A Study of the Corrosive Effect of Soldering Fluxes on Printed Circuit Boards

Six corrosions tests were evaluated as to their effectiveness in assessing the corrosive characteristics of commercial rosins used in the electronics industry

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ABSTRACT. The corrosiveness of six commercial rosins used by the electronics industry was studied. The copper sheet test, drop test and copper electrodeposition test were used. The chloride content, pH and conductivity of the aqueous rosin extracts were determined. Finally, the electrochemical impedance spectroscopy (EIS) method was used. All six tests allowed rosin corrosiveness to be studied. The EIS method allowed the corrosion rate to be quantified.

Introduction

The advent of the printed circuit board (PCB) has turned electronics into the major field for application of soft solder. In fact, a host of devices ranging from the smallest electronic devices to vast telephone switchboards include many soldering points.

A soldering flux serves three main purposes: 1) to dissolve the corrosion film that hinders contact between the base metal and soldering alloy, 2) to prevent reoxidation of the metal surface during soldering, and 3) to alter the equilibrium surface tension in order to facilitate the spread of the solder (Refs. 1, 2).

The fluxing properties of rosins are typically improved by mixing them with additives called "activators." Unfortunately, the activator also leaves a corrosive residue that it is impossible to remove in many cases (Refs. 3–6).

The purpose of this paper is to report the results of a study of the corrosiveness of six commercial rosins widely used in soldering PCBs. The rosins have specific applications and are not all used interchangeably. Five conventional tests for PCB technology were used, along with a sixth more recent test, based on the EIS method, which makes it possible to study the corrosive effect of a rosin.

Experimental Procedure

The compositions of the fluxes used are indicated in the German DIN Specification 8511 T2 (Ref. 7). According to the manufacturer, R-3 and R-4 are type F-SW-31 "water white" rosins (nonactivated), R-0 and R-00 are type F-SW-26 halide-based activated rosins, R-1 is a type F-SW-32 halogen-free activated rosin, and R-2 is a type F-SW-25 organic flux rosin. The six solder fluxes are typically used in the electronics industry. R-0, R-00 and R-2 also are used in structural applications (Ref. 2). Table 1 shows information about the six commercial soldering fluxes studied and their national specifications, United States QQ-S-571E (Ref. 6), Germany DIN 8511 T2 (Ref. 7), and British BS 5625 (Ref. 8).

KEY WORDS

Rosin
Soldering Flux
Copper Sheet Test
Drop Test
Electrodeposition
Chloride Content
pH Aqueous Solution
Conductivity
Impedance
Corrosion Rate

Copper Sheet and Drop Tests

Six 50 x 50 x 0.5-mm sheets of semi-hard copper with a cupping in the middle were prepared. The sheets were degreased in 5% H_2SO_4 at 60–70°C for 1 min and subsequently immersed in 25% $(NH_4)_2S_2O_8$ containing 0.5% H_2SO_4 at 20°C. After rinsing in distilled water, the sheets were placed in a 5% H_2SO_4 solution at 25°C for 1 min, followed by rinsing with distilled water and acetone, and air-drying.

One gram ±0.05% of 60:40 Sn-Pb soldering alloy and 0.040 g ±0.005% of flux were placed in the middle of each copper sheet and the sheets were then floated on the surface of a molten metal bath at 235°C ± 5°. Five seconds after the soldering alloy had melted, the copper sheet specimen was removed from the bath and allowed to cool for 15 min. Finally, the specimens were placed upright in a humidity chamber at 91–95% relative humidity (RH) and 40°C ±2°. Corrosion was observed in the appearance of a bluish green color on the copper sheets or white stains in the soldering alloy or flux residue (Refs. 8–12).

The drop test was carried out as follows: a 30 wt-% rosin solution in benzyl alcohol was prepared and a drop was placed in the middle of each copper

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sheet. Finally, the sheets were placed in a humidity chamber at 100% RH and room temperature (Ref. 10).

Copper Electrodeposition Test

A volume of 0.05 mL of rosin solution was placed on a copper-coated stainless steel sheet. Two copper film thicknesses were studied: 0.1 μm and 0.6 μm. The stainless steel sheets were then placed horizontally in a humidity chamber at 50% ±5% RH and 23°C ±2°, for 24 h ±0.5 h. After exposure to the humidity chamber, the specimens were visually examined and finally immersed in isopropyl alcohol, according to the MIL-F-14256C specification (Ref. 5).

Determination of the Chloride Content, pH of Aqueous Solution, and Conductivity of the Water Extract

One gram of flux was added to 50 mL of benzyl alcohol and the mixture was heated until the dissolution of the flux was complete. Fifty milliliters of distilled water was then added, and the solution was filtered through a separation funnel and allowed to stand for 24 h.

The phase containing the aqueous extract was collected and diluted to 100 mL. The resulting solution was then used to determine the chloride content (Ref. 13), the pH by use of a glass electrode pH-meter (Ref. 14), and the conductivity by means of a commercially available conductivity meter (Refs. 5, 6).

Electrochemical Impedance Spectroscopy (EIS)

The specimen used was a 2.3 x 1 x 0.1-cm PCB (Fig. 1) with two soldering points for establishing a two-electrode configuration (Ref. 15). A sketch of the setup is included at the bottom of Fig. 1. One-tenth gram of 60:40 Sn-Pb soldering alloy was placed at each soldering point, together with an approximate quantity of 0.03 g of flux, and melted in place using an electronic soldering iron. The specimens were stored in a humidity chamber at 100% RH and 40°C ±2°.

The PCBs used in this work simulated real service conditions. In fact, they contained the galvanic couple formed by the copper tracks in the printed circuit and the soldering alloy, as well as the rosin-activator residues. These features and the high sensitivity of the EIS method make this approach a very promising choice.

By applying a single-frequency voltage $\Delta v = V_m \sin\omega t$, where ω is the angular frequency in radians/s ($\omega = 27\pi f$, f is the frequency in Hz), the phase shift, ϕ, and amplitude of the resultant current $\Delta i = I_m \sin(\omega t + \phi)$ can be determined. Impedance is a vector whose modulus is defined as $|Z| = V_m/I_m$ containing resistive (R) and reactive (C) components. Impedance can be defined as a complex number $z = z' - jz''$, where z′ and z″ are the real and imaginary components, respectively, and $j^2 = -1$ (Ref. 16).

Measurements were made using a Solartron 1250 frequency response analyser (FRA) connected to an EG&G PARC 273A potentiostat/galvanostat. The frequency range used was from 55 kHz to 1 Hz, and the signal amplitude was ±10 mV (rms). Impedance measurements were generated at the open-circuit potential.

Table 1 — Identification and National Specifications of the Six Categories of Solder Fluxes Studied

Rosin	QQ-S-571E Standard	DIN 8511 T2 Standard	BS 5625 Standard
R-0	RA	F-SW-26	5a
R-00	RA	F-SW-26	5a
R-1	RMA	F-SW-32	5b
R-2	RA	F-SW-25	5a
R-3	R	F-SW-31	6
R-4	R	F-SW-31	6

United States QQ-S-571E (Ref. 6). Germany DIN 8511 T2 (Ref. 7). British BS 5625 (Ref. 8)

Results of Experiments

Copper Sheet Test

The intensity of the bluish green halo formed on the copper sheet was the criterion for estimating the corrosiveness of the soldering fluxes according to British specification 5625 (Ref. 8). After three days, the copper specimens coated with rosins R-0, R-00 and R-2 showed a bluish green halo, whereas R-1 exhibited no signs of corrosion.

Table 2 summarizes the results obtained at 30 days. The halo developed on R-0, R-00 and R-2 at 30 days may have resulted from the condensation of moisture and the solution containing the ionic residues from the rosin activators agree with British specification 5625 (Ref. 8).

The soldering alloy was more readily melted on the copper specimen coated with rosin R-2 than on the other specimens, to the extent that it spilled over — Fig. 2A. On the other hand, the solder did not wet the copper sheet or spread widely on the specimens coated with rosins R-3 and R-4 — Fig. 2B. This is an indirect measure of flux corrosiveness.

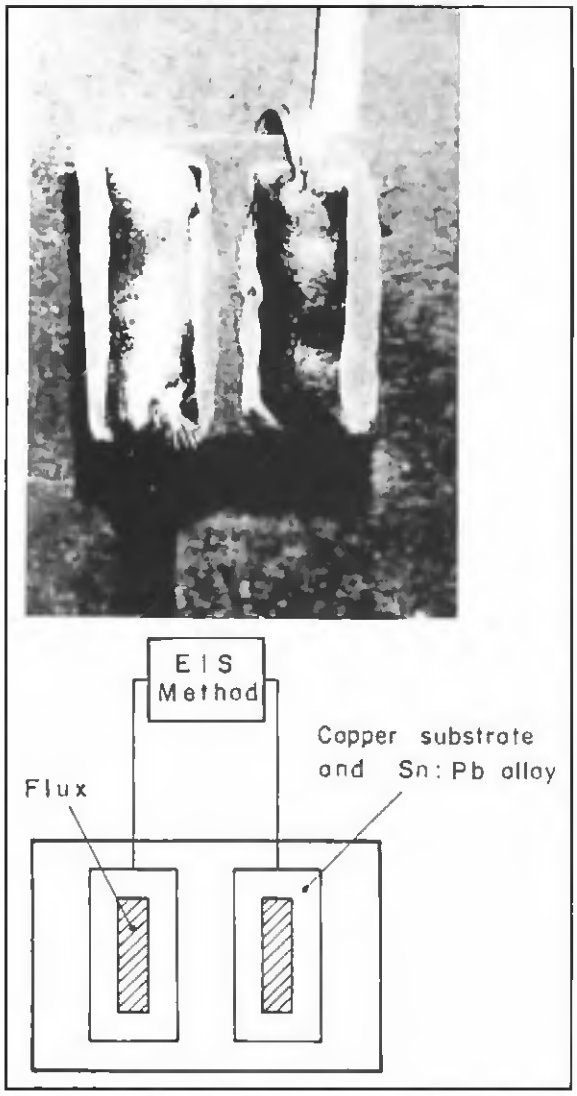

Fig. 1 — Specimen containing two soldering spots used in the EIS Method and the setup of the arrangement.

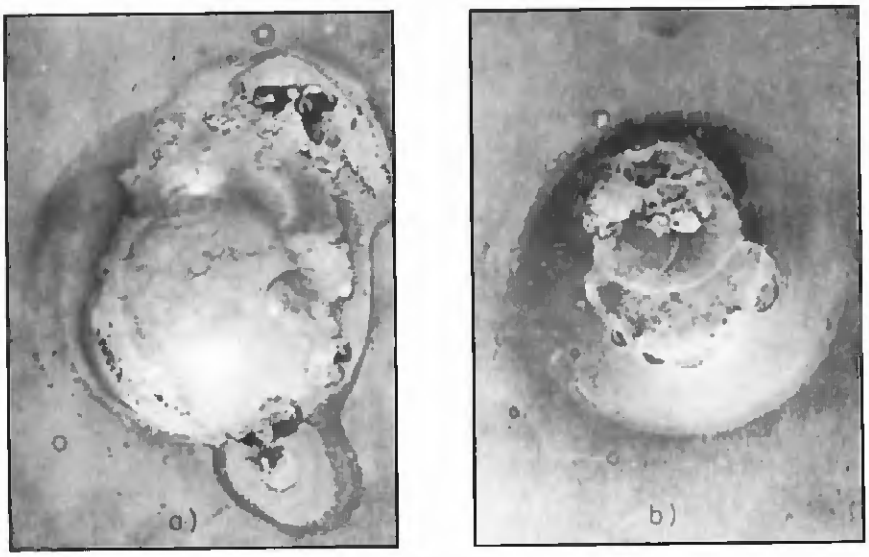

Fig. 2 — Copper sheets containing soldering alloy and rosin. A — Rosin R-2; B — Rosin R-3.

Table 2 — Copper Sheet Test Results at 30 Days

Rosin	Corrosion Grade at 30 Days Associated to Sheet Color
R-0	1
R-00	1
R-1	2
R-2	0
R-3	0
R-4	0

0: No change, 1: Bluish green color, 2: White color (Ref. 8).

Table 3 — Drop Test Results

Rosin	Experimentation Time 2 days	10 days	30 days
R-0	1	1	2
R-00	1	1	2
R-1	1	2	3
R-2	2	2	3
R-3	0	1	1
R-4	0	1	1

0: No corrosion stain, 1: Slight trails of corrosion and color change, 2: Slight pittings, 3: High corrosion.

Table 4 — Modified Copper Electrodeposition Test Results Expressed as Time Needed to Dissolve a Thin Copper Film Using a Drop of Flux Dissolved in Benzyl Alcohol

Rosin	Thickness of Copper Film 0.1 μm	0.6 μm
R-0	7 min	30 min
R-00	30 min	60 min
R-1	45 min	6 h
R-2	4 min	25 min
R-3	16 h	>24 h
R-4	16 h	>24 h

Thus, rosin R-2 was seemingly the most active, whereas rosins R-3 and R-4 did not allow the solder to wet the metal properly as they contained no activator.

Drop Test

Table 3 shows the corrosion produced by the rosins tested as measured by means of the drop test. Within 1 h, rosins R-0, R-00 and R-2 gave rise to a light-colored halo around the drop, whereas rosin R-1 had changed the drop area to a very dark color. Rosins R-3 and R-4, however, resulted in no changes.

At two days, the drops of rosins R-0, R-00 and R-2 were thicker and darker and the original halo had spread and turned bluish. At 10 days, the drops of rosins R-0, R-00 and R-1 had a greenish blue veil. On the other hand, the drops of rosins R-3 and R-4 had evaporated.

At the end of the test the rosins were dissolved in benzyl alcohol in order to study the type of attack involved. Rosins R-3 and R-4 left a dark stain on the copper sheets, which was even darker for R-1 and R-2. The specimens coated with rosins R-0 and R-00 showed many pits.

Copper Electrodepositinn Test

The specifications commonly used to carry out the copper electrodeposition test are cited in United States specifications MIL-F-14256C, QQ-S-S71E and ASTM B284 (Refs. 5, 6, 17). However, none of the six rosins studied complied with these specifications, due to their excessive corrosiveness. A new method named the modified copper electrodeposition test was proposed. This new method involves measuring the time taken by a drop of flux solution in 20 wt-% of benzyl alcohol to dissolve a thin copper film. This proposed new method allowed the rosins to be classified according to their corrosiveness.

Rosin R-0 dissolved the 0.6-μm-thick film in half the time taken by R-00. On the other hand, rosin R-0 was approximately four times less corrosive than R-00 with a 0.1-μm film thickness — Table 4.

Corrosion in the specimens coated with rosins containing chlorine (R-0, R-00 and R-2) started around the drop and formed a halo that eventually exposed the underlying stainless steel. The other specimens showed a dark spot under the drop, where the copper coating started to dissolve — Fig. 3.

As can be seen from Table 4 and Fig. 3, rosins R-0 and R-2 were more corrosive than R-00 and R-1, which in turn surpassed R-3 and R-4 in this respect.

In order to simulate the changes occurring in a rosin during soldering, a parallel test was carried out, involving boiling a constant volume of rosin solution for 1 min followed by placing 0.05 mL of the solution on a copper-coated stainless steel sheet with a 0.1-μm and 0.6-μm film thickness. The results were identical to those for the nonheated rosins.

Activators are known to become inert above a given temperature (Ref. 18). In order to investigate this effect, a second parallel test was carried out, involving placing five drops of rosin on a stainless steel sheet coated with copper at a 0.1-μm and 0.6-μm thickness and heating with a soldering iron. The results thus obtained were similar to those of the modified copper electrodeposition test.

Determination of the Chloride Content, pH of Aqueous Solution, and Conductivity of the Water Extract

Table 5 shows the chloride content, pH, and conductivity of the aqueous extracts from the fluxes studied. All six rosins were acidic; also, three of them (R-0, R-00 and R-2) contained a chlorinated activator. As can be seen from the conductivity values, there were some differences between the fluxes. Thus, the activated rosins had a much higher conductivity than the unmodified rosins.

As can be seen from Table 5, the rosin R-2 was the least acidic and also the one containing the most chloride. Dunn, *et al.* (Ref. 9), claim that a rosin of pH 3.5 containing over 4% chloride is highly corrosive.

Electrochemical Impedance Spectroscopy (EIS)

In general, the diameter of the semi-

circle of a Nyquist plot is a measure of Rp value, and using the Stern-Geary equation ($i_{corr} = B/R_p$) the corrosion current density may be estimated. It can be concluded that the greater the diameter of the semicircle (R_p) the lower the i_{corr}. Thus, the evolution of a Nyquist plot with time allows the corrosion current density to be quantified (see below).

Figure 4 shows the typical Nyquist plots (Z' vs. jZ") for the rosins obtained at different experimental times. During the first 10 days of the test a very open arc is observed. It should be noted that all the Nyquist plots obtained in these first 10 days were similarly shaped. However, after 15 days the plots started to exhibit some differences. Thus, the approximate semicircle for R-2 and R-1 rosins was defined with time, with less definition for R-0 and R-00 rosins and almost no change for R-3 and R-4 rosins.

Discussion of Results

While the drop test can be used as a rough approach to studying corrosiveness in rosins employed by the electronics industry, it is better suited to stronger fluxes such as those used in plumbing, where pit depth can readily be measured by metallographic microscopy (Ref. 19).

In soldering two metals, the liquid flux wets the surroundings of the molten solder front, thus bringing both metals and the corrosion layer potentially present into contact. The soldering process may alter the composition and activity of the flux. On the other hand, some of the residues left after the flux cools are highly hygroscopic and may lead to galvanic corrosion. Therefore, the basic purpose of the copper sheet test is to measure galvanic couples formed in soldering. Because copper is more noble than the soldering alloy, approximately 300 mV (Ref. 20), the galvanic effect will further enhance solder corrosion in the presence of chloride ions, thereby increasing the risk of failure in the electric contact at the soldering joint.

As can be seen from Table 6, the results provided by the modified copper electrodeposition test and copper sheet test were quite consistent. In addition to these tests, the water extract chloride content, aqueous solution pH, and water extract conductivity should be determined (Ref. 14) since residual ionic contaminants in the solder can trigger corrosion in the presence of moisture. The results of these tests (Table 5) were also consistent with the corrosion tests: copper sheet test and modified copper electrodeposition test.

In order to interpret the EIS measurements, the electrolyte (water adsorbed from the atmosphere)/rosin/metal system may be described by an equivalent circuit relevant for the conditions of the experiment, *i.e.*, some network containing ideal resistive and capacitive components which can represent the properties of the test system and model the collected data. To approximate the electrical

Table 5 — Chloride Content, pH, and Conductivity Test Results

Rosin	% Cl-	pH	Conductivity μS cm⁻¹
R-0	1.60	3.5	56
R-00	0.40	2.4	139
R-1	0.00	3.3	17
R-2	4.04	4.1	122
R-3	—	3.5	8
R-4	—	3.1	10

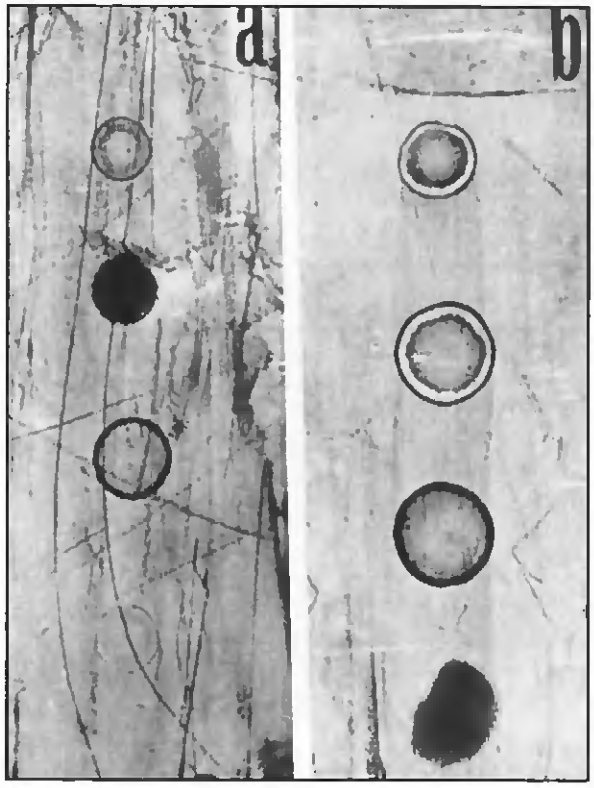

Fig. 3 — Effect of the attack by different rosin drops on a copper film of 0.6 μm thick. A — Spots left by rosins R-0, R-1, R-00 and R-2 (top to bottom) at 30 min; B — Spots left by rosins R-0, R-2, R-00 and R-1 (top to bottom) at 60 min.

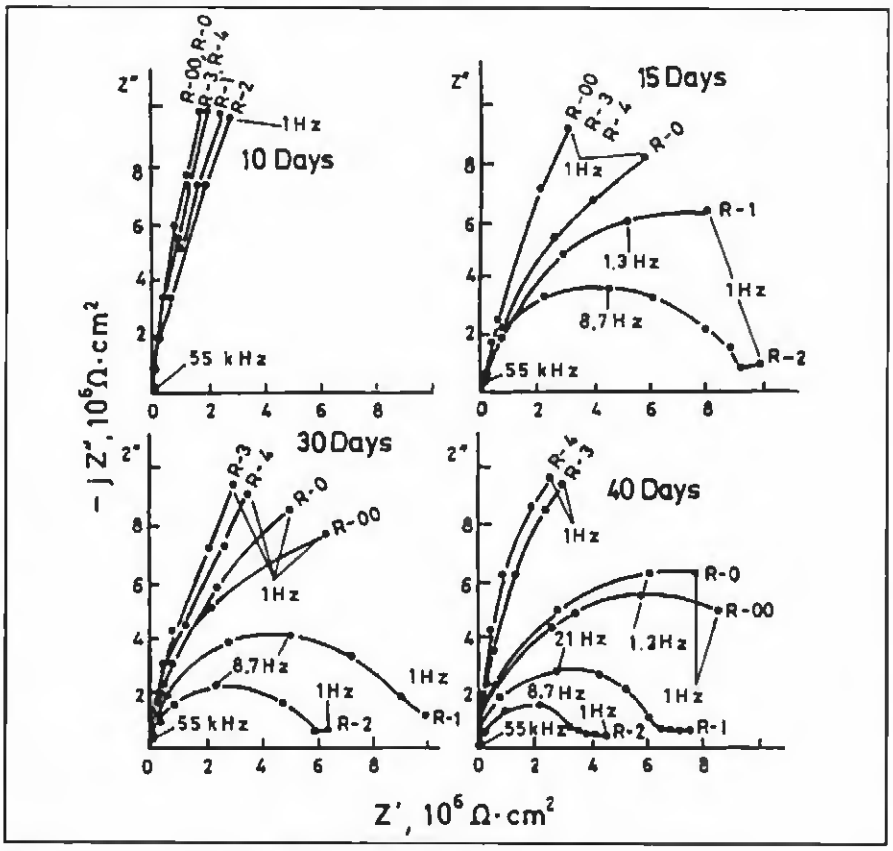

Fig. 4 — Nyquist plots for the rosins studied at different times.

Table 6 — Classification of the Rosins Studied in Decreasing Order of Corrosiveness

Copper sheet test	R-2>R-0>R-00>R-1>R-4=R-3
Drop test	R-2>R-1>R-0=R-00>R-4=R-3
Modified copper Electrodeposition test	R-2>R-0>R-00>R-1>R-4>R-3
Chloride content of water extract	R-2>R-0>R-00>R-1=R-4=R-3
pH of aqueous solution	R-2>R-0=R-3>R-1>R-4>R-00
Conductivity of water extract	R-00>R-2>R-0>R-1>R-4>R-3
EIS method	R-2>R-1>R-00>R-0>R-4=R-3

Table 7 — Rosin Corrosion Current Density Estimated by the EIS Method

Time	Rosin R-0	R-00	R-1	R-2	R-3	R-4
	Corrosion current density, nA cm^{-2}					
15 days	7.9	4.1	0.3	17.6	4.1	4.0
20 days	11.0	5.5	12.7	20.6	3.8	3.9
30 days	11.3	8.2	15.0	25.8	4.1	4.2
40 days	11.8	13.7	23.6	37.5	4.1	4.0

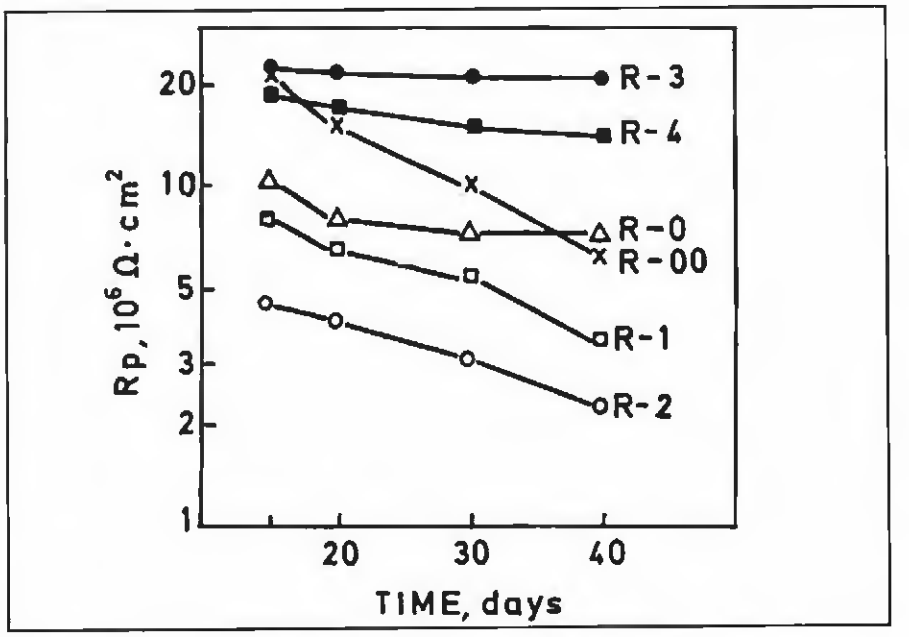

Fig. 5 — Variation of the apparent polarization resistance, Rp, with time.

double-layer and the faradaic impedance of a quasireversible reaction (corrosion process) a resistor and a condenser (electrical double-layer) in parallel can be used. Nyquist plots provide a wealth of information. Thus, as can be seen from Fig. 4, the behavior of the electrolyte/rosin/metal system at 10 days was essentially capacitive, the rosin appears to show a certain inertia to starting the corrosion process and a very open arc close to the imaginary axis is obtained (10 days, Fig. 4). The Nyquist plot shape can be ascribed to the absence of corrosion; otherwise, part of the current would have shunted along the faradaic branch parallel to the capacitive branch of the equivalent circuit, as was indeed the case later, which accounts for the gradual definition of the semicircle. Thus, for 15 days experimentation, the Nyquist plot of R-2 rosin draws a semicircle. The diameter of the semicircle gives an apparent polarization resistance, R_p, equal to 9 x 10^6 Ω cm^2. Finally, for 40 days experimentation, the R-2 and R-1 rosins define a depressed semicircle, at high frequencies, and a small diffusion "tail" at low frequencies. The depression of the Nyquist plot may be due to dispersion in the time constant (Ref. 16). For 40 days experimentation R-00 and R-0 semicircles continue to be very open and the R_p value may be obtained by extrapolation. For this experimentation time, the least corrosive behavior is shown by R-3 and R-4 rosins. Figure 5 depicts the variation of R_p with time.

Once R_p is known, the corrosion current density can be estimated by using the Stern-Geary equation ($i_{corr} = B/R_p$). For this purpose, we assumed an approximate value of the constant B of 0.026 V, which is very commonly used in atmospheric corrosion studies (Ref. 21). The apparent surface area was 32 mm^2. Table 7 shows the corrosion current density thus estimated for each type of rosin.

Tentative weight loss and average corrosion may be calculated using Faraday's law. In this way, we found an average annual corrosion of 0.43 μm $year^{-1}$ for copper, and 0.99 and 1.11 μm $year^{-1}$ for tin and lead, respectively, all at the maximum corrosion current density measured, *i.e.*, 37.5 nA cm^{-2} (Table 7). Obviously, lower values of i_{corr} cause less corrosion. Because these are mean values, the corrosion rate may be greater at some points.

Conclusions

The rosins studied in this work are employed by the electronics industry, and the activators they contain are moderately corrosive, so use of the modified copper electrodeposition test is to be preferred as it is more sensitive than the drop test and performs similarly in all other respects. On the other hand, the copper electrodeposition test fails to measure the effect of contact between the metals forming the soldering joint, so it must be used in combination with the copper sheet test.

The EIS method is potentially useful for assessing the corrosiveness of rosin activators used as soft soldering fluxes. The corrosion system made up by the copper, solder and flux residue is adapted to an equivalent circuit essentially consisting of a parallel condenser and resistor. Consistent with the theoretical predictions, the resulting Nyquist plot is roughly semicircular. The estimated apparent polarization resistance, R_p, provides a semi-quantitative measure of flux corrosiveness. Thus, rosins R-1 and R-2 proved to be the most aggressive of the six tested, whereas R-3 and R-4 were found to be the most reliable, with R-0 and R-00 lying between the two extremes. These results are consistent with those obtained using conventional techniques.

References

1. Moshkova, G. E., Oparina, R. A., and Stakhovsky, S. A. 1975. Effect of the flux on the surface tension of a solder. *Svarochnoe Proizvodstvo* 7: 11–12.

2. Manko, H. H. 1973. Soldering fluxes.

Past and present. *Welding Journal* 52(3): 163–166.

3. ASTM Standard D 509. 1975. Rosin sampling and grading. American Society for Testing and Materials. Philadelphia. Pa.

4. British Standard DTD-599A. 1961. Non-corrosive fluxes for soft soldering. U. K.

5. United States MIL-F-14256C. 1963. Flux solutions of rosin or mildly activated rosin.

6. United States QQ-S-571E, specification. 1972. Solder, tin alloy: tin-lead alloy; and lead alloy.

7. German Standard DIN 8511 T2, specification. 1967. Fluxes for brazing, braze welding and soldering metallic materials; fluxes for soldering of heavy metals.

8. British Standard 5625. 1980. Specification of purchasing requirements and methods of test for fluxes for soft soldering. U. K.

9. Dunn, B. D., and Chandler, G. 1980. The corrosive effect of soldering fluxes and handling on some electronic materials. *Welding Journal* 59(10): 289-s to 307-s.

10. Luder, E., and Krell, A. 1965. Zur frage der korrosion von weichlötstellen an kupfer. *Metallwissenscheft und Techink* 19(11): 1156–1159.

11. Krell, A. 1973. Soldering fluxes and corrosion. *ZISMitteilungen* 11(4): 370–375.

12. Krell, A. 1979. Weichlöt flubmittel und korrosion. *Schweisstechnik* (Berlin) 6: 249–252.

13. ASTM Standard D 512. 1989. Test methods for chloride ion in water. American Society for Testing and Materialss. Philadelphia. Pa.

14. Studnick, W. R., and Foune, C. C. 1973. Testing for corrosivity in activated liquid soldering fluxes. *The Western Electric Engineer* 17(1): 3–8.

15. Marsh, G. A. 1963. The measurement of instantaneous corrosion rates. *Proc. 2nd Inter. Congr. on Metallic Corrosion*, New York, pp. 936–941.

16. Macdonald, J. R. 1987. *Impedance Spectroscopy*. pp. 1–12 and pp. 27–42, New York, N.Y., Wiley.

17. ASTM Standard B 284. 1971. Standard specification for rosin flux-core solder. American Society for Testing and Materials. Philadelphia. Pa.

18. Okamoto, I. 1975. Studies on flux action of soldering. *Transaction of IWRI* 4(1): 85–91.

19. Costas, L. P. 1981. An accelerated test method for evaluating the corrosiveness of soft solder fluxes. *Materials Performance* 20(4): 39–41.

20. Dunn, B. D. 1976. Product assurance and choice of materials for satellite construction. *Metallwissenscheft und Technik* 30(9): 711-720.

21. Bastidas, J. M., Mora, E. M., and Feliu, S. 1990. The protective action of two vapour phase inhibitors on the corrosion of mild steel. *Werkstoffe und Korrosion* 41(6): 343–347.