
EIA BULLETIN

Contamination of Printed Wiring Boards

CB2

JUNE 1959

**ELECTRONIC INDUSTRIES ASSOCIATION
ENGINEERING DEPARTMENT**



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ABSTRACT

Contamination of printed wiring boards is defined, and examples are given of the causes of such contamination. The electrical effects of such contamination are then reviewed. Specifications are given for tests which may be used to evaluate the causes of contamination. Electrical tests for evaluating the effects of contamination are detailed.

This report was prepared by Messrs. Edward B. Saubestre* and Saul W. Chaikin**, Chairmen of Eastern and Western Subcommittees on Contamination of Printed Wiring Boards.

The report was subsequently reviewed and formally approved by the full membership of EIA Committee 40C on Printed Wiring. Mr. R. A. Geshner***, Chairman, and recommended for issuance as an EIA Engineering Bulletin.

*Enthone Inc., (work done while employed with Sylvania Electric Products Inc., Flushing, New York).

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CONTAMINATION OF PRINTED WIRING BOARDS

1. Introduction

1.1 Definition

For the purpose of this paper, contamination will be defined as a chemical or metallurgical material change or deterioration on the board, occurring before or after assembly. These changes may arise in (a) the raw material, (b) processing or (c) from environmental conditions.

1.2 Sources of Contamination

1.2.1 Raw Material

Organic decomposition of the laminate may occur. This is especially true of partially cured, thermoplastic materials. If the copper-coated board is manufactured by a plating technique, rather than by use of a pre-clad laminate, contamination may arise as a result of the cleaning and plating procedures used. The susceptibility of a board to the effects of contamination is dependent on the type of laminate used, since some react with, or absorb contaminants more readily than others, and/or absorb moisture more readily.

1.2.2 Processing

In producing etched boards, the principal sources of contamination are etching solution residues. This is particularly true with ferric chloride etchants, but is also true to varying degrees for other etchants as well. Residual electrolyte from cleaning, sensitizing, chemical plating, and electroplating solutions is often a major factor in contamination of the printed circuit board.

Among lesser sources of contamination are solder flux residues, metallic migration of silver, and growth of whisker formations on cadmium, zinc, and tin plated surfaces, extraneous contamination, as from fingerprints, spillages, etc., and decomposition of organic protective coatings.

1.2.3 Environment

After the printed wiring board has been completely processed, and is ready to be placed in service, further contamination of the board may arise as a result of the environment to which the completed assembly is subjected. For example, oxidation and tarnishing of the metal surfaces may occur, making subsequent soldering operations more difficult, and further metal migration may occur as a result of humidity conditions to which the board is exposed. In tropical or other high-humidity, high-temperature environments, fungus and similar growths may give rise to troublesome contamination problems. Corona discharges give rise to ozone and nitrogen oxides in the air which can also cause deterioration of the electrical properties of the wiring assembly.

1.3 Effects of Contamination

Contamination of a printed wiring board may cause many undesirable effects, but the principal one by far is associated with electrical performance changes, such as bridging and leakage between adjacent conductors on the assembly, and changes in both the surface and bulk conductivity of the laminate.

In extreme cases, actual mechanical failure of the board can occur as a result of contamination. Another important effect of contamination on the board is decreased solderability of copper or plated surfaces, and increased resistance of contact tabs. Finally, some processing procedures may weaken the adhesive bond between the laminate and the copper conductor.

2. Tests for Determining the Sources of Contamination

Such tests can be divided into two types: Those which determine the total amount of contamination present on the board, and those which determine the presence of specific contaminants on the board.

2.1 General Tests

Tests which determine the total amount of contamination on the board are based on the assumption that contamination which leads to altered electrical properties of the board is due to the presence of ionized or ionizable matter. The presence of such matter may be detected in two ways: the ionized matter may be extracted in boiling water, and the resulting change in conductivity of the water measured, or, a potential may be applied between adjacent conductors at high humidity, so as to cause corrosion of the copper conductor, and the amount of dissolved copper determined analytically.

2.1.1 Extraction Tests

The following procedure may be employed to carry out the water extraction test:

Thoroughly clean five 180 ml. electrolytic beakers, five watch glasses for beaker covers, one 50 ml. graduated cylinder. Cleaning shall be performed as follows: wash in a hot water detergent solution, wash several times with tap water and rinse at least five times with distilled water. Perform all of the following operations in a laboratory maintained at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Pour 50 ml. of distilled water at 23°C into each of the five beakers and cover with watch glasses. Measurements of the resistivity of the water in each beaker shall be made to determine if the beakers have been thoroughly cleaned. The specific resistance of the distilled water in each beaker shall be equal to or above 500,000 ohm-cm at $23 \pm 2^{\circ}\text{C}$. If the resistivity of the water in any beaker is less than 500,000 ohm-cm, the beakers shall be re-washed, 50 ml. of distilled water again added, and the resistivities re-measured. This procedure shall be repeated until the resistivity of the water in each beaker is equal to or more than 500,000 ohm-cm. Cover all beakers.

2.1.1 Extraction Tests (Cont'd.)

A conductivity cell, whose cell constant is approximately 0.1 and a conductivity bridge similar to Model RC-1C (Industrial Instruments Co.) may be used for these measurements. The conductivity cell should be thoroughly washed in distilled water prior to use. The distilled water employed shall have a specific resistance of approximately 500,000 ohm-cm or higher, at $23 \pm 2^{\circ}\text{C}$. In each of the five beakers, each containing 50 ml. of distilled water, place one $1\frac{1}{2}$ " x $1\frac{1}{2}$ " test specimen. Cover the beakers with the watch glasses. Heat the five beakers at one time on a hot plate until the distilled water begins to boil and continue boiling for one minute. Remove the beakers from the hot plate and allow to cool at room temperature for 10 minutes. Place the beakers in a bath of cool ($15-18^{\circ}\text{C}$) running tap water and allow contents of beakers to cool to 24°C . Remove beakers from the bath immediately after reaching 24°C . Remove specimens from the beakers using clean forceps and determine the resistivity of the water extracts in the following manner. Thoroughly wash the conductivity cell with distilled water and immerse it in the water extract of one sample. Make instrument reading. Thoroughly wash conductivity cell in distilled water and immerse in a water control. Make instrument reading. Thoroughly wash conductivity cell in distilled water and immerse in a water extract. Make instrument reading. Wash the conductivity cell in distilled water and continue measuring resistivities of the remaining controls and water extracts. The specific resistance of each of the controls shall not be below 500,000 ohm-cm at $23 \pm 2^{\circ}\text{C}$. If the latter value is below 500,000 ohm-cm, it indicates that the test was contaminated with water soluble, ionized materials and the entire test shall be repeated. Calculate the mean of the specific resistivities of the water extracts. This value is a measure of the amount of ionizable matter extracted from the test specimens.

2.1.2 Copper Corrosion Test

This method assumes that the degree of contamination can be evaluated by measuring the amount of metallic copper transformed into copper compounds by the action of contaminants being assumed to be ionized or ionizable. This chemical attack on copper can be accelerated by high humidity and the application of a d.c. potential to adjacent conductors on the board. If a precise micro-analytical method of copper determination is utilized, it should be possible to obtain correlation with the amount of contaminant present.

The method employed is as follows:*

The test specimen is exposed in a humidity cabinet at 95°F and 95% relative humidity. A d.c. potential of 220 v. is applied to adjacent conductors. Although this treatment accelerates corrosion, there may be superimposed on this still another corrosion accelerating factor consisting of making the surface more moisture receptive by the application of a hymectant, such as glycerine or ethylene glycol in very diluted form.

* Dr. Leo Pessel, Chemical and Physical Laboratories, Tube Division, RCA, Camden 2, New Jersey, Unpublished (1957).

2.1.2 Copper Corrosion Test (Cont'd.)

After 24 Hours, the printed wiring board is removed from the humidity chamber, and the board is rapidly washed with a solvent which removes any copper corrosion product formed on the board as well as rosin flux residues, without exerting significant attack upon metallic copper itself. A suitable solvent for this purpose is a mixture of:

2,4 Pentanedione -- $\text{CH}_3\text{COCH}_2\text{COCH}_3$ -- 50% (vol)
Diacetone alcohol -- $\text{CH}_3\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$ --- 25%
Water -- 25%

The washing is accomplished by using a very small quantity of the solvent mixture and a rubbing action by means of a rubber policeman. Several small batches of solvent are utilized and are carefully collected in a small porcelain dish. Rubbing may also be accomplished by using very small wads of cotton which are added to the contents of the dish.

After evaporating the solvent, the contents of the dish are ignited and ashed. The subsequent procedure is carried out in the same dish without removal of its contents. The ash is dissolved in a small amount of concentrated HCl containing about 20% of concentrated H_2SO_4 . After evaporation to the disappearance of the hydrochloric acid odor, water is added, the solution made alkaline with ammonia, and then acidified with acetic acid. Potassium iodide and starch are added and the solution titrated with 0.01 N sodium thiosulfate solution. For titration a microburette permitting an estimate of 0.002 ml. of liquid volume is utilized. The method is accurate to 0.01 mg (10 micrograms) of copper.

2.2 Specific Tests

Specific tests of the type discussed below are used to detect presence, not of ionizable matter in general, as in the case of the previously discussed tests, but of specific contaminants.

2.2.1 Test Papers for Copper and Iron

One of the most common sources of contamination on printed wiring boards is the presence of etching residues. Since ferric and cupric chloride etches are commonly employed, and since, in any etch, copper builds up in the solution, the two metals most commonly tested for are iron and copper. A convenient way to determine the presence of these materials on a board is by use of sensitized test papers. The paper is pressed against the board and a "contact print" of contamination on the board results: blue for iron ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$) and red-brown for copper ($\text{Cu}_2(\text{Fe}(\text{CN})_6)$). Detailed instructions for preparation and use of the paper follow:*

Reagents: 1. Zinc acetate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$
2. Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$

* Dr. Saul W. Chaiken, Stanford Research Institute, Menlo Park, Calif.

- Equipment:
1. FR Adjustable Film Developing Tank, 4" x 5"
 2. Glass plate
 3. Glass Photographic Developing Tray
 4. Hydraulic Press
 5. Dye Transfer Paper, Eastman Kodak Type G, double weight
 6. Filter Paper

- Solutions:
1. 0.25 M Zinc Acetate: Dissolve 109.5 g of zinc acetate dihydrate in enough distilled water to make 2 liters of solution.
 2. 0.25 M Potassium Ferrocyanide: Dissolve 211.2 g of potassium ferrocyanide trihydrate in enough distilled water to make 2 liters of solution.
 3. 0.1 M Hydrochloric Acid: Dissolve 8.3 ml of concentrated hydrochloric acid (s.g. 1.18) in enough water to make 1 liter of solution.

To prepare the sensitized paper, insert dye transfer paper in the developing tank. Close the tank and fill with the zinc acetate solution through funnel in the top. Allow to stand for 30 minutes with occasional gentle agitation. Pour the zinc acetate off, saving it for re-use. Fill the tank with potassium ferrocyanide solution, and allow to stand 45 minutes with occasional gentle agitation. Pour off the ferrocyanide solution, saving it also for re-use. (The precipitate of zinc ferrocyanide will settle out and the potassium ferrocyanide can be decanted and used again.) Rinse the paper by alternately filling and emptying the tank with distilled water three times. Remove the paper and air dry it face up on a clean glass plate.

When ready to use the paper on a board, moisten the dried paper for 30 seconds in 0.1 M HCl in a developing tray. Drain and blot the excess acid with filter paper. Place the gelatin side of the paper against the sample. Place a resilient surface which is flat and iron-free against the paper and apply a pressure of 25-50 psi for 5 minutes ($\frac{1}{4}$ " neoprene sheet covered with Saran Wrap has been found suitable for this purpose). Remove the paper from the sample.

A positive test for iron is indicated by a blue color, and copper by a red-brown color. This test is sensitive to 0.001 micrograms/mm² of both iron and copper.

A variation of the above test is the following:*

The test area on the board is first moistened with 10% (wt) HCl (with low iron analysis). Then, the moistened areas are immersed in 10% (wt) potassium ferrocyanide solution or 10% (wt) ammonium Thiocyanate solution (the latter is used for iron detection only). The board is removed from the test solution, and blotted with filter

paper. The latter is then examined for evidence of iron or copper. Iron is indicated by a blue color, copper by a red-brown color. If the thiocyanate paper is used, iron is indicated by a red color.

2.2.2 Other Tests for Copper and Iron

The above test paper is very convenient in that it will simultaneously reveal the presence of iron and copper. If only one or the other impurity is being investigated, it is also possible to use reagents specific to one metal ion. For example, the following two reagents are specific for iron in the ferric state:*

The test paper is prepared as above, except that the paper is soaked in thioglycolic acid (mercaptoacetic acid), and, immediately before use, is moistened with 6N ammonia, rather than HCl. The presence of ferric ion is revealed by a purple-red color.

Alternatively, the test paper is prepared as above, except that the paper is soaked in an aqueous solution of 8-hydroxy-quinoline-7-iodo-5-sulfonic acid (ferron), and, immediately before use, is moistened with HCl as before. The presence of ferric ion is revealed by a green color.

The following reagents can be used for copper:*

The paper is prepared as above, except that it is soaked in 0.1 g/l solution of dithizone, (diphenylthiocarbazone) in CCl_4 and, immediately before use, is moistened with dilute ammonia solution. Presence of copper is indicated by a yellow-brown color.

Alternatively, the test paper is impregnated with diethyl-dithiocarbamate dissolved in CCl_4 , this reagent giving a brown-yellow reaction with cupric ion of great selectivity.

Two methods have been mentioned above for using these spot tests. One involved fixing the reagent on suitable paper by means of an insoluble zinc salt, the other involved conducting the reaction directly on the board, and applying filter paper to the board to detect the reaction. There are other, less satisfactory ways to accomplish such spot tests. For example, the board could be washed in water or suitable solvent, and a drop of test solution can then be reacted with a drop of the reagent solution on a spot plate, in a test tube, or on filter paper. Needless to say, such methods would provide no indication of the distribution of residual contamination, on the board.

2.2.3 Autoradiography

Radioactive iron and copper compounds can be used in making studies of etching residues and the like. If this is done, then trace contamination of copper and iron can be detected by autoradiographic techniques. In this method, a polyester film is placed over the specimen and Kodak Autoradiographic Stripping Film Type NTB is used to develop the image. About 10^6 disintegrations per cm^2 are needed to produce a measurable image. If Cu^{64} is used (3000 mc/g, where 1 mc = 3.7×10^7 disintegrations/sec), and Fe^{59} is used (1 mc/g), a one hour exposure would detect about 2.5×10^{-9} g/ cm^2 of copper on the surface, and 10^{-6} g/ cm^2 of iron.

* F. Feigl, Spot Tests, Vol. I (Inorganic), Elsevier Publ. Co. (1954).

2.2.4 Organic Decomposition

Operating temperatures of equipment may reach levels at which polymeric materials decompose, liberating vapors which condense on cooler portions of the equipment. The following method may be used to detect such decomposition of organic materials: *

The board is exposed to heat for a period of 16 hours, during which time any vapors liberated are allowed to condense on a cool glass plate. The presence of such matter is indicated by fogging of the plate. The deposit on the glass plate is made visible by dusting with a fluorescent powder, and photographs are then taken by exposure in ultra-violet light.

2.2.5 Fingerprints and Perspiration

Accidental human contamination of boards results largely from the presence of fingerprints and perspiration. Since fingerprints may be characterized by their amino acid content, the following test for amino acids is suitable: **

Fingerprints on the board are developed by immersing the board in a 0.2% solution of ninhydrin (triketohydrindene hydrate) in acetone, followed by heating of the board to 80°C for a few minutes. A pink color develops which becomes more intense with time, reaching maximum distinctness a day or two after the ninhydrin treatment. The color can be more easily seen by transferring the latent image to moistened filter paper.

2.2.6 Dust

Some plastic materials tend to pick up dust by electrostatic attraction. This dust may be observed by use of the following procedure: ***

The test plastic is exposed to a standard dust, containing a fluorescent component. Upon illumination of the test sample with ultraviolet light, the deposition of dust becomes easily visible because of the fluorescent powder. The fluorescent patterns may then be photographed.

2.2.7 Detection of Silver Migration

Migration of silver can cause failure of printed wiring boards. This type of contamination differs from the other types discussed above in that the contaminant is a metal, and in that silver migration does not lead to various degrees of contamination of the board: either migration has no effect, or else it causes short circuiting of the board.

Detection of silver is simple: it is merely observed visually, or at low (150X) magnification, by reflected or transmitted light. Somewhat better results are obtained by use of the latter. Alternatively, a sample may be gouged out and tested for silver by emission spectrography.

* V. J. Marchese and S. J. Klima, ASTM Bulletin, No. 172, 40-43 (1951).

** S. Oden and B. von Hofsten, Nature 173, 449-450 (1954).

*** P. C. Woodland and E. E. Ziegler, Modern Plastics 28, No. 9, 95; 169 (1951).

Another method for detecting silver is the following: *

Whatman No. 50 filter paper is impregnated with a saturated acetone solution of 5(p-dimethylaminobenzylidene) rhodanine, and allowed to air dry. In use, the paper is wet with 0.2 N nitric acid partially dried by being pressed momentarily between blotters, and then is pressed against the sample under 500# pressure in a hydraulic press for 2 minutes. After the pressure is released, the nitric acid is washed out of the paper with water. The presence of silver is indicated by an orange coloration on the background of the impregnated paper.

In order to test for the susceptibility of boards to silver migration, it is desirable to accelerate the rate of migration on the test board. This may be done by exposing the boards to 89% relative humidity (saturated potassium nitrate solution) at 40°C, and applying 480 v. d.c. to adjacent silver or silvered electrodes.** Following this, the above methods may be applied.

3. Tests for Determining the Effects of Contamination

As mentioned previously, the principal effect of contamination of printed wiring boards is bridging and electrical leakage between adjacent conductors. The electrical changes in d.c. characteristics are normally measured in terms of changes in surface and bulk resistivity, and the changes in a.c. characteristics are measured in terms of changes in Q.

3.1 Surface and Bulk Resistivity

In making studies of this type, it is conventional to employ standard test patterns and standard testing conditions.

3.1.1 Standard Pattern

The standard test pattern of Fig. 1 is customarily employed. Two commonly used values of D_1 , D_2 , and D_3 are:

D_1	0.5 in.	1.5 in.
D_2	0.75 in.	1.75 in.
D_3	1.0 in.	2.0 in.

3.1.2 Attaching Leads

Because high resistance measurements are being made, suitable leads must be employed. No. 28 silver plated standard wire with 10 mils of Teflon insulation is satisfactory.

To attach the leads to the sample, the leads are tinned and soldered to the land areas on the conductor pattern with rosin or rosin-alcohol flux using a 25-40W iron.

* F. Feigl, Spot Tests, Vol. I (Inorganic), Elsevier Publ. Co. (1954)

** S. W. Chaikin, "Study of Effects and Control of Surface Contaminants on Dielectric Materials," Stanford Res. Inst. (1958).

3.1.3 Standard Test Conditions

Following ASTM D 618-53, most testing is done for 96 ± 2 hours at $35 \pm 2^\circ\text{C}$, and at $90 \pm 2\%$ R.H. These conditions can be met by using a thermostatically controlled chamber, containing a pool of saturated sodium tartrate solution. For other humidity conditions, the following saturated solutions may be employed at $35-40^\circ\text{C}$:

96% R.H.	Potassium sulfate
75% R.H.	Sodium chloride
49% R.H.	Magnesium nitrate
32% R.H.	Magnesium chloride

There are also commercial test chambers on the market which may be conveniently used. An example is the Vapor Temp Chamber, made by the Blue M Electric Company, Blue Island, Ill.

3.1.4 Measuring Equipment

According to ASTM D 257-52 T, the resistance measuring equipment shall be accurate to $\pm 10\%$ up to 10^{11} ohms, and shall measure to 10^{12} ohms, at an applied voltage of 100-500 v. An example of suitable equipment for such purposes is the General Radio Megohm Bridge, Type 544B (General Radio Company, Cambridge, Massachusetts). For making continuous resistance measurements, an example of suitable equipment is use of Micromicroamplifier, No. 983-A (Leeds and Northrup, Philadelphia, Pennsylvania) used in conjunction with a 10 mv. Brown Elektronik Recorder (Minneapolis-Honeywell, Philadelphia, Pennsylvania).

3.1.5 Reporting Results

To permit comparison of values obtained by different experimenters, using different variations of the test pattern, it is preferable to report results in terms of resistivity, rather than resistance.

The surface resistivity is given as:

$$\rho_s = \frac{(D_1 + D_2) \pi R_s}{D_2 - D_1}$$

where R_s is the surface resistance measured between electrodes 1 and 2 (see Fig. 1).

The volume resistivity is given as:

$$\rho_v = \frac{(D_3^2 - D_2^2) \pi R_v}{4 t}$$

where t is the thickness of the specimen and R_v is the volume resistance measured between electrodes 1 and 3 (see Fig. 1). The units of length chosen for the surface resistivity are of no importance, but for volume resistivity it is customary to choose centimeters as the unit of length. Thus, surface resistivity is expressed in ohms, and volume resistivity in ohm-cm.

3.2 A.C. Measurements

Contamination of printed wiring boards affects the a.c. characteristics of the laminate by increasing the dielectric loss factor. In an ideal capacitor, the current flowing in is 90° out of phase with the voltage. To the extent that there is dielectric loss, the phase angle differs from this value, tangent of the change in phase angle being the dissipation factor. The reciprocal of the dissipation factor is Q. This factor can be conveniently measured on commercial equipment, an example of which is the Boonton Q-Meter, Type 260-A (Boonton Radio Company, Boonton, New Jersey).

4. Correlation Between Cause and Effect

It has been indicated above that many tests exist for detecting the possible causes of contamination, and also for detecting the effects of contamination. The important part of any program designed to study contamination is to be able to correlate between tests for cause and effect. Unfortunately, the question of predicting whether a given board, processed in a particular manner, will give rise to contamination in the field of a complex one, and no satisfactory methods have been developed to date.

4.1 Water Extraction Test

An attempt was made to correlate the results of the water extraction test with d.c. resistivity measurements.* It was found that this test will readily detect badly contaminated boards, but that boards with unacceptably low values of surface resistance will sometimes yield water extracts of high resistivity. Thus, the water extraction test is not a valid acceptance test at present. However, in view of the wide use of this test, some of the experimental details will now be given.

The test was run slightly differently than indicated on P. 2-3. The samples were 2" x 2" XXYP phenolic, cut in $1/2$ " wide strips after having been dipped in acetone for 10 seconds. These strips were then placed in a 250 ml distilling flask fitted with a ground glass connector. The samples were washed by swirling for 5 minutes in 200 ml of distilled water and the solution resistivity was checked on an Industrial Instrument, Model RC-16B conductivity bridge. The cell had a cell constant of 0.1. Following this, the sample and water were returned to the flask and refluxed for various times from five to thirty minutes with readings being taken at various intervals. When a reading was to be taken, the solution was cooled to 24°C and the reading corrected to 18°C . Before a test the flask was always washed with distilled water until readings of at least 6×10^5 ohms were obtained.

Fig. 2 shows the variation which results from using phenolic from different vendors. Fig. 3 shows a series of tests run on Richardson T-725. From these results, it was felt that not enough difference showed up to use this method as an acceptance test procedure except when boards were badly contaminated. Similar tests on etched boards confirmed the fact that in most cases, unless a board was badly contaminated, a separation could not be made by this method. In addition, it was felt that not enough difference was evident from refluxing the boards and the procedure

* V. P. McConnell, Defense Electronics Div., General Electric Company, Electronics Park, Syracuse, New York, Unpublished (1957).

might introduce factors which would lead to erroneous results, so the room temperature wash cycle was retained in further work, but the re-flux cycle was dropped.

Fig. 4 was used to relate the resistivity of the solution after washing, with the content of ferric chloride in the solution. Good checks were obtained between the resistivity of the water extract and the iron content, as analyzed, for a variety of poorly rinsed boards. Fig. 5 shows the effect of soaking in ferric chloride with the rinsing time remaining constant. In the tap water rinse, solution flow was 4000 ml/min. in an 800 ml beaker. Resistivity of the tap water was 5,800 ohms. It can be seen from the graph that prolonged soaking resulted in a leveling off over 40-50 minutes and no deterioration in values took place after that. Fig. 6 shows the difference in recovery rates between boards soaked in ferric chloride for 30 minutes and those soaked for 60 minutes. The boards which were soaked in ferric chloride for 30 minutes recovered at faster rates than those soaked for 60 minutes and indicated that the ferric chloride was entrapped; thus, the longer the soak in ferric chloride, the greater the penetration into the cracks and the longer the time needed to remove it in the rinse.**

It was found at this point that most of the contamination came from entrapped solutions in cracks in the phenolic caused by cutting the pieces, rather than by solution absorbed or absorbed at the phenolic surface. Samples which were sawed carefully, soaked in ferric chloride, rinsed, and then run through the testing procedure, showed resistivities which compared with those in Fig. 2 for each of the bare phenolic pieces. It was decided to cut the boards with a shear to check the effectiveness of rinsing, ferric chloride soaking, etc. where cracks would exist that might duplicate those resulting from a punching operation. An indication of the difference in sawing or shearing can be obtained from the fact that a plain, clean piece of phenolic which was soaked in tap water after sawing resulted in a reading of 5.1×10^5 ohms, whereas one which had been sheared resulted in a reading of 2.8×10^5 ohms. Both of these boards had started out with readings of 6.0×10^5 ohms.

In general, water extracts whose resistivity was less than 2.5×10^5 ohms came from boards in which the copper was visibly stained or darkened, and in which dip soldering was difficult to achieve. Such boards also had a lower leakage resistance. However, water extracts of a higher resistivity, such as 6.0×10^5 ohms, often came from boards with an unacceptably low value of surface resistance. Thus, the water extraction test, at the present, does not offer much promise as an acceptance test. It will readily detect badly contaminated boards, but the latter can usually be detected simply by other means.

4.2 Copper Corrosion Test

This test was used* to obtain good differentiation of the attack of printed wiring by various brands of solder flux of the rosin type,

** Measurements made by S. W. Chaikin at Stanford Research Institute at 96% R.H. showed little difference in contamination due to length of time of exposure to ferric chloride etches beyond the minimum required time.

* L. Pessel, Chemical and Physical Laboratories, Tube Division, RCA, Camden 2, New Jersey, Unpublished (1957).

including pure rosin flux and a number of activated rosin fluxes. Good correlation was found between the nature of the flux residue, its effect on the board, and the amount of copper corrosion obtained by this test. However, it was found that trace contaminants and the like did not produce a sufficient degree of copper corrosion to be detectable by this method. Thus, this method does not appear to be sufficiently sensitive to serve for the correlation of cause and effect of contamination on boards.

4.3 General Tests vs. Specific Tests

It is obvious from what appears above that the two general tests for contamination, the water extraction test, and the copper corrosion test, are useful only in detecting major amounts of contamination, and are not useful in detecting the minor amounts of contamination which may be present, which may nonetheless adversely affect the resistivity of the board. Probably the main reason for the disappointing results of these tests arises from the fact that equating electrical leakage of the board after a period of use with the presence of ionizable matter present on the board after processing represents too much of an oversimplification.

Thus, for the present, at least, more useful correlations between cause and effect can be obtained by comparing electrical leakage tests with tests for specific contaminants. However, unless meaningful knowledge exists as to the true cause of contamination in any particular case (and this rarely occurs in practice), correlations between electrical measurements and tests for specific contaminants could be dangerous and misleading.

4.4 Spot Tests for Copper and Iron

Considerable work has been done* on the correlation between copper and iron residues from etching operations and electrical leakage tests. For example, it was shown that after FeCl_3 etching, a 30 second rinse lead to a surface resistance (at 97% R.H.) of about 100 megohms. The chemical test cited above for iron gave moderate concentrations for the former case and light or very light concentrations in the latter case.

In another test, consecutive samples of XXXP boards were etched in a limited quantity of FeCl_3 , with the following results:

<u>Sample No.</u>	<u>Etching Time (min)</u>	<u>Resistivity after 24 hr. at 97% RH Megohms</u>	<u>Sensitized Paper Test</u>	
			<u>Fe⁺⁺⁺</u>	<u>Cu⁺⁺</u>
1	10	80.0 x 10 ⁶	No	No
2	11	100 x 10 ⁶	No	No
3	13	150 x 10 ⁶	No	No
4	25	0.4 x 10 ⁶	Yes	No
5	19	100 x 10 ⁶	No	No

* S. W. Chaikin, op.cit.

Sample No.	Etching Time (min)	Resistivity after 24 hr. at 97% RH Megohms	Sensitized Paper Test	
			Fe ⁺⁺⁺	Cu ⁺⁺
6	31	0.1 x 10 ⁶	Yes	No
7	40	200 x 10 ⁶	Yes (?)	Yes

It was also found that considerable variation in resistance can exist over the surface of the etched board, by as much as a factor of 4000 at 97% RH. If rinsing is adequate, it was found that the length of immersion in the ferric chloride bath is not critical. Adequate rinsing was found to be two minutes or more. It was also found that HCl, EDTA, and some wetting agents, such as Pluronic L-62, help reduce the degree of contamination after ferric chloride etching, when added to the rinse waters.

4.5 Autoradiography

At the present time, little formal use has been made of this technique. What use has been made to date indicates that, in chemical reduction plating of laminates to produce plated through holes, absorption of copper salts, and even reduction of copper may occur inside the laminate adjacent to the plated hole. Autoradiographic studies of surface contamination are inconclusive to date.

4.6 Fingerprints

A study of contamination by fingerprints applied in a standardized manner* showed that laminates of Teflon, silicone-glass, XXXP, polystyrene, cellulose acetate butyrate were good materials in this respect, while laminates of melamine-glass, epoxy-glass, and Kel-F were inferior.

4.7 Cleaning and Plating

The major contamination effects of cleaning and plating operations generally manifest themselves in terms of deterioration of bond strength between conductor and laminate, rather than in electrical leakage deterioration. It has been found** that non-ferrous electro-cleaners cause a 1/3 reduction in bond strength on epoxy-glass laminates when used cathodically. The nature of the damage was found to depend on the type of cleaning employed, however, Soak alkaline cleaning is least injurious, anodic cleaning is more deleterious, and cathodic cleaning is the worst of all, causing complete loss in bond strength after three minutes in a strong alkaline cleaner at 4v, 180°F, at a concentration of 6 oz/gal.

Regarding plating solutions, cyanide solutions are the most critical from the point of view of deterioration of bond strength. However, it was found** that even hot gold cyanide plating solutions are not very injurious in this connection, although epoxy-glass laminates were found better than XXXP (undoubtedly because of differences in the adhesive systems employed). For example, less than a 10% loss in bond strength was found on G-10 and G-11 epoxy-glass laminates before and

* S. W. Chaikin, op.cit.

** W. H. Hannahs, "Plating Considerations for Printed Wiring," 113th Meeting, Electrochemical Soc., New York (1958).

after cyanide gold plating at 160°F in a bath containing 1.6 oz/gal. gold salt (67% gold), and 2 oz/gal. potassium cyanide, after two minutes of plating (equivalent to 50 millionths of an inch of Au). When thicker amounts of gold were required, bond strength was affected deleteriously, and it is felt that it would be preferable to plate nickel or tin-nickel prior to gold plating, and deposit 50 millionths of an inch or less of gold.*

Assuming that bond strength is not adversely affected, plating treatments may also affect electrical properties. For example, it has been found** that of the commonly applied plating treatments, solder plating has no effect on electrical leakage, nickel-rhodium has a slight effect, and silver plating is the most harmful.

4.8 Dust, Fluxes, Protective Coatings

Dust, and other airborne matter is not critical, except when high humidity conditions are employed, in which case, deterioration in electrical properties may occur. In general, solder flux residues from rosin fluxes are not harmful. If highly activated rosin fluxes are used, electrical leakage may occur at high humidities.

Regarding organic protective coatings applied to prevent absorption of water by printed wiring boards, most varnishes are unsatisfactory, in that gradual absorption of water occurs, with resultant deterioration in electrical properties of the board. Epoxy-type coatings are much better in this respect.

It has been observed that epoxy-polyamide and epoxy-phenolic coatings tend to discolor (corrode) copper conductors on exposure to high humidity***. Some vinyl and acrylic resins are better in this respect.

With regard to use of organic protective coatings on the completed assembly, vibration and shock may lead to cracking of the coating, thus leading to absorption of water, arcing across the board, and the like. In addition, such coatings may permit long term reactions with the copper conductors, causing up to 15% reduction in conductor conductivity. When using such coatings, it is desirable to add various addition agents capable of preventing tarnishing of the copper due to absorption of water, oxygen, sulfur, etc.

4.9 Silver Migration

Direct observation of silver migration occurring after exposure to high humidity with an applied d.c. potential indicates that silver migration is promoted both by high relative humidities and high d.c. potentials. In order for migration to occur, the silver must be anodic. Silver migration is less likely to occur under a.c. fields, and will not occur significantly at a.c. potentials up to 650v. at

* E. A. Parker (Plating 45, 633 (1958) suggests use of a 1-3% silver gold alloy, since suitable baths for depositing such alloys can be operated at room temperature with very little free cyanide. Such solutions should have practically no effect on bond strength.

** S. W. Chaikin, op.cit.

*** B. G. Brand, "Organic Coatings in Printed Wiring," 113th Meeting, Electrochemical Soc., New York (1958).

60 cps, and up to 850 v. at 400 cps. In high frequency applications, there is essentially no problem of silver migration. XXXP, melamine-glass, nylon, and glass-bonded mica are most susceptible to silver migration. Teflon, nylon-filled phenolic laminates, and polystyrene are relatively inert to silver migration. Epoxy-glass materials are intermediate in behavior.

If silver migration will occur, it will occur no matter how the silver is applied, for example, it occurs on tube sockets with silver-plated terminals, on ceramic switches, nylon jacks, and other components in which silver is employed. An exception is silver-bearing solder, where the silver is present entirely as Ag_3Sn and not as free silver.

Although silver migrated more than other metals, copper, tin, and gold show traces of migration tendencies, while lead, nickel, indium, aluminum, platinum, cadmium, and rhodium do not migrate at all.

In the case of glass-filled laminates, the silver migrates in the interstices between the glass fibers, and the resin of the laminate. In the case of paper filled laminates, the silver migrates within the paper fibers.

Fig. 7 is a nomograph which illustrates the tendency of silver to migrate on XXXP boards. The nomograph takes into account the tendency of increasing humidity, temperature, and d.c. potential to accelerate silver migration.

5. Elimination of Contamination

It is a truism that half the battle in eliminating contamination of printed wiring boards is good housekeeping, and adherence to proper processing specifications. This is especially true of rinsing operations, after cleaning, etching and plating.

5.1 Cleaning Residues

Proprietary cleaners vary somewhat in their ease of rinsing. In this respect, strong alkaline cleaning solutions containing caustic are especially to be avoided. Similarly, strongly alkaline silicates should not be present. Proprietary cleaners designed for mild applications, such as the cleaning of non-ferrous metals, are generally satisfactory. Such cleaning residues are likely to increase electrical leakage on the board subsequently. However, an even more serious problem in the use of cleaners is their tendency to soften the adhesive bond between the board and the copper conductor, causing lifting of the conductor pattern. In this respect, it has been observed* that ferrous cleaners are worse than non-ferrous cleaners, and that electrolytic cleaning (especially anodic cleaning) is worse than soak cleaning. The problem also becomes worse the higher the temperature, pH and current density. Therefore, the cleaner used should not be any stronger than required, and the cleaning should be done by immersion only, at a temperature no higher than 160°F if this is practicable. Needless to say, the time of immersion should be the minimum compatible with removal of contaminants from the board.

* W. H. Hannahs, op.cit.

Where organic cleaners are used, such as solvent, and solvent-emulsion cleaners, care must be taken that the solvent has little or no interaction with either the laminate itself, or with the adhesive used in applying the copper foil, or with the adhesive applied to unclad laminates prior to metalizing. In this respect, some of the conventional solvents used in the cleaning field, such as tri- and perchlorethylene are not too satisfactory, for the very reason that they are effective solvents for organic compounds, i.e., they may soften or otherwise attack adhesives present, or swell the laminate, or remove desired markings and color codings. It may be preferable in such cases to use solvents or solvent-emulsions which are effective in removing contamination such as solder fluxes, fingerprints and the like, yet not effective enough to attack adhesives or laminates. Claims have been made for the use of fluorinated organics, such as Freons and perfluorinated compounds for such applications.

5.2 Etching Residues

The rinsing of etching residues, particularly after ferric chloride etching, is not simply a matter of being thorough. Consideration must be made of the problems of ion exchange and hydrolysis. Many laminates show ion exchange tendencies on their surfaces. Those which are of the cation exchange type are not of interest, because of the limited absorption which occurs. However, anionic ion exchange phenomena are of considerably greater interest. In a solution containing a high concentration of chloride, the ferric ion (undoubtedly in the form of an anionic complex such as FeCl_4^-) is readily taken up by ion exchange on the surface of a plastic which exhibits anionic ion exchange tendencies. On dilution of the ferric solution (as would occur during rinsing of the laminate), elution of the ferric ion takes place. This occurs both in water rinsing, and in rinsing with dilute HCl solutions. If no further reaction of the ferric ion occurred, the ferric ion contained at or near the surface of the laminate would wash away in the manner indicated. Unfortunately, the ferric ion displays a pronounced tendency to hydrolyze, and this results in serious contamination of the board. As the solution becomes more dilute in ferric ion and in chloride, a point is reached at which ferric hydroxide precipitates on the surface of the board, i.e., ion exchange is responsible for the presence of ferric ion on the board, and hydrolysis is responsible for its precipitation in such a manner as to contaminate the board. This problem of eluting the ferric ion from an anionically active laminate without precipitation insoluble salts can be largely resolved by adding complexing agents to the rinse. Some suitable complexing agents are given below.

In cupric chloride etches, a similar problem arises on rinsing, owing to the insolubility of the cuprous ion, unless the pH is low enough, or the excess chloride content is high enough to complex the ion. Naturally, this will not occur during rinsing operations. Thus, chloride etchants tend to leave deposits on the surface of the laminate after rinsing, no matter how thorough the rinsing may have been.

This problem may be minimized by adding wetting agents to aid in removal of contaminants by the rinse, by using acidified rinse waters for the preliminary rinse, prior to final rinses, and by use of suitable complexing agents, or chelating agents, to prevent or minimize precipitation of hydrous oxides or hydroxides of the respective metals present in the etchant. For ferric ion, suitable agents include ammonia, fluorides, cyanides, thiocyanates, citrate, oxalate, EDTA, phenol, and

catechol. For cuprous ion, suitable agents include ammonia, halides, cyanide, thiosulfate, thiourea, ethylene, maleic acid, and fumaric acid.

In a study of rinse water composition vs. subsequent electrical leakage*, it was found that, after etching in ferric chloride, it was helpful to add HCl, and Versene to the rinse. Most wetting agents, such as Tide, Aerosol OT, and Triton X-100 were ineffective. Pluronic L-62 was slightly effective.

5.3 Plating Residues

The rinsing of plating residues is subject to much the same criteria that were discussed above for etching residues. If care is not taken, insoluble salts of the metals present in the plating solution may precipitate on the laminate, and provide a source of trouble. However, no great degree of trouble should be encountered if proper rinsing practice is followed. In this respect, acid electrolytes are less troublesome than alkaline electrolytes, especially cyanides. The latter may be absorbed by the laminate, and produce a source of contamination.

A rather specific problem in rinsing of plating solution residues may arise in the production of "plated-through holes". In producing boards with conductors on both sides of the laminate, it is necessary to make electrical connection between the two sides of the board. This may be done by mechanical means, such as by eye-letting, or by means of "plated-through holes". In the latter process, the same procedures are followed as in the production of plated circuits, i.e., the hole is sensitized, rendered conductive by chemical plating of silver or copper, then electroplated with the desired thickness of copper. In this process, the laminations inside the board are exposed to the action of a variety of electrolytes, such as the cleaning solution, and the electroplating solution. In each case, there is a good opportunity for capillary action to cause considerable absorption of electrolyte. Such absorbed electrolyte may be very difficult to remove subsequently, and can considerably affect bulk resistivity of the laminate. At the present time, no completely satisfactory solution to this problem has been developed. Wetting, complexing and chelating agents help to remove some of the absorbed matter, but unfortunately, some of the electrolyte which is absorbed is reduced to the metallic form, and such material cannot be removed, though the latter is not a serious contaminant.

5.4 Soldering Residues

Solder fluxes do not generally provide for a major source of difficulty in contamination of printed circuit boards because of fairly rigid standards on the type of solder fluxes which may be employed. However, in some cases it may be necessary to remove solder fluxes to meet specifications, or military requirements. In such cases, solvents must be employed which will completely remove solder fluxes without affecting either the adhesives used between the laminate and the copper, or the laminate itself. As indicated above, fluorinated solvents seem to be finding some applications in this field. Other suitable materials which have been used for some time include toluene-isopropyl alcohol mixtures.

5.5 Potting Compounds

A widely used method of decreasing the effects of contaminants is the application of a final protective coating of organic material to

* S. W. Chaikin, op.,cit.

cover the entire assembly. For example, varnishes or epoxy-type coatings are applied. However, under conditions of high humidity, contaminated boards deteriorate gradually in electrical properties. This is probably due to moisture penetration of the organic coating. In this respect, silicone and epoxy coatings are the best known to date. Further research would be desirable in this field, to prepare coatings with a lower diffusion rate for moisture.

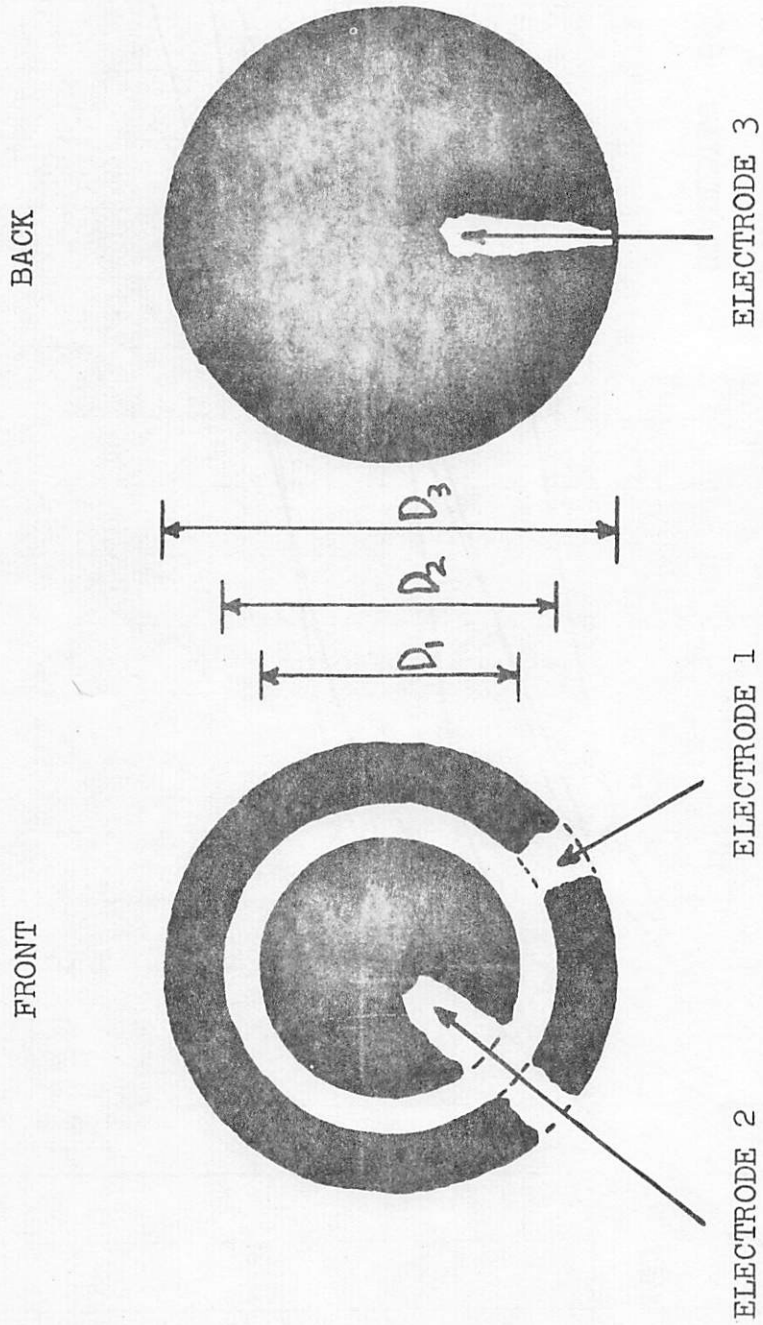
One advantage of epoxy-type potting compounds is their compatibility with the commonly used epoxy-glass filled laminated board.

5.6 Silver Migration

As pointed out above, silver migration is not a problem unless high humidity and a d.c. potential are present. However, if such is the case, silver migration can be greatly minimized by alloying the silver with 10% copper*. It has been found* that gold, cadmium, and copper greatly minimize or eliminate migration of silver when plated onto silver. Also, as mentioned before, silver-bearing solders are satisfactory. Solder plating of silver itself, however, is only partially successful. If 10% or more of copper is present in a Cu-Ag alloy, silver migration is reduced by 99% or more.

In addition to minimizing silver migration by alloying, it is also possible to minimize it by treating the surface of the board in such a way that moisture absorption is minimized, since migration required the presence of the electrolyte. Treatment* of the surface of XXXP with silicones reduces migration 75%.

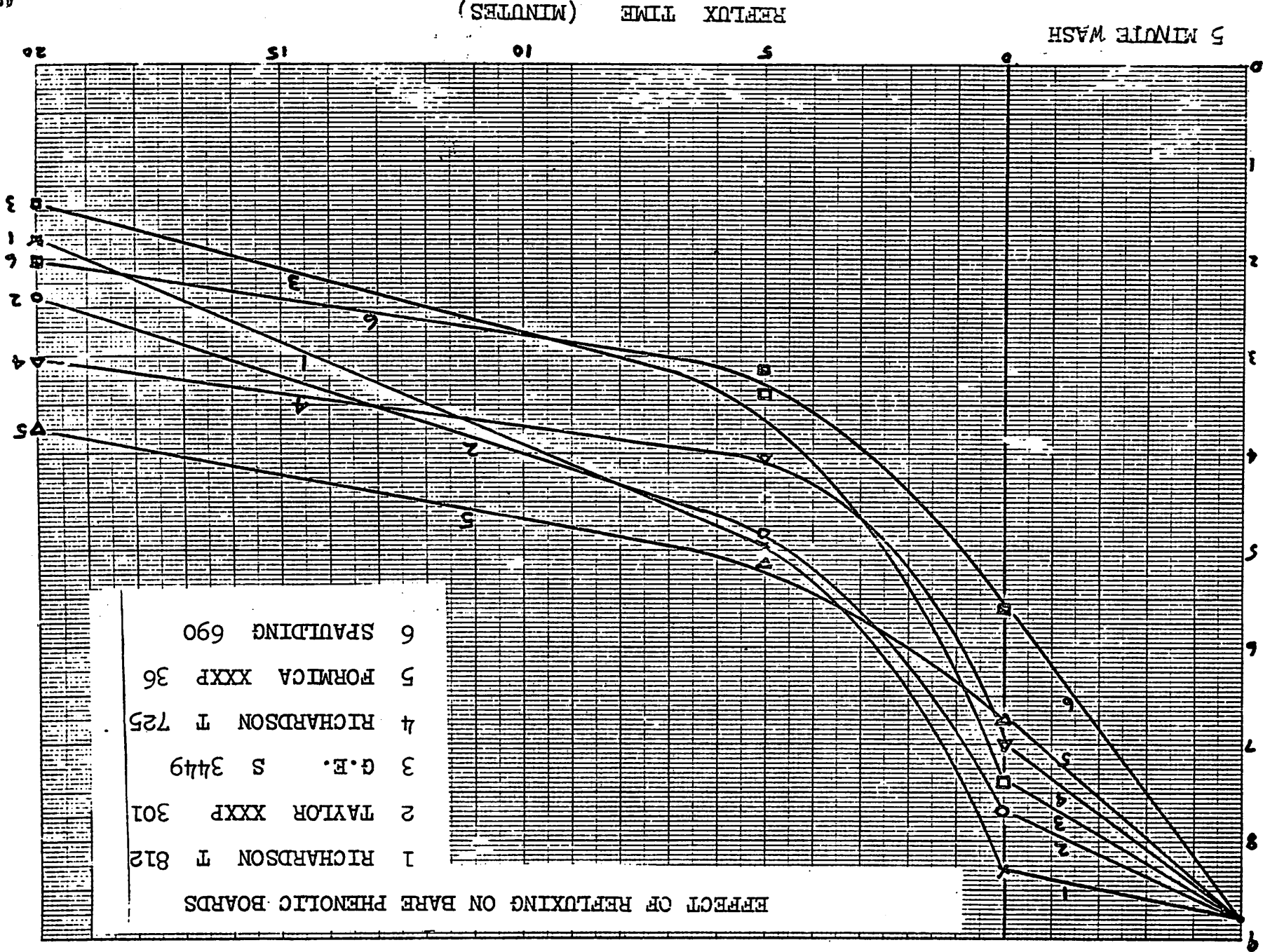
* S. W. Chaikin, op.cit.



STANDARD TEST PATTERN

FIGURE 1

RESISTIVITY X 10⁵ OHMS



EFFECT OF REFLUXING ON BARE PHENOLIC BOARDS

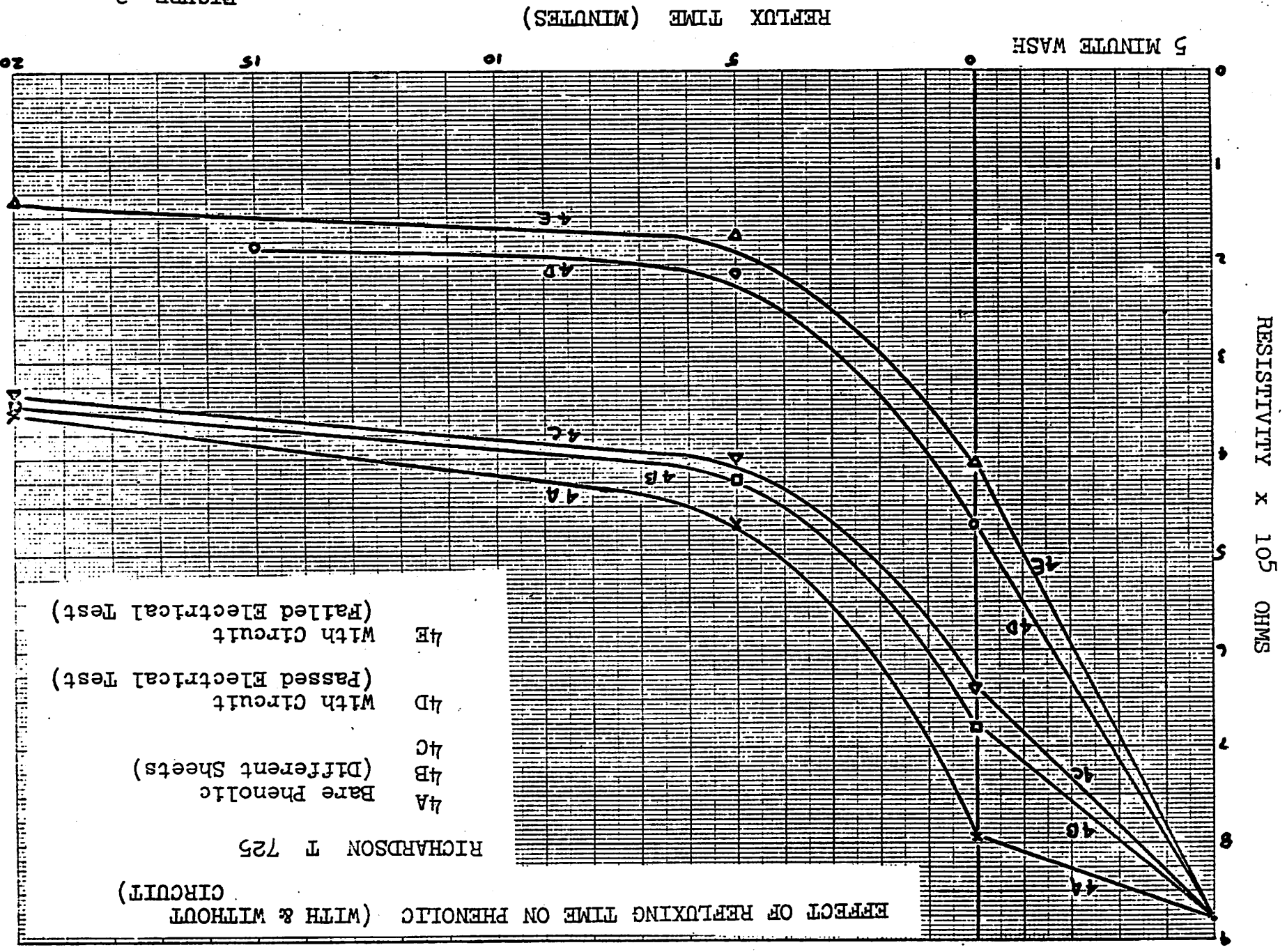
1	RICHARDSON T 812
2	TAYLOR XXXP 301
3	G.E. S 3449
4	RICHARDSON T 725
5	FORMICA XXXP 36
6	SPAUDING 690

REFLUX TIME (MINUTES)

5 MINUTE WASH

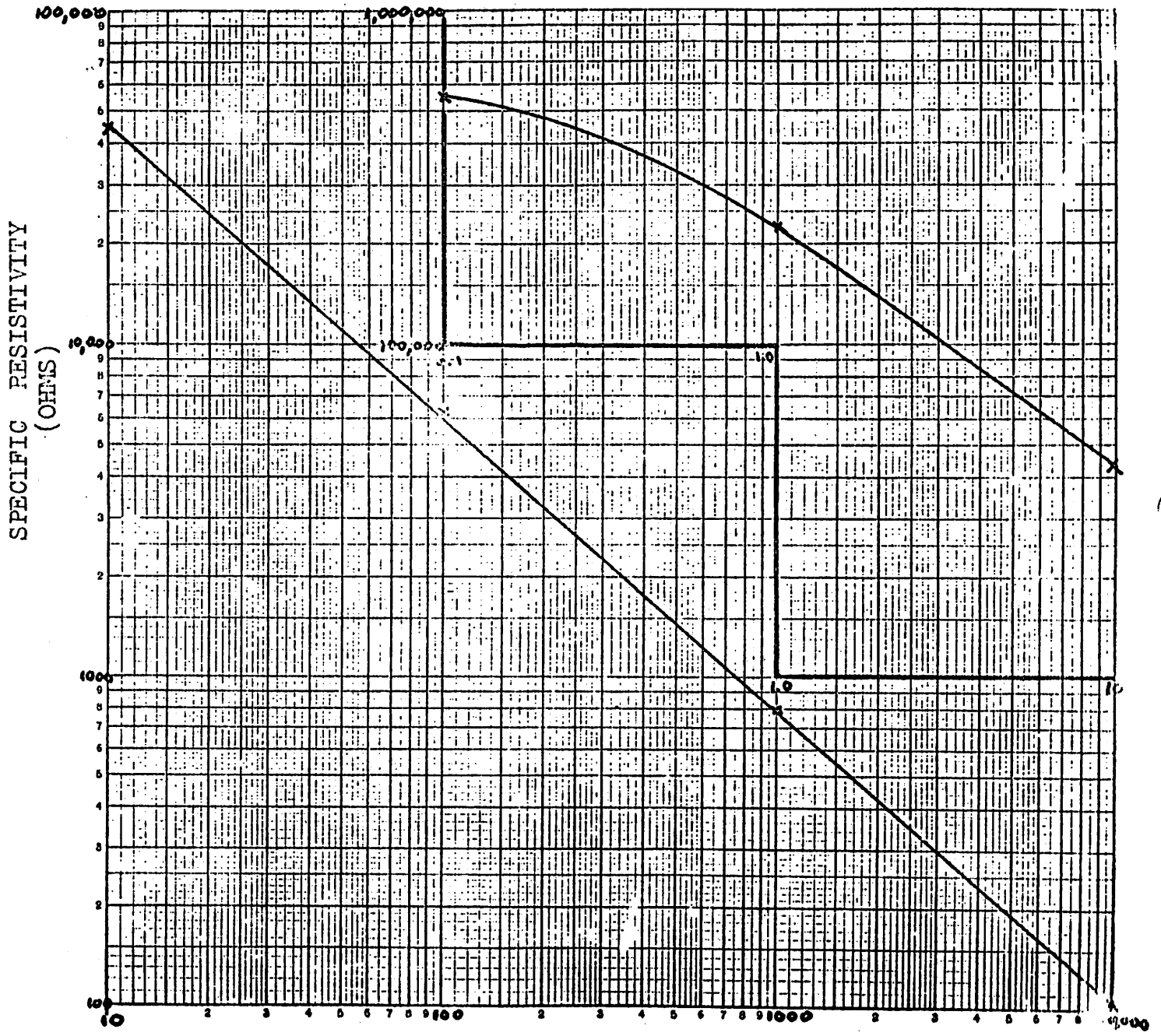
FIGURE 2

FIGURE 3



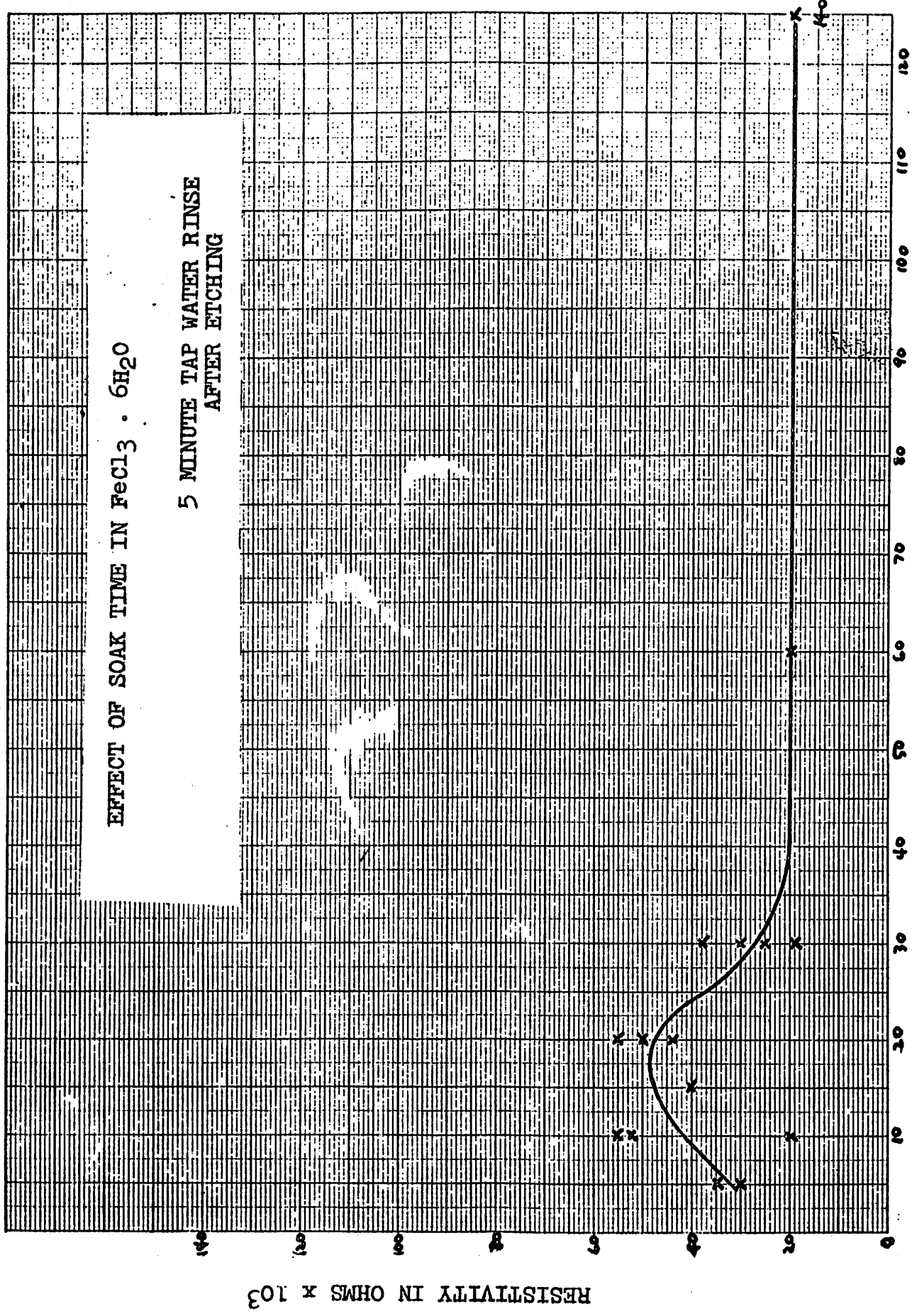
12

EFFECT OF FERRIC CHLORIDE ON RESISTIVITY OF WATER EXTRACTS



PARTS PER MILLION
(FeCl₃ . 6H₂O)

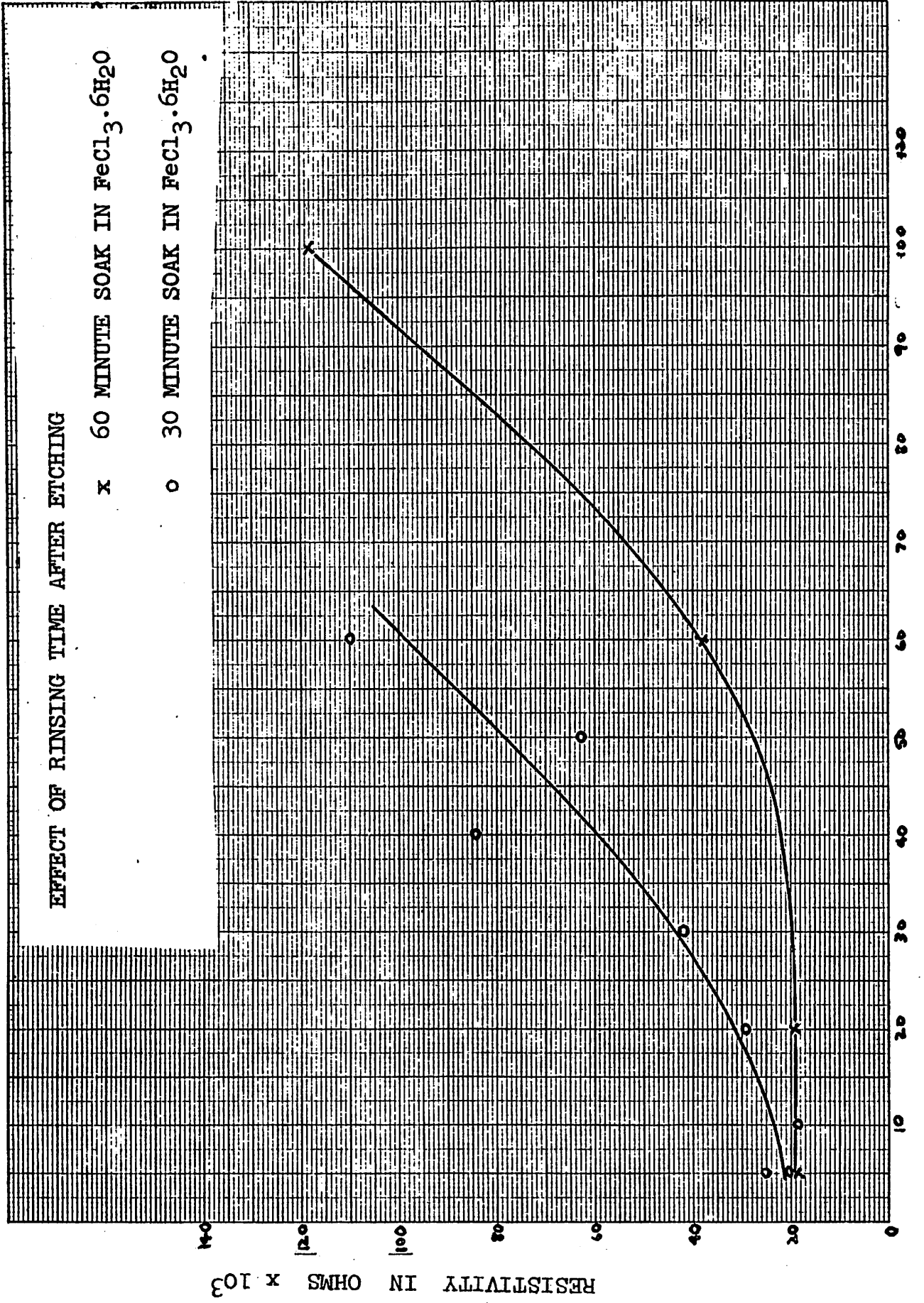
FIGURE 4



EFFECT OF SOAK TIME IN FeCl₃ · 6H₂O
5 MINUTE TAP WATER RINSE
AFTER ETCHING

FIGURE 5
TIME IN FeCl₃ · 6H₂O (MINUTES)

FIGURE 5



TIME IN TAP WATER (MINUTES)

RESISTIVITY IN OHMS X 10³

25

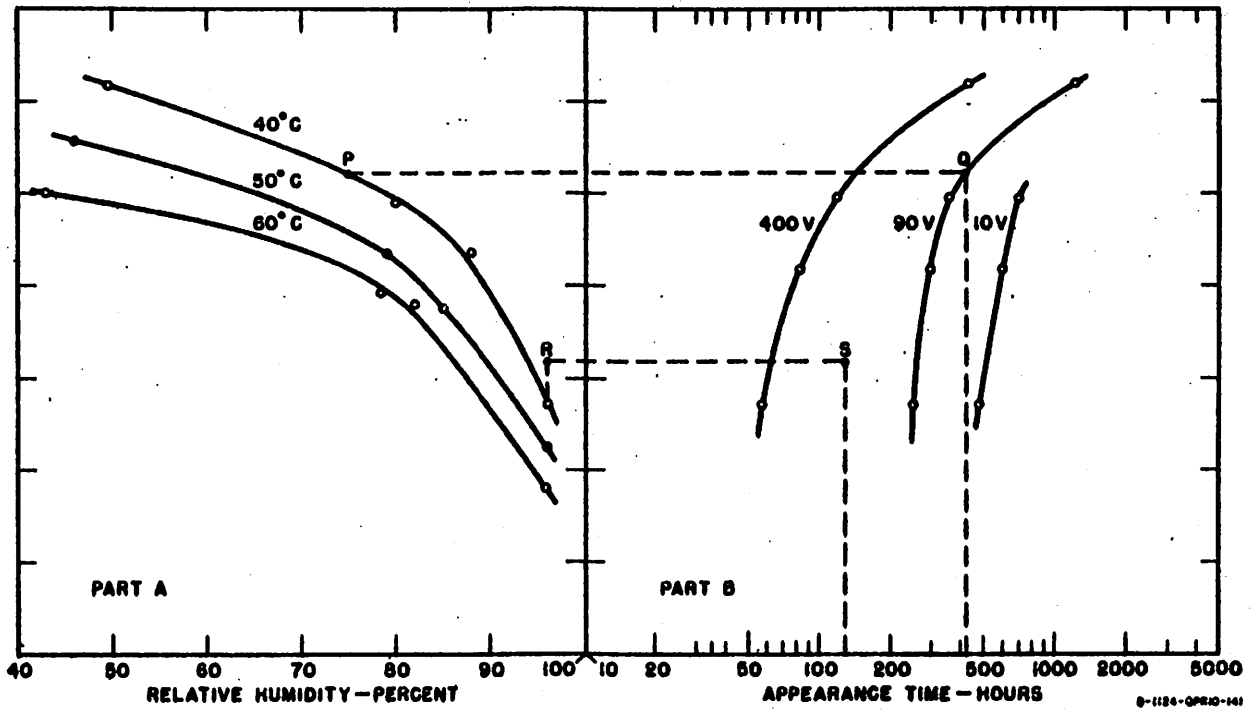


FIGURE 7

9-1124-OPR10-141



CONTAMINATION
OF
PRINTED WIRING BOARDS

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