# The Story of Nickel Plating – Part I

by George Dubpernell

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(Recompiled by J.H. Lindsay)

**Among the major metals electroplated in commerce is nickel. From decorative bright finishes to today's nanotechnology and MEMS applications, nickel is there. With all of the advanced technology involving nickel plating in our industry, it is somewhat surprising to learn that nickel plating has been going on for nearly 150 years. When the AESF (then the AES) celebrated the 50th anniversary of its founding in 1959, the June issue of Plating that year featured a series of articles relating the development of the important plated metals of the mid-20th century. The following article, written by Dr. George Dubpernell, one of the industry pioneers, relates the story of nickel plating, from its very inception to the 1950s. This first of two parts deals with the very early developments up to the point where the essentials of today's nickel baths were being understood. The reader will find the personal details to be as interesting as the technical ones.**

It is not commonly realized that nickel plating was discovered at Harvard University, about [150] years ago. It is also not appreciated that working out the first commercial process required ten years of intermittent effort on the part of Isaac Adams Jr., and came as the climax to a long period of struggle and disappointment, after innumerable tests and failures, tragedies and minor successes.[1]

Isaac Adams Jr. was born in Boston on February 20, 1836. His mother died a few years later, and he attended boarding schools during much of his adolescence. His father invented the Adams Printing Press a few years before the birth of Isaac Jr., and the manufacture and sale of these first successful power printing presses soon made the family wealthy.

Young Isaac was a good student, and his father intended that he should become a doctor. After his graduation from Bowdoin College in Brunswick, Maine, in 1858, he attended the Harvard Medical School where he received his MD degree in 1862. During this period he studied under Josiah Parsons Cooke, professor of mineralogy and chemistry, and during the years 1858 to 1860 he investigated the electrolytic possibilities of many nickel and cobalt salts, and made some electrotypes of these metals about 3.0 × 4.0 × 0.003 to 0.005 in. thick (7.6 × 10.2 cm × 76 to 127 $\mu$m thick).[2] Some samples made in 1860 were given to Professor Cooke, who placed them in his cabinet.[1]

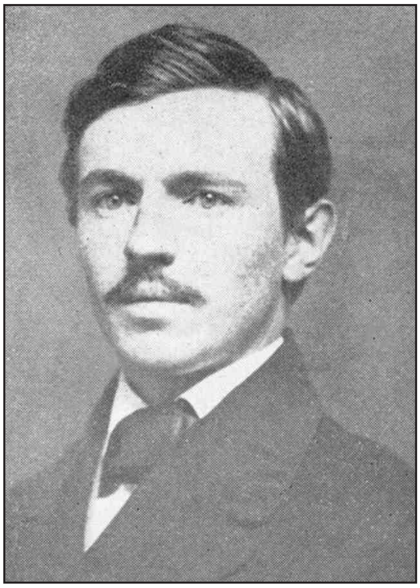
Upon graduating from Harvard Medical School in 1862, young Isaac went to Paris to continue his studies at the Êcole de Médicine until the fall of 1864. During this period he studied "mostly chemistry", and became proficient in glass blowing,[3] in addition to advanced medical studies. He was also said to have studied under Professor Bunsen in Germany.[4]

When he returned to the United States in the Fall of 1864, Dr. Adams immediately set up for the practice of medicine at 763 Federal Street, Boston, and lived with his brother Aquila at 43 Chester Square. He apparently failed to build up a good medical practice for one reason or another, perhaps because of his other activities. He established a laboratory in South Boston for work in chemistry and physics, and from 1865 to 1868 he put his knowledge of glass blowing to practical use by making a large number of Geissler tubes of various sizes and designs, which he sold to E.S. Richie of Boston, Chester Bros. of New York City, and Professor Cooke of Harvard University.[3]

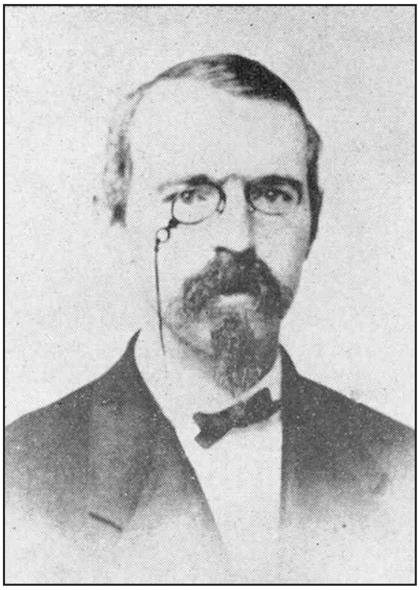
At this time he also made a number of vacuum tubes, "carbon burner" incandescent lamps, more than ten years before Edison. His electric light was essentially identical to Edison's with the exception that he did not develop a high voltage carbon filament, but instead used a thin "slip" of carbon lighted by a low voltage. Not visualizing any cheap source of electric power, he decided not to attempt the electric lighting business.

Dr. Adams became engaged to his cousin, Elizabeth Agry Adams, of Norridgewock, Maine, in the latter part of 1864, but she was the ward of his father's brother and business partner, Seth Adams. Uncle Seth was violently opposed to the marriage, and wrote to Elizabeth on February 23, 1865:

"He is now about twenty-nine years of age and up to this time his record of life is entirely what it ought not to be. He has never earned one cent towards his support and he is in no business that he manages in such a way that gives any evidence that he is likely to." Elizabeth became ill during 1865, and died at Uncle Seth's house in Newton, Mass., August 1, 1866. This must have been a great shock and tragedy to Dr. Adams, and perhaps influenced his decision a year or two later to give up the practice of medicine.



*Isaac Adams, Bowdoin, 1858*



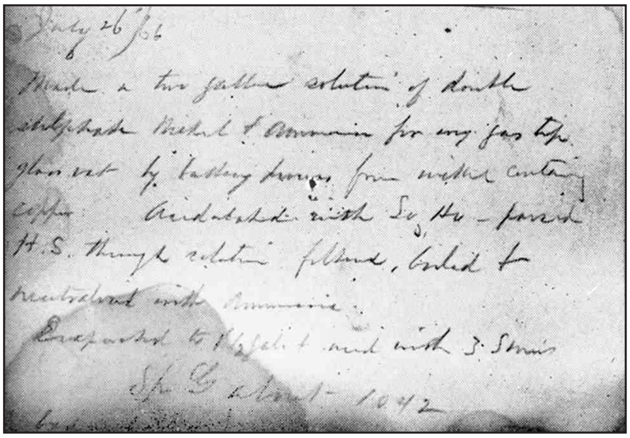
*Dr. Isaac Adams, Jr.*

*Mrs. Isaac Adams, Jr.*

Toward the end of 1865, Dr. Adams was approached by Joseph Smith of Boston, a dealer in gas fixtures, and asked to furnish a substitute for the lava gas-tip. He worked on it for several months, when it occurred to him that a nickel-plated iron tip might serve. Mr. Smith gave him some financial backing to set up about a 20-gal nickel solution, and perhaps also to file a patent application. In Dr. Adams' own words,[1]

"I commenced nickel-plating gas tips, I think, in the spring of 1866, but was not particularly successful, although I used, or supposed I used, a plating solution similar in its composition to the one I had used in 1860. I attempted, at that time, with the same solution, to produce an electrotype of nickel similar to the one I had given to Professor Cooke, and failed. The nature of the deposit which I produced was probably not such as to reassure Mr. Smith, or to give him a favorable impression as to the practicability of the process. However that may be, as far as he was concerned, he allowed the thing to drop there. The patent was issued to me soon after I undertook, at that time, to nickel-plate a lot of corset clasps and a patent finger guard, but the nickel deposit which I produced was not suited in quality to the purpose, and I was compelled to abandon its application to those articles. I afterwards silver-plated the finger guards to the number of about fifty thousand. This failure to produce what I had already produced six years before, namely, a reguline deposit of nickel, led me to experiment further, to determine the reasons why I succeeded in the one case and failed in the other. In experimenting with the commercial nickel which was to be had in the market of that day, I found that certain substances existing there had to be removed, or their effect in some way neutralized. The information obtainable from the books on this subject was exceedingly meager, and I found that I had to commence at the bottom and to determine experimentally the effects produced upon the nickel deposit due to the presence of the substances alluded to above; these were notably zinc, arsenic, copper and iron. This was not all. I found that the presence of the salts of the fixed alkalis and alkaline earths in certain solutions would have to be excluded or their decomposition prevented, as otherwise, owing to the facility with which such salts are decomposed, secondary products, nonmetallic, would make their appearance upon the cathode and injure or ruin the deposit. Further than this I found that the presence of any free acid produced an evolution of hydrogen, lessening the quantity of metal on the cathode, and that the presence of free ammonia, or more properly speaking, an alkaline state of the solution, tended to hinder or prevent the dissolving of the anode. It was only when I had fully completed these experiments that I considered I had such knowledge of the properties of the solution as to enable me to successfully nickel-plate as a business, or to impart such knowledge as would enable another person to produce a successful deposit. The experiments and discoveries to which I have just referred were completed in the winter of 1867-8."

Dr. Adams goes on to describe his work on the production of cast nickel anodes from 1859 to 1868, including the effect of carbon and silica to make the nickel easier to melt, and concludes: "... I found that the addition of a certain amount of iron (to the anodes) would practically prevent the deposition of copper and arsenic. The experiments, methods and directions, both as to solutions and anodes, were completed in the winter of 1867-8 - they were perfected and reduced to practice at that time."



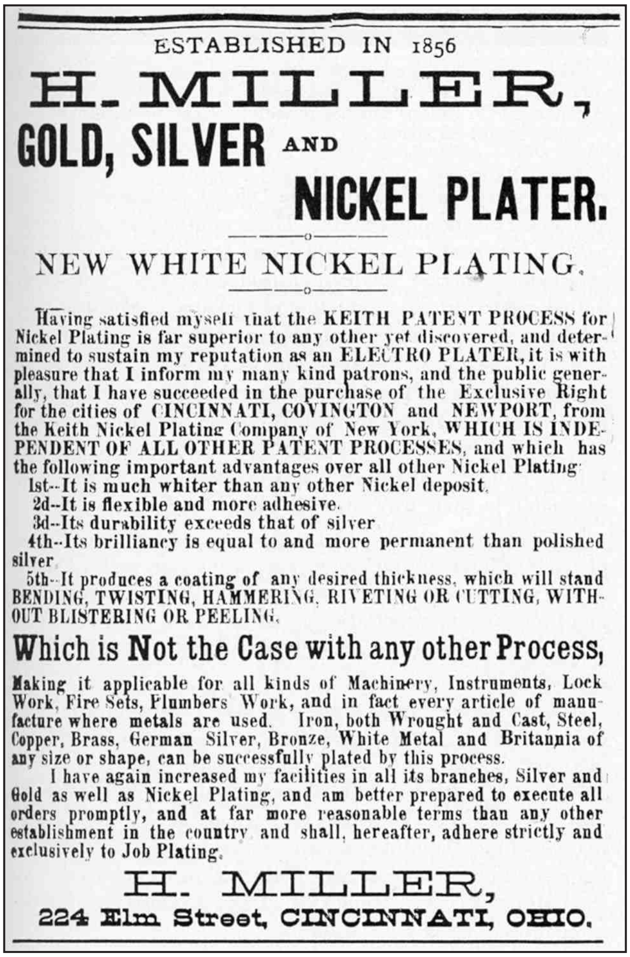
July 26/66
Made a two gallon solution of double
sulphate Nickel & Ammonia for my gas tip
glass vat by battery process from nickel containing
copper. Acidulated with $SO_3HO$ – passed
H.S. through solution filtered, boiled &
neutralized with Ammonia.
Evaporated to 1½ gall. & tried with 3 Smee's
Sp. G. about 1.042
[illegible]

*Original record of an early experiment from Dr. Adams' notebook No. 1 [transcribed by G. Dubpernell – Ed.]:*
*"July 26, 1866*
*Made a two-gallon solution of double sulfate of nickel and ammonia for my gas tip glass vat by battery process from nickel containing copper. Acidulated with $SO_3HO$ – passed. H.S. through solution, filtered, boiled and neutralized with ammonia.*
*Evaporated to 1½ gall. & tried with 3 Smee's*
*Sp. Gr. about 1.042*
*(bad as before)"*

The patent on nickel plating gas tips was filed July 16, 1866, and issued on August 21, 1866.[5] Dr. Adams stated that he plated more than 100 gross of the iron tips, but the business failed to grow because the lava tips were more profitable.

In the early part of 1867, Dr. Adams went to Europe with his brother Aquila and J.E. Thatcher. One purpose of the trip was to consider the commercial possibilities of incandescent lamps with A. Gaiffe, an instrument maker in Paris who later became his French backer for the sale of nickel plating.[3]

The next effort to commercialize nickel plating was made by William H. Remington of Boston late in 1868. Mr. Remington was convinced that nickel could not be cast into anodes, and his patent[6] related to an anode basket of platinum wire to contain the cube nickel of the day; and to a carbon plate covering the bottom of the tank and connected as anode, onto which the nickel grains or cubes were dumped. Another feature claimed was electroformed nickel anodes. The solution was made by dissolving nickel in nitric acid, precipitating nickel carbonate with potassium carbonate, filtering and washing, dissolving in a strong solution of sal ammoniac (ammonium chloride), and filtering. According to Dr. Adams, the solution was dark blue due to addition of excess ammonia, the same as the prior solutions of Boettger[7] and Becquerel,[8,9] thus making proper dissolving of nickel anodes impossible. Remington apparently plated some good samples and received some good publicity,[10] but was unable to stay in operation due to lack of knowledge of the need for a neutral or slightly acid solution, among other things.



ESTABLISHED IN 1856

H. MILLER,

GOLD, SILVER AND

NICKEL PLATER.

NEW WHITE NICKEL PLATING.

Having satisfied myself that the KEITH PATENT PROCESS for Nickel Plating is far superior to any other yet discovered, and determined to sustain my reputation as an ELECTRO PLATER, it is with pleasure that I inform my many kind patrons, and the public generally, that I have succeeded in the purchase of the Exclusive Right for the cities of CINCINNATI, COVINGTON and NEWPORT, from the Keith Nickel Plating Company of New York, WHICH IS INDEPENDENT OF ALL OTHER PATENT PROCESSES, and which has the following important advantages over all other Nickel Plating:

1st--It is much whiter than any other Nickel deposit.

2d--It is flexible and more adhesive.

3d--Its durability exceeds that of silver

4th--Its brilliancy is equal to and more permanent than polished silver.

5th--It produces a coating of any desired thickness, which will stand BENDING, TWISTING, HAMMERING, RIVETING OR CUTTING, WITHOUT BLISTERING OR PEELING.

**Which is Not the Case with any other Process,**

Making it applicable for all kinds of Machinery, Instruments, Lock Work, Fire Sets, Plumbers' Work, and in fact every article of manufacture where metals are used. Iron, both Wrought and Cast, Steel, Copper, Brass, German Silver, Bronze, White Metal and Britannia of any size or shape, can be successfully plated by this process.

I have again increased my facilities in all its branches, Silver and Gold as well as Nickel Plating, and am better prepared to execute all orders promptly, and at far more reasonable terms than any other establishment in the country and shall, hereafter, adhere strictly and exclusively to Job Plating.

H. MILLER,

224 Elm Street, CINCINNATI, OHIO.

*A competitive process.*

Remington's financial backer became frightened at the continued expense and called in Moses G. Farmer, a famous electrician of the day. M. Farmer in turn had Dr. Adams called in, in March, 1869 to straighten matters out at the shop at 14 Province Street, Boston. This was done during the next two months. The shop was finally reorganized with Dr. Adams in charge and called The Boston Nickel Plating Co., which was in business for about 100 years. It moved to 13 Bowker Street in 1872, and to 160 Portland Street about 1876 or 1878.

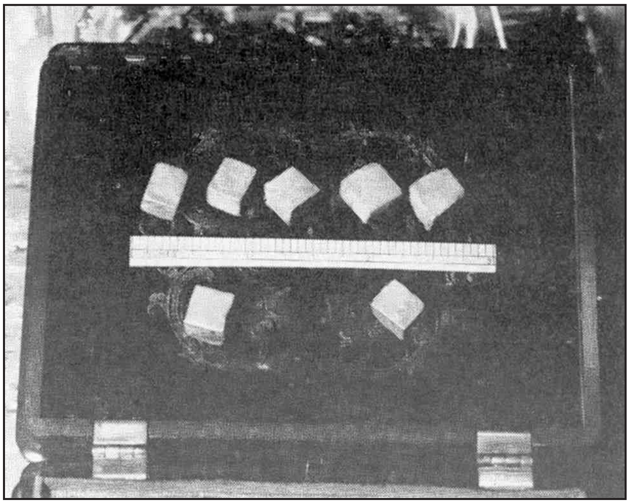
Some of the small nickel cubes shoveled out of Remington's tanks when the solutions were discarded are still in the possession of Mr. James Campbell of the Boston Nickel Plating Co. The International Nickel Company, Inc., analyzed two of these cubes with the following result:

| | |
|---|---|
| Copper | 4.76% |
| Iron | 0.85% |
| Carbon | 0.28% |
| Silicon | 0.18% |
| Sulfur | 0.12% |
| Manganese | 0.05% max. |

The percentage of copper above is eloquent of one of the difficulties of those times. Present specifications call for not over 0.10% copper in nickel anodes, and 0.02% maximum copper in nickel salts.[11,12]

Two patents were filed by Dr. Adams May 6, 1869 and issued May 25, 1869. One covered a sulfite solution for nickel plating[13] said to be advantageous when the anodes were contaminated with zinc; and the other related to combining nickel with silica or carbon, or both, in order to make it more fusible and get better castings.[14]

The United Nickel Company was incorporated in New York on June 14, 1869 by E.A. Quintard, George D. Allen, Charles C. Beaman, Jr., J. Trumbull Smith and Joseph Hayes, with capital stock of $1,000,000. The original trustees included William E. Learned of New York and Isaac Adams Jr. of Boston, in addition to the above five persons.[1] Dr. Adams owned about 10% of the stock and served as president, chemist and patent advisor until the company was dissolved in 1890.



*Nickel cubes from Remington's tank.*

The main patent on the Adams process of nickel plating was filed July 9, 1869 and issued August 3, 1869.[15] It describes the purification of nickel and of its salts, and the production of nickel sulfate. This is then converted to nickel ammonium sulfate (double salts) by combining with the requisite quantity of ammonium sulfate. The bath was made up to 1.5 to 2.0 oz/gal (11.2 to 15.0 g/L) nickel concentration, and should be neutral with the avoidance of strong acidity. The preparation of the double chloride of nickel and ammonium is also described, but the use of sulfate baths is preferred.

The production of nickel anodes is also described. Non-metallic impurities are removed as slag when the nickel is melted, and zinc is volatilized. Sufficient iron is added to the molten metal to be the chemical equivalent of the copper and arsenic present, and keeps them from interfering with the plating process.

Four precautions are given for good results:

1. Do not use too high a current density.
2. Keep potash, soda, or nitric acid from being dragged into the solution.
3. Use an anode area somewhat larger than the cathode, especially with the sulfate solution.
4. In plating zinc articles, plate them with copper first.

Electroforming is described and claimed as well as electroplating. The principal claim states that the nickel solution should be ". . . free from the presence of potash, soda, alumina, lime or nitric acid, or from any acid or alkaline reaction."

Another patent application was signed by Dr. Adams on October 7, 1869 and filed November 5, 1869.[16] It had the title "Process For Protecting, Hardening and Beautifying Various Metallic Articles," and enumerated most of the more important uses of nickel plating at the time. While the final fee was paid November 11, 1869, the application was rejected November 20th. On December 9, 1869 it was amended by cancelling all except the last paragraph and substituting an entirely new specification on plating gun parts only! This was granted, and issued on December 21, 1869.

Along with the formation of the United Nickel Company, a job shop was started in New York City in July 1869, having larger capacity than the Boston shop. It was called the New York Nickel Plating Company and was located at 133 to 135 West 25th Street with an office at 18 Park Place connected with the office of Greene, Tweed & Co. The new nickel plating became popular immediately, and business was good. Some records available indicate that the New York Nickel Plating Company did a business ranging from $4,000 to $8,000 per month in 1874 and 1875, in spite of the depression of 1873-1878.

Shortly after signing the last patent application above on October 7, 1869, Dr. Adams went to Europe with Mr. Quintard to establish the nickel plating industry there. A small experimental shop was started in Liverpool almost immediately and a larger plant of about 600 gallons capacity in Birmingham by the spring of 1870. A similar plant was opened for business in Paris in December 1869, under the management of A. Gaiffe.

Dr. Adams mentions that they had no competition at first, and that it came later on.[2] However, it was not very much later, as his English backer, Alfred Sellers of Sheffield, wrote him on May 1, 1872: "Verily! Friend Adams, thou hast stirred up the deep waters of nickel plating by the long pole of thy patents and now everyone, either knew of it before or can now do it better than thou canst." The influence of competition can frequently be seen in the numerous patent suits which followed, and even in the nature of some of the patents taken out.

*Picture printed from a nickel electrotype made in Paris in March 1870.*

*Bronze medal awarded at the International Industrial Exposition in Buffalo, New York. The medal was apparently nickel plated by Dr. Adams and has remained bright and untarnished in its case for 80 years [as of the date of this article – Ed.].*

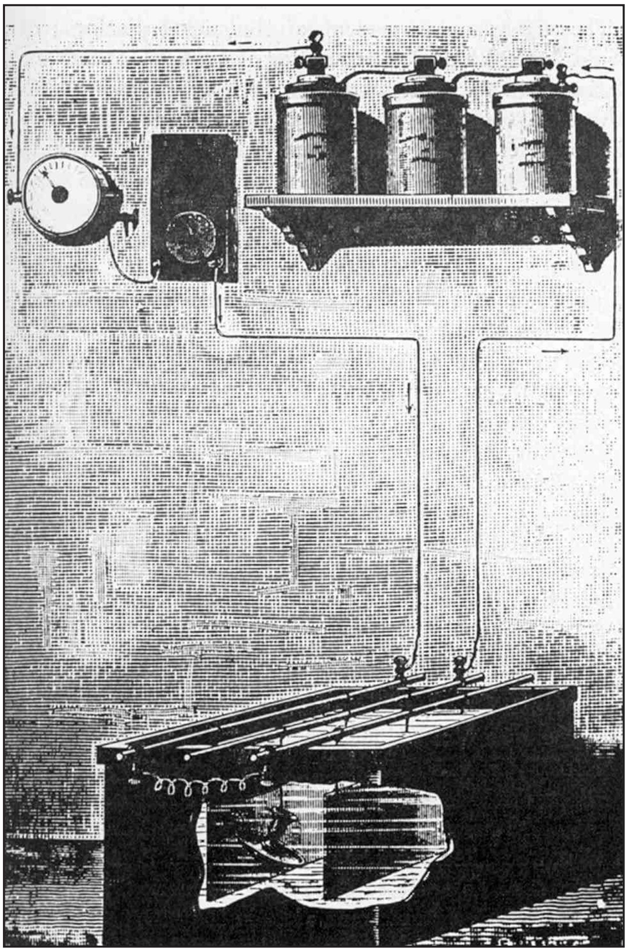
Two more American patents were filed while Dr. Adams was abroad. Both were signed in London February 1, 1870. One[17] covered the use of three other double salts of nickel sulfate, nickel aluminum sulfate, nickel potassium sulfate and nickel magnesium sulfate. These solutions are preferably used at temperatures over 100°F (38°C), and freedom from any acid or alkaline reaction was emphasized especially. The other patent related to the production of nickel anodes with better solubility characteristics by adding carbon to them.[18]

Aside from his activities in selling and establishing nickel plating in England, France, Germany and Austria, it appears likely that Dr. Adams married in December 1869, although one source[19] indicates December 1868. He married Lucille Emilie, daughter of George Lods of Hericourt, France, and associated in some way with his French backer, A. Gaiffe.

The story is told that arrangements were almost completed for a large contract for nickel plating guns for the French Army, when the Franco-Prussian war broke out in July 1870, and broke up the negotiations. At any rate, it appears that Dr. Adams probably returned to the United States in about August 1870.

Another patent application was filed December 19, 1870, claiming merely a cast nickel anode as a new article of manufacture.[20] Two other applications were filed October 8, 1870,[21,22] but due to an interference were not granted until July 4, 1871. That of Moses G. Farmer[21] related to the production of nickel plating solution or double salts by electrolyzing a solution of ammonium sulfate with a nickel anode "by the battery process," while that of Dr. Adams[22] covered the same process using a hot solution.

It is usually assumed that the Adams process consisted in the use of a solution of pure double salts alone. This is not true. The record shows that Dr. Adams commonly made a pure solution of single nickel sulfate, and added the desired quantity of ammonium sulfate, but less than that required to form double salts with all of the single salt. He was aware that it was frequently desirable to maintain a somewhat higher nickel concentration than afforded by pure double salts, particularly at low temperatures, and generally employed some of both.



*An early plating tank set up for plating with batteries as the source of power (1892).*

A patent application was filed January 17, 1873 on plating with single salt baths.[23] This reiterated the greater need for purity with single salts, and the poor anode solubility if the solution became alkaline. It was found that the single salts ". . . can be successfully used. . .," and such use was claimed.

Dr. Adams' last patent on nickel plating was filed October 21, 1872 but did not issue until August 25, 1874,[24] probably due to an interference with H.T. Brownell.[25] This patent related to heating nickel plated articles at a low red heat (about 700°F; 371°C) to improve the adhesion for more severe service. Brownell's patent[25] related to heating the article before nickel plating and then plating in a hot bath.

The still later patents are of lesser interest to us. One on cobalt plating claimed the use of various double salts of cobalt, and also disclosed a method of making cobalt anodes.[26] Another related to bonding rubber to clothes wringer rollers by means of the use of a cyanide copper plate,[27] and is understood to have been assigned to the Hood Rubber Company. The last patent related to the electric light bulb work and covered especially the use of a lead glass composition for sealing platinum lead in wires.[28]

Aside from job shops in Boston and New York, and numerous licensees, a job shop was also started in South Windham, Connecticut, in January 1872, called The Adams Nickel Plating and Mfg. Co. Dr. Adams was president, and part of the business was the plating of screen plates for paper pulp for the Smith & Winchester Company. A patent was granted on this use of nickel plate.[29] The shop also manufactured and sold nickel plated screws; and served as a headquarters for the United Nickel Company, in addition to the offices in Boston and New York.

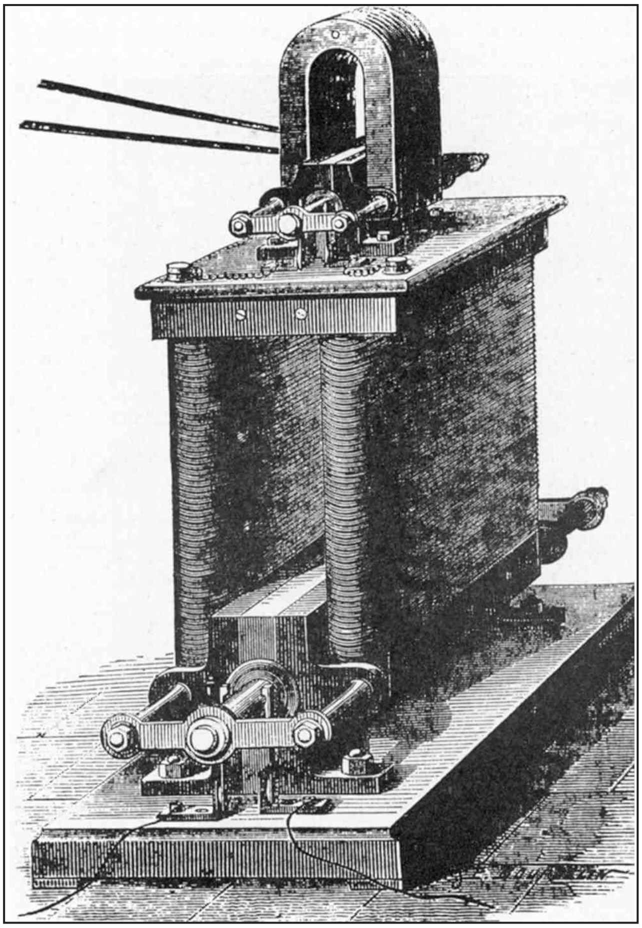
The United Nickel Company defended its position against all infringers promptly and energetically from 1871 to 1886. This was necessary if it was to survive. The times were those of the "robber barons" in American industry. The trade fought the patentees at every turn, and used every device to outwit them. Dr. Adams testified in 1890,[3] ". . . We carried on very extensive litigation in ten or twelve different states of the Union, and brought hundreds of suits - quite a number of them to final hearing. We had, all told, first and last over a thousand licensees . . ."

Some of the more important decisions in the patent suits are readily available[30-40] in addition to the complete record in the Weston suit. In many cases the effect of contamination with potassium, sodium, aluminum and calcium salts was argued rather endlessly, but the most important fact was that the baths should be free from any acid or alkaline reaction. At the time in question the only measure of acidity and alkalinity was by titration, a rather inadequate method for the purpose of controlling nickel baths.

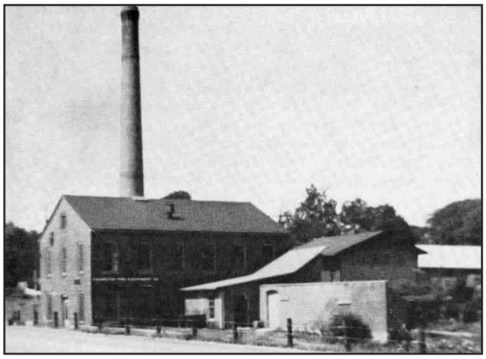
The suits were partly decided on the fact that there was no commercial process of nickel plating before Adams, and the success of his process was taken as a strong indication of the validity of his patents. Even the addition of a small amount of tartrate,[31] or of a larger amount of acetate and acetic acid[36] was held to infringe.

The vigorous enforcement of the nickel plating patents would seem to have left something of a "psychic scar" on the plating industry, or at any rate there has sometimes been a substantial aversion to paying royalties on new metal finishing processes. The royalty rates of the United Nickel Company were given[41] as 3¢/gal/month on 100 gallons of solution, and graded down to 2¢/gal/month for larger installations.[42]

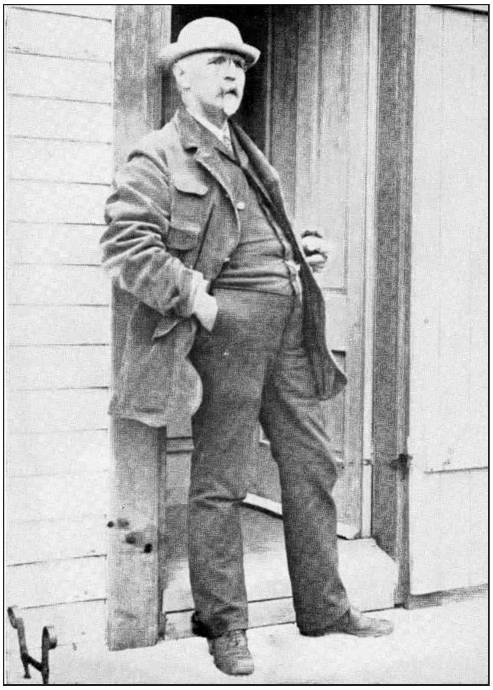
It may be of interest to know what was considered a good job of decorative nickel plating in those days. Gaiffe published an article[43] in which he stated that a nickel deposit of 1 g/dm$^2$ was generally considered satisfactory, and cost about 10 centimes (about \$0.02, or about \$0.20/ft$^2$). This would be a nickel plate about 0.0005 in. (12.7 $\mu$m) thick.



Wilde dynamo for generating electricity for plating. The New York Nickel Plating Company was said to have the only one of these machines in the country in the early 1870s. They were characterized by two armatures, the smaller one on top being used for excitation (1883).



Former factory of the Adams Nickel Plating and Mfg. Co. in South Windham, Conn. as it appeared in 1954.



Dr. Adams in 1888 in the kitchen doorway of his home in Annisquam, Mass.

After the patent suits ended and the United Nickel Company was disbanded in 1890, Dr. Adams retired from business and lived in a summer home at Annisquam, Mass., with a winter residence in Cambridge, Mass. He became a rather little-known figure by the time of his death, July 24, 1911, and only a few obituary notices have been found.[4,44]

## The use of boric acid

Edward Weston was born in England May 9, 1850. Like Dr. Adams he was trained for medicine; but coming from a poor family, it was by means of a three-year apprenticeship to a doctor in Wolverhampton. He rebelled against a medical career and sought employment at the Royal Institution in London, but failed to make any connection. Due to a chance acquaintance he resolved to come to America, and arrived in New York as a young man of 20 in May 1870, a year after Dr. Adams had successfully established his nickel plating process.[45]

Weston soon became an expert at nickel plating, but did not succeed in finding a way to avoid infringing Dr. Adams' patents. He did improve the nickel baths by adding boric acid to them, and patented this addition.[46] Boric acid was not widely used at first, and it is mentioned[45] that competitors used acetic acid to avoid infringement. The patent ran out in 1895, but it was many years later before the dependable action of boric acid as a mild brightener and as a buffer in the acid range, made it an almost universal constituent of nickel baths.

Langbein, in 1898 gave ten formulas for nickel baths with only one containing 4.0 oz/gal of boric acid.[47] W. Pfanhauser Sr. and W. Pfanhauser Jr.[48] gave five formulas for nickel baths in 1900, and used 2.67 oz/gal of boric acid in two of them. Brochet in 1908 did not include boric acid in his formulas, but favored the use of this chemical.[49]

In 1911, E.S. Sperry[50,51] investigated the use of boric acid in nickel baths and stated that its value had only been appreciated for the previous five years. Earlier workers were criticized if they used more than 1/8 to 1/4 oz/gal. Sperry found that the solubility of boric acid in nickel baths at room temperature was about 6.0 oz/gal, and recommended this concentration. The lack of greater solubility provided a simple means of control, since an excess would not dissolve, and too low a concentration was not very serious.

Nevertheless, the analysis of nickel baths for boric acid has received considerable investigation. Wogrinz and Kittel[52] proposed the removal of all nickel from the sample by electrolysis, and titration of the boric acid after adding glycerine or mannitol. Citrates do not interfere as they are destroyed at the platinum anode.

Baker[53] patented a mixed indicator of one part brom thymol blue to five parts brom cresol purple for the direct titration of boric acid in single salt solutions, after the addition of glycerine or mannitol. The writer used this indicator in plant control and obtained good results with it. It is still in use, and recommended in several textbooks.

Phenolphthalein can be used for this end point if the nickel solution contains a salt which will prevent the precipitation of nickel hydroxide at about pH 7.0. Willard and Ashworth[54] suggested the use of brom thymol blue alone, as it changes color at pH 7.0. They also suggested neutralizing the green color of the nickel salt by adding a red dye, fuchsine.

Willard and Ashworth especially point out the interference of ammonium salts, fluorides and citrates, if these are present, and give methods for their removal or avoiding the interference. The same problem is attacked by more recent workers. Vincke[55] suggested the removal of nickel by electrolysis before the determination. Raub, Bihlmaier and Nann[56] also depend on removing the nickel by electrolysis, and study the determination in the presence of citrate.

Longfield[57] proposed a method which he felt overcame most of the interferences. He titrated the boric acid directly, with 0.02 g of methyl red dissolved in glycerine as the indicator, and felt his results were accurate to 0.25 oz/gal of boric acid. Langford[58] complexes the nickel with sodium citrate and glycerine, and titrates to a phenolphthalein end point.

There is little standardization or agreement regarding the boric acid determination. Pfanhauser[59] advises against the determination, but also suggests a more recent direct titration based on work by A. Wogrinz and G. Kudernatsch,[60] using a brom cresol purple end point after adding invert sugar syrup. Fortunately there is not a very great need. The nickel bath can be kept saturated, or an inaccurate titration is satisfactory for control purposes.

AES Research Project No. 2 has suggested titrating to a phenolphthalein end point after removing nickel by precipitation as nickel ferrocyanide.[61] This is a good practical method for general use. A more recent suggestion[61a,62] to remove the nickel by ion exchange is probably less convenient in most cases.

## Chlorides and anode behavior

Bancroft[2] appears to have been the first (1906) to state clearly that a small amount of chloride in a nickel bath was sufficient to ensure that the anodes would dissolve with 100% efficiency regardless of their composition or structure. In the early days, Adams[15] and others used nickel ammonium chloride baths, but found the deposits somewhat dark and favored sulfate solutions. There must have been some awareness that the anodes dissolved better in chloride solutions, but this does not appear to have been explicitly discussed. Adams[15] suggested the use of an anode area somewhat larger than the cathode ". . . particularly in the sulfate solution." The common practice was to use such a low current density - only a few amperes per square foot - that the anodes dissolved satisfactorily.

Foerster[63] studied the electrodeposition of nickel with nickel anodes in 1897, but does not discuss the anode behavior quantitatively. It is probably significant that he uses slightly higher current densities with chloride than with sulfate baths. He bagged his anodes with parchment paper, but this deteriorated excessively in the chloride solutions. However, the anode sludge was more adherent with chloride baths, and unbagged anodes were satisfactory if the air agitation was placed a few inches away from them.

Langbein[47] points out that baths with a good concentration of ammonium chloride will dissolve even rolled nickel anodes freely, and tend to turn alkaline in operation. Pfanhauser[48] recommends a higher current density and an anode area only half that of the cathode in a solution containing chloride. According to O.P. Watts,[64] E.F. Kern in 1908 stated that pure nickel anodes could be used with 100% efficiency if a small amount of chloride is present. Brochet also pointed out in 1908[49] that even a low concentration of ammonium chloride is sufficient to make nickel anodes dissolve readily.

While ammonium chloride (sal ammoniac) was used in making up some of the early baths in 1868-1869, it does not appear to have become a common constituent of nickel baths until much later. Langbein[47] in 1898 only suggests ammonium chloride in three out of ten baths, and several of these were special solutions for plating over zinc, with rolled nickel anodes specified. Langbein describes an "American Nickel Bath" which consisted only of a 15 to 20% solution of ammonium chloride used with cast nickel anodes. This bath, also called the "Nickel Bath Without Nickel Salts," of course did not work until electrolyzed sufficiently to dissolve some nickel from the anodes, and then was used primarily for thin plating on cheap articles.

Pfanhauser[48] in 1900 recommended a bath containing 5.3 oz/gal double salts, 2.6 oz/gal boric acid and 2.0 oz/gal ammonium chloride. This general type of bath became the most common for several decades, frequently with the inclusion of some single nickel salts also in order to secure a higher metal content. Thus E.S. Sperry in 1911[50,51] gave as a typical nickel bath: 8.0 oz/gal double salts, 1.0 oz/gal single salts, 1.0 oz/gal sal ammoniac and up to 6.0 oz/gal boric acid. This formula is considered as good as any known.

Blum and Hogaboom in the 1949 edition of their book[65] give the following formula for a cold solution: 16 oz/gal single salts, 2.0 oz/gal ammonium chloride, and 2.0 oz/gal boric acid. The ammonium chloride serves the double purpose of increasing anode solubility and hindering the formation of basic salts on the cathode at high current densities. Blum and Hogaboom also give a special formula for nickel electrotyping consisting of 9.0 oz/gal single salts and 0.7 oz /gal ammonium chloride. The use of ammonium chloride has decreased radically with the advent of bright nickel plating, as ammonium salts are frequently incompatible with the brighteners employed.

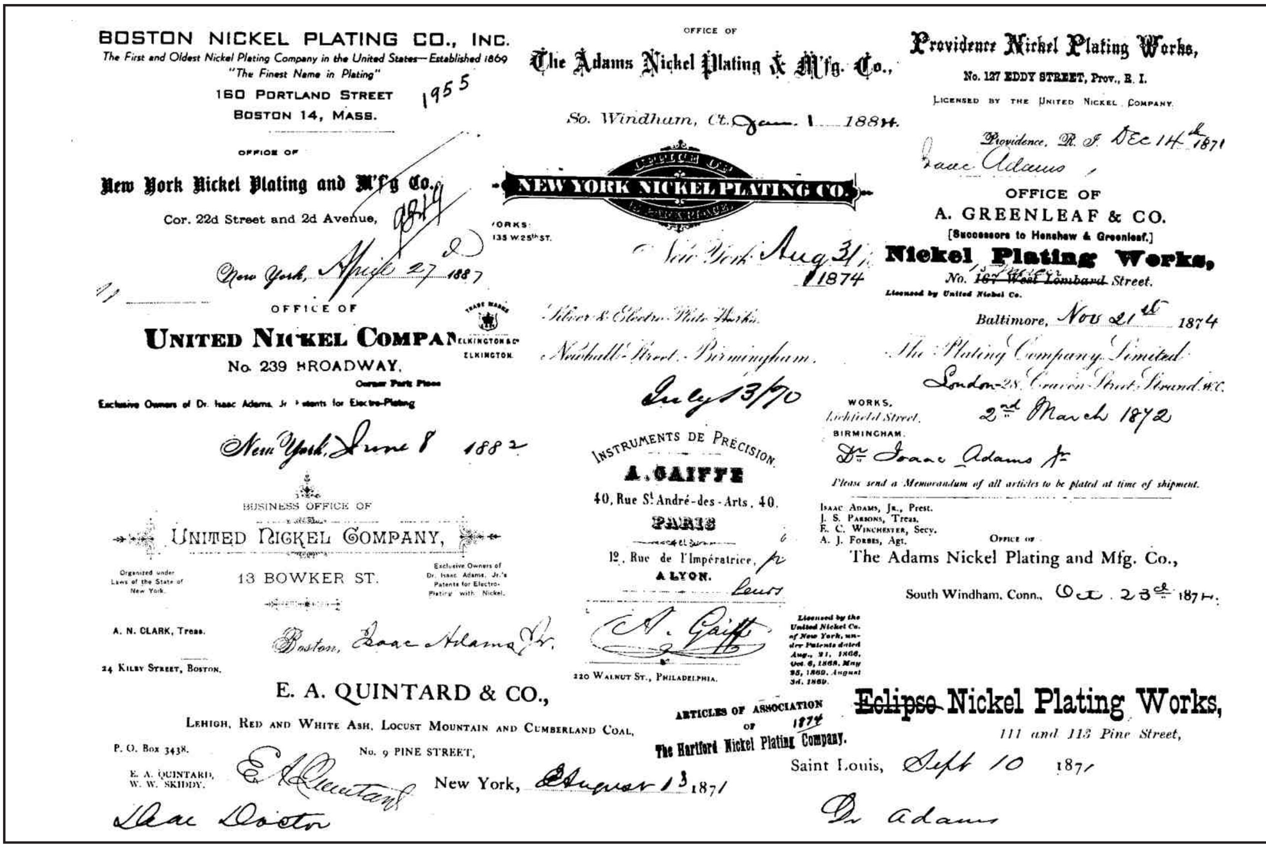
The first good modern investigation of the behavior of nickel anodes was that of Thomas and Blum.[56] Twenty different anodes were tested, and it was shown that any type of anode can be used if the bath contains some chloride. Not many additional studies of nickel anodes have been published. Several good investigations[67-70] were published in full in the AES Technical Conference Proceedings. Thews reviewed the subject in 1951[71] and Bauder[72] gives an extensive bibliography of both articles and patents.

## Acidity and the Control of pH

We have already noted that one of Dr. Adams' most important contributions was that nickel baths should be free from any acid or alkaline reaction whatsoever.[15] His precursors had used strongly ammoniacal solutions in which nickel anodes were insoluble, because they got no plate in acid solutions or very poor plates generally. Dr. Adams controlled the acidity or neutrality of his solutions by keeping them neutral or slightly acid to litmus paper, and alkaline to Congo Red paper. This became the practice for a long time.

Weston's addition of boric acid buffered the bath and made it easier to operate in a favorable range of acidity.[46] Langbein[47] discusses these matters in considerable detail. He also points out the tendency of rolled nickel anodes to make nickel baths turn acid, and cast anodes to make the baths become alkaline, and suggests the use of some of each for best maintenance.

Jordis[73] suggested the neutralization of all strong acids with ammonia, and then acidifying with weakly dissociated acids such as boric acid or citric acid, in order to get the best hydrogen ion



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*Providence, R. I.* Dec 14th 1871
Isaac Adams

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[Successors to Henshaw & Greenleaf.]
**Nickel Plating Works,**
*No.* ~~*167 West Lombard*~~ *Street.*
*Licensed by United Nickel Co.*
*Baltimore,* Nov 21st 1874

*The Plating Company Limited*
*London-28, Craven Street, Strand W.C.*
WORKS,
*Lichfield Street,*
BIRMINGHAM.
2nd March 1872
Dr Isaac Adams Jr
*Please send a Memorandum of all articles to be plated at time of shipment.*

ISAAC ADAMS, JR., Prest.
J. S. PARSONS, Treas.
F. C. WINCHESTER, Secy.
A. J. FORBES, Agt.
OFFICE OF
The Adams Nickel Plating and Mfg. Co.,
South Windham, Conn., Oct. 23d 1874.

*Licensed by the United Nickel Co. of New York, under Patents dated Aug., 21, 1866, Oct. 6, 1868, May 25, 1869, August 3d, 1869.*

**~~Eclipse~~ Nickel Plating Works,**
*111 and 113 Pine Street,*
Saint Louis, Sept 10 1871
Dr Adams

*Early nickel plating companies.*

concentration. Foerster[74] studied the effect of hydrogen ion concentration on the deposition potentials of cobalt, nickel and iron in 1916, but had no accurate measure of the concentration, as the pH scale was not developed until a few years later. He found that hydrogen deposited easier than nickel or cobalt and that in 1.0N and 2.0N nickel sulfate solution the hydrogen ion had more effect than in nickel chloride, while in 4.0N nickel sulfate there was less effect than in nickel chloride. Riedel[75] also varied the hydrogen ion concentration in an effort to improve the adhesion of nickel deposits from cold baths.

About 1920 the pH scale for measuring and indicating hydrogen ion concentrations had become well standardized in biological work,[76] and began to be used in other fields. McKay[77] and Mudge[78] state that the International Nickel Company started using it in the control of nickel refining solutions at this time. Within about five years the use of pH measurements became common for the control of nickel baths. Major credit for this step forward should be given to Dr. Blum and his collaborators at the National Bureau of Standards.

In 1921 Dr. Blum elaborated on pH measurement in a paper on the use of fluorides in nickel solutions,[79] and gave curves showing the buffering effect of boric acid and fluorides. The outstanding paper serving to introduce the method into nickel plating practice was that of Thompson in 1922.[80] This was followed by a series of investigations on the desirability of various methods of pH measurement and control,[81-90] and the introduction of inexpensive equipment for the purpose.[83-85]

Blum and Bekkedahl[91,92] reviewed the developments, and showed that the colorimetric methods in common use generally gave results about 0.5 pH unit higher than the electrometric measurements or the true pH.

The buffering action of various chemicals or weak acids in nickel baths was studied in some of the above investigations on the measurement of pH. O.P. Watts[93] discussed the subject at some length and suggested the use of acetates. D.A. Cotton reported an excellent investigation also.[94] While nickel baths are commonly acid, Saubestre[95] recently re-examined the possibilities of nickel plating from alkaline baths, a question which has received little consideration since the difficulties with such baths in the early days.

*The conclusion of this paper will be published in the May 2006 issue of **Plating & Surface Finishing.***

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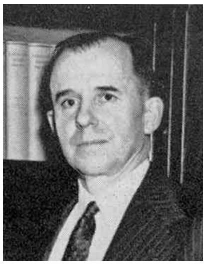
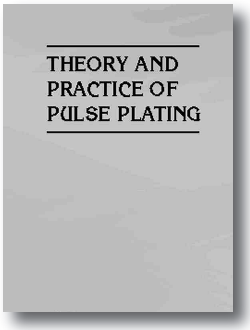


## About the Author

*George Dubpernell is a graduate of the University of Michigan (1924), where he was associated with the late Professor E.M. Baker. Dr. Dubpernell then worked and studied under Dr. Colin G. Fink at Columbia University and received the A.M. degree from that institution in 1927. Returning to Michigan he studied under Professor A.L. Ferguson and received the Ph.D. degree in 1933 for work on overvoltage. His early experience with plating which began in 1919 included work on lead plating (Detroit Battery Company), zinc (Harris Zinc Process Company and Apollo Metal Works), copper and nickel (C.G. Spring & Bumper Co.) and cadmium (The Udylite Corporation). He has been associated with the development of chromium plating since 1925, from 1933 on with United Chromium Inc., later Metal and Thermit Corp (M&T). Dr. Dubpernell has authored many papers on electroplating and overvoltage. He is a member of the American Electroplaters and Surface Finishers Society, American Chemical Society, the Electrochemical Society, the Institute of Metal Finishing, ASM and AIME. He was the recipient of the AESF Scientific Achievement Award in 1973.*



THEORY AND PRACTICE OF PULSE PLATING