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The Needs for, and Problems Experienced While Developing a Successful Low Palladium Activation System for Electroless Copper Deposition.

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Abstract.

The electroless deposition of Copper is widely used within the printed circuit board industry as it offers a simple and reliable method for metallizing holes, which subsequently enable multilayer PCBs. While the process as a whole continues to develop since its adoption, one point that has remained common is the need to activate those materials on which the Copper does not naturally deposit, namely the glass fiber bundles and epoxy matrix. Such activation processes are typically based on Palladium as this has been long proven to be a reliable method, however its use does not come without some penalties. The activation step is acknowledged to be one, and in some cases, the most expensive step within the electroless Copper process as a whole, and this is due to the cost of the Palladium metal itself. Historically this has always been a concern, but with the current cost of Palladium exceeding that of Gold, the desire for a "low cost" activator has increased dramatically in recent years.

Over the years, many suppliers have developed alternative processes utilizing conductive polymers or variations of carbon, and while these have been accepted within the market and have generally been found to operate at a lower cost, with decades of reliability data, and countless installations worldwide, the metallization of through holes with electroless Copper remains the preferred method for many applications. Hence the need for a "low cost" but high performance, Palladium based activator step remains as strong as ever.

This paper summarizes experiences gained while developing a new cost effective Palladium containing ionic activation system, we review the successes and issues found with early generations and then show that building on these experiences, a successful, low Palladium activation system can be provided that satisfies both the technical and commercial demands of today's PCB market.

Background.

Since the first double sided PCBs were introduced, there has been a desire for a "front to back" or "side to side" electrical connection as this primarily enables a higher densification of surface componentry. Historically this connection has been achieved through the use of leaded components, but as both PCB and component technologies developed, it became necessary that the PCB itself provide such a through connection, and the basis of the current "through via" was born. Ideally such a connection would have electrical properties comparable to the main conductor materials, and sufficient mechanical properties to withstand not only the exposure conditions arising from the final product use, but also the PCB production process, as well as any final assembly process such as soldering or resin encapsulation. In view of this, Copper was the obvious choice as it offers outstanding electrical conductivity with acceptable mechanical properties, but more importantly, does so at a reasonable cost compared to other metals such as Silver.

With both "old" and "new" laminate materials typically composing of conductive foils in combination with an insulating polymer matrix and a glass or ceramic reinforcement, it becomes clear that any process targeting full metallization of a drilled through hole or via, must function with both conductors and insulating materials, as such, this initially discounts the use of electroplating operations as a high proportion of any through hole would be non-conductive and so, cannot carry electrical current, and will not metallize. With these excluded, it falls to the immersion and electroless processes to act as the primary metallization route for through holes, and with the immersion processes not ideally suited due to their need for a compatible layer providing the exchange source, electroless processing of Copper became the predominant technology for PCB production. It should be noted that there are a number of successful direct metallization processes based on Carbon, Graphite[1] and conductive polymers[2] within the PCB industry, and while these do have a proven performance, they have not seen a universal acceptance similar to that of the electroless Copper processes.

In order for electroless deposition to occur, there needs to be a sufficiently active surface available that will accommodate, or catalyze that deposition. Historically this catalyst or activation step has been based on Palladium, either in colloidal or ionic form. Should the latter ionic form be utilized, it necessary to further reduce the Palladium from its ionic state to its elemental state in order that it can operate as a suitable catalyst. Figure 1 shows a typical process sequence for an electroless Copper processes utilizing an ionic based activation system.

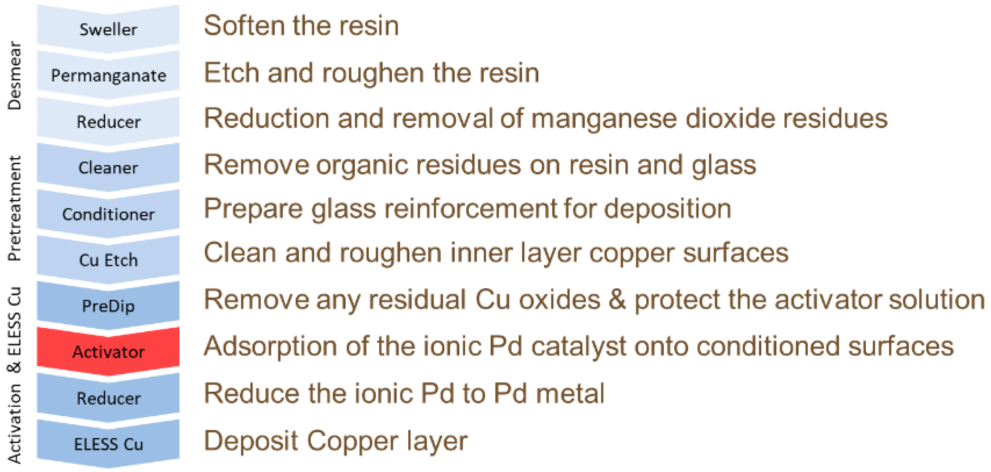

Figure 1 Typical Process Sequence for Electroless Copper Deposition Using an Ionic Activation System

Increasing Palladium Costs.

With decades of experience and reliability data surrounding the electroless Copper processes and the products produced using them, it is clear that there is a heavy reliance on the sustainability of such processes, however, there is an ongoing “thorn in the side” of the PCB industry, namely the cost of the Palladium used within the activation step.

Figure 2 shows the historical spot price for Palladium, and as can be seen there has been a steady increase over the last 20 years, which has had an obvious impact on the operational costs for electroless Copper processing. As a point of reference, at the time of writing, the current spot price for Palladium was $1791 per Ounce [3], while that for Gold was lower at “only” $1508 per Ounce. [4]

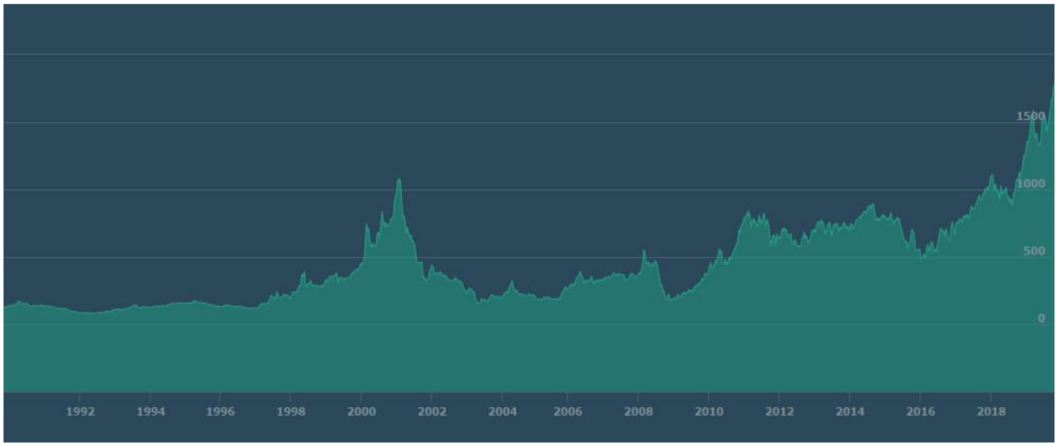

Figure 2 Palladium Spot Price [3]

From Figure 2, it is clear that a reduction in Palladium price, however welcome, is not anticipated to occur soon, and so, there has been an increasing demand on chemical suppliers to reduce the dependence of the electroless Copper process on the Palladium raw material price. As stated earlier, there are other metallization processes available, some of which are also based on Palladium, and there have also been disclosures recently relating to the development of activator systems not based on precious metals [5] but in the meantime, with the high reliance on the electroless Copper processes remaining, the applicable chemical suppliers are working on developing a new generation of activators, that are still based on Palladium, but do so at a much lower concentration than previously.

Low Palladium Containing Activator Systems.

Historically, and depending upon the technique used (ionic or colloidal), the Palladium content in a functional activator bath for electroless Copper processing has typically fallen in the region of 100 to 300ppm, with the products towards the lower end of the scale being based on colloidal Palladium and the higher on an ionic Palladium. This has obviously made the colloidal systems attractive as their lower Palladium content offers a seemingly lower process costs, however, there has been evidence to suggest that the Palladium deposit arising from their use is not as even as one arising from an ionic based activation bath (see figure 3) bringing their suitability into question for a number of high reliability applications, so there are a high number of PCB producers utilizing ionic Palladium which operate towards the higher concentrations.

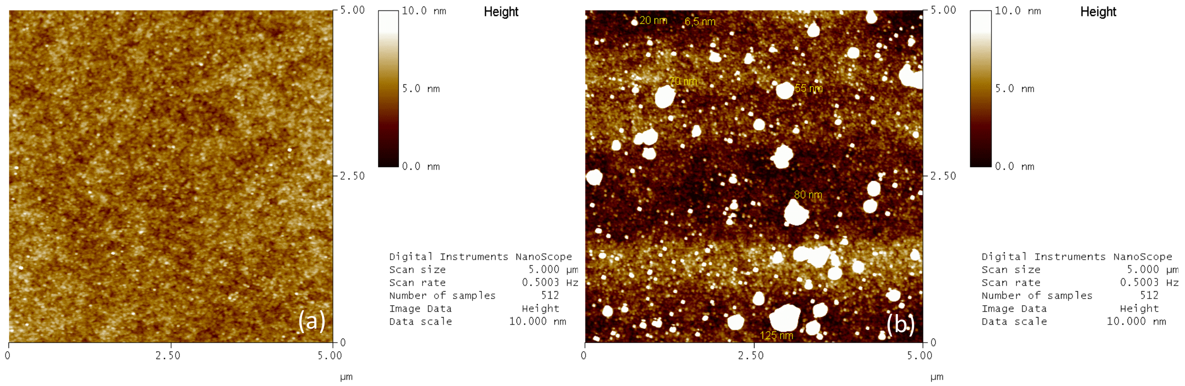

Figure 3. Palladium Deposition Arising from Ionic (a) and Colloidal (b) Activation Systems

In principal, the reduction of Palladium content in the activator bath would appear a simple thing to achieve, simply put less Palladium into it, however there are a wide number of interactions occurring within the process tank that make it no so straightforward.

As stated above, the primary function of the activator is to deposit or adsorb Palladium onto the dielectric system in order to enable subsequent Copper deposition. In order to achieve this, in an acceptable time frame, there is a minimum amount of Palladium needed within the activator solution itself, and traditionally, a Palladium content marginally higher than this is utilized in order to ensure an excess of Palladium is always available in the process solution. Additionally, the higher the Palladium content of the process bath, generally, the more effective the adsorption and coverage of Palladium onto the dielectric system. So while it can be understood why an elevated Palladium content is beneficial, it would seem a simple case of reducing the Palladium content closer towards the minimum level, and then maintaining it would yield a low Palladium activation process.

Unfortunately, there are a number of counterproductive mechanisms which are constantly in affect and are actively diluting or consuming the Palladium in the activator bath, and these mean that while a low Palladium activator that works initially is easily achievable, maintaining it as a stable working solution offers more of a challenge.

Table 1. – Factors Effecting Palladium Content and Consumption in Electroless Copper Activation Bath

1	Consumption due to Palladium deposition on the panel
2	Dilution due to solution drag in from previous process steps
3	Consumption due to solution drag out on panels leaving the bath
4	Consumption due to undesirable reactions occurring in the bath itself

In sequential wet processes, it is reasonable to say that “there is no such thing as a truly isolated bath”. As a single panel, or a basket of panels passes from one process tank into another, it will carry with it a volume of liquid from the preceding tank, known as drag in, and then when it leaves the tank it is assumed that the panel or basket will take a similar volume of liquid with it, which is known as drag out. In the case of the activator bath, this means that the predip is dragged into the activator, effectively diluting the bath, and then it will drag out functional activator, further depleting all active components. While these dilution volumes can be measured and counteracted through a regimented replenishment protocol, their volumes can be appreciable (20-100ml/M^2), which can lead to high operating costs.

It is clear that Palladium is the critical and main active component of the activator bath and is constantly being diluted through drag in, it is also however, prone to cross reactions with contaminants arising from that drag in as well as general operation. As such the Palladium is constantly being consumed due to undesirable side reactions occurring in the process tank.

Figure 4. shows the total Palladium content within the process solution for an early generation of low Palladium based activation baths, recorded while under normal operation, and as can be seen it remains reasonably constant across the period examined. Superimposed on the same curve is the relative Palladium adsorbed onto test vehicles processed regularly throughout that loading, and clearly, this drops somewhat dramatically to the point where less than 40% of the original Palladium level is adsorbed. Clearly this raises concerns, as less adsorbed Palladium equates to lower activation levels and thus risks quality and performance issues of the final electroless Copper layer.

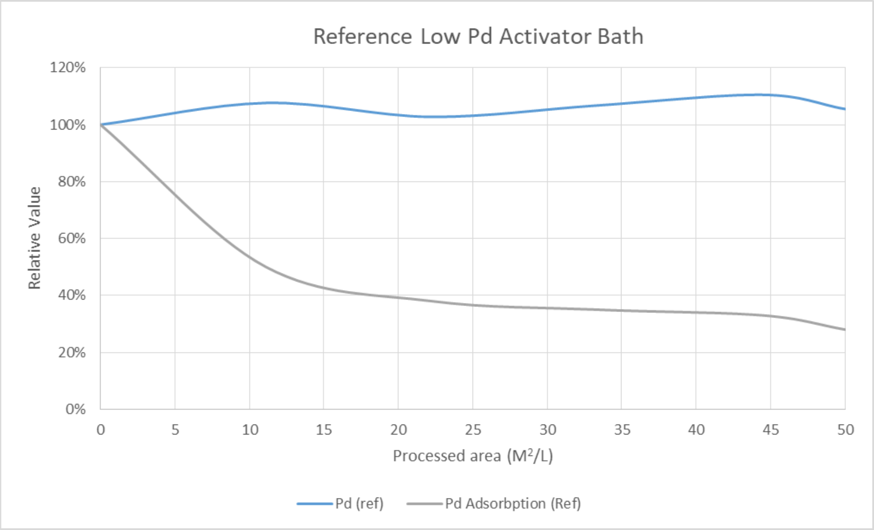

Figure 4. Relative Palladium Content and Palladium Adsorption During Bath Loading for an Early Generation of Low Palladium Activator

Performance of New Low Palladium Activation Process.
Figure 5 shows comparable analysis for the newly developed activation process operating with a Palladium content of approximately 80ppm, the Palladium adsorption for the reference bath above is also shown.

Clearly, there is no drop in the Palladium adsorption levels for the newly developed solution, implying that the new process bath is not only more chemically stable, but would yield a more consistent activation performance for the subsequent electroless Copper process.

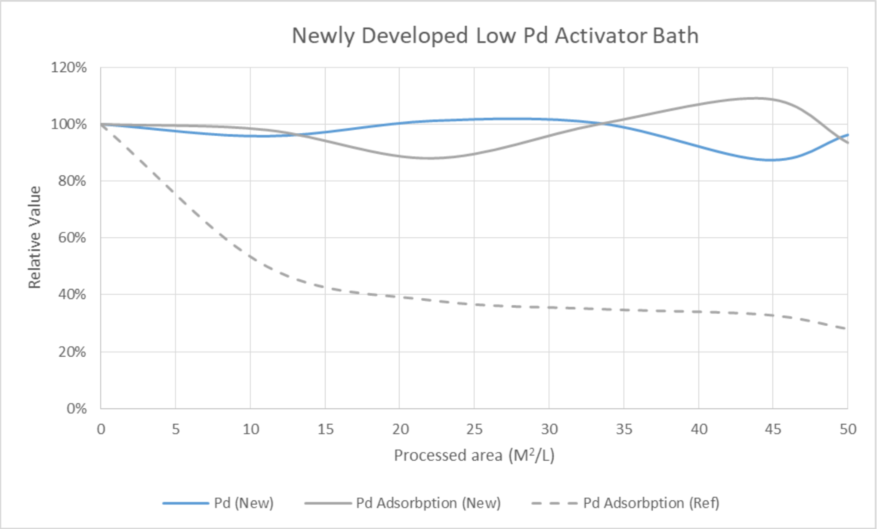

Figure 5. Relative Palladium Content and Palladium Adsorption During Bath Loading for the Newly Developed Low Palladium Activator

Palladium Adsorption on Other Dielectrics.
While the Palladium adsorption has been stabilized for the new low Palladium activator bath, it is interesting to compare its performance relative to that of a more traditional high Palladium containing bath. Figure 6 shows the Palladium adsorption levels measured on two commercially available, and widely utilized FR4 materials, with a representative high Palladium containing activator (>200ppm) and the newly developed low Palladium bearing bath (80ppm). It can be seen that while the Palladium level within the process solutions are at very different concentrations, this does not have any dramatic impact on the actual Palladium adsorbed onto the dielectric material, with both the high Palladium containing reference and the newly developed bath showing comparable levels of Palladium detected on the dielectric surfaces, suggesting that the activation performance of the two solutions would also be comparable.

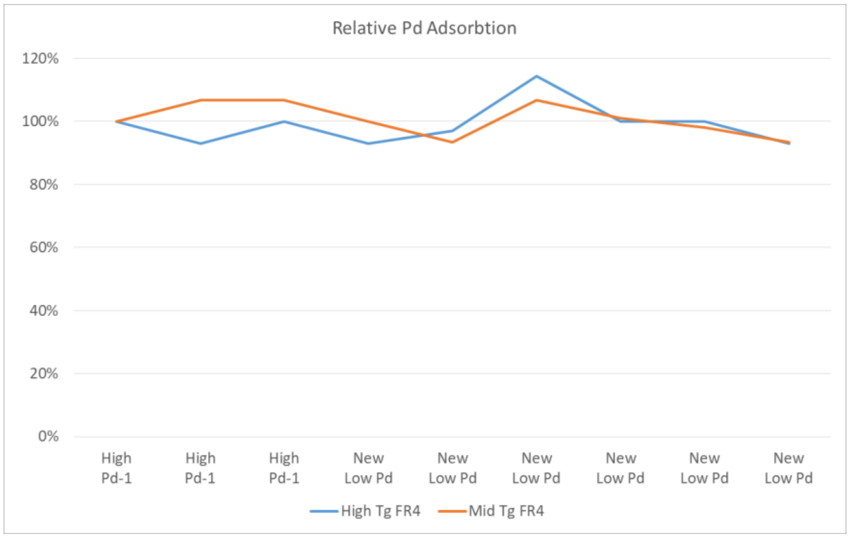

Figure 6. Palladium Adsorption on Two FR4 Dielectrics for a Reference High Palladium Containing Activator and the Newly Developed Low Palladium Activator

Deposition and Coverage with Electroless Copper.

When an extended investigation was made using a commonly used electroless Copper bath in combination with the reference high Palladium and new low Palladium activator, on a larger selection of dielectrics (Figure 7) it is confirmed that the lower level of Palladium in the active working solution has little or no impact on the activation function for the electroless Copper deposition as the coverage ratings via “back light” tests are comparable for both the high and low Palladium activation systems.

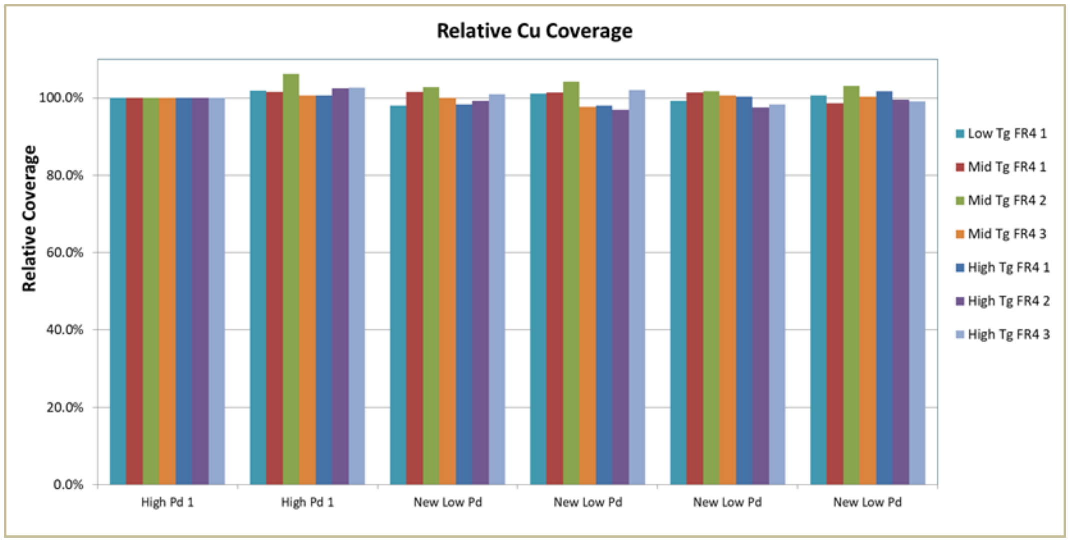

Figure 7. Copper Coverage on a Number of FR4 Dielectrics for Reference High Palladium Containing Activator and Newly Developed Low Palladium Activator

While coverage has been shown to be independent of the Palladium content in the activators examined, it is essential that the new low Palladium activator process not affect the deposition speed or thickness characteristics of the electroless Copper deposit, as this could impact its compatibility with existing processes and equipment, and thereby limit its interest within the market. Figure 8 shows the deposition thickness measured through titration for two commercially available electroless Copper baths utilizing the new low Palladium activator and the reference high Palladium activator. As can be seen there is no appreciable difference in terms of Copper thickness for the two conditions used, and all parts were processed for the same contact time, indicating no dramatic impact on deposition speed.

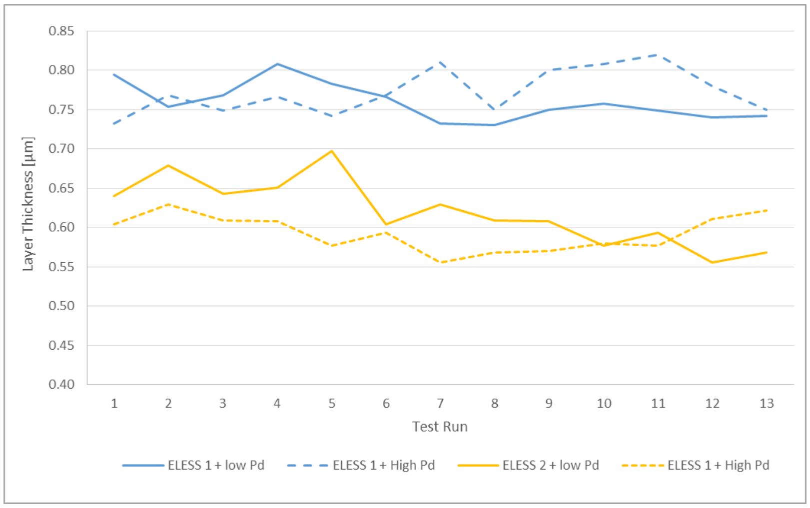

Figure 8. Electroless Copper Thickness for Two Copper Baths Utilizing the Newly Developed Low Palladium Activator and a Reference High Palladium Activator.

Reliability.

When testing for outline reliability requirements typical to the PCB industry, it can be seen from Table 2 that a reference electroless Copper process [6] in combination with the newly developed low Palladium activator is more than capable of passing such demands and is suitable for use in a wide range of electronic applications.

Table 2. – Reliability Test Data for Electroless Copper Process Utilizing the Newly Developed Low Palladium Activator.

Test Type	Method	Conditions	Test Criteria	Defect rate	Result
Solder Shock/Float	IPC TM 650.2.6.8	6 x 10 sec @ 288ºC	No ICD during inspection	0	Pass
	Based on IPC TM 650.2.6.8	9 x 10 sec @ 326ºC		16.1% Low Pd 32.3% High Pd	Pass
Cu-Cu Adhesion (BMV)	Internal Quick Via Pull	75, 100, 125, 150um Dia BMV	Target Pad Lift	0	Pass
Interconnect Stress Test	Based on IPC TM 650 2.6.26	2000 cycles 150ºC/ TR	Resistance Change <3%	Mean ΔR < 2.43%	Pass
Thermal Cycling	Based on IPC TM 650 2.6.7	1000 cycles -40/+125ºC (15/15min)	Resistance Change <3%	Mean ΔR < 1.85%	Pass

Summary.

With the current high price of Palladium not showing any signs of decreasing in the near future, in order to minimize ongoing process operational costs, there is increasing pressure to reduce the Palladium content used in electroless Copper activation processes. While a number of low, or reduced Palladium activators have been introduced previously, they have generally seen limited market acceptance due to poor or inconsistent performance.

A new low Palladium activation process has been developed, which overcomes the issues reported with earlier generations, and is shown to offer comparable performance to the current high Palladium containing equivalents. The testing reviewed within the paper, shows that the Palladium adsorbed onto a range of dielectric materials can be maintained at a stable level across the operational life of the process bath, and is, not only equivalent to that arising from traditional activation series, but is sufficient to enable a reliable and robust electroless Copper deposition.

References

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