Eliminating VOCs and CFCs at the AT&T Printed-Circuit Board Headquarters

Louis S. DiMarino, Jr.
Philip A. Joseph
Earl J. Sherwood

In the early 1980s, the Richmond Works—now known as the AT&T Printed-Circuit Board Headquarters, Richmond, Virginia—began efforts to reduce and/or eliminate environmentally damaging chemicals then in common use in the printed-circuit board industry. As a result, it was one of the first AT&T manufacturing facilities to exceed the company's environmental goals to reduce toxic air emissions and phase out the use of chlorofluorocarbons.

Introduction

The AT&T Printed-Circuit Board Headquarters—Richmond, Virginia (hereafter referred to as Richmond), is one of the largest printed-circuit board manufacturing facilities in the world. Its products include multilayer boards, double-sided rigid boards, and backplanes (connectorized printed-circuit boards). These products become part of equipment that ranges from telephone handsets to digital switching systems and computers. Traditionally, the manufacture of these products required large quantities of volatile organic compounds (VOCs) and chlorofluorocarbons (CFCs). (See Panel 1 for definitions of abbreviations, acronyms, and terms.)

During the past ten years, Richmond launched environmental programs that have placed the facility among AT&T's leaders in the campaign to reduce toxic emissions and eliminate CFCs. The programs have virtually eliminated the need for VOCs in the manufacture of circuit boards and have removed CFCs from the manufacturing process.

Converting to Aqueous-Based Production

For most of the past twenty years, circuit board manufacturers relied heavily on chlorinated solvents for many of their operations. These VOCs were used primarily to develop and remove photosensitive polymer films, clean flux residues, and develop permanent covercoat polymer films. The photopolymer materials were solvent-based systems that required the use of 1,1,1-trichloroethane and methylene chloride. Rosin fluxes, used as an aid in fusing solder to finished circuit boards, were removed with 1,1,1-trichloroethane.

Since the early 1970s, AT&T has looked for ways to replace these solvents with aqueous-based materials. The earliest efforts to introduce aqueous systems preceded construction of the Richmond site. Aqueous-based photopolymers that are used to define circuit patterns were first tested at AT&T's Greensboro, North Carolina, Plant, Richmond's predecessor. Aqueous systems used in the early 1970s by smaller shops in the printed-circuit board industry were more accurately called "semi-aqueous" because short-chain organic solvent additives were still employed. Small shops used these semi-aqueous systems to avoid the more capital-intensive solvent systems, which required distillation units, storage tanks, evaporators, dryers, etc. However, for large printed-circuit shops with solvent recovery equipment, semi-aqueous systems were not cost-effective. Also, the additives used in the semi-aqueous systems had suspect toxicological effects. A few fully aqueous systems were available, but they could not provide the operating windows (wide range of operating conditions) and process capabilities needed for the increasingly difficult printed-circuit designs.

The electronics industry's rapid growth in the early 1980s accelerated the drive to replace solvent systems. The investment in solvent recovery equipment needed to support expanded production had become cost-prohibitive. In the late 1970s, research at AT&T Bell Laboratories and by proprietary chemical vendors yielded the first aqueous fluxes. Hot water mixed with a mild detergent easily removes these aqueous fluxes from the circuit boards. In 1980, Richmond imple-

Table I. Timeline of Aqueous-Based Process Technology

Year implemented	Process
1980	Aqueous flux
1983	Innerlayer process—aqueous liquid photoimageable system—Accutrace
1987–1988	Primary imaging process—aqueous dry film—Dynachem HG
1988–1989	Secondary imaging process—PDD liquid film or du Pont 8130 dry film

mented its first aqueous flux and stopped using rosin fluxes (see Table I).

Multilayer Board Expansion. In 1982, Richmond was enlarged to increase multilayer board production. An important part of this expansion was the conversion of the innerlayer imaging process from a solvent dry film photopolymer system to an aqueous system. (Innerlayers, which are very thin printed-circuit boards, are laminated together in various combinations to produce multilayered circuit boards.) A partnership with W. R. Grace Company was established to develop an aqueous liquid photoimagable system, now known as Accutrace®. (Accutrace is a registered trademark of W. R. Grace Company.) Implemented in 1983, the new aqueous system significantly increased product yield and production efficiency and avoided large capital expenditures for solvent recovery equipment.

Hard-Board Process. Several hard-board (multilayer and double-sided rigid) operations continued to require chlorinated solvents (VOCs). Throughout the 1980s, more federal, state, and local restrictive environmental regulations were imposed on permissible levels of toxic organics in fugitive emissions, wastewater effluent, and in shop operating atmospheres. The regulations imposed significant pressure on solvent photopolymer vendors and users to find fully aqueous-based alternatives. Richmond tested aqueous photopolymers at

different times during the 1980s. A 1984-85 review of primary imaging polymers showed that the Dynachem® HG photopolymer had good circuitry resolution (could resolve clearly defined circuit traces) and an operating window and process capability that could support the printed circuit technology in use at that time. (Dynachem HG is a registered trademark of Morton International, Inc.)

Primary Imaging. In 1985, Richmond launched a program to convert the hard-board primary imaging operation from a solvent-based to an aqueous-based imaging process (see Table II). The program, which involved conversion of the existing photopolymer application, print exposure, developing, and stripping processes, was complicated by the incompatibility of the new aqueous-based polymers with chemical processes that had to be applied before and after the imaging operation. All plating equipment had to be modified for new acid-based cleaning chemistries that could be used with both solvent- and aqueous-based polymers. All production equipment and processes had to be modified with a minimal effect on day-to-day production.

The first step toward the use of an aqueous primary imaging process was the introduction of a new electroless copper-plating bath. A thin deposit of copper must be plated into the through-holes of printed-circuit panels (a printed-circuit panel may contain more than one printed-circuit board) to provide electrical continuity from one side to the other. Because aqueous photopolymers require more aggressive chemical processing in subsequent operations, the copper-plate's thickness in the through-holes had to be increased. High-deposition baths are supposed to yield an electroless copper deposit thick enough for aqueous processing.

In the late 1970s, attempts to introduce a high-deposition, electroless copper-plating bath in Richmond

Table II. Changes in the Hard-Board Process

Process steps	Solvent process	Aqueous process
1. Raw material selection 2. Hole drilling 3. Electroless copper plating	Low-deposition plating	High-deposition plating
Primary imaging		
4. Pumice scrubbing 5. Photoresist lamination 6. Printing 7. Developing	Solvent-based film 1,1,1-trichloroethane	Aqueous-based dry film (Dynachem HG) Sodium carbonate
8. Electrolytic copper plating 9. Resist removal 10. Ammoniacal etchant bath	Alkaline cleaner Methylene chloride	Acidic cleaner and a microetchant Sodium hydroxide
Secondary imaging		
11. Solder mask application 12. Printing 13. Developing	Solvent-based film 1,1,1-trichloroethane	PDD liquid film and du Pont 8130 dry film Sodium carbonate
14. Solder levelling 15. Board routing 16. Final testing	Rosin flux	Aqueous flux

had failed because of the poor chemical stability of such dynamic chemistry. During January 1987, a new electroless bath was developed for Richmond by MacDermid, Inc. The bath provided the needed thickness of copper and the chemical stability necessary for a high-deposition electroless bath. By June 1987, the new bath was in use throughout the plant.

After the printed-circuit boards have been through the electroless copper-plating operation, they move to the primary imaging operation. This is actually a series of operations in which the boards are scrubbed, laminated with an aqueous photopolymer (Dynachem HG), and exposed to the printed-circuit image in an ultraviolet printing unit. The unexposed portions of the polymer are then dissolved ("developed") in an aqueous solution of sodium carbonate. At this point, a polymer film covers all areas of the board that will not contain circuitry.

Trace residues of organics and oxides may remain on the copper surface after the aqueous photopolymer has been dissolved. These must be cleaned before additional copper is deposited electrolytically on the board. Before aqueous polymers were introduced, the chemical cleaning steps of the electrolytic copper-platers incorporated an alkaline bath in which a small amount of copper was electrolytically removed from the surface and holes. Because the aqueous polymers were also removed by this bath, a

new cleaning chemistry had to be developed.

The new cleaning chemistry had to be compatible with both solvent and aqueous polymers and could not have an adverse effect on production capacity. However, the new chemistry required two steps to clean the circuit boards as thoroughly as the single-step alkaline cleaner. In addition, the aqueous cleaning process was removing two to three times more copper than its alkaline-based predecessor. Not all plating equipment at Richmond had enough spare tanks to permit addition of this new chemistry. In one year, each plater was removed from production, modified, and reinstalled with all the necessary physical changes required for the new chemistry.

After two years of preparation, all production lines were running with the compatible chemistry in place. By that time, new aqueous developing and stripping equipment, drain services, chemical supply systems, and waste treatment had also been installed. After the aqueous polymer was introduced late in 1987, the aqueous process window was found to be narrower than expected and process limitations became apparent. Photopolymer lamination and printing equipment now had to be modified. By June 1988, most of the hard-board solvent-based process had been replaced by the aqueous system.

Secondary Imaging. The remaining solvent-based polymer films were used during the secondary imaging

(solder mask or covercoat) process. This process used a dry-film photopolymer and involved an imaging operation similar to that used for primary imaging. However, conversion to an aqueous-based material was complicated by the need to meet the surface insulation resistance standard set by Bell Communications Research (BELLCORE), as well as by the needs of individual customers' soldering operations.

Converting to an aqueous solder mask process encountered another obstacle. Circuit board production at Richmond had as many as five solder masks—two dry films and three screen inks—in the production stream at any one time because of differing requirements established by designers or customers. To simplify the conversion, the number of masks had to be reduced to a more reasonable number.

The decisions needed to convert the solder mask operation were complicated by the many available process alternatives. In some instances, customer or designer requirements precluded the use of some aqueous films. Also, Bell Laboratories and various solder mask vendors were working to develop a fully aqueous, liquid solder mask. After a careful economic analysis of the different solder mask technologies, a multi-track strategy was adopted. Three solder mask technologies would be pursued: screen printing, an aqueous dry film, and an aqueous, photodefinable liquid film.

Several dry films were tested for surface insulation resistance and solderability, but no film met the surface insulation resistance requirement. The problem was due to inadequate rinsing after the aqueous developing step. The rinsing portion of the aqueous developer was redesigned, and a dry film solder mask (produced by E. I. du Pont de Nemours) that could meet the surface insulation resistance standard was selected. However, the rinse uses large volumes of water.

Research throughout the 1980s by Bell Laboratories resulted in an aqueous-based, photodefinable dielectric (PDD) liquid film. Implementation of this material involved a lengthy customer approval process to assure product reliability. By the end of 1989, all solvent-based covercoat operations at Richmond had been converted to the aqueous-based solder masks.

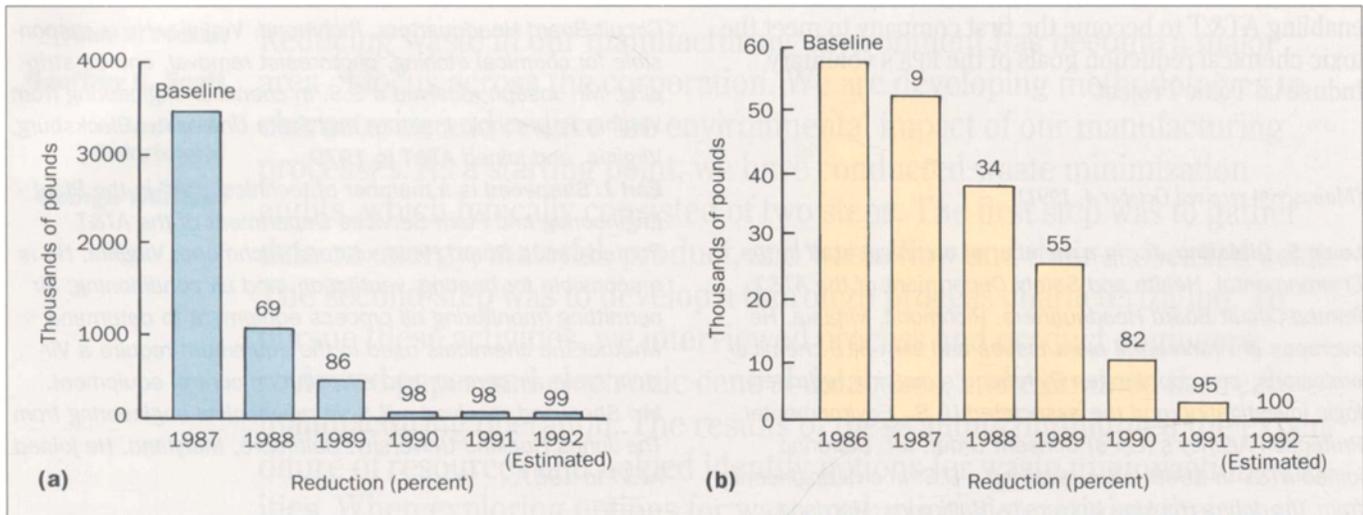The decade-long effort to convert from solvent-based manufacturing to aqueous-based manufacturing required a high level of motivation, as well as great flexibility, from Richmond's personnel. During that time, they dealt not only with aqueous-based materials that were technologically inadequate, but also with expanding production requirements, corporate and local restructuring resulting from divestiture, and increasingly restrictive regulatory requirements. The final elimination of all solvents represented a collective effort by everyone at Richmond. The extent and depth of the necessary changes involved virtually every aspect of the plant's operation. The effort required close support and cooperation by the various chemical and polymer film vendors before, during, and after the conversion phases. Work that began with the conversion has resulted in closer ties to Richmond's chemical and polymer film vendors. In turn, these ties have continued to yield dividends in process improvement and technological advancements. This effort enabled Richmond to reduce VOC emissions by 4.6 million pounds per year from the peak year 1985.

Eliminating CFCs in the Manufacturing Process

The other area in which Richmond implemented changes to improve the environment was the elimination of CFCs in the manufacturing process. Since 1986, Richmond has reduced its annual use of CFCs regulated by the Montreal Protocol from 57,800 pounds to total elimination during the last half of 1991. (The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer calls for a 50-percent reduction from 1986 rates of CFC consumption by July 1, 1998. To date, the protocol has been ratified by 59 nations.) CFC reductions were first made through conservation. Now, substitutions or process change has completely eliminated the need to use CFCs in the manufacturing processes.

The two areas where initial conservation took place were degreasing in the Final Mechanical Shop and the cleaning of artwork.

- A CFC-113 degreaser was used to clean small circuit boards in the final mechanical process. The equipment had a vapor trap comprised of a set of cooling coils fed by a self-contained refrigeration unit and wrapped around the top of the degreasing tank. The refrigeration unit operated only when the degreaser was in use. Studies showed that even though the tank had an air-tight closure, the CFC-113 still vaporized and leaked out when the equipment was not in use. By running the refrigeration unit continuously, the loss

(a) Baseline 1987; 1988: 69; 1989: 86; 1990: 98; 1991: 98; 1992 (Estimated): 99
Reduction (percent)

(b) Baseline 1986; 1987: 9; 1988: 34; 1989: 55; 1990: 82; 1991: 95; 1992 (Estimated): 100
Reduction (percent)

Figure 1. (a) The percent by which toxic air emissions were reduced at Richmond from 1987 to 1991. (b) The percent by which CFCs were reduced at Richmond from 1986 to 1991. Projections are included for 1992.

of CFC-113 was substantially reduced.

- During the production and use of artwork, CFC-113 was used to clean the artwork. By changing the type of applicator and the method of cleaning the artwork, Richmond reduced CFC usage substantially.

 The next step was to investigate process changes or materials that could be substituted for CFC-113 in the above operations, as well as in other operations that use CFCs at the plant.

- The Final Mechanical Shop now cleans small boards using a water-based ultrasonic cleaner, thereby eliminating the need for the CFC-113 degreaser.
- After investigating several different materials for cleaning artwork that were not cost-effective (methyl alcohol and isopropyl alcohol), a heptane-based film cleaner was found to be the best overall cleaner and is now being used.
- In the hard-board print process, a combination of mechanical cleaning rollers and a heptane-based film cleaner are now used. The artwork is run through the mechanical cleaner and then cleaned with the film cleaner. In the Model Shop, a hand-held cleaning roller is now used to clean the artwork.
- Before drill spindles were rebuilt, they were cleaned in

a degreaser that used CFC-113. An aqueous-solution substitute was tested and has now replaced the CFC-113.
- Isopropyl alcohol has replaced the CFC-113 mold release now used in the Multilayer Stack-up/Lamination Shop.

These are just a few of the substitutions and process changes that were made at the Richmond Printed-Circuit Board Headquarters to eliminate CFCs from its manufacturing processes.

Conclusion

 The elimination of three chemicals —1,1,1-trichloroethane, methylene chloride, and CFC-113—will make it possible for Richmond to reduce total SARA 313 emissions by more than 3.5 million pounds per year from the initial base year of 1987 and CFC usage by more than 57,000 pounds per year from a 1986 base year. These reductions of 99 percent (see Figure 1a) and 100 percent (see Figure 1b), respectively, far exceed the Corporate Environmental Goals. Richmond was one of the first AT&T locations to exceed the Corporate 1995 total toxic air emission reduction goal of 95 percent and to exceed, by several years, the Corporate goal of 100-percent CFC phaseout by 1994. Richmond's work in eliminating CFCs helped AT&T be recognized at the President's Environmental and Conservation Challenge Awards with a Presidential Citation. These reductions also far exceed the EPA's 33/50 Program and were instrumental in

enabling AT&T to become the first company to meet the toxic chemical reduction goals of the EPA's voluntary Industrial Toxic Project.

Louis S. DiMarino, Jr., is a member of technical staff in the Environmental, Health and Safety Department of the AT&T Printed-Circuit Board Headquarters, Richmond, Virginia. He oversees environmental plant issues and SARA 313 chemical emissions, and coordinates Richmond's ongoing hydrogeologic investigation and the associated U. S. Environmental Protection Agency's (EPA's) Consent Order. Mr. DiMarino joined AT&T in 1969, after receiving a B.S. in civil engineering from The Johns Hopkins University, Baltimore, Maryland.

Philip A. Joseph is a member of technical staff in the Chemical Internal Business Unit Department at the AT&T Printed-Circuit Board Headquarters, Richmond, Virginia. He is responsible for chemical etching, photoresist removal, and tin stripping. Mr. Joseph received a B.S. in chemical engineering from Virginia Polytechnic Institute and State University, Blacksburg, Virginia, and joined AT&T in 1979.

Earl J. Sherwood is a member of technical staff in the Plant Engineering and Plant Services Department of the AT&T Printed-Circuit Board Headquarters, Richmond, Virginia. He is responsible for heating, ventilation, and air conditioning; air permitting (monitoring all process equipment to determine whether the chemicals used in the equipment require a Virginia state air permit); and air pollution control equipment. Mr. Sherwood received a B.S. in mechanical engineering from The Johns Hopkins University, Baltimore, Maryland. He joined AT&T in 1967.