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EPA Office of Compliance Sector Notebook Project

PROFILE OF THE ELECTRONICS AND COMPUTER INDUSTRY

September 1995

Office of Compliance Office of Enforcement and Compliance Assurance U.S. Environmental Protection Agency 401 M St., SW (MC 2221-A) Washington, DC 20460

This report is one in a series of volumes published by the U.S. Environmental Protection Agency (EPA) to provide information of general interest regarding environmental issues associated with specific industrial sectors. The documents were developed under contract by Abt Associates (Cambridge, MA), and Booz-Allen & Hamilton, Inc. (McLean, VA). This publication may be **purchased** from the Superintendent of Documents, U.S. Government Printing Office. A listing of available Sector Notebooks and document numbers is included at the end of this document.

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Contacts for Available Sector Notebooks

The Sector Notebooks were developed by the EPA Office of Compliance. Particular questions regarding the Sector Notebook Project in general can be directed to the EPA Work Assignment Managers:

Michael Barrette US EPA Office of Compliance 401 M St., SW (2223-A) Washington, DC 20460 (202) 564-7019 Gregory Waldrip US EPA Office of Compliance 401 M St., SW (2223-A) Washington, DC 20460 (202) 564-7024

Questions and comments regarding the individual documents can be directed to the appropriate specialists listed below.

Document_Number	Industry	<u>Contact</u>	<u>Phone (202)</u>
EPA/310-R-95-001.	Dry Cleaning Industry	Joyce Chandler	564-7073
EPA/310-R-95-002.	Electronics and Computer Industry	Steve Hoover	564-7007
EPA/310-R-95-003.	Wood Furniture and Fixtures	Bob Marshall	564-7021
	Industry		
EPA/310-R-95-004.	Inorganic Chemical Industry	Walter DeRieux	564-7067
EPA/310-R-95-005.	Iron and Steel Industry	Maria Malave	564-7027
EPA/310-R-95-006.	Lumber and Wood Products Industry	Seth Heminway	564-7017
EPA/310-R-95-007.	Fabricated Metal Products Industry	Greg Waldrip	564-7024
EPA/310-R-95-008.	Metal Mining Industry	Keith Brown	564-7124
EPA/310-R-95-009.	Motor Vehicle Assembly Industry	Suzanne Childress	564-7018
EPA/310-R-95-010.	Nonferrous Metals Industry	Jane Engert	564-5021
EPA/310-R-95-011.	Non-Fuel, Non-Metal Mining Industry	Keith Brown	564-7124
EPA/310-R-95-012.	Organic Chemical Industry	Walter DeRieux	564-7067
EPA/310-R-95-013.	Petroleum Refining Industry	Tom Ripp	564-7003
EPA/310-R-95-014.	Printing Industry	Ginger Gotliffe	564-7072
EPA/310-R-95-015.	Pulp and Paper Industry	Maria Eisemann	564-7016
EPA/310-R-95-016.	Rubber and Plastic Industry	Maria Malave	564-7027
EPA/310-R-95-017.	Stone, Clay, Glass and	Scott Throwe	564-7013
	Concrete Industry		
EPA/310-R-95-018.	Transportation Equipment	Virginia Lathrop	564-7057
	Cleaning Industry	_	

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ELECTRONICS AND COMPUTER INDUSTRY (SIC 36) LIST OF ACRONYMS

- AFS AIRS Facility Subsystem (CAA database)
- AIRS Aerometric Information Retrieval System (CAA database)
- BIFs Boilers and Industrial Furnaces (RCRA)
- BOD Biochemical Oxygen Demand
 - CAA Clean Air Act
 - CAAA Clean Air Act Amendments of 1990
 - **CERCLA** Comprehensive Environmental Response, Compensation and Liability Act
 - **CERCLIS CERCLA Information System**
 - CFCs Chlorofluorocarbons
 - CO Carbon Monoxide
 - COD Chemical Oxygen Demand
 - CSI Common Sense Initiative
 - CWA Clean Water Act
 - D&B Dun and Bradstreet Marketing Index
 - **ELP Environmental Leadership Program**
 - EPA United States Environmental Protection Agency
 - EPCRA Emergency Planning and Community Right-to-Know Act
 - FIFRA Federal Insecticide, Fungicide, and Rodenticide Act
 - FINDS Facility Indexing System
 - HAPs Hazardous Air Pollutants (CAA)
 - HSDB Hazardous Substances Data Bank
 - IDEA Integrated Data for Enforcement Analysis
 - LDR Land Disposal Restrictions (RCRA)
 - LEPCs Local Emergency Planning Committees
 - MACT Maximum Achievable Control Technology (CAA)
 - MCLGs Maximum Contaminant Level Goals
 - MCLs Maximum Contaminant Levels
 - MEK Methyl Ethyl Ketone
 - MSDSs Material Safety Data Sheets
 - NAAQS National Ambient Air Quality Standards (CAA)
 - NAFTA North American Free Trade Agreement
 - NCDB National Compliance Database (for TSCA, FIFRA, EPCRA)
 - NCP National Oil and Hazardous Substances Pollution Contingency Plan
 - NEIC National Enforcement Investigation Center
 - NESHAP National Emission Standards for Hazardous Air Pollutants

NO₂ Nitrogen Dioxide

NOV - Notice of Violation

National Priorities List

National Response Center

Nitrogen Oxide

NO_X _

NPDES -

NPL -

NRC -

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ELECTRONICS AND COMPUTER INDUSTRY (SIC 36) LIST OF ACRONYMS (CONT'D)

National Pollution Discharge Elimination System (CWA)

LIST OF ACKONTINS (CO

NSPS -	New Source Performance Standards (CAA)
OAR -	Office of Air and Radiation
OECA -	Office of Enforcement and Compliance Assurance
OPA -	Oil Pollution Act
OPPTS -	Office of Prevention, Pesticides, and Toxic Substances
OSHA -	Occupational Safety and Health Administration
OSW -	Office of Solid Waste
OSWER -	Office of Solid Waste and Emergency Response
OW -	Office of Water
P2 - Pollu	tion Prevention
PCS -	Permit Compliance System (CWA Database)
POTW -	Publicly Owned Treatments Works
RCRA -	Resource Conservation and Recovery Act
RCRIS -	RCRA Information System
SARA -	Superfund Amendments and Reauthorization Act
SDWA -	Safe Drinking Water Act
SEPs -	Supplementary Environmental Projects
SERCs -	State Emergency Response Commissions
SIC - Stand	lard Industrial Classification
SO ₂ Sulfu	r Dioxide
-	Total Organic Carbon

- TOC Total Organic Carbon
- TRI -Toxic Release Inventory
- TRIS Toxic Release Inventory System
- TCRIS Toxic Chemical Release Inventory System
- TSCA Toxic Substances Control Act
- **TSS Total Suspended Solids**
- UIC Underground Injection Control (SDWA)
- UST Underground Storage Tanks (RCRA)
- VOCs Volatile Organic Compounds

ELECTRONICS AND COMPUTER INDUSTRY (SIC 36)

I. Introduction to the Sector Notebook Project

I.A. Summary of the Sector Notebook Project

Environmental policies based upon comprehensive analysis of air, water, and land pollution are an inevitable and logical supplement to traditional single-media approaches to environmental protection. Environmental regulatory agencies are beginning to embrace comprehensive, multi-statute solutions to facility permitting, enforcement and compliance assurance, education/outreach, research, and regulatory development issues. The central concepts driving the new policy direction are that pollutant releases to each environmental medium (air, water, and land) affect each other, and that environmental strategies must actively identify and address these interrelationships by designing policies for the "whole" facility. One way to achieve a whole facility focus is to design environmental policies for similar industrial facilities. By doing so, environmental concerns that are common to the manufacturing of similar products can be addressed in a comprehensive manner. Recognition of the need to develop the industrial "sector-basedO approach within the EPA Office of Compliance led to the creation of this document.

The Sector Notebook Project was initiated by the Office of Compliance within the Office of Enforcement and Compliance Assurance (OECA) to provide its staff and managers with summary information for eighteen specific industrial sectors. As other EPA offices, States, the regulated community, environmental groups, and the public became interested in this project, the scope of the original project was expanded. The ability to design comprehensive, common sense environmental protection measures for specific industries is dependent on knowledge of several inter-related topics. For the purposes of this project, the key elements chosen for inclusion are: general industry information (economic and geographic); a description of industrial processes; pollution outputs; pollution prevention opportunities; Federal statutory and regulatory framework; compliance history; and a description of partnerships that have been formed between regulatory agencies, the regulated community, and the public.

For any given industry, each topic listed above could alone be the subject of a lengthy volume. However, in order to produce a manageable document, this project focuses on providing summary information for each topic. This format provides the reader with a synopsis of each issue, and references where more in-depth information is available. Text within each profile was researched from a variety of sources, and was usually condensed from more detailed sources pertaining to specific topics. This approach allows for a wide coverage of activities that can be further explored based

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upon the citations and references listed at the end of this profile. As a check on the information included, each notebook went through an external review process. The Office of Compliance appreciates the efforts of all those that participated in this process and enabled us to develop more complete, accurate, and up-to-date summaries. Many of those who reviewed this notebook are listed as contacts in Section IX and may be sources of additional information. The individuals and groups on this list do not necessarily concur with all statements within this notebook.

I.B. Additional Information

Providing Comments

OECA's Office of Compliance plans to periodically review and update the notebooks and will make these updates available both in hard copy and electronically. If you have any comments on the existing notebook, or if you would like to provide additional information, please send a hard copy and computer disk to the EPA Office of Compliance, Sector Notebook Project, 401 M St., SW (2223-A), Washington, DC 20460. Comments can also be uploaded to the Enviro\$en\$e Bulletin Board or the Enviro\$en\$e World Wide Web for general access to all users of the system. Follow instructions in Appendix A for accessing these data systems. Once you have logged in, procedures for uploading text are available from the on-line Enviro\$en\$e Help System.

Adapting Notebooks to Particular Needs

The scope of the existing notebooks reflect an approximation of the relative national occurrence of facility types that occur within each sector. In many instances, industries within specific geographic regions or States may have unique characteristics that are not fully captured in these profiles. For this reason, the Office of Compliance encourages State and local environmental agencies and other groups to supplement or re-package the information included in this notebook to include more specific industrial and regulatory information that may be available. Additionally, interested States may want to supplement the "Summary of Applicable Federal Statutes and Regulations" section with State and local requirements. Compliance or technical assistance providers may also want to develop the "Pollution Prevention" section in more detail. Please contact the appropriate specialist listed on the opening page of this notebook if your office is interested in assisting us in the further development of the information or policies addressed within this volume.

If you are interested in assisting in the development of new notebooks for sectors not covered in the original eighteen, please contact the Office of Compliance at 202-564-2395.

II. INTRODUCTION TO THE ELECTRONICS/COMPUTER INDUSTRY

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the Electronics/Computer industry. The type of facilities described within the document are also described in terms of their Standard Industrial Classification (SIC) codes. Additionally, this section contains a list of the largest companies in terms of sales.

II.A. Introduction, Background, and Scope of the Notebook

The electronics/computer industry is classified by the U.S. Bureau of Census as SIC code 36. SIC 36 includes manufacturers of electrical distribution equipment, household appliances, communication equipment, electrical industrial apparatus, radio and television receiving equipment, electronic components and accessories, electrical wiring and lighting equipment, and other electrical equipment and supplies. The electronics/computer industry is comprised of five major sectors: telecommunications, computers, industrial electronics, consumer electronics, and semiconductors. Many segments of the electronics/computer industry are interdependent and share common manufacturing processes.

The Department of Commerce provides the following three-digit breakout for industries in SIC 36:

SIC 361	- Transformers
SIC 362	- Motors/Generators
SIC 363	- Household Appliances
SIC 364	- Electrical Wiring and Lighting Equipment
SIC 365	- Household Audio and Video Equipment and Audio
	Recordings
SIC 366	- Communication Equipment
SIC 367	- Printed Wiring Boards (also commonly called Printed
	Circuit Boards), Semiconductors, Integrated Circuits, and
	Cathode Ray Tubes
SIC 369	- Storage Batteries, Primary Batteries (wet and dry).

In 1988, the U.S. Bureau of Census reclassified some of the manufacturing of computer parts, such as semiconductors, printed wiring boards, and integrated microcircuits, and included them with the component industries in SIC code 36. For the purpose of this profile, computer equipment (SIC 35) and the electronics/computer industry (SIC 36) have been combined because of the overlapping industry segments. Currently there is no SIC code for electronic assemblies manufactured by the electronic manufacturing services industry (EMSI), otherwise known as contract

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assemblies. Electronic assemblies are sometimes classified under SIC 3679 as indicated by the Institute for Interconnecting and Packaging Electronic Circuits (IPC).

Due to the vast size of the electronics and computer industries, this profile will focus on the distinct equipment and products that raise environmental concerns.

II.B. Characterization of the Electronics/Computer Industry

The electronics/computer industry produces a variety of products such as batteries, televisions, computer chips/components, and household appliances. During the manufacture of many of these products, chemicals are released into the environment. This profile will focus on three products:

SIC 3674	-	Semiconductors and Related Devices
SIC 3672	-	Printed Wiring Boards (PWBs)
SIC 3671	-	Cathode Ray Tubes (CRTs).

The profile focuses on semiconductors and not integrated circuits because integrated circuits are used to produce semiconductors and most electronic devices manufactured today are multiple devices/circuit chips. Semiconductors, although accounting for only a small portion of total industry sales, are crucial to all electronic products and to the U.S. economy and pose numerous environmental concerns. PWBs and CRTs also raise environmental concerns from their manufacturing processes.

The following sections describe the size and geographic distribution, product characterization, and economic trends of the electronics/computer industry and specifically semiconductors, PWBs, and CRTs. The information provided in the following sections was compiled from a variety of sources including the Bureau of Census, documents developed by The World Bank, U.S. International Trade Commission, and the U.S. Department of Commerce.

II.B.1. Industry Size and Geographic Distribution

Variation in facility counts occur across data sources due to many factors, including reporting and definitional differences. This document does not attempt to reconcile these differences, but rather reports the data as they are maintained by each source.

Size Distribution

The U.S. has the largest electronics (including computer) workforce in the world, although Japan, the Republic of Korea, and other Asian nations are experiencing rapid growth in their electronics workforces. The size of the U.S. domestic electronics workforce for SIC 36 was estimated to be 2.39 million in 1991, while the number of worldwide employees was estimated to be four million. In addition, the electronics/computer industry is estimated to provide four million additional jobs to people who support and service U.S. electronics firms. The electronics/computer industry provides more jobs than any other manufacturing sector in the U.S., three times as many jobs as automotive manufacturing, and nine times more than the steel industry. The electronics/computer industry has not, however, experienced growth in domestic employment for the past two and one-half years. In fact, since 1989, the industry has lost 210,000 jobs.

IPC states that this stagnation in job growth is caused primarily by two factors: increased productivity and increased competition by foreign manufacturers that may have fewer government regulations. IPC also notes that the U.S. electronic manufacturing services industry or contract assembly industry is one of the fastest growing industries in the country, employing over 150,000 people.

The following exhibit lists the segments of the industry highlighted in this profile, as well as the number of facilities with fewer than and greater than 20 employees. Just under 50 percent of semiconductor and PWB manufacturing facilities have greater than 20 employees.

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Facility Size E	istribution of Electronics/Computer Industry				
SIC Code	Number of Facilities with <20 Employees	Number of Facilities with > 20 Employees	Percentage of Facilities with > 20 Employees		
3674 Semiconductors and Related Devices	484	439	48%		
3672 Printed Wiring Boards	734	591	45%		
3671 Cathode Ray Tubes	120	69	37%		

Exhibit 1 Facility Size Distribution of Electronics/Computer Industry

Source: Based on 1992 Bureau of the Census data, Preliminary Report Industry Series.

Exhibit 2 lists the top ten electronics/computer industry companies worldwide according to a 1992 addition of *Electronic News*. The companies are listed in descending order of electronic sales during the latest available four quarters in 1992. Many of these top ten companies are not from the United States. However, a representative from the Electronic Industries Association (EIA) noted that many of these international companies have manufacturing facilities in the United States. Corporations that are among the top 25 in terms of electronic sales include AT&T, General Motors, Xerox, Apple Computer, Hewlett Packard, Motorola, and General Electric.

Company Name	1992 Electronic Sales in Millions of Dollars
IBM	\$53,600
Matsushita Electric	\$48,668
Toshiba	\$29,232
NEC	\$28,375
Fujitsu	\$25,879
Philips	\$25,747
Hitachi	\$25,107
Siemens	\$24,550
Sony	\$22,959
Alcatel Alsthom	\$20,892

Exhibit 2 Top 10 Worldwide Electronics/Computer Industry Companies

Source: Based on 1992 Electronic News.

Geographic Distribution

Exhibit 3 displays the number of electronics/computer industry facilities in each State for SIC 3671, 3672, and 3674. As seen in Exhibit 4, approximately 38 percent (3,689) of the facilities in the electronics/computer industry are located in EPA Region IX¹. Region V has approximately 13 percent of the electronics/computer industry facilities. Across the U.S., approximately 60 percent of the facilities in the electronics/computer industry are located in six States: California (34 percent), Texas (6.5 percent), Massachusetts (6.4 percent), New York (4.5 percent), Illinois (4.4 percent), and Pennsylvania (4 percent).

The U.S. semiconductor industry is concentrated in California, New York, and Texas, specifically to be near primary users, transportation routes, utility and telecommunication infrastructures, and engineering experts. Texas, Oregon, and Colorado also received a large portion of capital investments by semiconductors producers during 1986-1992. Manufacturers have selected these States because of low tax rates, land values, and energy prices.

California has the largest concentration of industry workers, accounting for almost one-third of the semiconductor industry's employment. Texas, Arizona, New York, and Massachusetts also have high employment in the semiconductor industry. The majority of PWB manufacturers are located in Texas, California, Illinois, New York, Minnesota, and Massachusetts. According to Dun & Bradstreet, approximately 51 manufacturers produce cathode ray tubes (CRTs) in the U.S.; most of them are located in Illinois, Indiana, Ohio, Kentucky, Pennsylvania, and California (1994).

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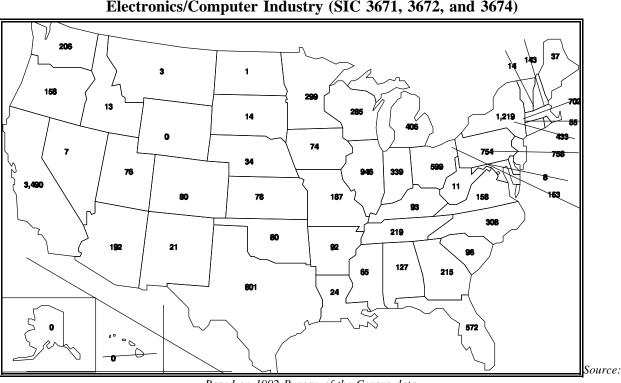


Exhibit 3 Geographic Distribution of and Number of Companies in the Electronics/Computer Industry (SIC 3671, 3672, and 3674)

Based on 1992 Bureau of the Census data.

Exhibit 4 Percentage of Companies in the Electronics/Computer Industry (SIC 3671, 3672, and 3674) by Region

Region I:	10.8%	Region VI:	7.2%
Region II:	8.0%	Region VII:	1.4%
Region III:	6.0%	Region VIII:	3.4%
Region IV:	7.6%	Region IX:	37.6%
Region V:	13.1%	Region X:	4.8%

II.B.2. Product Characterization

Semiconductors

Although semiconductors account for only a small portion of electronics/computer industry sales, this product is crucial to all electronic products and to the U.S. economy. Semiconductors can serve one of two purposes: they act as a conductor, by guiding or moving an electrical current; or as an insulator, by preventing the passage of heat or electricity. Semiconductors are used in computers, consumer electronic products, telecommunication equipment, industrial machinery, transportation

equipment, and military hardware. Typical functions of semiconductors in these products include information processing, display purposes, power handling, data storage, signal conditioning, and conversion between light and electrical energy sources. According to EPA's Design for the Environment (DfE) initiative, computers are the principal end use of semiconductors, constituting 40 percent of the market in 1992.

Printed Wiring Boards

Computers are also the major U.S. market for PWBs, with communications being the second largest application market. The Institute for Interconnecting and Packaging Electronic Circuits (IPC) indicates that nearly 39 percent of printed wiring boards produced in 1993 were used by the computer market, while 22 percent were used by the communication industry. PWBs and assemblies are used in many electronic products such as electronic toys, radios, television sets, electrical wiring in cars, guided-missile and airborne electronic equipment, computers, biotechnology, medical devices, digital imaging technology, and industrial control equipment.

Cathode Ray Tubes

According to EPA's Common Sense Initiative (CSI) subcommittee, the CRT industry produces tube glass, color picture tubes and single phosphor tubes, television sets, and computer displays. Currently, nearly all projection television tube and computer display manufacturers and the majority of CRT glass manufacturers are located outside the United States. Therefore, this CRT industry profile focuses on the production of color picture tubes, single phosphor tubes, and rebuilt tubes (collectively called CRTs and categorized under SIC 3671). These products are the video display component of televisions, computer displays, military and commercial radar, and other display devices.

II.B.3. Economic_Trends

For the past two decades, worldwide production of electronics (including computers) has grown faster than any other industrial sector. The American Electronics Association (AEA) estimates that domestic sales of U.S. electronics companies increased from \$127 billion to \$306 billion during the period from 1980 to 1990. According to the U.S. Department of Commerce, the value of shipments (sale of computer products and services) in the computer industry declined during the 1990-1991 recession, but has experienced growth since then. The value of shipments increased two percent in 1993 to \$8.3 billion and is expected to increase another two percent in 1994, to \$8.48 billion. U.S. exports of the electronics/computer industry have increased at an average rate of 18 percent since 1977.

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EIA indicates that the U.S. electronics/computer industry has experienced a 13 percent growth in production in 1994. Japan now holds the largest share of global consumer electronics production; 49 percent in 1990. Although the U.S. produced a little over 10 percent of global consumer electronics equipment, it is one of the two largest consumers of such products, with purchases totaling \$33 billion in 1990.

Semiconductors

The U.S. semiconductor industry has experienced growth since 1992. The U.S. global market share of semiconductors, semiconductor processing equipment, and computer systems fell between 1980 to 1991. Japanese firms gained most of the market share lost by U.S. firms. Although the U.S. continues to be the world's largest consumer of electronics products, as a result of Japan's growth in consumer electronics production, Japan is now the world's largest consumer of semiconductors. The U.S. is the second largest market in the world for semiconductors, with consumption at \$17.4 billion in 1990. The five largest U.S. producers are Motorola, Intel, Texas Instruments, National Semiconductor, and Advanced Micro Devices. According to the Department of Commerce, the value of shipments of U.S. semiconductors is estimated to be \$37.6 billion in 1993 and is expected to grow 12 percent in 1994 to over \$42.1 billion.

Printed Wiring Boards/Electronic Assemblies

Japan and the U.S. now have equal market shares, 27 percent each. IPC notes that the U.S. was the largest PWB market in the world with a value of approximately \$5.5 billion in 1993. According to the Department of Commerce, the value of printed wiring board shipments produced in the U.S. was \$6.75 billion in 1993 and is expected to grow by three percent, to \$6.95 billion, in 1994. According to IPC, the U.S. electronic manufacturing services industry or contract assemblies industry generates over \$9 billion in revenue.

Cathode Ray Tubes

According to 1994 U.S. Industrial Outlook data, the total value of CRT shipments was \$3 billion in 1993 and is expected to increase six percent to \$3.2 billion in 1994. The total value of CRT shipments is expected to increase more than 3.5 percent per year due to a projected rising demand for television sets and computer displays.

III. INDUSTRIAL PROCESS DESCRIPTION

This section describes the major industrial processes within the electronics/computer industry, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and Federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of reference documents that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the processes. This section also describes the potential fate (air, water, land) of these waste products.

III.A. Industrial Processes in the Electronics/Computer Industry

The products discussed in this section, semiconductors, printed wiring boards (PWBs), and cathode ray tubes (CRTs), pose significant environmental concerns during the manufacturing processes and/or comprise a large portion of the electronics/computer industry. This section will describe and distinguish these products as well as the steps followed to manufacture them. This discussion also includes an explanation of the wastes generated during the manufacturing processes.

III.A.1. <u>Semiconductor Manufacturing</u>

Semiconductors are made of a solid crystalline material, usually silicone, formed into a simple diode or many integrated circuits. A simple diode is an individual circuit that performs a single function affecting the flow of electrical current. Integrated circuits combine two or more diodes. Up to several thousand integrated circuits can be formed on the wafer, although 200-300 integrated circuits are usually formed. The area on the wafer occupied by integrated circuits is called a chip or die.

Information in this section is from a variety of sources including the following: U.S. EPA's DfE initiative, U.S. EPA Common Sense Initiative (CSI), California Department of Toxic Substances Control, McGraw Hill Encyclopedia of Science and Technology, *Integrated Circuits, Making the Miracle Chip, Microchip Fabrication:* A Practical Guide to Semiconductor Processing, and Microelectronics and Computer Technology Corporation (MCC). The semiconductor manufacturing process is

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complex and may require that several of the steps be repeated to complete the process. To simplify this discussion, the process has been broken down into five steps:

- ¥ Design
- ¥ Crystal processing
- ¥ Wafer fabrication
- ¥ Final layering and cleaning
- ¥ Assembly.

The primary reason that semiconductors fail is contamination, particularly the presence of any microscopic residue (including chemicals or dust) on the surface of the base material or circuit path. Therefore, a clean environment is essential to the manufacture of semiconductors. Cleaning operations precede and follow many of the manufacturing process steps. Wet processing, during which semiconductor devices are repeatedly dipped, immersed, or sprayed with solutions, is commonly used to minimize the risk of contamination.

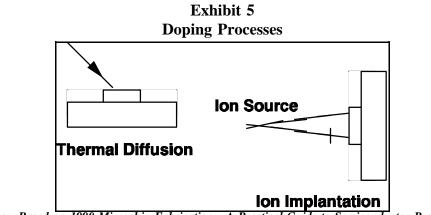
Step One: Design

As with any manufacturing process, the need for a particular type of product must be identified and process specifications must be developed to address that need. In the case of semiconductors, the circuit is designed using computer modeling techniques. Computer simulation is used to develop and test layouts of the circuit path. Then, patterning "masks," which are like stencils, are fabricated, manufacturing equipment is selected, and operating conditions are set. All of these steps occur prior to actually producing a semiconductor.

Step Two: Crystal Processing

Wafers, which consist of thin sheets of crystalline material, are the starting point of semiconductor production. Silicon, in the form of ingots, is the primary crystalline material used in the production of 99 percent of all semiconductors. Silicon crystals are actually "grown" using controlled techniques to ensure a uniform crystalline structure. Because crystals of pure silicon are poor electrical conductors, controlled amounts of chemical impurities or **dopants** are added during the development of silicon ingots to enhance their semiconducting properties. Dopants are typically applied using **diffusion** or **ion implantation** processes (See Exhibit 5). Dopants eventually form the circuits that carry the flow of current.

¥ <u>Diffusion</u> is a chemical process which exposes the regions of the silicon surface to vapors of the metal additive (dopant) while maintaining high temperatures. The process ends when the additives (represented by the arrow in Exhibit 5) migrate to the proper depth and reach the appropriate concentration in the silicon wafer. ¥ <u>Ion implantation</u> is a process that allows for greater control of the location and concentration of dopants added to the wafer. Metal dopants are ionized and accelerated to a high speed. As shown in Exhibit 5, the ions penetrate the silicon surface and leave a distribution of the dopant.



Source: Based on 1990 Microchip Fabrication: A Practical Guide to Semiconductor Processing.

Either doping process can be used in semiconductor manufacturing. Antimony, arsenic, phosphorus, and boron compounds are the dopant materials most commonly used for silicon-based semiconductors. Other dopants include aluminum, gallium, gold, beryllium, germanium, magnesium, silicon, tin, and tellurium. Wastes including antimony, arsenic, phosphorus, and boron may be generated in the wastewater as a result of ion implantation or diffusion. Excess dopant gases, contaminated carrier gases, and out-gassed dopant gases from semiconductor materials may also be generated.

Most semiconductor manufacturers obtain single crystal silicon ingots from other firms. Ingots are sliced into round wafers approximately 0.76 mm (0.03 inches) thick and then **rinsed**. The wafers are further prepared by mechanical or chemical means. A wafer's surface may be **mechanically ground**, **smoothed**, and **polished**, as well as **chemically etched** so that the surface is smooth and free of oxides and contaminants. Chemical etching removes organic contaminants using cleaning solvents and removes damaged surfaces using acid solutions. Chemical etching is usually followed by a **deionized water rinse** and **drying** with compressed air or nitrogen. In some cases, bare silicon wafers are cleaned using ultrasound techniques, which involve potassium chromate or other mildly alkaline solutions.

Etching is a method of cutting into, or imprinting on, the surface of a material. Several etching processes can be used on semiconductors, as well as integrated circuits and printed wiring boards. Wet etching uses acid solutions to cut patterns into the metal. Dry etching involves reactive gases and is rapidly becoming the method of choice for high resolution. Dry etching processes use various halogenated or nonhalogenated gaseous compounds.

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In the semiconductor industry, dry plasma etching, reactive ion etching, and ion milling processes are being developed to overcome the limitations of wet chemical etching. Dry plasma etching, the most advanced technique, allows for etching of fine lines and features without the loss of definition. This process forms a plasma above the surface to be etched by combining large amounts of energy with low pressure gases. The gases usually contain halogens.

Materials used during the wet etching process may include acids (sulfuric, phosphoric, hydrogen peroxide, nitric, hydrofluoric, and hydrochloric), ethylene glycol, hydroxide solutions, and solutions of ammonium, ferric, or potassium compounds. Materials used during the dry etching process may include chlorine, hydrogen bromide, carbon tetrafluoride, sulfur hexafluoride, trifluoromethane, fluorine, fluorocarbons, carbon tetrachloride, boron trichloride, hydrogen, oxygen, helium, and argon. Typical solvents and cleaning agents include acetone, deionized water, xylene, glycol ethers, and isopropyl alcohol. The most commonly used cleaning solution in semiconductor manufacturing includes a combination of hydrogen peroxide and sulfuric acid.

Acid fumes and organic solvent vapors may be released during cleaning, etching, resist drying, developing, and resist stripping operations. Hydrogen chloride vapors may also be released during the etching process.

Step Three: Wafer Fabrication

Wafers are usually fabricated in batches of 25 to 40. Wafer preparation begins with an **oxidation** step.

¥ <u>Oxidation</u> is a process in which a film of silicon dioxide is formed on the exterior surface of the silicon wafer. Thermal oxidation takes place in a tube furnace with controlled, high temperatures and a controlled atmosphere. Oxidation is a reaction between the silicon wafer surface and an oxidant gas such as oxygen or steam. This process may be needed as a preliminary step before diffusion or ion implantation (doping). This layer protects the wafer during further processing. Following oxidation, the wafer surface is thoroughly cleaned and dried.

Materials used during oxidation, include silicon dioxide, acids (hydrofluoric), and solvents. Materials such as oxygen, hydrogen chloride, nitrogen, trichloroethane, and trichloroethylene may also be used. Wastes that may be generated from this process include: organic solvent vapors from cleaning gases; rinsewaters with organic solvents from cleaning operations; spent solvents (including F003); and spent acids and solvents in the wastewater.

Next, patterns are imprinted onto the substrate using **photolithography** (also referred to as lithography) and **etching** processes. Photolithography is the most crucial step

in semiconductor manufacturing because it sets a device's dimensions; incorrect patterns affect the electrical functions of the semiconductor.

Photolithography is a process similar to photoprocessing techniques and other etching processes in that a pattern is imprinted. The silicon wafer is coated uniformly with a thin film of resist. A glass plate or mask is created with the circuit pattern, and the pattern is imprinted in one of several ways. One type of optical photolithography is the projection of x-rays through a special mask close to the silicon slice. Another type of optical photolithography, one that does not need a mask, is electron-beam direct patterning, which uses a controllable electron beam and an electron sensitive resist. Once the pattern is developed, some areas of the wafer are clear and the rest are covered with resist (See Exhibit 6).

P	Process Step	Purpose	Cross	Se	ctic	on
			· · · · · · · · · · · · · · · · · · ·			
1.	Alignment and exposure	Precise alignment of mask to wafer and exposure to U.V. light. Negative resist is polymerized.				
2.	Development	Removal of unpolymerized resist.				
3.	Etch	Selective removal of top surface layer.				
4.	Photoresist Removal	Cleaning of photoresist from the wafer's surface.				
5.	Final Inspection	Inspection of wafer for correctness of image transfer from photoresist to top layer.				

Exhibit 6 Photolithography Process

Based on 1990 Microchip Fabrication: A Practical Guide to Semiconductor Processing.

Two types of photoresists can be used during semiconductor production:

- ¥ <u>Positive</u> photoresists are chemicals that are made more soluble, with regard to a solvent (i.e., developer), after exposure to radiation. During development, the developer removes the resist that was exposed to radiation.
- ¥ <u>Negative</u> photoresists are chemicals that polymerize and stabilize upon

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exposure to radiation. During development, the developer removes the resist that was protected from radiation.

After photolithography, chemical **developers** are used to remove unnecessary coatings or resist material that remains on the substrate. Development can be conducted by liquid methods (dip, manual immersion, or spray coating) or dry methods (plasma). The wafer is then **etched** in an acid solution to remove selected portions of the oxide layer to create depressions or patterns. The patterns are areas in which dopants will be applied. The wafer is **rinsed**, typically by immersing in a stripping solution to remove unwanted photoresist, and then dried. See Exhibit 7 for a list of materials used during the photolithography process.

		Solvents and
Photoresists	Developer	Cleaning Agents
Positive:	Positive:	Deionized water
Ortho-diazoketone	Sodium hydroxide	Detergent
Polymethacrylate	Potassium hydroxide	Isopropyl alcohol
Polyfluoroalkylmethacrylate	Silicates	Acetone
Polyalkylaldehyde	Ethylene glycol	Ethanol
Polycyanoethylacrylate	Ethanolamine	Hydrofluoric acid
Polymethylmethacrylate	Isopropyl alcohol	Sulfuric acid
oly (hexafluorobutylmeth-acrylate)	Phosphates	Hydrogen peroxide
	Tetramethyl-ammonium	Hydrochloric acid
Negative:	hydroxide	Nitric acid
Isoprene	Alkyl amine	Chromic acid
Ethyl acrylate	Ethyl acetate	Ammonium hydroxide
Glycidylmetharcylate	Methyl isobutyl ketone	Hexamethyldisilazane
Copolymer-ethylacrylate		Xylene
	Negative:	Cellosolve acetate
	Xylene	n-Butyl acetate
	Aliphatic Hydrocarbons	Ethylbenzene
	N-Butyl acetate	Chlorofluorocarbons
	Cellosolve acetate	Chlorotoluene
	Isopropyl alcohol	Glycol ethers
	Stoddard solvent	
	Glycol ethers	

Exhibit 7 Chemicals Used in Photolithography for Semiconductors

Source: Based on EPA DfE 1993: <u>Industry Profile and Description of Chemical Use for the</u> <u>Semiconductor Industry: Preliminary Draft</u>.

During the next step, **dopants** are applied to the patterned wafer surface typically using <u>diffusion</u> or <u>ion implantation</u>. See Step two for a list of materials used and wastes generated during the doping process.

Additional layers of silicon may also be applied to the wafer using **deposition** techniques, typically epitaxial growth or chemical vapor deposition.

¥ Epitaxyl allows the growth of another layer of silicon on top of the wafer. A

silicon layer is grown using high temperatures and dopant compounds. This top layer of silicon is where the final device will be formed. Not all semiconductors need this layer.

¥ Chemical vapor deposition deposits a thin coating on materials by a chemical process. Vapor deposition is a low pressure process that combines appropriate gases in a reactant chamber at elevated temperatures to produce a uniform film thickness.

Materials that may be used during deposition include silane, silicon tetrachloride, ammonia, nitrous oxide, tungsten hexafluoride, arsine, phosphine, diborane, nitrogen, and hydrogen.

Wastes that may be generated from these processes include: acid fumes from etching operations; organic solvent vapors from cleaning resist drying, developing, and resist stripping; hydrogen chloride vapors from etching; rinsewaters containing acids and organic solvents from cleaning, developing, etching, and resist stripping processes; rinsewaters from aqueous developing systems; spent etchant solutions; spent solvents (including F003) and spent acid baths.

Many products require that steps two through three be repeated several times in order to create the specified structure.

Step Four: Final Layering and Cleaning

Once the wafer is patterned, the wafer surface is coated with thin layers of metal by a process called **metallization**. These metal layers perform circuit functions within the finished semiconductor. External connections to the silicon wafer are provided by evaporation of thin metal films onto areas of the semiconductor chip surface in a vacuum. Almost every metal can be used to make this electrical connection to the silicon; aluminum, platinum, titanium, nickel/chromium, silver, copper, tungsten, gold, germanium, and tantalum are most common. Argon gas is also used in some operations. **Sputtering** and **high vacuum evaporation** are two types of metallization.

- ¥ <u>Sputtering</u> (also called partial vacuum evaporation) is a physical, rather than chemical process. This process occurs in a vacuum chamber which contains a target (solid slab of the film material) and the wafers. Argon gas is introduced in the chamber and ionized to a positive charge. The positively charged argon atoms accelerate toward and strike the target, dislodging the target atoms. The dislodged atoms are deposited onto the wafer surface. A uniform thickness of the coating is produced over the silicon slice.
- ¥ <u>High vacuum evaporation</u> is a process that uses an electron beam, a ceramic bar heated by thermal resistance, or a wire heated by electrical resistance. This method coats the surface of the wafer with metal.

Photolithography and etching are also used to remove any unnecessary metal using

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chlorinated solvents or acid solutions. Wastes generated include: acid fumes and organic solvent vapors from cleaning, etching, resist drying, developing, and resist stripping; liquid organic waste; aqueous metals; and wastewaters contaminated with spent cleaning solutions.

In the next step, **passivation** is used to apply a final layer of oxide over the wafer surface to provide a protective seal over the circuit. This coating protects the semiconductor from exterior influences and may range in thickness from a single layer of silicon dioxide to a relatively thick deposit of special glass. It also insulates the chip from unwanted contact with other external metal contacts. Materials used to form the passivation layer are silicon dioxide or silicon nitride.

After all layers have been applied to the wafer, the wafer is typically **rinsed** in deionized water. The back of the wafer is then mechanically ground (also called **lapping** or **backgrinding**) to remove unnecessary material. A film of gold may be applied to the back of the wafer by an evaporation process to aid the connection of leads to the bonding pads during a later process step.

Testing with alcohol compounds is conducted to ensure that each chip is performing the operation for which it was designed. Chips that do not meet specifications are marked with an ink droplet for discard during assembly operations. The wafer is cleaned again after testing, using solvents such as deionized water, isopropyl alcohol, acetone, and methanol.

Wastes generated from these processes include: spent solvents and acids in the wastewater and rinsewater from cleaning, developing, etching, resist stripping, and rinsing processes; acid fumes and organic solvent vapors from cleaning, rinsing, resist drying, developing, and resist stripping; spent silicon dioxide or nitride; hydrogen chloride vapors from etching; rinsewaters from aqueous developing systems; spent etchant solutions; spent acid baths; and spent solvents.

Step Five: Assembly

Semiconductors are assembled by mounting chips onto a metal frame, connecting the chips to metal strips (leads), and enclosing the device to protect against mechanical shock and the external environment. There are many types of packaging; such as plastic or ceramic. Plastic packages comprised more than 90 percent of the market in 1990.

Each package contains five parts: the die (e.g., chip), the lead frame of the package, the die-attach pad, the wire bond, and the molded encapsulant (i.e., plastic housing) (See Exhibit 8). This section describes how plastic packages are assembled. All semiconductor packages whether plastic or ceramic share the same basic parts and are assembled using the same general processes.

Plastic Package Components

Exhibit 8 Plastic Package Components

Source: Based on 1993 <u>Environmental Consciousness: A Strategic Competitiveness Issue</u> for the Electronics <u>Industry</u>.

The lead frame consists of a rectangular-shaped metal frame connected to metal strips or leads. The leads connect the chip to the electronic product. Plastic package lead frames are fabricated from sheets of metal, either copper or alloy 42, that is either **punched** or **etched**. The lead frame and leads provide the connections for the electronic components.

- ¥ The <u>punching</u> process consists of an array of small mechanical punches that remove sections of the metal sheet until the lead frame is complete. The leads are cleaned with water-based cleaning systems. In the past, manufacturers used chlorinated fluorocarbons (CFCs) or other solvents to remove cutting fluids. The lead frame is coated with a layer of photoresist, exposed, and developed. The manufacturer etches the lead frame, removes the photoresist, and cleans the lead frame again with water based cleaning systems.
- ¥ If the lead frames are <u>etched</u>, the process is similar to that used during PWB manufacturing. Acids or metal chlorides are usually used during etching. Sometimes ammonia is used to stabilize the metal chloride. The photoresist contains solvents (such as trichloroethylene or TCE) that are baked out and generate VOC emissions. Developers that are typically used include either an amine or metal hydroxide. Once the photoresist is removed, it is cleaned with solvents such as a mild hydrochloric acid (HCL) solution or with a brightener that contains sulfuric acid.

Wastes generated during punching or etching may include: spent organic vapors generated from cleaning, resist drying, developing, and resist stripping; spent cleaning solutions; rinsewaters contaminated with organic solvents; and spent aqueous developing solutions. Scrap copper or alloy 42 may be recycled during the punching process.

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The chip is then **attached** to an "attach pad," with a substance such as an epoxy material (thermoset plastic). Once mounted, the chips are inspected. The chip parts are bonded to the leads of the package with tiny gold or aluminum wires. A package may have between 2 and 48 wire bonds. The assembly is cleaned and inspected again. The combined components are then placed into a **molding press**, which encases the chip, wire bonds, and portions of the leads in plastic. The plastic-molding compound used in the press contains primarily fused silica. After the molding compound cures and cools around the package, the package is heated again to ensure that the plastic is completely cured. Excess material is removed using a chemical or mechanical **deflash** process. M-Pyrol is one organic solvent used during the deflash process. The final steps in package fabrication include **trimming** and **forming** the leads.

Waste generated during these steps includes excess epoxy/thermoset plastic; antimony trioxide (from the molding process); and spent organic solvents. Excess gold or aluminum from trimming processes can be reclaimed and reused.

Final computer tests are conducted to evaluate whether the product meets specifications. Even though the chips are produced using the same process, some may work better (e.g., faster) than others. As a result, packages are separated into low-and high-quality circuits. Often, low-quality circuits can still be sold. Final process steps include marking the circuits with a product brand. The finished product is then packaged, labeled, and shipped according to customer specifications.

III.A.2. <u>Printed Wiring Board Manufacturing</u>

Printed wiring boards (PWBs) are the physical structures on which electronic components such as semiconductors and capacitors are mounted. The combination of PWBs and electronic components is an electronic assembly or printed wiring assembly (PWA). According to Microelectronics and Computer Technology CorporationÕs (MCC) *Environmental Consciousness: A Strategic Competitiveness Issue for the Electronics and Computer Industry*, PWB manufacturing is the most chemical intensive process in the building of a computer workstation.

PWBs are subdivided into single-sided, double-sided, multilayer, and flexible boards. Multilayer boards are manufactured similarly to single and double-sided boards, except that conducting circuits are etched on both the external and internal layers. Multilayer boards allow for increased complexity and density. PWBs are produced using three methods: additive, subtractive, or semi-additive technology. The subtractive process accounts for a significant majority, perhaps 80 percent, of PWB manufacturing.

The conventional <u>subtractive</u> manufacturing process begins with a board, consisting of epoxy resin and fiberglass, onto which patterns are imaged. In most operations,

conducting material, usually copper, is bonded onto the substrate surface to form copper-clad laminate. After drilling holes through the laminate and making those holes conductive, unwanted copper is etched off, leaving copper patterns. The patterns on the board form the electric circuits that conduct electricity. Multilayer boards typically use metals such as platinum, palladium, and copper to form electric circuits. Specialized PWBs may use nickel, silver, or gold.

<u>Additive</u> technology is used less often than substractive technology because it is a more difficult and costly production process. This capital-intensive technology is used primarily for small interconnection components used in multi-chip devices. The production process begins with a base plate upon which a dielectric material is deposited. An interconnecting layer of copper is plated onto the dielectric layer which connects the layers of dielectric material and copper. Copper posts are plated-up and another layer of dielectric material is deposited exposing the posts. The next interconnect layer is plated and makes contact with the posts. Layers of dielectric material, copper, and copper posts are added to complete the interconnect. A lithographic process, similar to the one used in semiconductor manufacturing, diminishes the spaces and widths of the PWB.

This section provides a simplified discussion of the steps commonly performed during conventional subtractive manufacturing. The actual steps and materials used by a PWB manufacturer vary depending on customer requirements and the product being manufactured. The information provided in this section comes from various sources, including documents developed by MCC, IPC, EPA's Center for Environmental Research Information, EPA's DfE Program, California Department of Toxic Substances, EPA's CSI, and EPA's Office of Research and Development. PWB manufacturing can be grouped into five steps:

- ¥ Board preparation
- ¥ Application of conductive coatings (plating)
- ¥ Soldering
- ¥ Fabrication
- ¥ Assembly.

Step One: Board Preparation

Board preparation begins with a **lamination** process. Two-side etched copper dielectric boards (consisting usually of fiberglass and epoxy resin) are separated by an insulating layer and laminated or bonded together, usually by heat and pressure. Photographic tools are used to transfer the circuit pattern to the PWB, and computer control programs are used to control the drilling, routing, and testing equipment. Preparing the copper-clad board involves **drilling** holes to establish an electrical path between the layers and to mount components. The boards are then mechanically **cleaned** to remove drilling wastes (i.e., fine particulate contaminants, such as copper).

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Vapor degreasing, abrasive cleaning, chemical cleaning with alkaline solutions, acid dips, and water rinses are techniques used to clean the boards and prepare them for the next process, **electroless plating**. See Exhibit 9 for a list of materials used during lamination, drilling, and cleaning processes.

Lamination	Drilling	Cleaning
Epoxies	Sulfuric Acid	Acetone
	Potassium Permanganate	1,1,1-Trichloroethane
	Ammonium bifluoride	Silica (and other abrasives)
	Oxygen	Sulfuric acid
	Fluorocarbon gas	Ammonium hydroxide
		Hydrochloric acid

Exhibit 9 Chemicals Used in Lamination, Drilling, and Cleaning

Source: Based on EPA DfE 1993: <u>Industry Profile and Description of Chemical Use for the</u> <u>Printed Wiring Board Industry: Preliminary Draft</u>.

Wastes generated include: airborne particulates, acid fumes, and organic vapors from cleaning, surface preparation, and drilling; spent acid and alkaline solutions; spent developing solutions, spent etchants, and waste rinsewaters in the wastewater; and scrap board materials and sludges from wastewater treatment. Drilling and routing dust (copper, aluminum, and gold) are collected and recycled.

Step Two: Electroless Plating

The first process in this step is to prepare the surfaces of the drilled holes. The holes are prepared by an etchback process to remove smeared epoxy resin and other contaminants using one of the following: sulfuric or hydrochloric acid; potassium permanganate; or carbon tetrafluoride, oxygen and nitrogen. The holes are then coated with a material such as copper or graphite carbon, by a chemical process called **electroless plating.**

Electroless plating coats a uniform conducting layer of copper or other material on the entire surface including the barrels of the holes of the prepared board without outside power sources. According to *Printed Circuit Board Basics*, this coating of copper is not thick enough to carry an electrical current, but provides a base upon which additional copper can be deposited electrolytically. According to DfE, copper is the industry standard, but many are switching to direct metallization processes. Chemical deposition is the technique used to coat the board. After the electroless plating, the boards are dried to prevent the board from oxidation (e.g., rusting). The board may also be cleaned to prepare for a following electroplating processing. See Exhibit 12 for a list of materials used. Waste generated include: spent electroless copper baths; spent catalyst solutions; spent acid solutions; waste rinsewaters; and sludges from wastewater treatment.

Step Three: Imaging

During imaging, circuit patterns are transferred onto the boards through **photolithography** or a **stencil printing** process. Photoresist (i.e., a light sensitive chemical) is applied to the board in areas where the circuit pattern will not be set. The board is exposed to a radiation source and **developed** to remove the unwanted areas of the resist layer. Stencil printing uses a printing process, such as silk screening, to apply a protective film that forms the circuit pattern.

After photolithography, the boards are subjected to a light **etching** process, typically using ammoniacal etchants, to remove rust inhibitor (applied by the company that produced the material from which the board is made) or other metals (usually copper). After the stencil printing process, the protective film is dried, and the exposed copper is etched away. Sulfuric acid and hydrogen peroxide are common etchants used during imaging. After plating or etching, the photoresist is removed with an photoresist stripper.

See Exhibits 10 and 11 for a list of materials used during photolithography and etching processes. Wastes generated during the cleaning and etching processes include: RCRA listed F001, F002, F003, F004, and F005 depending on the concentration of the spent solvents and the mixture of spent halogenated and non-halogenated solvents; spent resist material; and wastewater containing metals (copper). Other wastes generated include organic vapors and acid fumes, spent developing solutions, spent resist material, spent etchant, spend acid solutions, and sludges from waste water treatment.

Resists	Photopolymer Developers	Photopolymer Strippers
Mylar	Isopropyl alcohol	Sodium hydroxide
Vinyl	Potassium bicarbonate	Potassium hydroxide
Photoresists	Sodium bicarbonate 1,1,1-Trichloroethane Amines Glycol ethers	Methylene chloride

Exhibit 10
Chemicals Used in Photolithography for Printed Wiring Boards

Source: Based on EPA DfE 1993: <u>Industry Profile and Description of Chemical Use for the</u> <u>Printed Wiring Board Industry:</u> Preliminary Draft.

Exhibit 11 Materials Used During Etching

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Ammonia	Cupric chloride	Nickel	Permanganates
Ammonium chloride	Hydrochloric acid	Nickel chloride	Sodium citrate
Ammonium hydroxide	Hydrofluoric acid	Nickel sulfamate	Sodium hydroxide
Ammonium persulfate	Hydrogen peroxide	Nitrate	Stannous chloride
Ammonium sulfate	Lead	Nitric acid	Sulfuric acid
Boric acid		Nitrogen	Tin
Carbon tetrafluoride		Orthophosphate	
Chlorine		Oxygen	
		Peptone	

Source: Based on EPA DfE 1993: <u>Industry Profile and Description of Chemical Use for the</u> <u>Printed Wiring Board Industry:</u> Preliminary Draft.

Step Four: Electroplating

Electroplating is a process in which a metal is deposited on a substrate through electrochemical reactions. Electroplating is required to build up the thickness and strength of the conducting layers to provide reliable electrical conductivity between inner layers or from one side of the PWB to the other. Electroplating can also protect against corrosion, wear, or erosion. This process involves immersing the article to be coated/plated into a bath containing acids, bases, or salts. The industry standard for this process is copper, although many are switching to direct metallization techniques according to DfE.

The **electroplating** process for PWBs usually begins with the copper laminate which is coated with a plating resist (**photolithography**), by stenciling, leaving the area exposed to form the circuit pattern. The resist prevents the conductive material from adhering to other areas of the board and forms the circuit pattern.

The PWB plating process typically uses as copper and tin-lead as plating materials, although silver, nickel, or gold can be used. Copper in a plating bath solution is deposited to a sufficient thickness, and a solvent or aqueous solution is applied to remove the plating resist. The copper coating forms interconnections between the layers and provides electrical contact for electronic parts mounted or assembled on the PWB surface. PWB manufacturers then typically electroplate a tin or tin-lead solder on the board to protect the circuit pattern during the following etching or stripping processes. An acid etch solution (ammoniacal, peroxide solutions, sodium persulfate, cupric chloride, or ferric chloride) removes the exposed copper foil, leaving the thicker copper plating to form the circuit pattern. Ammoniacal and cupric chloride are the primary etchants used by PWB manufacturers. Fluoroboric acid is used in the tin-lead plating process to keep the metals dissolved in the solution and to ensure a consistent deposition of the tin-lead alloy onto the circuit board.

After the plating bath, the board is **rinsed** with water, scrubbed, and then dried to remove the copper, spray etch solutions, and other materials. Rinsing ends the chemical reactions during plating and prevents contamination or dragout from being released in the next bath or rinse water (dragout is the plating solution that sticks to

parts after taken out of the plating bath). Dragout can occur in any bath step, not just in one plating bath. The tin-lead layer is generally removed and the panel is electrically tested for discontinuities in the electrical pathway and shorts. See Exhibit 12 for a list of materials used during the electroplating process.

Electroless Plating Processes					
Type of Plating	Electroplating Chemicals	Electroless Chemicals			
Copper	Copper pyrophosphate Orthophosphate Pyrophosphate Nitrates Ammonia Acid copper Copper sulfate Sulfuric acid	Hydrochloric acid Palladium chloride Stannous chloride Metallic tin pellets Sodium hydroxide Copper sulfate Formaldehyde			
Tin-Lead	Tin-Lead Fluoroboric acid Boric acid Peptone	Tin chloride Sodium hypophosphite Sodium citrate			

Exhibit 12		
Materials Used in Copper and Tin-Lead Electro- and		
Electroless Plating Processes		

Source: Based on EPA DfE 1993: <u>Industry Profile and Description of Chemical Use for the</u> <u>Printed Wiring Board Industry: Preliminary Draft</u>.

The primary RCRA hazardous wastes generated during plating include: photoresist skins, F006 sludge from plating wastewater treatment, D008, F007, and F008 from plating and etching; spent acid solutions, waste rinsewaters, spent developing solutions, spent etchant, and spent plating baths in the wastewater; organic vapors from spent developing solution and spent resist removal solution; and acid and ammonia fumes. According to IPC, photoresist skins or the stripped resist material are exempt from categorical F006 classification if the skins stripping is separate from electroplating and if the boards are rinsed and dried.

Step Five: Soldering Coating

Solder coating is used to add solder to PWB copper component before component assembly. Fabricators use several methods of solder coating, but all of them involve dipping the panel into molten solder. The solder, an alloy consisting of 60 percent tin and 40 percent lead, coats the pads and holes not covered by solder mask. The excess solder is removed with a blast of hot oil or hot air. However, the hot oil or hot air does not remove the solder that has formed a chemical (intermetallic) bond with the copper. The removal of the excess solder is called Òsolder leveling.Ó The

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most common process is hot-air leveling. According to *Printed Circuit Board Basics: Quick and Easy Guide*, final solder coating thicknesses of 50 to 1,200 microinches can be achieved with most solder-leveling processes. Solder is only applied to desired areas so there is no metal or Òobjectionable fluidÓ discharged to the wastestream, according to MCC. MCC considers it to be the most environmental friendly solder application method.

Step Six: Electrical and Mechanical Testing

A cross section is cut from a sample panel from each lot using a grinding process called **routing**, and the plated holes are examined with a photomicrograph. Individual circuit boards are cut out of panels that pass quality control. Routing generates dust which may contain copper, lead, or other metals plated to the panel, but the dust is recycled. Electrical tests, dimensional and visual inspections, and quality audits are performed to ensure compliance with customer requirements. Finally, the finished PWBs are packaged, labeled, and shipped to the customer which in most cases is the original equipment manufacturer (OEM) or contract electronic assembly company.

Step Seven: Printed Wiring Board Assembly and Soldering

After the PWBs are manufactured, the electrical components are attached during **assembly**. Adhesives are applied to the boards, and then the components are attached and soldered to the boards. Components are attached to the PWB by a process called **soldering**. There are several different kinds of soldering processes, including wave, dip, and drag. In wave soldering, the PWA is passed over the crest of a wave of molten solder, thereby permanently attaching the components to the board. A type of chemical known as "flux" is used before soldering to facilitate the production of the solder connection. Not only does flux clean the surface and remove oxidized material, it prevents oxidation from occurring during the solder process. After the solder has been applied, flux residue may be removed from the board. According to a leading PWB manufacturer, deionized water instead of CFCs (such as Freon 113) and trichloroethane (TCA), are now used to remove flux. Although the residue may not affect the PWB's performance, it may lower the board's cosmetic quality. After soldering, the board may be cleaned and dried. Many assemblies, however, are looking at no-clean soldering operations.

The wastes generated during assembly include: solder dross, post-solder scrap boards, filters, gloves, rags, and spent gaseous or semi-gaseous solvents from cleaning processes. The wastes that may be generated during soldering, flux application, and cleaning include: organic vapors and CFCs (although CFC usage will be eliminated by 1996); copper, lead, spent solvents, and spent deionized water into the wastewater; solder dross; and wastewater treatment sludge. Solder dross is primarily oxidized solder skin that forms on any molten solder exposed to oxygen and can be recycled off-site.

III.A.3. <u>Cathode Ray Tube Manufacturing</u>

Cathode Ray Tubes (CRTs) have four major components: the glass panel (faceplate), shadow mask (aperture), electron gun (mount), and glass funnel. The glass funnel protects the electron gun and forms the back end of the CRT. In response to electrical signals, the electron gun emits electrons that excite the screen. The shadow mask forms a pattern on the screen. The shadow mask itself is a steel panel with a mask pattern applied through one of several kinds of photolithography.

This section summarizes the manufacturing process for color CRTs. Information used to describe CRT manufacturing comes from a variety of sources such as MCC, EPA's Common Sense Initiative (CSI), Corporate Environmental Engineering, and EPA's Effluent Guideline Division. For this discussion, the process is grouped into six steps:

- ¥ Preparation of the glass panel and shadow mask
- ¥ Application of the coating to the glass panel interior
- ¥ Installation of the electron shield
- ¥ Preparation of the funnel and joining to the glass panel/shadow mask assembly
- ¥ Installation of the electron gun
- ¥ Finishing.

Color CRTs

Exhibit 13 presents the steps for manufacturing a color CRT. The names of the operations may vary by manufacturer, but the basic processing sequence is identical in all color CRT manufacturing facilities. Lead in CRT display components and end-of-life concerns have been the most significant environmental issues in CRT manufacturing.

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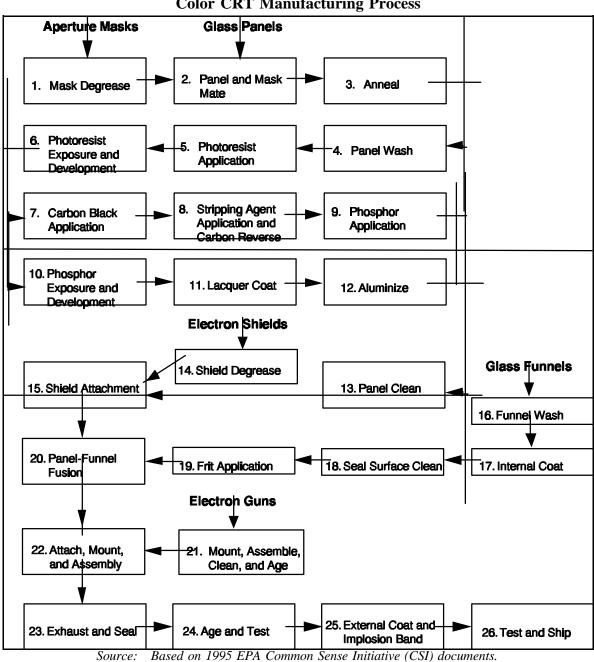


Exhibit 13 Color CRT Manufacturing Process

Step One: Preparation of the Panel and Shadow Mask

The shadow mask is constructed from a thin layer of aluminum steel (referred to as a flat mask) which is etched with many small slits or holes, and a metal frame that supports the flat mask. The shadow mask serves as a template for preparing a pattern on the glass panel surface. Shadow masks are commonly manufactured overseas and shipped to CRT manufacturers in the United States. The shadow mask is then **molded** to match the contour of the glass panel's interior surface and "blackened" in an oven to provide corrosion resistance. Finally, the shadow mask is **welded** to a blackened metal frame, usually steel, that provides support. Degreasing solvents and caustics are frequently used for **cleaning** the shadow mask assembly and production equipment. Oils are used for lubricating the press and other production equipment.

The front end glass panel is purchased from a glass manufacturer and shipped to the CRT manufacturer. Metal "pins," provided as part of the glass panel, are attached to the inside of the glass to serve as connection points for the shadow mask.

The shadow mask is carefully positioned inside the glass panel. Steel springs are then placed over the pins in the glass panel and attached to "hook-plates" or "clips" located on the mask assembly frame. With the glass panel and shadow mask assembly positions fixed in relation to each other, the springs are **welded** to the hook-plates. The glass panel and mask must remain as a matched pair through the remaining processes. The glass panel and shadow mask preparation operation frequently uses organic solvents or caustic cleaners for degreasing, oil for equipment maintenance, and oxidizers, such as hydrogen peroxide, for cleaning reclaimed masks.

Wastes generated during this step include spent solvents in the wastewater, vapors from solvent degreasing tanks, and waste glass from breakage.

Step Two: Application of Coating to Panel Interior

For the panel-mask to create images, a special coating is applied to the interior surface through a process called screening. Screening, the most complex part of the manufacturing process, is comparable to a photographic development process.

The screening operation begins with a **panel wash**. The mask is removed and the glass panel is washed to remove dust, oil, grease, and other contamination. The glass panel wash commonly uses acids and caustics followed by deionized water rinses for cleaning the glass.

The glass panel undergoes the **carbon stripe** process, which uses organic photoresist, chromate, deionized water, dilute acids and oxidizers, carbon slurry with binding agents, and surfactants to produce the black and clear striped pattern called the "black matrix." The clear areas will eventually be filled with color-producing phosphors. The glass panels are coated with a photoresist, which contains chromate (a toxic

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heavy metal compound) as a catalyzer. The panel is spun to even out the photoresist and then dried.

The shadow mask is re-inserted in the glass panel and a series of exposures are made on the panel surface using ultraviolet (UV) light in a **photolithography** process. The light passes through the mask openings to imprint the mask pattern on the photoresist. The mask also shadows the areas of the photoresist that will not be exposed. When UV light contacts the photoresist, polymerization occurs, and the exposed areas become less soluble in water than the non-exposed areas.

After the exposure, the shadow mask is removed and the glass panel is sprayed with water to remove the non-polymerized material. The imprinted pattern of exposed photoresist remains on the glass panel. The glass panel is then coated and developed again. The resulting image is essentially a "negative image" of the original photoresist exposure pattern.

During the **phosphor stripe** process, three phosphor colors (green, blue, and red) are used to make a color CRT and are applied using the same steps as the carbon stripe process. The phosphor stripe process uses various chemicals, including phosphor slurries containing metals (such as zinc compounds) and organic photoresists, chromate, deionized water, dilute oxidizers, and surfactants. The phosphor materials that are spun off the panels and removed in the developers are recovered and reclaimed either onsite or by a phosphor vendor. The reclaiming process involves the use of acids and caustics, chelating agents, and surfactants.

Two **coatings** are then added to the glass panel, which now has the black matrix and the three phosphor colors on it: lacquer (a wax-like layer) to smooth and seal the inside surface of the screen, and aluminum to enhance brightness. The panel is then ready to be joined to the back end of the CRT, known as the funnel. In preparation for joining, the panel edges must be **cleaned** to remove all traces of contaminants. A clean edge is critical to ensuring a good panel-to-seal connection in the finished CRT. The shadow mask and glass panel are reattached. Chemicals used in these processes include organic solvents and alcohol, caustics, silica-based coatings, aluminum, acids, ammonia, and deionized water. The material removed in the cleaning process is sent to a smelter to recover metals and sulfites.

Wastes generated during this step include: vapors from the lacquer area; wastewater containing deionized water, acids, oxidizers, carbon slurry, surfactants, chromate, phosphor solutions, chelating agents, caustics, organic solvents, alcohol, silica-based coatings, ammonia, zinc, and aluminum; process cooling waters, liquid wastes from precipitation, washing, filtration, and scrubber blowdown; lacquer wastes from spun off and over-sprayed lacquer; and lacquer remaining in lacquer containers.

Step Three: Installation of the Electron Shield

Most CRT manufacturers employ an internal **electron shield** to prevent stray electrons from reaching outside the screen area. Computer monitor CRTs often use external shielding, which is installed on the outside of the CRT's glass bulb. Before installation, the shields are cleaned with degreasing solvents or caustic cleaners. The internal-type electron shield is made of thin aluminum and is typically **welded** to the shadow mask assembly before the panel and shadow mask are connected with the funnel. Metal (steel) springs are also **welded** to the mask frame at this time. The springs provide an electrical connection between the mask and the funnel interior surface. Wastes generated from these processes include electron shield degrease wastewaters and metals from the welding.

Step Four: Preparation of the Funnel and Joining to Panel-Mask Assembly

The back end of the CRT (funnel) is purchased from a glass vendor and washed prior to use. The funnel is made of high lead content glass and the resulting wash water contains elevated lead levels. After the funnel is **washed**, the interior surface is **coated** with a black graphite coating which is a good electrical conductor and a nonreflective coating. The seal edge of the funnel is **cleaned** to facilitate bonding with the panel, and **frit** or **solder** glass is applied in a bead along the entire surface of the seal edge. The frit, approximately 70 percent lead, has the consistency of toothpaste or caulking. The viscosity of the frit is controlled by the addition of organic solvents. The frit serves as an adhesive to join the panel-mask assembly to the funnel.

After the frit is applied, the panel-mask assembly is connected to the funnel, and the whole glass package is placed in a positioning clamp to hold the two parts in place. The connected panel-mask and funnel assembly is then exposed to high temperatures in an oven to fuse the frit joint between the panel and funnel at the seal edges. The frit forms a strong bond between the two pieces of glass. During the **frit-seal fusion** process, the organic chemicals from the screening operation and in the frit are "burned out" of the CRT. The organic materials must "burn" cleanly to minimize any remaining residue. Wastes generated include wastewaters contaminated with spent black graphic, lead, and chemicals associated with the funnel wash, frit application, and seal surface cleaning. Wastes generated include frit contaminated clothing, instruments and utensil used to prepare the frit, unusable frit glass, and waste glass from breakage.

Step Five: Installation of the Electron Gun

Each CRT contains three guns: one dedicated to each of the phosphor colors used in the screen (red, green, and blue). To produce an electron gun, several metal components are **assembled** and loaded onto spindles to align the various elements. Glass parts are placed into fixture blocks and **heated**. When the glass reaches the proper temperature, the metal parts are embedded in the glass. The combination of metal parts and glass make up the gun. The guns are **cleaned** with organic solvents

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or caustic cleaners before they are mounted in the neck of the CRT funnel. Materials commonly found in the gun assemblies include metals, high lead glass stem (for electrical connection feed-through and exhaust purposes), ribbon connectors, and other manufacturer-specific parts.

The gun assembly is then inserted in the neck of the CRT funnel. The gun is aligned and the CRT funnel neck is **fused** to the gun by rotating the parts in front of open flame burners. An additional component is **welded** to the gun assembly to allow for removal of gases from the electron gun in subsequent steps. Wastes generated from this step include waste glass from breakage and wastewaters contaminated with spent organic solvents and caustic cleaners from mount cleaning.

Step Six: Finishing

The CRT "bulb" is still open to the atmosphere after the gun mount is sealed in the neck of the funnel. To complete the tube, the gases are removed by applying a vacuum to the bulb. Organic solvents are used to clean and maintain the vacuum pumps.

The bulb is "aged" by an electronic treatment applied to the gun or mount. The CRT is then coated with an external carbon black paint, and a metal band is placed around the outside of the panel with adhesives for implosion protection and safety. The band also provides mounting brackets for installing the CRT. The finished tube is tested in a high voltage testing station, and the CRT tested thoroughly to ensure that it meets all specifications before shipment. Each tube is packaged prior to shipment to the customer. Wastes generated from finishing processes include spent solvents and VOC emissions.

In some cases where the bulb face needs a special application, such as reference lines for an oscilloscope, a separate panel and funnel are used. A photoresist and mask are used to apply the reference lines on the panel. The single phosphor is applied in the same way as for a one-piece bulb, using a settling solution that contains potassium silicate and, usually, an electrolyte.

Tube Salvage

Cathode ray tubes may or may not be salvaged. Picture tube salvage operations reclaim spent or rejected picture tubes and return them to production. Salvage operation processes include a panel-funnel acid defrit, acid cleaning of panels and funnels (i.e., nitric acid), and cleaning of the shadow mask. These reclaimed components are returned to the process for reuse or are returned to the glass manufacturer for recycling. A product with knocks, scratches, chips, etc., is repaired. New necks are spliced onto funnels. Electron guns are usually discarded. Glass that cannot be used because of serious defects is recycled back to a glass plant directly or is sent off-site for cleaning and segregation before going to a glass plant.

CRT technology is a mature and efficient process; however, the use of a new technology called Flat Panel Displays (FPD) is becoming more common. FPDs offer certain environmental advantages over CRTs because of the tenfold reduction in glass used and substantial power savings. Existing performance deficiencies, such as poorer screen brightness and substantially higher prices, are limiting the widespread incorporation of FPDs into electronics products.

III.B. Raw Materials Inputs and Pollution Outputs

Outputs from the electronics and computer industry manufacturing processes affect the land, air, and water. Exhibits 14-16 describe the wastes generated during each manufacturing process.

Process	Air Emissions	Process Wastes (Liquids/Waste Waters)	Other Wastes (Solids/RCRA)
Crystal Preparation	Acid fumes, VOCs, dopant gases	Spent deionized water, spent solvents, spent alkaline cleaning solutions, spent acids, spent resist material	Silicon,
Wafer Fabrication	VOCs and dopant gases	Spent solvents, spent acids, aqueous metals, spent etchant solution, and spent aqueous developing solutions.	F003
Final Layering and Cleaning	Acid fumes and VOCs	Spent deionized water, spent solvents, spent acids, spent etchants, spent aqueous developing solutions, spent cleaning solutions, aqueous metals, and D007 (chromium).	Spent solvents
Assembly	VOCs	Spent cleaning solutions, spent solvents, aqueous developing solutions, and P & U wastes.	Spent epoxy material and spent solvents

Exhibit 14 Semiconductor Pollution Outputs

Exhibit 15 Printed Wiring Board Pollution Outputs

Process	Air Emissions	Process Wastes (Liquids/Waste Waters)	Other Wastes (Solids/RCRA)
Board Preparation	Particulates, acid fumes, and VOCs	Spent acids and spent alkaline solutions	Sludge and scrap board material
Electroless Plating		Spent electroless copper baths, spent catalyst solutions, spent acid solutions	Waste rinse water and sludges from waste water treatment

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Imaging	Organic vapors and acid fumes	Spent developing solutions, spent resist material, spent etchants, spent acid solutions, and aqueous metals	F001-5, depending on concentration and mixture of solvents. Sludges from waste water treatment
Electroplating	Acid fumes, ammonia fumes, and VOCs	D008 (lead), D002, D003, spent etchants, spent acid solutions, spent developing solutions, spent plating baths	F006, F007, and F008

Process	Air Emissions	Process Wastes (Liquids/Waste Water)	Other Wastes (Solids/RCRA)
Solder Coating	VOCs and CFCs		
PWB Assembly And Soldering	VOCs and CFCs	Metals (nickel, silver, and copper), D008 (lead), flux residue, spent deionized water, spent solvents	Solder dross, scrap boards, filters, gloves, rags, waste water treatment sludge

Exhibit 15 (cont'd) Printed Wiring Board Pollution Outputs

Exhibit 16				
Cathode Ray Tubes Pollution Outputs				

Cathode Ray Tubes Tonution Outputs					
Process	Air Emissions	Process Wastes (Liquid/Waste Waters)	Other Wastes (Solids/RCRA)		
Preparation of the Panel and Shadow Mask	Solvent vapors	Spent solvents	Glass (lead) from breakage		
Application of Coating to Panel Interior	Vapors from lacquer area	Spent photoresists, deionized water, acids, oxidizers, carbon slurry, surfactants, chromate, phosphor solutions, chelating agents, caustics, solvents, alcohol, coatings, ammonia, aluminum, and process cooling waters	Lacquer wastes		
Installation of Electron Shield		Electron shield degrease and metals			
Preparation of Funnel and Joining to Panel-Mask Assembly		Funnel wash, seal surface cleaning, and frit application wastewaters	Frit contaminated clothing, instruments, utensils, unusable frit glass (lead), glass (lead) from break-age		
Installation of Electron Gun		Spent solvents and caustic cleaners	Glass from breakage		
Finishing	VOCs	Spent solvents			

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III.C. Management of Chemicals in Wastestream

The Pollution Prevention Act of 1990 (EPA) requires facilities to report information about the management of TRI chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in Section 8 of the TRI reporting Form R beginning with the 1991 reporting year. The data summarized below cover the years 1992-1995 and are meant to provide a basic understanding of the quantities of waste handled by the industry, the methods typically used to manage this waste, and recent trends in these methods. TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention compliance assistance activities.

While the quantities reported for 1992 and 1993 are estimates of quantities already managed, the quantities reported for 1994 and 1995 are projections only. The EPA requires these projections to encourage facilities to consider future waste generation and source reduction of those quantities as well as movement up the waste management hierarchy. Future-year estimates are not commitments that facilities reporting under TRI are required to meet.

Exhibit 17 shows that the electronics/computer industry managed about 122 million pounds of production-related waste (total quantity of TRI chemicals in the waste from routine production operations) in 1993 (column B). Column C reveals that of this production-related waste, 44 percent was either transferred off-site or released to the environment. Column C is calculated by dividing the total TRI transfers and releases by the total quantity of production-related waste. In other words, about 81 percent of the industry's TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns D, E and F, respectively. The majority of waste that is released or transferred off-site can be divided into portions that are recycled off-site, recovered for energy off-site, or treated off-site as shown in columns G, H, and I, respectively. The remaining portion of the production-related wastes (6.7 percent), shown in column J, is either released to the environment through direct discharges to air, land, water, and underground injection, or it is disposed off-site.

Α	В	С	D	Е	F	G	Н	Ι	J
	Production Related Waste	% Reported as Released		On-Site			Off-Site		Remaining Releases
Yea r	Volume (10 ⁰ lbs.)	and Transferred	% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated	and Disposal
1992	121	49%	8.27%	0.41%	70.75%	3.21%	3.96%	4.83%	8.52%
1993	122	44%	9.38%	0.20%	72.12%	3.41%	3.77%	4.41%	6.70%
1994	121	Ñ	7.63%	0.13%	74.99%	4.33%	3.88%	3.58%	5.44%

Exhibit 17 Source Reduction and Recycling Activity for SIC 36

	1995	129	Ν	8.87%	0.59%	74.45%	4.61%	3.65%	3.04%	4.78%É
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