Electroless Nickel: Past, Present And Future

By

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During the last fifty years, the growth of electroless nickel has been rapid and exciting. That which began as a laboratory curiosity during World War Two, flourished and became the fastest growing segment of the metal finishing industry in the 1970's and 1980's. Today, electroless nickel has become a more mature product and its growth of has slowed. It still has great potential, however, as new coatings and applications are developed.

This paper describes the evolution of electroless nickel and how the present industry grew from this process. The state of today's market, including its size, the types of baths used, and the types of the parts and substrates plated, is also discussed. In addition, some thoughts on the future direction of the industry are provided.

THE PAST

The development of electroless nickel can be divided into three stages of evolution. It began with the commercialization of the coating in a few, large, consolidated facilities. Its development continued with the introduction of easier to operate baths and their growing use in traditional plating facilities. Finally the industry's evolution culminated for the present with electroless nickel coatings designed for specific applications.

Commercialization. The reduction of nickel by hypophosphite had been observed as early as 1844 by A. Wurtz[1] and again by Francois Roux[2] in 1913. Abner Brenner and Grace Riddell of the National Bureau of Standards, however, are generally credited with the discovery of electroless nickel during World War II.

Roux produced shiny, adherent deposits, and was granted a patent[2] in 1916 for the deposition of nickel on aluminum and other metals. His results, however, did not lead to any commercial application, because the reaction could not be controlled and because his solutions always decomposed. Accordingly Roux's patent and his coating were soon forgotten.

In 1944, Brenner and Riddell discovered electroless plating accidentally, without any knowledge of the previous studies. They were investigating the use of reducing agents in a new process for electroplating the bore of gun barrels. When sodium hypophosphite was added to the bath, they were surprised that the outside plated, and that the cathode efficiency was greater than 100 percent. The researchers soon realized, however, that chemical reduction had occurred and that they had discovered a new process[3].

Brenner and Riddell continued to study this new type of plating for several years and published their results in 1947[4]. A patent for the process was awarded to them in 1950[5]. After the original results were published, several companies began investigating the possible commercial uses of the process. Among these were GM Allison (which developed the Ni-Chem process), Curtiss Wright, Eastman Kodak, Dow Chemical (the Dow process), GE Gas Turbine, North American Aviation, American Locomotive (the Alcoplate process), and the General American Transportation Company (generally called GATX after the insignia on their rail cars)[6]. This work continued through the 1940's and early 1950's.

GATX was primarily responsible for the commercialization of electroless nickel. At the time of the announcement of Brenner's discovery, they were actively investigating cheaper alternatives for the nickel cladding in some of their tank cars. They had considered electroplating, but concluded that it was impractical for their application and too expensive. Electroless nickel, however, appeared ideally suited for inside plating and especially for tank cars[7].

After several years of careful research, Gregoire Gutzeit and his group at GATX developed a completely new plating bath and installed a pilot plating line in their East Chicago plant. The bath, which they named Kanigen (for catalytic nickel generation) was a significant improvement over that proposed by Brenner[7]. It was stable, had a long life, plated at a rate of one mil/hr, and was inexpensive to make. GATX received 40 different patents for this bath and its improvements over the next decade.

Based upon the successful operation of the pilot line, GATX built two large production plants in 1953, one for general work in East

Chicago and another specifically for tank cars near Sharon, Pennsylvania. Later a third shop was opened in Los Angeles. During the next eight years, over 1,200 tank cars were plated at Sharon, and all types of parts were plated at the other plants[6].

During the 1950's, GATX actively promoted their Kanigen electroless nickel process and its deposit for use by other industries. They conducted extensive research on the properties of the coating, and published many articles to document its advantages for potential users. GATX also ran a full page advertisement in the New York Times to introduce the coating to American industry. The results of their research were the basis of most that was known about electroless nickel for the next 25 years.

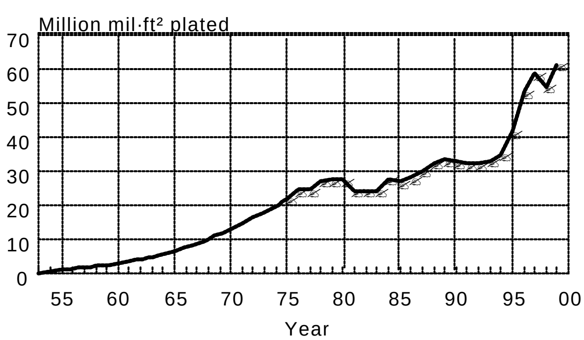
GATX not only became a large job shop, but they also licensed their process to other commercial platers and captive operations, both in the USA and overseas. Some prominent licensees were IBM, the Atomic Energy Commission's Oak Ridge National Laboratory, Gillette[6], and Fescol and Seurec in Europe. Worldwide there were approximately 25 licensees of Kanigen technology[8]. Effectively all of the growth of electroless nickel during the 1950's was due to this process, and its originators at GATX.

Expansion. By the early 1960's, the traditional metal finishing suppliers had taken notice of electroless nickel coatings. Abe Krieg, from Gutzeit's original research group, had joined Shipley, and in 1961 introduced their first formulation. Concurrently, Enthone obtained a license from GATX to use Kanigen's stabilizers and began producing their own solutions. Enthone had been an early proponent of this technology and aggressively fostered its use in plating shops. Soon afterwards, MacDermid and several smaller suppliers also entered the market[8].

The immediate thrust of the suppliers was to make the solutions more easily operated by traditional platers. They especially wanted the baths to operate in simple, stand alone tanks, and to be replenished by over the side additions during operation.

GATX and its Kanigen licensees were still a powerful force in the market during the 1960's and early 1970's. The growth of the industry, however, was due more to the metal finishing suppliers. They produced *plater friendly* baths, placed them into many job shops, and made the coating available to more users. Consequently, the growth of electroless nickel increased rapidly. By the mid 1970's, the growth rate of the industry had doubled over that of the previous decade. This is illustrated by Figure 1[9], which shows the volume of electroless nickel plated during the last forty-five years.

Figure 1
Electroless Nickel Plating in North America



Unfortunately, however, the industry's growth during this period was not matched by an increase in its knowledge. Too little work was done to characterize electroless nickel coatings and their uses. In the United States, the suppliers' research usually was directed toward bath operation and that conducted by users often was not published. The lessons which had been learned by GATX were not available to non Kanigen facilities. As a result, many new electroless nickel platers lacked the information to do their jobs properly, and there were some bad applications. These failures affected the reputation of the entire industry and left many user engineers reluctant to try the coating.

Specialization. In about 1973, the industry began to change again. A new metal finishing company, Elnic, had begun promoting the use of high phosphorus electroless nickel coatings for more demanding applications. Elnic's entry into the market, happened to coincide with the expanding need of oil and gas producers for longer lasting methods of combating corrosion. As the demand for energy and its cost were rising rapidly, the producers were beginning to explore in more aggressive environments, and to try to improve the reliability of their equipment.

As these users, and their equipment suppliers, began to realize that this *improved* electroless nickel could solve some of their problems, they begin using increasing amounts. By 1980, most valve and oil tool manufacturers were specifying electroless nickel coatings extensively, and several had installed their own in-house plating lines.

By the early 1980's, the established metal finishing suppliers, had developed their own baths for high phosphorus deposits, and had begun to promote their use. Concurrently, the industry began studying the coating again to try to confirm its benefits and encourage its growth. Both the American Electroplaters Society and Products Finishing Magazine established forums for the results of these studies. In addition, some suppliers began programs of seminars and short courses to help educate users and platers.

The 1970's were the emotional heyday of the electroless nickel industry. Sales of the coating were increasing at an annual rate of 10 to 15 percent, and electroless nickel was thought to be one hope for an otherwise declining metal finishing industry. This growth is also illustrated by Figure 1.

Both domestic manufacturers of sodium hypophosphite had expanded their plants to ready themselves for the expected rise in electroless nickel sales. There was much excitement among suppliers, platers and users alike, and the World Electroless Nickel Society (called WENS) was formed to unite these groups in promoting the coating. Unfortunately this excitement was not to be long lasting.

Decline. In 1980 and 1981 two outside influences came together to undermine electroless nickel's prominence and its sales in the USA. The first was the collapse of the petroleum market. As the price of crude oil fell from more than $30 per barrel to less than $20, so did the need for additional output, production equipment, and plated components.

The second change was not as sudden, but was far more damaging. This change was the progressive loss of component manufacture from North America to offshore locations, especially in the Far East. As these facilities left the United States, so did their need for electroless nickel coatings.

Together, these two factors caused a severe retrenching of the industry. Within 12 months, the amount of electroless nickel plating in the USA declined by more than 10 percent. Some platers, however, lost one half their sales. For many, the knowledge that electroless nickel was not immune to market swings, and would not always provide growth, was more harmful than the loss of their markets. This knowledge caused the industry to lose its sense of invulnerability.

The decline would have been even more severe if rigid memory disks had not been commercialized. Hard disks, along with the rapid growth of personal computers, produced a new market for electroless nickel and offset some lost business. Without the introduction of this new technology, the decline of electroless nickel production in 1981 and 1982 would have been twice or perhaps three times as severe.

These lost sales, combined with increasingly more demanding regulations from the Environmental Protection Agency, had a pronounced effect upon platers. Across the country, metal finishers had to decide whether to invest in expensive waste treatment systems to keep declining sales, or to simply leave the market. Many chose the later course. It has been estimated that 5,000 metal finishing companies were at work in the United States in 1981. By 1987, however, the industry had declined greatly and had only about 4,000 members[10]. Today the total number of finishers in the USA and Canada may be as low as 3,500.

Nickel-Boron Coatings. During the 1950's, coatings reduced using sodium borohydride or its derivatives were being studied independently by Farkenfabriken Bayer in Germany and by DuPont in the United States. The first patents for these coatings were issued in 1955, but it was not until 1963 that commercial plating was began.

The first plant was the Nibodur facility at Paul Anke AG in Essen, Germany. It was followed shortly by others in East Germany and the Soviet Union. By 1970 there were 10 operating plants in Europe with a total capacity of 10,000 liters (2,600 gallons)[11]. This process produced coatings containing about 5 percent boron and 5 percent thallium, which were notable for their high hardness and wear resistance.

By the middle 1970's the Nibodur process was responsible for approximately 10 to 15 percent of the electroless nickel plating in Germany[12]. By the 1980's, however, waste treatment concerns and regulations had forced many of these operations to close or to convert to nickel-phosphorus technology[13].

One similar process also opened in the United States in the early 1980's. This was the Nibron facility at Southeastern Coatings (Secoa, now Pure Coatings) in Florida. The Nibron process was based upon DuPont technology, but also used sodium borohydride as its reducing agent and produced high boron and thallium coatings. Secoa developed several applications for it in the aerospace industry, where of its high wear and temperature resistance were useful. A competitive plant later opened in Indianapolis, but ceased operations in 1990. The Pure facility is now the only operating borohydride plant in North America.

Also in the 1960's, DuPont commercialized its Nibel process, which used dimethylamineborane (DMAB) as its reducing agent. This process usually produced coatings containing less than 1 percent boron without other alloying agents. The deposits had excellent conductivity and solderability and found uses in many electronic applications.

While DuPont subsequently left metal finishing, DMAB reduced electroless nickel processes were continued by Allied Kelite and Shipley. Because of their high cost, however, the growth of these coatings was slow and usually limited to alternatives to precious metals. Together, borohydride and DMAB reduced coatings represent less than 1 percent of today's electroless nickel market in North America.

THE PRESENT

Since 1983, there has been a steady resurgence in electroless nickel plating, both in the job shop and captive segments, which has driven total sales to levels greatly surpassing that of 1980. While, the increasing importance of personal computers and their hard disk drives has provided the largest part of this growth, there were other contributors.

The strength of the worldwide economy in the 1980's created a general need for manufactured goods and for plated components. Rising defense spending during the cold war drove the aerospace and electronics sectors to new heights of production and increased their use of electroless nickel coatings.

The slow revival of the oil and gas industry since 1985 also helped the recovery of electroless nickel. During the last few years, although the number of active production rigs has stayed very low, manufacture of valves and tools has more than doubled. Together these factors have produced an annual growth rate of about 7 percent for the industry during the late 1980's.

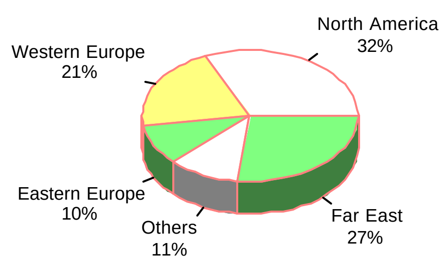
Because of the success of high phosphorus coatings, suppliers and users began looking at other alloys and types of electroless nickel coatings which might better suit specific applications. Boron based coatings, various ternary alloys, mineral and polymer composites, and alternate phosphorus contents were all considered. Of these, so far only Teflon® composites and low phosphorus coatings have shown any significant growth.

The recession beginning in 1990 caused the electroless nickel industry to again stagnate. Sales of coatings in North America through 1993 were flat at about 32 million mil-ft² per year. There were no specific causes for this slowdown, only the general sluggishness of the world economy. With the recovery beginning in 1992, sales of electroless nickel again began to grow rapidly, driven primarily by the ever increasing sales of personal computers. Since 1994, the growth rate of the industry has been greater than 10 percent. Today, the annual sales of electroless nickel coatings exceeds 60 million mil-ft². This increase is also illustrated by Figure 1.

World Market. Historically, the largest market for electroless nickel plating has been North America. In 1987 almost 40 percent of all the electroless nickel produced in the world was plated in the United States and Canada. This amount was nearly equal to the combined production of Western Europe and the Far East[14 15].

By 1993, however, the tremendous growth of industry in the Far East and the political unification of Europe have served to equalize usage of electroless nickel through the world. Today, about 30 percent of the coatings applied are used in each of the three major economic blocks -- North America, the Far East and combined Europe[16]. This is illustrated by Figure 2.

Figure 2
World Electroless Nickel Market



Australia and the industrialized areas of Africa and South America are also expanding markets for electroless nickel coatings. Their growth rate during the 1990's has been higher than most of the world and is second only to the Far East. Today their combined use equals about 10 percent of the world's production[14 16].

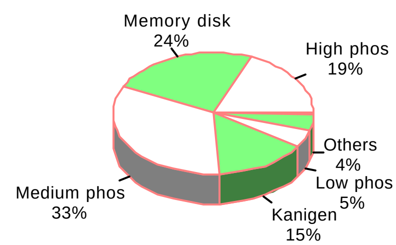
North American Market. There are today more than 900 electroless nickel plating facilities in North America. Of these, approximately two-thirds are job shop platers and the remainder are captive facilities for manufacturing plants. A few captives also compete for outside jobs, especially when their own work load is low.

Regionally, electroless nickel plating is evenly divided in the United States, with about one quarter of the production facilities located in the northeast, the mid west, the south and the west. Within these regions, however, plating is concentrated in centers. The principal ones are California, Dallas and Houston, Minneapolis, Chicago, Detroit, the New England to Philadelphia corridor, Ohio and Florida.

Most platers use solutions purchased from proprietary suppliers. Only about 15 percent of the coatings applied are produced from Kanigen or other plater formulated baths. Of the proprietary solutions, approximately 5 percent is purchased as a matrix package, while the remainder is either a full proprietary or a semi additive solution[17].

The traditional, bright or non bright, medium phosphorus coatings are still the most commonly used type of electroless nickel. As shown in Figure 3, the combined sales of Kanigen and other mid phosphorus coatings amount to one half the electroless nickel in the United States. Most of the balance are high phosphorus coatings, which are nearly equally divided between those used for memory disks and those used for other purposes. Low phosphorus coatings and specialty products, like PTFE composites, are a fast growing segment of the market. Together, however, they so far only represent about 9 percent of the solutions sold. Boron reduced coatings represent less than 1 percent of the electroless nickel market in North America[17].

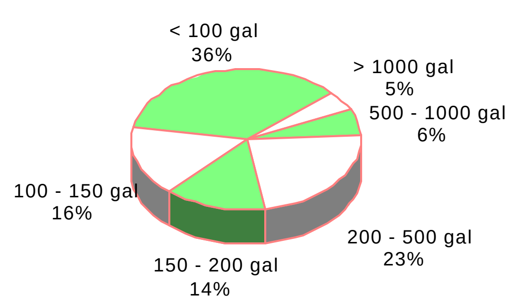
Figure 3
Types of Baths Used



Based on mil·ft² plated

As shown in Figure 4, the maximum capacity of the electroless nickel tanks in one half the plating facilities in North America is 150 gallons or less. In another one third of the shops, the largest electroless nickel tank is between 150 and 500 gallons. Only five percent of the shops have tanks with capacities of 1000 gallons or more[17].

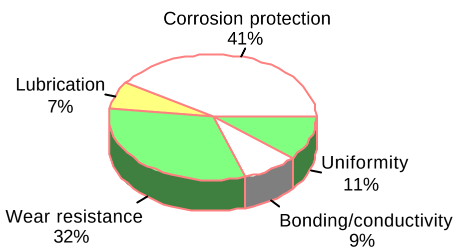
Figure 4
Sizes of Electroless Nickel Tanks



Based upon the largest tank in a facility

Applications. Electroless nickel has many unique properties, which are used by most segments of industry, either separately or in combination. As shown in Figure 5[17], in United States the most common use of electroless nickel is for corrosion protection. Applications requiring a hard finish or wear resistance, however, are almost as common. Together these properties make up three quarters of the use of the coating in non memory disk applications. The remaining one quarter is divided between conductivity, lubricity, magnetic response, bondability, uniformity and adhesion enhancement.

Figure 5
Uses of Electroless Nickel

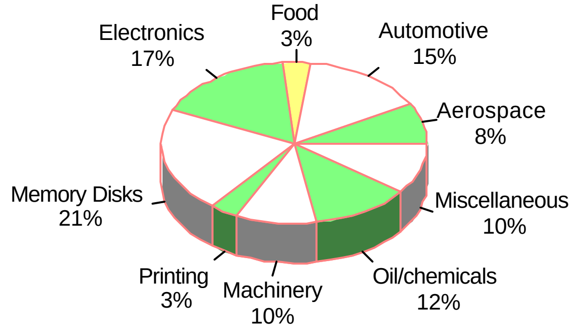


Excludes coatings used for memory disks

Figure 6 shows the results of a survey conducted in 1993 of job shop and captive facilities in the United States to find the types of parts plated and the industries that use them. By far the largest users of electroless nickel coatings are the memory disk manufacturers. These facilities apply more than one fifth of all of the coatings in the United States. Little if any of this type of plating is done in job shops.

Other electronic applications make up the next largest use of electroless nickel with almost 17 percent of the market. Job shop and captive facilities share equally in this segment. This volume, however, represents a drop of about one fifth from that reported in a survey conducted in 1979[18], mostly due to the movement of some of this business to offshore locations.

Figure 6
Uses of Electroless Nickel



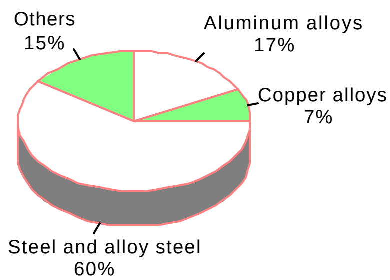
The next most common application is components for the automobile industry with 15 percent of the total. This is a significant increase from 1979, when ECI's survey showed this use to be only 9 percent. Much of this growth has occurred in job shops during the last five years. Few suppliers to the automobile industry have in house electroless nickel facilities.

The fourth largest user of the coating is the petroleum, chemical and valve industries. Together they consume about 12 percent of the electroless nickel produced in the USA. Even with the severe downturn that this segment experienced in the early 1980's, the amount of coatings applied by job shops for this application is about the same today as in 1979.

The remainder of the coatings used are divided between many different applications. Aerospace, food, machinery and power transmission, plastics, printing and textiles all use significant quantities of electroless nickel. One strength of the industry is the many markets it serves.

Substrates. Another way of looking at applications is by the type of substrate being plated. A survey was also conducted in 1993 of job shops to estimate the types of metals being plated[17]. The results of this study are summarized in Figure 7.

Figure 7
Substrates Plated With Electroless Nickel



Excludes coatings used for memory disks

In job shops, most of the work is on ferrous substrates. Approximately 60 percent of the parts that are plated are made from plain steel, iron and alloy steels. This equals a reduction of one quarter from that reported in 1979[18].

Of the remaining work, about 18 percent is on wrought and cast aluminum, and about 8 percent is applied to copper, brass and bronze. The balance is divided between ceramics, plastics, magnesium, zinc die casts, sintered metals, titanium, and other metals. Together non ferrous alloys amount to about 40 percent of the market, which is nearly twice that reported in 1979.
With one exception, the division of substrates in captive facilities is probably very similar to that in job shops. The exception is memory disks. These devices represent one fifth of the coatings applied and are made from aluminum. If this quantity is added to the aluminum substrates plated by job shops and other captives, the combination would equal 40 percent of the total market.

THE FUTURE

The future of the electroless nickel industry is far from clear. It will depend largely upon the state of the worldwide economy, and on political decisions made in Washington and other national capitals. There are two factors, however, which are expected to negatively affect the industry in the future.

Reduced defense spending in the United States has significantly reduced the amount of electroless nickel plating needed. This reduction has been and will continue to be most severe in the aerospace and electronic sectors, especially in New England and the West Coast. With the present political climate, it is unlikely that federal spending on defense or other high tech projects will increase in the future. This factor will continue to result in losses of production for the industry.

The second sector that will experience losses is magnetic memory disks. Many manufacturing facilities have been relocated to overseas. Also, one major manufacturer has announced that they are converting from the traditional aluminum disk to a non plated glass substrate. The plans of the other manufacturers is not yet known. These changes will cause a significant reduction in the amount of electroless nickel plated in North America. While non disk platers see no direct benefit from these sales, the revenue they provide suppliers does help support research and efforts to find new markets for electroless nickel.

Several factors will help to compensate for some of these losses. Component manufacture has begun to slowly return to North America which will require increased plating. Added investment of European and Japanese companies in American production facilities will also increase the use of electroless nickel in the United States.

The oil and gas industry will continue to order more tools, valves and equipment, many of which are exported. In addition, the domestic consumption of petroleum is increasing, further fueling demands for equipment. The chemical manufacturing industry has also shown a growing interest in electroless nickel coatings for maintenance and should use increasing amounts.

One industry that should see significant growth is automotive. Their use of electroless nickel has doubled in the last decade. With the American automotive companies' increased emphasis on quality and reliability, even more opportunities for electroless nickel will develop.

If these trends and the economic recovery continue for several years, the growth rate of the non disk segment of the electroless nickel industry should continue to remain between 5 and 10 percent. The disk segment is more uncertain. Its decline will depend upon how much of the disks are converted to glass and upon how much of their manufacture moves overseas.

CONCLUSION

To provide more applications for the coating and to help ensure its success, the electroless nickel industry needs to continue to provide answers to functional problems. To accomplish this goal, suppliers and platers must work together to ensure the quality of the coatings they provide. We must educate the users of the product and explain what it will and what it will not do. Lack of quality and of knowledge lose opportunities for the industry.

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BIOGRAPHICAL SKETCH

In Memory of Ron Duncan

Ron Duncan served as Vice President of Palm International, Inc., where he led the company's technical and educational initiatives. Prior to joining Palm, he was Director of Research at Elnic, Inc., focusing on electroless nickel formulation and materials research.

Before entering the metal finishing industry, Ron spent 12 years in the oil sector with Exxon and Caltex Petroleum Corporations, tackling materials and corrosion challenges. His work took him across the globe—including the United States, Middle East, Europe, South America, and Africa—where he developed a reputation for his deep expertise and practical problem-solving.

Ron held a BE in Mechanical and Metallurgical Engineering from Vanderbilt University. He was a Registered Professional Engineer and a certified Corrosion Specialist through NACE. A leader in technical standards, he chaired NACE task groups T-1G-19 and T-6A-53, contributing to authoritative reports on electroless nickel and other metallic coatings. He also served on the AESF's Electroless Committee.

Throughout his distinguished career, Ron authored more than fifty technical papers on corrosion, coatings, and electroless nickel. His work appeared in Materials Performance, Plating and Surface Finishing, Metals Progress, Products Finishing, and Finishers Management, as well as in numerous industry conferences. He was the principal author of the electroless nickel chapter in Volume 5 of the Metals Handbook and was honored with the AESF Gold Medal in 1996 for the best paper published in Plating and Surface Finishing.

Ron also directed the Electroless Nickel School, a comprehensive four-day seminar presented by Palm, which educated professionals in all aspects of electroless nickel technology.

Ron Duncan passed away on December 15, 2006. He is deeply missed by his family, colleagues, and the broader surface finishing community. His legacy of innovation, mentorship, and integrity continues to inspire all who had the privilege of working with him.