

Background documents on three key elements of the electronics manufacturing sector: semiconductors, printed wiring (circuit) boards and TFT-LCD screens

Adam Walters, David Santillo, Iryna Labunska & Kevin Brigden

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Introduction and summary

We live in an age of electronics. In the industrialised world, and increasingly in industrialising nations, our daily lives revolve more and more around the use of a variety of electronic consumer goods, from mobile phones and entertainment devices to desktop and laptop computers and personal digital assistants (PDAs). At the point of sale, electronic goods have a very clean and energy- and material efficient image compared with many other consumer goods. But behind the products lie the lifecycles of a myriad chemicals, materials and components which are all too often far from clean and efficient.

Previous reports have focused on the end-of-life consequences of the massive growth in the global electronics market and its continued reliance on hazardous chemicals, namely the mountains of e-waste (see e.g. [‘Recycling of electronic wastes in China and India: workplace and environmental contamination’](#), and [‘Environmental and Human Health Concerns in the Processing of Electrical and Electronic Waste’](#)). This series of background documents focuses attention at the other end of the lifecycle, on the processes used in the manufacture of one increasingly ubiquitous electronic device, the personal computer.

A typical computer can be seen to comprise an external casing and peripherals, including a screen, and internal circuitry and wiring, including printed wiring boards, semiconductors, hard drives, interface sockets, cables, etc. Each and every computer, desktop or laptop, is an incredibly complex construction assembled from hundreds or even thousands of individual manufactured components, which themselves may also be highly complex arrays of micro-circuitry.

The following background documents are designed to provide an outline of production processes commonly used in the manufacture of just three elements integral to modern computers, namely semiconductors (or ‘chips’), printed wiring boards (PWBs) and thin film transistor liquid crystal display (TFT-LCD) screens. Whereas the first two are common to all computers, the third (LCD screens) are rapidly replacing more conventional cathode ray tube (CRT) displays for desktop computers, primarily because of the much smaller desk space they occupy.

In each case, the documents are intended to provide a brief description of the main production processes employed as standard in the sector, including inputs of process chemicals and other raw materials, the origin and nature of waste streams generated and a discussion of the available information, though somewhat limited, concerning human health and environmental impacts associated with working practices and waste emissions from manufacturing facilities. These backgrounders do not attempt to provide an exhaustive description of any one sector or, indeed, any single step in the processes, a near impossible task given the overall complexity, diversity, commercial confidentiality and speed of change which characterize the industry. Rather their intention is to act as an introduction to the processes in common use in order to provide a framework for discussion and understanding of the concerns for the environment and human health arising from the sector.

Furthermore, the number and complexity of the processes involved, make it extremely difficult to summarise further than the level of information already offered in the background documents without losing the resolution necessary to gain that understanding. It is therefore highly recommended that the reader refers to the full background documents in each case. Rather than trying to provide a synopsis, therefore, this introduction and summary instead presents some overarching concepts and observations to complement the background documents themselves.

1. Processes used in the manufacture of semiconductors, printed wiring boards and LCD screens are highly diverse and complex, utilizing a wide range of techniques, purpose-built equipment and process chemicals to produce compact, three dimensional components to increasingly high specifications. The precise processes and raw materials used are expected to vary significantly from plant to plant, depending on specific design and performance demands, intended applications and legislative requirements, among others.
2. Although some of the processes used in laying down series of layers of fine circuitry on printed wiring boards, semiconductors and within LCD screens are superficially similar, there are nevertheless quite fundamental differences in practice, including differences in the raw material demands and, ultimately, the wastes generated.
3. Nevertheless, it is reasonable to conclude in general terms that electronics manufacturing has a high resource intensity, in terms of chemicals, energy and water demands. Commonly, only a very small proportion of the raw materials used are ultimately incorporated into the finished product, the remainder being recovered for reuse or going to waste. For example, it has been estimated that it takes up to 30kg of raw materials (including water) to manufacture a single semiconductor chip weighing just 2 grammes, a ratio of 15 000 to 1. Behind the clean and efficient image, therefore, lies a markedly inefficient and potentially highly polluting network of manufacturers.
4. Although the full diversity of chemicals in use in any one of these sectors has never been documented, many of those chemicals which are known to be in common use have hazardous properties. Large quantities of organic solvents, including chlorinated solvents, etching bath acids, halogenated gases, lead-based solders, surfactants and perfluorinated compounds used in specialist applications such as photoresists, developers

and antireflective coatings are just some of those commonly encountered and addressed in further detail in the background documents which follow.

5. Many of these chemicals present substantial concerns both for potential exposure in the workplace and the possible environmental consequences of their release in waste streams. Emissions of chemical wastes to water and to air are known to occur from electronics manufacturing facilities throughout the supply chain, though such waste streams are so far poorly studied and characterized. Among the chemicals in common use are metals and organic compounds which are environmentally persistent and, therefore, resistant to degradation in conventional wastewater treatment plants. If waste streams containing these persistent chemicals are directed to such plants, it is very likely that these chemicals will either bind to particulates and accumulate in the treatment plant sludges, rendering them highly contaminated, or simply exit the plant unchanged in the final effluent.
6. Although case studies remain very few in number and highly controversial, there is some clear evidence of environmental contamination arising directly from chemical spills at semiconductor manufacturing facilities, as well as indications from epidemiological studies of impacts on the health of workers involved in certain operations. One of the best known pollution events was the leak of 15 000 litres of 1,1,1-trichloroethane from storage tanks at Fairchild Semiconductor in Silicon Valley into the underlying aquifer used as a drinking water supply. Far less is known about the overall scale and diversity of the environmental impact of these sectors or the potential for adverse effects on the health of residents of areas surrounding such facilities.
7. Electronics manufacturing is a global industry, and one in which there are complex and ever changing chains of supply. Moreover, the industry is one of the fastest developing of all, feeding the continuous demand for ever faster, smaller and more sophisticated electronic devices. This inevitably means that any description of the processes and chemicals used can only ever provide a fairly general overview, especially as a more detailed description would inevitably become rapidly outdated. Where relevant information is available, the background documents reflect recent and current trends in process changes and chemical use, though the secrecy surrounding research and development of new technologies clearly limits this insight.
8. Despite its high demand for resources, including a diverse array of hazardous chemicals, the electronics industry at a global level appears to remain relatively free from environmental regulation. This may, in part, be a consequence of the very rapid evolution and development of the sector, such that the rate of introduction of new industrial processes outpaces the development of regulatory controls. Even within the European Union (EU), where many major industrial sectors (including textiles, pulp and paper, glass and organic chemical manufacture) are subject to controls under the Integrated Pollution Prevention and Control (IPPC) Directive (Council Directive 96/61/EC), there appears to be little if any co-ordinated monitoring or control of waste management in the electronics manufacturing sector. Indeed, given the rate of change of technologies and processes in electronics manufacture, the definition and enforcement of BAT (best available techniques) under the IPPC approach could prove unworkable. In

the United States, the Semiconductor Industry Association (SIA) successfully negotiated around limits on copper concentrations in effluents from metal finishing processes under the Clean Water Act by arguing for semiconductor manufacture to be dealt with as a separate case, subject to no limits on copper discharges. Overall, however, there is currently insufficient information available on which to document the workplace and environmental regulations which apply within the sector within any one country or region, or to allow comparison of how such controls vary across the globe.

When it comes to worker and environmental protection, there are some signs of change within the electronics industry. The EU Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment, or the RoHS Directive, has had a substantial impact on the industry well beyond Europe and, in the case of some companies at least, well before its official entry into force on July 1st 2006. But this Directive, which prevents the use of the heavy metals lead, mercury, cadmium and hexavalent chrome and of the brominated flame retardants PBBs and PBDEs (with exceptions for deca BDE and some designated uses of metals), addresses only a very small part of the problem, with a heavy focus on avoiding the presence of these hazardous chemicals in the final products put on the market in the EU. Aside from the upstream changes these specific prohibitions require, RoHS alone is likely to have little impact on the use of the majority of the hazardous chemicals used in the manufacturing processes themselves, nor on the overall efficiency and resource intensity of those processes.

What is urgently required is a much more fundamental shift in thinking and emphasis by those companies engaged in electronics manufacture to ensure that concerns regarding chemical and other raw material use, workplace exposure and waste management become a routine part of company planning, research and development cycles, without waiting for legislative measures to catch up and without pursuing derogations from existing law. In technological terms, electronics manufacturing remains at the cutting edge and has a strong economic future. There is no reason why it should not also be at the cutting edge when it comes to clean designs and technologies, substitution of hazardous chemicals, increased resource efficiencies, greater worker health protection and the prevention of environmental pollution at source. In short, it is vital that, in the inevitable race for technological advances, the electronics manufacturing industry does not remain blind to the parallel need for pollution prevention and sustainability.

An Overview of Semiconductor Manufacture

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An Overview of Semiconductor Manufacture

“Semiconductor manufacture is a dynamic industry in which manufacturing processes undergo continual innovation. A new technology is introduced every 18 – 24 months requiring the constant introduction of new chemicals, equipment and processes” (Dietrich 2004).

“The reality of a fabrication plant is that it’s a huge chemical factory” (Brumfiel 2004).

“The need to develop and deliver new process technologies at a breakneck pace necessitates that the technologists focus almost exclusively on developing a process with the efficiency and robustness to deliver maximum yield. Optimal utilization of input commodities – chemicals, water, power, exhaust – receives only cursory consideration in the drive to establish a workable process for the manufacturing floor” (Dietrich 2004)

1. Introduction

We live in an age of semiconductors. From the moment a digital alarm clock wakes them, the lives of many people in the industrialised world depend on the use of electronic devices of some description. They have permeated most aspects of society and reached a state of ubiquity. And sitting at the heart of almost all electronic devices is a semiconductor chip, or ‘microchip’.

Due to their unique properties, these devices are able to control the flow of electronic information in the solid state and have been increasing in complexity at astounding rates ever since their inception in the 1950s. Likewise, the economic value of the associated manufacturing industry has grown rapidly, at an average rate of 16% per annum between 1970 and 1999 (SIA 2006a).

However, since the first major chemical contamination incidents associated with semiconductor manufacture emerged in the early 1980s, attention has been drawn increasingly to the disproportionately high resource demands of the industry. The clean image of the silicon revolution hides a plethora of problems, including vast quantities of process chemicals, water and energy required for the stepwise processes by which chips are manufactured. Input analysis has shown that over 30 kg of materials (including water) are required for the manufacture of each single 2 gramme memory chip (Williams *et al* 2002). Such devices require an energy intensity at least an order of magnitude greater than many other conventional electrical products.

Production of semiconductors now occurs in fabrication plants, or ‘fabs’, in many countries right across the globe. It is sometimes speculated that, because of the need for use of cutting edge manufacturing processes in all locations, environmental impacts will have been addressed consistently and minimised also. There is little evidence to support such assumptions, however, especially if the total footprint of the industry, including waste management, is taken into account.

The relationship between constant technological evolution and environmental impact is also unclear. On one hand, each successive redesign or change to manufacturing equipment provides an opportunity to incorporate enhanced health and environmental protection measures.

However, the constant change also inevitably introduces new chemical inputs, generally with poorly characterised environmental profiles.

The wide range of hazardous chemical agents employed indicates a high potential for detrimental worker health effects and a variety of environmental impacts. However, use and exposure scenarios are complex and it is notoriously difficult to link observed health trends with chemical exposure, even in the workplace, as discussed below.

2. Steps in the semiconductor manufacturing process

A semiconductor is a material whose electrical properties may be greatly changed by the addition of small amounts of chemical impurities, or ‘doping’ agents. Careful addition of these impurities (doping) allows complex patterns of different electrical conductivities to be created within an extremely small area. In turn, this makes possible the construction of so-called ‘solid state’ versions of many conventional electrical components on a far smaller scale. Semiconductor chips, or ‘microchips’ therefore comprise a complex array of microscopic components that both respond much more quickly and use less electricity than the equivalent conventional circuitry.

Semiconductor ships are constructed from ultra pure materials in a step-wise process, typically consisting of between two and three hundred steps but essentially involving three basic elements: layering, patterning and doping. Firstly, layers of insulating, semiconducting, or conducting material, depending on purpose and design, are initially deposited on the surface of a slice of silicon crystal. Semiconducting layers are generally doped using an array of chemicals in order to tune their electrical properties. Each layer is then patterned by masking and etching processes, leaving the required material covering selected areas of the chip’s surface only, in a process analogous to that described for constructing PWB circuits, before subsequent layers are applied.

3. Environmental and health concerns arising from semiconductor manufacture

3.1 *Resource consumption*

Demand for water

Massive volumes of water are required for semiconductor manufacture. In some cases this consumption has placed a burden upon local supplies. Droughts in Taiwan are reported to have pitted high-tech firms and farmers against one another in competition for limited water resources (Williams 2003). Pure water is required to have low parts per trillion levels of metals such as iron. Purifying water to this degree greatly increases the embedded energy of the process from the very outset.

Use of chemicals

Similarly, as sophistication has increased and semiconductor size has decreased, tolerable levels of impurities in process chemicals have fallen from parts per million (ppm) in the 1950s and 60s to sub parts per billion (ppb) today (Plepys and Schischke 2004). Large volumes of high purity gases and of solvents such as hydrogen peroxide (H₂O₂), hydrogen fluoride (HF), sulphuric acid (H₂SO₄) and isopropyl alcohol (IPA) are required during manufacture. To produce them requires

additional purification technologies, often within dedicated facilities, compared to the standard industrial grades. The energy intensity of the upstream manufacture of ultra-pure chemicals, though poorly documented, is therefore also likely to be relatively high.

Some recycling /reclaiming processes exist. These typically involve large capital investments, but payback periods may be economically favourable and some evidence of industry uptake exists (Williams 2000). However, in many cases the recovered solvents and gases are likely to contain such a spectrum of impurities that clean-up to ultra-high purity may prove impracticable (Timms 1999).

3.2 Emissions to water and air

Water

Water is generally used for rinsing following etching and cleaning stages during manufacture (Williams 2000). Due to the high purity levels that must be maintained this use scenario generates large volumes of wastewater containing a wide range of chemical contaminants. VOCs such as acetone have been detected in wastewater discharge at concentrations as high as 4ppm (Wu *et al* 2003). A wide range of acids and metals may also be present.

One process, termed ‘chemical-mechanical planarization’, may account for 30-40% of the overall water discharge from semiconductors facilities. This process occurs after metallization (deposition of metals to provide electrical connections) and both reduces the thickness and ensures uniformity of the deposit. A slurry of abrasive particles and a range of chemicals (chelating agents, surfactants, oxidizing agents) are used, generating waste streams which are complex and difficult to treat. Typically the wastewater discharge may contain 50-500mg/l abrasive particles (SiO_2 , Al_2O_3 and CeO_2) and 0.5-100 mg/l soluble copper (Hollingsworth *et al* 2005). The industry has only shifted to copper interconnects within the last 10 years. The potential environmental impact of the discharge of large amounts of the metal has sparked a variety of reactions, including the publication of a number of papers tackling the issue of how to treat this waste stream (Yang 2002).

A different approach to the problem is reported by the Semiconductor Industry Association (SIA 2006b). The American trade body responded by ensuring that the US EPA did not treat this process as metal finishing (which it is, at least, analogous to) for which strict copper discharge requirements exist (due to the element’s environmental toxicity). Instead the process is treated separately as semiconductor manufacturing, for which no copper limitation exists. This circumvention of the US Clean Water Act is openly admitted by the SIA. When the required specialised treatment does occur, sludge laden with copper, other chemicals and a high content of submicron and nanoparticles is formed (Huang and Wang 2005), a waste that must be handled as hazardous waste (Hollingsworth *et al* 2005).

Evidence reported by Chang *et al* (2004) states that discharges from a Taiwanese Science Park within which semiconductors are manufactured has seriously degraded the quality of local waterways, causing events such as fish mortality and altered sexual characteristics in shellfish.

However, as is often the case, there is insufficient evidence to link any one plant to these observed environmental consequences.

During the early 1980s, a number of cases of groundwater contamination arising from the semiconductor industry were identified (Williams 2003). The main source of pollution was leakage of chemicals from storage tanks. One of the most publicised incidences occurred at Fairchild Semiconductor in Silicon Vally. Between 1977 and 1981, 15,000 litres of 1,1,1-trichloroethane leaked from underground tanks and via wells enter drinking water supplies. Epidemiological studies reported noticeable rises in the rates of miscarriages and birth defects in the affected areas (Rudolph & Swan 1985). However this conclusion was not confirmed by a later, more comprehensive, study (Wrensch *et al* 1990). Court cases brought by local residents were settled out of court by a multimillion-dollar payment in 1986. Other groundwater contamination cases have occurred in Japan, also involving chlorinated solvents but without compensation-seeking lawsuits (Williams 2003).

Air

Semiconductor manufacturing generates a number of different gaseous waste streams potentially containing a wide range of hazardous air pollutants including heavy metals, perfluorinated compounds, inorganic acids and volatile organic compounds (VOCs) (Chein & Chen 2003). VOCs are mainly generated during wafer surface cleaning, etching and photoresist processes. A study of VOC emission from Taiwanese semiconductor plants reported direct emissions as high as 9900 kg/month. In most cases, IPA (isopropyl alcohol - widely used for cleaning and drying) was found to be the dominant constituent (Chein & Chen 2003). The relative amounts of other VOCs emitted, such propyl glycol ethers and acetates, acetone, dimethyl sulphide and 2-heptanone varied greatly depending upon the specific processes employed by the plants.

The appreciable amounts of VOCs emitted by semiconductor manufacturing plants may be responsible for the presence of these compounds in ambient air over a Taiwanese Science Park (Chiu *et al* 2005). IPA and acetone were detected at parts per billion by volume concentrations (29-135 ppbv and 12-164 ppbv respectively) with a range of other contaminants found to be also be present at lower levels. VOC emissions though exhaust systems may not be abated by traditional condenser systems. However it has been shown that through careful control of the condenser conditions and the use of integrated zeolite concentrators, 90% removal of total hydrocarbons can be achieved (Lin *et al* 2005).

Plasma processes use halogenated gases to generate highly reactive species that allow the controlled removal of layers from the surface of wafer. Similar ranges of gases may be used in automated plasma cleaning to remove deposits from inside process chambers. Employment of plasma etching within electronics production has increased, because the “dry” process affords both better control and achieves finer resolution than its “wet” chemical equivalent. However due to the reactive nature of the plasma environment complex mixtures of waste gases are generated. Predominantly these contain halides of the etched material (such as SiF₄). However the presence of carbon either in the feed gas or in organic photoresists upon the wafers surface results in the formation of a wide range of halogenated organic compounds including aromatic and heterocyclic species.

A study in which rats were exposed to exhaust gases from reactor chambers revealed genotoxic effects such as sister chromatid exchanges and chromosomal aberrations (Bauer *et al* 1996). Although this study only evaluated the process gases from aluminium etching, it is probable that similarly toxic and complex mixtures arise from the dry etching of other layers and from processing with fluorine (rather than chlorine) containing etchants.

Due to the large amount of electricity consumed by semiconductor manufacturing the industry's indirect emissions of greenhouse gases are considerable (Williams 2003). However the utilisation of fluorinated gases in plasma etching and automated tool cleaning processes provides the potential for direct emission of very potent greenhouse gases. Due to their long environmental half lives and strong infrared absorption cross-sections the gases commonly used have global warming potentials (GWP) orders of magnitude greater than that of CO₂ (IPPC 2000):

Process Gas	100 year GWP
CF ₄	5820
C ₂ F ₆	12010
C ₃ F ₈	8690
C ₄ F ₈	8710
CHF ₃	12240
SF ₆	15290
NF ₃	10970

Reported industry estimates suggest that, in the early 1990s, the global warming impact of these direct emissions (CO₂ equivalent) was of an equivalent order of magnitude to that of the generation of the electricity used by the industry (Williams 2000). The industry, through the World Semiconductor Council, has committed itself to a 10% reduction from the 1995 baseline by 2010. Given the growth rate of the semiconductor industry this is a considerable commitment and is being pursued in a variety of ways, including shifting to inherently less potent greenhouse gases, process optimization and the installation of abatement technologies (Allgood 2003, Tsai 2005 Worth 2000). There are no signs that industry is planning to shift away from fluorinated processes, so some form of abatement technology will always be necessary. These generally involve the production of significant amounts of HF gas and other harmful waste products (Wang *et al* 2005).

Waste (solvents etc shipped off site)

Due to the large quantities of chemical agents required, semiconductor plants generate significant amounts of contained waste. Processing of this waste is often out-sourced to other companies, adding complexity to the environmental footprint of manufacturing. Reclamation of solvents may be possible in some cases (Lin and Wang 2004) though evidence suggests that the waste may often be incinerated. Wastes generated may be contaminated with a wide range of compounds. Some, such as contaminated oils from vacuum pumps used to extract etching fumes, have been found to be highly genotoxic, causing genetic mutations in laboratory studies (Bauer *et al* 1996). Significant pollution incidences have occurred due to the illegal activities of some solvent processing companies (Chang *et al* 2004).

Perfluorinated Substances

The electronics industry uses a number of perfluorinated substances, including PFOS (perfluorooctane sulphonate) and related compounds, in a variety of specialist applications. Due to their unique characteristics, these substances have found application as performance chemicals in photolithography processes, including in photoresist, developer and anti-reflective coating formulations. PFOS-based photo-acid generators (PAGs), an integral part of the photolithographic etching process, have been introduced to facilitate the use of ever smaller wavelengths of ultraviolet (UV) light, necessary in turn to enable further miniaturisation of circuits on semiconductor chips. Other applications include use as surfactants in developers, etch mixes and photoresists (as, unlike many potential alternatives, they are silicon-free), as well as in surfactants used for surface cleaning (especially edge bead cleaning, RPA 2004).

Among the various perfluorinated compounds in use, PFOS has been found to be particularly persistent and bioaccumulative (classifying as very persistent, very bioaccumulative, or vPvB) and toxic substance and, as a result, has been proposed for addition to the Stockholm POPs Convention. Draft European legislation to restrict the use of PFOS and its derivatives (Directive 76/769/EEC Com(2005) 618) remains under consideration by the Parliament and Council. However, this proposed Directive contains a derogation allowing the continued use of PFOS in photoresists and anti-reflective coatings for photolithography (among other non-electronics applications) on the basis that the chemical is considered to be of critical importance to current processes, that there are no viable alternatives and that such uses are considered by the Commission not to pose a major risk due to the relatively small quantities used in those applications (estimated at under 200 kg per year for the EU as a whole, OSPAR 2005). In any event, there is evidence that at least some within the European industry are in the process of phasing-out the use of PFOS and related substances voluntarily.

3.3 Occupational Health

Semiconductor manufacture is a light industry causing fewer injuries heavier industries. However, incidence of occupational illness is significantly higher than average (LaDou and Rhom 1998).

In general terms, clean-room operators are exposed to low concentrations of many different substances. Though the possibility of chronic exposure through leaks and spillages exists, it is typically maintenance and cleaning staff that run the greatest exposure risks. Therefore, the major health concern for most employees is the potential impact of long-term, low level exposure to a wide and frequently changing range of chemicals. Clearly, the establishment of cause-effect relationships relating to health impacts of chemical exposure is extremely difficult in such circumstances.

A large epidemiological study (Schenker *et al* 1995) found that female fabrication workers had an increased risk of spontaneous abortion compared with their non-fabrication co-workers. Analysis of specific exposures revealed a dose-response association between ethylene glycol ethers (solvents often used in photoresists) and spontaneous abortion. Following this study, many companies reportedly stopped using the compounds (Williams 2003), though hard evidence for this change is limited. The study also discovered reduced fecundability (probability of achieving

pregnancy in a typical menstrual cycle) and increased menstrual cycle length amongst workers. These effects were only slight when measured across the entire cohort of workers, but were statistically significant for some specific task sub-groups.

A study of workers in Taiwan also reported a relationship between exposure to ethylene glycol ethers and increased time to pregnancy amongst workers (Chen *et al* 2002), as well as with increased menstrual cycle length (Hsieh *et al* 2005). Examination of 249 workers at a semiconductor plant in Taiwan in 1995 suggested that those workers whose tasks put them at risk of short-term, high exposure (ion implantation and photolithographic engineers) suffered from a greater prevalence of restrictive lung abnormality (Luo *et al* 1998) and had significantly lower white blood cell counts (Luo *et al* 2002) than their colleagues employed in different processes.

Cancer is another concern amongst workers. A large number of workers in the US have taken legal action against both semiconductor manufacturers and their chemical suppliers. Epidemiological studies investigating possible links between the 'fab' environment and cancer are limited in number and not without controversy.

One publicly funded study was conducted in the UK by the Health and Safety Executive (HSE) as a result of fears raised by former employees of National Semiconductor. The study found cancer incidence amongst employees to be comparable to the general Scottish population (HSE 2001 and McElvenny *et al* 2003). However, incidences of certain cancers were found to be unexpectedly elevated, such as increases in cases of brain, stomach, breast and lung cancer. The work has been criticised due to the small sample size (71 deaths) and the potential for a lack of distinction between workers with different duties to hide important trends (Watterson *et al* 2003).

An earlier HSE study, this time into the rates of spontaneous abortion at 6 UK semiconductor manufacturing plants, has been similarly criticised. The report (Elliot *et al* 1999) concluded that there was no convincing evidence of increased spontaneous abortion rates. Fowler *et al* (1999) criticised the HSE for failing to distinguish between workers with different exposure scenarios and for using too small a sample size to disprove convincingly any absence of risk.

In the USA, an attempt to publish an analysis of the mortality records of 32,000 IBM employees over 32 years has been refused by the courts. The data formed part of the evidence submitted to a court case which two former employees brought against IBM, alleging that they had contracted occupational cancer. The analysis reportedly found significantly greater deaths from several cancers amongst former employees than would be expected in the general population, with further increases observed amongst workers who spent at least a month in chip manufacturing facilities. The decision to refuse publication is suspected to have been influenced by industry pressure (Wadman 2004).

A detailed analysis, supported by IBM, of cause-specific mortality among 127,000 workers at 3 IBM facilities between 1965 and 1999 reported overall mortality to be 35% lower than the mortality rates in the general population of the states in which the facilities were located (after appropriate adjustments for age, gender and race) (Beall *et al* 2005). Cancer mortality was 22% less after the same adjustments. This could well be a case of the so-called 'well worker effect' (i.e. the fact that workers in this sector are generally in a better state of health than average). In

some ways, however, this adds significance to the fact that excesses in mortality in some subgroups for some cancer types could still be detected (though it has been speculated by some that the excesses may simply be due to chance). The investigators consider that the increased rates warrant further investigation, specifically associations of central nervous system cancer with equipment maintenance workers at one facility and prostate cancer with laboratory workers at another.

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An Overview of Printed Wiring Board (PWB) Manufacturing

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An Overview of Printed Wiring Board (PWB) Manufacturing

“[Printed wiring board] manufacturing is the most chemically intensive process in the building of a computer workstation” (EPA 1995a)

For bare-board fabrication, about 7 percent of the materials used actually go into the product and the remaining 93 percent are emitted as process waste (Allen 1997 cited in Lau et al 2003)

Introduction

Printed wiring boards (PWBs), otherwise known as printed circuit boards (or, rather confusingly, PCBs) provide both the physical structure and electronic circuitry that connects most components together in electronic devices. Manufacturing involves producing mazes of copper connections on thin layers of insulating material. These are then stacked, laminated together, and holes drilled through them to receive components and to allow communication between layers. Production requires multiple processes and chemicals, many of which are not incorporated into the finished PWB itself.

This report provides an overview of the processes involved in making PWBs and highlights some of primary environmental concerns. Reliable published information concerning the environmental and health impacts of current practices in the industry remains scarce. The techniques applied undoubtedly vary according to size and location of the companies involved, as well as the specifics of commercial demand and regulatory pressure. This should therefore be taken as an indicative overview of the most common materials and techniques, rather than an exhaustive description of all processes in use.

PWB manufacture is a multistage process which may be divided into six basic steps:-

1. base board manufacture – synthesis of the glass fibre epoxy or other insulating material (dielectric) which forms the main structure of the board
2. inner layer circuitisation – laying down the complex network of copper circuitry on each layer of base board
3. lamination – stacking and pressing together a number of circuit board layers to form the multilayered circuit
4. drilling – to make desired connections between copper circuitry on different layers of the board and to allow attachment of other components
5. outer layer circuitisation – laying down additional copper circuitry on the outer surfaces of the board, and coating the drilled holes to provide electrical connectivity between layers of the laminate
6. finishing – application of a range of finishing materials to clean, strengthen and protect the board from dust and oxidation

In simple terms, the laying down of a circuit pattern on any one layer involves coating the base material with copper and then selectively stripping it back off from everywhere except where circuit connections are required. The copper which is to remain is temporarily protected from

the stripping (etching) solutions by a template or 'mask' of etch resistant material laid on top of the copper in the shape of the desired circuit.

Building up, laminating and finishing circuit boards in this way involves a number of chemical intensive processes and can generate a mix of hazardous wastes. This document focuses on processes used in steps 2 to 6 above. Manufacture of the base board itself involves the use of other hazardous chemicals, including very common use of brominated flame retardants (especially tetrabromobisphenol-A, or TBBP-A) and can also generate hazardous waste streams. However, there is relatively little specific information available on emissions from this stage of the production process.

Steps in the PWB manufacturing process

Copper clad laminate production

PWBs consist of layers of insulating (dielectric) material sandwiched between copper foils. Boards may be divided into four types; single-sided, double-sided, multilayer, and flexible. Most circuit boards produced today have between two and ten layers. Multiple layers of circuitry allow more complex (or dense) communication between devices to occur whilst ensuring that boards remain compact. Flexible boards are used when space is of a premium (hearing aids etc) or when a flexible connections providing multiple channels of communication between moving parts is required.

The dielectric material provides structural strength to the board as well as electrical insulation. A range of different materials is used, offering different levels of technical performance. Historically, rigid PWBs were formed from a composite of resin impregnated paper. Today, woven glass fibre epoxy resin-based composites predominate for all but flexible board production. PTFE and perfluorinated-hydrocarbon mixed-monomer polymers are used for high frequency, high performance electronic circuits because of the excellent dielectric properties of these materials (Hu & Griffith 1999), whilst polyimide films (such as DuPont's 'Kapton') are often used as the base layer for flexible circuit boards.

Production of copper clad laminates, the raw materials for PWB manufacture, involves bulk chemical polymerization and, often, solvent based glues to bind copper foil to the laminate. This process is potentially one of the most noxious processes in PWB manufacturing in terms of solvent emissions (Lau *et al* 2003). In some very large vertically integrated manufacturing facilities (such as those sometimes seen in China), laminate production may occur on the same site as PWB production. However, given the different nature of the enterprise, it is more likely to be carried out by other manufacturers.

Some form of flame retardant system is added to most polymers produced for electronic applications, and circuit boards are no exception. As noted above, tetrabromobisphenol-A (TBBP-A) is the most commonly used in epoxy resins. This compound reacts with other monomers during resin production, becoming largely chemically bound into the polymer. However, it must be noted that chemical reactions rarely go to completion and it is therefore possible that some unreacted TBBP-A remains unbound in the finished resin sheet and printed

wiring boards. For example, Sellstrom & Jansson (1995) detected approximately 4ppm free (unbound) TBBP-A in circuit board filings using a weak alkaline extraction method. Although whole boards have a much smaller surface area ratio than filings (per unit mass), the harsh chemical environments to which they are exposed during production may be expected to lead to some leaching of unreacted monomer. In addition, the polymer manufacturing process itself is likely to generate waste streams contaminated with TBBP-A and possibly other organic chemicals. There is, however, remarkably little published information in this field.

Inner layer circuit production

The first stage in the production of a typical multilayer PWB is the laying down of the copper circuitry that is to form the inner ‘buried’ layers of the final circuit board. This may either be achieved by subtractive or additive processes. Approximately 80% of PWBs are fabricated using a subtractive process whereby unwanted copper is stripped (etched) from a uniform layer of copper leaving a pattern of conducting tracks. Additive processing, selectively laying down circuit areas, is more difficult and expensive (EPA 1995a) and so is generally reserved for producing small, dense components for multi-chip devices. Some evidence indicates that additive processing generates less chemical waste (EPA 1995b). This section, however, provides an overview of the more conventional subtractive manufacturing.

In order to selectively remove copper from a uniform ‘foil’, some sort of template or ‘mask’ is required. This is achieved by coating the (cleaned) copper clad dielectric with a layer of photoresist compound (a mixture of monomers, cross-linking agents and photocatalysts) that changes its solubility upon exposure to UV irradiation. Typically, the photoresist is applied as a dry film layer attached to an optically transparent backing plastic such as Mylar. UV light is then shone on the photoresist layer through a mask or as a narrow beam which traces out the intended circuit routes. In the most common type of photoresist used in PWB manufacture (negative photoresist), areas exposed to UV light polymerise, becoming insoluble (Shaw *et al* 1997). Unexposed photoresist remains soluble and is washed away in a suitable solvent, leaving the required circuit imprinted.

The remaining resist pattern now shields copper foil that is to form the circuit pattern and the exposed foil may be etched away. It is estimated that at least 60% of the copper foil originally applied to the board is typically removed almost immediately by such etching processes (Lau *et al* 2003). After etching, the remaining photoresist is removed using other chemicals (‘film stripping’), leaving the final copper circuit upon the dielectric backing material.

Lamination

Lamination is the process of stacking and fixing together layer upon layer of individual circuits produced in this way, using semi-cured (‘B-stage’) epoxy resin to bind the layers together. Lamination takes place in a press, using pressure and high temperatures (sometimes in a vacuum) to cure the B-stage substrate and ensure effective bonding. A typical press cycle may take 1 hour to complete with several boards stacked together to form a “book” separated by aluminium coated release sheets. Any environmental issues with this process are likely to be associated with the emission of volatile compounds from the curing B-stage substrate.

Drilling of Through Holes ('vias')

So far, the PWB consists of a number of two dimensional layers of copper circuitry separated, in the third dimension, by non-conducting dielectric (glass fibre resin). Holes drilled through the PWB (sometimes called 'vias'), allow attachment of components and/or electrical interconnection of the layers. Interconnection is achieved by copper coating the insides of the holes. In order to allow the efficient deposition of an electroplated layer of metal, the holes must first be prepared, including cleaning and deposition of a thin 'seed' later of conducting material, after which a thicker, conducting layer of copper can be deposited by electrolysis.

Hole coating was traditionally carried out using the so-called 'electroless copper process', associated with significant environmental concerns. Over the last decade, industry has been encouraged to switch to other methods of making holes conductive, including direct metallization, carbon and graphite based techniques (EPA 1998a). These alternatives are often quicker, simpler (less process chemistry) and have a better environmental profile, but are less suitable for complex boards with many layers and narrow holes (Graphic 2005, Hui *et al* 2003).

Outer layer circuit production

Outer layer circuitry is laid down in a similar manner, though a range of surface finishes may be applied depending on the PWB's intended application and the assembly methods to be used when it is loaded with electronic components. Two distinct methods are used to etch the circuits.

The simpler method employs copper electroplating in order to coat the holes and board surfaces entirely. A photoresist mask is then applied in the same way as with inner layer circuitisation, covering both the intended circuit areas and the holes. Unwanted copper is etched and the mask removed, just as for inner circuits. However, this method, known in the industry as 'tent and etch', has certain limitations. Due to the indiscriminate plating of copper, a large amount must subsequently be etched away. This is not only inefficient, but causes technical challenges on modern fine line boards as the corrosive etching chemicals eat away copper horizontally as well as vertically, damaging the remaining circuit tracks.

A more involved process, known as 'print, pattern-plate and etch', is reportedly more commonly used. In this case, a photoresist mask is placed *over the area to be etched* and further copper electroplated where the circuits will be formed (i.e. building up a thicker layer). In order to remove the now thinner copper layer present between the intended circuit lines, an additional mask is applied to the thicker copper. This second etch-resist mask is typically a metal coating applied in a second electroplating process immediately after copper plating. Traditionally a mixture of lead and tin were deposited, though a number of alternative etch-resists perform equally well and are less environmentally damaging. Electroplated nickel/gold, a commonly used surface finish, can also be used as an etch resist.

Commonly, the area of circuitry that is not required to make contact with components is then protected from corrosion by applying an insulating organic solder mask, following careful cleaning and polishing of the surface circuitry.

Surface finishing

Once all circuitry is in place surface finishes are applied. These perform a number of functions, primarily preventing copper oxidation, facilitating the attachment of components, preventing defects during the assembly process, and providing hardness to circuitry that may be subjected to mechanical stresses such as edge connectors. A range of surface finishes and application techniques exist.

Solder Mask Over Bare Copper

Solder masks physically and electrically insulate the areas of circuitry which are not needed to be exposed for electrical connection to the board. The density of modern circuitry necessitates these coatings in order to ensure that solder does not make rough or unintended connections.

Hot Air Solder Levelling

Hot air solder levelling (HASL) is a very common technique for applying solder to a board. After the application of a solder mask, the PWB is immersed in molten solder. Solder in contact with exposed copper forms a metallic bond. A jet of hot air is then used to remove the excess leaving only the pads that are to receive electrical connectors coated. This process is considered the most efficient means of solder application by industry as only minimal amounts enter waste streams.

In 2003 it was reported that about two thirds of the PWBs produced had a HASL finish (Lau *et al* 2003). HASL is possible with lead free solders as well as the standard Pb-Sn solder. However the solder coating is often insufficiently thick for soldering or attaching microchips, such that additional deposition may be required.

Nickel-Gold

Nickel is often used in surface finishes. The metal is very hard, corrosion resistant and aids solderability retention. However, the surface of plated nickel is susceptible to oxidation in air. Therefore nickel coating is immediately followed by deposition of a thin layer of noble metal (gold or palladium). This ensures that solderability is retained (Milad 1997). Electroplating of gold upon nickel (referred to as Hard Gold) produces a surface suitable for edge connectors; surfaces likely to be subject to various environmental and physical stresses. Other methods of depositing gold or palladium over nickel produce surfaces suitable dense component connection arrays. In these cases the component is often attached by methods such as chip-on-pad (ultrasonic/thermosonic bonding), not soldering.

Immersion Bismuth-silver

Both silver and bismuth coatings have been shown to preserve the solderability of pads and provide alternatives to precious metals such as palladium and gold. Deposition of either produces a coating of pure metal upon the pad surface. As silver easily tarnishes an organic inhibitor is also deposited (Biegle 1997)

Organic Solderability Preservative

Benzotriazole and substituted benzimidazole coatings provide non-metal alternatives for preventing copper oxidation. These coatings provide cheaper alternatives to precious metal

finishes (Reed 1997), possess some unique technical qualities and do not produce metal waste streams (DeBaise 1997)

Tin Lead Reflow

Historically a very common finish, reflow subjects tin-lead solder (originally applied as the etch resist) to heat either in a hot oil bath or oven causing the solder to melt ensuring that any copper exposed by etching is covered. Use of this finish has reduced over the last decade.

Environmental and health concerns arising from PWB manufacture

Printed wiring board production is therefore a lengthy and chemically intensive. Fabrication of modern multilayer PWBs requires numerous wet chemical processes producing complex waste streams that may be loaded with a wide range of metal and organic contaminants. The necessity of a very large number of rinses compounds the problem by greatly increasing the volume of waste water which may contain low concentrations of processing chemicals from all production stages.

A complete environmental audit of the production process is difficult and none are reported in the literature. No detailed analyses of the content of PWB production facility waste water were available at the time of writing. What is provided here is a brief overview of the types of compounds that may be encountered either, as components of waste water or as air emissions.

Production of dielectric and copper laminate

Production of the commonly used glass fibre resin composite is by its very nature a chemically intensive process. Conventional production requires the use of large quantities of organic solvents to apply resin to the glass fibre cloth. For this reason the process is judged to cause the greatest environmental air emissions of the whole PWB manufacturing process (Lau *et al* 2003). Commonly used raw materials are listed below.

Fibre glass components

Aluminium oxide, silica dioxide, boron trioxide, fluorine. Fluorine and boron trioxide can cause hazardous particulate and toxic vapour emissions during manufacture (Wallenberger *et al* 2004). Boron trioxide exposure can cause nasal irritation, conjunctivitis and erythema (NIOSH 1990)

Solvents

Volatile organic compounds such as methyl ethyl ketone (MEK), and acetone are commonly used to dissolve the resin. Glass cloth is dipped through the resin bath, impregnated and subsequently dried, a process resulting in the volatilization of large quantities of solvent. Depending on the particular facility, these are generally either incinerated or simply vented (Lau *et al* 2003)

Hardeners

These include dicyanamide and aromatic diamines (Bosch 1999).

Ethylene glycol ethers

Reportedly used (in combination with acetone) as a coating adhesive (Shih *et al* 2000). The compounds have been found to have haematological, reproductive and teratogenic toxicity. Haematological toxicological effects of commonly used ethylene glycol methyl ether (EGME) include leukopenia, lymphocytosis, panocytopenia, marrow depression and decreased counts of red blood cells, haemoglobin, and platelets (see Shih *et al* 2000). A study of workers in two Taiwanese copper clad laminate factories using EGME found significantly reduced red blood cell count, haemoglobin and packed cell volume. The incidence of anaemia amongst exposed workers (26.1%) was significantly higher than in the control group (3.2%) (Shih *et al* 2000). Ethylene glycol ether releases from electronics facilities occur through both fugitive and point air emissions (EPA 2003). Exposure to glycols is regulated in some countries, though their use remains widespread.

Resins

Epoxy resins can be produced from a wide range of compounds (at least two different monomers, hardeners, catalysts, flame retardants and other additives), depending on the required physical characteristics of the resin. Flame retardancy is most commonly provided by incorporation of a brominated analogue of the epoxy monomer bisphenol-A, namely tetrabromobiphenol-A (TBBPA), which reacts similarly to bisphenol-A and is incorporated into the resin (commonly known as FR-4 resin). This use accounts for most of the TBBPA produced worldwide (BSEF 2000, Birnbaum & Staskal 2004), though it is also used in additive mode in some other applications. Even in reactive form, some TBBPA remains unreacted in the final product and can be released back to the environment.

TBBPA is highly lipophilic and acutely toxic to aquatic life (Canesi *et al*. 2005). It can be found, albeit at relatively low concentrations, in human blood (Thomsen *et al*. 2001). TBBPA has been shown to be immunotoxic and neurotoxic to mammalian systems *in vitro* (Birnbaum & Staskal 2004). Although only weakly oestrogenic, TBBPA is a potent inhibitor of the binding of triiodothyronine (T₃) to thyroid hormone receptor (Ghisari & Bonefeld-Jorgensen 2005). While the significance of this to whole organisms has been challenged, recent evidence indicates significant anti-thyroid hormone effects even *in vivo*, such as the inhibition of tail shortening in amphibians (Kitamura *et al*. 2005, Goto *et al*. 2006). Since the thyroid hormone system is so central to proper growth and development, including brain development, chemical interference with the system is clearly a major concern.

Alternative water-based resin systems have now been developed with similar performance properties to the organic solvent based resins. Other areas of environmentally motivated research include biopolymeric dielectrics (polymers derived from renewable resources) and reworkable encapsulants (thermosetting polymers that may be dissolved, allowing recovery of both chips and copper circuitry) (Lau *et al* 2003).

‘Kapton’ (DuPont’s polyimide brand used widely for flexible boards) is synthesized by polymerizing an aromatic dianhydride and an aromatic diamine. Though some fully imiditized polyimides are approved for medical and food contact applications the monomers used for their production are often hazardous. Dianhydride monomers are skin and eye irritants and several aromatic diamines are suspected carcinogens (Lakatchev & Vera-Graziano 1999).

For the production of fluoropolymers such as PTFE, used in high specification boards, a polymerisation aid is necessary. PFOA (perfluorooctanoic acid) or APFO (ammonium perfluorooctanoate) is used to improve physical properties of the polymer and increase the rate of polymerisation. PFOA is currently the subject of a major risk assessment being conducted by the US EPA. The draft version (released January 2005) of this reported that there was “suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential” based on evidence from two dietary carcinogenicity studies in rats. However the EPA’s Scientific Advisory Board has suggested that the evidence is strong enough to suggest that the compound is a “likely” human carcinogen. The common anion of both PFOA and APFO bioaccumulates in organisms (Martin *et al* 2003).

Photoresists

Photoresists probably make up the highest volumes of those chemicals which are used only in processing and are not ultimately incorporated into the PWB. A large proportion of the film laid down on each layer is almost instantly ‘developed’ and removed, with the remainder stripped using harsher chemistry after etching.

The chemical composition of typical dry film resists is difficult to identify. A diversity of organic chemicals appears to be used. Some publications report that the waste generated by contemporary photoresist stripping operations is not hazardous, though such conclusions remain very much open to question (EPA 1998b).

Historically, photoresists were developed in organic solvents (Shaw *et al* 1997) such as glycol ethers (such as EGME, previously discussed), 1,1,1-trichloroethane, and dichloromethane. (EPA 1995a, Lau *et al* 2003). Aqueous base-developable systems are now available and their use reported to be commonplace, though the extent of continued use of organic solvents is not known. Aqueous systems use warm alkaline solutions to remove soluble resist (i.e. that proportion not exposed to UV radiation).

Spent developing solution containing dissolved photoresist compound is one of the largest liquid waste streams generated by PWB manufacturing (EPA 1995b). A plant located in the UK concentrated this fluid to produce a “cake” that was then sent to landfill. It is not known whether this reflects common practice in the sector regionally or worldwide.

An alternative to alkaline photoresist stripping involves the use of 20% 2-amino-ethanol in alcohol (EPA 1995b). Spent resist stripper may contain approximately the same concentration of 2-aminoethanol as virgin resist stripper (EPA 1998b) and, if the spent solution is sent for disposal without further processing, a significant source of organic waste may result.

Waste water streams

As is clear from the discussion above, the circuitisation of PWBs essentially consists of metal deposition followed by selective metal removal (etching). Baths used to strip metals receive very high concentrations of dissolved metal ions. These are usually either captured by continuous bath replenishing processes or by on or off site processing (EPA 1998b). However, numerous rinse

cycles are present in the production cycle and loss of metals and process chemicals into rinse waters is thought to represent a significant source of environmental pollution (EPA 1995b).

Metals

A number of different metals may be used in PWB production depending upon required finishes. A short summary is provided detailing those either ubiquitously or extensively used. The list is not exhaustive, particularly as catalyst and process chemistries may require others not mentioned here. Concentrations of metal ions present in waste water will depend upon process performance, ease of recovery (both practicality and financial cost) and recovery incentives (such as the metal value and local environmental/water legislation) (Centi & Perathoner 1999).

Copper

PWB production obviously generates large amounts of wastewater rich in dissolved copper. In the case of copper etch baths, technology exists to allow the constant extraction of metal salts, maintaining bath performance and recovering the valuable metal (EPA 1998b). Aside from the main etching process, both electroless copper and micro-etching processes involve dissolved copper chemistry. Micro-etching uses chemical agents to remove a fine layer of copper from exposed circuitry, thus priming the surface by removing copper oxide build-up and producing a roughened surface. Whilst management of copper in these baths may make financial sense, they greatly increase the number of rinse cycles and, hence, the overall volume of wastewater.

Iron

Iron chloride is employed as a micro-etchant in the hot air solder levelling process due to its compatibility with solder flux (EPA 1998b). Other uses exist, including the sacrificial exploitation of iron's greater binding potential over copper to the chelating agent EDTA, allowing the more valuable copper to be recovered with greater ease from electroless copper waste streams (Chang 1995)

Nickel

Nickel plating is a common component of metal surface finishes (EPA 1998b). Processing involves baths of nickel salts. Escape of these into waste waters is a concern due the toxic nature of nickel and its salts and compounds (ASTDR 1997). Some nickel compounds have been classified as carcinogenic to humans, whilst the metal itself is considered possibly carcinogenic (IARC 1990). Nickel plating often uses the particularly toxic salt nickel sulphate (EPA 2001).

Palladium

The electroless copper process employs palladium chloride as an activating catalyst (Hui *et al* 2003). Palladium is also deposited in some surface finishes due to its inertness (as a 'noble' metal) and relative cheapness compared to gold (Milad 1997).

Tin

Tin is extensively used as an etch resist, historically in combination with lead and, increasingly, independently (Lau *et al* 2003). When a tin (or tin/lead) finish is not required the metal is etched away after copper etching – often with nitric acid (Lee *et al* 2003). Lee *et al* (2003) report of a method of disposing of spent etching solutions in South Korea containing: 250 g/L HNO₃, 30–40 g/L Cu, 30 – 40 g/L Sn, 30 – 40 g/L Pb and 20 – 25 g/L Fe. The solution is neutralized with

sodium hydroxide to produce a sludge which is then incinerated. This process emits nitrous oxide gas and produces a very metal-rich waste product which is then dumped. This practice is also reported elsewhere in the literature (see Scott *et al* 1997).

Lead

Lead solder use is discussed elsewhere in this document in greater detail. Lead – tin hot air solder levelling is a well established and routine surface finish (Lau *et al* 2003). After solder application the board is cleaned in hot water, a potential source of lead in waste streams (EPA 1998b). However, this is of minimal concern compared to lead-tin etch resist where this is still applied (EPA 1998b).

Silver

Silver plating provides an alternative, technically viable, surface finish to HASL (Biegle 1997). However, silver contamination of waste streams would cause concern due to its potent toxicity to bacteria and other simple aquatic organisms (Merk 1999).

Gold

Gold electroless and electroplating are commonly used finishes.

Surfactants

Surfactants and wetting agents are likely to be used in PWB production to ensure consistent and complete coating of surfaces during processing. This is especially important when making drilled holes conductive.

Complexing agents

Electroless copper plating uses EDTA as a chelating agent to maintain high copper concentrations in the process solutions (EPA 1995b). Its presence in waste streams both impedes metal recovery (Chang 1995) and increases the mobility of metal ions in waste streams. As noted above, iron salts can be used to bind selectively to EDTA in order to decrease copper solubility and thereby increase copper recovery.

EDTA is persistent in the environment (Nowack 2002), resulting in detectable background levels in European and other waters. Its persistence allows the chelating agents' effect upon metal chemistry to continue well beyond the point of application, even after release of wastewaters to the environment (Bedsworth 1999). Remobilisation of metal ions from sediments potentially leads to contamination of ground and drinking water (Nowack 2002).

Alternative biodegradable chelating agents do exist, apparently offering similar technical performance, and there is some evidence that these may be suitable for use in electroless plating (EPA 1998b). The extent to which they are being taken up by the industry, however, is not currently known.

Other inorganic compounds

A very diverse range of other inorganic chemicals may be employed in printed wiring board production leading to complex and often highly acidic waste streams, loaded with dissolved

metals. The range of inorganic compounds present in any given effluent will vary depending upon the particular process chemistries used in a facility.

Phosphoric acid: Employed as a cleaning agent in large quantities in the electroless copper process (Hui *et al* 2003), nickel plating (EPA 2001) and elsewhere. This compound, a source of phosphates, may produce detrimental effects in the aquatic environment by upsetting nutrient balances and stimulating rapid algal growth. Similarly the wide use of nitric acid chemistry may result in large releases of algal growth-stimulating nitrates.

Fluoboric acid: Fluoboric acid may be used in electroless copper processing as an accelerator (Hui *et al* 2003) and in tin (and tin-lead) plating along with its tin salt (EPA 1995b). The compound has a strong caustic action on skin and mucous membranes and is irritating to eyes and the respiratory tract (Merk 1999).

Other Acids: A range of other acids are commonly employed in PWB manufacture including hydrochloric, concentrated sulphuric, hydrofluoric, nitric, boric and the organic methyl sulfonic acid.

Sodium hypochlorite: More commonly known as a bleaching agent, this compound is also reportedly used in electroless copper lines (Hui *et al* 2003)

Sodium Chlorite This powerful oxidizer is used to prepare copper surfaces for lamination (EPA 1995 b). The compound is a source of ClO₂ gas (the active oxidizer). Chlorine dioxide is chemically unstable, highly toxic and can even attack stainless steel (Stringer and Johnston 2001).

Cyanides The preparation of gold surface finishes often entails the use of cyanide salts of gold (EPA 1998b)

Potassium Permanganate Used extensively to clean smeared epoxy resin from drilled holes prior to plating (EPA 1995b)

Formaldehyde

Formaldehyde is used as a reducing agent in the electroless copper process (Lau *et al* 2003). This compound, a known human carcinogen (IARC 2004), is both volatile and highly soluble in water (Merk 1999). Because of the hazards presented to workers, formaldehyde has been one of the main factors causing regulatory authorities (such as the US EPA) to try and steer industry away from the electroless copper process.

Other organic compounds

A range of organic solvents and reagents may be used in the production of PWBs. A large number of these compounds may be proprietary or at least dependant upon individual formulations. For this reason no complete inventories of those that may be encountered exist. The now common place use of aqueous photoresists has greatly reduced the need for organic solvents in PWB manufacture. However a number of uses remain with the particular solvents used depending upon product formulations.

Glycol ethers

As stated above, these epoxy resin solvents exhibit a range of toxic effects. As well as in dielectric glass-fibre boards, epoxy resins may also be used as solder masks.

Dimethyl formamide

Employed in electroless copper plating, DMF exposure can cause hepatotoxicity, male reproductive cancers, disrupted sperm motility and possibly embryotoxicity and teratogenicity in animals and humans (See Chang et al 2005).

2-aminoethanol

Reportedly common in photo resist stripping chemistries (20% solution in isopropyl alcohol) (EPA 1995b), this compound is known to be toxic via a variety of exposure routes. It is a corrosive irritant and has been linked to genetic mutation in humans (Lewis 2004).

Plasma Etching

Used to remove both smeared epoxy resin and glass fibres from drilled holes, plasma etching provides an alternative to wet chemical techniques. Replacement of wet chemical de-smearing and etch-back baths from PWB production is often reported as environmentally positive (EPA 1995b). However, the alternative plasma etching systems often employ fluorine species such as CF₄ (CFC 14) and produces a range of reactive species, including other fluorinated chemicals. Emission capture technologies exist for plasma etching, but no data were available regarding their global use.

A note regarding post-manufacturing PWB assembly: soldering and conformal coatings

Printed wiring board assembly (or 'board stuffing'), the loading of manufactured boards with components, is more labour than chemical intensive. Nevertheless, there are concerns relating to soldering and the application of so-called 'conformal coatings'.

Soldering

A wide range of techniques are used to apply the solder that connects components to PWBs. Lead in solder presents an environmental hazard, including through leaching or atmospheric emissions during and after waste recycling and/or disposal. Moreover, during manufacture of PWBs, fumes may be evolved and solder dross produced. Both lead and flux fumes present a toxicological hazard to workers. Dross, the term for solid impurities which accumulate in solder baths, is considered hazardous and must be recycled in an appropriate manner (EPA 1998b).

The use of lead free solder is set to increase dramatically as manufacturers who supply to Europe comply with the RoHS directive (which came into force 1st July 2006). However given that a number of suppliers have shown that complicity with RoHS is possible (Lau *et al* 2003), there is no need for the continued use of lead solder anywhere except in some specialist applications for which alternative methods are yet to be proven.

Conformal Coatings

Finally, loaded PWBs may be coated with a thin layer of polymeric material. These coatings protect the sensitive components from thermal shock, moisture, humidity, corrosion, dust, dirt and other damaging elements (Lau *et al* 2003). A high degree of electrical insulation is also provided if the coating is well applied, providing protection from short circuits caused by foreign bodies upon the PWB's surface. Due to the increased density of connectors on modern boards and the increasing delicacy of components, these coatings have become widespread and routine.

Coatings may be based upon a number of polymer chemistries, commonly materials like acrylic, epoxy, urethane, parylene and (inorganic) silicone. Often applied as an atomized spray, many coatings are solvent based. Typical spray formulae are 60 to 70% solvent, all of which is evaporated upon application. A range of solvent free coatings are now available, use of which may reduce volatile organic compound (VOC) burden of manufacturing.

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An Overview of Thin Film Transistor–Liquid Crystal Display (TFT-LCD) Manufacturing

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An Overview of Thin Film Transistor–Liquid Crystal Display (TFT-LCD) Manufacturing

Introduction

Thin-film transistor liquid-crystal displays (TFT- LCDs) have increased in popularity at a remarkable rate over the last 10 years. Maturity of manufacturing technologies has allowed affordable mass marketing of these devices. Less information is available describing the environmental impact of TFT- LCD manufacture than for printed wiring boards or semiconductors. This probably reflects the relative infancy of mass production of these devices.

TFT-LCDs are composite products containing not just a screen, but also fluorescent lights (miniature, 2-3mm diameter tubes in the case of laptops), control circuit boards loaded with components, wiring and, in the case of stand-alone models, electric transformers. All of these elements are (normally) housed within a plastic enclosure. The fluorescent tubes used within TFT- LCD screens typically contain a total of 4-12 mg of mercury (Williams 2003). This usage has received exemption from the RoHS directive (EU directive 2002/95). Some evidence of the development of alternative light sources free from mercury exists, though commercial viability of these is unclear (Socolof *et al* 2001). Plastic components of electronic products may contain flame retardants, including brominated flame retardants, which may be released to the environment during manufacture, use and disposal of the screens (in common with other flame-retarded plastics used in electronic goods).

Steps in the TFT-LCD manufacturing process

The actual display element of TFT- LCD screens consists of a viscous layer of liquid crystal sandwiched between two glass plates. Onto the rear of these a series of control transistors are printed (using similar techniques to semiconductor manufacture). These manipulate the light transmitting properties of the liquid crystal thus producing a grey scale image from the white light emitted by the fluorescent tube. Colour is provided by electrically activated filters printed on to the front glass layer (Williams 2003).

There is very little published information specifically addressing chemical use during TFT-LCD manufacture. However, production of the control transistors and colour filters uses techniques analogous to those used in semiconductor manufacture. Carried out in a ‘clean-room’ environment, these production steps include chemical vapour deposition, masking, etching and doping. The main difference is the large surface area and relatively uniform nature of the required pattern.

Environmental and health concerns arising from TFT-LCD manufacture

Consequently a number of environmental problems associated with semiconductor fabrication plants (‘fabs’) may also be associated with TFT- LCD production. For example, a wide range of chemical agents are required, including acids, alkalis, heavy metals and organic solvents. On particular concern is the routine use of the very potent greenhouse gas, sulphur hexafluoride

(SF₆) during etching and cleaning operations. SF₆ has a global warming potential some 15000 times that of CO₂ over a 100 year timeframe (IPPC 2000). Other concerns relate to the use of toxic gases such as phosphine.

Of the few available studies, one has reported that workers in clean-rooms of TFT- LCD fabrication plants are exposed to a range of volatile organic compounds, including propylene glycol methyl ether acetate (PGMEA), xylene, IPA and acetone (Wu *et al* 2004). The waste water from fabrication plants is known to contain a range of organic chemicals, including dimethyl sulphoxide and acetone. It is often characterised by the large concentration of organic nitrogen present in the form of compounds such ethanolamine and tetra-methyl ammonium hydroxide (Chen and Chen 2004).

The unique element of TFT- LCDs, namely the liquid crystal compounds, have been poorly evaluated in terms of toxicity (at least within the peer reviewed literature). Hundreds of different compounds are suitable for application in displays. Typically a mixture of around 20 chemicals is applied at a rate of 0.6 mg of liquid crystal per square centimetre of panel surface (Socolof *et al* 2001). The compounds are generally large chiral organic molecules, often polycyclic aromatic or halogenated aromatic hydrocarbons (Williams 2003). Their size is considered to render them non-volatile, such that concerns regarding worker exposure are thought to be limited to ingestion and dermal absorption (Socolof *et al* 2001). Of 588 liquid crystal compounds tested by industry, only 25 were found to have a LD₅₀ (dose that is lethal to 50% of the population) of less than 2000 mg/kg body weight (work reported in Socolof 2001). However, such studies of acute toxicity may underestimate chronic toxicity, and their potential to cause sub-lethal effects, perhaps following long-term occupational exposure, has yet to be evaluated.

The US EPA commissioned a life cycle analysis comparing TFT-LCD screens with conventional cathode ray tubes (CRT) (Socolof *et al* 2001). The results of this showed that, overall, the CRT has a more significant environmental impact. Partially this may be attributed to the greater energy consumed during all stages of the lifecycle of these devices. During manufacture, however, the difference between the two is not so clear. This may be due to the range and nature of the chemical inputs required. For example, despite the significantly greater energy consumption of CRT display manufacture, LCD production (due to the use of potent greenhouse gases) may have a comparable global warming impact.

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