

Adhesives in Printed Circuit Applications

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Introduction

A printed circuit is generally defined as a conductive pattern formed on the surface of an insulating base. The term "print" is loosely employed to refer to any process whereby a design is applied to a surface. Having thus set the stage for the underlying subject of this paper, one can see that our present approach to electronic circuitry is really not so new in principle after all. Indeed, it would be very difficult to assign even an approximate date to the invention of the first printed circuit. If we are willing to overlook the real end purpose of circuitry, it becomes apparent that pottery decorated with patterns of precious metal constitutes "printed circuitry" by definition. In fact, the techniques currently employed in the manufacture of ceramic circuits are, for practical purposes, techniques lifted out of the pages of history:

It is quite generally accepted that printed circuitry, as we know it today, received its real impetus from the manufacture during World War II of proximity fuses. Since then, the growth of printed circuitry has been phenomenal. Today many millions of printed boards are produced annually in this country alone. There are obviously reasons for such interest, so let us review a few of these.

A printed circuit begins with a form of art work—the product of a draftsman employing normal drafting techniques to reduce a circuit designer's brainchild to two dimensions. Since the final product is normally generated from this art work by conventional graphic arts methods, it must be quite apparent that changes during the development and modification of the final circuit can be introduced by simple drafting changes in the original drawing. At the same time, since the location of component interconnections is controlled by the lines drawn by the draftsman, the need is greatly lessened for the use of highly trained labor

on the assembly line, and for extensive inspection after assembly. The highly reproducible placement of conductors also means that the prospects of stray capacitances in high frequency circuits is minimized. In addition, of course, the use of a rigid insulating base provides a physical form which can be handled readily in automated machine assembly. The very concept of printed circuitry yields a nearly ideal first step toward rugged, compact circuit packaging, a factor of increasing importance in the coming space age.

With this background, let us now see how adhesives fit into the picture. It will be difficult to draw a sharp line setting "adhesives" as such apart from resins which are used to bond fibrous reinforcements together in the formation of insulating base materials, and from thermoplastic dielectrics which adhere to treated metal surfaces without the addition of bonding agents. Also, some resin formulations will be found to serve the dual purpose of adhering components to boards and protecting the boards from contaminating environments. Consideration will be given to these applications in the course of this paper.

Undoubtedly, the most obvious major use of adhesives in printed circuitry is in adhering conductors to the insulating base.¹ In the case of etched foil circuitry, the problem is generally one of bonding copper foil to a laminated thermoset plastic. The etched foil method can be thought of as a subtractive process, i.e., one in which extraneous conductive material is removed. Additive processes are also employed. These are processes in which the conductor patterns are selectively applied to the insulating base where required. Although the adhesive serves the same purpose in each case (namely, to adhere the conductor pattern to the insulator) the specific properties required are somewhat different, as will be seen later. Adhesive compounds may also be employed for anchoring components to the insulating base, for reinforcing printed circuit packages, and for

laminating insulating bases together or to other supporting structures. These might best be thought of as secondary applications of adhesives in printed circuitry, and as such will occupy only a small part of the discussion.

Discussion

Processes

Let us take a brief look at a few of the printed circuit processes in which adhesives play an important part, so that we may have a better appreciation of the demands placed on the adhesive. The processes considered are not necessarily indicative of the most widely used methods, but rather were selected to give a broad picture of the way in which adhesives can be used.

The schematic diagrams shown in Figures 1, 2, 3, and 4 illustrate four typical production techniques employing adhesives. There are an unlimited number of variations of these processes,² but the limitations of time and space do not permit description of all conceivable ramifications of these basic methods. The figures should serve to indicate the major underlying differences between these techniques, while Table I summarizes some of the aspects of processing which may control adhesive selection.

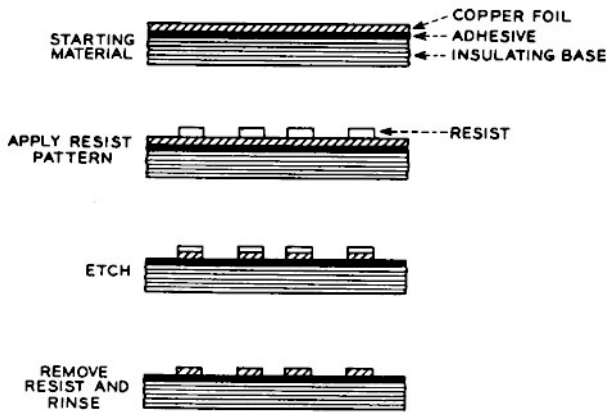


Fig. 1. Etched foil circuit process.

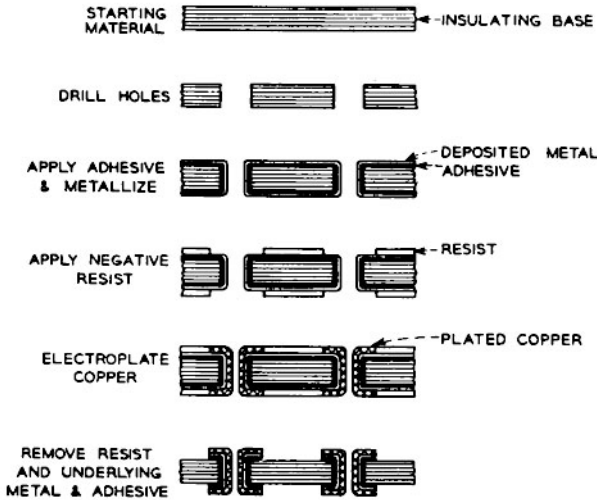


Fig. 2. Plated circuit process.

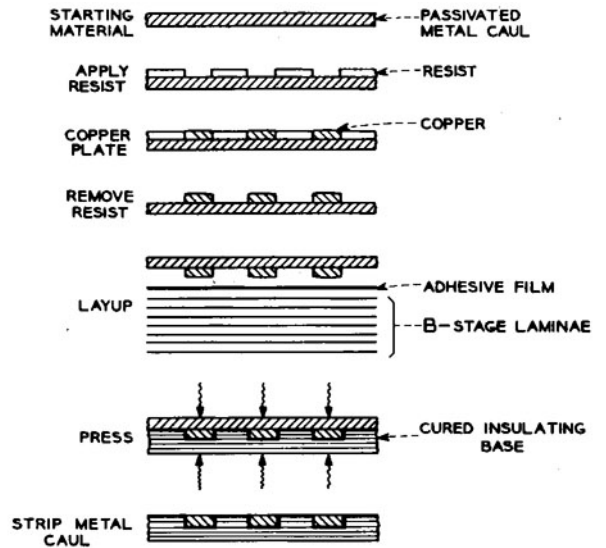


Fig. 3. Transfer circuit process.

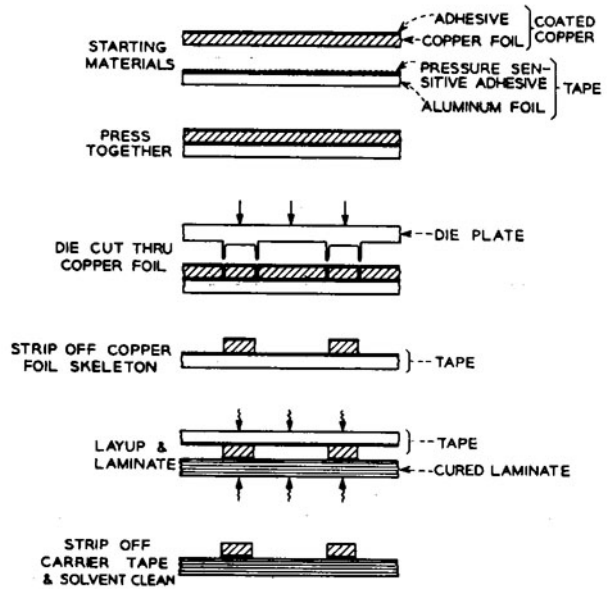


Fig. 4. Appliqué circuit process.

TABLE I
Summary of Process Characteristics Affecting Selection of Adhesive

	Process used			
	Etched foil	Plated	Transfer	Appliqué
Type laminate adhered to	<i>B</i> -staged	Cured	<i>B</i> -staged	Cured
Adhesive layer on surface of board	Yes	No ^a	Yes ^b	No
Mechanical anchorage	No	Through board	At conductor edges	No
Exposure to electrolyte	Yes	Yes	No ^c	No

^a Plated circuit process based on copper-clad laminate will leave adhesive on surface.

^b Modifications of process illustrated may not leave adhesive on surface.

^c Other techniques may be used.

Adhesive Requirements

At this stage we should be able to establish some general requirements for printed circuit adhesives used to hold printed conductors to the insulating base. Unfortunately, there is no unanimity of opinion as to which specific method of processing should be used, but if we assume the worst possible conditions relative to the adhesive requirements, we shall at least err on the safe side for purposes of our general discussion. Table II shows these requirements.

TABLE II
Summary of General Adhesive Requirements

Electrical properties at least equivalent to insulating base.
Good bond to copper and to laminated thermoset plastic.
Retention of bond:
In process (i.e., through soldering, electroplating, etc.).
In service (e.g., under thermal degradation, thermal shock, vibration, etc.).
No corrosion of copper or other metals.
No harmful volatiles.

Other requirements could undoubtedly be added, but those listed in Table II are the main ones to consider in a general presentation such as this.

Adhesive Types

For purposes of copper cladding printed circuit boards, there are three major types of thermosetting adhesives used in commercial practice. They are vinyl-modified phenolics, acrylonitrile rubber-modi-

fied phenolics, and modified epoxies. Each type has particular attributes, and at the risk of over-generalization, an attempt will be made to indicate their pros and cons.

Perhaps the most widely used circuit cladding adhesives through the years have been polyvinyl butyral-modified phenolics. These types generally exhibit very low electrical leakage coupled with moderate bond strength and moderate solder dip resistance. They have poor resistance to alkaline gold-plating baths but cause no corrosion and yield no vapors which might foul electromechanical devices or cause electrical leakage.

Acrylonitrile rubber-modified phenolic adhesives normally have relatively poor insulation resistance at high humidity,³ hence their use should be limited to processes which leave no surface residue of adhesive. They generally exhibit better solder dip resistance than the vinyl-phenolics and have higher peel strengths. They are somewhat more resistant to alkaline gold-plating baths, but less resistant to organic solvents used to remove resist residues. They will also generally bond to a somewhat less clean substrate surface. Some nitrile-phenolics do not permit the use of copper oxide surface treatments, but they are generally satisfactory from the standpoint of corrosion and volatiles.

Modified epoxy adhesives are of such a wide variety as to defy generalization. Some have poor peel resistance, some are corrosive to copper, some have poor heat resistance, some are toxic prior to cure, etc. Excellent properties in any individual category, however, can be built into these materials. The problem, of course, is to form a suitable combination of properties appropriate to the given application.

In the plated circuit process illustrated, general purpose, partially thermosetting rubber-resin cements can be employed. As in the case of the modified epoxies, these materials cover a broad spectrum of compositions and properties. In general, however, commercial resin-modified, neoprene base cements may cause some corrosion of copper. Resin-modified acrylonitrile rubber cements are generally used in the plated circuit process. These types, however, cannot be employed blindly because some are very poor around electromechanical devices. Outgassing tests have shown that some adhesives of this type can evolve up to 10% of their dry weight in low boiling, ionic fractions which will cause electrical and mechanical fouling of associated devices, components or electrical contacts.⁴ Other chemically similar ad-

hesives which are superficially alike in bonding characteristics evolve only trace amounts of nonionic materials which are nongummy and electrically clean. It is this latter type that should be employed in printed circuit applications.

Evaluation

So far, we have been discussing properties such as insulation resistance, solder dip resistance, resistance to plating baths, etc., all factors which do not normally enter into the evaluation of adhesives. It is pertinent then to give some consideration to methods of testing. Several references are available in the literature relative to details of the various test methods peculiar to printed circuitry.⁵⁻⁷ Therefore we shall deal here mainly with those aspects of evaluation and properties on which there appear to be serious differences of opinion.

Where an adhesive residue remains on the insulating surface of a processed printed circuit board, it becomes important to know something of its electrical leakage characteristics. This property is generally determined as insulation resistance using an interlocking comb pattern,⁵ or as surface resistivity or insulation resistance using a standard guard ring electrode pattern.^{7,8} It is imperative that test equipment be so designed as to permit measurement of insulation resistance in the conditioning environment, since surface resistivity, which is generally the main contributing factor in electrical leakage, will recover almost instantaneously upon removal to normal humidity.⁹

Bond strength serves as a measure of the ability of a clad material to withstand processing and service without delamination. Stresses may be imposed on the bond through thermal shock, physical abuse, chemical attack, and long time exposure to elevated temperatures, with shock and vibration loading also factors. Although superficially a reasonably straightforward property, bond strength has been the source of much confusion.

Since we are dealing with the bonding of metal foils, resistance to peel stresses would appear to be the most appropriate bond strength characteristic to determine, yet there are those who have placed considerable emphasis on "pull-off" or flatwise tensile tests.¹⁰ More often than not this method will result in interlaminar failure in the insulating base rather than in failure in the glue line. Not once has this writer observed a case of the former type of failure in a printed circuit board. On this

basis, it would seem questionable whether a bond strength test which produces this form of failure is really meaningful. In addition to this, of course, there is a very broad scatter in results produced by the pull-off test.¹¹

Peel tests have most often been run on 1 in. wide strips of clad laminate. The test strip is usually supported horizontally and the metal foil is then peeled off using a spring scale or a tensile test machine. At times a shot-bucket method will be employed in which the load is applied by slowly adding lead shot or sand to a container suspended on the foil.¹² Other variations are also used.^{11,13,14}

The spring scale technique leaves much to the judgment of the operator in determining the average peel strength, because no autographic record is available. The use of an autographic tensile test machine is much to be preferred, but those with spring or pendulum-type loading mechanisms should be avoided if greatest accuracy is desired. The shot-bucket method yields only the load required to initiate peel at a given point in the bond. It has been found that this load will generally exceed the average load required to sustain peel by means of a test machine, by approximately 10 to 15%.⁵

In using 1 in. wide strips for peel testing, it is important to remember that actual printed conductors will generally measure only 3 to 10% of this width. Thus 1 in. strips can completely mask small defects capable of causing ready delamination of normal printed conductors. Furthermore, it has been shown that chemical and oxidative attack occurs at the exposed edge of the glue line and may extend under the conductor as much as $1/32$ in. from either edge.¹⁵ This would imply possible attack on more than half of the bond under a conductor 0.100 in. wide, but the same amount of attack would affect only about 6% of the bond area of a 1-in. wide strip. In addition, stress distribution across the strips will vary somewhat with width, hence values obtained on 1 in. wide strips are not strictly comparable to those actually encountered with narrow conductors.

For these reasons, some workers have concentrated on peel measurements made on $1/8$ in. wide conductors.^{5,16} Because of the small loads involved, test equipment must be accurate at low range (full scale about 2-5 lb.), and loads should be recorded autographically for accurate determination of average peel strength. For best results, with the least dependence on operator variables, a planimeter can be used for this determination. With

TABLE III
Effect of Foil Thickness on Peel Strength

Insulating base	Average peel strength ^a	
	1.4 mil thick	2.8 mil thick
PBE-P (phenolic-paper)	9.5	13.2
GEE (epoxy-glass)	10.9	13.5

^a In lb./in. width, using $\frac{1}{8}$ in. wide conductors peeled by test machine and autographically recorded.

experience, however, the operator can establish the average very accurately by visual estimation with the aid of transparent grids. In any case, the load required to initiate peel should be disregarded.

In comparing peel test data, it is important to realize that the thickness of the foil is a major factor, as shown by the typical data in Table III.

Peel strength of the unprocessed clad laminate does not provide a full picture of bond quality, since the materials may be exposed to chemical attack during etching and plating, and to thermal degradation during printing, assembly, or repair operations, as well as in service. Of considerable interest therefore is the resistance of the bond to various plating and cleaning baths. Due to the need for low contact resistance on plug-in connections, use is often made of gold-plated contacts. Other plated metals (e.g., rhodium over nickel, solder, etc.) are used for wiping switches, corrosion protection, etc., but generally their application causes little trouble with the foil adhesion.

Although there is relatively little reliable data available in the literature on the subject, there is ample evidence to indicate that the main cause of chemical attack on the bond is alkalinity. Dytrt¹⁴ reports rough data which indicates that acid gold plating baths have appreciably less deleterious effect on bonds than do the conventional high pH, gold cyanide baths. Pape¹⁷ in an unpublished report, found no significant bond deterioration with vinyl-phenolic or epoxy bonds in an acid gold citrate plating bath.¹⁸

The effect of pH on deterioration was brought out in a paper presented by Hannahs,¹⁹ in which he showed that an alkaline electrocleaner used at 180°F. would degrade the bond at the cathode by as much as 60%, as against about 15% degradation at the anode. The significance of this is to be found in the fact that the pH at the surface of the cathode is considerably increased during electrolysis, while a marked reduction in pH is experienced at the anode. In general, vinyl-modified phenolics are

least resistant, while certain modified epoxies display the greatest alkali resistance. Schlabach et al.⁵ indicate that the extent of visible edge attack by alkaline gold on a vinyl-phenolic bond may amount to 0.0066 in. at each edge of the conductor.

In the case of thermal effects on the bond, there is the problem of transient bond strength reduction at elevated temperatures, encountered in baking resists, in soldering, and in service around heat-emitting components (see Table IV).

TABLE IV
Effect of Temperature on Peel Strength

Insulating base	Average peel strength, lb./in., at	
	23°C.	90°C. ^a
PBE-P	13.2	10.3
GEE	13.5	12.1

^a After 15 min. conditioning. Two ounce copper, $\frac{1}{8}$ in. wide, autographically recorded.

As long as the bond strength is sufficient to prevent blistering of the foil or flagging of the conductors at the exposure temperature, there is little cause for concern.

Of perhaps more importance is the thermal degradation of the bond with time. Schlabach and Rider¹⁵ report a study of thermal degradation at temperatures of 82°C. (180°F.) approximating the maximum storage temperature normally required for military equipment, 105°C. (221°F.), the AIEE maximum continuous operating temperature for paper and other organic base laminates, and 120°C. (248°F.), the maximum continuous service temperature often recommended by suppliers of clad epoxy-glass laminates. At the higher temperature, degradation of peel strength was marked and rapid, with only about 20 to 60% of the original strength being retained after 13 weeks conditioning. The exact amount of degradation appears to be highly dependent on the specific adhesive and base material involved. Continuous, long-time operation at 82°C. (180°F.) should cause no serious problem, but for service at higher temperatures, consideration must be given to the particular products used. It should be remembered then that the controlling factor in the determination of the maximum service temperature of a clad laminate is likely to be the adhesive rather than the laminate.

An oven blister test is another technique used to assess the tendency of the clad material to delaminate at elevated temperatures. This test, which generally consists simply of exposing a piece of

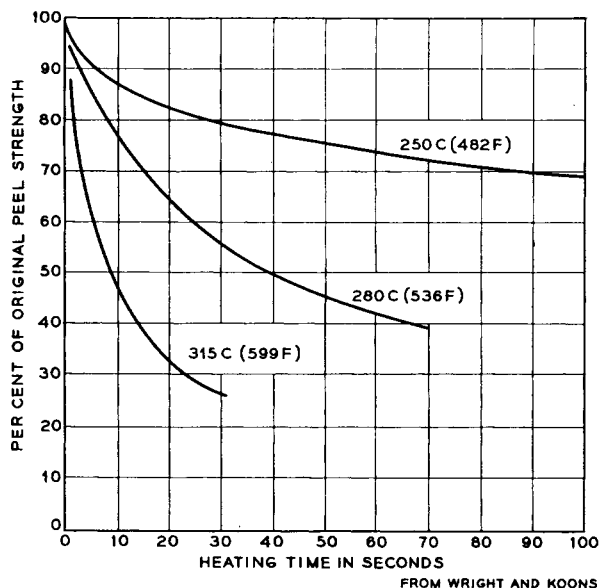


Fig. 5. Degradation of peel strength at soldering temperatures (measured at room temperature). Epoxy glass (GEE) clad with 2 oz. electrolytic copper foil.

clad material (either 2 by 2 or 6 by 6 in.) to a temperature of 120–140°C. for 30–60 min., is not primarily a measure of bond quality, but rather is a check on the quality of the laminate itself. The exact dimensions and test conditions depend on the method referenced.^{7,13}

Since component leads must be attached to printed terminal pads by soldering, a means must also be employed to determine whether the bond will withstand soldering temperatures. Solders are readily available which will melt at temperatures as low as 95°C. Unfortunately, to be effectively employed at this temperature, they must be used with a highly activated flux. Since such materials are also very corrosive, their use is not recommended in circuitry. Unactivated (water white) rosin fluxes are safe to use, on the other hand, but they require high temperatures to make them effective. Hence, for high reliability, circuits are generally soldered at temperatures of at least 450°F., using tin-lead eutectic solder.

It has been found that 1-in. squares of clad laminate solder dipped at this (or higher) temperatures for appropriate times (usually 5–10 sec.) will provide a good measure of the solder dip resistance of the material. Visual examination after the specimen has cooled will show blisters if the material is substandard. Peeling the foil back will then indicate where the blister occurred. This is a go, no-go type of test, however, and to provide a more

definitive measure of solder dip resistance, replicate specimens are frequently dipped at times increasing by 5 sec. increments to determine how long the material will resist the heat of a soldering bath at a specific temperature. In attempts to avoid coating the surface of the copper with solder, some investigators have resorted to hot oils in place of solder, but it should be noted that the thermal effects are not the same due to the differences in thermal conductivity and specific heat between the oil and the solder.

Considerable improvement has been made in clad laminates in recent years. When they were first employed in printed circuitry, solder dip resistance at 450°F. was likely to be marginal when only a 10-sec. dip was employed. Today, periods of 30–60 sec. are fairly commonplace, and higher temperatures can be employed (Fig. 5). Since higher temperatures and longer times generally mean better solder joints, improved reliability is the result. An additional factor, of course, is the ability to make repairs by hand soldering without causing lifting of the conductors. It might be noted that the form of the conductor pattern can have much to do with repairability. Wright and Koons²⁰ have shown that $\frac{1}{8}$ in. wide conductors can be heated with an iron up to four times as long as individual $\frac{1}{8}$ in. diam. terminal pads (lands), without their falling below a 6-lb./in. peel strength limit. This is apparently due largely to the heat sink effect of the larger conductor pattern. Bond degradation at soldering temperatures appears to be a cumulative effect, i.e., heating for 30 sec. continuously has the same effect as three 10-sec. heat cycles, with cooling in between.²⁰

Up to now we have dealt at length with the various adhesive problems encountered in foil clad circuitry. It would perhaps be appropriate at this point to backtrack a bit and take a closer look at the copper foil itself as it relates to the problem of bonding.

The foil used for printed circuitry is produced by one of two processes. It is either continuously electrodeposited on a lead drum or it is rolled by conventional metal rolling techniques. The former process is merely an extension of a method long employed in the manufacture of copper flashing, shields, and valleys for the building trades. Initially, little attention was paid to the specific needs of the embryonic printed circuit industry. The thin foils were often full of pinholes and inclusions of dirt and tramp metals. To retard oxidation of the foil in storage, a solution of fish oil in

mineral spirits was wiped onto the foil. It was apparent that the oils had to be eliminated and more attention had to be paid to the overall cleanliness of the manufacturing operation if bonding and general quality were to be improved. At this stage, rolled copper foil entered the picture, but rolling also required the use of oils, which then had to be removed prior to bonding.

Electrolytic foil presents a nearly ideal physical surface for bonding, with the dendritic surface structure formed on the solution side during electro-deposition. The same is not true, however, with rolled foil, which is relatively smooth on both sides. Through the expenditure of considerable research effort, improved prebonding techniques were developed for copper which are effective on both types of foil.^{3,21}

As a result of this work, and through the demands of the various services and companies requiring electronic circuitry, the attention of suppliers to the printed circuit industry has been focused on the need for higher quality clad laminates. Solder dip resistance has consequently been vastly improved, as was mentioned earlier, and peel strengths have been increased by two or three times. Electrical properties have also improved, with the result that printed circuitry is now entering into more and more consumer and military products.

It has been suggested that adhesives can be employed to reinforce printed circuit assemblies. Crandell and Koons²² screened various adhesive materials on the basis of working characteristics (including cure temperature), corrosion, adhesion, and toughness, and then evaluated the most promising material for resistance to thermal shock and acceleration forces. Thermal shock tests consisted of subjecting standard printed circuit assemblies, containing nine components, to ten cycles from -54°C . (-65°F .) to $+85^{\circ}\text{C}$. (185°F .), with a 1-hr. dwell at each temperature. Vibration tests were run on the same type of assemblies, in three planes, over a series of constant accelerations, with frequency increasing from 30–2000 c.p.s. at a rate of one-third octave per minute. The majority of failures occurred while vibrating in a plane normal to the board. Failures were monitored electrically by checking for opens during vibration. Table V shows the effect of the method of applying the adhesive on weight and on acceleration forces which can be imposed on the board without failure of printed conductors or component leads. All tests were on $1/16$ -in. single clad (2 oz. copper) epoxy-glass boards. The adhesive was an unmodified

TABLE V
Effect of Adhesive Application on Limiting Acceleration Force and Weight

Adhesive application	Limiting acceleration force, G	Wt. increase, %
None	9	—
Spotted at four corners of each component	20	8
Full fillet around each component	>30	14
Conformal dip coat over entire board	>30	20

epichlorohydrin-bisphenol A resin cured with a bisphenol modified hydroxy-aliphatic amine for 1 hr. at 66°C . (150°F .).

Different specific circuit assemblies, insulating bases, mountings, adhesives, etc., would all have profound effects on the absolute values of force and weight, but the relative picture should remain the same. Meek et al.²³ claim protection of small components up to 20,000 G, using a polysulfide-modified epoxy resin. They used a brush applied conformal coating. They also employed various other combinations of modified and unmodified epoxies for protection against mechanical shock and adverse environments. They found that complete encapsulation permitted reductions in overall weight through the elimination of mechanical supporting structures.

Mention was made earlier of the need to use adhesives which would not corrode copper. Experience has shown that adhesives employed by suppliers in cladding laminates have not caused corrosion of the foil conductors. Exceptions have involved secondary bonds where a general purpose rubber cement was used in the plated circuit process, or where copper was bonded with a low temperature curing epoxy adhesive.

Many corrosion tests have been developed for evaluating adhesives and plastics,^{24,25} but perhaps the simplest and most direct method for our use is one based on printed circuit specimens.²⁶ Modified interlocking comb insulation resistance test patterns (Fig. 6) are etched on both surfaces of a double-clad epoxy-glass laminate, and leads are soldered to the bus bars using water white rosin flux. Following thorough cleaning, rinsing, and drying of the specimen, a $3/4$ -in. wide strip of adhesive is applied across the conductors of one of the patterns midway between the terminals. After curing the adhesive, the board is suspended over a saturated salt solu-

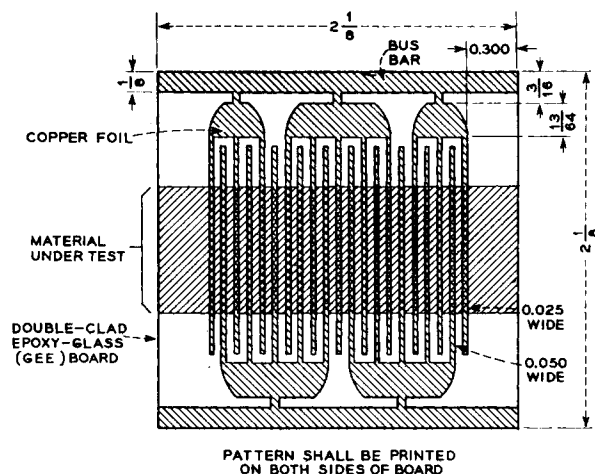


Fig. 6. Printed circuit test pattern for corrosion of copper by adhesives, encapsulating compounds, and organic finishes.

tion in a sealed jar to provide a controlled high humidity.²⁷ The leads are then connected externally to the terminals of a 45-v. battery. The jar is placed in an oven to provide a controlled temperature with some acceleration. Conditions commonly employed are 35°C. (95°F.) and 90% relative humidity. After specified periods of conditioning the specimens are examined visually for the formation of characteristic green corrosion products. The uncoated side of the specimen serves as a control to show that the clad material and the processing have not contributed to any corrosion which may be observed.

Although epoxies are highly regarded as metal adhesives, care must be taken in their formulation for use around circuitry. Many compositions have proved corrosive, among them ones containing: polyamide-amines, 3,3'-iminobispropylamine, diethylenetriamine, triethylenetetramine, and aliphatic-based triglycidyl ether resins. If we may generalize further, we find that epoxies formed from diglycidyl ethers of bisphenols, of themselves, cause no copper corrosion even with fairly high (0.32%) values for hydrolyzable chlorine. Polysulfide liquid polymers are satisfactory provided an appropriate amine is used. Hydroxy-aliphatic amines are generally satisfactory, but in specific formulations some may prove marginal. Aromatic primary amines, aliphatic primary-tertiary amines, and common reactive diluents generally appear to be clean. For further information relative to the chemistry of epoxy resins and curing agents see refs. 28-33.

In some cases, increasing the cure temperature is enough to prevent corrosion of copper (see Table VI). The presence of other platings over copper or high copper alloys should not be allowed to delude one into feeling that copper corrosion has ceased to be a problem. The slightest porosity in a protective electroplate often proves to be the Achilles heel when corrosive adhesives are used. There are, of course, other metals which are employed in printed circuit applications, but copper is by far the

TABLE VI
Corrosion Tests on Typical Epoxy Compounds

Compounding ingredients ^a	Curing agent(s)	Cure	Corrosion	Time
BGE ^b	Polyamide-amine + bisphenol-modified hydroxy-aliphatic amine + TPP ^b	16 hr./23°C. 1/2 hr./85°C. 1 hr./85°C.	Severe Sl. blackening None	16 hr. 21-30 days 30 days
None	Aliphatic polyamine + bisphenol-modified hydroxy-aliphatic amine	1/2 hr./85°C.	None	30 days
BGE ^b + inorganic filler	Polyamide-amine + 3,3'-iminobispropylamine	1/2 hr./85°C.	Slight	21 days
BGE + inorganic filler	Polyamide-amine + TETA ^b	1/2 hr./85°C.	Moderate	21 days
AGE ^b + PVAc ^b + inorganic filler	DEAPA ^b	2 hr./82°C.	Severe	<1 day
None	DEAPA ^b	2 hr./82°C.	None	30 days
None	Salt of phenolic tertiary amine	2 hr./82°C.	None	30 days
None	Mixture primary aromatic amines	3/4 hr./120°C.	None	30 days
PO ^b + TGE ^b	TETA ^b	1 hr./65°C.	Severe	<1 day
None	Bisphenol-modified hydroxyaliphatic amine	2 hr./60°C.	None	30 days
PSu ^b	Tertiary amine	24 hr./23°C.	None	30 days

^a Reactive diluents, fillers, unreactive modifiers, etc.

^b BGE = butyl glycidyl ether, TPP = triphenyl phosphite, TETA = triethylenetetramine, AGE = allyl glycidyl ether, PVAc = polyvinyl acetate, DEAPA = diethylaminopropylamine, PO = propylene oxide, TGE = triglycidyl ether epoxy resin, PSu = polysulfide liquid polymer.

most troublesome with regard to corrosion. Different test techniques would have to be adopted in the case of other metals.²⁵

It must be apparent that materials which cause corrosion under the conditions outlined above may also introduce problems of electrical leakage, although not all corrosive constituents are necessarily conductive. It does not necessarily follow, however, that electrical leakage is an appropriate tool to employ in corrosion testing. Actually, many adhesives which produce excessive electrical leakage do not cause corrosion. It was stated earlier that vinyl-modified phenolics generally have better insulation resistance than the nitrile rubber-modified phenolics, but there is no apparent correlation with corrosion.

Other Applications

There are many other applications for adhesives in printed circuitry including use as a replacement for solder in making electrical connections. These "cold solders" are normally based on epoxy resins loaded with silver powder,^{34,35} although some adhesives have been offered which contain other conductive fillers. Most metal powders form non-conductive oxides and sulfides, hence the use of silver. In general, it is necessary to employ silver pigment volume loadings of 25 to 30% in order to provide adequate conductivity. Even then the average resistance may be approximately 50 times that of a tin-lead eutectic solder.³⁵

There is a recent, growing trend in printed wiring which has important implications for the future. This is its use in microwave applications.³⁶ It is not the intent of this author to enter into a discourse on the function of these components. Schlabach and Colardeau³⁷ have described the application of low dielectric loss materials for such uses. The chief advantages of this approach over conventional wave guide or coaxial structures are reported to be: marked reductions in weight, volume, and cost and increased design flexibility. Because of the relatively high loss, electrical anisotropy and moisture sensitivity of conventional clad laminates, it has been necessary to resort to unfilled fluorocarbon or hydrocarbon polymers for most such applications.

This subject is perhaps not an appropriate topic for a paper on adhesives, since the bonding is generally achieved by fusing the polymer to chemically oxidized copper foil, without benefit of an adhesive.^{38,39} The same technique is applicable to the manufacture of flexible printed circuits for use in cables and wiring harnesses.^{40,41} Another

type of printed wiring which sidesteps the use of adhesives is molded wiring.⁴² Small copper alloy balls are sintered onto one side of the copper foil. The insulating material is then molded against the sintered surface to produce a high-strength mechanical bond.

There are many other bonding applications in the field of printed circuitry, but the foregoing pages have given an overall picture of the field with sufficient detail to permit the reader to avoid major pitfalls and hopefully to aid him in the intelligent selection and evaluation of adhesive materials. There are two texts now in print⁴³ or in preparation⁴⁴ which should be of assistance to anyone requiring additional information relating to the field of printed circuitry.

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Synopsis

This paper discusses the technology of adhesives employed in printed circuitry. The chemical types of adhesives are described and their general characteristics are given. Typical printed circuit processes are used to spotlight the demands placed on the adhesives. Test methods and requirements peculiar to printed circuitry are discussed in detail, and particular emphasis is placed on those properties which will not be too obvious to the adhesives technologist unfamiliar with circuitry. Secondary applications of adhesives in printed circuitry are touched on briefly, and mention is made of bonding methods in use or under development which do not employ adhesives. Numerous literature references are given.

Résumé

On discute dans cette publication la technologie des adhésifs employés en circuits imprimés. On décrit les types chimiques d'adhésifs et on donne leurs caractéristiques générales. Les procédés typiques des circuits imprimés sont employés pour répondre aux demandes concernant les adhésifs. On discute en détail des méthodes d'essais et les exigences particulières aux circuits imprimés, et on place particulièrement l'accent sur ces propriétés qui ne devront pas être trop évidentes aux technologistes non familiers des adhésifs pour circuits. On effleure brièvement les applications secondaires des adhésifs en circuits imprimés et on fait mention des méthodes de liaison en usage ou en développement qui n'emploient pas d'adhésifs. On donne de nombreuses références de la littérature.

Zusammenfassung

In der vorliegenden Mitteilung wird die Technologie der bei gedruckten Schaltungen verwendeten Klebstoffe behandelt. Die chemische Natur der Klebstoffe wird beschrieben und ihre allgemeine Charakteristik gegeben. Typische Verfahren für gedruckte Schaltungen werden benützt, um die an die Klebstoffe gestellten Anforderungen zu erläutern. Testmethoden und Spezialanforderungen für gedruckte Schaltungen werden im einzelnen besprochen und besonderer Nachdruck wird auf diejenigen Eigenschaften gelegt, die dem mit der Schaltungstechnik nicht vertrauten Klebstoff-technologien weniger bekannt sind. Sekundäre Anwendungen von Klebstoffen bei gedruckten Schaltungen werden kurz berührt und gebräuchliche oder in Entwicklung befindliche, klebstofffreie Bindungsmethoden werden erwähnt. Zahlreiche Literaturhinweise werden gegeben.