LB-978

AN EXPERIMENTAL HIGH-SPEED PHOTO-RESIST TECHNIQUE FOR PRINTED CIRCUITS

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Approved

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Introduction

This bulletin describes a new electrophotographic photo-resist technique directly applicable to the high-speed production of printed (etched) circuit units. The procedure described furnishes a method of photo-selective masking with a light sensitivity many times that of current methods. Exposure requirements are reduced from minutes with high-intensity arc or other ultraviolet sources to fractions of a second with ordinary tungsten or fluorescent bulbs. Projection printing thus becomes possible.

The system is based on the RCA "Electrofax" process of dry electro-photographic printing, in which special zinc oxide pigment dispersed in a resin binder serves as a photoconductive coating to store a charge pattern corresponding to a light image projected on the surface. A second resin, in powdered form and having an electrostatic charge opposite to that initially placed on the photoconductor, is dusted on the light-formed charge pattern and fused in place. It is this fused powder image which forms the acid resist for subsequent etching of printed circuit patterns, after solvent removal of the photoconductive film in background areas.

The process furnishes sufficient speed, definition, reproducibility and ease of operation for use in the production of point-to-point wiring boards on a mechanized basis. Because of its ability to produce completed resist patterns, ready for etching, in a few seconds by either contact or projection printing, it has also proved valuable in the quick production of pilot model circuit boards for experimental or evaluation purposes. In the current stage of development it is not recommended for the production of units involving narrow lines and close spacings, such as bifilar coils or the like.

General Discussion

Advances in materials showing photoelectric sensitivity, so well used in television pickup tubes, are now pointing the way to new dry-processing photographic methods which are independent of silver halide chemistry. The methods depend on a photoconductive layer which is electrically charged, exposed to produce a latent electrostatic image, and then dusted with fine charged particles to make the image visible. The best-known system, called xerography[1,2] employs a selenium-coated metal plate, a pigmented powder for ink, and a transfer to paper for the final print. Commercially available phosphors and especially prepared cadmium sulfides have also been used to prepare plates for continuous-tone electrophotography.[3]

Work has been in progress at RCA Laboratories on an improved system of dry photography called "Electrofax".[4] One phase of this work has led to the development of an experimental high-speed photo-resist technique using the same equipment and materials as those developed for Electrofax copying paper. Photographic exposure times are 10,000 to 100,000 times less than those for previous photo-resists, thus greatly simplifying and speeding up processing and mechanization. The application of this technique to the production of printed circuit boards is described in the following sections.

Outline of the Process

The steps involved in the production of printed circuit boards by the Electrofax system are outlined below. These steps are further illustrated in Figs. 1 and 2.

1. *Coating of the metal surface of the copper-clad phenolic sheet with a thin layer of a powdered photoconductor in a plastic binder.* This may be accomplished by any standard coating procedure, such as spraying, dipping, flow-coating, or spin-coating.

2. *Electrophotographic printing of the fused resin resist image.* The coated surface is now electrostatically charged in the dark, exposed with a positive optical image of the circuit pattern to be reproduced (e.g., black where copper is to remain in the final circuit), powder-developed with a fusible acid-resistant resin (toner) and the powder image heat fused. For optimum resist action, the fused powder should penetrate into or through the photoconductive layer, and should completely cover the areas to be masked. Pinholes in the fused image will result in pitting of the copper surface beneath during etching.

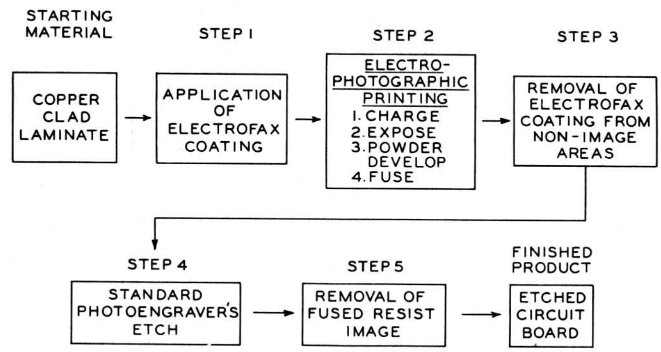

Fig. 1 - Steps involved in production of printed (etched) circuit boards by the Electrofax high-speed photo-resist method.

3. *Solvent removal of the photoconductor-resin from background areas.* The surface is next washed with a solvent which will attack the resin binder in the photoconductive layer, softening or dissolving the resin sufficiently to allow physical removal of the resin and the photoconductor particles from background areas. This removal has been accomplished thus far by use of a cotton swab. Brushes, splash etch equipment, solvent jets, vapor degreasers or the like might also be used to accomplish this job.

During this step the fused image acts as a resist to prevent removal of any underlying photoconductor-resin.

4. *Etching.* The exposed copper is now etched away with a standard etching solution, such as a ferric chloride solution with a strength of about 40 degrees Baumé. Other acid mixtures may also be used.

5. *Removal of resist.* The fused image covering the copper circuit components is now removed by swabbing with a suitable solvent.

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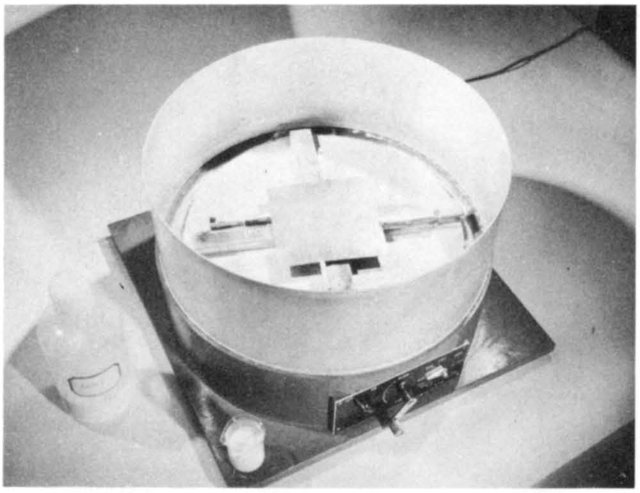
[1] R. M. Schaffert and C. D. Oughton, "Xerography: A New Principal of Photography and Graphic Reproduction", *Jour. Opt. Soc. Amer.*, Vol. 38, pp. 991-998, December, 1948.

[2] U. S. Patent 2,297,691.

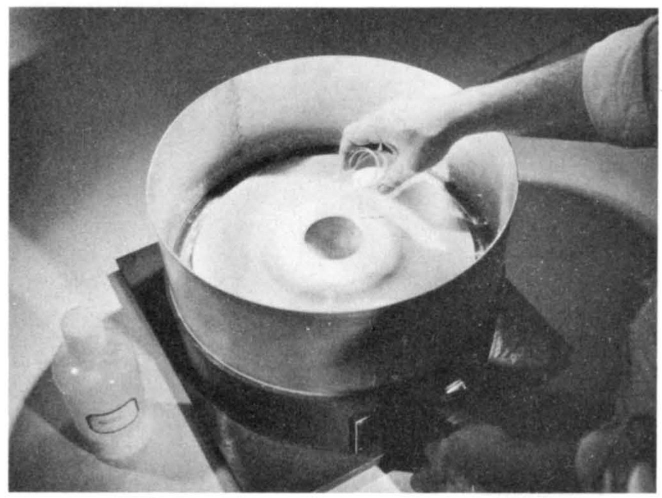
[3] Eugene Wainer, "Phosphor-Type Photoconductive Coatings for Continuous Tone Electrostatic Electrophotography", *Photographic Engineering*, Vol. 3, No. 1, pp. 12-22, 1952.

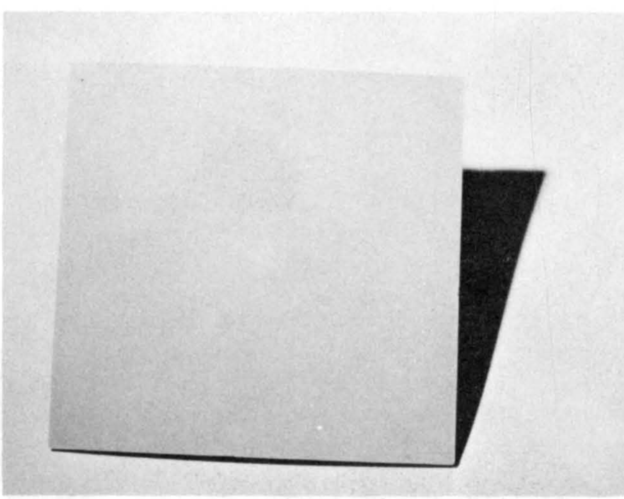
[4] C. J. Young and H. G. Greig, "Electrofax --- Direct Electrophotographic Printing on Paper", *RCA REVIEW*, Vol. XV, No. 4, Dec. 1954.



a. The copper clad insulating base placed in a suitable spin coating apparatus.

b. Spin coating the copper surface with a liquid suspension of zinc oxide and a resin binder.

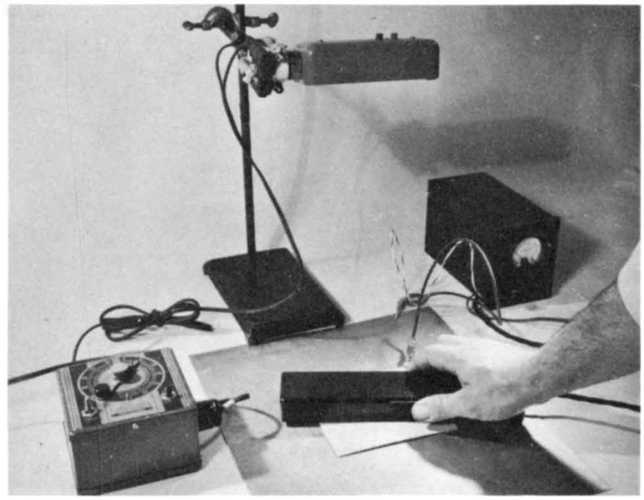


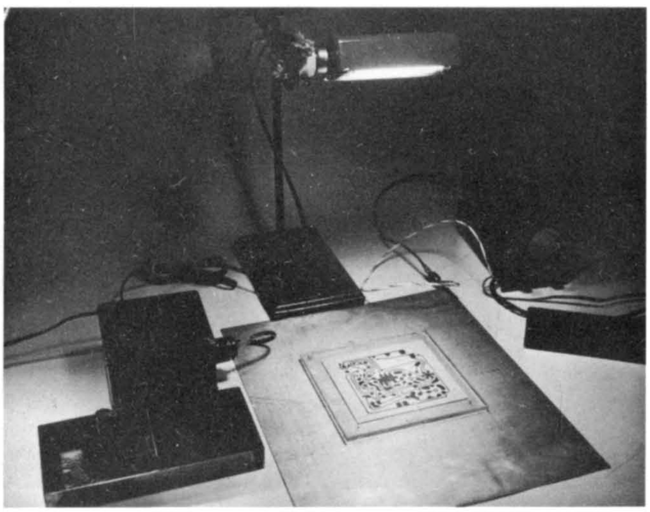


c. The copper clad sheet with the thin dry photoconductive coating applied. This coating becomes light sensitive only after electrostatic charging.

Fig. 2 - Step 1--Applying the electrophotographic coating.

d. Placing a uniform electrostatic charge on the coated copper surface by "spraying" with negative ions from a corona discharge unit. This is done in the dark, or under a suitable safelight.





e. Exposing the plate to a light image of the circuit to be reproduced in copper. In this case, the sample is being "contact printed" through a film, using two 4-watt fluorescent tubes. With this source, the exposure time is about five seconds.

f. Developing the charge image remaining after the exposure by use of an acid resistant fusible powder bearing a positive electrostatic charge. This powder is being applied by brushing with the RCA magnetic brush.

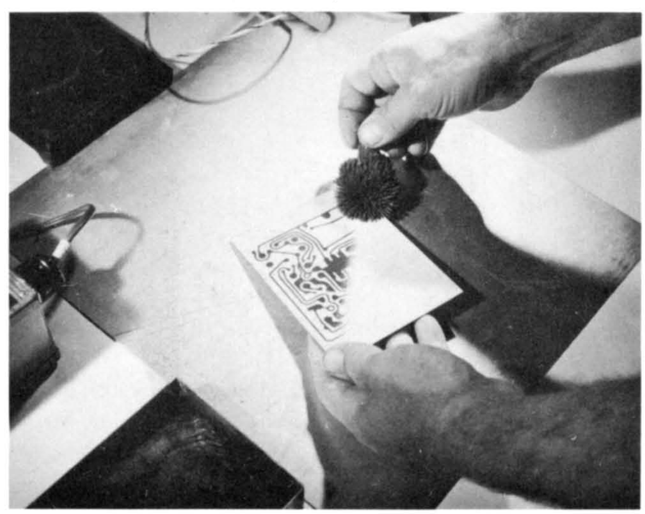
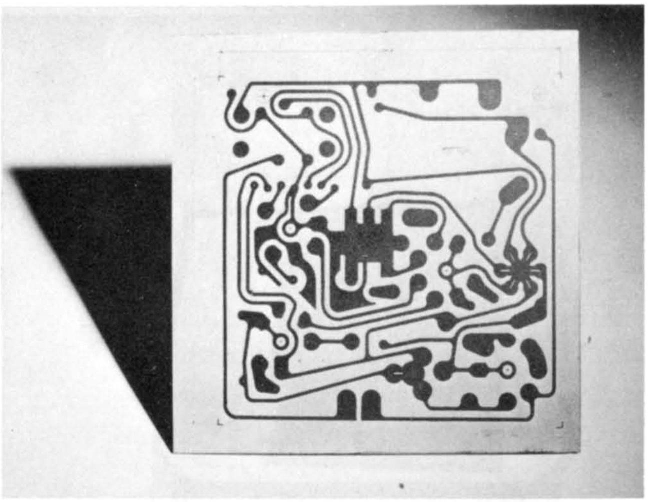
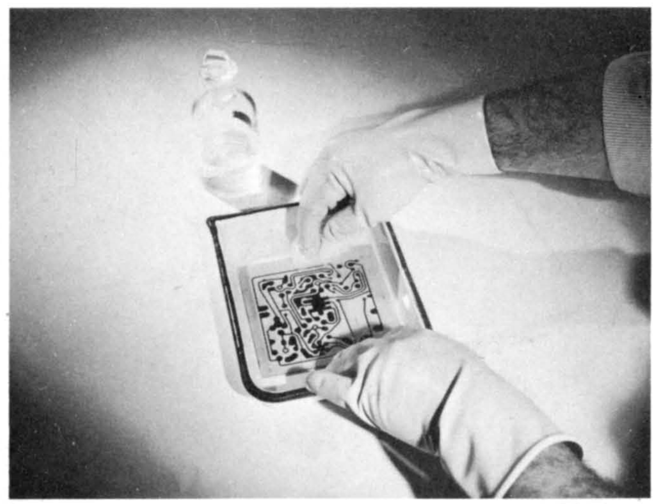


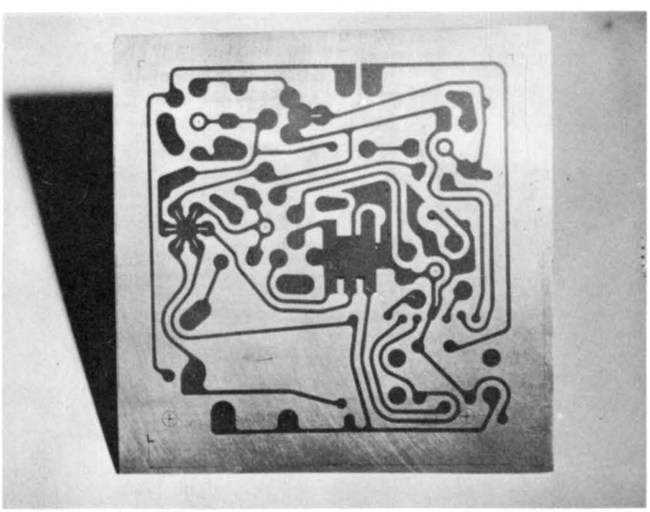
Fig. 2 - Step 2--Applying the resist image by the Electrofax process.



g. The coated copper clad sheet after the acid-resistant powder image applied in Step 2 has been thoroughly heat fused.

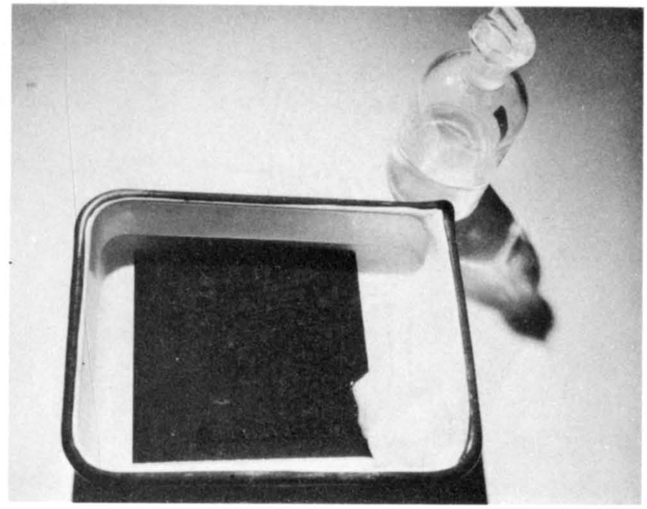
h. Swabbing with a selective solvent to remove the photoconductor-resin coating from copper areas to be etched away.



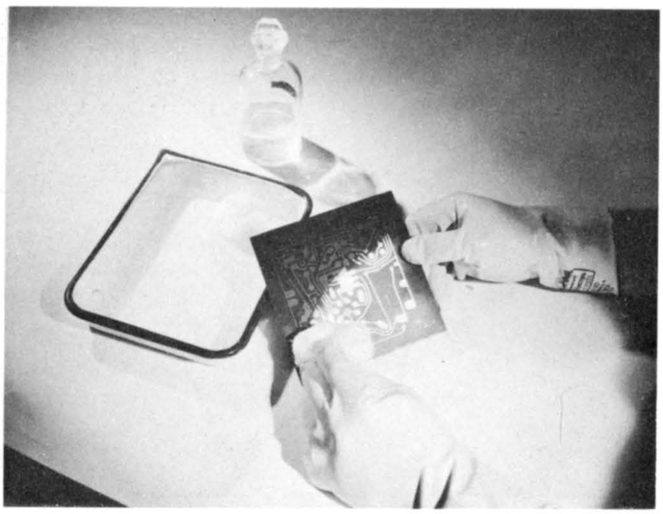


i. The plate with the photoconductive coating removed from background areas, ready for etching.

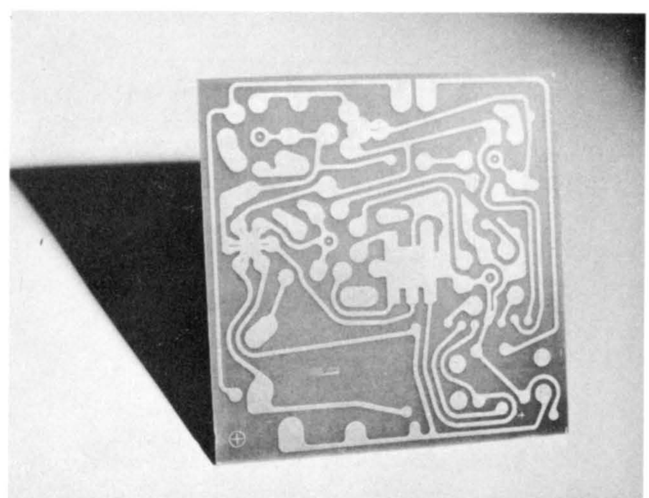
Fig. 2 - Step 3--Clearing the background areas.



j. The plate with copper etched away in all areas except those protected by the fused electrophotographic image. Etching is accomplished by standard photo-engraving methods.



k. Removing the acid-resistant resin image by use of an organic solvent.



l. The finished circuit board, ready for punching or drilling, component insertion and dip soldering or other treatment.

Fig. 2 - Step 4--Etching.
Step 5--Removing the resist image.

Detailed Description of Processing Techniques

The best procedures to date for preparation of typical printed circuit units are as follows:

1. A coating mixture (sensitizer) is prepared by thoroughly mixing

G.E. Silicone Resin Sr-82 (60% in Xylene) (General Electric Co., Chemical Devision, Pittsfield, Mass.)	65g.
Toluene (Toluol)	200g.
White ZnO (Florence Green Seal-8) (New Jersey Zinc Sales Co., 160 Front St., New York, N. Y.)	100g.

The above is ball-milled for 3 hours or mixed in a Waring Blendor (or the equivalent) for about 5 minutes.

If desired, wavelength sensitivity of the coating may be extended by addition of a suitable dye sensitizer. A typical sensitizing procedure consists of the addition of 5 ml. of a 1 per cent solution of Rose Bengal (CI No. 779) in methanol to the above mix before ball-milling or blending.

The addition of Rose Bengal in this proportion increases the tungsten sensitivity of the coating about 30 times, by extension of the wavelength response into the visible region or the spectrum. Ultraviolet sensitivity is relatively unaffected. This effect is shown graphically in Fig. 3.

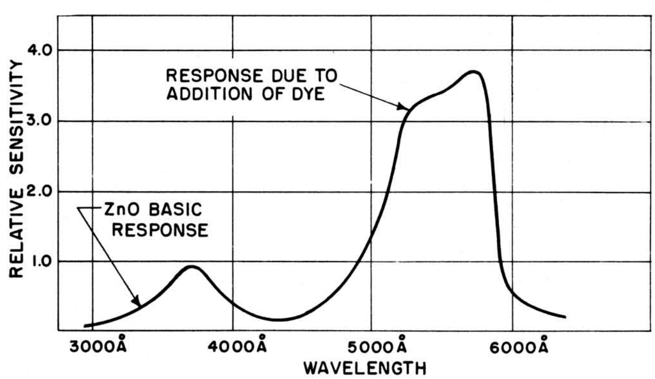


Fig. 3 - Spectral response of Electrofax coatings sensitized with rose bengal.

Other examples of dye sensitizers are given in reference 4.

2. The above coating is applied to standard commercial copper-clad phenolic or other suitable metal-clad stock of the desired characteristics, and air dried. Application may be by any conventional coating method, such as spin or flow coating, spraying, or dipping. Coating thickness is adjusted to be as thick as possible consistent with good electrophotographic printing properties. For a white ZnO-silicone mixture in a ratio of 2.5-to-1, this is estimated to be about 0.1 to 0.3 mil. Spin coating the above mix at 300-700 RPM gives a satisfactory coating thickness. Other formulations may allow use of even thinner coatings.

3. The photoconductive surface is next uniformly charged in the dark (or under suitable safelights), using a corona unit such as that described in Appendix A and illustrated in Fig. 4, exposed with a positive (black-on-white) optical image of the circuit to be reproduced, and powder developed (toned) with a suitable electroscopic fusible acid-resistant resin-base powder. A typical exposure time in contact printing is four seconds under two 4-watt white fluorescent tubes at 20 inches, or 1/10 second to two 4-watt "Black Light" tubes at the same distance, using the mixture in step 1 without dye addition. For the silicone-bound mixture in the example above, satisfactory resist images have been obtained with a developing powder consisting of a low cost

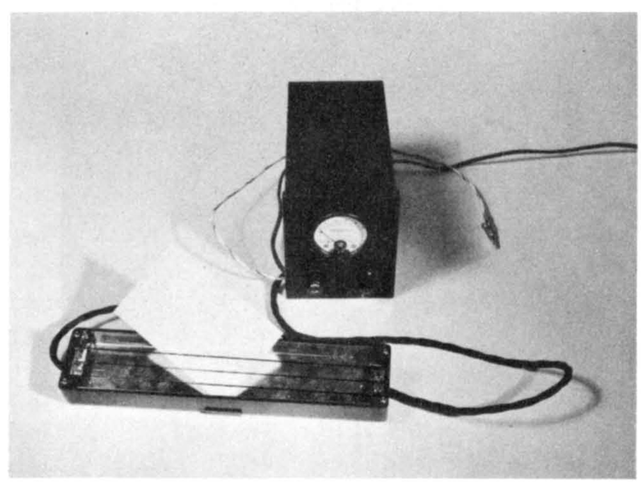


Fig. 4 - Corona unit and power supply for use in applying a uniform surface charge to Electrofax coatings. The hand corona unit is shown overturned from its normal use position and with a piece of paper inserted, to emphasize the three fine wires from which the corona discharge emanates.

resin base combined with carbon black and certain black dyes. Instructions for preparing this toner are contained in Appendix B.

Powder development (toning) may be by any of the methods well known in the electrophotographic art, such as powder cloud, charged droplet spray, cascade, roller development or the RCA "Magnetic Brush". All of these systems are described in some detail in reference 4. The magnetic brush method, however, furnishes by far the most convenient and practical system of those evaluated thus far. In its practical use for photo-resist development, about 2 to 4 grams of the toner described above, or any other suitable toner, are mixed with about 100 grams of powdered iron magnetite, or other magnetic carrier and the resulting mass is picked up on a magnetic structure so arranged as to direct the magnetic "bristles", which follow the magnetic field lines, against the latent charge image to be developed on the photoconductor coated surface of the circuit boards. For hand work, this magnetic structure may be simply one end of an Alnico magnet. A

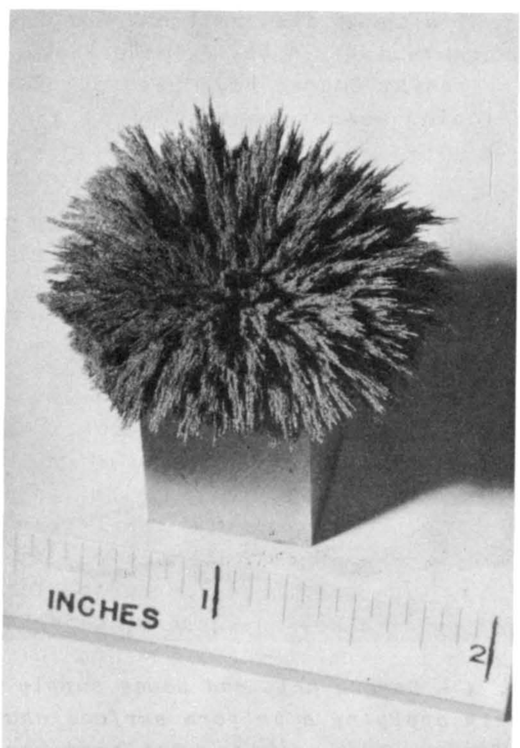


Fig. 5 - A hand magnetic brush suitable for developing Electrofax images.

close-up of such a hand magnetic brush is shown in Fig. 5. Other structures may be devised for machine operation. In designing such systems, it should be kept in mind that the iron powder and toner supply must be easily, and preferably continually, remixed, since the toner supply on the ends of the ferro magnetic "bristles" becomes depleted during development. Arrangements must also be made for replenishment of toner as the supply in the brush mixture is used up. For hand work, this may be accomplished by merely dipping the brush in pure toner powder and agitating therein. The iron or other magnetic carrier is not depleted, since it remains attached to the parent magnetic pole during development.

4. The powder image is now thoroughly fused. Best results in the laboratory have been obtained by heating for 2 to 4 minutes in an oven at about 200 degrees C. Satisfactory fusing has also been obtained with infrared lamps and by induction heating, and with much shorter heating times. This, of course, is a function of toner formulation and softening and melting points of the photoconductor resin binder. Ideally, the image resin should fuse completely through the photoconductive film and attach itself directly to the copper surface beneath. The toner described above approaches this condition.

5. Background areas are next cleared by wiping away the photoconductor-resin with a cotton swab wet with a solvent which softens or dissolves the silicone or other photoconductor binder without affecting the image areas. For silicone resin and the image powders currently used, aliphatic alcohols are suitable. Image fusing by oven baking at 200 degrees C polymerizes the silicone binder to some extent. A suitable procedure for cleaning the silicone-ZnO coating from background areas is a 2-minute soaking in denatured ethyl alcohol, followed by rubbing with a cotton swab wetted with the same mixture. Use of a higher alcohol, such as pentanol, or preferably of alcoholic sodium hydroxide, increases the efficiency of the clearing process and allows longer or more intense baking.

6. From this point on, the sheet is handled by standard etched circuit techniques. The copper or other metallic film is etched away by any of the usual etch baths, and the sheet

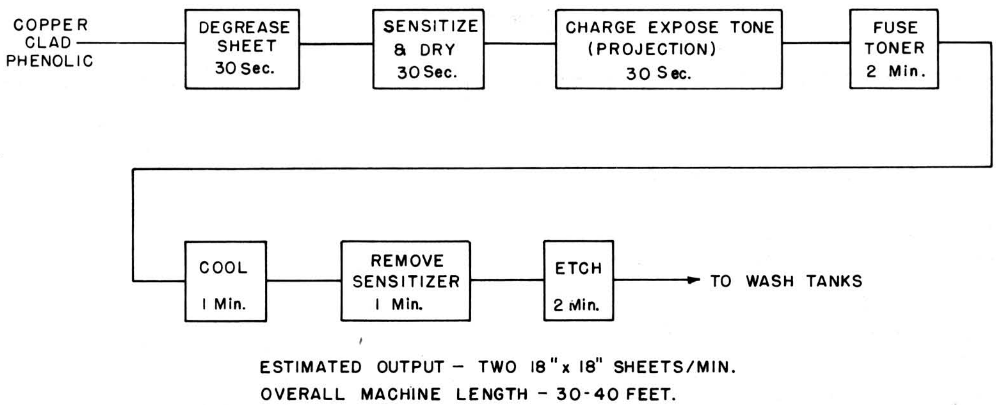


Fig. 6 - Continuous printed-circuit production by Electrofax.

washed and dried. Finally, the fused resin resist may be removed completely or locally, as desired, by means of an aromatic solvent, such as toluene.

Advantage of the Process

This new method has the following principal advantages:

1. Exposure requirements are orders of magnitude less than those for present commercial counterparts. This makes possible projection printing and complete mechanization of the process. Photographic processing is dry and quick. Because of the high photographic speed of the photo-resist process, and its positive-to-positive nature, direct use of drawings for projection or contact printing is readily possible.

2. Cost of the basic sensitizing material and processing are comparable with present photo-resists.

3. Techniques involved in the process are similar to present methods, allowing easy adaptation of commercial equipment and personnel.

4. Intrinsic resolution and contrast are sufficient for present printed circuit requirements.

5. Wavelength sensitivity of the coating may be extended or controlled by use of appropriate dye sensitizers or by choice of photoconductor.

6. Because the photoconductor-coated copper laminate sheets are chemically and physically stable they may be stored indefinitely before use.

A preliminary estimate of the factors involved in continuous printed circuit production by this method has resulted in a flow sheet for a possible continuous-operation machine as shown in Fig. 6. The time factors involved in any particular stage may be reducible, depending on design of equipment and techniques used.

The exposure station in such a machine might consist of a lens, a mirror, and suitable lighting arranged so as to project a reflected image from an enlarged drawing of the desired circuit pattern in the desired size and position directly on the surface of the electrostatically-charged photoconductor-coated copper laminate. Exposure times may be few seconds or a fraction of a second, depending on the light source, optical system and coating formulation used.

M. L. Sugarman, Jr.

M. L. Sugarman, Jr.

Appendix A

Suggestions for Corona Charging Equipment Suitable for Use in the Electrofax Process

Below are descriptions of some of the units that may be used for Electrofax printing:

Power Supply Unit

Any high-voltage power supply which will supply from -5 kv to -10 kv at 100 microamperes to 500 microamperes will be satisfactory for Electrofax processing.

Two sources of commercial power supplies are:

1. Model No. PS10
   Condenser Products Co.
   Chicago, Illinois
2. 0-10 kv positive or negative output
   Spellman Television Co., Inc.
   New York 67, New York

A small power supply designed at RCA and shown in Figs. 2 and 4 may also be used. The circuit diagram for the unit appears in Fig. 7.

Corona Unit

One design for a corona charging unit consists of three 0.003-inch wires strung taut between insulators. They are 1/2 inch apart and 7/16 inch from the surface to be charged. The wires are shielded by a grounded metal cover spaced 1/2 inch from the plane of the wires. Such a unit is illustrated in Figs. 2 and 4.

It has been found that approximately -6 kv is needed to charge the Electrofax surface satisfactorily with the above unit.

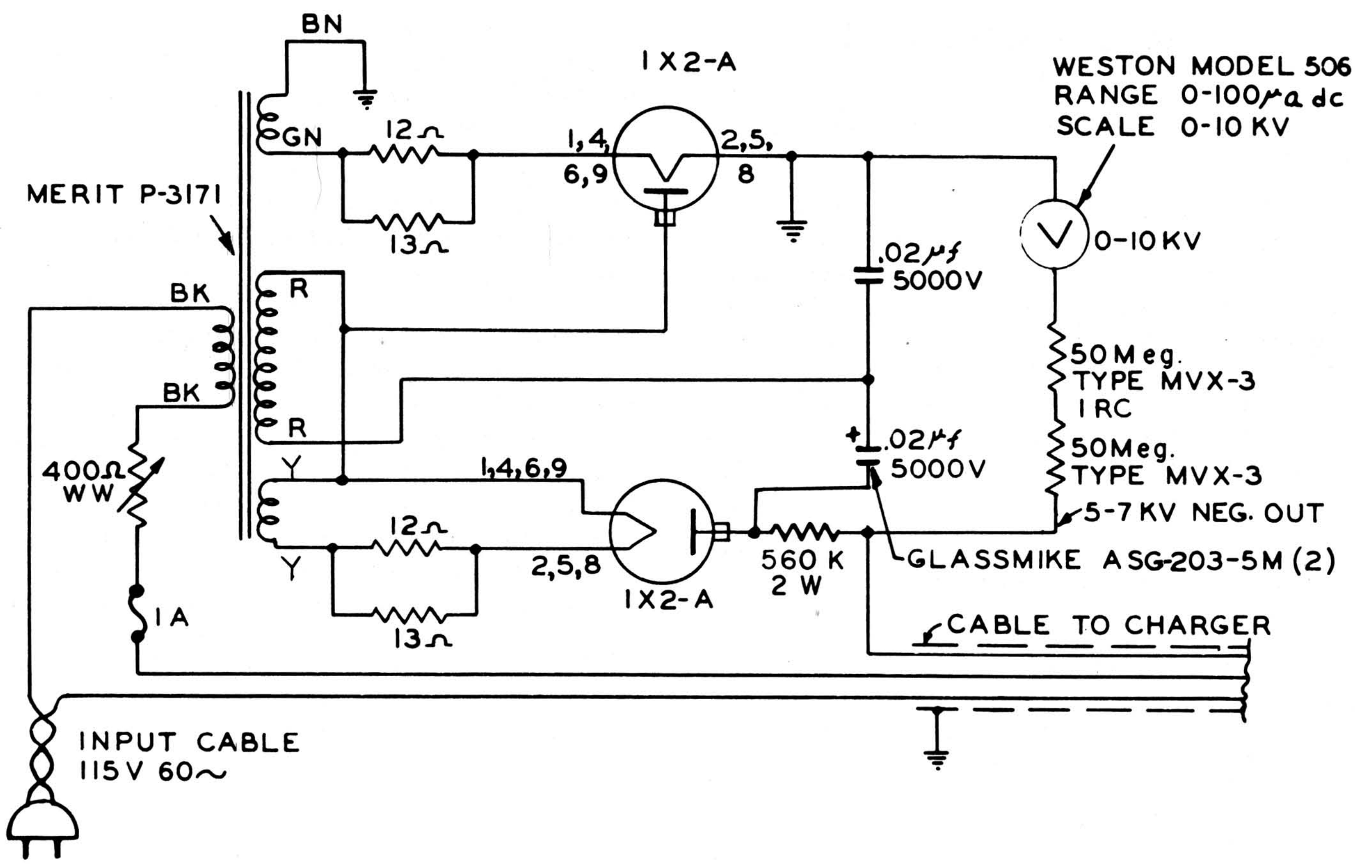


Fig. 7 - Rectifier for corona charger.

Appendix B

Preparation of RCA Experimental Developer Powder

1. The following materials are thoroughly mixed in powder form:

200 grams Piccolastic Resin 4358A* (200 mesh)
12 grams Carbon Black G**
12 grams Spirit Nigrosine SSB***
8 grams Iosol Black***

2. The mixed powders are melted and thoroughly mixed in a stainless steel beaker. (180° - 200°C). This melt is quite thick and tar-like in consistency. There is some smoking, probably due to the organic colors, so mixing and heating should be as short a time cycle as possible.

3. The melt is emptied onto a brass tray and allowed to cool and harden.

4. The hardened mass is broken up and coarse ground. The material grinds readily.

5. The coarse ground material is ball-milled for about 20 hours in a one-gallon capacity Ball Mill with porcelain balls.

6. The milled powder is screened through 200 mesh screen. Recovery is about 76 per cent of 200 mesh powder. This powder takes on a positive charge when mixed with the iron powder currently used for magnetic brush development. It therefore develops a direct positive image on the electrophotographic ZnO - resin coating which carries a negative charge.

Note: When using the above toner in a magnetic brush system, the particle size of the magnetic carrier with which the toner is mixed is somewhat critical. Optimum size range for powdered iron or magnetite is 100 to 200 mesh.

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*Pennsylvania Industrial Chemical Corp., Clairton, Pa.
**Fisher Scientific Co., 63J Greenwich, New York 14, N.Y.
***National Aniline Div., Allied Chemical & Dye Corp., New York 6, N. Y.