



NASF SURFACE TECHNOLOGY WHITE PAPERS
80 (1), 1-19 (October 2015)

The 11th William Blum Lecture
Presented at the 57th AES Annual Convention in Montréal, Québec,
June 22, 1970

Some Contributions of U.S. Supply Houses to Plating Science and Technology

by
Arthur H. DuRose
Recipient of the 1969 William Blum
AES Scientific Achievement Award





NASF SURFACE TECHNOLOGY WHITE PAPERS
80 (1), 1-19 (October 2015)

The 11th William Blum Lecture
Presented at the 57th AES Annual Convention in Montréal, Québec,
June 22, 1970

Some Contributions of U.S. Supply Houses
to Plating Science and Technology

by
Arthur H. DuRose
Recipient of the 1969 William Blum
AES Scientific Achievement Award

Editor's Note: Originally published as A.H. DuRose, *Plating*, 57 (8), 793-802 (1970), this article is a re-publication of the 11th William Blum Lecture, presented at the 57th AES Annual Convention in Montréal, Québec, on June 22, 1970.

ABSTRACT

The origins of several developments in the plating field are reviewed, based on available information. An attempt is made to show why and how the processes and concepts evolved, with particular attention to inside stories and the people concerned. The developments and new concepts are analyzed in terms of whether they originated from chosen problems, accidental observations, random experimentation or adaptation. Curiosity and imagination are seen to be important attributes of many of the persons involved.

Introduction

By precedent it might be expected that the subject matter of this paper should cover some past or new and unreported work by the author or his laboratory. This of course was considered. But, although I am familiar with most of the developments in my own company, I am also aware of and appreciate the significance and importance of developments and discoveries in the laboratories of other supply houses. Also, in many cases, there is interaction such that the research in one company cannot be separated from that in other companies. In addition, there is an interest in personal and background stories behind inventions.

It was for the above reasons that the title subject was chosen. In addition to the supply houses, there are at least three other sources of plating knowledge equally important. These are the large manufacturing users of plating supplies, the universities, and the profit or non-profit research organizations, including government agencies. These will not be directly covered in this paper.

I have chosen a few of those developments of which I am most cognizant; those that have made an impression on me either in my formative learning process or which seem to have been commercially important. I hasten to admit that different developments may be of more importance and interest to other platers. I must apologize for omitting reference to contributions from some sources, the reasons being that there has to be a limit to the length of this paper and that it is written from a personal and possibly narrow viewpoint.

In soliciting information, I was particularly interested in how and why ideas originated and the continuum from these ideas into new concepts or processes. I was only partially successful in this. More information became available from some sources than others or was known first-hand, and this, to an extent, accounts for the disproportionate lengths of some topics.

Contrary to the usual custom, it will be understood why proprietary names are used in some cases, but intentionally the more recent developments have not been covered.

Several of the persons whose contributions will be discussed, are so well-known to the trade by their first names or nicknames, that it would seem inappropriate to refer to them otherwise.



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

The Grasselli-Roessler and Hasslacher-Du Pont Groups

In 1915, Clayton Hoff joined the analytical laboratory of Grasselli in Cleveland, and in 1921 Christian (Chris) Wernlund became associated with Charles Proctor at the Roessler and Hasslacher Company (hereafter called R & H) in Perth Amboy. Although active interest in plating processes did not emerge for several years, this era, in my opinion, marked the beginning of one of the most productive laboratory and service groups in the history of plating. From these laboratories came the Halogen Tin process and the first bright cyanide zinc, bright high-speed copper, and practical alkaline tin solutions. Other developments were bright cyanide cadmium, Molyblack and the Hull Cell. Also, largely through the efforts of Dick Hull, a plating symposium was organized, which in its book form became the really first edition of *Modern Electroplating*.¹

Because this was one of the first and largest plating research groups, more than the usual space will be given to description of its developments.

Actually, the Grasselli laboratory at Cleveland and the R & H laboratory at Perth Amboy, and later at Niagara Falls, should be considered separately. Grasselli was taken over by Du Pont in 1929, and R & H absorbed a few months later. For a few years, there was little communication between the two laboratories. Both departments offered cadmium and zinc cyanide plating processes to the trade, Grasselli being interested in promoting sales of the metals and salts, and R & H of cyanides. Coordination between the laboratories culminated in 1939 when the Du Pont Electroplating Division was formed to take over all activities except manufacturing. During World War II, further moves were being made for consolidation, and plans were made to locate all research at Wilmington. However, after a period of apparent confusion, the move was made instead to Niagara Falls in 1946. This change of plans and the possibility that Du Pont might discontinue extensive work on plating processes had much to do with the resignation of several members of the Grasselli team.

Leon Westbrook had arrived at Grasselli in 1923 in time to contribute to the early development of "Cadalyte." Dick Hull came in 1933, Ray Hoffman in 1934, Ernest Schweikher in 1937, Allen Gray in 1940 and Don Swalheim, the baby of the group and one of the few remaining with Du Pont, came in 1941. At Niagara Falls were Chris Wernlund, Floyd Oplinger, Bob Bair, Harry Benner and others. Don Swalheim went to this laboratory in 1947. All of these names are well-known to the plating trade or science. Wernlund and Oplinger had become well-known for their work with the stannate plating process.¹ Two Grasselli patent attorneys, George Lutz and later Albert Griggs are given much credit by the Cleveland research workers. These men kept in close touch with the laboratory, envisioned the breadth of patent coverage needed and suggested fruitful lines of research. This kind of interest can be invaluable.

Bright cadmium and zinc

Long before Clayton Hoff arrived at Grasselli, that company was a producer and processor of cadmium, zinc and their compounds. One of his first problems was to develop new and faster methods for the analysis of zinc ores. Out of this evolved some electrochemical methods for separating and determining quantitatively the zinc and cadmium contents. Word came that General Electric-Schenectady was having difficulty with its cadmium plating operations and Clayton was asked to assist. By employing some of the principles involved in his analytical methods along with the use of materials such as goulac, starch or dextrine, he was able to introduce to industry the "Cadalyte" process. This was an ammoniacal cyanide solution^{2,3} and one infers that, in the analytical technique, ammonia had been found to restrict the deposition of zinc. (This was not the first proprietary cadmium bath in the field; Marvin Udy had earlier introduced a bath⁴ containing sodium cadmium cyanide and protein⁵ on which the Udylite Company was later based. Gus Soderberg has told how wool and tobacco juice were found to be brighteners for cyanide cadmium and how bright dips were developed.³⁷)

About this time, Leon Westbrook arrived on the scene and he and Hoff were practically the "whole show" for almost ten years, Westbrook in the laboratory, and Hoff, joined later by Howard Blouch, mostly on sales and service. Leon became fascinated with the effects of addition agents and in 1926 introduced the use of traces of nickel and cobalt⁶ in the Cadalyte bath containing goulac, for further brightness. By 1927 he had discovered the combination of nickel and "sulfonated castor oil" which gave a brilliant cadmium deposit.^{7,8} This is interesting because, although this material is essentially a sulfate ester instead of a sulfonate, it led to the testing of many sulfonated materials, not only for cadmium but also for zinc and nickel.^{9,10} Westbrook, Lutz



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

and Hoff of course wanted to pursue the use of sulfonates in nickel solutions but were overruled by management because Grasselli had no established position in nickel and could see no profit in selling addition agents.

The story is told that it soon was surmised that goulac contained aldehyde or keto groups and, since goulac had a beneficial effect on cadmium, this led to experimentation with aldehydes. It was also suspected that ammonia and amines played a part in the addition agent action. In 1934-35, several patent applications were filed by Henricks, Hull, Vaughen and Lutz, covering aldehydes and ketones and their reaction products with cyanide and amines.

During the late 1920s, Hoff and Westbrook had become interested in doing work on cyanide zinc. Fearful that this would interfere with the Cadalyte profits, they were given no encouragement although Grasselli owned a zinc smelter in West Virginia. Finally, about the time Ray Hoffman arrived in 1934, a possible shortage in cadmium was foreseen because of the use of cadmium alloys for bearing purposes, and the green light was given for work on zinc.

Westbrook had previously found that molybdenum and other metal compounds¹¹ were beneficial ingredients in the zinc solution, but realized from analogy with cadmium that an organic additive might also be needed. He had found that furfural was active but unstable. The breakthrough came about 1935 when Ray Hoffman ordered some heliotropin along with other organic compounds from Eastman Kodak. This^{12,13} in combination with molybdenum became the basis for the first bright zinc solution, "Zin-o-Lyte." Other brighteners were discovered by Hoff¹⁴ and Hull¹⁵ and in 1937 an important patent application was filed by Hull¹⁶ covering the use of oxygen-containing heterocyclics in combination with protective colloids. This became the basis for barrel plating formulations.

An interesting sidelight is that piperonal was imported from Japan, so, after Pearl Harbor, more expensive but available aldehydes were used for a time. Ray Hoffman had previously found these to be at least as good as piperonal, so, after Pearl Harbor, he soon devised simplified methods for their manufacture. However, patents were not allowed on these new aldehydes and this left the way open for other companies at a later date to exploit the use of such compounds as anisaldehyde for zinc plating.

Although all of this work on zinc had been done at Grasselli-Cleveland, it should be noted that in 1921 Wernlund at R & H had reported¹⁷ the results of an extensive study on zinc cyanide solutions. In 1936, now with duPont, he filed on the use of polyvinyl alcohol.¹⁸

The Hull Cell

The origin of the concept for the Hull Cell is uncertain. A plausible account has it that there may have been some connection with a plating cell commonly used at Grasselli. This was a small storage battery case about two inches in width with an anode at one end. The cathode was longer than two inches, so it was placed diagonally at the opposite end of the cell. From this, Dick Hull elaborated and perfected the Hull Cell.¹⁹ The Hull Cell normally used is only one variation of several designs broadly covered by the patent. It is said that the first cell was made of paraffin-coated cardboard.

The Hull Cell was used extensively at Grasselli. Frank MacIntyre became so skilled in its use that he could guess the approximate analysis of a bath, including impurities, merely by looking at one or two Hull Cell plates.

High speed bright cyanide copper

Those who plated zinc die castings with bright nickel-chromium before 1939 can well remember the difficulties in obtaining a fully-bright deposit over the dull copper deposits common at that time. It was known that for proper corrosion protection the copper should be at least 5 μm (0.2 mil) thick so resort could not be made to use of thin deposits. The demand was present and R & H produced cyanide so, in retrospect, it is obvious that R & H should develop a better cyanide copper solution. Such a process was introduced in 1938 and described in the first *Modern Electroplating* symposium.

Originally, Pan's high concentration bath was modified and the best conditions found to be high temperature, low free cyanide and pH of 12.5. Oplinger then operated such a bath at the Buckeye Bumper Plant in Springfield, Ohio. This trial was a failure



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

but it did indicate the need for brightness, better solution conductivity and an antipitting agent. The bath was then improved, Benner suggesting the use of thiocyanate as a brightener, Bair, the use of high pH, and Wernlund, the use of carbohydrates.²⁰ Oplinger had previously suggested the use of high concentration and high temperature, and later Holt²¹ recommended the use of betaine-type wetting agents.

The carbohydrate was originally intended to form a gelatinous film around fine solid particles and prevent deposit roughness. This made it almost impossible to filter the solution, so it was eliminated and filtration alone was used to control roughness.

In 1941, the benefits of the potassium ion were realized and covered by another patent.²² (At about the same time, Lowenheim was using potassium in the stannate bath.^{23,24})

Halogen tin

There were two reasons for the development of the "Halogen Tin" process. First there was the need, because, under war conditions, a tin shortage was inevitable. Second, stannous chloride was a Grasselli product. In my opinion, this was one of the more important Grasselli-duPont plating developments, although to many platers it might be relatively unknown. It was largely developed under "crash" conditions requiring cooperative efforts among individualistic and creative men. It also required and received cooperation from industry which needed the process, and much credit is given to Sam Johnston of Weirton Steel in this respect. The choice of stannous chloride, a Grasselli product, as a tin source is surprising to others who have worked with tin solutions, since one of the best solutions for producing dendritic treelike growths is that of stannous chloride.

United States Steel was developing its Ferrostan process and Crown Cork and Seal was developing the use of alkaline tin for strip plating. From Weirton Steel, Howard Blouch brought the problem to the Grasselli laboratory, and Allen Gray did some preliminary work evaluating the stability of various solutions and studying anode corrosion. One of the premises was that the normal acid tin baths, which required high acid concentration in order to prevent stannous tin precipitation, were not very responsive to addition agents. So, Ernie Schweikher set out to find a new electrolyte in which tin was reasonably soluble at a reasonable pH and which was amenable to addition agents. From this developed the SnCl₂-F-pH combination,²⁵ which Hoff christened "Halogen Tin." Ray Hoffman and others found that polyglycol and similar water soluble polymers were suitable addition agents.^{26,27} It was observed that traces of copper in the solution accelerated the oxidation of tin, and another patent²⁸ was issued to Schweikher claiming the use of thiocyanate for sequestering copper, and ferro or ferricyanides for sequestering iron in solution. These four patents formed the original basis for the Halogen Tin process; all were filed in July, 1943.

At Weirton, three large strip plating units capable of operating at 1000 ft/min were being installed without having available a demonstrated electrolyte. So, before the "Halogen Tin" process was completely developed, Sam Johnston in 1942, persuaded Westbrook and Hoff to try the solution in his pilot line. With some reluctance this was done and it worked so well that Sam stepped the line up to full capacity the first day of continuous operation. Weirton immediately made plans for use of this process in their large units that would run at higher speeds and current densities than the pilot line. The Grasselli Group was then faced with a dead-line for working out the inevitable problems. Hull headed the program, Schweikher refined the process in the laboratory, Swalheim took over the work at Weirton assisted as necessary by others, Hoffman went after addition agents, Gray looked into variations and other applications and Aaron Johnson studied the operating characteristics of the bath with Swalheim when he was not at Weirton. This necessitated the development of a Rotating Cathode Cell to simulate line plating conditions in the laboratory, which was described by Swalheim²⁹ in a paper for The Electrochemical Society at Buffalo.³⁰

Full scale production in the large units was started early in 1943. This translation through the pilot line and into production within one year represents a real tribute to the research team, Sam Johnston and the production division at Weirton Steel. The units are now operating at 2000 ft/min.

The early organic-type bright nickel

While Dr. Max Schloetter³¹ is usually, and rightfully, given credit for the introduction of the modern bright nickel about 1933, it should be remembered that several years earlier Lutz and Westbrook had proposed the use of alkyl naphthalene sulfonates for bright nickel.



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

Schloetter's process using aromatic polysulfonates was introduced into the United States in 1934 by the Pyrene Manufacturing Company and is said to have produced acceptable bright deposits only after it had been properly electrolyzed and aged. It would appear that metallic or organic impurities had to accumulate which acted as brighteners (brighteners of the second class) in conjunction with the sulfonate.

In those depression years, processes such as this were sorely needed by industry but on the other hand it can be understood why some labor-conscious job shop owners asked "Why do you not wake up to the fact that these patents . . . should be destroyed immediately?"

The likely success of this bright nickel caused fast action among the United States supply houses and many sulfonates and sulfuric acid treated materials were tried quickly as nickel plating addition agents. By late 1934, Paul Pine³² of Harshaw had developed "Nibrite" using such agents as sulfuric acid treated retine and rosin oil and by 1935 a bath was installed at Chrysler. This addition agent, which was really a mixture of several compounds, had several characteristics different from Schloetter's. A bright deposit was produced without aging, although by today's standards it was not very bright. Also, as mentioned in the patent, the solution had a low surface tension and gave pit-free deposits. Not realized at that time was the fact that the deposit was low in sulfur and had excellent corrosion resistance compared with later bright nickels. Nibrite had one fatal fault - it would not maintain its brightness. The minor constituent which acted as the brightener became depleted; more addition agent was added but eventually a point was reached where nothing could be done except to treat the bath with permanganate.

Several years earlier, Mr. McGean had separated from Harshaw but had maintained an interest in plating supplies. In 1934 Virgil Waite with McGean Chemical Company filed³³ on the use of aromatic sulfonates with cadmium and/or zinc as brighteners. This, then, was the first of the bright nickel solutions as we know them today; that is, containing separately-added control agents and brighteners. Of interest today is that this patent disclosed the carbon and sulfur contents of the deposit.

Waite and Martin continued work on improvement of the McGean solution and one of the addition agents tried as a brightener was Duponol. It was, of course, ineffective as such, but they noticed that the hydrogen gas bubbles did not adhere to the nickel deposit and a pit-free deposit was obtained. Waite and Martin immediately recognized the importance of this discovery and in 1935 filed on the use of sulfate esters of aliphatic alcohols for eliminating pitting. The patent application ran into interference with Harshaw and General Motors, but was finally issued to McGean.³⁴

The realization that better deposits and better control could be accomplished by use of separately-added control agents and brighteners led to further research in this direction at Harshaw. It had been observed previously that lower valent sulfur and sulfurized compounds were useful as brightener extenders in the Nibrite solution. Therefore, when K.E. Long was preparing colloidal selenium for rectifier use, the thought occurred to add this to a nickel solution. Very rough deposits resulted, but when he tried selenium dioxide, good brightness was obtained. This led to the patent application³⁵ in 1936 by W.J. Harshaw and K.E. Long on the use of selenium and tellurium compounds as brighteners with aromatic sulfonate control agents. This solution using selenium dioxide as the brightener produced a fully-bright deposit even by present-day standards. Excellent results were obtained in large (120 gal) laboratory tanks and a large commercial installation was quickly made. Then, "the roof fell in," the chromium over this deposit was grey and dull. One can imagine the scurrying and overtime work when this information was telephoned back to Cleveland. In a matter of a few days, K.E. Long found that an invisible selenium film on the bright nickel was the cause and could be removed by an activating treatment in sodium cyanide.

After this, except for the necessity of educating platers and analysts, this solution was well-accepted. Gradually, however, it became apparent that the deposit had poor corrosion resistance and afforded poor protection to the basis metal. Today, we would put the blame on the relatively high sulfur and selenium contents of the deposit. Although irritating on the receiving end, much credit must go to Carl Heussner of Chrysler for coercing the supply houses into attempts to improve corrosion protection. Improvements were made over subsequent years but he was not fully satisfied until sulfur-free deposits were introduced.

In my opinion, the next important contribution, and it became very important, was the aryl sulfonamide-sulfonimide patent filed in 1937³⁶ by Henry Brown of Udylyte. It was the first of a series of patents in which Henry discussed the chemistry and



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

electrochemistry of nickel plating addition agents. He points out the catalytic effect of nickel, the modifying effect of position and type of other groups present, and the importance of unsaturation.

It had been observed³⁷ that peroxide had a tendency to brighten nickel deposits and, therefore, other oxidizing agents were considered as brighteners with Henry Brown in charge. Henry knew that Thomas Edison had used chlorine to obtain improved plating results³³ and based on this he tried the disinfectant chloramine T, the N-chloro derivative of p-toluene-sulfonamide. It appeared to be better than aromatic poly-sulfonates and continued to give good semibright luster even after the chlorine had dissipated. One can readily see, then, how this led to the discovery of the use of sulfonamides and saccharin.

The next step at Udylite was to find a brightener to use in conjunction with the sulfonamide. Since formaldehyde was known to be partially effective, other aldehydes and ketones were tested. One of Udylite's first bright nickel processes used a combination of aldehydes as the brightener along with sulfonamide control agents. It was found that unsaturated aldehydes were more effective than saturated aldehydes. This in turn led to Henry's ideas and speculations on un-saturation not only in the brightener but in the sulfo-oxygen control agents.³⁹

In the following years, several other patents were issued to Henry and in 1944 he filed on the use of unsaturated aliphatic sulfonates,⁴⁰ another milestone. These, like the sulfonamides, are very effective in increasing tolerance to brighteners and, unlike saccharin, increase the tolerance to metallic impurities.

An interesting interlude was the almost simultaneous discovery of the use of sulfonated aryl aldehydes at Seymour Manufacturing Company, Du Pont and Udylite. This, of course, led to a three-way patent interference case which lasted several years. The case was finally decided in favor of M. Freed⁴¹ (Seymour) for his application filed in 1939. However, Ernie Schweikher (DuPont) was allowed a more restricted patent⁴² for the use of m-sulfobenzaldehyde in high chloride solutions.

In Schloetter's patent, the first claim was broad and covered a high gloss nickel deposit having a crystal size less than 0.0001 mm. On the basis of this, it was argued that other processes using sulfonates at that time were dominated by the Schloetter patent and the Bright Nickel Corporation was formed in 1938 to handle licensing arrangements. There may be exceptions, but it appears that most technical people in the supply houses objected to any license payments but were overruled by their managements. It is interesting to speculate what would have happened with today's knowledge of bright nickel and its structure. The sublicensing firms consisted of Harshaw Chemical Company, McGean Chemical Company, Pyrene Manufacturing Company, Seymour Manufacturing Company and the Udylite Process Company. In a very short time, The Udylite Corporation was formed and took over the Bright Nickel Corporation.

The bright and semibright nickel-cobalt deposits

It is probably not accidental that the bright nickel-cobalt deposits came into being at the same time as the so-called "organic-type" bright nickel. History has shown that when a need or use becomes apparent, that need is usually satisfied from several and diverse directions. This has been termed "multiple discovery."

One day in 1934, while Bill Stoddard was "the laboratory staff" of the Weisberg and Greenwald consulting firm, a man named Otto Hinrichsen came to the penthouse laboratory in New York City with a secret substitute for chromium plating. Bill remembers opening numbered packages while making up one or two gallons of the plating solution, and recognizing all of the ingredients except what later turned out to be sodium formate.

This Hinrichsen solution contained nickel sulfate, nickel chloride, cobalt sulfate and sodium formate and was operated "warm" and without agitation. The limiting current density was about 1.5 A/dm². The deposit had excellent ductility, was bright when plated over a buffed surface, and had the white color of the 17 per cent alloy.

An arrangement was made with Hinrichsen, and Bill Stoddard commenced work to speed up the rate of deposition. By increasing the temperature and using agitation, current densities of 4-6 A/dm² were attained, but after a few ampere-hours, full brightness was lost.



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

In discussing this problem with Dr. Weisberg, it was conjectured that possibly formaldehyde was involved in the cathode reaction due to the presence of formate. So, formaldehyde was added to the solution and immediately improved brightness was obtained. There also seemed to be an optimum pH and, after a considerable number of adjustments, the optimum pH was found to be 4.2-4.4 by a colorimetric method.

Being satisfied and pleased with these results, a 35-1 bath was made up in an enameled steel tank and plating of samples was started. In a short time, the deposit became hazy.

After recovering from this shock, Bill reviewed in detail his past notebook records to find what had been overlooked. It gradually dawned on him that, while determining the optimum pH, he had used ammonium hydroxide several times for pH adjustment. After totaling the amount of ammonium hydroxide added in his previous work, he added the equivalent amount of ammonium sulfate to the 35-1 bath and once again the deposit became fully bright.

Thus evolved the Weisberg-Stoddard Bath⁴³ and unlike the secrecy which usually surrounded the "organic type" solutions, this and subsequent modifications were fully described in non-patent literature.⁴⁴⁻⁴⁶

About the time of the first field trials at Jaque Kreisler and Washburn Wire Goods, a bewhiskered gentleman, Van Winkle Todd, was invited to the Weisberg office to see the bright plated samples. Hanson-Van Winkle-Munning was in a position to cast the cobalt-nickel alloy anodes. An agreement was reached between Weisberg and H-VW-M and, soon after, the latter took over the marketing and servicing of the process. This was handled by licensing arrangements with the users.

During the period that Weisberg and Stoddard were perfecting the bright alloy solution, Barney Case at Eaton Manufacturing Company in Cleveland was finding that less pitting in the Watts deposit could be attained by alloying with small amounts of other metals.⁴⁷ He ordered small alloy anodes from H-VW-M and after testing, settled on the #9 anode which contained 1 per cent cobalt. Variations were then made on this anode from A to H and the variation H chosen. Thus originated the name "9-H" for the anode and the nickel bath. When Barney approached Hanson to make the production anodes, he was informed of the Weisberg-Stoddard development. This led to cooperation between Weisberg and Case and the commercialization of the 9-H bath for semibright nickel deposits containing about 1 per cent cobalt.⁴⁵

A problem which had troubled Weisberg, H-VW-M, and Case was the purification of solutions by other than high pH and oxidizing treatments, and, here again, Weisberg and Case worked together. Electrolytic refining of copper and nickel gave them the clue and this led to the now well-known electrolytic purification methods. Later, while employed by Hanson, Barney refined and elaborated on these methods so that they could be used for continuous purification.⁴⁸ Barney did much to teach "good housekeeping," its methods and benefits to the plating industry.

Reduction of hexavalent chromium in alkaline solutions

The method by which M. Beckwith discovered the use of sodium hydrosulfite for reducing chromium is an excellent and orderly example of the creative process. First was the definition of the problem and recognition of the need for its solution. This was followed by the "incubation period" and development of hypotheses. The method of testing was obvious. The actual testing was, as in most cases, by trial and error using those agents which the hypothesis had indicated. After verification, the method was generalized, in his case, to its use in alkaline cleaners.

In 1938 while at Guide Lamp, Division of General Motors, Anderson, Indiana, "Beck" became aware that blistering and poor adhesion could be traced to the presence of hexavalent chromium in the copper strike.⁴⁹ The usual reducing agents were ineffective in reducing the chromium and the remedy was to frequently discard the cleaner and copper strike. The problem had not been solved when "Beck" joined the Wyandotte Chemical Company in 1939.

"Beck" continued working on this problem whenever new ideas occurred and, early in 1941, while looking through a handbook, he "stumbled onto Lykopen," a trade name for hydrosulfite, and which was described as a textile dye remover. He tried this first in a beaker, and finding it effective, deliberately contaminated a copper solution in a small job shop and then reduced the chromium with hydrosulfite.



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

The next move was a demonstration for the late Guy Cole at the Ternstedt Laboratories. Two days later Guy called to tell "Beck" that Guide Lamp was shut down because of chromium in their copper strike and lack of more copper cyanide in stock. "Beck" took the plane for Anderson the next morning with a small amount of hydrosulfite in his pocket, and had them back in production an hour after his arrival.

Others were informed of this treatment method and it "took like wildfire." "Beck" was asked to present a paper^{50,51} on the subject at the 1941 American Electroplaters' Society Convention and for it received the Proctor Memorial Award.

Today, this treatment method has been partially replaced by other methods but this does not detract from the fact that it was a novel and important contribution to the plating industry.

Chromium and the Dubpernell test

We know George Dubpernell for his associations with United Chromium, Inc., now M&T, for his very completely referenced histories of nickel and chromium plating,^{52,53} for the original work on chromate conversion coatings,⁵⁴ and for the Dubpernell Test.

There is no need to repeat the early and more recent accounts of United Chromium and its chromium plating processes. One should be aware, however, of the many papers and patents authored by Jesse Stareck, Frank Passal, Ed Seyb, Ron Dow, Bob Couch and others. From these United Chromium-M&T research workers came such developments as self-regulating chromium solutions, crack-free chromium, and dual chromium. Jesse Stareck is known also for the development of Electrocolor and Patternplate based on cuprous oxide deposits, and, when he found the pyrophosphate solution would not produce cuprous oxide, he then developed it into a commercial copper plating bath. The service by this company and its well-staffed laboratories was and is not only valuable to the users of chromium solutions, but has led to the accumulation of much practical "know-how."

Although other accomplishments and interests have been of more importance to George, the Dubpernell test for detecting cracks in chromium deposits has been useful in the past and with the coming of microcracked chromium, has recently become even more useful. In 1924, while doing some work for E.M. Baker at the University of Michigan, George observed that, while cyanide copper would plate (nonadherently) on chromium, acid copper would not. Then, in 1925 and 1926, in Colin Fink's laboratory he used this peculiarity of acid copper to detect pores and cracks in chromium plate. This work was not published.

In 1927, while working on his Ph.D. in Ann Arbor, he commuted to and from Detroit four days a week to work for the General Chromium Corporation. One day, when returning to Ann Arbor, he rode with Professor Baker. Baker "was puzzling about how to show the cracking in decorative chromium plate." "I felt free to describe the Dubpernell test to him and it was like touching a match to some gasoline fumes." The next January the test was described⁵⁵ and credited to George.

George completed his work for the doctorate under Professor Ferguson in 1933 and went to work for United Chromium. He has recently retired, but at present is writing an article on electroplating for the *Encyclopedia Britannica*.

Leveling, duplex nickel and corrosion

Leveling

In the years 1938-1940, it became increasingly apparent that the so-called organic-type bright nickel was inferior in corrosion resistance and protection to the normal Watts nickel deposit. It was also inferior to the bright or semi-bright nickel-cobalt deposits being marketed by Hanson. It was quickly recognized that sulfide in the deposit was an important factor and spot tests were used by the author to show qualitatively the presence of sulfur in the deposit. The results of these spot tests correlated well with corrosion results.

A large potential outlet at that time for a suitable proprietary nickel process was for nickel plating bumpers. These were plated with a high chloride Watts nickel or the 9H semibright low cobalt alloy, then buffed. A nickel deposit for this use had to be ductile,



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

have good corrosion resistance and be easy to buff. It was obvious to bumper manufacturers that the organic-type bright nickel was not suitable.

Because of the poor polish on the hot formed and pickled bumpers at that time, an easy-to-buff nickel deposit was required. During the war years, of course, no research was possible on nickel plating for bumpers, but toward the close of the war, thoughts were given to the requirements for a buffable nickel. As described in a later paper,⁵⁶ it was conjectured that such factors as hardness and surface luster or coarseness would affect the ease of buffing. To test the relative importance of these factors, various solutions were chosen that would give "dull to lustrous semibright and hard to soft" deposits.

These thoughts were discussed with Paul Pine, my superior, and he made arrangements with C.L. Lancaster for a cooperative plating and buffing test program. Chet Lancaster was the manager of the Buckeye Bumper Plant, a division of Electric Auto-Lite Company. Tribute must be given to Pine and Lancaster not only for making possible these arrangements, but also for the encouragement they gave Bob Miller of "Auto-Lite" and me.

One of the semibright deposits was plated using a solution containing naphthalene disulfonate even though its corrosion resistance was suspect. Toward the end of the plating part of the program, it was found that there were enough of the 2.5 × 18 in. panels so that another solution could be added to the program. It was decided to use another semibright but sulfur-free deposit and, fortunately, coumarin was chosen as the additive. This compound had attracted our attention some time previously during routine testing of organic compounds. It was almost by chance that it was chosen because of several other possible choices.

The buffing tests were performed at Buckeye Bumper Company in 1945 using an armor plate cut-off saw. This had been adapted with spring scales by Bob Miller so that buffing wheel pressure and drag could be measured. After a few trials, reproducible results were obtained.

By measuring drag, luster and coverability of polish and scratch marks, the original thoughts regarding buffability were verified. However, deposit B (from the solution containing coumarin) added another unforeseen factor, namely, the ability to fill in scratch marks. This was not realized at first. The buffing tests showed this deposit to have excellent coverability compared to the others. Then it was noted that the unbuffed deposit had more luster than other semibright deposits when compared on coarsely-polished or rough surfaces. It was several weeks after this before microscopic examination and surface analyzer charts showed that we were getting what is now called leveling.

The cooperative buffing test program had been well-planned and executed but the discovery during this program that coumarin was a leveling agent was almost accidental. It is true, however, that it was chosen partly because it was realized it would not introduce sulfur into the deposit.

A subsequent paper⁵⁷ gave more leveling data for this deposit and in another paper⁵⁸ an attempt was made to explain leveling in terms of throwing power into small surface irregularities. While adsorption of addition agents on peaks was mentioned as a possibility, it was not explained how this could be a continuous process and it remained for Kardos⁵⁹ and Edwards⁶⁰ to describe it in terms of a diffusion controlled process.

In our 1950 paper,⁵⁸ in addition to describing what is now called geometric leveling, it was shown geometrically that leveling would be more pronounced on closely adjacent scratches than on single scratches. More recently, this has been verified and explained⁶¹ in terms of adsorption area and diffusion.

This leveling nickel process was widely accepted in spite of the reduction product which gradually accumulated. It was known that this formed at the cathode and its composition was surmised, but not proven until Dr. J. Alexander at Harshaw showed by UV analysis that it was hydroxy phenyl propionic acid. Dr. Alexander had been one of the first to use UV for analysis of aromatic nickel addition agents.



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

Duplex nickel

Probably the first to plate duplex nickel as we know it today was Walter Karash in our laboratory. This was about 1946. However, there were several reasons why this did not attract our immediate interest. Foremost of these was that our bright nickel at that time had very little leveling and the required bright nickel thickness seemed excessive. Second, it was not realized immediately that this combination would lead to superior corrosion protection.

It was realized that, if a good bright nickel deposit could be applied over the leveling semi-bright nickel, there would be many cases where buffing could be eliminated. With this in mind, work was started to improve our bright nickel. Several advances were made, but it was not until 1952 that such a bath was developed. This was a team effort by a group of individualistic but cooperative and enthusiastic workers.

In 1953, again in cooperation with Electric Auto Lite Company, various sets of steel panels were plated and submitted to Chrysler Corporation for corrosion tests. The results were quite favorable for the duplex nickel and to my knowledge this was the first inkling that duplex nickel might afford superior corrosion protection. It is of interest that the first corrosion test used was the neutral salt spray; the CASS and Corrodkote tests had not yet been developed. By this test, duplex nickel does not reveal corrosion protection much superior to single layer sulfur-free nickel. It was only after outdoor exposure, and later CASS and Corrodkote, tests were made that the superiority of duplex nickel was fully realized.

It did not take long for us to show that the superior corrosion protection was due to galvanic protection by the more active bright nickel between the chromium and sulfur-free semibright nickel. We had long been aware of the effect of sulfur in nickel. The bright nickel had a laminar structure and the semibright nickel a columnar structure and, for several years, we gleefully enjoyed seeing our competitors try to obtain the superior corrosion protection by using columnar, but sulfur-containing, semibright nickels.

This enjoyment did not last long; in a few years, both Hanson and Udylite⁶² had developed sulfur-free semibright nickel solutions using acetylenic leveling agents. These were used successfully in their duplex nickel processes. Udylite followed this in 1962 with their "Tri-Ni"⁶³ where an even more electronegative nickel deposit was interposed between the semibright and bright nickel layers.

In the last section of this paper, "adaptation" will be mentioned as a method for invention. This method is well-illustrated by the account of how Henry Brown and coworkers developed a process for producing microporous chromium. In 1959 they were interested in developing a "satin" nickel plate. Various addition agents were tried but difficulty was encountered in obtaining a uniform satin finish over a reasonable current density range. At about the same time, for possible engineering uses, they were studying the codeposition of fine insoluble, nonmetallic particles with nickel. Using very fine silicon carbide particles, they noticed the surprising smoothness and uniformity of the dispersion coating especially when using bright nickel addition agents. One can see then how this led to dispersion-type satin nickel deposits and thence to microporous chromium.⁶⁴

Corrosion and addition agents

In 1959 and 1960⁶⁵⁻⁶⁷ we determined and published corrosion potentials and corrosion currents of couples, which largely explained the corrosion mechanism for duplex nickel-chromium layers. It was also shown that SO₂ could sulfidize deep into the surface of sulfur-free deposits and cause them to act like sulfur-containing nickel. These studies led to an interest in how sulfur gets into bright nickel deposits and how the concentrations of sulfo-oxygen control agent and brightener affect the sulfur and carbon contents of the deposit. It was shown⁶⁸ that the commonly-used control agents contribute the sulfur but, excluding allyl sulfonate, practically no carbon, and that the carbon is largely contributed by the brightener (polarizer), if it is organic. It was shown that the sulfur increases rapidly at first and then more slowly with increasing control agent concentration corresponding to adsorption equations and that the brightener frequently enhances the cleavage of sulfur from the control agent. In spite of some contrary evidence, I attempted to explain the latter effect by the polarizing action of the brightener. Within a short time, Edwards⁶⁹ had shown this to be an inexact interpretation, and proposed his mechanism involving competition for adsorption sites. Subsequently, several "polarizers" have been found which decrease the cleavage of sulfur from control agents.



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

A supply house is constantly on the lookout for quick and easy methods for evaluating solutions and deposits. An example of this is the use Harshaw has made of corrosion potentials of nickel deposits for indicating relative corrosion tendencies. It is easier to survey a large number of deposits by potential measurements and then verify or disprove the results by a few actual corrosion tests than it is to make many cathodic and anodic polarization measurements. The use of corrosion potentials as criteria presupposes that the anode and cathode $E-i$ slopes (reactions) for different nickel deposits are approximately the same. Recently, possible exceptions to these premises have been found. By choice of a suitable potential measuring solution⁷⁰ and a standardized procedure, we have been able to predict corrosion results for single, duplex, and triplex deposits. In fact, for sulfur contents in the range of 0 to 0.1 per cent, it is believed that potential measurements are at least as reproducible as sulfur analyses and of more significance.

By static potential measurements it has been found that phosphorus in nickel has a peak activating effect at about 3.5-4 per cent. Cobalt in nickel deposits has only a slight activating effect up to about 60 per cent, a moderate effect from 60 to 90 per cent, and above this the electronegativity increases very rapidly. Only deposits above about 93 per cent cobalt are useful as sacrificial layers in triplex coatings, but they cause blistering. Also, in some nickel deposits, absorbed hydrogen and its fast or slow release can be detected by simple potential measurements, and there is an interrelation between the potential, absorbed hydrogen, ductility, stress and corrosion rate.

B.F. Lewis and the cleaning of zinc die castings

This is a story of a development we are likely to forget, but to me it marks one of the milestones in plating technology.

In the years prior to 1932, any plater knew that zinc die castings could not or should not be cleaned anodically; *i.e.*, any plater except Bert Lewis.

Bert had grown up with the pre-chromium era of plating on die castings. He had had analytical and practical plating experience with die cast alloys, and the direct nickel plating of these in the cold, low metal, high sulfate nickel solutions.

Copper striking and plating came into use but in the years 1920-1932, cathodic treatment in mild trisodium phosphate-soda ash solutions remained the usual method of cleaning die castings. The electrocleaner inevitably became contaminated with zinc and thereby became a zinc electroplating bath. The deposited film was very active and would readily become immersion plated with copper. Such cathodically-treated surfaces were subject to interdiffusion of the zinc and copper and this frequently led to blistering of the copper and nickel. Minimal time of exposure in the cleaner and its frequent replacement were the only remedial actions.

When the use of chromium over nickel became common after 1927, the stresses created by chromium revealed the need for better adhesion of deposits and the need for new concepts in surface preparation. It was with this purpose in mind that Bert in 1932 became the cofounder and technical director of Northwest Chemical Company.

The idea that zinc die castings might beneficially be cleaned anodically had probably occurred to others, but anodic treatment in trisodium phosphate was corrosively-destructive to the surface. Bert's premise, therefore, was that the constituents of the cleaner, while effecting the cleaning action should also inhibit harmful attack of the surface.

The method of approach was largely by trial and error, although by now a considerable background of basic cleaner chemistry had been accumulated and was helpful. This was largely an individual effort; group effort was of more use in the development of pre-cleaners. Actual die castings were used in the cleaning trials, followed by complete plating and heat treatment. The parts were then inspected visually and by microscopic examination of cross sections. The results of one trial would indicate the direction of the next trial or trials.

The widely held theory that the buffed die cast surface should not be discolored in electrocleaning was proven untenable; a properly-anodized surface was found to be desirable. The anodic film, blue-gray in color, was not removed in the weak acid neutralizer; it remained to serve as a protective film until removed by the reducing effect of the copper strike, with simultaneous replacement by the copper electro-deposit.⁷¹



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

While it is not generally known, Bert Lewis was probably one of the first to show that most corrosive attack through copper-nickel chromium deposits starts from the outside and penetrates toward the basis metal. This developed in the 1940s when Carl Heussner, with good reason, had concluded that the failure of plated parts was at least partly caused by silicates used in electrocleaners. Through the years, Bert Lewis had learned much from microscopic examination of new and aged plated parts. Using an ordinary plater's microscope and a 35mm camera, he made color transparencies of cross sections showing the gradual penetration of corrosion with ultimate perforation and, in the case of die castings, the consequent formation of the blister. With this graphic evidence, he was able to satisfy Carl Heussner as to the true cause of blisters.

Acetylenics and leveling theory

In July 1955, a United States Patent⁷² was issued covering the use of water-soluble acetylenic compounds as brighteners for nickel plating. This has become one of the famous patents in the plating field and is the "parent and grandparent" of many other patents. It also has led to several patent controversies which bear witness to its importance. Many of the acetylenics are leveling agents, so it is not surprising that after they had been put into commercial use, thought was given again to an explanation for the phenomenon of leveling.

In the summer of 1949, Dr. Otto Kardos, working for Hanson-Van Winkle-Munning, noticed an advertisement for the first acetylenic alcohol available in commercial quantities. It intrigued him because of the symmetrical balance between the presumably "metallophilic" acetylenic group and the two hydrophilic hydroxyl groups. Also the $-C \equiv C-$ group resembled the $-C \equiv N$ group which he knew to be active as a nickel brightener. A sample was ordered, and on testing as a single addition agent, the results were found encouraging. By 1951, a field test was made using acetylenics in a barrel nickel plating process, and a patent application was filed.

Work continued on other acetylenics and, in the fall of 1952, Otto was told that because nickel had become more plentiful, he should concentrate on an organic-type bright nickel (in contrast to Hanson's bright nickel-cobalt bath). He then tackled the matter in a more systematic way using the acetylenic compounds in conjunction with Class I brighteners. Before Christmas, he was able to write in his note-book "excellent, brilliant, uniform, no bending noise" and his notice of conception was written on December 26.

In March of 1953, the continuation-in-part application was filed which became United States Patent 2,712,522 and shortly thereafter, the first installation of "Nickel-Lume" was operating very successfully at S.E. and M. Vernon Company in Elizabeth, New Jersey.

Two years went by and, in the fall of 1955, a period came when there was not too much pressure from process development or trouble shooting. Under these more relaxed conditions, Otto and Dr. Don Foulke were able to muse on the phenomena of microthrowing power and leveling for which no satisfactory explanation existed. They were especially puzzled by cyanide baths which have poor microthrow and good macrothrow.

In thinking about the difference between macro and micro-profiles, the idea eventually developed that the diffusion layer thickness might be the critical dimension. The diffusion layer boundary could follow the profile of a macro-groove but not of a micro-groove. Consequently, the diffusion layer would be thinner over micropeaks than over microrecesses, and diffusion of metal ions, addition agents, and hydrogen ions to micropeaks might be faster than to microrecesses.

From here on, the development of these hypotheses and their proof is well known.⁷³⁻⁷⁵ Worth repeating, however, and although it may seem very apparent now, an important and novel step in the thought process at that time was that one should be able to produce variations of current density by variation of agitation rate over a flat cathode, which correspond to the variations of deposit thickness between microrecess and micropeak.

While interest and curiosity are of prime importance, Otto has aptly shown that the diffusion theory of leveling originated from the bringing together of several available, but apparently unrelated, concepts and facts known in 1955:



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

1. The known experimental facts of leveling, microthrowing and macrothrowing power.
2. The variation of diffusion layer thickness over microprofiles in electropolishing.
3. The experimental values of diffusion layer thickness.
4. Polarization at various agitation rates.
5. Concept that over a microprofile, polarization can overwhelm the influence of ohmic resistance and lead to practically uniform current distribution.
6. Concept of the rate-determining step in a reaction sequence.

INCO and its publications

Over the years, we as platers have come to expect research publications from The International Nickel Company (INCO) which not only contain useful data but which are also informative in our understanding of basic plating principles. A young plater in research or production today would be well advised to read and study many of the fine publications contributed by workers in the INCO research laboratory.

INCO was one of the first of the large corporations to institute research on a large scale. This was not out of any sense of obligation to industry but for self-preservation. In the last year of World War I, the sales of INCO nickel were about 71 million lb. Three years later, this had dropped to 13 million lb. The Bayonne laboratory was opened in 1924 to develop, by modern research methods, new uses and data on nickel which would eventually increase its peacetime use.

While many of the initial projects at Bayonne were of a metallurgical nature, electrodeposition was also definitely considered important. Wesley⁷⁶ reports laboratory records which show that R.J. McKay in 1919 had plated sound nickel in a low pH solution at 454 A/ft².

One of the first projects started under Wesley was the study of the mechanical properties of electrodeposited nickel. We take such data for granted today but, at that time, little was known and techniques for determining such data had to be developed. Four papers⁷⁷⁻⁸⁰ gave results on tensile properties, hardness, structure, and effect of annealing for various Watts, all-chloride, hard and moderately-hard nickel deposits. A more modern paper⁸¹ gives properties at elevated and subzero temperatures.

Other papers were published concerning the characteristics of the all-chloride nickel solution,⁸² adhesion of nickel deposits as affected by various cleaning methods,⁸³ and the development of methods for replenishing the nickel content when using insoluble anodes.⁸⁴

Research which is extremely instructive in an understanding of throwing power was given in a publication in 1944.⁸⁵ This shows the relative effect of cathode polarization, efficiency, and conductivity on throwing power. By means of Gardam's approximation equation, Wesley and Roehl calculated the metal distribution ratio on the near and far cathodes of a Haring Cell for Watts, hard and all-chloride nickel solutions. These values were then compared with experimentally-determined Haring Cell ratios and the agreement was good. This paper and that of Gardam should be read by anyone trying to understand throwing power.

Another paper, which leads to a better understanding of the plating process, involves the electrodeposition of nickel at high current densities.⁷⁶ Here, the authors determine the limiting current density of all-chloride and Watts nickel solutions under various degrees of agitation. Although current densities of the order of 5000 A/ft² were obtained, of more basic interest was their discussion showing how the concentration, diffusion coefficient, diffusion layer thickness, and transport number, affect the limiting current density.

In Wesley's Hothersall Memorial Lecture⁸⁶ he discusses the phenomenon of nickel anode corrosion; why are some nickels easier to corrode than others? He speculates as to the role played by (electron) vacancies in the third level and their effect on polarization and passivity. By this approach, he further speculates on why chlorides in solution and sulfide in the nickel metal improve anode corrosion. This is one of those papers which creates new ideas each time it is read.

The above speculations had some influence in leading INCO into further work on corrosion⁸⁷⁻⁸⁹ and the effect of other elements in the nickel on anode behavior. This brings us to fairly recent times and we should all be aware of the papers coauthored by



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

Petrocelli and their masterful treatment of corrosion problems. The work reported in the paper by DiBari and Petrocelli⁸⁹ contributed to an understanding of the role of sulfur in SD electrolytic nickel.*

Two papers by Burt Knapp⁹⁰⁻⁹¹ are of much importance to those interested in corrosion of decorative nickel-chromium deposits. These papers are replete with actual corrosion data for many deposit combinations. The first paper suggests that nickel deposits may be far less porous than had previously been thought and that pitting from the surface, eventually leading to perforation, is the chief cause of failure. The pitting may frequently be accelerated by galvanic action of the nickel-chromium couple, but is influenced by the chemical composition and microstructure of the nickel.

The second paper describes corrosion results of "sandwich" coatings where thin layers of such metals as cobalt, silver, lead, copper, chromium, and others were interposed between two layers of nickel. Some of the better results were obtained with chromium and cobalt as the intermediate deposit; cobalt, however, was so effective galvanically that small blisters formed.

Other publications out of INCO, but not completing the list, are on choice of electrodeposited coatings,⁹² corrosion testing,^{93,94} and plating on nickel and nickel alloys.⁹⁵

Other supply house contributions

Because of space and time limitations, it is regretted that background information was not assembled on other equally-important contributions, such as periodic reverse current, conversion coatings, thickness testing methods, stripping solutions, plating on plastics, precious metals, and cleaning developments.

Review

In the introduction, an interest was expressed in how these inventions and discoveries originated. It would be impossible to analyze each invention and inventor in the light of the many volumes that have been written on creativity but it might be of interest to outline briefly the reasons and methods for invention and discovery and some of the conditions or environment for creativity.

Inventions originate from:

1. *Problems* - Thinking up" the problem and defining it are frequently half of the problem. Be dissatisfied; as soon as a process works well, it should be considered obsolete.
2. *New creations* - Entirely new concepts, articles or processes which did not exist before. These are not common and except for concepts have been very rare in the field of metal finishing.
3. *Accidental observations* - One may start off to work on inhibitors but end up with the best metal stripping solution on the market.
4. *Curiosity and random experimentation* - A random observation may lead to an answer to a problem which had not been realized to be a problem.
5. *Generalization and adaptation* - The answer to one problem can frequently be adapted for use in other problems (processes).

An inspection of the developments reviewed in this paper shows that about 60 per cent originated in part from the "problem" source. About 50 per cent involved accidental or random observations, and 25 per cent had some element of adaptation in their origin. There were, of course, several which could be classified under more than one heading. A few of the concepts (unsaturation of brighteners, leveling) might be considered "new creations" but even these originated for other reasons.

Methods for invention and creativity

Although in recent years new operational techniques (discussion methods, mechanical systems, forced relationship) have been devised to solve problems and aid creativity, the classical method still dominates. It consists of several steps; desire or interest;

* TM, International Nickel Company.



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

recognition and definition of problem; preparation or information-gathering; manipulation (putting together of apparently unrelated information); incubation (letting the imagination and subconscious go to work); illumination (the answer may come slowly or suddenly); verification (experimental); generalization (where else can this idea or phenomenon be used?).

Some or all of these steps were used in all of the developments covered in this paper. Variation was always present and cyclic application and feedback were no doubt necessary. Some information gathering, some incubation and some verification are usually necessary at each step of the classical method.

Characteristics and environment

I have taken the liberty to attempt to list some of the attributes which seemed to contribute to the creativity of those workers mentioned in this paper. The most universal characteristics were curiosity, enthusiasm, and the ability to be interested and puzzled. They were also courageous (even to the point of spending their company's money), assertive but not afraid to be wrong, and not afraid to ask questions or question the answers. They were energetic workers, and persistent. Persistency sometimes can be a fault in industry, but this does not appear in any of the developments reviewed. Creative persons have been described as egocentric, asocial and nonconforming. If there was a tendency in this direction, it was not invariably evident to any extreme degree.

In a few cases, team effort was used but in most cases the developments were largely the result of individual effort. The group effort can be seen to be very effective, however, when the proper interest and motivation existed. Motivation was important; the interest or lack of interest, as shown by fellow workers and management, could be a great help or hindrance in this respect. Plush surroundings did not seem to be a significant factor.

In recent years, there is a change coming over plating research as well as research in general. Research today is tending to be based more on basic knowledge than on experience, although it is difficult to distinguish between the experience of yesterday and the knowledge of today. The fact remains that the new research worker today has more fundamental knowledge than those of yesterday and this is shown by the recent exponential increase in technology. It is submitted, however, that it is the imaginative and curious person, whether he be highly-knowledgeable or not, who makes the breakthrough discoveries and inventions.

Acknowledgement

I thank the following for information and help given in the preparation of this paper: L. Westbrook, C. Hoff, R. Hoffman, E. Schweikher, D. Swalheim, R. Bair, R. Hull, B. Martin, K. Long, H. Brown, W. Stoddard, B. Case, M. Beckwith, G. Dubpernell, B. Lewis, O. Kardos, W. A. Wesley, E. Roehl, B. Knapp and K. S. Willson.

References

1. *Modern Electroplating*, The Electrochemical Society, New York, 1942.
2. C. Hoff, U.S. Patents 1,564,413-4 (1925).
3. C. Hoff, *Trans. Am. Electrochem. Soc.*, 50, 301 (1926).
4. M. Udy and F. Nicholson, US Patents 1,383,174-5-6 (1921).
5. C. Humphries, US Patents 1,536,858-9 (1925).
6. L. Westbrook, US Patent 1,681,509 (1928).
7. L. Westbrook, US Patent 1,826,159 (1931).
8. L. Westbrook, *Trans. Am. Electrochem. Soc.*, 55, 333 (1929).
9. L. Westbrook, US Patent 1,818,179 (1931).
10. G. Lutz, L. Westbrook, US Patent 1,818,229 (1931).
11. L. Westbrook, US Patent 2,080,520 (1937).
12. L. Westbrook, US Patent 2,233,500 (1941).
13. L. Westbrook, US Patent 2,218,734 (1940).
14. C. Hoff, US Patent 2,080,479 (1937).



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

15. R. Hull, US Patent 2,080,483 (1937).
16. R. Hull, US Patent 2,196,588 (1940).
17. C. Wernlund, *Trans. Am. Electrochem. Soc.*, **40**, 257 (1921).
18. H. Barrett and C. Wernlund, US Patent 2,171,842 (1939).
19. R.O. Hull, US Patent 2,149,344 (1939).
20. C. Wernlund, H. Benner and R. Bair, US Patent 2,287,654 (1942).
21. D. Holt, US Patent 2,255,057 (1941).
22. C. Wernlund, US Patent 2,347,488 (1944).
23. M.M. Sternfels and F.A. Lowenheim, *Trans. Electrochem. Soc.*, **82**, 79 (1942).
24. F. Lowenheim and M.M. Sternfels, US Patent 2,424,472 (1947).
25. E. Schweikher, US Patent 2,407,579 (1946).
26. R. Hoffman, US Patent 2,457,152 (1948).
27. A. Gray, W. Gresham and D. Loder, US Patent 2,461,507 (1949).
28. E. Schweikher, US Patent 2,402,185 (1946).
29. D.A. Swalheim, *Trans. Electrochem. Soc.*, **86**, 395 (1944).
30. Communication from L. Westbrook.
31. M. Schloetter, US Patent 1,972,693 (1934).
32. P.R. Pine, US Patents 2,029,386-7 (1936).
33. V. Waite, US Patents 2,112,818; 2,114,006 (1938).
34. V. Waite and B. Martin, US Patent 2,254,161 (1941).
35. W.J. Harshaw and K.E. Long, US Patent 2,125,229 (1938).
36. H. Brown, US Patent 2,191,813 (1940).
37. K.G. Soderberg, *Plating*, **53**, 1262 (1966).
38. T. Edison, US Patent 964,096 (1910).
39. H. Brown, *Trans. Inst. Metal Finishing*, **47**, 63 (1969).
40. H. Brown, US Patent 2,523,190 (1950).
41. M. Freed, US Patent 2,409,119 (1946).
42. E. Schweikher, US Patent 2,426,416 (1947).
43. L. Weisberg and W. Stoddard, US Patent 2,026,718 (1936).
44. L. Weisberg, *Trans. Electrochem. Soc.*, **73**, 435 (1938).
45. L. Weisberg, *ibid.*, **77**, 223 (1940).
46. L. Weisberg, *Proc Am. Electroplaters' Soc.*, **37**, 185 (1950).
47. E.D. Viers and B.C. Case, US Patents 2,199,304 (1938); 2,183,384 (1939).
48. B.C. Case, *Proc Am. Electroplaters' Soc.*, **34**, 228 (1947).
49. R. Wagner and M. Beckwith, *ibid.*, **25**, 147 (1938).
50. M. Beckwith, *Monthly Rev. Am. Electroplaters' Soc.*, **28**, 543 (1941).
51. M. Beckwith, *Proc Am. Electroplaters' Soc.*, **28**, 80 (1941).
52. G. Dubpernell, *Plating*, **46**, 599 (1959).
53. G. Dubpernell, *ibid.*, **47**, 35 (1960).
54. G. Dubpernell and K.G. Soderberg, US Patent 2,021,592 (1935).
55. E.M. Baker and W.L. Pinner, *S.A.E. J.*, **22**, 331 (1928).
56. R.D. Miller and A.H. DuRose, *Proc Am. Electroplaters' Soc.*, **34**, 281 (1947).
57. K.S. Willson and A.H. DuRose, *Plating*, **36**, 246 (1949).
58. A.H. DuRose, W.P. Karash and K.S. Willson, *Proc Am. Electroplaters' Soc.*, **37**, 193 (1950).
59. O. Kardos, *ibid.*, **43**, 181 (1956).
60. S. Watson and J. Edwards, *Trans. Inst. Metal Finishing*, **34**, 167 (1957).
61. *Interfinish '68*, p. 54 (International Metal Finishing Conference).
62. R. Clauss and H. Brown, US Patent 3,140,988 (1964).
63. H. Brown, US Patent 3,090,733 (1963).
64. T.W. Tomaszewski and H. Brown, US Patents 3,152,971-2-3 (1964).
65. M.M. Beckwith, *Plating*, **47**, 402 (1960).
66. A.H. DuRose, *Proc. Am. Electroplaters' Soc.*, **47**, 83 (1960).

NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

67. A.H. DuRose and W. Pierce, *Metal Finishing*, 57 (3), 44 (1959).
68. A.H. DuRose, *Trans. Inst. Metal Finishing*, 38, 27 (1961); 38, 84 (1961).
69. J. Edwards, *ibid.*, 41, 169 (1964).
70. A.H. DuRose and R. Stern, US Patent 3,183,067 (1965).
71. B.F. Lewis, *Proc. Am. Electroplaters' Soc.*, 27, 66 (1940).
72. O. Kardos, T. Menzel and J. Sweet, US Patent 2,712,522 (1955).
73. D.G. Foulke and O. Kardos, *Proc. Am. Electroplaters' Soc.*, 43, 172 (1956).
74. O. Kardos, *ibid.*, p. 181.
75. O. Kardos and D. Foulke, in *Advances in Electrochemistry and Electrochemical Engineering*, Ed. C. Tobias, Vol. 2, New York, Interscience, 1962; p. 145.
76. W.A. Wesley, W. Sellers and E. Roehl, *Proc. Am. Electroplaters' Soc.*, 36, 79 (1949).
77. W.A. Wesley, *Monthly Review Am. Electroplaters' Soc.*, 25 (8), 581 (1938).
78. W.A. Wesley and E. Roehl, *J. Electrochem. Soc.*, 82, 37 (1942).
79. E. Roehl, *Monthly Rev. Am. Electroplaters' Soc.*, 34, 1129 (1947).
80. E. Roehl, *Plating*, 35, 452 (1948).
81. C.H. Sample and B.B. Knapp, *ASTM Special Tech. Publ. No. 318* (1962).
82. W.A. Wesley and J. Carey, *Trans. Electrochem. Soc.*, 75, 209 (1939).
83. E. Roehl, *Iron Age*, 146 (13), 17; 146 (14), 30 (1940).
84. W.A. Wesley, D. Carr and E. Roehl, *Plating*, 38, 1243 (1951).
85. W.A. Wesley and E. Roehl, *Trans. Electrochem. Soc.*, 86, 419 (1944).
86. W.A. Wesley, *Trans. Inst. Metal Finishing*, 33, 87 (1956).
87. V. Hospadaruk and J. Petrocelli, *Plating*, 48, 479 (1961).
88. J. Petrocelli, V. Hospadaruk and G. DiBari, *ibid.*, 49, 50 (1962).
89. G. DiBari and J. Petrocelli, *J. Electrochem. Soc.*, 112, 99 (1965).
90. W.A. Wesley and B. Knapp, *Trans. Inst. Metal Finishing*, 31, 267 (1954).
91. B. Knapp, *ibid.*, 35, 139 (1958).
92. C.H. Sample, *Plating*, 37, 482, 618 (1950).
93. F.L. LaQue, *Proc. Am. Electroplaters' Soc.*, 46, 141 (1959).
94. F.L. LaQue, *Mater. Methods*, 35 (2), 77 (1952).
95. W. Sellers and C. Sanborn, *Proc. Am. Electroplaters' Soc.*, 44, 36 (1957).

About the author



One of America's most widely known and highly regarded electrochemical and electroplating scientists, Arthur H. DuRose, was announced as the recipient of the 1969 AES Scientific Achievement Award at the opening session of the AES Detroit Convention, June 16, 1969, by Dr. A.M. Max, chairman of the Scientific Achievement Award Selection Committee.

The members of the committee who assisted Chairman Max to make the choice were Dr. Henry Brown, Dr. Burton B. Knapp, Dr. Joseph V. Petrocelli, Dr. Edward B. Saubestre, and Mr. Perry J. Sloan.

Mr. DuRose, director of electroplating research of Harshaw Chemical Company, briefly acknowledged the announcement of the honor. He delivered the Eleventh William Blum Lecture at the Opening Session of the 57th AES Annual Convention in Montreal in June 1970. The award consists of a commemorative plaque and a \$1500 honorarium.

Arthur DuRose was born in 1912 to recently arrived English parents in the Auto City of Flint, Michigan where he received his early schooling. He attended Graceland Junior College in Lamoni, Iowa where he was president of the Engineer's Club, and graduated with high honors. He then went to Michigan State College in 1932. Here he became interested in electro and colloid chemistry under Dr. D.T. Ewing and was elected a member of Tau Beta Pi, graduating in 1934 with a B.S. in engineering.

For a little over a year he was employed by Chevrolet-Flint on tin plating of pistons, and on hard chromium plating. He then went to the University of Cincinnati and with the help of a graduate assistantship, graduated with an M.S. in 1937. With the interest in



NASF SURFACE TECHNOLOGY WHITE PAPERS 80 (1), 1-19 (October 2015)

electrochemistry instilled in him by Dr. Ewing and G. Spencer at Chevrolet, he joined the then small Electroplating Division of Harshaw Chemical Company. His intention was to work one or two years and go back to school, but the work was so fascinating, he has never left.

Except for the war years when he worked on Manhattan District Projects, he has been closely associated with Harshaw's Electrochemical and Plating Research and Technical Service but in recent years he has concentrated on research. During the latter part of the war he was associated with a War Metallurgy Committee for evaluating and stimulating the use of lead deposits and this developed into an active interest in Committee B-8 of ASTM. He was a member of several technical societies and has held offices in the AES, both locally and nationally. These included Research Board Chairman, National Director, and President of the Cleveland Branch.

Mr. DuRose authored or coauthored some 20 papers or chapters and more than 25 United States Patents on chemical or plating subjects, and is listed in American Men of Science. Although most of his time had been devoted to applied research, he contributed much to basic understanding in electroplating. He was first, or one of the first, to demonstrate leveling and geometric leveling, to show reasons for the superior corrosion protection by duplex nickel, and to study the effects of types and mechanisms of addition agents on the composition, structure and leveling of nickel deposits.

In 1969, he lived in Richmond Heights, Ohio with his wife Helen. They had three grown children, Dick a lawyer, Barbara a teacher, and Betty a legal secretary. He had a patient and understanding wife who allowed him to use most of his spare time keeping up with his work and the electrochemical literature; in those years there was little time for outside activities except for an occasional game of golf and reading history or philosophy.