United States Patent

Brand et al.

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[54] MANUFACTURE OF PRINTED CIRCUITS

[72] Inventors: **John Seemann Brand**, Cranbury; **Vladimir Paul Honeiser**, Lawrenceville, both of N.J.

[73] Assignee: **American Can Company**, New York, N.Y.

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[52] **U.S. Cl.** **117/212**, 29/620, 117/216, 117/226, 117/DIG. 9, 174/68.5, 338/308

[51] **Int. Cl.** **B44d 1/18**, H01h 37/36, H05h 3/12

[58] **Field of Search** .....174/68.5; 317/101 B, 101 C; 338/307, 308, 211, 212, 210; 29/620; 117/212, 217, 70 R, 76 P, 226, 216, DIG. 9

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Primary Examiner—Darrell L. Clay

Attorney—Robert P. Auber, George P. Ziehmer, Leonard R. Kohan and Leonard G. Nierman

[57] **ABSTRACT**

Circuits including conductors and impedance elements are printed on paper. Component values are maintained within acceptable limits of variation by correlated selection of substrate porosity and ink to produce a high degree of absorption of the liquid ink vehicle into the porous substrate while producing relatively little penetration of the pigment. Resistance values are lowered, and their reliability and consistency greatly improved, as compared with printing on either impermeable or excessively porous substrates.

7 Claims, 6 Drawing Figures

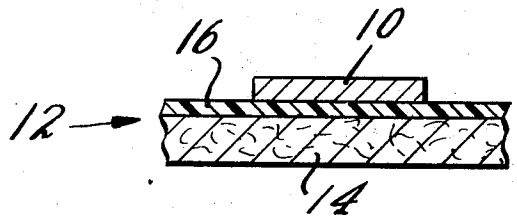


Fig. 1

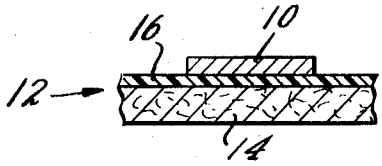


Fig. 4

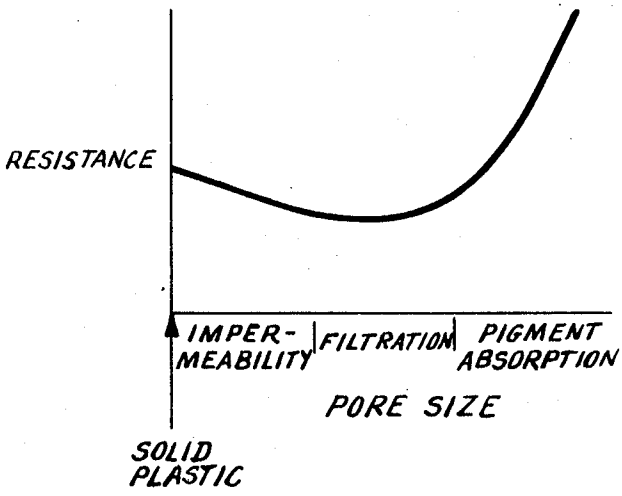


Fig. 2

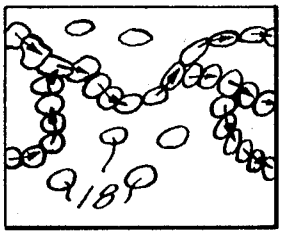


Fig. 5

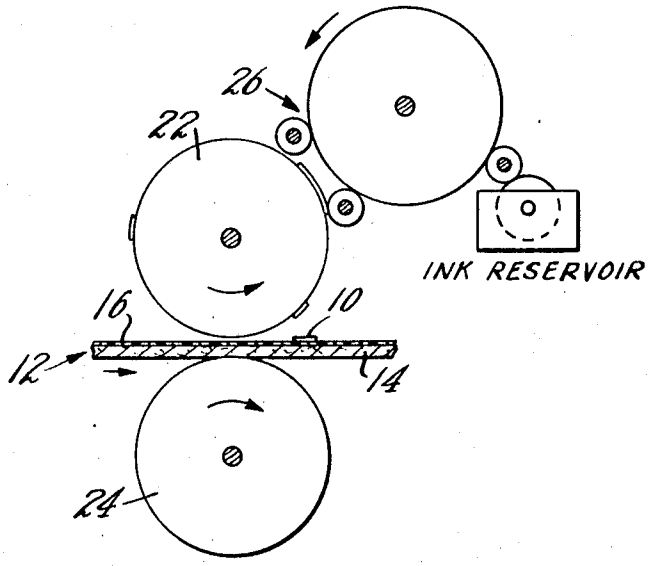


Fig. 3

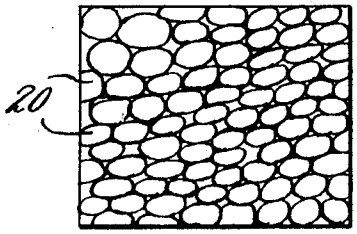
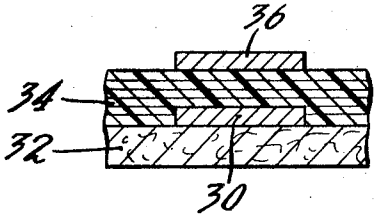


Fig. 6



INVENTORS
JOHN SEEMANN BRAND
VLADIMIR PAUL HONEISER
BY
Leonard G. Norman
ATTORNEY

MANUFACTURE OF PRINTED CIRCUITS

This invention relates to the manufacture of electrical components and circuits, and more particularly to low-cost production thereof by use of high-speed printing equipment.

The concept of employing a printing-press for mass production of electronic components and circuits is extremely old, having been mentioned in numerous papers and books in the earliest days of development of "printed circuits." A few early experimenters apparently attempted to implement this idea, but were so unsuccessful that the efforts appear to have been abandoned as hopeless within a few years after early widespread predictions that printing-press production of electronic circuits would shortly be commonplace. A number of early papers report experiments with printing presses attempting to print electronic circuits, but usably reliable reproduction does not appear to have been achieved.

Paper is a wholly natural or obvious choice as a printing substrate, and appears to have been contemplated in the early speculative predictions mentioned above. However, there have been found no reported experiments with such a substrate. In view of the results of the investigations which have led to the present invention it may be speculated that the early workers considered substrate porosity as such a handicap that the failures with substrates such as plastics made it appear obvious that results with porous substrates must be even more remote from acceptability. It appears obvious (misleadingly, as shown by the present invention) that if difficulty is encountered in reasonably reproducing a resistance value (the most difficult problem as hereinafter discussed) on a highly stable and non-absorbing substrate such as a plastic plate or sheet, the difficulties in doing so on a porous substrate should be completely prohibitive. The findings of the present invention demonstrate that this is not the case.

The early mentions in the literature discussed above appear to treat the difficulties encountered in using a printing press as arising primarily from limitations on the thickness of the ink layer which can be deposited on a substrate surface. On this premise, it is indeed concludable that best results from the standpoint of reproducibility from one sample to the next should be obtained by deposition on a smooth surface, rather than effectively losing a portion of the deposited film in a porous substrate. However, as demonstrated by the present invention, the failure of earlier workers in the art to achieve satisfactory results with a printing press appears to have been attributed to the wrong cause.

In the same early period of printed circuit development in which some workers in the art unsuccessfully attempted to employ printing presses, they and others developed other graphic methods which came into common use for differing products. The product to which the term "printed circuit" (PC) is now most commonly applied is neither "printed" nor a "circuit" within the meaning of these terms as hereinafter used. This is the now-familiar type of circuit board limited to printed wiring for attachment of conventionally-manufactured impedance components. A second main line of development, in which impedance elements are also deposited as films by graphic-derived techniques, normally employs a glazed ceramic or similar substrate upon which the films are deposited in various manners which have become known in recent years as "thick film" and "thin film" deposition methods. The present invention is in essence an improvement in "thick film" technology. (It will of course be understood that the term "thick film" as used in the art to contrast with "thin film" does not alter the ordinary meaning of "film" as describing a layer which is in either case thin relative to the substrate.)

The invention is based on experimental investigation of the electrical characteristics of circuit components, particularly resistors, mass-produced by a printing press. The experimental data demonstrate that the production of satisfactory electrical circuits in this manner is feasible provided the inks and substrates employed are properly correlated in accordance with the criteria of selection which the invention provides. Although it was the principal object of the experimental work which resulted in the invention to make the use of a printing press in such circuit production practical, the broader aspects of the teachings may be employed to improve and simplify other production methods, such as those employing silk-screening and similar methods of deposition of films on substrates.

The satisfactoriness of any graphic method of film deposition for the production of electronic circuits requires the meeting of a large number of requirements, some of which are met rather easily and some of which are extremely difficult to meet. Irrespective of the process employed, there are three basic types of film compositions required, which may be characterized as conductive, resistive, and dielectric. (The invention may be ultimately employed for the deposition of semiconductors, at such time as pigments of this type may be developed.) The conductive films or patterns generally serve the same electrical function as wires and metallic capacitor plates and coils in wired circuits. The primary requirement of such films is one of minimum conductivity. Although the meeting of this requirement is not simple from an absolute standpoint, the difficulty is relatively small as compared with the requirements in the deposition of films in which variation from uniformity in either direction is unacceptable. In the case of the dielectric films, normally employed between conductors to provide capacitance, close tolerances must be held to provide uniformity of capacitance value from one sample to the next; also it is necessary to avoid pinhole imperfections, etc., which can produce arcing. However, such problems are relatively easily solved as compared with the problem of producing reliable resistance films.

The production of satisfactory resistance films has, at all times since the earliest days of development of graphic methods of circuit production, been a difficult problem. It would appear that the difficulties encountered in this regard were a major factor in the apparent early abandonment of efforts to produce satisfactory component circuits with a printing press, and the shift of effort to inherently less economical processes, such as silk-screening of paints and vacuum deposition of resistive metal films. Even with the complexities thus introduced, presently known processes are in general incapable of closely reproducing resistance values without measurements made on each specimen. Much effort has long been devoted, and is still devoted, to control of the resistance value of each individual specimen in response to a measurement made after or during the film deposition, either employing various techniques of "trimming" or fixing an end-point for discontinuance of a sputtering or similar process.

The present invention flows from observation that a printing-press has a greater inherent capability for producing wholly uniform film deposition than other pattern-producing methods, followed by investigation of the manner in which this potential superiority can be realized in terms of reliability of electrical characteristics of the deposited films. As a result of experimental investigation of parameters producing a wide range of results as regards useability of the printed circuit output, it has been ascertained that the assumption apparently heretofore made that non-porous materials are superior to porous materials as regards ability to produce electrical uniformity of deposited films of inks and paints is erroneous if the porosity characteristics of the substrate are properly related to the composition of the ink or paint employed. By variation of porosity there are found to be produced with a given ink composition used in printing a wide variety of qualities of electrical characteristics of visually similar films, particularly as regards reproducibility of resistance values, varying from products which are essentially useless to products of quality generally comparable to that produced by much more expensive methods of production. The employment of either an insufficiently porous or an excessively porous substrate produces a wholly unsatisfactory product. Although the physical phenomena which produce this great difference in useability of the printed circuit product are not readily directly observable, available experimental evidence appears to demonstrate the theory of operation hereinafter to be discussed.

The type of film-pattern deposition typified by employment of a printing press, silk screen, etc., employs a liquid or semi-liquid composition of the type known variously as an ink, a paint or a paste, dependent primarily on the general degree of viscosity or plasticity. Such a medium in general consists of particles of solid material, herein called the pigment, along with liquid components in which the particulate matter is dispersed to give the overall composition the liquid or semi-liquid character required for the process employed and to provide an ultimate binder for the particles and adherence to the substrate. After deposition of the film, whether by spraying, brushing, printing-press operation, or otherwise, the liquid components are partially solidified and partially eliminated by evaporation, etc., with the solidified portion forming a binder or matrix holding the pigment particles and adhering to the substrate. As a practical matter, most compositions for forming such films have substantially more than two components. Ink and paint compositions commonly employ separate constituents for the binder material and a diluent employed to impart the desired viscosity properties, and there are also present additives to speed the drying or curing and for similar purposes.

It is theoretically possible to employ only sufficient liquid in such a composition to form, when solidified, a binder for the pigment of the minimum concentration which will hold it together. However, the ink compositions employed in printing presses desirably contain a considerable component of liquid beyond this minimum. Further, even were such an ideal to be achieved, there is doubt whether it would be practically useful on a fluid-impervious smooth substrate, since the concentration of binder required to give assured bonding to a smooth impermeable substrate is prone to be substantially higher than that which is required for mere cohesiveness of the dried film.

Where a film is produced on an impermeable substrate from a liquid composition having a much higher concentration of binder than the minimum required for cohesiveness of the ultimate film, electrical performance is found to suffer wide variations in successive samples. Consider, for example, the conductivity of a film of metallic pigment particles. A theoretically optimum conducting film so deposited would have no more binder than that required to fill the interstices or voids inherent in a packed-particle structure. Current flow distribution in such a structure is generally similar to that through a wire of comparable metal content. But with even mildly excessive binder, contact between adjacent particles is no longer assured, and successive short lengths of a conductor so formed can exhibit wide variations in conductivity. The current pattern through such a conductor is wholly different than that through a wire, the overall conductivity of such a conductor being primarily determined by randomly-occurring regions of low conductivity. Nevertheless, because the primary performance requirement of a conductor is some minimum of conductivity, i.e., a maximum resistance, a small excess of binder can be tolerated, although not desirable.

In the case of a resistor, the adverse effects of excess binder in the dried film are much more prohibitive. Random variations in resistance from sample to sample will occur even with an ideally uniform deposition producing wholly identical patterns and volumes of deposition of identical composition. It is believed a practical impossibility to deposit a film, particularly with a printing-press, having so little excess of binder present in the composition as deposited that reliable resistances can be achieved.

In the method of the present invention, the film is deposited with substantial excess liquid vehicle and the excess vehicle is removed from the film prior to solidification by a filtering action which leaves the pigment in a relatively low concentration of binder material on the surface of the substrate to closely approximate the idealized film-production already discussed. The ink is deposited with an excess of binder on a porous substrate surface having a pore-size selected to act as a filter passing the excess binder while admitting relatively little of the pigment from the surface of the substrate. The liquid of the ink composition is removed to the point where the film, upon drying, contains an amount of binder closely approximating the theoretical optimum earlier described. The constancy of resistance values from one circuit to the next obtained in the printing-press production of circuits compares favorably with that obtained by far more complex and expensive production methods.

The pore-structure for producing the filtering action is selected by experimental matching to the characteristics of the particular ink composition, particularly in accordance with the size of the particles of the resistive pigment (normally carbon). The most readily available and inexpensive type of porous substrate material is of course paper. It is found, however, that most ordinary papers are not suitable with the pigments most practical for use. As in the case of an ordinary discrete carbon resistor, the employment of relatively coarse carbon particles produces resistors of prohibitively high noise-generation, as well as making reproducibility of resistance values difficult or impossible. It is found that papers selected without care, when employed with pigments of relatively fine particle-size giving the best resistor performance, produce wholly insufficient filtering action. Where the pore structure is so coarse as to permit fairly free penetration of the pigment particles, the ink is absorbed in the paper with little or no filtering action, and the results are at least as unacceptable as in the case of impervious substrates. With proper pore structure at the surface of the substrate, the pigment is retained in the surface while the excess binder is absorbed into the body of the substrate. Upon solidification of the binder, there remains on the surface a matrix containing the pigment particles with approximately the minimum amount of binder required to provide cohesiveness. This is securely bound to the substrate by the absorbed binder material, which contains relatively little pigment. The concentration of binder in the surface film can be well below that required to obtain adherence to a non-porous substrate.

It will of course be understood that neither the pores of the substrate nor the pigment particles are in practice wholly uniform in size, so that there is no abrupt interface between pigmented and unpigmented binder at the surface of the substrate. However the volume proportion of pigment to binder in the pores of the ultimate product is substantially less than the volume proportion of pigment to binder in the surface film, the pigment concentration decreasing very rapidly with depth of penetration of the binder.

Various types of porous substrates may be employed successfully. The most desirable are papers having a small-pored coating on the surface upon which the circuit is printed, the fineness of pores required being difficult to obtain in the body of a paper. Among commercially available papers, clay-coated papers appear most suitable for use with the fine-ground carbon pigments which are preferred for resistive components.

The invention further provides certain improvements or refinements of the general process as above described. Practical printing of electronic circuits requires a plurality of successive layers or superimposed films. Conductor patterns are coupled to margins of resistive patterns and capacitors are desirably formed by a number of successive layers of deposition. Layers above the first layer cannot employ the filtering action described above. This is found to constitute no major restriction on the utility of the invention, since it is only the resistance elements in which the filtering action is found highly critical to acceptability. Accordingly, the over-printing of successive layers of non-resistive ink patterns may, if so desired, be performed with inks of the same composition as the base layer. For best results it is found desirable to employ, for the deposition of overprinted patterns, inks which permit substantial removal of liquid by means other than fluid flow. One manner of accomplishing this is by employment of a combustible liquid as a primary constituent, deposition of the film being followed by flaming or "flashing." Such a printing process is greatly advantageous in that it provides very rapid curing of the binder constituent and overall drying of the film. However, as hereinafter discussed more fully, it is frequently desirable to

employ for resistive films, where precision is required, a type of ink which dries more slowly but gives somewhat better compaction of the pigment particles as a result of the filtering action of the substrate.

As will hereinafter be seen, additional factors enter into the selection of inks and substrates and other aspects of the present method, such as assuring that the desired degree of removal of liquid from the deposited film occurs prior to solidification of the binder.

In addition to the aspects above briefly described, the invention also provides further features best understood from the description below, illustrated in the annexed drawing.

In the drawing:

FIG. **1** is a schematic enlarged fragmentary sectional view of a printed circuit element made in accordance with the invention;

FIG. **2** is a schematic illustration of the random-contact orientation of pigment particles when incorporated in a substantial excess of binder;

FIG. **3** is a schematic diagram corresponding to FIG. **2** but illustrating a more ideal relation of pigment particles;

FIG. **4** is an idealized graph illustrating the general approximate relation between resistance and substrate pore-size for film patterns formed by identical deposition of a given printing ink;

FIG. **5** is a schematic illustration of the operation of a rotary letterpress printing press employed in the printing of circuits in accordance with the invention; and

FIG. **6** is a fragmentary schematic sectional view of a capacitor formed by overprinting a number of layers in accordance with the invention.

Referring first to FIG. **1**, there is there illustrated in schematic form a greatly magnified section of a printed circuit element of the invention comprising a resistance element film pattern **10** on a substrate generally indicated at **12**. Appropriate film pattern shapes for formation of circuit elements are well-known, for example as shown in U.S. Pat. No. 3,484,654 of Vladimir Paul Honeiser, and accordingly not illustrated. The substrate is here a coated paper, the body **14** being coated with a surface layer of a filter coating **16**, such as the clay coating of certain commercially available papers later mentioned. Although a coating on only one side is illustrated, it will of course be understood that coatings on both sides are employed where circuit patterns are printed on both sides of a substrate.

As schematically shown in FIG. **2**, where a film pattern is formed which has a substantially higher proportion of binder than the minimum required to hold the pigment particles **18** in a cohesive matrix, contacts between adjacent particles **18** occur in a random manner to form distinct paths for current flow (the direction of current flow is arbitrarily selected as left to right in the illustration of FIG. **2**, with arrows representing exemplary complete current paths). Much of the particulate content contributes nothing to the conductivity. The resistance value through such a structure cannot be expected to be closely reproduced from one sample to the next, irrespective of the precision with which deposition conditions are duplicated in each successive specimen. By contrast, where the packing of the particles more closely approaches the ideal, as in the particles **20** of FIG. **3**, the fluctuations of resistance value from sample to sample may be expected to be much lower, in addition to the fact that the resistance itself will be much lower. In accordance with the invention, conditions closely approaching those of FIG. **3** are obtained by removing from the film, after its deposition but before completion of drying or curing, substantially all of the excess binder (shown as voids in FIGS. **2** and **3**).

The expected general or gross effect of varying the porosity characteristics of substrates upon resistance values of a resistive film, with deposit of a given quantity of the same ink in a predetermined pattern, is shown in the graph of FIG. **4**. As there shown, the porosity or pore-size characteristics may be considered to have three general regions. The lowermost region is designated that of "impermeability" and has as its lower limit a substrate which is wholly impermeable, such as a solid sheet of smooth plastic, a paper with a coating of solid plastic, or a glazed ceramic. As a very small degree of porosity is introduced and then increased, the resistance of the dried film decreases due to binder absorption prior to curing, until there is reached the porosity region producing a high degree of filtration. In this region essentially all of the excess liquid over that required for binding of the film is absorbed in the substrate so that upon solidification of the binder the pigment in the film approximates the ideal packed condition. When the pore size becomes too coarse, a substantial portion of the pigment itself penetrates into the paper, wherein it is lost as a factor of conductivity, to a degree which cannot be exactly controlled, this region demonstrating a rise of resistance due to such pigment absorption. In principle, if the porosity were to be increased to the point where the substrate is effectively merely a very loose fibrous mass with substantially no isolation of the regions into which the liquid flows, there would be a further region (not shown) in which the resistance would again approach the value on a non-porous surface. However, such a substrate cannot preserve the shape of the original deposited pattern with sufficient precision to be of utility.

The existence of the three general regions shown in FIG. **4** has been verified experimentally, but there are found to be too many practical variables to permit the obtaining of experimental data closely delineating a smooth idealized curve such as shown. No method of deposition is presently known for exactly reproducing the amount of ink deposited on substantially differing substrates while at the same time maintaining constant all of the other variables which may affect the result. For example, although a printing press, as later mentioned, is fully capable of leaving substantially identical quantities of an ink on extremely large numbers of successive substrates of the same compositions, a substantial change of surface composition greatly affects the amount of ink deposited in each impression. Although such factors as impression pressure may be adjusted and correlated with observed ink consumption to equalize the amount of ink deposition on varying substrates, such adjustments in themselves represent changes of conditions which can materially affect the data. In addition, porous materials are not sufficiently calibratable in exact pore size to permit construction of a continuous curve such as that illustrated from experimental data. However, the validity of the general shape of the plot of FIG. **4** appears to be demonstrated by the experimental evidence hereinafter described, obtained in experiments with substrates falling in the two high-resistance regions as well as a number of clay-coated paper substrates appearing to possess varying degrees of close approach to optimum porosity characteristics with the inks employed.

There is shown in FIG. **5** a schematic illustration of the rotary letterpress printing process. Although the invention in its broad aspects may be employed with printing processes and equipment of other types, these presently appear to be less satisfactory. It is found that the reproduction of resistance values is a far more sensitive indicator of uniformity of deposited films than any other known, and that best results are obtained with the rotary letterpress process.

The illustrated rotary letterpress will be recognized as conventional by those skilled in the printing arts. The plate cylinder **22** and the impression cylinder **24** rotate at constant speed to deposit on the substrate, on the plate pattern, the ink delivered to the patterned plate by the train of inking rollers **26** from a suitable ink reservoir and fountain rolls. The constant-speed rotary motion of all components produces a uniformity of film deposition from sample to sample which cannot be achieved in any other known manner. However, for the basic reasons already outlined, assuring constancy of film deposition from sample to sample has been found to be wholly insufficient in itself to produce corresponding uniformity of the electrical characteristics of circuits so printed. Despite the precision of repetition of deposited ink films inherent in such a press, no fully satisfactory results are found to be obtained

with either impervious substrate materials or with papers not giving the filtering action earlier described.

The commercially available papers found most desirable are papers having a coated surface of much finer pore structure than the body or core. Particularly advantageous are papers having a surface layer of fine-ground particles, such as clay-coated papers. Even among papers of this description there are appreciable differences in merit as measured by variation of resistance values among a large number of samples printed on each particular paper. However these differences in merit (as measured by the statistical variation of individual samples about the mean resistance value obtained with the particular paper) are relatively minor as compared with the superiority of any of such coated papers over either uncoated papers, on the one hand, or impermeable substrates, on the other.

Exact comparison of the merit of papers having only small differences in structure or composition is difficult. There are various factors, later discussed, which enter into selection of particular papers for use with any given ink. Also there are a number of variables which make close quantitative comparison between reproducibility results achieved in runs with respective papers extremely difficult when they are in the central or optimal region of porosity of FIG. 4. Were the ideal single-variable comparison of FIG. 4, with all else held constant, practically possible to measure, mere mean resistance value would be an inverse indicator of reproducibility merit. As hereinafter seen, however, the variables of the printing process cannot be controlled sufficiently accurately to permit the obtaining of detailed data points clearly demonstrating this correlation among papers of closely comparable porosity.

The discussion thus far is simplistic in describing the requirements which must be met in practical printing of circuit patterns, particularly resistance patterns, whether with a printing press or by other means for deposition of the films. At least equally important with the preservation of resistance value of a given resistor of a circuit from one sample to the next is preservation of a constant ratio of resistance values. Where deviations from the mean value occur on a random statistical basis, the deleterious effects on circuit performance are in essence multiplicative in many circuits. The preservation of wholly exact identity of such printing conditions as pressure at the point of impression, etc., over a pattern of substantial size is found to be difficult, even with presses of precision sufficiently high so that there existed, prior to the present invention, no manner of detecting nonuniformities except by an instrument such as an optical densitometer. It is accordingly desirable to select papers and inks so that the effects of any such variations which occur will be minimized. Thus a selection of parameters which produces the best results from the standpoint of identity of successive samples of a single resistor is not necessarily an optimum selection for the printing of an overall circuit.

Experiments were performed with letterpress printing on high-grade commercial rotary presses of two different manufacturers (Davidson and Heidelberg). The similarity of results indicated that differences in detail of press construction do not have any major effect on product quality, so long as the full precision of reproduction of which the letterpress process is capable is closely approached. Experiments with other printing processes, namely offset and flexographic, indicated these to be less satisfactory.

The experiments which resulted in the invention employed a substantial number of ink formulations (for each of the three general types of films) on a large variety of paper substrates, ranging from wholly impermeable plastic-coated papers to fairly coarse uncoated papers. Papers at these extremes of the porosity range were found incapable of producing satisfactory circuits with any type of ink composition. Although passable results could be obtained with a few uncoated papers as regards conductive films, by selection of pigment having a large effective size for purposes of producing the filtering action, and although the conductive films thus deposited can, with certain precautions, be overprinted with dielectric films and a further conductive film to form fairly acceptable capacitors, no success was obtained in printing commercially satisfactory resistors on any uncoated paper. The papers found to produce the best resistive films (with the inks hereinafter described) were commercially available papers of the type generally called "clay-coated," having a fine-pored smooth printing surface overlying the more coarsely porous body. Even within this group, which are sufficiently similar so that quantitative information on relevant structural differences is not available, there were observed differences in merit of the circuits produced, even though these differences were relatively small as compared with the differences between this group as a whole and papers lying outside the porosity range wherein wholly useable resistors are obtained.

A diversity of inks were employed in the tests. It was found that the most desirable pigments for use in resistive, conductive, and dielectric ink, respectively, were to a great extent independent of the other ink constituents present, although the optimum selection of the other constituents, herein collectively called the "vehicle," substantially varied with the type of pigments, i.e., the most desirable resistive ink would not provide the most desirable conductive ink or dielectric ink by mere substitution of one pigment for another. Two general classifications of vehicles, based on drying or curing mechanism, were found most satisfactory. These are the types known as "oxidizable" and "heatset." In an oxidizable ink, curing of the binder is effected by polymerization and air oxidation, either at room temperature or, for somewhat greater speed, in a suitable oven. Common components of the binder of such an ink vehicle are certain alkyds, vegetable oils, hydrocarbons and linseed oil. The type of ink known as "heatset" normally employs as the binder a suitable varnish thinned to the desired consistency by a relatively non-volatile hydrocarbon composition of fairly low flash point, and is dried rapidly by a burning-off of the hydrocarbon by flaming. As hereinafter pointed out, it is found that each of these types of inks has its own distinctive advantages in the printing of circuits, and it is further found that a vehicle adapted to be cured and dried by a combination of these processes produces results which partake highly of the advantages of both. In principle, it is of course possible to print the various patterns employed in circuit-forming with inks of greatly different vehicle characteristics, but such an approach is practically undesirable for economical production printing of circuits.

Where a slowly-dried oxidizable ink is used, the beneficial effects of the filtering action of the paper are generally minimized. With such inks, the drying or curing is normally delayed until there is reached more or less of an equilibrium between the capillary action of the pores of the paper and the capillary action produced by the pigment itself upon reaching a fully compacted condition. However slow drying introduces the necessity of substantial delay between application of successive film patterns and also complicates handling of output sheets, which cannot be directly stacked for handling until drying has proceeded to the point where there will be no transfer ("offset") of ink from the drying film to the back of the succeeding sheet. Drying of a heatset ink by flame treatment can be much more rapid. However, if the flame treatment is applied shortly after the time of impression, the filtering action of the invention may not proceed to completion and the degree of compaction of the pigment obtained is not quite as high. The result is that resistors printed with heatset inks and cured by flaming tend to have a somewhat higher deviation of resistance values from one sample to the next than the best results obtainable with the oxidizable inks. (Note that it is not generally possible to produce an exact match of the amount of pigment deposited on a given pattern area with different types of inks but with the same settings of other press conditions so that correlation between mean resistance value and absence of sample-to-sample variations cannot be expected in such comparisons).

In the case of oxidizable inks, papers found best for use, with proper press adjustment, show as little as less than 3 per-

cent average deviation of resistance values over a large number of samples in some runs. Average percentage deviations with heatset inks were somewhat higher, but the oxidizable inks were found less satisfactory when sought to be employed for overprinting a layer already printed, particularly in building up a large number of layers, as in a capacitor construction such as shown in FIG. 6. Such a construction employs a conductive film **30** directly deposited on the substrate **32**. Over this are deposited a number of layers (of the order of five to ten) of dielectric films to form the overall dielectric **34**, upon which is printed a further conductor **36** forming the upper electrode of the capacitor. In printing such multilayer circuit elements, the heatset inks and the oxidizable inks were found to each have certain problems regarding interaction between layers. The fresh application of oxidizable ink excessively attacked the layer already dried, while heatset overprinted layers frequently would not adhere. These problems were satisfactorily solved with mixtures of the two types of inks.

Exemplary oxidizable ink formulations suitable for use with clay-coated papers for direct surface application (i.e., as the first film or layer deposited) are:

Resistive ink: 17 parts carbon black (Cabot XC727R); 40 parts alkyd (LV498); 31 parts "Magie Oil" No. 470; 10 parts boiled linseed oil; and two parts dryer (337).

Conductive ink: 59 parts flake silver (Silflake 135); 10 parts alkyd (V172); 10 parts "Magie Oil" No. 470; 10 parts boiled linseed oil; and one part dryer (337).

Dielectric ink: 75 parts barium titanate; eight parts alkyd (V498); eight parts alkyd (V172); seven parts boiled linseed oil; and two parts dryer (337).

Desirable compositions for heatset inks are:

Resistive ink: 15 parts carbon black (Cabot XC727R); 78 parts varnish (E14–24A); and seven parts "Magie Oil" No. 400.

Conductive ink: 70 parts silver flake (Silflake 135); 20 parts varnish (E14–24A); and 10 parts "Magie Oil" No. 440.

Dielectric ink: 80 parts barium titanate; 11 parts varnish (E14–34A); five parts "Magie Oil" No. 440; 3½ parts alkyd (V172); and one-half part dryer (337).

For composite-type inks, mixtures of equal parts of the respective resistive and conductive inks above are found suitable. For the dielectric ink, a desirable formulation is: 67 parts barium titanate; 19¾ parts varnish (E14–B34A); eight parts "Magie Oil" No. 440; five parts alkyd (V172); one-fourth part dryer (337); and one-fourth part non-dryer (Eugenol).

The group of coated papers mentioned above were: Appleton Letterpress Offset; Appleton Masterful Offset; Over-print Label; Lustro Gloss Offset Enamel Finish; Lustro Gloss, Offset Dull Finish; Lustro Gloss (regular finish); Northwest Mountie; and Cumberland Gloss.

Satisfactory results were obtained in printing resistors, employing the resistive inks above described, with all of these papers, although in somewhat varying degree, to some extent dependent upon the type of ink. It was found that results obtained with the oxidizable ink were somewhat more sensitive to exact characteristics of the paper than the heatset ink. The papers producing the best results with the oxidizable ink displayed substantially lower sample-to-sample deviations of resistance value than were obtainable with any paper using heatset inks, but certain papers produced less desirable (although acceptable for many purposes) results with oxidizable inks than any of the mentioned papers produced with heatset inks. Resistance measurements were made on runs of a pattern of eight rectangular resistors distributed to appear at widely separated portions of a letter-size sheet. For each resistor of the pattern, a large number of individual samples of each paper were measured as to resistance and the average percentage deviation about the mean resistance value calculated. In all cases, variations of this average percentage deviation were observed in some degree from one resistor of the pattern to another. Such variations were not, however, consistent from one paper to the other. It is presently hypothesized that these differences result from differences of degree of uniformity at various locations on samples of the same paper which are not observable in any other known manner. Under these circumstances, it was of course impossible to wholly isolate the effects of type-of-paper variations from random resistance variations flowing from inadequate compaction of the pigment particles. The effects of possible variations in impression pressure at various portions of the printing plate were minimized by employment of an elastomeric plate producing very light pressure at the point of impression.

As a general indicator of relative merit of the various papers, the average percentage variations of the values of individual resistors were themselves averaged for all locations on the paper. For the heatset inks, the range of overall percentage deviations of all resistances was from 5.23 percent (Lustro Gloss regular finish) to 8.41 percent (Cumberland Gloss). For the oxidizable inks, the range was somewhat broader at both extremes, ranging from 4.03 percent (Lustro Gloss regular finish) to 10.26 percent (Appleton Masterful Offset). Although the order of merit of the various papers was not wholly identical with the two types of inks, the differences in merit produced by differences in vehicle were small.

Dependent upon the degree of precision required in any particular circuit design, most or all of the papers in this group thus produce satisfactory printed resistors. By contrast, no comparable results were obtained with substrates of substantially different surface structure. With uncoated papers, resistance values were unusably high, and so widely distributed from sample to sample as to make the production process useless. With an impervious substrate such as a polyethylene coated paper, the results were similarly useless when oxidizable inks were employed; with certain heatset inks, it was found possible to print runs of individual resistors of values reasonably clustered about a relatively high mean value, but the results obtained were poorer than the poorest obtained within the group of clay-coated papers, in addition to the fact that adherence of the printed films could not be made reliable.

Details of the manner of curing and drying of the films are found to produce little effect on quality if certain basic principles are observed. It is important that sufficient vehicle penetrate into the substrate to produced the desired pigment compaction on the surface before the drying and curing of the binder is completed. Where light printing impression pressure is used, as with an elastomeric plate, such penetration occurs relatively slowly, and excessively rapid drying, such as by immediate flaming of a heatset ink, or by too-rapid oven baking, should be avoided. The speed of penetration varies substantially from paper to paper and from ink to ink, and the minimum desirable drying time of a resistive film for a particular ink-paper combination should be experimentally determined, being generally a substantial number of minutes to an hour or more. It should be noted that with a coated paper, the time for completion of the filtering action is not determined wholly by the porosity of the coating, but depends on a number of other factors such as the coating thickness and the coarseness or fineness of the body of the paper. With desirable carbon resistive pigments, it is believed that the end-point of penetration is more or less automatically established by the capillary counter-force exerted by the filtered pigment residue as it reaches its compacted condition. However with coarser pigments, it may be possible to reach a condition of over-extraction of vehicle, in which case cohesiveness of the film will be adversely affected.

The printed circuits so produced are desirably encapsulated both for protection against moisture and abrasion and to provide the rigidity required in most practical uses. A conventional encapsulant may be employed, one example being the thermosetting resin commercially marketed for such purposes as Durez. However, direct application of the encapsulant to the printed components, particularly resistors, is found to produce excessive shift of values. The procedure devised for preventing substantial resistance change is to enclose the printed circuit or component in a sealed envelope (with leads

or terminals extending), preferably a multilayer laminate of plastics designed to prevent all types of substances, as well as thermal effects, from producing change in the film resistance. A laminate including polyethylene, Saran, Surlyn, and nylon was found particularly desirable for this purpose. The encapsulation may be done by dipping, and a suitable wax applied for additional moistureproofing after curing of the encapsulant. The leads or terminals, preferably attached to the printed film structure by a conductive epoxy cement, are of course embedded in the encapsulant except for their extending ends, as is conventional.

As will be observed by those skilled in the art, the basic teachings of the invention may be employed in manners substantially different from the embodiments herein described in accordance with the patent laws. Accordingly, the scope of the protection to be afforded the invention should be determined in accordance with the definitions thereof in the appended claims, and equivalents thereto.

What is claimed is:

1. In the method of manufacturing printed electronic circuits including the steps of depositing on all portions of a patterned area of the surface of each of a succession of substantially identical substrates a layer of an ink comprising a settable liquid vehicle bearing a uniform concentration of solid pigment particles of desired electrical characteristics and setting the vehicle on each substrate to form a surface film of pigment particles in a vehicle matrix covering the predetermined area,

the improvement for producing uniform electrical characteristics comprising the steps of depositing the ink with substantial excess of vehicle and filtering from the surface film on said area, prior to setting of the vehicle, a portion of the liquid vehicle with substantially lesser pigment concentration than said uniform concentration to produce a solidified film on the predetermined surface area of substantially higher pigment concentration than is produced by setting of the vehicle at deposition concentration.

2. The method of claim 1 wherein the vehicle is filtered from the surface film by absorption in a porous body.

3. The method of claim 2 wherein the porous body is the substrate.

4. The method of claim 3 wherein the porous body is paper.

5. The method of claim 4 wherein the paper comprises a body portion having a porous coating on said surface of substantially smaller pore-size than the body portion.

6. The method of claim 5 wherein the paper is clay-coated.

7. The method of claim 1 wherein the pigment particles are carbon and the printed elements are resistors.

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