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Číslo II

# IMPROVEMENT OF THICK PRINTED COPPER SUBSTRATES SOLDERABILITY BY FORMIC ACID

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### Anotace:

Tento článek se zabývá pájitelností užitím par kyseliny mravenčí v kombinaci s technologií vakuového pájení na keramických substrátech s měděným motivem vytvořením technologií TPC (Thick Printed Copper). Téma pájených spojů s nízkým, ideálně nulovým obsahem voidů vzniklých v průběhu pájení v oblasti elektroniky je důležité z důvodu rostoucí poptávky ve vysoko výkonových aplikacích. Přítomnost voidů může způsobit mnoho negativních účinků jako je lokální přehřívání nebo zranitelnost vůči mechanickému namáhání, což může vést k prasklinám a trhlinám. Pokud jsou pájené spoje poškozené nebo zničené, je produkt nefunkční a může vést k jeho úplnému zničení. To může mít za následek i život ohrožující situace.

#### Annotation

This paper deals with solderability of thick printed copper substrates using formic acid vapours in combination with vacuum soldering technology. The topic of low void, preferably void free joints in the field of electronics is important, because of rising demand in high-power applications. Void presence can cause many negative effects such as localized overheating or mechanical stress vulnerability which can result into cracks and splits. If the joints are partially or fully destroyed, the product is non-functional and can lead to its total destruction. This condition can result even in life threatening situation.

# **INTRODUCTION**

The necessity of low void, preferably void free, joints in the field of electronics is exponentially rising. This requirement is caused by continuous miniaturization of components, increasing density of parts on substrates and high-power applications [1]. All these factors are resulting in large heat dissipation, which cannot transfer through voids as effectively as through solder itself and can lead to localized overheating. Other severe issue is mechanical stress vulnerability, which can result into cracks and split [2]. Vacuum reflow soldering is proved way to achieve low void and high-quality connections. Further improvement can be reached by using fluxless solder in combination with formic acid vapours as an active atmosphere [3].

# VACUUM SOLDERING USING FORMIC ACID

Regularly used methods for soldering of micro components, eg. preform soldering with flux or traditional reflow soldering with rosin based paste result in many problems. Flux contained in the soldering process contributes to creation of voids in the joints, which can result in the complications mentioned in the beginning of the article. It is possible to reduce the size and volume of these voids, by using vacuum reflow soldering. Flux presence in the soldering process still can cause troubles by polluting the soldered samples. Necessity of pre- and after process cleaning is imminent. The after process cleaning is very problematic because of substrate and components damaging risk. All of these difficulties can be avoided by soldering in formic acid vapours, since elements created during the soldering process can be evacuated from the chamber. [1]

The chemical composition of formic acid is HCOOH, it can be found in nature, but in larger scale is industrially produced from methanol. Main use is during chemical synthesis, in power cells or, as in our case, for oxide reduction. The reaction of common metal oxide (MO) with formic acid is:

$$\begin{array}{l} \text{HCOOH}(g) + \text{MO}(s) \rightarrow \text{M}(\text{COOH})(s) + \\ \text{H2O}(g) \end{array} \tag{1}$$

$$M(COOH)(s) \rightarrow M(s) + CO2(g) + H2(g)$$
(2)

First equation describes formic acid reaction with the metal oxides at a lower temperature  $(150 \text{ }^{\circ}\text{C} - 190 \text{ }^{\circ}\text{C})$  and creation of carboxyl compounds. Second equation shows further temperature rise (200  $^{\circ}\text{C}$  and higher), which causes decomposition of the mixture into carbon dioxide and hydrogen. All these elements created during the process are in a form of a gas and can be evacuated from the chamber using pure nitrogen. [4]

Typical reflow profile using formic acid vapours can be seen in *Figure 1*. and consist of several parts. Firstly, the chamber is evacuated using vacuum pump and filled with pure nitrogen. This step is usually executed twice, to ensure lowest possibility of contamination of the chamber atmosphere with oxygen and air humidity. Temperature in the chamber is then raised to 175 °C. At the same time, formic acid vapours are introduced into the chamber and begins to react with the oxides on the surface of the samples. Next step is further temperature rise to melting level of the soldering compound. At the second part of this step, evacuation of the chamber is executed for possible voids created during the process to be lapped out of the solder. Last phase is combination of cooling with nitrogen filling of the chamber, which speeds up the cooling and flushes away any residues of formic acid. [5]

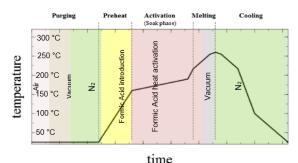


Fig. 1 Schematic diagram of typical reflow soldering process [3].

### MATERIALS AND PROCEDURES

Ceramic substrates (96% Al2O3; 0,63 mm thick) with thick film copper conductive patterns realized by the TPC (Thick Printed Copper) technology were used. Ceramic has specific property benefits, e.g. high heat dissipation, chemical and heat resistance, high dielectric strength. All the benefits are making the ceramic substrates brilliant in high power applications, where high heat is occurring. High conductivity in combination with thick copper layer greatly affects necessary modification made to reflow profile. For the possibility of customization of the soldering profile, vacuum reflow oven VSU20 from Invacu company was used. Its ability to hold formic acid in separated closed container, connected to nitrogen source and full variability in settings was a must.

Pre-process cleaning using citric acid checked the influence of acid concentration and time of exposure on the individual samples. Three different concentrations (1 %, 5 %, 10 %) and three-time durations (1, 5, 10 minutes) were set. After the exposure, all samples were rinsed with demineralized water or isopropyl alcohol. Then, the cleansed samples were placed in the reflow oven. Spread test method was used for the solderability test after the reflow process. This method allows spread measuring of solder ball with defined diameter (500  $\mu$ m) on soldered surface. Results evaluation was executed by measuring of solder ball spread and wetting contact

angle. After the soldering process was carried out, all samples were observed by the stereomicroscope SZX10 and confocal laser scanning microscope LEXT OLS5000. For wetting evaluation is applicable plot shown in Figure 2.

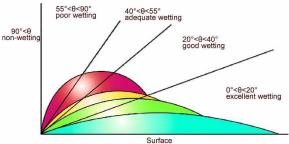


Fig. 2 Wetting proficiency dependent on wetting angle [6]. **RESULTS AND DISCUSSION** 

From each sample, spread and wetting contact angle was measured from solder balls and put in the graphs. The results of samples that were rinsed with demineralized water can be seen in Figure 2 and 3. In Figure 4 and 5 can be found results of samples, that underwent rinsing with isopropyl alcohol.

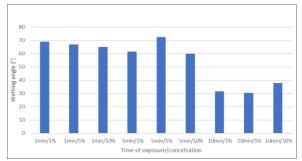


Fig. 3 Wetting angle dependency on the time of exposure and concertation of the samples rinsed with H2O.

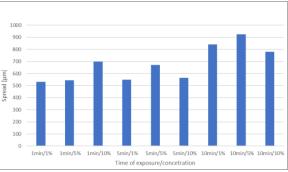


Fig. 4 Spread dependency on the time of exposure and concertation of the samples rinsed with H2O.

The results of rinsing the samples with demineralized water after the cleaning process shows that it is unsuitable for shorter time exposures of citric acid. Difference between one and five minutes' time duration is almost negligible as for wetting angles and also spread after the soldering process. But the trend can be seen as with rising exposure time and concertation, the wetting angles are slightly dropping and spread values are going in the opposite direction. With 10 minutes' exposure, the quality of spread ability and wetting angle is rising exponentially.

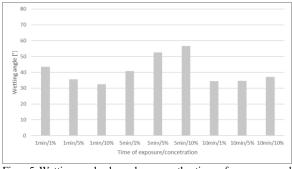


Fig. 5 Wetting angle dependency on the time of exposure and concertation of the samples rinsed with IPA.

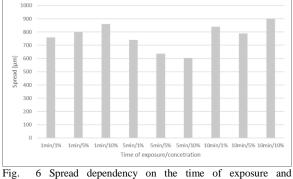


Fig. 6 Spread dependency on the time of exposure and concertation of the samples rinsed with IPA.

The results of samples that underwent rinsing with isopropyl alcohol shows, that even with shorter time durations of exposure to citric acid during cleaning, the wetting angles and spread ration is higher than when demineralized water is used. When the longer time interval is applied, the results do not differ that much in comparison with demineralized water, as both achieve great results.

# CONCLUSION

The experiment proved that pre-process cleaning is indispensable part when using formic acid as active atmosphere during vacuum soldering on ceramic substrates with copper conductive patterns. Citric acid has proven itself as an effective cleaning solution for this type of samples but results are dependent on the circumstances of exposure. The influence of used liquid for rinsing has shown as well. For preservation of great results, short time exposure is applicable only when isopropyl alcohol is used, otherwise results are mediocre. With the ten minutes' time interval for cleaning, the dependence on the rinsing solution is diminishing, as for achieved results are above average with wetting angles ~  $35^{\circ}$  and spread of the solder balls ~ 800 µm from the default value of 500 µm.

### ACKNOWLEDGMENTS

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