Zinc is among the “workhorse” metals plated today. In the automotive industry alone, zinc is the mainstay in providing corrosion resistance to everything from automotive body panels to fasteners, brackets and other small parts. It is plated on everything from steel coils to small screws. The use of zinc as a sacrificial corrosion agent dates back to the first half of the 19th century. 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 for the AES Golden Jubilee by Ernest W. Horvick, who spent most of his career at the American Zinc Institute, relates the history of zinc plating in all of its incarnations, including barrel, rack and continuous strip plating.

In the 19th century, as iron and steel came into more extensive use, their susceptibility to rusting was quickly realized to be a serious problem. The need for suitable protective coatings was early recognized and zinc was employed for this purpose over a century ago.

Zinc coatings applied by various methods have been regarded as the most practical method for retarding corrosion of iron and steel throughout the years. While some historians state that the electroplating of iron and steel with zinc for protection against corrosion was first proposed in 1840, as indicated by the following classical reference, zinc was electrically deposited prior to this date.

“In 1829, Dr. John W. Revere of New York, brought before the Lyceum of Natural History of that city, samples of zinc-coated spikes and small plates attached to wood, the whole having been exposed to the action of sea, air and water since 1827. Revere was convinced that the coating of zinc formed an excellent protection for iron articles. The mention of electrochemical terms in Revere’s work indicates that the coating was accomplished by what is known as the electrogalvanizing process.”

It was in the year 1800 that the power of the electric current to decompose water was first observed, the discovery being made by Nicholson and Carlisle. It is interesting to note from the description of this first electrochemical experiment that the voltaic battery furnishing the current was made up of plates of zinc and silver.

Shortly after, Sir Humphry Davy became engaged in electrochemical research. His work in this field was well along by the end of 1807 and included indications that one metal could be deposited upon another. The name of the first man to deposit zinc on steel electrically is lost in history. However, Dr. Revere’s reference to 1827 established it as having been done prior to that date.

The first patents relating to electrogalvanizing were issued in England in 1852. English patent No. 951 issued to Wall in 1852, describes a solution for electrically depositing zinc upon iron and states that the work of deposition is to be carried out by means of voltaic cells. Other early English patents namely Person, No. 951* of 1854; Puls, No. 1276 of 1855 and Brown, No. 1175 of 1857, all show that the problem of depositing zinc upon iron by electrochemical means received considerable study.

An alkaline zinc cyanide plating bath was patented as early as 1855, although baths of this type did not attain commercial importance until 1916. The first American zinc plating patent was granted in 1862, but extensive use of the electrolytic process of galvanizing was a physical impossibility in these early days prior to the advent of the electric dynamo because of the limited electrical power...
available from batteries. Then, a battery of six Daniell cells in series parallel was only capable of delivering 120 A-hr in 10 hr. This was only enough power to deposit 4.8 oz. of zinc. **The weak current used for the purpose of depositing or plating came exclusively from batteries until the practical work on copper refining of Elkington in 1867.**

The first practical dynamo appeared about 1880, but some 20 years of development passed before they became reliable. The plating of most metals upon another by electrochemical means requires the use of an electrogenerator or dynamo having low voltage combined with large capacity in amperes of current delivered. It required much research to develop this particular type of dynamo and generate a suitable level of efficiency. The possibility of the electrodeposition of zinc was therefore unappreciated until that time. However, after the invention of the dynamo and while its improvement was taking place, a revival of electrogalvanizing ensued. This is manifested in the patents issued to Elmore in 1881, Classen in 1882, Philip in 1890 and Cowper-Coles in 1893. Other patents for the electrodeposition of zinc, mainly for solutions, were subsequently issued in England, Germany, France and the USA. From 1880 to 1903, the total of these from the above countries was 49. However, the early zinc electroplating solutions permitted the use of current densities of only 5 to 20 A/ft² of surface being coated, so that zinc was deposited at too slow a rate for general

** Now, with modern [1959] electrolytic DC power sources, 12,000 A at 18 V could deliver 120,000 A-hr in 10 hr, and would deposit 4,800 oz. of zinc in the same time on one fully automatic machine.

---

**How Zinc is Applied Electrically**

Forty wires moving continuously are held immersed in the electrolyte solution. They make contact with the negative side of the electrical current as they pass through a series of porcelain contact fingers. The electrical energy for the galvanizing is furnished by large motor generator sets delivering 15,000 amperes each at low voltage.

The weight of the zinc coating is accurately controlled by the amount of electric current and by the speed at which the wire travels. The result is a tight, adherent, dense, smooth and uniform zinc coating as bright as unpolished silver.
application. Not only was the plating slow, but the control was so uncertain that the work was frequently unsatisfactory. In effect, the zinc coatings generally produced then were dull, non-uniform, unattractive and limited in corrosion resistance because they were deposited from inefficient baths or inadequately cleaned work.

**The development of the industry**

Early in the 20th Century, the zinc electroplating industry began to develop and grow from its humble inheritance of the previous century. The development stems from the creation and invention of various electroplating processes. A brief discussion of these processes will show how their development contributed to the advancement of the zinc electrocoating industry.

**The Meaker process**

Confronted with the necessity of rust-proofing certain steel products which existing methods of electrogalvanizing could not handle in 1905, Guy L. Meaker developed a new process and solution which soon gained recognition as the first successful electrogalvanizing. This process combined an advanced, high-speed electrolyte of the sulfate type with scrupulous precleaning of the steel, without which the adherence of the zinc is faulty and its corrosion resistance is impaired. For many years careless pickling had been regarded as adequate before electroplating, since it was thought that the remaining dirt and scale were covered by the plate anyway. However, because this did not permit good plating, stringent cleaning was required in the Meaker process.

**Tainton and Bethanizing process**

The Tainton or Bethanizing process, developed in 1932-1933, is a special application of acid sulfate zinc plating, using insoluble silver lead anodes. In this process the raw material is roasted zinc concentrate containing about 65% metallic zinc. The zinc content of the plating bath is derived from roasted zinc ore concentrates which are dissolved in sulfuric acid. The solution is then highly purified. The zinc does not appear in metallic form until it is deposited from the electrolyte onto the carefully cleaned steel wire.

The process is carried out in long bath cells through which the wire passes. The current employed is of very high amperage. Since the plating solution is highly conductive and highly agitated by the fast moving wire, current densities from 1000 to 2000 A/ft² can be used. The current passes to the wire from the insoluble anodes and is taken off by sliding cathode contacts at close intervals.

The coating obtained is never less than 99.99% pure zinc. It is uniformly and continuously built up on the steel base as the wire passes through the solution. The weight of the coating which can be two, three or more times heavier than other zinc coatings and still not be affected by the most severe fabricating operations, is determined by the speed of the wire. As this speed can be accurately regulated at all times, the weight of the coating can be controlled with precision. In order to improve appearance, the plating can then be compacted and burnished, or drawn through tungsten carbide dies for smoothing and brightening the coatings.

**The Herman process**

The first electrogalvanizing process used on a large commercial basis was that developed at the Langbein-Pfanhauser Works in Germany. This very important development in the history of the zinc plating industry, known as the Herman process, uses a nearly neutral sulfate bath as an electrolyte and plates with zinc anodes at moderate current densities from 50 to 100 A/ft². The Herman Process was apparently the first to develop the necessary wire handling method combined with a more advanced wire cleaning method, making possible the production of reasonably heavy coatings in a commercial scale operation.

With certain variations in electrolyte composition and methods of wire cleaning, essentially similar processes employing soluble zinc anodes have been used in electroplating plants set up in the United States.

**The Marino process**

The Marino electrogalvanizing process is a development in the zinc plating field which is considered similar in procedure to the Meaker process.

**The Hubbell and Weisberg process**

The Hubbell and Weisberg process was developed around 1940. It was introduced as a new method of electroplating zinc on steel by utilizing waste materials instead of new metal for coating. The advantage of the process lies in its ability to use cheap sources of
zinc instead of zinc anodes. The zinc is dissolved from galvanizer’s skimmings, brass foundry fume, organic reduction residues or by a solution of ammonium chloride and ammonia. Insoluble graphite anodes are used in the plating tank, but iron or stainless steel anodes may be used.

The zinc plating takes place from this alkaline electrolyte which is first purified. Plating reduces the zinc content of the electrolyte which is then returned to the leaching plant where the zinc removed by plating is replaced. The plating tank is specially designed to take advantage of the fact that the anodes seldom have to be changed, and to provide covers that prevent escape of ammonia fumes, and at the same time permit easy rethreading of wires and strip.

High current densities are employed in the Hubbell and Weisberg process, an aspect which together with the high conductivity of the solution, and the design of overall equipment, makes the process highly economical in use of electrical power.

A significant advantage achieved in the process is that savings increase as the amount of zinc used increases, considering that a special plant has to be provided to put zinc in the skimmings or other products into solution. Also, the operating costs of this plant must be added to the purchase price of the zinc, in skimmings and other waste materials, to obtain the actual cost of zinc used in the plating tank.

**Rapid zinc process**

In the early 1940s, the Hanson-Van Winkle Company developed a new type of acid bath and method of application known as the “Rapid Zinc Process.” The electrolyte is simple in composition, consisting of zinc chloride and zinc acetate without addition agents. Coatings are deposited at current densities of 40 to 1000 A/ft².

When zinc-aluminum anodes are used, as explained in another section, no chemical attack is incurred when the electrolyte bath is idle. This, in conjunction with practically 100% anode and cathode efficiencies and the inherent stability of the chemical constituents of the bath, results in almost constant solution pH. The rate of solution flow depends upon the particular application. A simple method of analysis for bath control is also included in the process.

**The Corronizing process**

Corronizing is a process in which a composite electroplated coating is used. This is comprised of a layer of nickel plated on the basis metal, followed by a layer of zinc (or tin). The process was developed and introduced in the early 1940s. The dual coating is heated for a period up to six hours at a range of temperatures in excess of 260°C (500°F), depending upon the thickness of the basis metal and the conditions which it must meet. The operational sequence, similar to conventional plating procedure, consists of cathodic cleaning, pickling for scale removal, anodic pickling, nickel plating, zinc plating from an acid bath and then heat treatment.

**Plating solutions**

The various zinc electrocoating processes and applications that have been developed over the past half century have been and still are characterized by the compositions of the plating baths. These are of two general types: one utilizes an acid electrolyte, and the other an alkaline electrolyte. The former are known as sulfate, sulfate-chloride, chloride, chloride-acetate and fluoborate baths, depending upon their chief constituents. The alkaline electrolytes are mostly cyanide baths, although zincate and pyrophosphate baths also have their advocates.

The choice between the types used is based upon a number of factors. For instance, in considering which bath to use, the higher plating rate and low operating costs of acid baths have to be balanced against the superior throwing power of the alkaline cyanide baths. Thus, the acid baths, although having poor throwing power, are used largely for plating strip and wire because of their high plating rate and lower operating costs. Alkaline cyanide baths, with their better throwing power, are used in plating objects of irregular shape.

**Acid baths**

Of the acid baths, the sulfate solution is the most widely used. Reasonably priced zinc sulfate is the principal salt in this bath and because it is highly soluble in water, solution can be highly concentrated, with the advantage that the general ratio of zinc to other type ions makes possible an increased rate of zinc deposition. Because of high anode efficiency and the tendency of anodes to corrode, additions of sulfuric acid must be made periodically to maintain acidity. Also, sodium acetate or aluminum chloride are added to the bath because their buffering action helps regulate solution pH.

The sulfate bath is the most commonly used electrolyte for zinc electrodeposition. As mentioned earlier, it is used extensively for coating wire and strip. Deposits from this bath are whiter but coarser-grained than those deposited from cyanide baths.

Chloride baths made from solutions of zinc, sodium and aluminum chlorides yield very good deposits. The higher conductivities of these baths allow them to be run at high current densities, without requiring agitation or other precautions to prevent overheating the electrolytes.

Chloride acetate solution is the electrolyte used for the “Rapid Zinc Process.” Only zinc chloride and zinc acetate without additive agents are used in this solution. The bath may be operated with zinc-aluminum alloy anodes so that no chemical attack of the anodes takes place when the bath is not in use.

Fluoborate baths provide a comparatively new method of zinc electroplating. They can be operated at very high current densities without impairing the deposits. It is claimed that the fluoborate electrolyte gives good results with cast and malleable iron, where plating in a cyanide bath is a problem.

*Electrogalvanizing or electroplating zinc on steel has made considerably progress in recent years and is becoming an important factor in the electrocoating field.*
Alkaline baths

The alkaline baths are generally used for batch zinc electroplating, and are capable of providing a variety of deposits. While the cyanide baths have formed the basis for most of the alkaline electrolytes, comparatively recently baths employing ammonium salts have been developed. The relative advantages of alkaline baths such as superior throwing power and disadvantages with respect to plating rates and operating costs have already been discussed.

Alkaline cyanide baths are made up largely of zinc cyanide in solutions of sodium cyanide and sodium hydroxide. They are found to be the most easily controlled of all the zinc plating baths. The cyanide electrolytes are employed with comparatively low current densities and soluble anodes. They yield fine grained deposits which, from the plain baths, are quite dull. With small additions of mercury, however, a white matte can be produced [but not in this day and age — Ed.].

An important development in the electroplating of zinc was the introduction of bright zinc coatings directly from the plating bath. However, these coatings are frequently given a bright dip to further enhance their decorative qualities. Bright zinc plating is obtained from cyanide baths free from heavy metallic impurities or by the use of special agents in the bath which act in brightening the deposit and improving the throwing power at low current densities. The brightening additives are composed of organic compounds such as gelatin, glucose, dextrin and condensation products of phenols and aldehydes. They are normally used with soluble salts of chromium, molybdenum, cobalt, nickel and germanium. Superior corrosion resistance is claimed for these bright deposits.

Pyrophosphate and sodium zinicate baths which have been developed are described in the literature. The zinicate bath contains additions of various chemicals including sodium cyanide which acts to refine the grain size of the coating.

Anodes

Anodes used for electrodeposition of zinc are of two types - soluble and insoluble. The soluble anodes are obviously of zinc to provide the metal to be plated. With insoluble anodes, the zinc is furnished to the electrolyte by leaching material containing zinc oxide, as explained in the section on the Tainton or Bethanizing process.

In the electrodeposition of zinc with soluble anodes, the zinc ions in the electrolyte are maintained during operations by electrolytic dissolution of the zinc of which the anodes are comprised. The plating or electrogalvanizing solution automatically maintains itself by dissolving zinc from the anodes in the exact quantities being plated out on the steel that is being coated. Over the years there has been, however, considerable change in opinion as to what the anode composition should be.

In the early days the composition of the zinc used for anodes differed widely, containing impurities of varied types and amounts. Neither zinc of high purity, nor the means of controlling exact composition were available, and as a result, film quality was often inferior. In more recent years, soluble zinc anodes have been commonly made from cast or wrought metal of such grades as Prime Western (98.5%), Intermediate (99.5-99.8%) and higher purity of the order of 99.95 to 99.98% zinc. With these, continuous filtration has been customary in large continuous installations but not in still tank operation, although suspended material must be removed periodically to prevent pitting, roughness and poor deposits. Sludge represents loss of zinc metal and must be removed to permit high quality of work. Certain metallic impurities also may go into solution, and in codeposition with zinc have adverse effect on corrosion resistance and appearance of the deposit.

While over the years all grades of zinc have been used for anodes, it has been found that best results are undoubtedly obtained with Special High grade (99.99% pure) zinc. The advantages of pure zinc for anodes have been realized since the beginning of the zinc electroplating industry but could not be exploited until modern methods rendered the manufacture of such high purity zinc a commercial reality. Now, with 99.99% purity zinc, the formation of sludge from local action of zinc with metallic contaminants is minimized. Sludge not only represents loss of zinc but also detracts from efficiency in that it must be removed from the bath to permit consistently smooth deposition.

With Special High grade zinc anodes, in addition to this advantage, higher plating efficiency is achieved, and it is possible with various proprietary solutions (to be discussed in a later section) to secure extremely bright zinc coatings. In general, with these anodes higher quality if obtained irrespective of the type of zinc plating produced.

All zinc anodes, but least of all high purity zinc, tend to be dissolved by direct chemical attack when the plating bath is not in operation, resulting in loss of the metal by corrosion, and saturation of the electrolyte to such a high degree that it cannot be operated efficiently. With Special High grade zinc, because of the high anode efficiency, the electrolyte gradually tends to become supersaturated with zinc. As a result of demands from industry for improvements, research was carried out to ascertain the effects of alloying anodes with certain metals which are not harmful to the bath. To minimize anode dissipation during idle time, and promote uniform corrosion during operation, anodes alloyed with aluminum and mercury for cyanide solutions or magnesium and calcium for acid electrolytes were introduced. [Again, mercury is out of the question today — Ed.]. These additions were found to eliminate excessive differences between anode and cathode current efficiency. Excessive anode dissolution has also been minimized by use of auxiliary sheet steel, nickel plated sheet steel or sheet nickel anodes along with the zinc anodes. Auxiliary anodes have likewise been found to be helpful when plating steel with zinc, if recessed parts are being treated, in that they ensure a uniform deposit over an irregularly shaped surface.

Electrogalvanizing of Strip Steel

Developments in the steel industry at the end of the 1920s, which provided inexpensive metal with deep drawing properties, set the stage for large scale electrogalvanizing of strip steel. After the introduction of the continuous hot mill in 1927 came the develop-
ment of means for cold reduction of the bands in 1929. These two innovations were the basis for the modern high speed continuous hot and cold tandem mills which convert a 17,000-lb. slab to a ribbon of steel of uniform desired width and thickness at a fabulous speed - in excess of a mile a minute. Thus, large tonnages of wide strip steel were made available for different processes including electrogalvanizing. Research was immediately carried out to devise means of electrodepositing zinc on continuously moving strip. Originally, the widths produced were less than 20 in., with the majority less than 12 in. It is believed that one steel company had a pilot line in the 1930s devoted to electroplating wider strip. It was rumored that the process utilized insoluble anodes and the zinc content of the electroplating was maintained by cycling through a leaching and purification step, using low grade zinc ores and tailings as a source for zinc.

In 1939 a pilot line for tin plate installed at Weirton Steel Company was converted to plate zinc. For this, the Hubbell-Weisberg electrolyte was used, to which an ammoniacal zinc chloride complex was added. The outbreak of the war brought the Weisberg electrolyte was used, to which an ammoniacal zinc Company was converted to plate zinc. For this, the Hubbell-W...
Today’s mechanical devices and automatic equipment for zinc electroplating have indeed been developed to a high degree of efficiency. In the early days everything was done by hand. As mechanisms were developed and introduced, hand labor was gradually augmented or replaced. Now mechanical handling and processing equipment is available which operate partially or completely automatically so that very little operational attention is required.

Since the beginning of the century, equipment manufacturers for zinc electroplating have met production problems of every conceivable nature - some relatively simple, others so intricate as to need unusual, original and ingenious solutions. With improvements and new developments in plating apparatus, there have been commensurate advantages - increased and standardized production at lower cost; reduced labor requirements and labor turnover; increased salability of product through improved quality and finish, simplified and standardized solution equipment; reduced chemical and acid consumption; lower equipment upkeep; less unit and floor space; and with all clean, sanitary operating conditions. The characteristic features of design, construction and operation of the equipment now available are based upon the most advanced principles of mechanical, electrical and chemical engineering. These principles are applied to meet actual operating conditions as they exist in everyday plant operations. New, fully automatic machines are in operation, designed for the whole zinc plating cycle - electrocleaner, cold water rinse, electrified acid dip, cold water rinse, cyanide dip, zinc plating, cold water rinse or reclaim, cold water rinse, cold water rinse and spray, hot water, load and unload. Citing a representative installation, the parts to be processed are placed on the plating racks and carried to the zinc plating machine on a continuous conveyor. After plating, they are carried to the final assembly point by the same means of transportation. Electric current for the zinc plating tank is consumed at the rate of 8500 A at 6 V. The electrocleaner tank requires 4000 A at 6 V. Production and quality problems in the plating room are now reduced to a minimum as a result of the installation of such automatic machines.

Of course, the cycle will vary in accordance with the demands of the cycles previously discussed. The majority of electroplated zinc coatings run from 2.5 to 12.7 µm (0.1 to 0.5 mil) thickness. For outdoor applications, zinc coatings of 12.7 to 50.8 µm (0.5 to 2 mils) thick are applied. This type coating is usually preferred for close dimensional or threaded parts.

Zinc-plated pennies
An interesting sidelight on zinc coated steel is that during World War II zinc-coated steel pennies were produced to save 4600 tons of copper normally used for the production of copper pennies. The pennies were made from steel sheet which had been zinc coated electrolytically. However, the electroplated zinc on steel sheets was also used as a satisfactory substitute for the more scarce materials - nickel, tin and chromium among other strategic metals. According to an article which appeared in November 1942, ‘the zinc plated sheet is new in that pure zinc applied by an electroplating process to steel sheets has not been widely commercialized before.’

Specifications
The first recorded specific studies by ASTM on electroplated coatings were started about 1927 by a Subcommittee on Hardware Specifications (now Subcommittee XIII). In this investigation steel articles of many shapes were coated by many methods including electroplated zinc. Specimens were exposed in several locations, including New York, NY, Sandy Hook, NY, Pittsburgh, PA, State College, PA and Key West, FL, and were inspected at intervals by interested members of the sub-committee.

However, because of certain circumstances, two years later a special study of electroplated coatings was carried out subsequently and exposure tests of electroplated steel were conducted under the direction of a joint committee consisting of representatives of ASTM Committee A-5, B-3 and B-6, and the Research Committee of the AES. The specimens were to be prepared at the National Bureau of Standards. It was truly a cooperative effort. A simple system of rating on a logarithmic scale of 1 to 5, later modified to 10, was employed with special reference to the appearance and extent of rust. This system made it possible to draw objective conclusions, based on arithmetic averages of the successive ratings of electrodeposited zinc and other metallic coatings. The results of the exposure tests were published by the National Bureau of Standards. These results and knowledge gained by industry served as the basis for specifications for electroplated coatings that were first prepared by the joint committee in 1935 and have since been revised and extended.

Because the joint committee was made up of the representatives of the other groups previously mentioned, its official actions were sometimes cumbersome and slowed down. This dilemma was solved in 1941 by the formation of ASTM Committee B-8 on electrodeposited metallic coatings. Since then it has functioned successfully and effectively in maintaining specifications up-to-date.

The electro-process, whose coating is applied by means of electric power, offers continued promise of advancement as improved methods and equipment become developed. Not only is the prospect continually brightening in this respect, but with continued opportunity to replace manual handling of items to be coated, increased rates of production at lower production cost can be envisioned.

Tremendous studies have been made on the electroplating and electrogalvanizing of zinc, as evidenced by the replacement of large electric power generating units for the weak batteries first employed and the continued innovations and improvements of plating solutions. There is every reason to feel that further improvements will be forthcoming under this process.

About the Author
Ernest W. Horvick graduated From Princeton University in 1935 as a chemical engineer. Before coming to the American Zinc Institute, he was with Weirton Steel Company, Bell Aircraft and Minneapolis Honeywell, in technical, supervisory and marketing capacities. He was a member of the American Chemical Society, the American Society for Metals (ASM International) and the Society of Die Casting Engineers.