of SOC also has obvious advantages. Overall, the cost of SOC is about 44% lower than that of traditional PTH.
3.4. Actual Operation of Two Processes

Based on above PTH and SOC process design and analysis, we take the SOC of the PCB manufacturer Guangzhou EE factory and the PTH line of Huizhou GCS factory as an example (the average production capacity is 30,000 square meters / month) and further conduct the actual operation inspection. To produce the same amount of PCB, statistical analysis of its water and electricity consumption, waste water discharge, waste disposal, labor costs, etc., as well as efficiency, yield power and other quality management. It can be seen that the SOC process exhibits significant advantages in practical applications.

The SOC process has been applied in the PCB manufacturing plant for more than five years. Compared with the traditional PTH process, it has obvious quality, environmental protection and cost advantages. The following results are obtained through statistics: Firstly, from the perspective of quality control, the traditional Vertical electroless copper plating line needs to check the back-light every 4 hours. When the quality control is fine, the average back-light check is at least 2 times per month. 0.1% to 0.3% of the PTH process rejection is caused by hole skipping plating. The SOC process only needs to check backlight per shift, basically no backlight problems, and the proportion of the SOC process affected by the finished product scrap is below 50 ppm, which not only improves the yield power, but directly reduce the loss caused by the quality scrap. It ensures on-time delivery and produces significant economic benefits.

Secondly, from the perspective of environmental protection, for production scale of 30,000 m² of circuit boards per month, the amount of waste solution and waste water produced by statistics are shown respectively in Table 5 and Table 6. It can be seen that the SOC waste discharge types and emissions quantity are significantly reduced. Among them, the total amount of SOC waste liquid is less than 1/3 of PTH and the discharge of waste water is only 1/2 of PTH.

| Process          | Chemical             | Consumption      | Daily waste solution (T) | Daily waste water (T) | Main Pollutant          |
|------------------|----------------------|------------------|--------------------------|-----------------------|-------------------------|
| Conditioner      | 2613A/B              | 0.8 kg/100m²     | 0.01                     | 9.6                   | COD                     |
| Micro-etch       | Na₂S₂O₈              | 6.0 kg/100m²     | 0.075                    | 9.6                   | Oxidant, Cu²⁺           |
| Pre-dip          | 2624                 | 2.2 kg/100m²     | 0.0275                   | 9.6                   | Inorganic               |
| Activator        | 2616B                | 1.0 L/100m²      | 0.0125                   | 9.6                   | Pd²⁺                    |
| Acceleration     | 2627                 | 2.0 L/100m²      | 0.025                    | 9.6                   | Reducing agent          |
| Electroless Copper | 2638A/B/C          | 21.57 L/100m²    | 0.2695                   | 9.6                   | Cu²⁺, EDTA, HCHO, COD   |
|                  |                      |                  | Total (T/day)            | 0.4195                | All above               |
|                  |                      |                  | Total (T/month)          | 10.907                | 1497.6                  |

*The data were acquired at the production scale of 30,000 m² PCB per month

| Process          | Chemical             | Consumption      | Daily waste solution (T) | Daily waste water (T) | Main Pollutant          |
|------------------|----------------------|------------------|--------------------------|-----------------------|-------------------------|
| Micro-etch       | Na₂S₂O₈              | 7.7 kg/100m²     | 0.096                    | 7.2                   | Oxidant, Cu²⁺           |
| Conditioner      | 2301A/B              | 0.74L/100m²      | 0.01                     | 7.2                   | COD                     |
| Initiator        | 2302                 | 1.1 L./100m²     | 0.014                    | 7.2                   | Oxidant                 |
| Polymerization   | 2303A/B/C            | 0.5 L./100m²     | 0.006                    | 7.2                   | COD                     |
|                  |                      |                  | Total (T/day)            | 0.126                 | 28.8                    |
|                  |                      |                  | Total (T/month)          | 3.276                 | 748.8                   |

*(a) A micro-etching process was added in the front of SOC process for the production of multi-layer boards. (b) The data were acquired at the production scale of 30,000 m² PCB per month.
4. Conclusion

Through research and running case analysis, it can be found that under the premise of ensuring product quality, the SOC process is convenient to operate, the process is short, and the production process is easy to be automatically controlled, which can greatly reduce the production cycle of the product, reduce the production cost, and improve the production efficiency. At the same time, the production process has low emission of toxic waste and is environmentally friendly, which greatly reduces the wastewater discharge and environmental pressure during the PCB production process. Therefore, whether it is from the perspective of technology, economy or environmental protection, SOC technology has obvious advantages, it is general trend of SOC TO replacing the traditional PTH process.

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