

GREEN RESIDUES AND ELECTRICAL RELIABILITY

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Abstract

Green residues on circuit boards or SIR and copper corrosion coupons may indicate serious corrosion and electrical reliability problems or limited and benign copper corrosion products that do not cause electrical reliability problems. Although this subject was discussed many years ago, no electrical evidence was given that certain green copper/flux residues do not degrade circuit reliability. Some liquid and solder paste fluxes give high SIR values in testing per J-STD-004 and IPC-TM-650 section 2.6.3.3, yet leave green residues on copper surfaces after soldering or exposure to heat and high humidity. The copper surfaces under such green flux residues are shiny and unpitted.

In this work, the FT-IR-spectrum of the green residue that was produced on an SIR coupon reflowed with solder paste flux, after exposure to seven days of 85°C, 85% R.H. and -48V bias, was compared to the spectrum of a synthetically prepared copper-rosin salt. These spectra have similar features that are not found in unreacted rosin or the inorganic copper salts most indicative of potential electrical failures. The copper-rosin salt is hydrophobic. SIR coupons prepared, in this work, with the salt had SIR values about a half order of magnitude above those of similar bare copper control coupons and an order of magnitude higher than the reflowed flux. Hence, this green copper-rosin salt does not degrade circuit reliability and limits further corrosion of copper surfaces.

INTRODUCTION

The appearance of green oxides and salts on copper surfaces is often considered an indication of detrimental corrosion processes. This can be the case in the presence of high concentrations of halide ion or hygroscopic materials on electronic circuits, where a continuous corrosion process may occur. Such corrosion processes may cause electrical failure of the affected circuit. However, some corrosion processes are self-limiting, and hence relatively benign. Manko found that unactivated and mildly activated rosin fluxes in the presence of copper wire and oxygen turned green because the abietic and other organic acids in the rosin reacted with oxidized copper to form the copper-rosin acid salts [1]. Since copper rosin salts are electrical insulators, the formation of green discoloration on copper surfaces by pure rosin and mildly activated rosin fluxes was not considered detrimental to an electronic assembly. While this is a logical conclusion, no electrical measurements were made at elevated temperature and humidity to prove this.

Turbini found that a rosin flux residue on copper turned green when exposed to elevated temperature and humidity [2]. FT-IR spectroscopy was used to compare the unprocessed flux and the resulting green flux residue (Figure 1). Although peak assignments were not given in

Turbini's work, examination of this data shows that the most important features of this comparison are the shift of the carbonyl stretch going from free carboxylic acid ($\sim 1700\text{ cm}^{-1}$) in the rosin flux to the copper carboxylate ($\sim 1600\text{ cm}^{-1}$) and shifts in the O-H stretching region ($4000\text{--}3000\text{ cm}^{-1}$) associated with changing hydrogen bonding owing to a decrease of free carboxylic acid moieties in the green flux residue. The copper surfaces under the green corrosion products were found to be shiny and unpitted.

Recently in our laboratory, ROL0 and ROL1 type solder paste flux (without solder powder) residues on bare copper surface insulation resistance (SIR) have turned dark green following exposure to 85°C and 85% RH during routine J-STD-004 classification testing per IPC-TM-650 section 2.6.3.3 [3]. This green discoloration is nearly independent of bias, and occurs on anodic, cathodic and unbiased portions of the SIR coupons. Tarnished copper often will have green rosin flux residues only after exposure to a solder paste reflow temperature profile. This greening effect is particularly strong for fluxes containing hydrogenated rosin. Despite the green discoloration of the test coupons, the SIR values for these fluxes are relatively high, and no evidence of electrochemical migration is found. The copper surface under the green flux residue is also found to be shiny and unpitted. This green

discoloration is either absent or very slight for solder paste, i.e., mixed paste flux and solder powder, tested under the same conditions. Since tin salts are not colored, this is not unexpected.

In this work, FT-IR spectra and J-STD-004/ IPC-TM-650 section 2.6.3.3 SIR values are compared for a solder paste flux containing hydrogenated rosin and a synthetic copper hydrogenated rosin salt.

EXPERIMENTAL PROCEDURES

Synthesis of copper hydrogenated rosin salt

The synthetic procedure was developed by R. Smith [4]. A slight stoichiometric excess of copper (II) acetate was added to hydrogenated rosin dissolved in butyl cellosolve. The mixture was boiled with stirring for several minutes. The butyl cellosolve was evaporated, and the reaction products were dissolved in tetrahydrofuran and washed with water to remove excess copper (II) acetate. Evaporation of the tetrahydrofuran yielded an extremely viscous, dark green substance. This substance is insoluble in water and only slightly soluble in isopropanol.

FT-IR spectroscopy

All spectra were measured with a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer with a microscope attachment.

J-STD-004 / IPC-TM-650 - 2.6.3.3 SIR testing

For solder paste flux, a thin layer of paste flux was spread on three IPC-B-24 coupons. For the copper rosin salt, a 25% solution in butyl acetate was pipetted on three IPC-B-24 coupons. The fluxed coupons were then subjected to a solder paste reflow temperature profile. Teflon-insulated wires were soldered to the coupons with an unactivated rosin flux. The coupons were connected to a Model 300 Sirometer and placed in a temperature humidity chamber set at 85°C and 85% RH. After temperature and humidity had stabilized, -48V bias voltage was applied to the circuit. SIR values were measured at 100 V after 24, 96 and 168 hours of bias application.

Frequent-measurement SIR testing

A thin layer of solder paste flux was spread on ten IPC-B-25 comb B coupons, then subjected to a solder paste reflow temperature profile. Teflon-insulated wires were soldered to the coupons with an unactivated rosin flux. 1 Mohm current-limiting resistors were placed in series with the SIR coupons. The coupons were placed in a temperature humidity chamber set at 85°C and 85% RH. Temperature and humidity were monitored with independent wet and dry bulb measurements using T-type thermocouples. After temperature and humidity were stabilized, 100V bias/measuring voltage was applied to the circuit. SIR values were obtained via IR drop measurements across the 1 Mohm resistors with a National Instruments SCXI datalogger system. SIR was measured every 15 minutes for the first day of measurement and hourly thereafter.

EXPERIMENTAL RESULTS

Figure 2 shows an FT-IR spectrum of the green copper

residue scraped off an SIR coupon exposed to 85°C 85%RH. Figure 3 shows the FT-IR spectrum of the synthetic copper rosin salt and Figure 4 shows the FT-IR spectrum of the hydrogenated rosin starting material. Like the spectrum of the rosin flux given in Figure 1, the hydrogenated rosin spectrum shows a sharp spike at 1700 cm⁻¹ for the free carboxylic acid, but no peak at 1600 cm⁻¹ for copper carboxylate. The copper-rosin salt spectrum shows a strong peak at 1600 cm⁻¹ and a smaller peak at 1700 cm⁻¹, indicating that, while most of the rosin acids reacted with the copper acetate, some unreacted rosin remained in the mixture. Likewise, the green flux residue spectrum also had both peaks present, indicating that the rosin in the flux residue had partially reacted with copper on the coupon, causing the green discoloration observed.

Table 1 summarizes SIR results for a rosin-resin type solder paste flux and the synthetic copper rosin salt per IPC-TM-650 section 2.6.3.3. The SIR values for coupons prepared with the copper-rosin salt had SIR values about a half order of magnitude above those of similar bare copper control coupons and an order of magnitude higher than the coupons prepared with solder paste flux.

Table 1

Sample	Average SIR at 85°C 85% RH -48 V bias, 100 V measure		
	24 hrs	96 hrs	168 hrs
Solder Paste Flux	4.4x10 ⁹ Ω	4.5x10 ⁹ Ω	5.9x10 ⁹ Ω
<i>Controls</i>	2.2x10 ¹⁰	2.0x10 ¹⁰	1.8x10 ¹⁰
Copper Rosin Salt	1.8 x10 ¹¹	1.1x10 ¹¹	2.1x10 ¹¹
<i>Controls</i>	4.1x10 ¹⁰	5.3x10 ¹⁰	5.8x10 ¹⁰

SIR vs time measurements for the solder paste flux on ten IPC-B-25 comb B patterns at 85°C, 85%RH and 100 V bias are given in Figure 5. During the 5 day test period, most SIR values remained above 10⁹ ohms and all values were above 5x10⁸ ohms. No sudden decreases in SIR indicative of electrochemical migration were observed.

DISCUSSION OF RESULTS

The FT-IR spectrum of the green solder paste flux residue on the SIR coupons shows that some of the rosin acids

present reacted with the oxidized copper surface of the conductors to form the intensely green colored salt. Additionally, the SIR values for the copper rosin salt/rosin mixture are very high, resembling those of a conformal coating. This corroborates Manko's conclusion that copper rosin salts are hydrophobic and electrical insulators, unlikely to cause electrical failures of printed circuit boards. Finally, the J-STD-004/IPC-TM-650 - 2.6.3.3 SIR values and the SIR vs time curves for the solder paste flux on bare copper suggests that the presence of the green flux residues is not likely to cause corrosion related failures in copper circuits.

CONCLUSIONS

Rosin-containing flux residue on copper can become green during exposure to elevated temperatures and humidity because a strongly colored copper rosin salt is formed. The high SIR values obtained for a synthetic copper rosin salt indicates that the material is hydrophobic and an electrical insulator, even under extreme temperature and humidity conditions. This suggests that presence of green flux residues does not indicate a deterioration of printed circuit board electrical reliability for many rosin-containing fluxes including those used in some solder pastes.

REFERENCES

1. H. Manko, "Color, Corrosion and Fluxes," Electronic Packaging and Production, February 1969
2. L. Turbini, Final Report, "Reliability Impact Study for Alternative Cleaning Solutions" to Warner Robins Air Logistics Center/LYPRE, June 1994
3. Joint Industry Standard J-STD-004 "Requirements for Soldering Fluxes," January 1995
4. R. Smith, unpublished results, 1987

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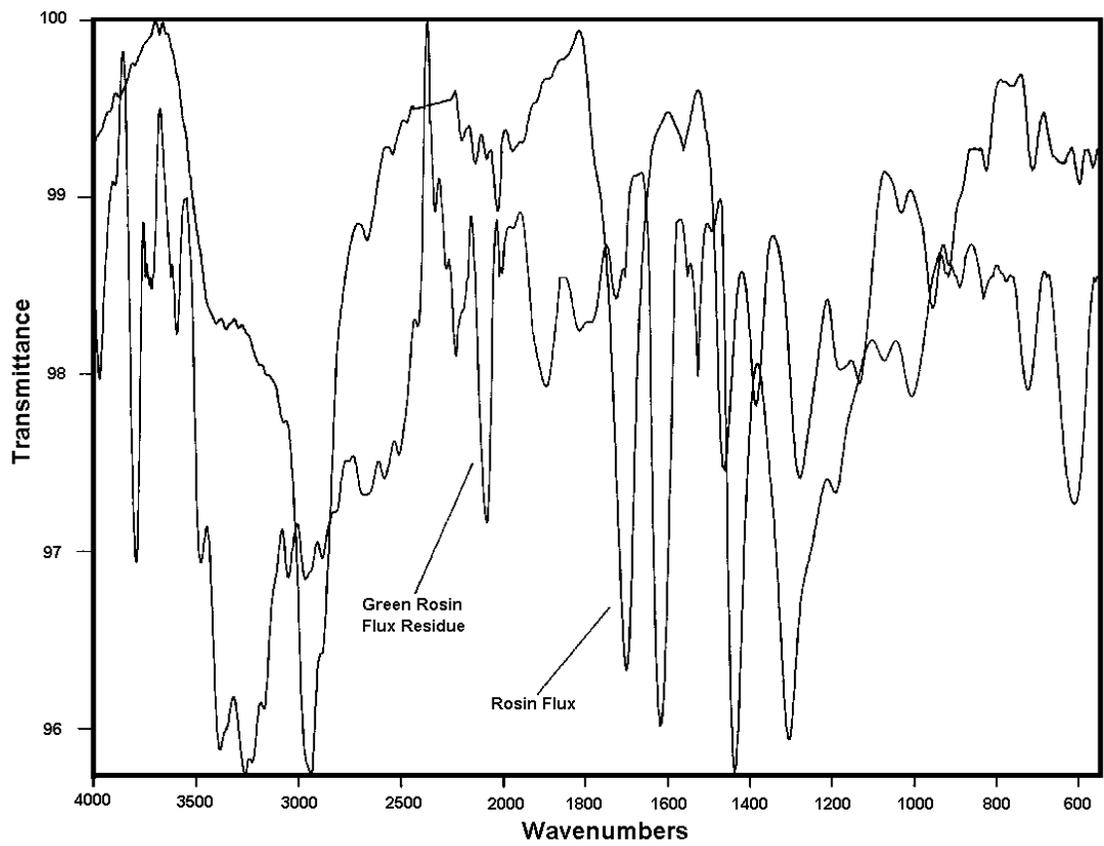


Figure 1. FT-IR spectrum of a rosin flux and the green residue of this flux on copper after exposure to elevated temperature and humidity (taken from reference 2.)

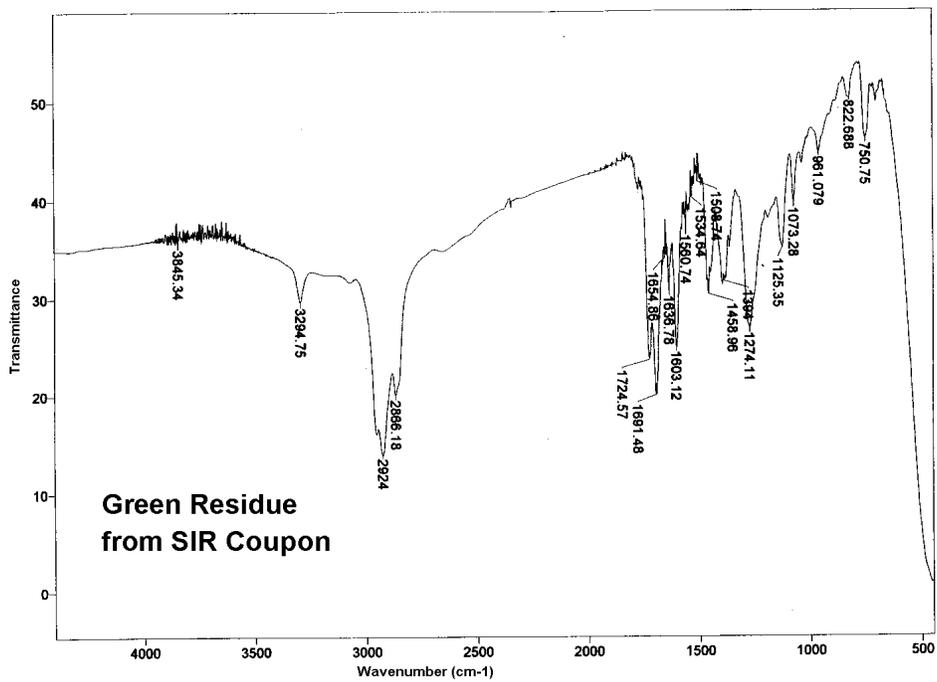


Figure 2. FT-IR spectrum of green residue scraped off an SIR coupon with solder paste flux that turned green during exposure to 85°C 85% RH.

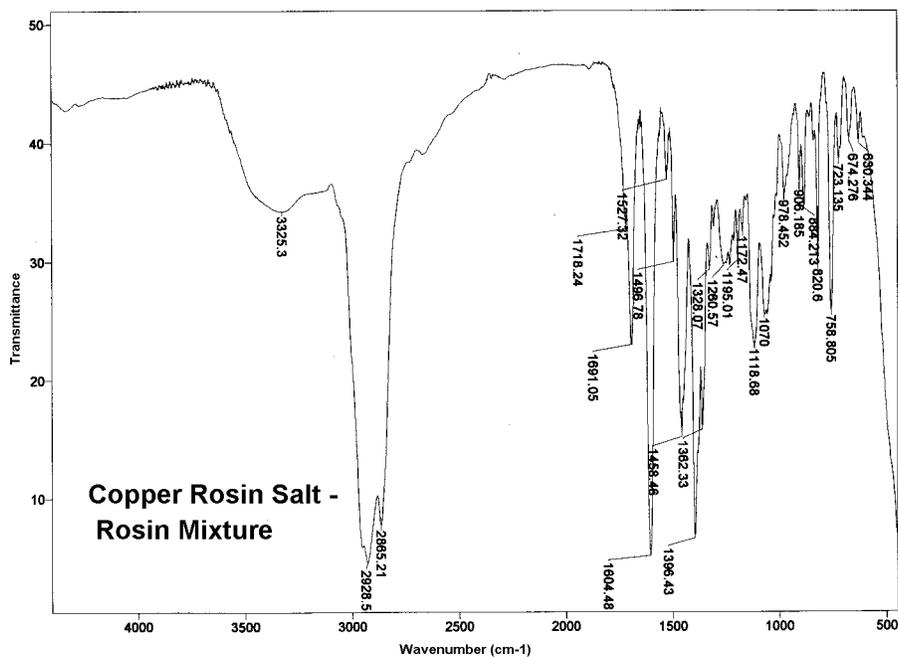


Figure 3. FT-IR spectra of copper-rosin salt / rosin mixture.

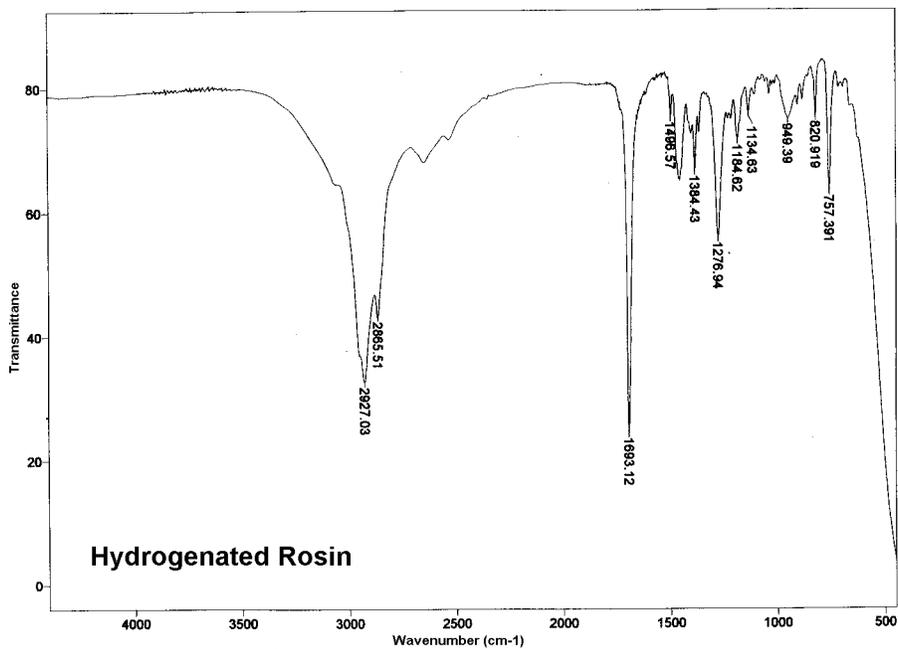


Figure 4. FT-IR Spectrum of hydrogenated rosin.

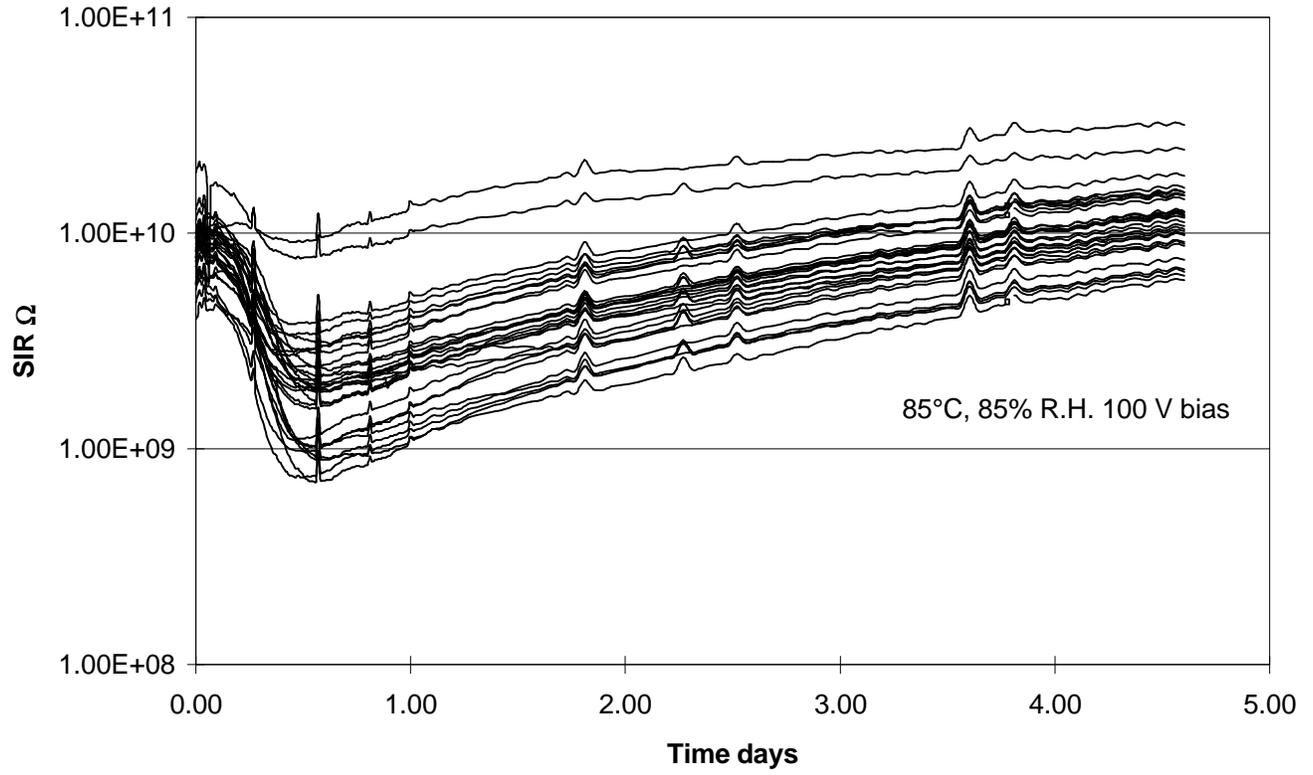


Figure 5. SIR vs. Time for a rosin-resin solder paste flux .