FINAL DRAFT
1994

Generic Scenario: Material Fabrication Processes for Manufacture of Printed Circuit Boards

Background

There are three general manufacturing stages in creating a final printed circuit board assembly: (1) the fabrication of the basic materials used in the printed circuit board; (2) the fabrication of the basic printed circuit board; and (3) the fabrication of the printed circuit board assembly, which is used in almost all electronic equipment manufactured today. Each of these three stages is a separate industry that usually is independent of the other two. Due to the broad scope of these three stages and the chemical processes involved (especially printed circuit board fabrication), this presentation covers only the first stage – the material fabrication processes.

Process Description

The materials required by printed circuit board manufacturers are basic reinforced plastic sheets (laminates), laminates that have copper foil (or other metals) bonded to one or both sides (metal clad laminates), and a partially cured resin preimpregnated fabric (prepreg) used in the buildup of multilayer printed circuit boards. The steps in the material fabrication processes are shown in Figure 1.

Material fabrication starts with preparation of the reinforcement material, which is in the form of yarn made from either glass, fused glass (quartz), aramid (Kevlar™), polyester, or cellulose paper [1]. Other types of materials may be used as reinforcements to obtain special characteristics either mechanically or electrically, but these are insignificant in quantity. The yarns are received by the material fabricator on bobbins or in packages that are brought together and wound onto a steel cylinder in a process called *warping*. Next the yarns are cut into the two lengths used in the weaving process: the warp yarn (along the machine direction) and the filling yarns or pick (cross machine direction). This step is called *slashing*. As part of this process, the yarns are dipped in an aqueous solution of starch, passed through squeeze rollers, and dried. The protective coating, called *sizing*, protects the yarns from abrasion during weaving. The yarns are then sorted into sizes and are fed to the weaving loom where the warp yarn and filling yarns are woven together to form a fabric.

In the processes leading up to and through weaving, the fabric has picked up starch and lubricants used in the various steps amounting to 2 to 3% of the total yarn weight. This added weight is driven off by first heating the fabric to 1000°F and then placing it in a 700°F oven for 3 days. As the last step in fabric production, a chemical coupling agent (silane) is added to the fabric to make the reinforcement adequately bond to the organic resin systems used in forming the prepreg or laminates. The silane coupling agent is hydrolyzed and applied from an aqueous solution. As the fabric dries, the silane is deposited on the surface at about 0.1% by weight of the fabric.

The second constituent of the material used is the organic resin that binds the layers of fabric together into sheets. These resins are predominantly epoxy, polyamide, and polytetrafluoroethylene and are combined with other chemicals (less than 2.5% by weight) to provide opacity, fire resistance, quick curing, etc.[2]. The prepared resin is combined with the fabric and is metered to combine at a percent by weight, depending on the electrical and mechanical characteristics required (see Figures 2 and 3). This combination is then partially cured to the prepreg condition in an oven. A minimum of two layers of fabric are required to form the prepreg. At this point the prepreg is either shipped to the board manufacturer for use as a bonding ply in the buildup of multilayer boards or is moved on to the material manufacturing process for buildup into laminated sheets that are bare or metal clad. In either case the prepreg is completely cured by pressure and/or beak-dry driving off the remaining volatiles. Depending on the degree of automation, all of these processes can be self-contained, therefore minimizing exposure levels to the volatiles (see Figure 2).

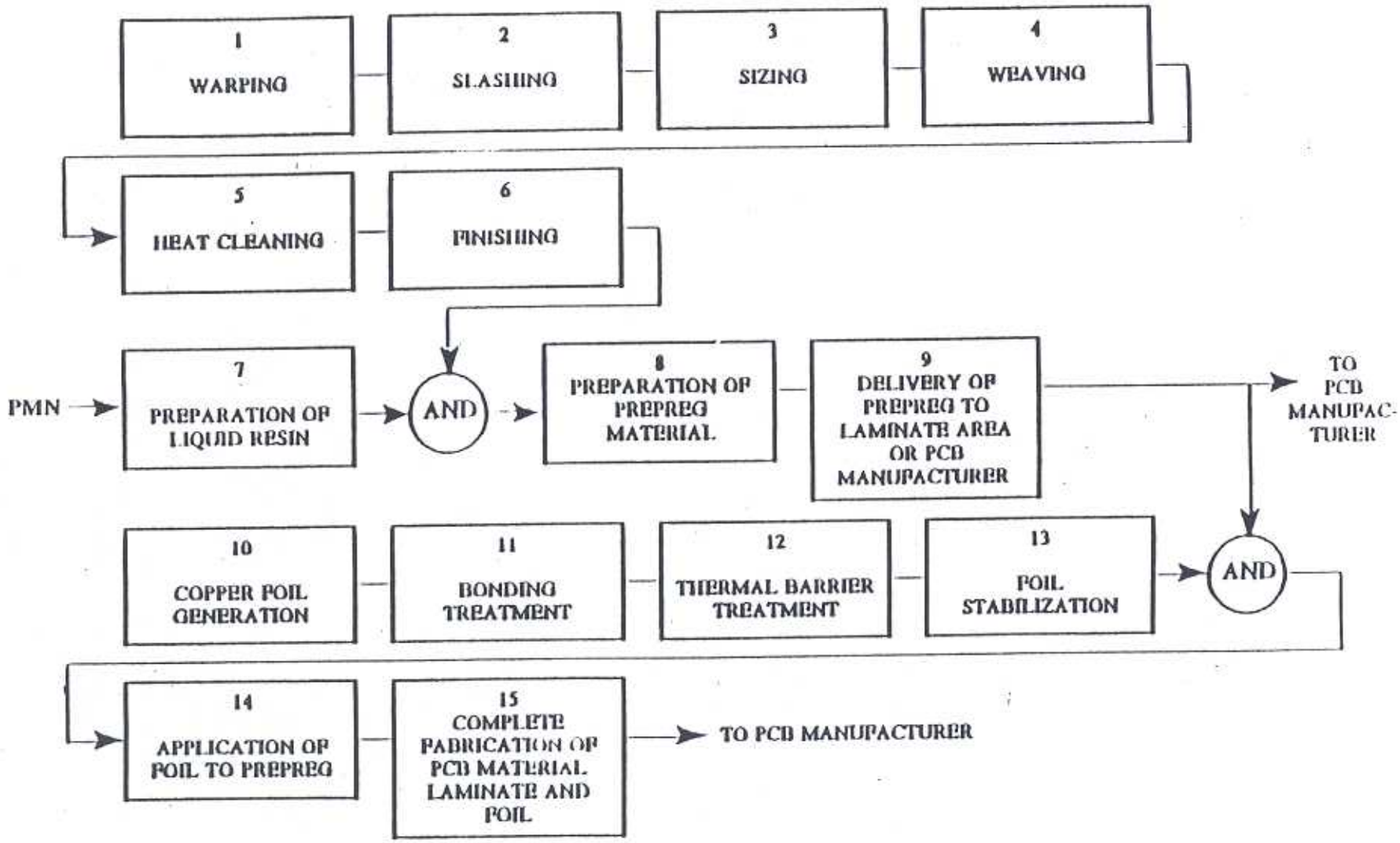

Figure 1. Printed circuit board material fabrication processes.

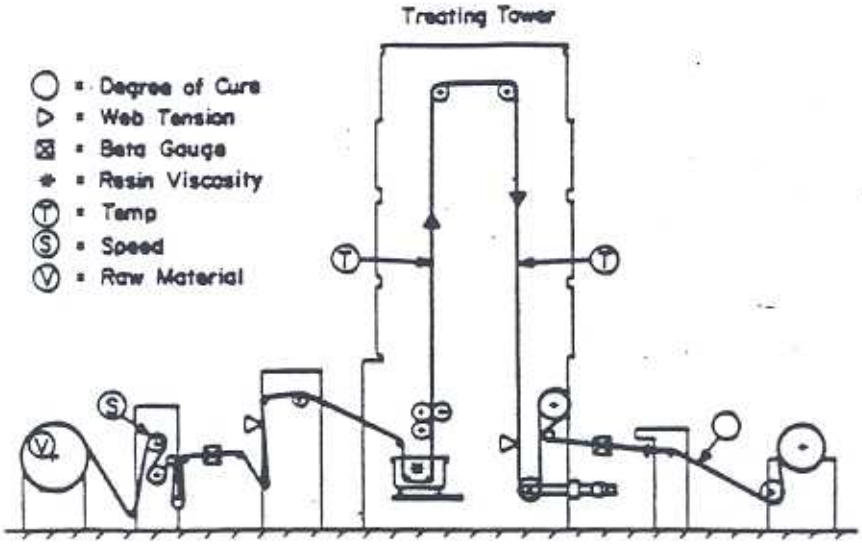

Figure 2. Location and type of process controls on the vertical tower processing system ***(Westinghouse Electric Corp.).***

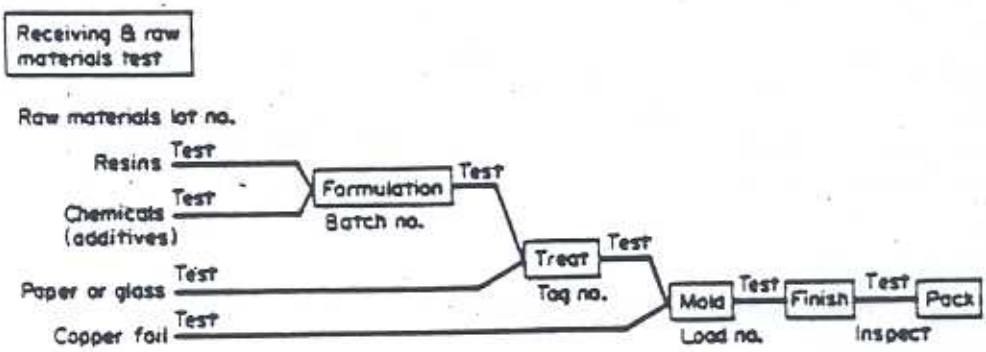

Figure 3. Laminate flowchart for laminate quality control.

The majority of the cladding metal is copper and can be either wrought or electrodeposited in thicknesses varying from 0.0004 to 0.004 inch [2]. The wrought copper foil is formed by rolling copper ingots down to the required thickness. Various foil characteristics can be obtained in terms of ductility, hardness, and surface roughness by heat treatment during the stages of the rolling process. Wrought foils are more expensive than electrodeposited foil. Electrodeposited foil is made using a sulfuric acid solution in which pure copper has been dissolved along with other additives that control the copper foil characteristics. This copper solution is pumped into an electroforming cell where the application of current between the anode and cathode causes copper ions from the chemical bath to plate onto the cathode surface. The cathode is a cylindrical stainless steel drum that rotates while partially submerged in the solution. The foil is deposited on the drum surface as it rotates through the solution and then is stripped from the drum to form the copper foil sheets. The thickness of the foil is determined by the rotational speed of the cathode drum. The anode conforms to the curvature of the cathode so that uniform, consistent plating takes place.

After the foil has been formed, it is given a bonding treatment to provide an adhesive surface between the foil and the laminate material. The drum side of the foil is shiny and the deposited side is microscopically roughened. The latter side is treated with metallic copper and copper oxides to increase its adhesion properties. To provide a barrier between the copper and the resin laminate during the soldering of the printed circuit card assembly, a deposition of brass, zinc, or nickel is made over the bonding treatment. Finally, a foil stabilization treatment is added to both sides of the copper foil to prevent oxidation and staining during the high-temperature steps associated with laminating the copper foil to the laminates. The treatments usually are chromium based and are applied in thicknesses in the 100 micron range. This material must be removed by the laminator or the printed circuit board manufacturer so that good solderability of the copper foil can be attained during printed circuit board assembly.

The foil is now ready to be combined with prepreg material. The foil of the desired thickness and size is mated with the same size prepreg material of the desired thickness. The foil can be placed on one or both sides. These layers are stacked with steel plates between each laminate/foil combination. The stack is placed in a press or an autoclave where the combination is heated and pressure is applied for a specific time. When the laminates are cooled they are inspected for conformity to thickness, warp, foil adhesion, and any other properties specified on the fabrication order such as water absorption or dielectric constant. The completed sheets are then shipped to the circuit board manufacturer to complete the process.

Extent of Production

The estimated total of laminates used in North America in 1992 was 30 million square meters [3], and the amount of copper foil used was estimated at 60 million square meters [4]. These numbers came from two different sources, and it is more than likely that the ratio of foil to laminate is 1.2 to 1.5 rather than the 2.0 number, so the numbers are only approximate as stated. There are 20 to 30 major, manufacturing sites in the USA, with the majority located in southern California and the northeastern coastal states. A typical company would be one of the Allied Chemical or Arlon facilities with 25,000 to 50,000 square feet of manufacturing space and would produce 60,000 to 90,000 square feet of laminate and 40,000 to 50,000 square feet of prepreg per year. The number of workers in the mixture/curing area would be 3 to 5 maximum of each site of this size.

Waste Generation, Environmental Releases, and Exposure-Level Calculations

Waste Generation

PMN chemicals may be used in several of the steps involved in materials fabrication for the manufacture of printed circuit boards. Specifically, PMN chemicals may be used in preparing the reinforcement material, in

the organic resin, or in the cleaning and/or treatment solutions. To calculate the environmental releases and worker exposure calculations for this generic scenario, the PMN chemical is assumed to be a component of the organic resin used to bind layers of the reinforcement sheets to form the prepreg, which may be combined to form multilayer boards or laminated sheets. The organic resin has been selected as the point of introduction of the PMN chemical because it is an important constituent, by weight, of the prepreg or laminate. Consideration of the resin preparation and application steps suggests that these steps are likely to be the most significant with respect to air and waste emissions, and worker exposure from the overall material fabrication process.

The organic resin is prepared from a mixture of chemicals to provide the necessary combination of opacity, fire resistance, quick-curing properties, etc. Components of the resins are epoxy, polyamide, and Teflon™ mixed with unknown solvents that are driven off in the curing process after being combined with the laminates. No data are available on the resin-to-solvent ratio at the start of the process. When the output is laminate, it is fully cured at the end of the process and prior to shipping. When it is prepreg, the material is only partially cured. The printed card manufacturer lays up layers of prepreg and laminate to make up multilayer board, and the stack is completely cured in an autoclave under pressure and high-temperature conditions. In this scenario, it is assumed that the PMN chemical is mixed on site at the printed circuit board material fabrication facility to yield the organic resin. This assumption probably is valid based on information collected from our review of medium-size manufacturing facilities. The quantity of resin mixed per day varies greatly with the size of the company. Large quantities of solvents and other chemicals are likely to be mixed in drums or other large containers on site. Some chemical constituents of the resin, such as acrylics or epoxies, are skin irritants and may be corrosive. Workers typically are equipped with skin-protective gear including gloves.

Impregnation of the fine cloth reinforcement material (1 to 2/1,000-inch thickness) with the resin typically is conducted as follows: 30-inch-wide cloth, in lengths up to 200 inches is fed through equipment that allows a controlled thickness of resin to envelop the fabric. Impregnation may be automated and is likely to be contained due to the noxious odor associated with the resin during curing. The resin-impregnated fabric may then be passed through squeeze rollers to remove excess resin, and is partially cured in an oven (at 140°F) to form the prepreg. When removed from the oven, the prepreg may be trimmed for sizing purposes and to remove unwanted resin overflow sections, combined to form boards of varying thickness, with foil on one or both sides, and cured to a laminate at high temperature. Alternatively, the prepreg materials may be shipped to a circuit board manufacturer to make up multilayered printed circuit boards. The curing ovens used in fabrication facilities generally are vented to the outside atmosphere; it is not known whether any control equipment is used on these vents. Water usage is minimal, because there are no known cleaning steps during resin impregnation.

Assumptions:

%PMN	: weight percent of PMN chemical in the resin
W	: weight in pounds of resin used per day at the facility
D	: number of days per year of operation of the facility

Environmental Releases (total lb/year at a single manufacturing facility)

Solid Wastes: Solid wastes containing the PMN chemical will arise from trimming of the prepregs for sizing the circuit boards or for removing resin overflow sections. Solid wastes containing PMN could arise from cleaning and maintenance of the resin impregnation equipment, and from unused resin that is disposed of for any reason. The amount of PMN chemical released as solid waste from a single manufacturing facility can be estimated roughly as follows:

$$\%PMN/100 * SW * RF * D = ?\ lb/year$$

where SW is the amount of resin solid waste in lb/day generated at the facility, and RF (between 0 and 1) is the fraction of PMN remaining in the resin after impregnation and curing. Highly reactive or volatile PMN chemicals are likely to have a small RF value because they are likely to be removed by the time the resin has solidified.

Some manufacturing facilities may operate in a closed loop whereby the solid resin waste is returned to the original liquid resin and dissolved using appropriate solvents. Under these conditions, PMN releases must be reduced to reflect reuse of the chemical in the manufacturing process.

Air Emissions: Air emissions of a PMN chemical component in the resin could arise if the PMN chemical is volatile. Such emissions would occur when mixing the chemicals to prepare the organic resin, during resin impregnation, and when the resin-impregnated fabric is cured to form the prepreg. These emissions are likely to be fugitive, except for the case of the vented ovens, and in the typical manufacturing facility would be vented to the atmosphere by a ventilation system.

It is difficult to estimate the extent of air emissions for a PMN chemical with the current information available. However, if the PMN chemical is volatile, a large fraction of the air releases would likely arise during resin curing in the elevated temperature oven. The amount of PMN chemical released as air emissions could be estimated as:

$$\%PMN/100 * W * \%Volatilized/100 * D = ?\ lb/year$$

where %Volatilized is the percentage of PMN chemical that is volatilized during resin preparation, impregnation, and curing.

Water: Liquid waste containing PMN is expected to be negligible because there are few liquid cleaning steps but could arise when cleaning process equipment, tanks, and other containers. Because these operations are nonroutine, PMN emissions would have to be estimated on a case-by-case basis.

Worker Exposure

Worker exposure to the PMN chemical potentially could occur during the resin preparation, resin impregnation, and curing steps where workers may be involved in application and handling operations. The extent of worker exposure would depend on the type of process equipment and the extent to which the workers come into direct contact with the resin. Accurate quantification of the various potential exposure routes is difficult with the limited information available. For this generic scenario, the various potential routes are discussed qualitatively.

Inhalation (mg/day): Inhalation is expected to be an important route of worker exposure and will be significant if the PMN chemical is volatile. To determine the extent of inhalation exposure, typical air concentrations of PMNs during resin preparation, impregnation, and curing are measured. If data on the PMN air concentrations are not available, concentrations of suitable surrogate chemicals used in current resin formulations could be utilized. If the volatility of the surrogates is similar to the PMN volatility, and if both chemicals are mixed to form the resin using similar process steps, then measurements of the air concentrations of the surrogate chemical could be used to estimate potential exposure to the PMN chemical.

Assuming that the work involved in handling prepregs and supervising process operations is medium-duty work in terms of the level of physical activity required, an inhalation rate of 1.75 m^3/hr can be assumed [6]. Further, assuming that H is the fraction of the hours in a process day during which resin mixing, application, and curing occur, inhalation exposure of a worker during an operating day to PMN chemical in the resin is:

$$C\ (mg/m^3) * \frac{\%PMN}{\%Surrogate} * 1.75\ (m^3/hr) * H * N = ??\ (mg/day)$$

where C is the concentration of the surrogate chemical in the workplace air.

Dermal Exposure (mg/day): Dermal exposure can arise during mixing of the PMN chemicals with other chemicals to prepare the organic resin, during loading and unloading of the resin-impregnated fabric from the oven where it is partially cured, during trimming of the prepreg, and when building up the prepregs for multilayer boards. Because some of the chemical constituents in the organic resin, such as acrylics and epoxies, are corrosive/skin irritants and pose dermal hazards, and to minimize circuit board contamination, workers in printed circuit board manufacturing facilities typically use protective gloves when handling chemicals and the resin-impregnated materials.

Assuming that the organic resin containing the PMN chemical is corrosive, CEB (1991) guidelines can be used to characterize dermal exposure as follows [6]. Direct contact with the PMN chemical is expected to be negligible because of the use of protective equipment. In qualitative terms, dermal exposure of workers at the facility may be best characterized as *incidental contact* [6] from the contact of protective clothing with the PMN in the resin.

Alternatively, if the resin is noncorrosive, dermal exposure from the PMN chemical may be calculated using typical factors for dermal exposure from the types of routine contact operations involved [6], as during the mixing of chemicals to prepare the resin and the handling of the resin-impregnated material just before and after partial curing to the prepreg state. If routine contact with the resin (and PMN chemical) occurs in these operations with a frequency, FT (number/day), the dermal exposure is:

$$(1{,}300\text{-}3{,}900)\ \text{mg/m}^3 * \text{FT} * \%\text{PMN}/100 = ??\ \text{mg/day}$$

These estimates of dermal exposure would be mitigated if workers wore dermal protective gear, such as gloves. Because resin materials are, at the least, skin irritants if not actually corrosive, it is likely that skin protective gear will be used at most circuit board manufacturing facilities.

Disposal Concerns

The containers used to transport the PMN chemical to the facility are assumed to be recycled, cleaned to remove contamination, and appropriately landfilled or incinerated. All liquid and water wastes are assumed to be reused, reprocessed, or air-dried and disposed of as solid wastes. Solid wastes containing the PMN chemical are assumed to be disposed of using appropriate mechanisms.

Release of the PMN chemical to the environment could also occur as a result of the retention of PMN in the cured printed circuit board. The implications of this release may need to be addressed for the PMN chemical.

References

[1] William L. Glover, "Prepreg and Laminate Manufacturing," *Nepcon 1993 Proceedings*, pp. 80-81.

[2] Ronald D. Savage, "Copper Foil Manufacturing," *Nepcon 1993 Proceedings*, pp. 71-79.

[3] "U.S. PCB Industry Demographics," *Printed Circuit Fabrication Magazine*, Vol. 16, No. 5, May 1993, pp. 48-53.

[4] Harvey S. Miller, "The Board Industry 1943-1993-2043, Market Technology Interactions," *Nepcon 1993 Proceedings*, pp. 61-68.

[5] W. Coombs, *Printed Circuit Handbook*, 3rd ed., McGraw Hill, 1988, New York, NY, pp. 32.1 - 32.3.

[6] CEB, 1991. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessments*, Volume 1, Contract No. 68-D8-0112, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, February 1991.