The electrochemical protection of iron and steel against corrosion

by **Colin G. Fink**[1]).

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In the utilization of materials for the construction of a wide diversity of products characteristic of the modern highly technically developed age, metals are a very important factor. Our sky-scrapers, our bridges, our railroads, airplanes, agricultural machinery, electrical equipment, etc., all incorporate metals as an essential constituent. The metals available to us in a sufficiently large quantity and at a cost sufficiently low to be considered for most of these structures and products are relatively limited. Out of a total of about 80 metals which occur in the earth's crust, there are only about 9 that come into account. The chief basis metals today are iron, copper, and aluminum. Of these three, iron far out-weighs the other two not only in quantity available, but in mechanical properties which the other two do not possess—aside from the cost of iron which is far below that of the other two. The world's annual output of iron now approaches 100,000,000 tons; that of copper, 2,000,000 tons; and that of aluminum, ½ million tons. Engineers have long recognized that the one metal that we must primarily take into consideration as a metal of construction is iron, or its alloy, steel. The other six metals that enter chiefly into modern structures and products are tin, zinc, and lead—used mainly for protective purposes; and manganese, chromium, and nickel—important as steel alloy constituents.

The one inherent defect or weakness in the case of iron and steel is the low resistance to corrosion, as compared with that of copper, aluminum, tin, zinc, lead, chromium, manganese, or nickel. As is well-known, there are copper and zinc roofs that have been exposed to the elements for many generations and are still in good condition. Chromium is not only resistant to corrosion at atmospheric temperatures, but at white heat; tin forms a protective coating which is very insoluble under ordinary conditions; etc. We shall discuss the properties of these metals in more detail below.

This one outstanding defect on the part of iron—not to withstand corrosion—and on the other hand, its high tensile strength, high fatigue value, and its mechanical properties, with which no other metal can compete, has been an incentive to chemists and engineers to devise various means of protecting iron and steel against corrosion.

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[1]) Head, Div. of Electrochemistry, Columbia University, New York City.

Although there have been a half dozen different methods in commercial use for the protection of iron and steel, including oiling and painting of the exposed parts of the metal, we are going to confine ourselves to electrochemical methods, since we consider these the most practical, as well as the most efficient, if properly applied. During the last ten years very important improvements have been made in a number of the electrochemical methods. We will consider first the cathodic processes, including the application of coatings of nickel, chromium, zinc, etc.; and then the anodic processes, which are rapidly being adopted by many metal concerns.

Coatings of Electrodeposited Nickel.

The lasting properties of solid nickel are well known. We have compared solid nickel with solid copper, tinned iron, and galvanized iron, exposing the samples to severe intermittent corrosion tests:— salt spray followed by drying, then water spray and drying, and again salt spray, drying, etc., repeating the cycle over and over again, each step in the cycle occupying at least fifteen minutes. This test simulated, although in a very much more intensive manner, the conditions prevailing on any small island in the tropics. Under such severe conditions, the solid nickel samples outlasted by far the other samples tested. With this fundamental valuable property of nickel as a basis, it seemed to us that methods and means should be found for the application of a coating of nickel to iron and steel that would effectively protect the underlying steel against corrosion, not only in the temperate zones where the largest percentage of iron and steel products are consumed, but also in the tropical zones where galvanized iron is " ruined within the brief space of a year".

Accordingly, a systematic investigation was undertaken by the writer to determine the underlying cause or causes for the common failure of nickel coatings on steel. One ever present factor to be contended with in the electrodeposition of nickel is hydrogen: It is most uncommon indeed to deposit nickel without hydrogen. The injurious effects of hydrogen are not confined to the embrittling of the nickel deposit, but more objectionable still are the deep pits or holes due to hydrogen. The embrittling effect may be regarded as being primarily due to the codeposition of nickel and hydrogen— the latter being either adsorbed or dissolved in, or chemically combined with, the nickel. The other, by far more destructive effect of hydrogen on the nickel plate, that of producing pinholes, pores, or pits, is most commonly brought about or initiated by a mere speck or fine scratch on the surface of the steel:

Finely divided particles of dust or of other material, insoluble in the acid sulfate nickel bath, will migrate to and deposit on the surface of the cathode by electrophoretic forces. Each such particle, upon anchoring itself to the surface, immediately becomes the focus center of hydrogen. Upon close inspection of the cathode surface during electrolysis, a minute gas bubble attached to the dust particle soon becomes visible. The bubble slowly grows in size and no nickel is deposited at that point. A pit or hole in the nickel plate is the result.

By carefully guarding against the contamination of the nickel bath, and by the judicious and regulated supply of a cathode depolarizer, such as ozone or hydrogen peroxide, we succeeded in producing nickel coated steel sheets that developed no rust specks even after two years' continuous exposure on the roof of one of the buildings in the business district of New York City. The nickel solutions were carefully filtered before use, the cells were covered to prevent the introduction of atmospheric dust, and finally, the nickel anodes were surrounded by a finely porous diaphragm to avoid loosened, insoluble constituents from the anode from migrating to the cathode and attaching themselves to its surface.

We found that under these conditions nickel deposits as thin as 0.001 inch (0.025 mm.) rendered splendid protection to the steel underneath. One of the outstanding advantages of nickel for electrodeposition as compared with most other metals is its high throwing power. During nickel deposition, the metal will fill every pit and crevice, assuming proper cleaning and plating conditions.

The objections that have been lodged against nickel is its marked tendency to become dull and unattractive in appearance, even under relatively dry atmospheric conditions. Another objection to nickel plate is its comparative softness and consequent ease with which it is scratched. Both of these objectionable features of nickel plate are readily counteracted nowadays by the super-electrodeposition of a thin coat of chromium (0.00001 to 0.0005 inch, or 0.00025 to 0.013 mm.).

Coatings of Cobalt and of Cobalt-Nickel Alloy.

Cobalt is readily deposited from an acid sulfate solution containing a little chloride and borate. The plate retains its bright lustre better than nickel, and can be made relatively hard. On account of the high price of cobalt, as compared with that of nickel or of chromium, the metal is not commercially employed as such to any great extent. However, in combination with nickel, it has recently found wide application. Thus one of the standard " bright nickel " baths extensively used in the United States is an acid sulfate bath containing both nickel and cobalt, in the proportion of four to one. The valuable characteristics of the nickel-cobalt alloy plate were reported upon by us a few years ago[1]). The plate protects steel better than either nickel or cobalt alone. The plate is relatively hard and very attractive in appearance. It is the whitest plate known. By direct comparison with other " white " plates, including silver, we found the cobalt-nickel plate to rank above all. We attribute the whiteness of the plate to the compensating effect of the yellow cast of nickel and the blue cast of the cobalt—the same principle that is daily utilized in the laundry, of dipping yellow linen into bluing water.

Other applications of cobalt in conjunction with chromium and tungsten will be discussed below. In general, the precautions prescribed for nickel plating apply equally as well to cobalt or cobalt-nickel alloy plating.

Electrolytic Copper Coatings.

From time to time suggestions have been made to deposit copper on steel as a protective coating, but it is only within recent years that copper-plating steel has become an industry. In the United States, large sheets of steel are electrodeposited with copper and these sheets are subsequently made up into cans to serve as containers for oil. However, in comparison with chromium or nickel, the copper is not as serviceable. On the other hand, copper-plated steel has found an important application in the automobile industry. Here copper serves primarily as a metal to reduce the cost of burnishing the tempered steel parts such as bumpers. The usual procedure is to remove the scale of the bumper parts with the aid of an emery wheel. This results in relatively deep scratches on the steel. Now if this hard steel were polished, it would be very expensive. Accordingly, a relatively heavy electrodeposit of copper is applied to the bumper steel surface and then, due to the malleability and tendency of the copper to flow, the bumper parts can readily be brought to a high polish. The polished parts are then nickel-plated, and finally chromium plated.

We might include another application of copper on steel, namely that of copper-coated steel telephone wire. Here the copper performs a double purpose. It not only protects the steel which gives the wire its high tensile strength, but it serves as the electric conductor. The electrolytic apparatus in which the steel is plated is almost a quarter of a mile long.

Electrolytic Chromium Coatings.

Chromium is a relatively new-comer in the field, but within a short time it has become very important commercially, and thou-

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[1]) *Colin G. Fink* and *K. H. Lah,* Tr. Electrochem. Soc. **58,** 373 (1930).

sands of applications for chromium-plate have been found. One of the outstanding advantages of chromium over all other of the common metals being used to protect steel is its great wear-resistance. On this account, various mechanical devices, including steel dies for drawing wire and tubing, have their bearings chromium-plated. We have exposed chromium-plated steel parts to atmospheric corrosion for several years, and the articles are still in first-class condition. Chromium may be deposited with copper and nickel as is the practice in the bumper industry. An interesting application of chromium-plated steel parts will be described below under the caption " Heat Treatments". Not only have we deposited chromium on the outside of steel pipes, but also on the inside of these pipes, through which thousands of gallons of corrosive liquids have passed. Another interesting application is the chromium-plating of the inside of gun barrels, thereby extending the life of the rifling many times. Finally, those interested in golf may know that the shafts of the best golf clubs are made with steel, chromium-plated. Under properly controlled conditions, chromium plate on steel can be made absolutely free from pinholes.

Electrolytic Zinc and Cadmium Coatings.

For a long time, the hot galvanizing process was so well established that it was difficult for the electrolytic zinc methods to compete. However, within recent years, there have been an increasing number of plants changed over from the hot galvanizing process to the electrogalvanizing process. For one thing, carefully tempered steel and steel parts, shaped and built to close specifications, cannot be hot galvanized without injuring both the temper and the shape. Accordingly, articles such as the automobile tire rims and many machine parts are electrogalvanized in preference to hot galvanized. The Bethlehem Steel Company has now been in operation for over two years on electrogalvanizing steel wire, and the product, is in every respect superior to the hot galvanized. The process employed is the Tainton process, and a novel step in this is the use of the zinc ore as a starting material, which is leached with spent sulfate liquor. In other words, the zinc in the ore is deposited directly on the wire, without ever being in the ingot or molten state. Among the valuable properties of this new product is its outstanding malleability. Sharp bends can be made in the wire without cracking the coating. Important, too, in the Tainton process is the use of sulfate in place of cyanide, thus doing away with the unstable, poisonous bath.

A close competitor of zinc, especially for smaller iron and steel parts is cadmium, either as such or alloyed with zinc. Many thousands of iron outlet boxes used in electric wiring are now being plated with cadmium-zinc alloy, and the performance is exceptionally good. There is some discoloration, but there is no tendency for the iron underneath to show through, even after six or eight years of service.

Electrolytic Tin Coatings.

What applies to electrolytic zinc, applies in great measure also to electrolytic tin. Another important advantage of electrodeposited tin on iron and steel, as against hot tin as ordinarily practiced, is the relative freedom from pinholes in the electrolytic process. There is every indication in the United States that electrolytic tin will displace hot tin dipping methods within the next few years. A bright mirror surface is obtained[1]).

Electrodeposition of Hydrogen.

Although hydrogen has often been characterized as belonging to the metals, very few investigators have ever considered using it as a protective coating for iron and steel. Although the film of hydrogen deposited on the steel has a very short life and it is, therefore, necessary to continue plating hydrogen as long as it is desired to protect the steel, this objection is not as serious as it would seem on first consideration. As a matter of fact, a number of steam boilers and condensers in the United States are today protected from corrosion, and also from boiler scale formation, by applying an invisible hydrogen film on the surface of the boiler tubes. A small generator of six volts is connected to the boiler tubes forming the cathode and to a carbon anode inserted into the boiler but carefully insulated from the boiler shell.

Miscellaneous Electro-Coatings.

On a small scale, cast iron and steel parts are being gold-plated and subsequently heated in hydrogen. Similarly, silver-plated parts are produced. Relatively new developments are the electroplating of steel with tungsten, molybdenum, and manganese. It is yet too soon to submit reports on the relative efficiency of these plates as compared with chromium, nickel, and others. Suffice it to say that every metal in the periodical system can be deposited from aqueous solutions, even though the conditions for deposition do vary from metal to metal. Thus, we have electrodeposited aluminium successfully from aqueous solutions.

Heat Treating Electrodeposits.

With the introduction of hydrogen and cheap ammonia into the metal finishing plants, heat treating in a reducing atmosphere soon became a relatively simple matter. The developments in this field

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[1]) *Colin G. Fink,* Patents pending.

point to radical changes in the application of various metals and alloys. To cite only a few cases: Upon heat treating chromium plated steel in hydrogen or ammonia, a surface alloy of chrome-iron is formed which is highly resistant to corrosion. In the same manner, iron and steel parts can be " stellited ": that is, a stellite alloy, composed of cobalt, chromium, and tungsten can be formed on the surface of the steel by first depositing the three metals and subsequently alloying the three metals together in a reducing atmosphere. Similar ideas have been worked out for tin-plated copper articles, producing on the surface of the copper article the familiar golden-bronze. The alloying of the electrodeposit with the basis metal requires very little time, and the hydrogen or other reducing gas acts as a flux and hastens the alloying reaction. In general, heat treating in a reducing atmosphere, even at relatively low temperatures not high enough to appreciably affect the temper of the steel, will greatly enhance the corrosion resistant properties of the plated metal, such as nickel, or chromium, or zinc.

Anodic Processes.

Aside from the cathodic processes discussed above, a number of anodic processes have been worked out which have given great promise of further development. The anodic deposition of rubber on steel is now a fully developed industrial process, both in Europe and in the United States. This deposition requires only a few minutes. The rubber deposit is subsequently vulcanized; it renders the steel resistant to our strongest acids, including hydrochloric acid.

Besides the rubber process there are other anodic processes, the basic principles of which are in full accord with the electrochemical theory of corrosion. The idea is to expose iron and steel parts to selective anodic dissolution, eliminating from the surface of the metal certain constituents, leaving behind a surface of uniform composition and low point to point voltage. Dr. F. J. Kenny, in our laboratory, investigated at length the anodic treatment of iron and steel in chromic acid1). By actual test, the corrosion resistance of steel was increased over 100-fold after the anodic treatment. In place of chromic acid, other acids may be used, notably phosphoric acid and oxalic acids. By carefully exploring the surface of the steel before anodic treatment and again after anodic treatment, we could definitely demonstrate that the potential variations, as the fine electrode point passed over the surface of the metal, were very much reduced in size after the treatment. It is our contention that the elimination of voltaic couples from the surface of the steel will eliminate corrosion. In this connection, it is interesting to record

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1) *Colin G. Fink* and *F. J. Kenny*, Tr. Electrochem. Soc. **60**, 253 (1931).

that electrolytic deposits of iron on steel greatly improved the corrosion resistance of the steel. Here, again, we attribute the improvement to the elimination, or at least to the decided reduction in the potential, of the point to point couples in the surface of the steel. Not only is the deposit of electrolytic iron on steel of uniform composition, but the crystals of iron are all orientated in the same direction. It might be well to recall that the potential of a metal crystal at the ends is not the same as it is at the side of the crystal, and that if two pure crystals of iron are so placed in the surface of an iron sheet so that the sides of some crystals are exposed and in other cases the ends, we will get a galvanic couple between two crystals of the identical composition.

Another interesting development which rightly belongs under the caption " anodic processes " is the so-called anodic coloring or dyeing of steel and other metals. Iron and steel are " anodized " in a sodium hydroxide solution¹), and a good, adherent oxide film is produced: Iron hydroxide is first formed and if at this stage the iron or steel article is dipped into a lake forming dye bath, pleasing results are obtained. Important, however, is the fact that steel surfaces thus " dyed " are much more resistant to corrosion than before dyeing. We attribute this fact to the same equipotentialization of the steel surface as brought about by the anodic treatment in chromic acid.

Methods of Testing.

We have already referred to the intermittent corrosion test in the case of nickel-coated steel. We strongly advocate the intermittent test in preference to the continuous salt-spray test. We find that the intermittent test approaches actual service conditions much more closely than the old spray test. Of course, it is important, in each case, to simulate actual service conditions as closely as possible and if the coated steel is to be exposed to sun, then laboratory tests in the dark are not comparable. Accordingly, a number of laboratories have added an ultraviolet lamp, an open arc, or mercury quartz lamp. It is usually desirable to know within a short time as to the quality of the electrodeposit and in that case, the Preece test, which is applied to zinc plate is very serviceable. In the Preece test, a copper sulfate solution is used, and the zinc-coated article is dipped into this. Copper is deposited by displacement. The samples remain in the copper sulfate solution for one minute, they are then washed in running water, and the copper deposit is lightly rubbed off. This test, although primarily used for zinc-coated steel, has been found to be valuable in many other plating plants. In the ferricyanide

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¹) *L. Revillon,* Rev. métal. **16**, 257 (1919).

test, filter paper or blotting paper is saturated with a weak solution of ferricyanide and this paper is laid on the plated steel. Wherever there is a pin hole and the steel is exposed, a little blue spot develops in the paper. The solution for this test is usually composed of 10 grams of sodium chloride and 1 gram of potassium ferricyanide in 1 liter of water.

When nickel-coated steel parts are to be used in alkali apparatus, it is, of course, important to test in alkali. We have found that if there are any pinholes, the alkali will reveal little rust spots in a very short time. We use as alkali testing solution ammonia water, to which we add a little ammonium chloride. Although this will attack the nickel plate, it will attack the basis iron more rapidly.

Relative Merits of the Various Electrodeposits.

Each one of the various electrodeposits has its own field of application. Thus, for example, tin-coated steel will continue to command first place in the food industries. Here zinc-coated and cadmium-coated steel are out of the question. For high wear resistance, the chromium plate is superior to all others. For color, the closest to white silver, the alloy of nickel and cobalt is the best. For lowest cost, especially for cheap articles such as wire fencing, we find zinc outstrips all the others. For severest atmospheric conditions, such as prevail in the tropics, we find chromium on nickel to be superior to all others. For the protection of steel molds used in rubber goods factories, we find chromium better than any of the others: Copper, nickel, zinc, all form sulfides readily during the vulcanizing operation, whereas the tendency to form chromium sulfide under these conditions is practically nil. Aside from tin, useful in the food industry, we find both nickel and chromium acceptable, especially where the ability to resist considerable wear due to frequent cleaning and scouring is important. In this case, a soft tin plate would not last very long and a hard nickel or nickel-chromium surface is preferable. For steel parts which must resist corrosion at high temperatures, chromium on steel is best. Other coatings, such as zinc and cadmium, soon disappear and even nickel and cobalt oxidize and flake off, whereas chromium-plated steel parts give a very long life.

Conclusion.

In years past, the electroplating industry was confined primarily to plating of small parts or articles made of brass or nickel silver. The plate applied was largely for decorative purposes. In recent years, the automotive industry has demanded a coating for steel that should be not only decorative, but also protective against corrosion—and besides, there should not be any change in the temper qualities of the steel during the process of applying the coating. Meeting this requirement of the automotive industry, together with the recent introduction of strip or " band " steel by the large steel companies, has greatly stimulated the electrodeposition of various metals on steel. We look to very rapid and important developments in this field, within the next few years.

The cost of applying electrolytic plates to steel will, in most cases be much lower than that for other coating processes and the results obtained will be much more lasting and satisfactory.

Columbia University, New York, N. Y.