



The William Blum Lectures

#05 - W. Andrew Wesley - 1963



The 5th William Blum Lecture
Presented at the 50th AES Annual Convention in Atlantic City, New Jersey,
June 23, 1963

Pitting of Decorative Nickel-Chromium Coatings
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Editor's Note: Originally published as W.A. Wesley, *Annual Technical Proceedings of the American Electroplaters Society*, 50, 9-16 (1963), this article is a re-publication of the 5th William Blum Lecture, presented at the 50th AES Annual Convention in Atlantic City, New Jersey, on June 23, 1963.

ABSTRACT

The status of the knowledge of the weathering of nickel-chromium coatings is reviewed, attention being focused on the process of corrosion of the chromium and nickel layers. This is not as well understood as is the subsequent attack of the basis metal. It is shown that the present theories are useful guides to investigators in their search for new coating systems. Surface pitting of the coatings is characterized by randomness of pit sites, a density of sites below 10,000 per cm² and a marked dependence upon exposure conditions. It is suggested that new experiments be based upon the hypothesis that the pitting process initiates with corrosion of the chromium layer. These would utilize instantaneous polarization techniques. They would include a search for a relationship between lattice defects and the nucleation of pits, also a study of the influence of the nature and structure of the metal layer just under the chromium on pit initiation.

I deem it a great privilege to be chosen to honor Dr. Blum by presenting the 5th William Blum Lecture. I am fortunate to have known Dr. Blum personally for more than thirty years. I admire him for his integrity and for his sustained devotion to the advancement and dissemination of knowledge of the science of electrodeposition. Any record of the long struggle to develop a science out of the old art of plating must be replete with references to the part played by Dr. Blum. His influence has been a major factor since the beginning.

Dr. Blum summarized the status of knowledge of the weathering behavior of decorative nickel-chromium coatings in a cogent paper published in 1961.¹ What I propose to do in his honor is to attempt to carry on from where the summary left off, to show what is not understood in this area and to speculate on the directions in which the truth may lie and should be sought.

What is known

It is clear from Dr. Blum's summary and from more recent literature that the breakdown of decorative nickel-chromium coatings during exposure involves a corrosion process which precedes the development of visible rust or other corrosion product of the basis metal. That process is the corrosion of the nickel layers. It is not instantaneous but takes time, longer for thicker nickel layers than for thinner. If this were not so then rust would appear quickly upon exposure, as indeed it does where there are gross accidental defects or breaks in the coating visible before exposure.

Let me summarize first what is known about the mechanism of this corrosion process, that is, the corrosion of the coating layers, not the subsequent attack of the base. The latter is well understood and needs no comment.

Initiation of the attack

It is commonly believed that chromium coatings in the range of thicknesses used commercially are not continuous but contain pores and/or cracks. There is no question that this is true on surfaces where the cracks are visible but the evidence that there are pores in a crack-free chromium layer is what the legal mind would classify as "circumstantial." More about this point later.

At the base of such cracks and pores nickel is exposed to moisture and begins to corrode. An important corollary to this is that the site of corrosion of nickel is determined primarily by the position of a breach in the chromium layer, not by the presence or absence of defects in the nickel layer.

Rate of corrosion of nickel

The mechanism of the corrosion of nickel in the pit which forms at a break in the chromium is electrochemical and is fairly well understood. The phenomenon is explainable by applying the "acid theory" of pitting corrosion first formalized by T.P. Hoar.² The principle can be illustrated by a sketch such as Fig. 1. When exposure conditions are such that the chromium layer is cathodic to nickel, hydroxyl ions are formed at the chromium surface, tending to raise the pH there. Within the pit, nickel ions are formed. The salts hydrolyze to form hydrogen ions. Being sheltered from the more alkaline cathode film, the electrolyte within the pit becomes more acid. Further corrosion of nickel results in further decrease in pH in the pit. The mechanism is self-perpetuating because the increasing acidity at the anode prevents precipitation of nickel hydrate, which would otherwise smother the reaction.

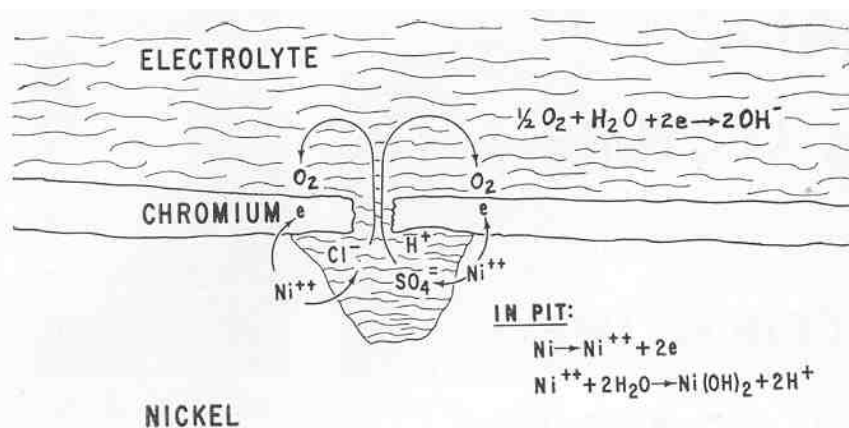


Figure 1 - Acid theory of pitting corrosion.

It is instructive to note that exposure to pure water instead of electrolyte would prevent galvanic reaction in such a cell, the pH could not drop in the pit and the reaction would be stifled. By this theory chromium-nickel coatings should be fully protective to steel in contact with pure water. This seems to be the case in practice.

Unfortunately, the life history of the nickel-chromium galvanic cell as it operates in weathering cannot be duplicated in the laboratory. The composition, pH, resistivity and thickness of film of moisture vary tremendously from one exposure to another and from time to time even in any one location.

Those who have examined many coated panels after exposure agree that the chromium surface must be predominantly cathodic to the nickel to produce pits of the shapes observed. Safranek and co-workers³ were able to set up small galvanic couples in which they observed currents in an electrolyte simulating industrial rain water. These currents were of the right direction of flow and order of magnitude to be compatible with recorded behavior of plated coatings. When the CASS electrolyte was used instead of the milder solution, the measured currents were much higher, as would be expected in an accelerated test.

If the CASS and Corrodokote tests are indeed reproducible it should be possible to predict the current flow in a nickel-chromium galvanic couple from first principles,⁴ namely, from polarization curves for each element of the couple obtained under the test conditions. Thus, curve ABC in Fig. 2, derived from data of Petrocelli, *et al.*,⁵ is an observed relationship of the cathode potential to current flow of a chromium electrode 1 cm² in area. JBK is the anodic polarization curve for a surface of semi-bright nickel 0.0001 cm² in area. The intersection of these curves, point B, represents the current which would flow if the two electrodes were coupled, neglecting any IR drop in the circuit.

Point B is at 0.7 μ A, which is equivalent to 7000 μ A/cm² on the tiny nickel surface or a penetration rate of 8 mils (203 μ m) per day. This is too high but not by more than an order of magnitude.

In an electrolyte of high resistivity, such as a thin film of industrial rain water, the effect of the resistance drop IR of the cell cannot be neglected. This could reduce the galvanic current well below the value at B. If the resistance R of the microscopic cell can be measured or estimated⁴ then the correction for IR can be made as shown in Fig. 2. The IR drop is represented by the distance between the two polarization curves at a current I . In the example in Fig. 2 the corrected current would be $0.2 \mu\text{A}$ instead of $0.7 \mu\text{A}$.

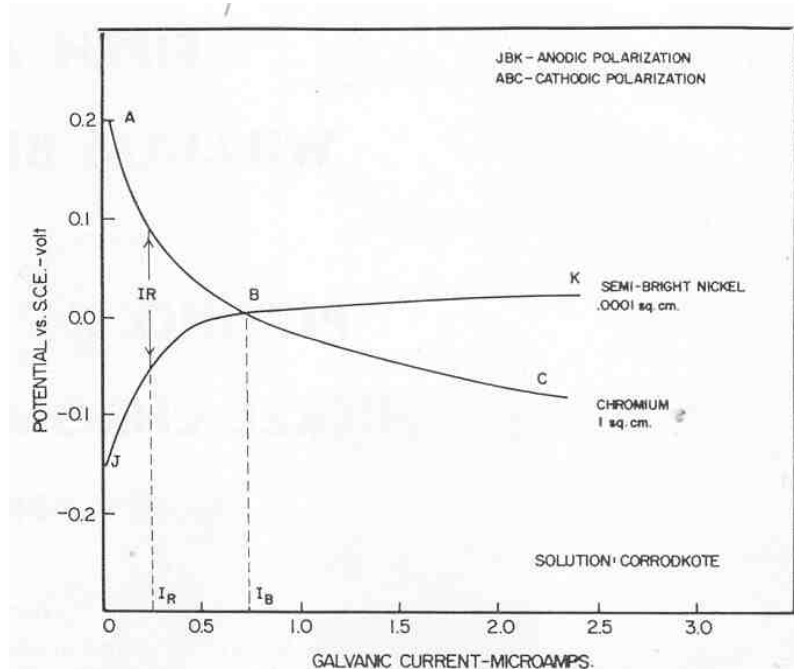


Figure 2 - Graphic estimation of galvanic corrosion current.

In AES Research Project 19 an important attempt is being made to observe directly the behavior of such galvanic pitting cells in operation out-of-doors.

Behavior of double nickel layer coatings

When two layers of nickel of different composition are employed under the chromium, the pitting cell action is complicated by the presence of a three-layer system. Here, again the variables are many. Nevertheless, the mechanism is well understood in principle, having been first delineated by metallographic study of sections cut through corroded exposure panels.

Let us look first at Fig. 3 which is a diagram from Melbourne and Flint⁶ showing hypothetical polarization curves for bright and semi-bright nickel deposits assumed to be of equal areas.

Quoting these authors; "If the two nickels are coupled together, the anode polarization curve for the couple (shown as a dotted line in Fig. 3) is the summation of these two curves. The intersection of the anode curve for the couple with the curve of cathode polarization defines the couple corrosion current O_X and the corrosion potential E_{corr} . At this potential the current passing to the semi-bright nickel is given by the intercept X_S and that passing to the bright nickel by X_B . It is evident that the ratio of the corrosion current flowing, respectively, to the bright and the semi-bright nickel depends on the relative slopes of the two polarization curves as well as on the potential difference between them."

This principle can be examined in the light of actual data from Petrocelli, *et al.*⁵ by adding to Fig. 2 a second anodic curve, this one for a bright nickel, to obtain Fig. 4. The two nickel layers in contact with the pit electrolyte tend to react as anodes versus the chromium cathodic area surrounding the mouth of the pit. The joint anodic curve in this case is so close to curve HC that it is not necessary to draw it separately. Neglecting resistance, the distance GC represents the total galvanic current ($2.2 \mu\text{A}$) of which only GF ($0.15 \mu\text{A}$) is generated by corrosion of the semi-bright layer, the balance by corrosion of the bright nickel.

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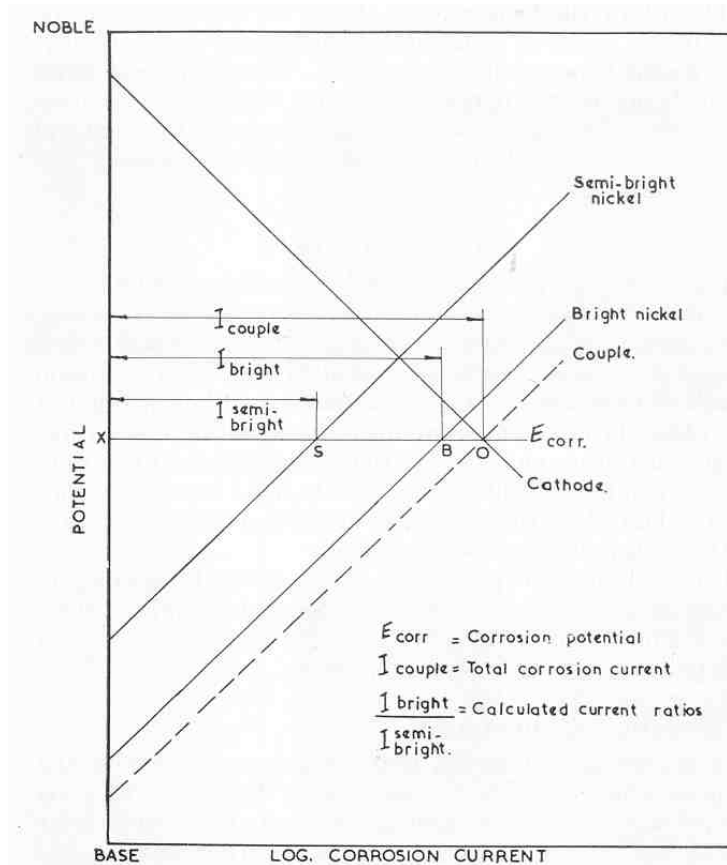


Figure 3 - Current ratio for double layer nickel system (Melbourne & Flint.⁶)

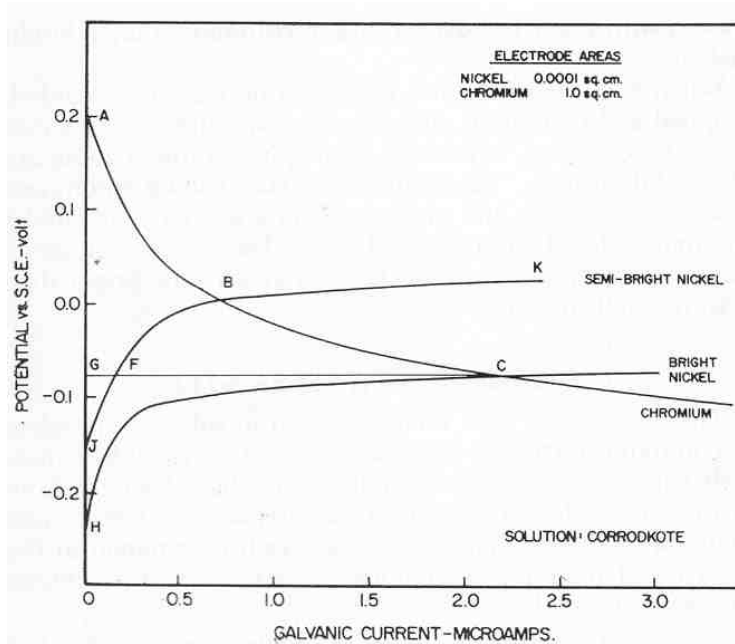


Figure 4 - Estimated galvanic currents in Corrodokote electrolyte.

From these diagrams alone one might question whether much is gained in substituting bright nickel with a higher corrosion rate for part of the less anodic semi-bright nickel. Consideration of the rate of penetration of the double coating shows why the net result is often beneficial. In Fig. 5b, corrosion of the bright nickel layer is seen to be detoured laterally in the double coating because there is sacrificial partial protection of the purer layer underneath.

The picture is complicated in a quantitative sense because there are so many factors which cause changes in the slopes of and potential differences between the three polarization curves. The variables include composition of the corrosive medium, temperature, composition of the nickel layers, thickness of the moisture film and prior history of the chromium surface. The result is that the superiority of a double nickel coating over a single layer system varies in different atmospheres, in different accelerated tests and with different kinds of nickel. No wonder there have been conflicting reports of the merits of multiple layer nickel-chromium coatings! Melbourne and Flint⁶ have explored this topic in some detail. They raise hope that two-layer nickel systems may be designed scientifically from potential diagrams.^{6,7}

The lateral corrosion or "detour" principle has been extended further experimentally by Knapp⁸ who interposed a layer of a third metal sandwiched between two layers of nickel as illustrated in Fig. 5c. Chromium performed better as the sandwich filler than any of the other metals he tried. This principle of lateral delay of penetration in multiple layer systems has since been confirmed experimentally by others.^{9,10}

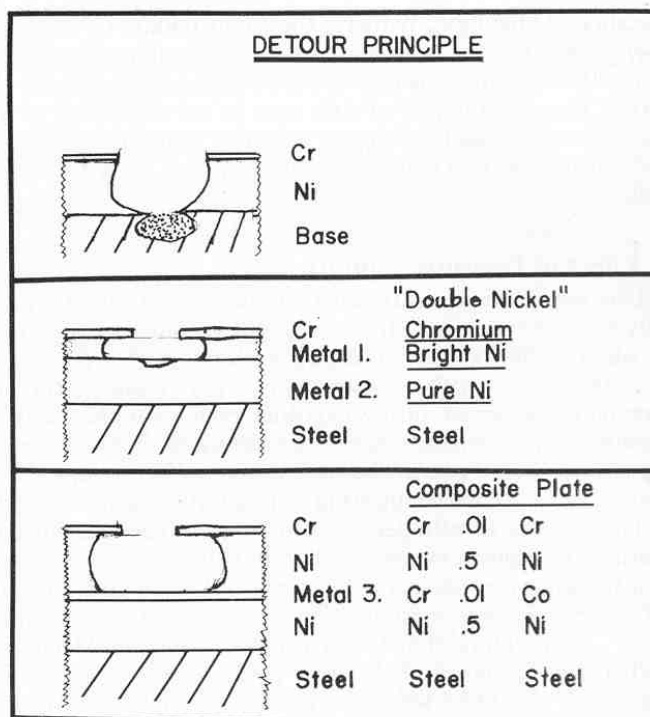


Figure 5 - Detour principle in pitting: (a) single nickel layer, (b) double nickel, (c) composite "sandwich" plate.

Principal remaining problems

The theory thus far reviewed here is useful to guide investigators in their search for coating systems which will show greater resistance to penetration by corrosion. One can imagine, however, that solution of two important remaining mysteries in the behavior of nickel-chromium combinations might lead to a breakthrough and open new avenues of improvement. One of these is to understand by what mechanism so small an amount of sulfur as 0.01% can radically alter the anode polarization characteristics of nickel.¹¹ This will not be discussed here today. The other problem is this: how is a surface pit started; what property of a point on the chromium surface determines that a pit will or will not start there?

Information relevant to surface pitting

Randomness of pit sites

Neglecting cracks and other gross defects which are detectable prior to exposure, it is known that the distribution of pits is random.¹² Attempts to design rating standards to be used in evaluating the condition of corrosion test panels failed until some were prepared by using a table of random numbers in choosing pit positions. Comparison of the two panel schematics in Fig. 6 makes this clear at a glance.

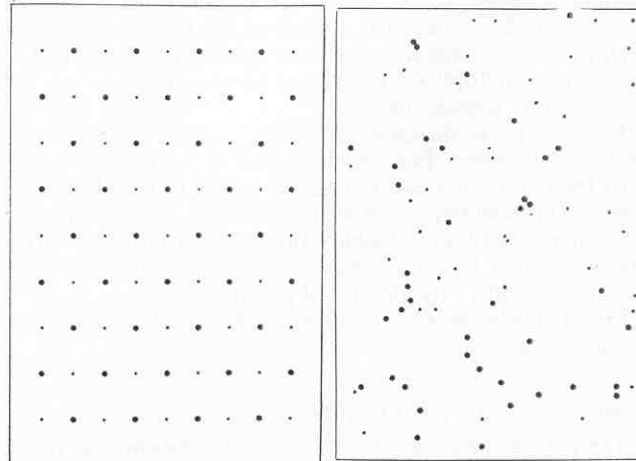


Figure 6- (Left) Unsatisfactory inspection standard; (Right) random spot standard. Defective surface area, 1.0%; 80 spots per panel (4 × 6 in. panel).

Density of pit sites

The number of pits observed in the surface of exposed nickel-chromium coatings varies by many orders of magnitude from less than one per cm² to a maximum reported number of 10,000 per cm², that is, from 10⁰ to 10⁴ pits per cm². The high value was reported¹³ for steel parts coated with bright nickel and chromium which had been exposed in the industrial atmosphere of Euston, England for one year. It is important to note that most of these minute pits were found not to have penetrated to the steel at this time. In my own experience with specimens exposed outdoors, I would say a value of 10³ would be high.

I have been watching for years for some indication in the technical literature of phenomena other than pitting which occur on metal surfaces with random distribution at sites numbering not more than 10⁴ per cm². There has been one instance of this kind, namely, the rapid boiling of water on horizontal surfaces.¹⁴ In nucleate type of boiling the population of boiling sites was measured experimentally. It was observed that the number of sites rose as the superheat of the water was increased. Starting with less than one per cm², the density rose to a value of about 300 per cm² with violent boiling.

Effect of exposure conditions

It is important to learn whether the sites of pits are fixed only by properties and structure of the chromium layer itself or whether the exposure conditions play a part. There is a paucity of data on this point. This is partly due to the unfortunate custom of rating exposure panels on the basis of numbers of pits penetrating to the basis metal without recording the number of pits in the surface layer. In retrospect this may have been good engineering testing but not good research.

The number of pits per cm² is usually much smaller in marine atmosphere exposures than in sulfurous atmospheres. It is not known whether the former would catch up to the latter if exposure were continued for longer periods at the marine sites. We do know that the density of surface pits increases with time of exposure.^{13,15} This point seems an important one which should be



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settled in future experiments. All that can be said at present is that the corrosive conditions affect the rate of nucleation of pits. We do not know that they affect the number of potential pit sites.

There is some evidence that exposure conditions do affect the density of perforations of coatings, that is, the number and size of pits penetrating to the basis metal. When a pit perforates the nickel-chromium layers and exposes the basis metal, a new galvanic cell is set up in which the basis metal is strongly anodic to the coating metals. The first pit to penetrate in a given area will thus tend to protect the surrounding area of chromium surface and slow down the corrosion of nickel in surface pits in that area. The effect of exposure conditions is this: the greater the conductivity of the moisture film, the further the protective action of the basis metal can be felt; hence, the fewer the number of rust spots per sq cm².¹⁶ A parallel effect is well known in the pitting of stainless steel where it has been demonstrated^{17,18} that corrosion pits are not mutually independent events and that pits interact with one another.

Effect of stress

While it is known that high stresses in plated coatings can markedly alter the shape and distribution of corrosion pits,¹⁵ it is not clear whether such stresses create additional pit sites. A marked reduction in density of perforations of exposed chromium-plated nickel foils was observed¹⁵ when chromium was deposited on the matte surface of the foil instead of the bright surface. This may not be a stress effect but one due merely to a multiplicity of pit sites on the matte surface, as observed by Hospadaruk.¹⁹

Here is another direction for future research in seeking the nature of pit sites. Bear in mind that we are not concerned with the effects of stress in causing cracks in the chromium layer. This phenomenon is well understood. It is made useful commercially in "double chromium" coatings.²⁰ The question raised here is: "Does stress in the chromium and nickel layers affect the density of pit sites?" .Put in another way: "Does stress play a part in creating a circular pit site?"

Structure of nickel layers

The nature of the nickel substrate under the chromium has a tremendous influence upon the number, size and distribution of pits in the chromium surface.¹⁵ More study of these relationships is needed. With chromium on buffed Watts nickel there are apt to be large numbers of very fine pits as contrasted with fewer but deeper pits in chromium-plated bright nickels.

When a Watts nickel foil is formed on a buffed mandrel, stripped and chromium plated before exposure, one observes a great density of extremely small pits in the chromium-plated dull surface. The bright side of such a foil if chromium-coated shows larger and much fewer pits so that it resembles chromium-plated bright nickel.^{15,21} The density of perforations formed, however, may be greater with the bright than with the dull surface.

Pitting of stainless steel

The investigator who would research to solve the problem of chromium pitting is fortunate in having available a masterly summary of the many studies which have been made on pitting of stainless steels. This was prepared by Greene and Fontana²² in 1958. There must be much in common in the behavior of these passive metals. The Greene and Fontana summary shows that:

1. Severe cold work increases the pitting attack of stainless steel but pitting is less likely to occur on polished than on etched or ground surfaces.
2. Pit sites appear to be almost randomly distributed in relation to metal structure with some preference for grain and twin boundaries.
3. The application of artificial pit techniques to the study of pitting corrosion has not been exploited completely. Studies of this type should be of great value in the understanding of the pitting corrosion process.
4. Time effects play an important part in applying the concepts of polarization and electrochemical control to pitting.

- Chlorides or other halides are almost always present when pitting is observed.

Initial stages of polarization

Greene and Fontana²³ suggested that the simplest concept of polarization and electrochemical control must be modified when applied to pitting attack because these characteristics change remarkably with time. They studied the behavior of a stainless steel pitting cell by making instantaneous polarization diagrams. Some of these involved measurements completed in as little as three seconds. They showed that the initial changes in the polarization curves were in the following directions: the cathode electrode became more noble with time while the anode became more active.

Since we are most deeply mystified by how a corrosion pit is started in the chromium layer, rather than how it propagates, measurements of instantaneous polarization values offer a promising research approach. Perhaps by extrapolating such measurements back to zero time a clue may be obtained to the condition required for pit nucleation.

Resistance polarization theory of pitting corrosion

If pitting takes place on a metal the anode reaction must be occurring faster at some places than at others. Edeleanu²⁴ pointed out that the unusual thing about pitting is that the anode reaction occurs fastest at the very place where the potential is lowest. He related this to the shape of the peculiar anodic curve for passive metals as in Fig. 7. With such metals the anodic area in the pit could have the potential B and corrode rapidly while the rest of the specimen could have the higher potential A but remain passive.

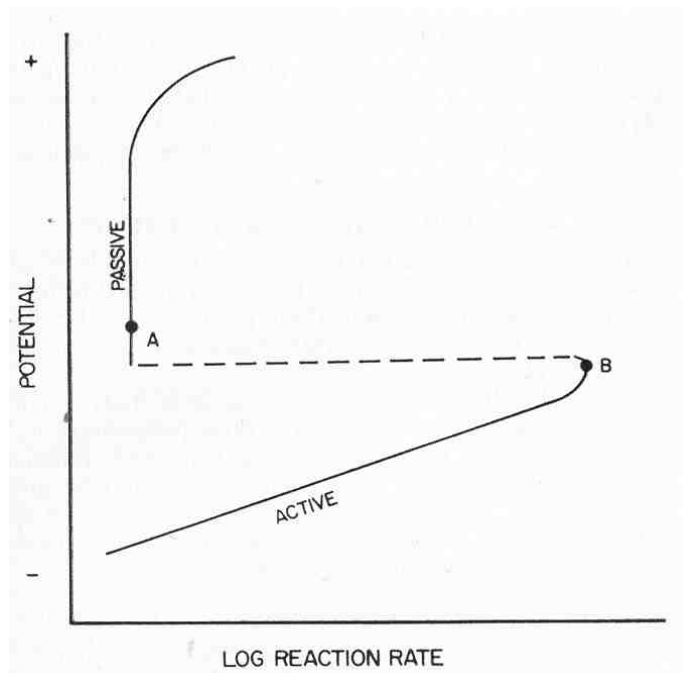


Figure 7- Anodic polarization curve for passive metals.

U.F. Franck²⁵ carried this analysis further by introducing the idea of a resistance IR drop in the electrolyte in the pit. As shown in Fig. 8 this can account for the part played by the non-pitting surface surrounding a pit, thus completing a cell diagram. The anodic polarization curve is for a very small stainless steel area in an environment such as exists within a pit. It is composed of an active part, a passive part and the unstable jump between them. The cathodic curve is for the large openly exposed surface around the mouth of the pit. It intersects both the passive and the active segments of the anodic curve. Resistance R of the electrolytic path in the little corrosion cell causes an IR drop which shows how the potential at the anode (E_a) can lie in the active region of the anodic curve while the potential of the cathode E_c remains at a level where stainless steel is stably passive.

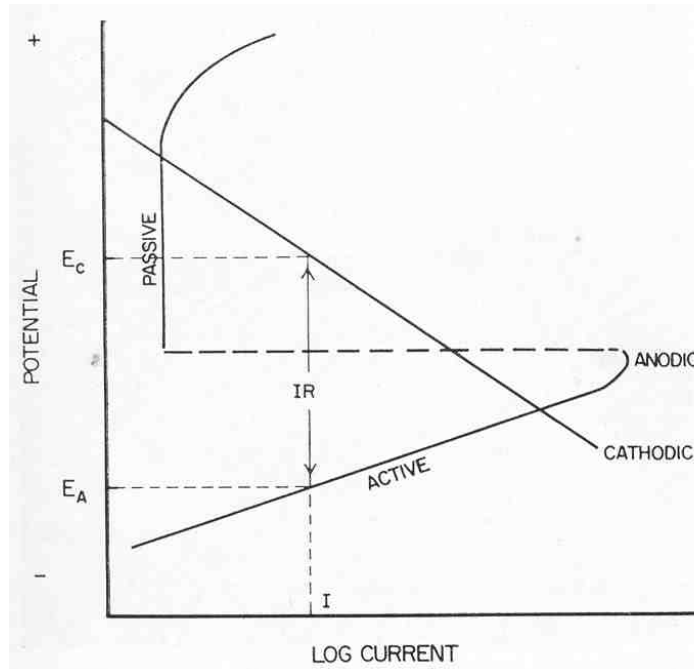


Figure 8 - Effect of resistance drop on galvanic pitting potentials.

Polarization of chromium

The outstanding characteristic of chromium polarization potential measurements is their lack of reproducibility in media of interest in atmospheric and accelerated corrosion studies. Most of these are of a pH greater than 2 or 3 whereas most of the published potentiostatic data for chromium were obtained in strong acid media. If one simply couples nickel and chromium in salt solutions in the laboratory, the chromium will usually be found to be anodic to nickel.^{3,5,26} On the other hand, long exposure out-of-doors seems to make the chromium surface noble. An odd effect is observed when as-plated chromium is rubbed with a suspension of magnesium oxide as is done in the CASS test. The open circuit potential becomes more noble while the cathodic overvoltage decreases. Figure 9 summarizes observations at Battelle Memorial Institute³ of such changes in single potential.

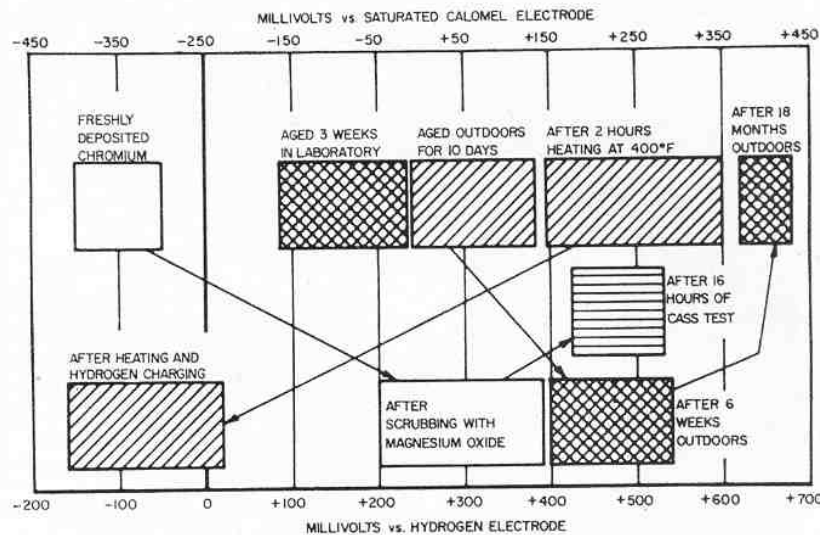


Figure 9 - Electrode potentials of chromium deposits on nickel in CASS solution (Safraneck, Hardy & Miller³).

Published potentiostatic curves for chromium anodically polarized in solutions of low pH are of the shape characteristic of metals showing passivity (Fig. 10). The critical potential for passivity BX is at a rather active level. Active chromium can corrode at very high rates with evolution of hydrogen at pH below 2. The dissolution rate of chromium in the passive condition, along the part of the curve labeled XY, is of the order of $10 \mu\text{A}/\text{cm}^2$ in strongly acid solutions, perhaps $1.0 \mu\text{A}/\text{cm}^2$ in the CASS solution and probably very much lower than this in areas boldly exposed to atmospheric moisture, possibly below $0.01 \mu\text{A}/\text{cm}^2$.

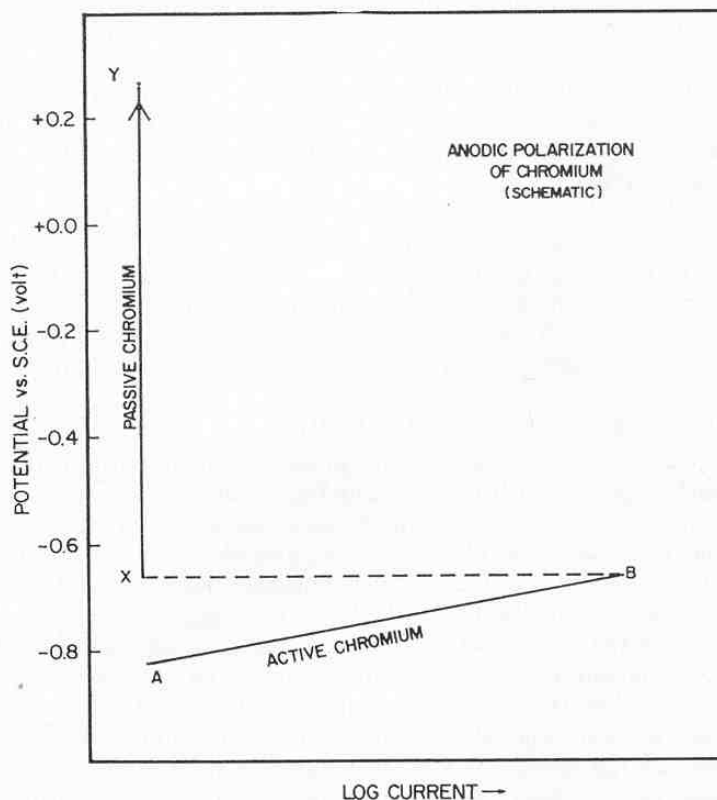


Figure 10 - Anodic polarization of chromium.

Cathodic potentiostatic curves are available for chromium in NH_4Cl , NaCl , Corrodokote and CASS solutions.⁵ While anyone specimen of the metal displayed a fairly steady potential in these controlled laboratory tests, the curves varied from piece to piece as much as 300 mV at the open-circuit end.

The cathodic curve in which we are interested is only that for passive chromium, that is, at potentials above $-0.75 V_{\text{SCE}}$. Chromium dissolution, if it is taking place at all on the surface remote from any pit, is so slow that the potential is unstable. Any change in the steady state applied current seems to cause an immediate large change in potential followed by a slow readjustment to a new steady state. The situation might be pictured as in Fig. 11 where we can assume one definite anode curve of characteristic shape reacting with a cathode curve which can move swiftly with changing conditions through positions S to U and back.

This kind of relationship basically satisfies the requirements of the "resistance polarization theory of pitting corrosion" discussed earlier. The chief difference is that the cathode curve of chromium is inherently unstable. Constantly changing corrosion conditions and interruptions experienced in atmospheric service render quantitative predictions out of the question.

The well-recognized rule can be mentioned at this point that a surface with few pits will suffer deeper penetration than one with profuse pitting. This relationship is to be expected in the pitting of the chromium layer just as it is in the subsequent penetration of pits into the nickel layer. It is compatible with the electrochemistry of chromium.

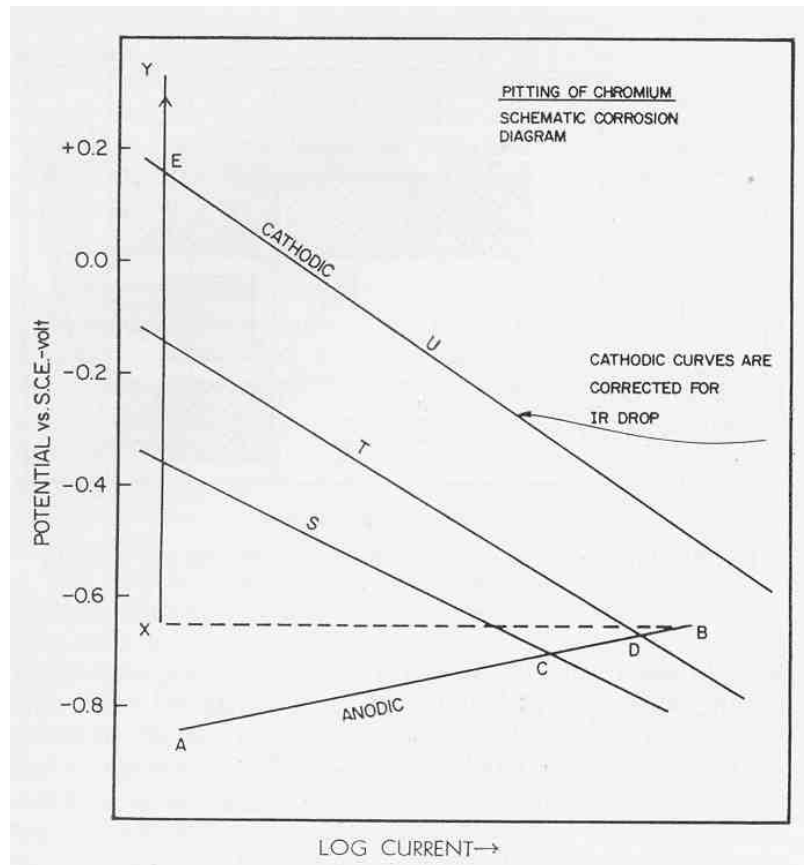


Figure 11 - Pitting of chromium.

Does chromium corrode at all?

Is there any factual basis for proposing the hypothesis that surface pitting of bright, uncracked chromium involves corrosion pitting of the chromium layer as its initial step? In the first place the idea seems compatible with the general picture of the behavior of such finishes. Knapp and I suggested this possibility in 1954¹⁵ to explain the fact that a thin film of chromium delays the initial perforation of nickel foils. Again, in CASS tests on panels coated with chromium thicker than 0.5 mil (12.7 μm), Saur²⁷ found that no nickel dissolution occurred but that the surface of the chromium lost luster and a large amount of Cr^{+3} was found in the run-off.

These observations were verified by exposure of an electroformed chromium sheet. There seems to be an excellent analogy between the pitting of stainless steels and the surface pitting of chromium-plated parts. One finds it difficult to believe that the mechanisms of the two phenomena are not similar. Yet if there be no corrosion of chromium there cannot be an analogous mechanism.

New approaches for research

There are times when it is necessary to take drastically different steps in research than have been applied before in attempting to solve an important problem. G.B. Shaw once said: "The man who waits to make an entirely reasonable will will die intestate."

I have already indicated the latent value of studying chromium pitting cells by the instantaneous polarization technique. Studies of the behavior of electroformed chromium foil exposed to various atmospheres should also be given high priority. They should include surface replica and thin film transmission examination of such foils in the electron microscope before and after exposure.

Do pits initiate at dislocations?

It has been suggested many times that corrosion pits in stainless steel and other metal surfaces initiate at the points where dislocations intersect the surface. This is based upon the fact that small, shallow pits can be formed at such points by critical etching procedures. The phenomenon is usually explained by stating that the free energy of the atoms in the distorted lattice around a dislocation is somewhat higher than elsewhere making that point of the surface anodic.²⁸

The actual reason must involve something more than a strain effect because most etching solutions do not give this type of attack. In addition, it appears necessary to have certain impurities segregated along the dislocation or adsorbed from the solution to permit its detection in this way. The electrochemist has no difficulty in visualizing an activation of a metal caused by segregation of specific impurities, so that the impure region will be anodic to the surrounding purer regions. The impurity requirement would seem to be more definitive than the structural one.

Mears²⁹ once suggested that since all metals contain dislocations one might expect all metals to corrode by pitting. He saw the problem not as: "why do metals pit?" but as "how can one explain it when they corrode uniformly?" It seems to me more likely that uniform corrosion starts as shallow etch pitting at a majority of dislocations. There are known to be 10^8 to 10^{11} dislocations per cm^2 in ordinary metals. If conditions were conducive to formation of a pit at every dislocation the pits would be so close together as to appear to merge if examined under an optical microscope. This kind of process is illustrated in recent work of F.W. Young, Jr.³⁰ who made the micrograph shown in Fig. 12.

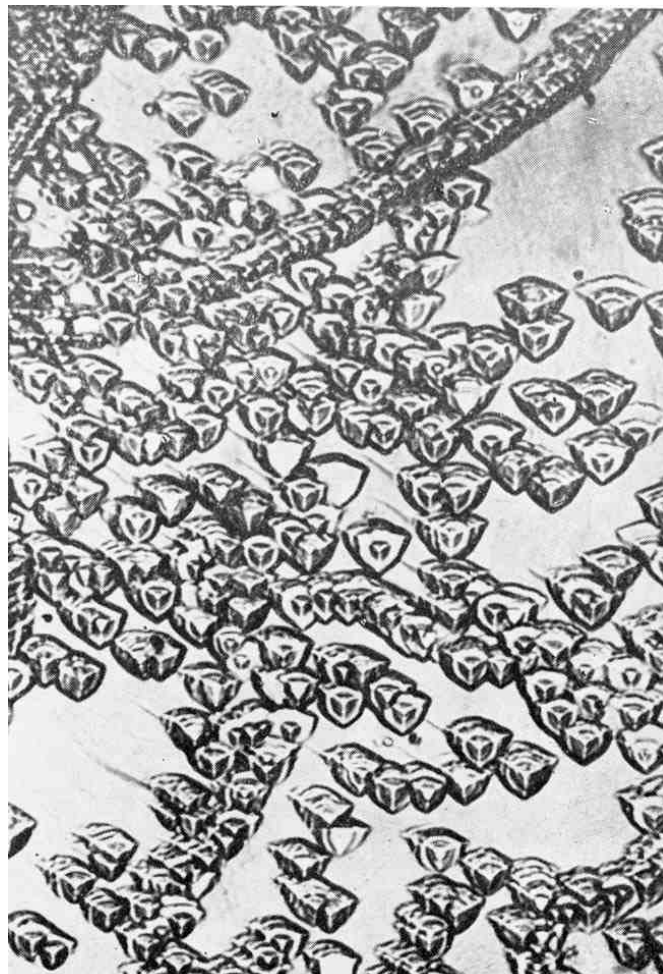


Figure 12 - Etch pits at dislocations in copper. Original magnification 160X (F.W. Young, Jr.³⁰).

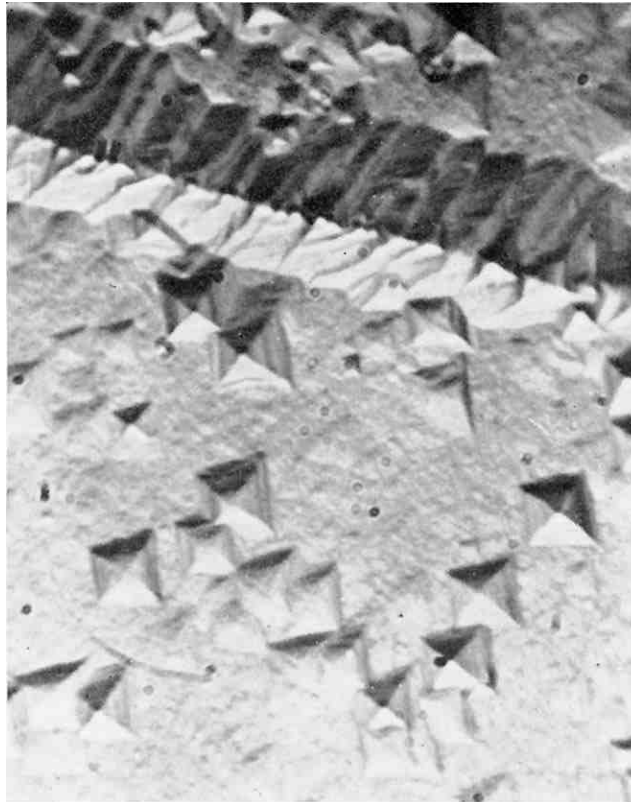


Figure 13 - Etch pits on (100) face of copper crystal. Original magnification 800X (F.W. Young, Jr.³⁰).

The appearance of the typical etch pit as seen in Fig. 13 does not suggest a geometry conducive to starting a self-perpetuating corrosion pit. For the latter to get underway it is necessary to have an area of metal sufficiently sheltered from the open body of corrodant that the pH in the sheltered zone can become and remain several units lower than that of the moisture film at the same time that oxygen or other cathodic depolarizer is restricted from access to the interior.

If there are 10^8 to 10^{11} dislocations per cm^2 , why do only 10^3 of these lead to corrosion pits? What difference could there be in the structure of these lattice defects which would occur only once in a million times?

One answer that cannot be ruled out *a priori* is that surface pits probably interact electrochemically as noted in the earlier discussion of pitting of stainless steel. The pits which get started first tend to blanket out the surrounding areas and prevent initiation of other pits. The range of such galvanic protection would vary with the nature and conductivity of the corrosion moisture film. A simple calculation shows that if one pit can protect a surrounding surface area only 10 mils ($254 \mu\text{m}$) in radius it would blanket a million neighboring dislocation sites!

Even if this interaction theory were correct we still lack the essential structural key. How can an etch pit which is characteristically an open pyramidal hole develop into a tunnel providing the necessary degree of shelter from the open surface? Working with aluminum, Edeleanu²⁴ succeeded in developing shallow pits into intricate tunnels under the very artificial conditions of applied current with the bulk of the surface anodized and lacquered. He explained the unexpected geometry of the pits by suggesting that they follow dislocations as best they can by advancing on a narrow front in certain crystallographic directions, choosing whichever plane has a suitable emerging dislocation. Similar studies should be made with chromium in environments not too remotely related to atmospheric corrosion.

The relatively small number of pits which develop in the atmosphere may possibly be due to the low probability of the simultaneous occurrence of the exact combination of factors required for a pit to become self-perpetuating. Consider the need

for segregation of the right kind and amount of impurity, the development of a pit shape sufficiently sheltered from the outer corrosive film, the requirement of chlorides and the proper sequence of exposure of the passive chromium surface to make it noble. How often can all these conditions be conducive at the same time and place?

Stacking faults

J. Nutting and coworkers³¹ have gathered evidence that stress-corrosion cracking of certain brass alloys involves preferential attack along stacking faults. Elements which decrease stacking fault energy tend to promote attack. They suggest a tendency for minor elements of the alloy composition to segregate along stacking faults. The possibility that such lattice defects can be related to the nucleation of surface pits in chromium should be investigated by someone competent to work in this field.

Effect of substrate

As noted earlier, the nature and structure of the metal layer just under the chromium exert a profound influence on the density of surface pits which develop on exposure. Study of these relationships should be profitable. It is interesting to recall that Dr. Blum showed as long ago as 1931³² that the response of coatings to a chromium porosity test varied with the nature of the basis metal. The test used was one in which the chromium surface was made cathodic at a controlled low potential in an acid copper solution. Deposition of copper was very localized and was considered to occur only at pores in the chromium so that the observed current flow in mA/dm² was taken as an index of the degree of porosity. Note in Fig. 14 that for ordinary chromium deposited at 45°C, porosity ratings were highest where the substrate was steel and copper but least on nickel. Even with the less porous chromium deposits made at 55°C, nickel proved to be the best undercoat.

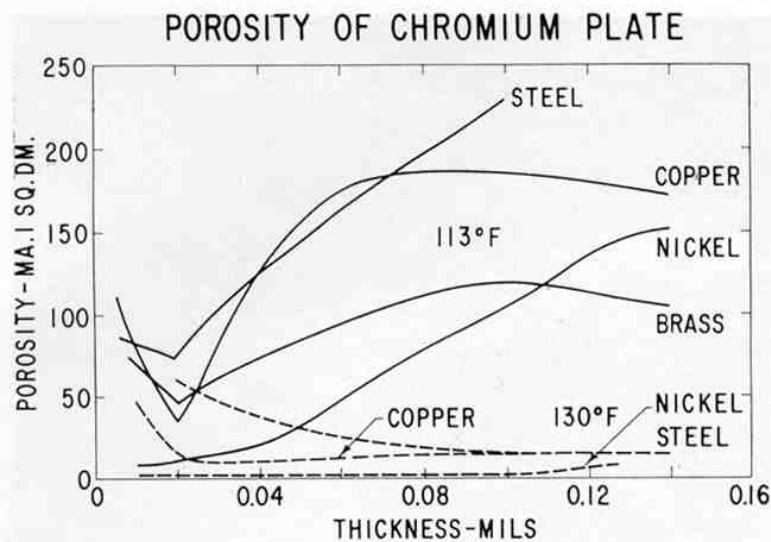


Figure 14 - Porosity of chromium plate. (Blum, Barrows & Brenner³²).

Again, Brown and Hoover³³ found that providing a layer of rhodium between a nickel layer and the final chromium made a great difference in the types of pores and cracks observed with a resultant amazing improvement in both salt-spray and outdoor exposure resistance. These workers also report inferior corrosion protection by chromium deposited directly on copper, brass or zinc, a result which is generally recognized in the industry.

The lead provided by Blum, *et al.*³² in focusing research attention on the properties and behavior of the chromium layer recommends itself as a potentially more useful approach than the study of the later stages in the life of a corrosion pit. It is possible that the number and distribution of lattice defects in the chromium bear some relationship to those of the substrate. I am unaware that anyone has ever demonstrated an epitaxial growth process in chromium electrodeposits. However, it is known that the overvoltage for deposition of chromium varies greatly on different surfaces so that lattice defects in the substrate may well cause local hiatus in the structure of the chromium.



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Stress

The role of stress in causing cracking of the chromium layer has been discussed often in the literature, along with the subsequent penetration of the nickel layer exposed at the base of the cracks. However, there are also many observations which indicate that stress may play a part in initiating the circular type of surface pitting. There has been no scientific study of this role of stress.

L'Envoi

All the research studies I have suggested in this lecture have for their broad objective a better understanding of the weathering of chromium finishes. I believe such studies justified by the importance of the nickel-chromium composite in industry. This team of metals continues to be the most promising component of bright metal finishes for several reasons:

1. Of the common commercial metals, including zinc, aluminum, copper, tin, iron, lead, cadmium and magnesium, none is as near to chromium in its corrosion and galvanic behavior as nickel. Copper is a close second but it has the disadvantages that its corrosion products stain a chromium surface and cause crater-type rust pits.
2. Nickel and chromium corrosion products do not stain the bright surface but wash away without causing blisters or craters.
3. Nickel plating can be made to give superior leveling action.
4. Nickel has physical properties admirably adapted for service under chromium, providing not only mechanical resistance to denting and impact but also some color match where the chromium is scratched through or gouged off.

In conclusion may I offer my opinion that nickel-chromium finishes are here to stay. Research to better understand their weathering behavior continues to be worthwhile.

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About Dr. W. Andrew Wesley (from the biography printed in 1962 at the time of his receiving the AES Scientific Achievement Award)



Dr. W. Andrew Wesley, a native of Yonkers, NY, graduated in 1923 from Cornell University with a degree of Bachelor of Chemistry. He received his Master of Science degree in 1924 and Doctorate in Philosophy in 1926 from New York University. He was elected to Sigma Xi and Phi Kappa Phi. He joined the staff of the Research Laboratory, International Nickel Co., Inc., Bayonne, NJ, in 1926, specializing in electroplating and corrosion research. In 1933, he was made head of the research groups working on these subjects. He became assistant director of the laboratory in 1939 and was named manager in 1954. He retired in 1963 from International Nickel and served the industry as a consultant on electrodeposition and corrosion.

At the time of his receiving the Scientific Achievement Award, Dr. Wesley was the author of over 40 publications. Over 25 American patents plus corresponding patents in many foreign countries had been issued in his name. He was responsible for many contributions to the advancement of the science of nickel plating including the development of new processes for electrodepositing nickel involving extremely high speeds and producing an especially hard type of the metal. One of these patents covered the process by which steel plates are clad with a layer of stainless steel to form an inexpensive composite metal widely used in the fabrication of chemical process equipment.

Dr. Wesley was very active in AES affairs, serving as the National AES President in 1960-61. From time to time he was active on the AES Research Committee (today's Research Board) and chaired that committee in 1950 and 1951. Among the honors he received from the AES in recognition of his work were two AES Gold Medal awards in 1939 and 1950, the Founder's Gold Medal in 1949, the AES Silver Medal in 1952 and a cash prize in 1943. He was made a National Honorary Member in 1964.

He was a Fellow of the American Institute of Chemists. Membership in technical organizations includes the American Chemical Society, The Electrochemical Society, the Armed Forces Chemical Association, the Institute of Metal Finishing, the Research Society of America, in addition to the American Electroplaters' Society. He received the Hothersall Memorial Medal of the Institute of Metal Finishing at its 1956 meeting in Blackpool, England. Dr. Wesley passed away in 1986.

In his lecture, Dr. Wesley covered what was then known about the weathering of decorative nickel-chromium coatings, at the time the most significant finish in the industry. In that era, technological breakthroughs in automotive bright work were coming to light in each issue of *Plating* magazine. Dr. Wesley's pioneering work at International Nickel was an integral part of this work, and thus his award and lecture was most timely.