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UNITED STATES DEPARTMENT OF COMMERCE • Sinclair Weeks, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Electrodeposition Research

Proceedings of the NBS Semicentennial Symposium on
Electrodeposition Research Held at the NBS on December 4-6, 1951

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Foreword

Electrodeposition processes have become an integral and important part of many industries—for example, the printing, metal refining, extractive metallurgy, hardware, automobile, and electronic industries. This has come about largely as a result of extensive research in the field of electrodeposition, especially during the past 25 years.

To encourage further research in this field, to present current research results and problems, and to facilitate the exchange of information, the National Bureau of Standards held the Symposium on Electrodeposition Research as the last of a series of twelve symposia conducted during the Bureau's semicentennial in 1951. The papers presented at the Symposium are published in this volume. These papers represent a cross section of research currently being conducted in electrodeposition by industrial, university, and government laboratories in Europe and the United States.

The cooperation of the Office of Naval Research in making possible the symposia series is gratefully acknowledged. The Symposium on Electrodeposition Research was planned and conducted by the Bureau's Electrodeposition Section—in particular by Dr. William Blum, Chief of the Electrodeposition Section until his retirement on December 31, 1951.

A. V. Astin, *Director,*
National Bureau of Standards.

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1. Research on Electrodeposition in Great Britain

By G. E. Gardam [1]

Introduction

The subject matter of this paper covers a wider field than others in the symposium, and it has therefore been thought useful to divide it into two parts. The first is a brief review of the type and magnitude of the research effort; and the second gives a more detailed description of a few important and recent researches.

Electroplating is quite a minor industry in Great Britain, yet it occupies an important place. The wider subject of metal finishing is becoming recognized as a key industry. The position of Great Britain is important from an international point of view, as she holds a premier place in the sterling block for export of equipment, chemicals, and thus for technological advice; Germany has shown little sign of recovering her prewar share of this business.

Research Effort

The effort intentionally devoted to scientific research for the electrodeposition industry in Great Britain is relatively small. The author, as an experienced but unprivileged observer, estimates it as equivalent to less than 100 full-time graduates. It must be clearly understood that this does not include any allowance for part of the time of the much larger number of research workers concerned with nonelectrodeposition metal-finishing processes, electroextraction and refining, electrolytic methods of analysis, corrosion of metals, etc., whose work often influences electrodeposition practice.

Distribution of Effort

This effort is divided between the following types of institution: (a) University and other academic institutions, (b) Government Departments: Department of Scientific and Industrial Research, defense departments, other departments, (c) Cooperative research associations, (d) metal-development organizations, (e) firms supplying plant, material, or advice for electroplating, (f) large users of electroplated articles, (g) large electroplaters, (h) users of electrodeposition for special purposes.

It will be obvious that much of the information obtained, especially by the groups (e) to (h), is not generally published. The remainder is disseminated by one of the following methods: (a) Publication in the leading scientific and technical journals, which are not, of course, specifically concerned with electroplating, (b) through the meetings and the Journal of the Electrodepositors' Technical Society, (c) through the pages of the four or five periodicals specializing in information

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[1] Director of Research, Design and Research Centre for the Gold, Silver, and Jewelry Industry, London, England.

on metal finishing, (d) by widely issued gratis publications of metal development or similar firms, (e) through patent specifications, (f) privately to a group of interested or participating persons.

University and Academic Institutions

The fundamental relations of matter and electricity, and the consideration of chemical reactions of an electrochemical character, are a frequent subject of physical-chemical research, but these do not have any noticeable effect, direct or otherwise, on practical electrodeposition. The results are published in the proceedings of the more learned societies, but especially in the Proceedings of the Faraday Society, established for this very purpose in 1903. It is noteworthy that when this Society held a special discussion on "Electrode Processes" in 1947 and published a volume of 338 pages, it raised little or no interest from the industrial research worker in electrodeposition.

Nevertheless, mention must be made in this section of the work of A. Hickling and his students at the University of Liverpool, of J. O'M. Bockris at the Imperial College of Science and Technology, London, and of F. P. Bowden, J. N. Agar, and T. P. Hoar at Cambridge University. The author considers that if only electrodeposition research workers spoke the same language or rather mathematics as these workers, rapid progress might be made.

Some university work shows an awareness of the electrodeposition industry. In this connection the work of U. R. Evans and his school at Cambridge University is mentioned later. Such work is, of course, free from either financial cost or directive control from the industry.

Workers in X-ray or electron diffraction, and in other branches of metal physics, sometimes interest themselves in the structure of electrodeposited coatings. The results have not been practically very useful so far, although for many years G. I. Finch at the Imperial College, London, has published an interesting series of papers by himself and his research students on the natural habit of the electrodeposited metal structure and the effect on it of the substrate, or basis, metal.

There is also intense interest in the theoretical basis of the polarographic method of electroanalysis, which involves much fundamental research in electrochemistry.

The polytechnic schools, which so effectively train operators for the electrodeposition industry, of which the most important are the Northampton Polytechnic, London, the Birmingham Technical College, and the Coventry Technical Institute, do not seem to carry out research work in the subject.

Great things are expected to follow from the endowment by Joseph Lucas, Ltd., of a research fellowship in electrodeposition in the Applied Metallurgy Department of the University of Birmingham, but the first holder has not yet been appointed.

The Government Departments

The Government maintains a Department of Scientific and Industrial Research, responsible to the Lord President of the Council, which operates directly a number of laboratories. The chief of these, the National Physical Laboratory, closely corresponds to, and shortly predates, your National Bureau of Standards. This, however, does not concern itself at all with electrodeposition, although the closely associated Chemical Research Laboratory has a strong corrosion section, and is therefore, interested in tests of protective coatings and the cause of their breakdown. However, it does not do any work on electrodeposition as such. It has recently applied some excellent work in inorganic chromatography to the analysis of electroplating solutions, especially for minor constituents or impurities.

The Department's Food Investigation Laboratory has shown a keen interest in coatings applied by electrodeposition on cans for foodstuff, both tin on steel, and other metals on aluminum. All the work of these institutions is freely published in appropriate journals. The Department of Scientific and Industrial Research also finances, and thus to some extent influences, the cooperative research organizations described below.

Government Defence Departments do not reveal the extent of their research work, which, however, is known to be great, perhaps 25 to 40 percent of the country's total research effort. Nor do they reveal the subjects, but it is believed that electrodeposition and allied subjects are an insignificant part of the total defense effort (except perhaps for the problem of protecting uranium slugs in an atomic pile). Nevertheless, the total amount may be large relative to industry.

The Ministry of Supply controls all work on atomic energy; it purchases and inspects all material for the Army and Air Force, and itself manufactures much of it. It also does most of the research on equipment and serviceability for the Army and Air Force. The Navy operates similar Departments, which maintain close liaison with the Ministry of Supply. Undoubtedly, much research work on electrodeposition and cognate subjects is done in a number of scattered laboratories; most of it is not published, and it is somewhat doubtful if it is collated.

Nevertheless, two Departments, at least, of the Ministry of Supply and two of the Navy have earned a reputation by actively working on the industrial applications of electrodeposition; they have undoubtedly profoundly affected its progress.

The first of these is the Electrodeposition Section of the Armament Research Establishment, Woolwich, near London, under D. J. Macnaughtan until 1931, then under A. W. Hothersall until 1950, and now under R. A. F. Hammond (who visited the U. S. A. in 1950). The published or revealed work of this laboratory may be divided into three groups.

(a) Fundamental work on the theory of electrodeposition, particularly nickel deposition, porosity, adhesion, and microstructure, partly done under contract for the British Non-Ferrous Metals Research Association and therefore first communicated privately to members of that body, but now almost all published, chiefly in the Journal of the Electrodepositor's Technical Society.

(b) Specific and detailed advice on the repair of worn and undersized machine and armament parts by electrodeposition with thick and adherent deposits of nickel or chromium, and on the chromium lining of machine-gun barrels, also on other subjects required by Ministry contractors during the late war. This precise information was clearly the fruit of much unpublished laboratory research. The information was partly published in an official series of Electrodeposition Memoranda, partly as process specifications, and much by written and verbal advice to contractors on specific problems.

(c) The devising and proving of a large number of tests, fully published in the Journal of the Electrodepositors' Technical Society, suitable for the enforcement of specifications and for research work on the various properties of electrodeposited coatings, especially means of determining the thickness, hardness, adhesion, porosity, and ductility of such coatings. The effect of these tests, and particularly of the representatives of the Section, on the formulation and adoption of specifications is not easy to estimate, but is undoubtedly outstanding.

Publication from this Section appears to be reduced at present, although its strength is known to be great. It must be presumed that increased security measures explain this, and that extension of valuable wartime work on the chromium lining of machine-gun barrels and similar work is being carried out.

The Royal Aircraft Establishment metallurgical laboratory at Farnborough, Hants, has also contributed much to the protection of light alloys, both aluminum and magnesium base, by long-term tests of various coatings, including electroplating and anodizing. The findings have been written into the famous series of D. T. D. and other specifications, which are vigorously enforced by the Aeronautical Inspection Department to the education of the electroplating industry.

Similarly, the Bragg Inspection Laboratory, Sheffield, of the Department for Inspection of Naval Ordnance, and the laboratories of the Engineer in Chief, Admiralty, have had an effect by advising controlling, and inspecting contractors' methods of electrodeposition, to their considerable improvement.

The use of electrodeposited coatings of silver for skin conductivity, and of rhodium or other platinum metal for contacts in radar and telecommunications, is known to have interested the research laboratories of the Service Department and the Post Office.

The Ministry of Works and other Ministries are buyers of electroplated wares have shown some interest in the formulation of specific performance tests for embodiment into specifications.

A certain amount of applied research work is done by the Post Office, which in Great Britain includes the telephone service, and for the nationalized cable and radio transmission industries, but few published data have arisen.

The Cooperative Research Associations

These associations, which have no exact parallel in the U. S. A., consist of a voluntary association of firms that contribute funds, handsomely augmented by the Department of Scientific and Industrial Research, to prosecute research on problems of mutual interest. The program is decided and controlled exclusively by the member firms, to whom the results are confidently communicated. Since they would eventually leak out, they are usually published after a time interval.

There are now over 40 such associations, and there has been talk of setting up a separate one for research in metal finishing. However, to date only the following have been extensively interested in electrodeposition.

The British Non-Ferrous Metals Research Association has, for some 26 years, devoted a part of its funds to this class of work. In the interwar years the actual research was done extramurally at the Armament Research Establishment. Some of this work has already been mentioned, but other work also arose in this way, e. g., on the theory of bright nickel plating, and on smoothing action, much of which is very relevant today; development of the well-known BNF Jet test for thickness measurement, and the BNF adhesion test for electrodeposits.

Since World War II all the research work has been done internally. Some is described later; other work has been on the roughness of bright nickel deposits. Work is starting on the economy of nickel, especially by a review of the relation of thickness and porosity of such coatings.

The BNFMRA has also for many years advised its members on electrodeposition difficulties and has thus disseminated much modern research work.

The British Iron and Steel Research Association (BISRA) is very large (budget $1,500,000) and fairly recent, although many of its constituent parts have functioned for many years. It has a section specifically devoted to metallic coatings on steel, but this section is more interested in hot-tinning and galvanizing than in electroplating.

Nevertheless, much of its work on porosity testing and on avoidance of defects that cause pores in the basis steel is of great importance to electrodepositors.

Its world-famous exposure tests of steel protected in various ways, which have been proceeding for many years under the direction of J. C. Hudson, have added greatly to our knowledge of atmospheric corrosion.

The Design and Research Centre for the Gold, Silver, and Jewelry Industries is a young and small cooperative research association. It has carried out some operational and other research on the high-quality polishing required in its industry and has published a simple test for "surface truth" of unpolished surfaces. (This was reprinted in *Metal Finishing*, N. Y.) It is also working on bright silver plating, gilding and gold-alloy plating, protection of silver and electroplate from tarnishing, and on chemical coloring processes.

The Printing and Allied Trades Research Association is interested in electrotyping, and in lithographing processes from electroplated metal plates. It has published several novel methods of importance.

The Production Engineering Research Association has recently begun to interest itself in metal finishing, including electroplating processes, as one of the normal stages of production engineering.

The Coil Spring Federation, working as a cooperative research association, is interested in protection of steel springs by electroplated coatings without embrittlement, or reduction of fatigue limit.

The Fulmer Research Institute is an independent research organization like the Mellon Institute. It has worked on electroplating of aluminium and the embrittlement of steel by electrolytic pickling.

Metal Development Organizations

In Great Britain there are a number of organizations disseminating information for the purpose of increasing the use of a particular metal, for example, the Tin Research Institute, the Mond Nickel Co., The Aluminium Development Association, The Copper Development Association, and The Zinc Development Association. The first two of these carry out extensive research, which is referred to below. The others support research in other organizations. Their influence is especially noteworthy because they issue technically sound literature at all levels, advocating the best use of their particular metal. Electrodeposition of the metal or on the metal (including anodizing) forms, therefore, a considerable part of their advice.

It is necessary to emphasize that the high integrity of the development organizations precludes normal advertizing, and they do not hesitate to recommend a competitive metal if impartial technical review suggests it to be preferable.

The Mond Nickel Co. has for many years published, and issued freely, a bulletin giving full abstracts on research in nickel plating. It has also done or financed much work on this subject, and, indeed, has pressed the results home by wide publication, exhibition, and technical advertizement. The Company has a virtual monopoly in the supply of nickel anodes and does much research on this subject. The results are not revealed except as patents, but they have undoubtedly influenced progress.

The Mond Nickel Co. is one of the larger producers ofthe platinum metals, which arise as by-products of nickel production. It therefore carries out research on rhodium plating and, to a less extent, on platinum and palladium plating. This is not widely published, but seems to be applied through the (British) Baker Platinum Co.

The Tin Research Institute has for many years carried out research work on the production, behavior, and testing of tin coatings on steel, cast iron, and copper by hot tinning and by electrodeposition. Some of this work was originally done extramurally at the Armament Research Establishment but all is now done internally in the Institute's well-equipped premises. It has included the well-known hydrochloric acid-antimony stripping test, the hot-water porosity test, several magnetic thickness tests, application of interference of light to surface contour tests, as well as the working out of practical processes in full detail for the alkaline stannate and acid stannous sulfate methods of depositing tin.

More recently, under J. W. Cuthbertson, the industrial electrodeposition of tin alloys has been attacked and complete processes made known for the following: Tin-zinc, which is claimed to have most of the advantages of cadmium plating, without the expense; tin-copper or speculum plating, which provides a hard, white, nontarnishing coating closely resembling silver; tin-lead plating, which facilitates subsequent soldering or provides a cheaper coating than tin. Tin-nickel coatings, which have such important advantages of appearance, tarnish resistance, and uniformity of composition, have just been announced. These are deposited in the bright condition without additional agent. A separate section, beginning on p. 11, is devoted to this subject.

Supply Firms

The British electroplating trade is supplied with most of its plant, chemicals, and other materials through five or six supply houses. One of these, W. Canning, is much larger and longer established than the others, some of whom, however, advocate American processes and presumably have American research contacts. Although all these firms undoubtedly do research for their own benefit, very little is published, or indeed does it appear as new proprietary processes. Their staff is not especially evident in technical meetings or at those to decide specifications. This is in contrast to certain firms supplying nonelectrodeposition metal-finishing processes (e. g., phosphating). Nevertheless, the supply firms, by their detailed and individual technical advice to their customers, profoundly influence the technical progress of the industry. They also generously support the British Non-Ferrous Metals Research Association.

A firm exploiting the French and Battelle patents on electropolishing is known to be doing research, chiefly on the development level, and presents papers on the results.

An important contribution of the supply firms is the development, on a pilot or full-scale, of processes that appear satisfactory from laboratory tests. Recording and discussion of such development seldom comes from the supply firms, except in the case of engineering experience in a few instances.

As well as the general supply firms, there are a few specializing in one or a few lines, e. g., the Westinghouse Brake Co., which supplies the bulk of the rectifier equipment. This firm has fully described some comparative tests on its equipment as compared with motor-generator sets and also special installations, including one designed to maintain constant current density with varying tank load.

There are also a number of large chemical firms, to whom the electroplating trade is a relatively small market, but who devote a reasonable amount of research to its needs. Imperial Chemical Industries have worked on cyanides, trichlorethylene, alkalis, indicators, wetting agents, etc., while some of the oil companies have evolved antipitting agents, emulsifiers, and antifingerprinting dips, especially for the industry. A few instrument firms have evolved instruments for the plating trade; with the exception of magnetic and electromagnetic thickness meters, little has come of this.

Large Users of Electroplating

As in the United States, the large users of electroplating do much of their own work and send the remainder to other platers. Many of the large automobile, cycle, radio, domestic appliance, and electrical firms have set up extensive laboratories to control their own processes, to inspect the "bought-in" material, and to investigate new processes and problems. The staff of these laboratories provide the majority of the authors of technical papers and those participating in the subsequent discussions; they are noticeably more open about their practice and difficulties than supply-house staff. Several textbooks have been written by the staff of such users or by the specialist consultants they often retain. In some cases the organization using electroplating is part of a large group possessing a more formal research department, such as the BSA Group. More academic types of papers often arise in such cases.

Reference must be made here to the publications of A. T. Steer, a research metallurgist of a large automobile manufacturer. He has published many and exhibited innumerable microsections of electroplated surfaces showing serious fragmentation of the basis metal. His dogmatic explanations of these as resulting from alleged high surface energy of the basis-metal surface have caused considerable controversy, although none can deny the excellence of his metallographic technique.

Large Electroplaters

The very large number of firms whose main business is the electroplating of other firms' products are usually not individually large enough, and seldom technically equipped, to do more than elementary "trouble shooting." There has lately been a movement, through their Trade Protection Association, the Metal Finishing Association, to sponsor or even to carry out electrodeposition research for their exclusive mutual benefit. It is believed that so far nothing has come of this.

Specialist Users of Electrodeposition

The numerous firms that employ electrodeposition for some special purpose, such as gramophone (phonograph) record production, electroforming, printing, metalizing of plastics, carry out some research and are usually willing to publish the results. The staffs are well-informed and contribute to technical discussions.

The use of electrodeposited brass for bonding of rubber to steel and the difficulty of control of the process produced much fine research work.

Publication of Scientific Information on Electroplating

A rather large number of books on electroplating have recently been published in Great Britain, few of which have contained new matter. Several were adversely reviewed and others only escaped on the grounds of systematic presentation or suitability for teaching.

Scientific journals of the more formal type seldom publish papers on electrodeposition. New research work is almost invariably published in the Journal of the Electrodepositors' Technical Society. Preprints appear a few weeks after the presentation, if indeed they do not appear before, but the formal Journal is often a year in arrear. These and other papers are usually verbally presented at one of the 10 meetings held annually by each of the three sections, where the good attendance insures a lively discussion. The best papers are retained for the annual conference, but the discussion is here often stifled by the number of papers presented. The Society circulates all printed papers and its Journal to some 1,200 members and many other subscribers.

The Society has recently tended to widen its purview to include most other methods of metal finishing, except painting and vitreous enamelling.

These meetings are fully reported as news in one or more of the technical periodicals especially interested in electrodeposition; they also publish original articles of fair interest, although seldom describing original research for the first time. The chief periodicals are *Electroplating*, a monthly entirely devoted to its name subject and closely related ones; *The Metal Industry*, a weekly published for the nonferrous-metal fabricator, gives several pages fortnightly to metal finishing; *Sheet Metal Industries*, a bulky monthly carrying much advertising, which often devotes lengthy and well-informed articles or series to electrodeposition, which are more detailed than those in its rivals; *Product Finishing* and *Industrial Finishing*, monthlies, chiefly devoted to paint finishing but sometimes carry articles on electrodeposition. Articles on electrodeposition research are sometimes published by metallurgical periodicals, e. g., *Metallurgia*.

Typical Recent Research Work in Electrodeposition

I have shown that electrodeposition research is carried out by many different types of organizations in Great Britain. The selected researches, typical as far as possible of each group, are now summarized. Although some have been published, it is believed that their full significance may not yet have been realized in America.

University Work

A research on the fundamental causes of the porosity of nickel coatings on steel has been proceeding at Cambridge University under U. R. Evans and S. C. Shome. They first showed, using the ferroxyl test, that an important cause of porosity was the surface roughness of the steel, especially such defects as scratches. They showed that this was due to the geometrical form of the roughness and not due to surface stresses, because the porosity increased with the depth of scratch, but it was not changed when the scratched specimens were annealed in vacuum before plating. The roughness caused by etching steel before nickel plating was also shown to increase the porosity of the coating. Nickel solutions having a high value of the rise of cathode potential with current density reduced the porosity in such cases because they had greater throwing power.

They then turned from consideration of pores as individual defects of the deposit to a consideration of the total uncoated area of steel. They showed that on theoretical grounds there were three likely ways in which a nickel deposit might cover a steel surface, viz: (a) deposition might take place anywhere from the first; (b) deposition might take place only on certain nuclei initially present, and also on others formed during deposition, and would spread laterally from them; (c) deposition might take place only on certain nuclei formed initially and grow laterally from them, but no further nuclei would be formed.

They then devised a very elegant method in which the uncovered steel of a thinly nickel-plated steel sheet was attacked, so that the amount of iron dissolved in a definited time was proportional to the uncovered area. They also devised another method by which the total amount of current flowing between the plated specimen and a very large cathode of noble metal was proportional to the total uncovered area. They then compared the rate of diminution of uncovered area determined by these methods with the increase of thickness; they showed that the form of the expression fitted only the third alrernative suggested, i. e., deposition starts on certain nuclei formed initially and the deposit spreads laterally from these, but none is formed thereafter.

Therefore, to decrease the porosity in a deposit of a certain thickness, two lines of attack are possible, viz: the number of initial nuclei can be increased and/or the rate of lateral growth can be increased. The second problem has not yet been tackled, but is a promising line. Evans and Schome showed that the number of initial nuclei was greater in nickel-plating solutions with a high value of rise of cathode potential with increase of current density; such solutions have good throwing power and are thus desirable for other reasons. A good example of such a solution is an ammoniacal nickel bath; unfortunately, Evans and Schome did not find these baths practical because the deposits were brittle and highly stressed. An alternative method of increasing the initial number of nuclei is to use a high initial current density, i. e., a "strike." The possibilities of PR plating seem important because of the frequent formation of nuclei.

This work is of the utmost importance, but is now held up by lack of funds.

Government Departments

The Armament Research Establishment has recently described a process for producing thick nickel deposits (up to 0.5 inch thick) in the bores of tubes up to 20 ft long and in enclosed vessels, using an insoluble anode which does not disintegrate, change in shape or require renewal.

The solution is virtually a Watts bath without chloride and contains nickel sulphate, sodium sulphate, and boric acid; it is used at a high acidity corresponding to pH 2, but this is determined by a titration method, because an oxidizing agent is formed in the solution, which destroys indicators. The anodes are of lead, lead-silver alloy, or lead-coated steel. Their construction, maintenance, and centralization are important. The chemical-engineering factors of the process are important and are fully described. The solution circulates from a head tank, through the tubes in parallel, then to a reaction tank, where the acidity produced by the action of the insoluble anode is counteracted by adding powdered nickel hydroxide. The solution is also heated in this tank, but not elsewhere in the system, and passes onward to a settling tank, pump, filter, and so back to the head tank. The throwing power of the process is poor, but this is easily offset by forming the anode. The deposits are soft (200 VPN, Vickers pyramid number), ductile, and quite free from pitting or "treeing" (provided the local current density is not excessive). Slightly harder deposits can be obtained by increasing the sodium-sulfate content of the solution or slightly changing the conditions. High current densities can be used except in narrow tubes. The method of cleaning the steel surface or a partially nickeled surface is described and insures adhesion of a very high order.

Another paper from the same laboratory will describe an average thickness test for the zinc deposit on small articles by measuring the time of gassing when they are immersed in a special acid mixture. This type of test has proved extremely satisfactory for small parts with cadmium plating, where local thickness tests are not possible. It has been metriculously tested, since it comes from S. G. Clark's laboratory, from which the B. N. F. Jet test came.

A new nonelectrolytic method of "smooth-etching", or "chemical polishing", of steel has also been developed at Woolwich.

Cooperative Research Associations

The British Non-Ferrous Metals Research Association has recently published results of the adhesion of electrodeposits to aluminum prepared by the zincate dip method. They find that the best adhesion is obtained at concentrations of zincate (i. e., caustic soda and zinc oxide) intermediate between the strong solutions advocated by the Aluminum Company of America and a much more dulute dip advocated in Great Britain.

They have examined the surface films formed on the aluminum in these dips by elegant photomicrographs and by electron diffraction, and have speculated on the mechanism of their formation.

Fundamental work on the cause of electropolishing is in progress. Existing theories are found wanting. A composite anode with adjacent microscopic hills and valleys electrically insulated from each other is being used and suggests that smoothing is not confined to electropolishing solutions.

The distinction is being carefully drawn between brightening and production of a lustrous surface that also gives sharp mirror images. Electropolishing will only do the former.

Metal Development Associations

The Tin Research Institute has recently announced full details of their research on a patented process for producing a bright alloy coating of tin-nickel—usual proportions 65 to 35 percent. They have also published considerable practical instructions for the industrial use of this process under license, and commercial units are in operation.

The coating is dark-white but mellow in color and has a faint rose-pink cast. It has extreme resistance to atmospheric tarnish and other corrosion, low porosity, and exceptional throwing power. It is deposited in a bright condition without the use of specific brightening agents.

The preferred electrolyte contains:

Stannous chloride	50 g/liter.
Nickel chloride	300 g/liter.
Sodium fluoride	28 g/liter.
Ammonium bifluoride	35 g/liter.

It is operated at 65° C and an average cathode current density of 25 amp/ft.^{2} Agitation is unnecessary. Alloy anodes or anodes of the separate metals may be used. Both anode and cathode efficiencies are almost 100 percent. Quite large variations in the composition of the solution or the condition of deposition do not markedly affect the composition or brightness of the deposit, so that control is not critical, but full analytical details are available. The coating has little leveling power.

The materials for construction of the plating tank, filters, and other equipment are unusual but have been fully tested. Perspex or Plexiglass is satisfactory. The solution does not fume strongly but should be draught-extracted.

The Tin Research Institute has also extensively tested the resistance of the coating to numerous reagents and published the results. The resistance to most corrosive agents is great and to atmospheric exposure is much better than nickel-chromium. The porosity is lower for a given thickness than for a nickel coating. A thickness of 0.0005 inch is sufficient on nonferrous metals. On steel a similar thickness is recommended but preceded by a deposit of copper 0.0005 inch thick.

Supply Houses

The research done by individual supply houses is understandably seldom disclosed. Messrs. Canning have recently marketed the first organic-addition bright-nickel bath to be widely used in Great Britain; previously the cobalt-nickel type was universally used.

They emphasize the leveling properties of the new bath and are doubtless working on this subject. Another supply house is agenting a Udylite bright nickel and have clearly done research on cleaning cycles to suit it.

A representative of another supply firm has recently published a textbook on industrial polishing of metals. Although an adequate account of known techniques is given, few original investigations are described. A forthcoming contribution, which should be helpful, is on consistent dyeing of anodized aluminium.

Large Users

Compliance with increasingly onerous thickness specifications has evidently caused several large users to institute detailed studies of deposit distribution and throwing power and to study practical methods of improving them. Some of the results disclosed have astounded experienced platers; they are somewhat optimistically being disclosed in the hope of influencing designers. A very useful experimental comparison of the accuracy of different methods of thickness testing of nickel deposits has been made by a larger user.

Perhaps the best indication of the steady investigational work carried out by large users is gained from public descriptions of their plant and process and the lively and informed discussion thereby aroused.

Large Platers

The investigational work of even the larger trade platers is apparently confined to economics and production efficiency, but these often disclose technical factors. Definite trials on the economics of different methods of polishing or barrel plating are examples.

Use of Electrodeposition for Special Purposes

A very full description has been given by P. Spiro of the London and Scandinavian Metallurgical Company of a commercially flourishing method of electroforming nickel moulds for plastics or diecasting. The large amount of prior research is frankly described. The masters or patterns are invariably made from cast phenolic or Perspex because of easy machineability, easy assembly with adhesives, easy removal from, or destruction in, the electroform, and dimensional stability.

The master is chemically silvered. (It is found essential finally to remove this chemically, even though the mould is buffed.) A number of baths were carefully examined for hardness of deposit, before and after annealing, brittleness, dimensional stability, throwing power, and especially stress, measured by the double-strip method. The optimum was found to be a Watts bath plus 2 oz/gal of cobalt sulphate, ¼ oz/gal of 1:3:6 sodium naphthalene trisulfonate, with additions of fluoride and wettting agent. This is used at a pH of 5.6 and 11 to 12 amp/ft.^{2}

Electroforms up to ¼ inch thick are regularly made, preferential deposition on outstanding portions being ingeniously prevented, usually without interruption, although deposition can be adherently restarted. The preferred deposit has a hardness of 520 VPN (still above 300 VPN after heating to 400° C) zero stress, considerable ductility, and dimensional stability. Methods of backing up have also been worked out.

A useful account has also been given by H. Silman of Joseph Lucas, Ltd., of the production lead plating of aluminium-bronze rotors for gas-turbine fuel pumps to prevent scoring. These operate under very heavy pressure against a steel face at high speed and cannot be lubricated. A curious pretreatment including double-flash pretinning with intermediate removal is used. (Probably dissolving out the aluminium from the surface.) Lead plating 0.0004 inch thick from the fluoborate bath and tin plating 0.00005 in. thick from the stannate bath is done in special jigs, with robbers, to achieve extreme uniformity of thickness. The coatings are alloyed by heating in oil (poor adhesion is shown here by blistering), lapped by hand to an optically flat surface, and tested under working conditions.

Discussion

Mr. W. A. Wesley, International Nickel Co., Bayonne, N. J. To go back to what you said about the insoluble anode process for a moment, I believe that you had some definite proof that an oxidizing agent is formed at the anode in that solution. How serious is that effect, and what do you do about it?

Dr. G. E. Gardam. Well, in answer to that we have the solution circulating around the system, and the oxidizing agent does no harm to anything. It stops pitting and oxidizes impurities. The only disadvantage is that it destroys an indicator, so that if you add an indicator, the solution becomes colorless again. It does not give any difficulty except in one case, Dr. Wesley, which is serious. If you try to do a restart adhesion of nickel onto nickel you just can't do it, because the oxidizing agent in solution forms on oxide film on the nickel before you can get some more nickel on it, and that applies to a certain extent to steel. Really, it did not cause us any trouble. It can be removed by circulating the solution over things like nickel turnings.

Mr. A. E. Carlson, General Chemical Division, Edgewater, N. J. I would like to ask, for the lead-tin alloy, why did you have to plate lead first and then tin and then diffuse them? Could you not have done it in the tin-lead alloy bath?

Dr. Gardam. Well, I am not quite sure of the answer to that one. Certainly they do not want a lead-tin deposit. It is rather like the diffused bearings where we have lead and infused indium or tin. Certainly, I don't think a lead-tin deposit would have done.

Mr. Carlson. They are plating a lead-tin alloy directly on bearings in this country, and it is perfectly satisfactory, at about 10 to 15 percent of tin. Is that your amount of tin?

Dr. Gardam. It would be about 30 percent, judging from thickness. I really do not know the answer to the question. It is not my own work.

2. Electroplating Research in France[1]

By Jean Salauze [2]

Introduction

A large part of the researches carried out in the electroplating field have been concerned with problems of surface protection that arise in various branches of industry, particularly in the automobile industry. France ranks fourth with the Western countries in industrial output, or third (after the United States and England but before Germany) if one considers only the automobile industry. France should therefore make an important contribution to the advancement of electroplating. In fact, however, electroplating researches in France are few and far between and are not in proportion to France's industrial output.

A comparison of the origins of electroplating researches in America and in France shows the causes of this. In America, electroplating researches are actively carried out in several universities, in research centers such as the National Bureau of Standards, the Battelle Memorial Institute, and in the laboratories of supply firms and large manufacturers. In addition, several scientific societies are active in the field. In France, very little electroplating research is done in corresponding institutions. However, the following should be mentioned:

1. Charles Marie (now deceased) of the Sorbonne formed a group of pupils active in electrochemistry, including such well-known men as N. Thon, M. Cymboliste [1],[3] and P. A. Jaquet [2].
2. The Centre de l'Aluminium, financed by Péchiney, and the laboratories of the business organization Tréfileries et Laminoirs du Havre, directed by Herenguel, have carried out work on anodizing of aluminum and have published their results, largely in the form of patents.
3. The French government has helped to establish a Centre du Chrome dur directed by Mr. Morisset, which is chiefly an information bureau for those interested in heavy chromium deposits. This organization arranges annual reunions and publishes work on hard chromium plating.

Work on Chromium Plating

As stated above, these papers on chromium plating are published by the Centre d'Information du Chrome Dur. The most important and the most original of them is incontestably that of P. A. Jacquet and Mrs. A. R. Weill; it is a joint work on the application of electropolishing and X-rays for the study of chromium deposits [3].

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[1] Presented by Vernon A. Lamb, National Bureau of Standards.

[2] Société des Accumulateurs, Romainville (Seine), France.

[3] Figures in brackets indicate the literature references on p. 20.

Up to the present, only the first part of this joint work has been published; it treats chiefly of the effect of the physical state of the basis metal surface, which is steel, on the physical properties of the coat of chromium deposited. Although it is too early to draw any definite conclusions, the results achieved are very interesting. The procedure adopted for examining the samples consists in taking oblique sections and electropolishing them in a bath containing, by volume, 5 percent of perchloric acid (specific gravity 1.59 to 1.61) and 95 percent of glacial acetic acid. The average conditions of electrolysis are: current density 15 amp/dm^2, voltage at the terminals 35 v, and temperature 20° C.

One unexpected result is that when we follow under the microscope the evolution of the network of fissures under the successive electropolishing actions, it appears that certain fissures remain, even after a considerable dissolution of the metal, of 0.01 mm, for example, but without producing any increase in their width, an increase which is, we must remember, a regular and classic phenomenon used during the fabrication of porous chromium deposits. It will be thus necessary in the future to try and establish a distinction between the different fissures in chromium deposits.

A second result that might have been foreseen, but of which the experimental confirmation is nevertheless very interesting, is that those fissures of the chromium deposit that reach the basis metal come into being through a peculiarity existing at the surface of this basis metal, which is revealed by examination under the microscope. This peculiarity is either a minute roughness, a heterogeneous structure, or a fissure, etc. Previously, Cymboliste had demonstrated by means of microphotographs [4] that the peculiarities of the basis metal induced peculiarities in the coating. In particular, the fissures that are produced in nickel deposits have their origin in a peculiarity in the surface of the basis metal that has induced, by disturbing the establishment of the normal crystallization of the metal, a line of least mechanical resistance which is opened in producing a fissure by the action of the internal stress of the deposit [5]. It is evident that this phenomenon may be extended and made general for all deposits that contain internal stresses. Jacquet and Weill have proved by experiment that this is actually the case with chromium deposits.

We know that electropolishing is a very useful tool for making smooth surfaces by doing away with as many as possible of the micro-irregularities. Whenever a mechanical procedure is employed, there is a weakening of superficial layers and a distortion, or lifting, of the metal grains. Jacquet and Weill have proved that chromium deposits formed on steel surfaces polished electrolytically have fewer fissures than those formed on surfaces polished mechanically. This point has important applications. It explains exactly a statement made by Eilander, Arend, and Sadrazil [6] that chromium protects better when deposited on a surface that has been polished by electrolysis.

Also, the examination of diffraction diagrams has revealed certain curious facts; when chromium is deposited on a steel surface mechanically polished, it is found that the chromium lattice is dilated from 0.15 to 0.2 percent and that the lattice of the steel base is itself dilated from 0.2 to 0.3 percent. On the other hand, when the surface of the basis metal is previously polished by electrolysis the lattices of chromium and of steel remain unaltered. However, Jacquet and

Weill recognize that it is too early and that their observations are insufficient to make it possible to draw definite conclusions.

This work deserves to be quoted in detail because it is very representative of recent work undertaken in many places on the physical properties of chromium deposits. It is said that between 1920 and 1940 study and research were mostly concerned with the chromium bath and its characteristics. Since about 1940, on the contrary, the study of the physical properties has taken first importance. M. Cymboliste [1] to a great extent initiated this line of work.

The other work concerned with the study of chromium deposits is less original than that which we have just discussed. Also, we are simply showing the trend.

The determination of the hardness of chromium deposits has interested many people. In particular, Girschig [7] has constructed a little apparatus called "microscleromètre" for measuring the hardness of light deposits. For this, the penetration of the point of the diamond must take place under the action of a very light load of only a few tenths of a gram. This small apparatus takes the place of the objective of the microscope. As a result, the impression is imposed on exactly that part of the sample previously chosen.

Cavé [8] has made many measurements for hardness with variable loads on deposits of different thicknesses. In particular, he has made a graph showing the load to apply in proportion to the thickness and the hardness of the deposit.

Mittenne [9] has taken over and completed this work, and has established, as a result of very many measurements, the variations in hardness found as a function of the load, and the influence of the machining of the deposit and of the basis metal. He has also drawn a graph relating the maximum load to the thickness of the deposit.

Le Rolland [10] has shown by judicious examples (e. g., rubber, which shows a hardness that is at once very low, because the point or ball penetrates without any effort, and yet very strong because the point or ball leaves no impression when it is removed) everything that is vague and indeterminate in the conception of hardness. He claims to determine the "superficial hardness" by the use of a pendulum on which is suspended a very hard rolling device (a cylinder, ball, or cone) that oscillates on the object to be tested. The deformation produced by the action of the weight of the pendulum has the effect of diminishing the time of oscillation. Le Rolland describes the various types of pendulums that he has used and gives some results for chromium deposits. However, there are not as yet sufficient results from which to draw conclusions.

We make brief mention of certain other work published by the Centre d'Information du Chrome Dur concerning the mechanical applications of hard chromium—the work of Meynier [11] on recent progress in chromium plating gages and two papers on the advantages and the effects of chromium plating cutting tools, one by Armagnat [12] and the other by Martin [13].

Work on the Electropolishing and Anodizing of Aluminum

As we have already remarked, this work is done mostly in the laboratories of Trefileries et Laminoirs du Havre, directed by Herenguel, and in those of l'Aluminium Francais, which is run by Pechiney.

In the first of these laboratories, Herenguel has made important discoveries on the conditions of preparation and on the nature of the alumina coating produced [14]. He has shown in particular that if the anodizing is carried out without special preparations, the anodic coat is heterogenous. While the outside is soft and sometimes powdery, the inside is hard. Such deposits have a poor resistance to wear and are unsatisfactory for dyeing purposes because they take dye rapidly on the surface and irregularly below the surface. He has demonstrated that for aluminum and its alloys, treated in a solution of sulfuric acid of a given concentration, if a graph of current density against the temperature is plotted, this curve divides the graph into three parts, which correspond with the formation of a continuous coating, of a discontinuous coating and of a heterogenous coating. This work has been done on pure aluminum, on alloys with 6.5 percent of magnesium, and on alloys with copper (duralumin) for baths containing, respectively, 10 and 15 percent of sulfuric acid by volume. The results of this research are protected by the French patent 913,486.

Patent 940,698 (Herenguel-Trefileries et Laminoirs du Havre et Societe Procol) gives the working instructions for electropolishing of aluminum. The bath has the composition:

Sulfuric acid (66° Bé)	70 percent by volume.
Phosphoric acid (60° Bé)	15 percent by volume.
Distilled water	15 percent by volume.

The temperature of the bath should be maintained between 75° and 100° C, 85° being the optimum temperature. The current density should be from 8 to 25 amp/dm^2. This varies according to the composition of the metal to be treated, 15 amp/dm^2 for aluminum of 99.5 percent and only 10 amp/dm^2 for duralumin. The agitation of the articles in the bath, at a linear speed of from 5 to 15 cm/sec, gives a uniform polish (with speeds less than 5 cm/sec the surface may be etched, and above 15 cm/sec there is no polishing). After this treatment, the surface is sometimes covered with a milky looking alumina coating. This must be dissolved by a chemical reagent. The polished article is then ready to be anodized as described in patent 913,486, to which we have already referred.

Although, strictly speaking, the procedure in question is not in the domain of electroplating, it is worthy of note that in a recent patent (984,863) Herenguel and the Association already referred to have described a method of chemical polishing of aluminum without current (by immersion). This discovery is the result of previous work that resulted in the French patent 798,721 on the electrochemical polishing of aluminum in a bath containing sulfuric, phosphoric, and nitric acids. Two methods have been perfected. One is suitable for rough polishing of very rough surfaces. The bath is a mixture with a very energetic reaction. It is operated at a temperature between 95° and 115° C:

Phosphoric acid (sp gr 1.71)	50 to 60 percent by volume.
Sulfuric acid (sp gr 1.84)	40 to 35 percent by volume.
Nitric acid (sp gr 1.50)	10 to 5 percent by volume.

The finishing is done in a much less energetic, but very selective bath, such as the following:

Phosphoric acid (sp gr 1.71)	70 percent by volume.
Sulfuric acid (sp gr 1.84)	25 percent by volume.
Nitric acid (sp gr 1.50)	3 to 8 percent by volume.

In either bath it is best to add from 0.2 to 1.5 g of a metal that is strongly electropositive to aluminum: for example, nickel in the form of sulphate.

Similar problems have been dealt with in the laboratories of the Société Péchiney. They have patented several solutions.

Concerning the brightening of aluminum, it is necessary to refer to the results quoted in the French patent 941,238, which describes a method applicable to wires and strips of aluminum and aluminum alloys. The composition of the bath is

Phosphoric acid (85%)	750 ml
Oxalic acid	300 g
Boric acid	150 g
Lead oxide (PbO)	1 g
Water	250 g

This bath is worked at 60° with a current density of 30 amp/dm^2. The bath is agitated and the article is treated for only a few minutes.

The Société Péchiney, in patent 961,236 describes a bath that operates at a low temperature (20°C) that can be used for very pure aluminum and for all aluminum alloys. The bath has the following composition, expressed in pure acids:

Nitric acid	30 to 45 percent
Phosphoric acid	8 to 24 percent
Chromic acid	3 to 10 percent
Water	Balance

It is worked with a high current density of between 10 and 50 amp/dm^2 with strong agitation. The length of treatment varies from 2 to 10 minutes.

In the recent patent 975,553 the Société Péchiney indicates an interesting modification to the classic anodizing bath of sulfuric acid. If the bath contains large quantities of halogen salts, and if very high current densities are employed, the oxide coat is formed with the same amount of current as in a normal bath, hence a great saving of time is achieved. The best halogen salts are alkaline chlorides and magnesium chloride. Also, for equal thicknesses, the anodic coat is much more supple. This is of interest for the electrical insulation of aluminum wire. Below is a comparison.

Normal bath	Modified bath
Sulfuric acid (66° Bé) 20 percent by weight. $t°=23°$ C. To form Al_2O_3 of 8-micron thickness requires 1.5 amp/dm^2, and $t=30$ min.	Sulphuric acid (66° Bé), 20 percent by weight + NaCl, 20 g/liter + KCl, 7.5 g/liter + $MgCl_2$, 0.5 g/liter. $t°=23°$ C. To form Al_2O_3 of 8-micron thickness requires 15 amp/dm^2, and $t=2$ min.

Other patents of the Society Péchiney are worth mentioning. French patents 898,758; 901,105, and 987,497 concern the various improvements in the applications of current in the installations for anodizing aluminum wire. Patents 985,496 and 985,918 concern, respectively, a procedure for closing the pores of the aluminum coat with barium sulfate (the article is quickly rinsed on leaving the anodic bath and plunged into a solution of 10 g/liter of barium nitrate), and the improvement of the physical qualities of the oxide coat deposited on wire, by heating from 100° to 600° C.

Miscellaneous Studies

These studies are nearly all connected with electropolishing. The reason for this specialization is certainly due to the influence, in France, of the researches of Jacquet.

From Jacquet we quote a recent work on the electropolishing of titanium [15] and its alloys, which is conducted in a nearly anhydrous solution of the following composition.

Anhydrous acetic acid	795 cm^3.
Perchloric acid	185 cm^3.
Water	48 cm^3.

The current density must be between 20 and 30 amp/dm^2, which requires a terminal voltage of 40 to 60 v. To avoid excessive heating it is operated for periods of 45 to 60 sec, each period corresponding to a dissolution of 10 to 12 microns.

Jacquet and Jean [16] by utilizing diffraction patterns have shown that metals polished electrolytically are sometimes covered with a thin oxide film. They have also shown by chemical analysis that the surfaces of copper, zinc, and magnesium, polished in a bath of phosphoric acid, contained small quantities of phosphate derivatives. In the case of copper, the film seemed to be fixed by adsorption and can be removed by sufficient rinsing. With zinc, and especially with magnesium, this appears to be a real chemical combination that is much more difficult to eliminate.

Mrs. D. Laforgue-Kantzler [17] has studied by various methods, such as the anodic potential, spectrography, polarography, and chemical analysis, the problem of copper in a phosphoric acid solution. She has arrived at the conclusion that copper passes into the solution in the cuprous state.

The electropolishing of nickel in solutions containing chloride ions has been the object of research by S. Tagima and T. Mori [18]. They have shown that polishing takes place at a normal temperature and with current densities of from 70 to 250 amp/dm^2 in solutions of hydrochloric acid or of chlorides of ammonia, aluminum, magnesium, nickel, or iron. These results confirm an observation already made by Evans, who succeeded in polishing aluminum in a bath of ammonium chloride.

Finally, in the field of pure electroplating, there is the French patent 976,801 of the Société Bozel-Maletra concerning nickel deposits that are thick and at the same time hard (from 400 to 450 Brinell) and ductile. These are obtained in a Watts bath worked hot and acid (pH=2 to 3) and containing a sulfamide, a sulfimide, or an aromatic sulfonate.

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Discussion

Dr. W. Blum, National Bureau of Standards, Washington 25, D. C. In the absence of Dr. Salauze, of course, it is very difficult to encourage any discussion.

Dr. W. R. Meyer, Enthone, Inc., New Haven, Conn. This is just a word of warning again because we do have short memories, and there has been a great deal of mention about perchloric acid. New people may be coming along and may be careless. You remember that big explosion, so I think we might mention that perchloric acid is very dangerous to work with.

Dr. Blum. Yes, it is not for large-scale work.

Dr. G. Dubpernell, United Chromium, Inc., Waterbury, Conn. I wanted to say a word in general about the relation of French work to that in other countries. While Dr. Salauze's paper points out some of the newer developments they are making now, in general, the present work in France follows that in other countries rather than leading the way, but it was not always that way. Antoine Becquerel, for example, was born 10 or 12 years before Faraday and lived longer than Faraday by over 10 years, and he was the first to work on chromium plating, for example, while Faraday had nothing to say on the subject. Both Faraday and Becquerel should have equal credit, I feel, as founders of electrochemistry.

I think it is owing to language difficulty that Becquerel's work is less well known. He did speculate about chromium plating in his books in 1843 and 1848. Then there was another Frenchman, Junot DeBussey, around 1850, who tried to use chromium plate as a foundation deposit for gold and silver on steel. In the 1890's there were Placet and Bonnet, and Moeller and Street, who formed a company for chromium plating and worked on both decorative and hard chromium plating. They had a kilogram of chromium, and claimed it was electrolytic chromium, which was exhibited at three different World Fairs, the last one being the St. Louis Exposition in 1904. When I correspond with present day French workers they don't seem to know a thing about the 1890 development.

Another first was Antoine Becquerel and his son Edmond, who have a very substantial claim to the discovery of nickel plating. They developed the double salt-nickel solution around 1860 or before, and carried on their claim against Isaac Adams of this country when he came to France with his process about 1870. The Frenchmen, I feel, deserve credit for developing nickel plating themselves and not waiting for Dr. Adams' development in this country.

Nowadays it is the reverse. If something new is developed here, within 5 or 10 years they investigate it in France, too.

Dr. Blum. We are glad to have this comment from Dr. Dubpernell. Most of us, because of the language difficulty, know too little of the work in other countries.

3. Electroplating Research in Germany, Belgium, and Holland

By P. Baeyens [1]

Introduction

In Germany, Belgium, and Holland there is not much being done as yet in the field of electroplating research. Germany has just started, after having been completely out of the picture. Belgium and Holland started work in this field during and since the war. In Belgium little has resulted to date, and in Holland it has developed to some extent, but the scope is still very limited.

The interest is mainly directed toward cheaper methods of obtaining brightness, for example, through use of bright-plating solutions, periodic reverse current, and electrolytic polishing.

Research in Germany

The information available about Germany is not sufficient to give a fully accurate picture. It is, however, evident that much work is being done, and it may be expected that this country is on the way toward taking its place among the other big metalworking communities.

Since World War II, research in Germany has been hampered by a number of factors, such as the destruction of facilities and the dismantling of industries. Langbein-Pfanhauser Werke, the most important supply house, was dismantled twice. The uncertainty of the German industrial and economic status also hampers research. Work did not start earlier than 1948–49, and it can hardly be expected to bear more fruit than it has in so short a time.

Subjects of study are mainly hard chromium plating and anodizing (which have always been pet German subjects), and bright nickel plating and electrolytic polishing.

Work is being done at supply houses, in the bigger industrial organizations, and in universities, often under sponsorship of industrial groups.

Among the supply houses that have well-equipped laboratories are Friedrich Blasberg, Dienert, Riedel, and Kampschulte. The last two of these have recently pooled their research work, and Riedel is also becoming the commercial outlet for the results of Siemens & Halske research.

Not much has filtered out yet about the work done in industrial laboratories. It is quite common that the first indications of this kind of research are found in patent applications, and to date not many have been published. Many of these industries work together with foreign groups with whom they exchange information.

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[1] Philips Gloeilampenfabrieken, Eindhoven, Holland.

More is known about the educational institutions. At the Max Planck Institute for physical chemistry and the University of Gottingen, Prof. Bonhoeffer works on problems of theoretical electrochemistry. Prof. Raub is still active in the field of noble metals. His work is being conducted at the Forschungsinstitut für Edelmetalle at Schwabisch Gmünd and at the Technische Hochschule at Stuttgart. His work also includes research in electropolishing and deposition of other than noble metals.

The Verein Deutscher Eisenhütteleute sponsors work at the University of Aachen, under the direction of Prof. W. Eilender.

Research in Belgium

In the past Belgium has never contributed materially to knowledge in the field of electroplating. The field was covered completely by foreign supply houses, and Belgian platers relied on them. Since the war, as a result of the closing of frontiers by the belligerents, a few individuals have started some research work on a modest basis. There are indications now that in the near future some organization in this field may materialize. Organized research may start there. Two groups that have come into being may stimulate it. The Centre Belge d'Etude de la Corrosion was created on July 11, 1951, by the metal industry, the big customers of this industry, the universities, and the banks. The purpose of CEBELCOR is to fight corrosion through scientific, technical, and educational means. In this picture electroplating has its place, too. At this time an electroplating committee is studying the possible research objectives as far as the Belgian plating industry is concerned. This committee also organizes educational lectures for the purpose of raising the general level of the industry. They are also preparing process specifications for guidance purposes.

The financial means of this organization are by no means negligible, and it can be expected that they will serve to promote research, probably in university laboratories.

The Comité International de Thermodynamique et de Cinetique Electrochimique (CITCE) was organized a few years ago. Although no actual financial support should be expected from this organization, one may hope that it will favorably influence such research by creating a sympathetic atmosphere for it.

The aim of the CITCE is primarily to be an international contact and good-will group, with adherents throughout the world. It has the support of notable electrochemical specialists everywhere. The promoters hope that eventually members will pool their knowledge and research facilities for the study of some worth-while objectives.

The CITCE has, as yet, no financial means and no laboratories. Its activity has mainly been the organization of conventions that have been quite successful.

As far as individual research is concerned, at this time, one school and a few industries are involved. The subjects are, once again, electropolishing and use of PR plating.

Work is done at the Faculté Polytechnique at Mons, where L. Meunier works on electrolytic polishing. His resources are, at this time, insufficient to warrant very extensive work.

The Bell Telephone factory and the Fabrique Nationale d'Armes de Guerre are believed to have a few people working on special plating problems.

Research in Holland

There is, at this time, no organized research in the field of electrodeposition in this country. The only existing technical institution where such work could be expected to take place has no plating group.

Supply houses, however, for the same reason as in Belgium, have started to pay some attention to this field since the war, and on a small scale are working on such topics as heavy silver plating, bright copper, conversion coatings on zinc, and the possibilities of PR plating. There is one factory where sieves are fabricated by electroforming, and here there is still a considerable amount of research being done to perfect the process.

The only factory where electroplating is an object of study of some importance is the Philips Gloeilampenfabrieken at Eindhoven. The plating laboratories of this industrial group have undertaken an extensive investigation in the field of electroforming in addition to their normal service work. This has already given birth to a modern plant for the forming of molds for phonograph records, to the electroforming of dies for plastics moldings, and to the fabrication by electrodeposition of thin-walled objects on a production basis.

In the field of finishing the activity of the laboratory is limited to those problems that are specific to this kind of industry, such as plating on uncommon base metals, or to the study of processes that are of general interest but not available on the Dutch market.

In this work, the plating laboratory has the help of the Philips research laboratory, where specialists are available in practically every field of science.

Two of the recent objects of study have been conversion coatings on zinc and cadmium and the metalizing of nonconductors by the method developed by A. Brenner at the National Bureau of Standards in the United States.

In the case of conversion coating of the type containing chromic acid and an "activator" anion (for example, sulfate ion), it was found that the solution could be perfectly controlled by keeping constant the pH, the hexavalent chromium content, and the "sulfate ratio." In the control of pH we discovered the fact—apparently known in the U. S. A.—that nitric acid is perfectly suitable as a pH controlling agent. With this kind of control a considerable amount of trivalent chromium and other contaminants can be tolerated in the passivating solution. An application of these principles to an automatic zinc-plating line has resulted in the continuous use of the passivating solution for more than 3 months on a 24 hours a day, 6 days a week basis. It has also been found that the consumption of chromic acid is very low and mainly a function of dragout, and that the rates of additions to the bath depend very much on the type of installation (objects, rinsing, dragin, and dragout).

Contrary to the experience of others, we found it perfectly feasible to apply electroless nickel plating to the coating of nonconductors. The major limitation is the high processing temperature in the nickel-plating solution. Because of this, materials and/or shapes that do not withstand this temperature cannot be used. The procedure, which is preferably preceded by a cleaning operation, consists of a treatment with a palladium chloride solution and electroless nickel plating. Successful deposits have been obtained on a great variety of materials like glass, Bakelite, ceramics, woods, etc. These deposits can be built to desired thickness either in the electroless bath or in any conventional plating solution.

Too many people have contributed to this review to permit naming them all. I must, however, mention the help of H. Krause and W. Kampschulte, who supplied most of the information about Germany, and M. Pourbaix, who helped on the Belgian side. I thank them, and the others herein omitted, very sincerely for their cooperation. I am indebted to the N. V. Philips Gloeilampenfabrieken for the permission to publish the foregoing details about their work.

4. Electrodeposition Research at the National Bureau of Standards

By William Blum [1]

The history and scope of the National Bureau of Standards Electrodeposition Section are summarized in an article in the Bureau's Technical News Bulletin, volume 35, page 180, December 1951.[2]

At present there are about 35 chemists and assistants employed in the National Bureau of Standards Electrodeposition Section. Their principal present activities are as follows.

Chromium plating of the bores of gun barrels. Chromium plating of gun barrels has been conducted for many years, generally with an improvement in performance and useful life. The object of the present research is to define the optimum conditions for preparation and plating and the optimum thickness and distribution of the coatings. These factors may differ with different caliber weapons and different firing schedules. The methods and equipment used are well known. In general, a cylindrical anode is centered in and insulated from the gun bore, the inner surface of which serves as the cathode. The anode consists of a steel or copper rod plated with a tin-lead alloy. The assembly is immersed in the chromium-plating bath after appropriate preparation and plated for the calculated period.

Electrodeposition of metals from nonaqueous solutions. Inspection of the periodic system shows that about 33 metals can be electrodeposited from aqueous solutions. About 15 of these are now electrodeposited commercially. Certain metals, notably molybdenum and tungsten, have not been deposited in a pure form from aqueous baths, but their alloys with iron, cobalt, and nickel have been so deposited.

There is a demand for coatings of such metals as aluminum, titanium, zirconium, molybdenum, and tungsten. If these can be produced by electrodeposition, they will find many military and industrial uses. Extensive studies of this subject, supported by the military agencies, are now in progress at the NBS (as well as in other laboratories).

A new type of bath for electrodepositing aluminum was recently developed at NBS and described at the October 1951, meeting of the Electrochemical Society. Smooth, dense, ductile deposits of aluminum were obtained from a bath consisting of aluminum chloride and lithium hydride dissolved in ethyl ether. The deposits may find applications in electroforming of waveguides and in coating other metals with aluminum.

At NBS some promising deposits of molybdenum have been obtained from a fused-salt bath operated at 600° C.

Special plating for Government agencies. During and since World War II there has been a great interest in the possibility of using

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[1] National Bureau of Standards, Washington 25, D. C.

[2] Available from the Superintendent of Documents, Washington 25, D. C., 10 cents. A mimeographed list of the NBS publications on electrodeposition, LP–14, may be obtained from the National Bureau of Standards, Washington 25, D. C.

electrodeposition for special purposes or to meet unusual conditions. In order to guide and assist various Government departments to determine whether their problems can be solved through the application of electrodeposition, the NBS conducts studies on many such problems. The results may then serve as a basis for large-scale tests for plant installations. Typical problems are those involved with the electroforming and silver plating of waveguides for radar equipment.

Tests and specifications for military supplies. While the Government departments, including the Department of Defense, employ Federal specifications where applicable, many special problems arise in connection with military equipment. The purpose of this project is to evaluate metal-finishing processes for these special applications and to develop tests that may be incorporated in appropriate specifications.

Instruments for measuring the thickness of coatings on metals. The appreciation of the great value and convenience of nondestructive methods of measuring the thickness of coatings on metals has led to a marked increase in the applications of the Magne-gage developed by the National Bureau of Standards in 1937. This instrument is made commercially, but their calibration is performed by the Bureau. Each calibration is accompanied by a card with four standard-thickness samples that can be used to check the calibration at intervals. The principle of the Magne-gage is employed in a special gage used to measure the thickness of metal coatings inside gun bores or other tubes.

Efforts are now being made at NBS to develop a nondestructive electronic method for measuring the thickness of nonmagnetic coatings on nonmagnetic basis metals, e. g., silver on brass. Promising results have been obtained, but more work is required to define the optimum design and the value and limitations of the method.

Applications of electropolishing. On many types of equipment, such as gears and turbine blades, it is desirable but very expensive to have a smooth, although not necessarily bright, surface. An investigation is being made of the favorable baths and conditions for electropolishing various steels and other metals, with special reference to the amount of metal that must be removed in order to obtain a desired improvement in surface finish.

Surface properties of molybdenum. Molybdenum has many desirable properties, including its hardness at elevated temperatures, but it is readily oxidized when heated in air. Efforts will be made at NBS to improve the surface behavior of molybdenum at high temperatures through the application of electroplated coatings of metals that may then be alloyed with the molybdenum by heat treatment.

Relation between permeability and protective value of electroplated coatings. This is Project 13 of the American Electroplaters' Society, a report of which, by Fielding Ogburn, paper 18, is included in these Proceedings. It is closely associated with AES Project 6, a report of which, by N. Thon, paper 17, is also included.

Physical properties of electrodeposited nickel. This is Project 9 of the American Electroplaters' Society, the complete report of which will be published shortly. A summary report by A. Brenner, paper 19, is included in these Proceedings.

5. Electrodeposition Research at Battelle Memorial Institute

By Charles L. Faust*

Introduction

Electrodeposition research at Battelle covers every aspect of the subject, as shown in table 5.1.

Much of the work was carried out for private industry or Government agencies and is not available for general disclosure. Some results have been published in the technical literature or in patents. Reference herein is made to three recent projects soon to be described in publications, either technical or patent. The work on the projects has been the direct responsibility of those named under the following three section headings.

TABLE 5.1. *Battelle's electrodeposition research*

Subject or field	Application or objective
Theoretical	Mechanism of hydrogen entry into metals; overvoltage; addition agents; properties of plates.
Electroforming Methods; engineering; procedures; new metals and alloys; aqueous and non-aqueous organic baths.	Electronic parts; fountain-pen caps; lipstick containers; molds; high-speed bearing liners.
Decoration Bright plates; high-speed plating.	Copper, nickel. zinc, silver, iron, copper-tin alloys, tin-nickel alloys, substitutes for shortage metals.
Protection	Substitutes for zinc and cadmium; substitutes for shortage metals; plating on unusual metals; protection for tropical exposure.
Alloy electrodeposition	Bright plating; bearing liners; cadmium-silver; zinc-tin; zinc-nickel; copper-tin; copper-lead; chromium alloys; gold alloys; silver alloys; silver-lead; copper-lead-tin.
Electrowinning and refining Aqueous and fused-salt baths.	Copper, manganese, special alloys, titanium, special metals.
Surface metallurgy Mechanical finishing and electropolishing.	Superior engineering performance of electroclad articles; better corrosion protection and appearance of plated parts; influence on plate structure and properties.
Graphic arts	Electrotyping; preparation of gravure surfaces; lithographic surfaces.

An Investigation of Electrodeposited Alloys and Pure Metals As Substitutes for Zinc and Cadmium for Protective Finishes for Steel Parts of Aircraft

By A. B. Tripler, Jr.[1]

During World War II it became apparent that, in the tropics, zinc and cadmium coatings offer inadequate protection to steel parts of aircraft. Shortly after the war a search was begun for coatings that would be superior to zinc and cadmium in protecting steel. Aside

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[1] Principal Electrochemist.

from this, the only further requirements were that the coatings give sacrificial protection, and that they be applied by electroplating.

Of the pure metals that can be electroplated, manganese and aluminum are the only ones, besides zinc and cadmium, that will provide sacrificial protection. Because of its chemical activity, however, the protection offered by manganese is of relatively short duration.

For the first phase of the project, the emphasis was placed on strengthening zinc and cadmium. Alloying these metals with some of the more noble metals was one possible way. Of the more noble metals, the following were considered: Nickel, tin, lead, antimony, indium, chromium, copper, and silver. Including the zinc-cadmium system, the total comes to 17 binary alloy systems.

To make as rapid a survey of these systems as possible, two electrochemical techniques were employed. The first was the measurement of single-electrode potentials in various media. These so-called "static potentials" told us at which composition an alloy ceased to be anodic to steel. Alloys that were cathodic were not of interest.

The second evaluation method was then applied to the alloys shown by the first test to be anodic. Each alloy was coupled with steel, and the corrosion current and polarization characteristics were measured. The "zero-resistance" circuit described by Brown and Mears was used for these measurements. From the second test, we learned the degree of cathodic protection, the amount of polarization, and the magnitude of the corrosion current that could be expected from an alloy coating of a given composition.

Preparation of plated specimens over a range of composition for each of the 17 alloy systems would have required a long investigation, because methods for codepositing the metals would have had to be worked out.

For many of the systems, preparation of cast alloys could be easily accomplished. The question arose, however, whether cast alloys would behave similarly to electrodeposited alloys of the same composition when tested by the two methods described above. Preliminary tests were made with several white brasses and with the zinc-tin alloys. The agreement between cast and electroplated alloys was fair in the case of white brasses and was good in the case of the zinc-tin alloys. Therefore, we proceeded with the cast alloys for the screening by electrode-potential measurements.

The electrochemical measurements indicated that a zinc-silver alloy containing 25 percent of silver and a zinc-tin alloy containing 80 percent of tin would give sacrificial protection to steel and yet would polarize to the extent that the corrosion current would be below that for pure zinc or pure cadmium. This was the situation we sought.

Cast specimens were not prepared for certain of the systems over a complete range of composition. Lead and zinc are almost completely immiscible, and preparation of the chromium alloys is made extremely difficult by the high melting point of chromium.

No successful method for the electrodeposition of zinc-silver alloys was known, so this became an objective of the research program. The attempts to devise a satisfactory alloy-plating process were not successful.

Up to this point, no study had been made of the intrinsic corrosion resistance of the alloys. We knew which ones would give sacrificial protection and how much they would give. But, what of the alloy itself, where the basis metal was not exposed, and no galvanic corrosion between basis metal and coating took place? This situation was studied next.

A new test was devised to provide alternate periods of condensation and dryness for the specimens. These conditions simulate most nearly the conditions in the tropics. Weight-loss measurements, following exposure in the cabinet, on certain selected cast-alloy specimens, including the zinc-silver, supported the conclusions drawn from the electrochemical measurements. Electroplated zinc-tin specimens exposed in the cabinet however, did not last for as long as the electrochemical measurements predicted. They were found to be superior to pure zinc coatings, but were not so good as cadmium. The electrochemical methods also predicted, for the conditions of the test, that cadmium-tin alloys would be about the same as pure cadmium. On the basis of recently published information and the results of incomplete tests at Battelle, electrodeposited cadmium-tin (75–25) coatings provide better protection for steel than either zinc or cadmium.

The electrochemical methods when applied to cast alloys are useful in eliminating those alloys that would not give sacrificial protection to steel. In predicting the life of plated alloys, one cannot be entirely certain when making measurements on cast alloys. This is because of minor structural differences between some electrodeposited alloys and the cast counterparts.

Since the preliminary work, certain manganese alloys have been studied. Manganese-zinc and manganese-tin alloy coatings prepared by diffusion appear to hold promise. Codeposition studies for these alloys are underway.

The Mechanism of Hydrogen Entry Into Metals

By L. D. McGraw[1]

Battelle Memorial Institute is engaged in a long-range program of fundamental studies designed to establish the mechanism by which hydrogen enters metals during chemical and electrochemical processing. The study is being sponsored by the National Advisory Committee for Aeronautics.

The initial work was exploratory and was intended to correlate the chemical behavior of atomic and molecular hydrogen with known methods of controlling the entry and exit of hydrogen in steel. As a result of the correlation, suitable reagents can now be chosen to increase or, for the first time, to significantly decrease hydrogen permeability and embrittlement of steel during cathodic pickling operations (in dilute sulfuric acid).

The entry mechanism proposed is that atomic hydrogen is deposited on the basis-metal surface and simultaneously disappears into the metal by diffusion alloying, as any metal alloys by diffusion into another when the ambient conditions are favorable. There is no need to postulate voids, fine cracks, or other defects into which a "gas" can slip. The mechanism can be expressed by hydrogen ion + metal + electron = hydrogen-metal alloy. There is no need to assume that atomic hydrogen existed for a finite period of time. When hydrogen does not alloy with a given metal there is no entry.

The rate of accumulation of hydrogen in steel during pickling is

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[1] Principal Physical Chemist.

dependent on the relative speeds of entry, diffusion, and exit under whatever environmental conditions prevail.

Any reagent or condition that prolongs the life of hydrogen in the "metallic" or "alloyed" state was found to cause an increased rate of accumulation of hydrogen in the metal. Accumulation was inhibited by environmental conditions which accelerate decomposition of the alloys. Thus, hydrogen accumulation in a metal could be controlled after it was assumed that the chemical behavior of hydrogen in metals is characteristic of the chemical behavior of atomic hydrogen. This behavior is close to that of a metal.

The chemistry of atomic hydrogen indicates that the decomposition of hydrogen alloys should be promoted by cathodic depolarizers which are oxidizing agents or catalysts for recombination of atomic hydrogen, and should be inhibited by cathodic polarizers which inhibit recombination of atomic hydrogen. Experiments have showed this view to be correct.

Reagents which were found to catalytically decompose hydrides of copper and arsenic inhibited the embrittlement of steel when they were added to the acid used for cathodic pickling. Likewise, reagents that inhibited hydride decomposition (hydrogen alloy decomposition) promoted embrittlement of steel during cathodic pickling in acid solution.

"Hydride" is used herein as referring to a hydrogen-metal alloy, either solid-solution or chemical-compound type, or both, as in a multiphase alloy. The term is not used loosely with the vague implication of "some gaseous atomic hydrogen in fine crevices in some solid."

The entry and exit of hydrogen from metals are equally influenced by the environment. When a cathode is subject to hydrogen deposition on only one side, the extent of embrittlement incurred depends on the rate of exit of hydrogen from the reverse side. The exit rate can be controlled. When it is decreased by substances that prevent decomposition of the hydrogen-metal alloy, such as dry potassium chloride, arsenic, or carbon tetrachloride, embrittlement is decreased because there is no "concentration gradient." The effect of dry potassium chloride and carbon tetrachloride relates to their property of preventing the recombination of free radicals, including hydrogen atoms.

The results of the research thus attach physical significance to the term "poison" in relation to hydrogen entry into metals and to hydrogen overvoltage. The "poisons" interact with atomic hydrogen reversibly to form definable free radicals of high-energy contents, such as CCl_3. Overvoltage is raised because the hydride (hydrogen-metal alloy) cannot decompose rapidly. That is to say, a sluggish irreversible transformation of protons to molecular hydrogen is promoted.

Hydrogen is removed permanently and overvoltage is lowered when a stable resonant system is formed, say by interaction of the hydrogen alloy with a quinoid dyestuff. The decomposition is speeded up, thus removing the cause of overvoltage.

Hydroxide has a strong catalytic influence on the rate of decomposition of hydrides. This explains why embrittlement is low in basic solution. We propose that rising pH in the cathode film is responsible for the decrease in rate of rise of overvoltage with increasing current density at high current densities. This phenomenon is not explained adequately by any modern theory of overvoltage but will be studied intensively in our future work.

Electroforming Aluminum

By W. H. Safranek[1]

The electrodeposition of aluminum was investigated with the objective of making lightweight waveguides that could be tested for radar wave-transmission characteristics. The work was sponsored by the Bureau of Aeronuatics, Navy Department.

A satisfactory process was developed for electrodepositing aluminum 0.65 mm or more thick. Aluminum waveguides with twists, bends, and/or tapers were electroformed by electrodepositing aluminum on electropolished, copper-plated, cadmium-nickel-alloy mandrels, followed by melting out the cadmium-nickel alloy and dissclving out the copper in nitric acid solution. This is a new procedure for obtaining mirror-like inner surfaces on electroformed articles. The plating baths consisted of a disperson of toluene in a toluene solution of the fusion product of ethyl pyridinium bromide and aluminum chloride with methyl tert-butyl ether or another addition agent for improving the physical properties of the aluminum electrodeposits.

By fusing 1 mole of ethyl pyridinium bromide with 2 moles of anhydrous aluminum chloride and adding benzene or toluene, a second layer formed on top of the plating solution, according to the procedure adopted by F. H. Hurley and T. P. Wier.[2] Attempts to electrodeposit aluminum thicker than 0.05 mm (0.002 in.), by the disclosed method, resulted in "lacey" nodular metal unsuitable for waveguide surfaces. The bath needed some kind of modification if electroforms of sound metal were to be achieved with the required wall thickness.

The ethyl pyridinium bromide-aluminum chloride fusion product dissolved in toluene was greatly improved by the use of an organic addition agent and by dispersing toluene in the solution of the fusion product and the addition agent.[3] The concentration of the addition agent (methyl tert-butyl ether) was between 1.0 and 2.0 percent by volume. The amount of excess toluene dispersed by nitrogen-gas agitation was approxixmately 40 percent of the total volume of the bath.

A new electrical system was also devised, incorporating 60- and 400-cycle alternating current for advantageous independent control of a-c density on the anodes and cathodes. This work was the first, to our knowledge, where alternating current was superpcsed between two sets of anodes independent of the cathodes.

With the proper current adjustments, the outer surfaces of the 1-mm-thick aluminum electrodeposits were very smooth and bright. With no alternating current superimposed on the direct current, the electrodeposits were highly stressed and were sometimes cracked. Excessive alternating current superimposed on the direct current caused nodular deposits. A deficient a-c density on the anodes caused the anode sludge (principally silicon) to dislodge, resulting in nodular plate. The details of the electrical and the gas-agitation

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[1] Associate Consulting Electrochemical Engineer.

[2] J. Electrochem. Soc. **98**, 203–207 (1951).

[3] Subject of patent application.

systems were published in the February 1952 issue of the Journal of The Electrochemical Society, and a patent application has been filed.

Waveguides produced with this new procedure had good ductility and strength. The microhardness of the cross sections was between 36 and 138 Knoop for the smooth deposits. Without an addition agent, but with toluene dispersed in the bath, 0.5-mm-thick plates were slightly nodular, and their microhardness was in the range of 28 to 36 Knoop. The addition agents caused a notable increase in the degree of orientation of the crystal planes (as determined by X-ray patterns), although they did not significantly change the microstructure, as viewed with the optical microscope.

The baths were used for as long as 560 amp-hr/liter (44 days) and could have been used longer, if necessary, indicating that extended use can be made of the solution-dispersal system employed in this investigation.

Aluminum waveguides were made for the first time by this procedure, which was the objective of the work. Other leads for baths were seen, but the project was not set up to study them. The results of this investigation are believed to be sufficiently encouraging for ultimate large-scale use of aluminum electrodeposition.

Discussion

Dr. G. E. Gardam, Design and Research Centre, London, England. In the binary anodic coatings I take it that the idea is to approach the potential of iron, and not have such a difference as with zinc. Is there not a danger that while you might get protection under normal conditions, you might get conditions where the potential reverses and therefore get the usual rusting? The other comment is that it is rather interesting that in England we have only one organization which is of the research type like Battelle and is much smaller, the Fulmer Research Institute. They had a project by Rolls Royce on hydrogen embrittlement under cathodic conditions, which is being published. No doubt Dr. Faust is familiar with that.

Dr. C. L. Faust. I might answer with a remark to the effect that we were aware of the condition which you have mentioned, Dr. Gardam, that the potential relationship can be varied by changing the environment, and that we must maintain some potential difference. The reason for using that special cabinet was an attempt to avoid that condition as much as we could in the direction we were working.

We had the privilege of talking with Dr. Hedges of the Tin Research Institute in Columbus about the time we started this testing as he has had some experience in exposure conditions and in attempting to set up a laboratory test to reproduce those tropical results. He thought that our test was superior in some respects to the K1110 test.

We have not at all satisfied ourselves, but the cabinet does operate as a quick screening method, and we have now exposed other panels in tropical conditions.

Mr. E. H. Lyons, University of Illinois, Champagne, Ill. You spoke of using carbon tetrachloride or dry potassium chloride on the back of the cathode to inhibit the decomposition of the hydride. Is there anything that will inhibit it on the solution side that you can mention?

Dr. Faust. Yes, there is. Methylene blue will inhibit the solution.

It has the effect of snatching the hydrogen atoms before they can diffuse into the metal.

Mr. F. L. Laque, International Nickel Co. New York, N. Y. I would like to ask a question and make a comment. The question is, what electrolyte or electrolytes were used for the potential measurements? The comment is, it seems to me that for a coating to be protective and have substantial thickness it does not have to be anodic. The important consideration is that it not be cathodic, so that the corrosion reaction can be forced within the pores. In this way the amount of damage is not likely to be as great as if you have a cathodic coating.

Dr. Faust. To answer your first question, distilled water and a 3-percent sodium-chloride solution were the media used. We attempted to simulate salt-water atmosphere and humid conditions from seacoast exposures. I agree that the coating does not have to be absolutely anodic. It can be a perfectly good envelope. As a matter of fact, the zinc-silver alloy is close to that potential and has lasted well.

6. Electrodeposition Research at United Chromium, Incorporated

By J. E. Stareck[1]

Abstract

Recent research work in self-regulating high-speed chromium plating baths, resulting in better throwing power, less lowering of fatigue resistance, and successful inhibition of basis-metal etching, was presented. Progress in the fields of porous chromium, crack-free chromium, and corrosion was outlined.

New developments in copper and zinc plating from mildly alkaline pyrophosphate baths were described. Special emphasis was given to a new zinc-plating process, which is characterized by better throwing power, low hydrogen embrittlement, and minimum requirements for waste disposal.

Recent developments in the field of chromate conversion coatings were brought out.

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[1] United Chromium, Inc., Detroit, Mich.

7. Electrodeposition Research at the Bureau of Mines

By Oliver C. Ralston [1]

Extractive metallurgy utilizes electrodeposition of metals as a recovery process and is not too vitally concerned with the finish of the surface of its cathodes. In the extraction of fine clays and some other suspensions, electrophoretic deposition is sometimes used as a means of recovering colloidal sizes of solids from aqueous suspensions of the washed minerals. These contributions to an electrodeposition symposium may not be of too great import to an audience made up largely of electroplaters, and so I shall be brief.

In a recently compiled index of 40 years of publications by the Bureau of Mines, there are only five entries of the word "Electrolytic" as the prime subject, although there are probably some hundreds of entries as subheadings under specific commodities. This gives emphasis to the fact that the Bureau of Mines uses electrodeposition as one of many tools in the study of conversion of mineral matter into forms that are salable.

The first important contribution to electrodeposition of metals by the Bureau of Mines was in 1914, with the first main subject assigned to the present writer—a study of losses of zinc in extractive metallurgy. The time was ripe to call a meeting of zinc metallurgists at Salt Lake City to consider the possible benefits of using an electrolytic process. The writer translated the only existing book, one by a German, Günther, "Die Darstellung des Zinks auf Electrolytischem Wege," and presented copies to the representatives of the more progressive companies at the meeting. Each went home and intensified efforts to develop workable processes for electrolytic extraction of zinc. The writer served as coordinator, visiting the various laboratories and disseminating information in order to accelerate the adoption of such processes. By the end of World War I, electrolytic zinc was firmly established in the United States zinc industry and has played an increasingly important role ever since.

This writer also prepared a book entitled "Electrolytic Deposition and Hydrometallurgy of Zinc," which is now well out of date and no longer available from publishers. The Germans returned the compliment, and Georg Eger translated the book into German, for sale in those countries where German was the principal technical language.

During those early years, with the help of Harry J. Morgan, the writer [2] worked out a method of making electrolytic zinc dust from sodium zincate solutions. Later, while in private employ, the E. I. du Pont de Nemours & Co., Inc., asked him for consultation on the design of a plant suitable for converting zinc carbonate precipitate back into zinc dust. On revealing the plan to their supplier, a better contract for zinc dust from retort smelters was obtained, and the zinc carbonate residue was accepted in partial payment. The first United States electrolytic zinc-dust plant thus died a-borning. However, in more recent years the problem of utilizing low-grade zinc carbonate, zinc silicate, and other oxidized ores which usually are not concentratable by mechanical means, has become more important. A caustic-

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[1] Chief Metallurgist, U. S. Bureau of Mines, Washington 25, D. C.

[2] H. J. Morgan and O. C. Ralston. Electrolytic zinc dust, Trans. Am. Electrochem. Soc. **30**, 231 (1916).

soda leaching and electrolysis process is under active development in the Bureau of Mines and has been fairly well studied on a pilot-plant scale. It is not yet ready for publication, but to arouse industrial interest a translation has been published[3] of a captured German document from the research files of the I. G. Farbenindustrie A.-G., Ludwigshafen. Several industrial firms needing zinc dust are now studying the proposition, and several possible operators of oxidized zinc ore mines in the West are also investigating.

Deposition of electrolytic zinc on aluminum cathodes is beset with difficulties due to unstable condition that results in re-solution of part of the deposited zinc after the deposit has built up for from 1 to 3 days. In the Albany, Oreg., laboratory of the Bureau of Mines, Ware and Higbie[4] have studied the deposition of zinc on thin zinc starting sheets. The results have been startling. The current efficiency remained high for periods of 10 days to a month, and final cathodes are as thick as the usual cast slabs of zinc. Being deposited on zinc, the manual labor of stripping from the usual aluminum cathodes is avoided, and, if the cathodes do not require melting into slabs, the usual drossing loss of 2 to 5 percent will be avoided. The cell room of an electrolytic zinc plant is the only location in such a plant that swarms with workmen, opportunity for economy in labor is great.

Other studies of depositing zinc on sheet cathodes of titanium and zirconium have been made by Ware. The deposit can be so easily loosened that, if the cathode is made narrower at the bottom than at the top, gentle tapping will release the zinc, and the deposit drops from around the cathode, leaving the complete zinc deposit from both sides of the titanium blank united, and a slot is left where the cathode originally was. This stripping phenomenon may be of value in electroforming.

Electrolytic lead powder from concentrated sodium chloride solutions saturated with lead chloride or lead sulfate was studied in 1916 by Sims and Ralston,[5] but there was less interest in spongy lead then than now, and the project was forgotten. Powder metallurgists and storage-cell manufacturers might well find in this contribution something usable at present.

Electrolytic manganese deserves mention in this record. It was developed by S. M. Shelton, who had transferred from the National Bureau of Standards shortly before being assigned to the job in the Bureau of Mines, and the process has been in use for nearly 10 years by the Electromanganese Corp., Knoxville, Tenn. A second plant is the prospect at Marietta, Ohio, and will be operated by the Electrometallurgical Division of Carbide & Carbon Corp. Pure manganese in noncarbonaceous alloys can fulfill many of the functions of nickel or copper. Stainless steels with partial or complete substitution of manganese for nickel are known, but none too well evaluated as yet. White brasses are also indicated, with their economy in copper. Price of metal has been coming down as the scale of operations has grown.

Electrolytic cobalt was developed as one way of recovering the metal from hydrometallurgical solutions in connection with the development of extractive metallurgy for an Idaho deposit. This product has not yet been taken up by industry.

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[3] Walter Eckart, Electrolytic preparation of zinc dust. Translation by O. C. Ralston. Bureau of Mines Information Circular 7466 (May 1948) 6 p. From Publication Board Document 41411, FIAT microfilm MM 106, frames 82–89 (Library of Congress).

[4] G. C. Ware and K. B. Higbie. The relative reliability of aluminum and zinc starting sheets for the electrodeposition of zinc, J. Electrochem. Soc. **97**, 425 (Dec. 1950).

[5] C. E. Sims and O. C. Ralston, The electrolytic recovery of lead from brine leaches, Trans. Am. Electrochem. Soc. **30**, 185 (1916).

Electrolytic chromium was developed through a period of years at the Boulder City, Nev., Station of the Bureau of Mines. In the beginning it was adapted to extraction of the metal from hydrometallurgical solutions. The scheme demands trivalent chromium in the electrolyte instead of the hexavalent chromium used by platers, which is one obvious economy. More recently, it has been found that, owing to the great volume of chemicals produced by dissolution of magnesium, aluminum, and iron from low-grade chromites the hydrometallurgy can be greatly simplified by starting with the cheapest grade of ferrochromium—the high-carbon "no-ratio" ferrochromium. This improved process has been licensed by the Electrometallurgical Division of Carbide & Carbon Corp., to go into a plant under erection at Marietta, Ohio. Other industrial enterprisers are considering it.

In my opening paragraph I mentioned electrophoretic deposition of clays from slurries formed in washing out impurities. The average white kaolin requires 1 faraday of electricity for each 10,000 grams of clay deposited. This is a rough measure of the average particle size of the clay being deposited on the anode. One faraday will deposit only 65.38 grams of zinc ions on a cathode. It seems strange to worry about the faraday equivalent of a colloidal suspension, but if its faraday equivalent gives some measure of particle size, it is a very useful datum. This twist in electrochemistry was contributed by the Bureau of Mines.

Discussion

Mr. R. A. Hoffman. Allied Research, Baltimore, Md. You mentioned the deposition of chromium. I would like to ask a question. What type of solution was used in the baths?

Mr. O. C. Ralston. The solution has changed considerably during the life of this development. Originally sodium sulfate, now ammonium sulfate, is the extra salt in the bath.

Mr. Hoffman. An aqueous solution then?

Mr. Ralston. Yes.

Mr. Hoffman. What do you use as an anodic material?

Mr. Ralston. Lead. The lead has to be alloyed with silver, or silver and arsenic, as is the case with lead anodes in chloride electrolytes.

Dr. G. E. Gardam, Design and Research Centre, London, England. I would like to ask Mr. Ralston if he can tell us the approximate price ratio of electrolytic manganese and nickel, and how that would change if electrolytic manganese was widely bought? I think that electrolytic manganese developed by the Bureau of Mines has a very great importance to electroplaters, especially today when nickel is not available. Just straight copper manganese has very much the properties of nickel-silver. Unfortunately, owing to certain legislation, we have only tried out 35-percent copper, and there is so much manganese that the alloys are rather difficult to plate. They are base metals and you can't easily get adhesion.

I think that the Bureau of Mines work is producing a new metal, not a substitute. It increases the potential total amount of metal by a very convenient electrolytic method.

Mr. Ralston. Your estimate is correct. It is a different metal. The purest manganese commercially available is the aluminathermic or silico-thermic manganese, which might be 97 percent manganese. To have 99.9-percent-pure material is quite important, and you are not carrying in some silicon that may be undesirable.

Of course, it is exceedingly low in carbon. Phosphorus, which occurs in most of the thermic manganese, is present to a very slight extent in electromanganese.

You asked about the current price situation. I haven't checked up on the price of electromanganese perhaps for 2 years. It was 28 cents a pound a couple of years ago. The price of nickel has been going up.

Now, in substituting manganese for nickel in a stainless steel, for instance, it takes about 10 percent of manganese by weight to do the work of eight parts of nickel, so that you have to take into consideration that there has to be a little longer lever arm on price to make it attractive, but there is plenty of difference at the present time as nickel is above 50 cents right now. It would be worth a lot more if we had a natural market. So, there is a considerable temptation now to employ electrolytic manganese to at least supplement the nickel supply in stainless steel. The 50-percent substitution seems to be more imminent than a 100-percent substitution.

Dr. W. Blum, National Bureau of Standards, Washington 25, D. C. In connection with the substitution of manganese for nickel, I will remind you of a fact some may have forgotten. During the war synthetic nickels, that is, nickel-less nickels, consisted, if I recall correctly, of about 65 percent of copper, 27 percent of silver, and 8 or 9 percent of manganese. The manganese was necessary to give the hardness and other properties to imitate the regular nickel-copper alloy. I don't know whether that is coming back, but it is just an interesting case where the manganese served a very useful purpose.

Mr. L. Weeg, National Lock Co., Rockford, Ill. The significance of something that Mr. Ralston said escaped me, and I am wondering if he would explain a little more in detail. You were talking about the starting sheets for the electrorecovery. You mentioned that the first starting sheets used were made of aluminum, but you could only continue the plating for about 3 days when there was a stripping effect, whereas, when you changed to a zinc starting sheet, you went several days without stripping. What was the mechanism?

Mr. Ralston. I wish I knew, but there are things that happen there. There will be local centers where the re-solution of zinc will occur, and you may have holes as large as 2 inches eaten from otherwise thick cathodes. That happens particularly when cobalt is present in sufficient amounts. You have a zinc-aluminum couple involved there, and then you have the chance for other ions to be deposited. If you have any bare aluminum, it accelerates the effect. Those holes show more corrosion on the back side next to the aluminum than on the outside. You can have a tiny pinhole and look under it, and it may be that half an inch has been eaten away from the back of the cathode.

Mr. Weeg. After 3 days of electrolysis, isn't the aluminum pretty well sealed up by the deposit?

Mr. Ralston. It should be, but those things happen otherwise.

Mr. L. Gilbert, Rock Island Arsenal, Rock Island, Ill. I would like to ask what sort of iron content you get in your electrolytic chromium?

Mr. Ralston. It depends upon how carefully we remove it, but from a few tenths up to 1½ percent, depending on the conditions of running a plant continuously.

8. Electrodeposition Research in Progress at Armour Research Foundation

By William H. Colner [1]

Electrodeposition on Titanium

The objective of this project, sponsored by Watertown Arsenal, is the development of a method to obtain adherent metallic coatings on titanium by electrodeposition. A question you might ask is, "Why would anyone want to plate on a metal that already has such excellent corrosion resistance?" The answer is that although titanium has good corrosion resistance, all its other properties are not necessarily as good. For instance, erosion and wear resistance are not outstanding in titanium, so that if a method of obtaining adherent electrodeposits were known, these properties might be improved. Thus the problem of plating on a relatively active metal enveloped in a tightly adherent, thin oxide is posed. The requirements of the method are to remove the oxide and strike the metal before it can reoxidize.

Obviously, the initial stages of the project were concerned with trials of presently known methods of plating on oxide-covered reactive metals, such as stainless steel, magnesium, and aluminum. Cathodic reduction of the oxide and simultaneous deposition of a strike metal (nickel) as is practiced with stainless steel gave nonadherent plates. Formation of an insoluble fluoride and subsequent plating in a fluoride bath, as is practiced with magnesium, likewise gave nonadherent plates. Zinc immersion plates in alkaline baths or acid fluoride baths gave similar unhappy results. We reasoned from these experiments that the presence of water was causing oxidation of the titanium as fast as the oxide was being reduced or removed. The program was accordingly directed toward nonaqueous baths.

As hydrofluoric acid is quite effective in removing titanium oxides in aqueous solution, it was used as the activating agent in the nonaqueous bath. Furthermore, because the more-active metals form better strikes than the noble metals when plating on an active metal, zinc was used as the strike metal. Finally, anhydrous hydrogen fluoride requires a polar molecule to manifest its acidic properties; therefore, a polar organic solvent was required. The bath that gave best results from the standpoint of adherence was accordingly one composed of zinc chloride, hydrogen fluoride, acetic acid as solvent, and a small amount of water. The small amount of water was added to give the bath an appreciable d-c conductivity. The water was present in small enough quantity to be tied up by the hydrogen fluoride, and therefore was unavailable to oxidize the titanium.

The adherence of specimens struck in the nonaqueous bath and subsequently copper-plated was excellent. The specimens were 1 by

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[1] Research Metallurgist, Armor Research Foundation, Chicago, Ill.

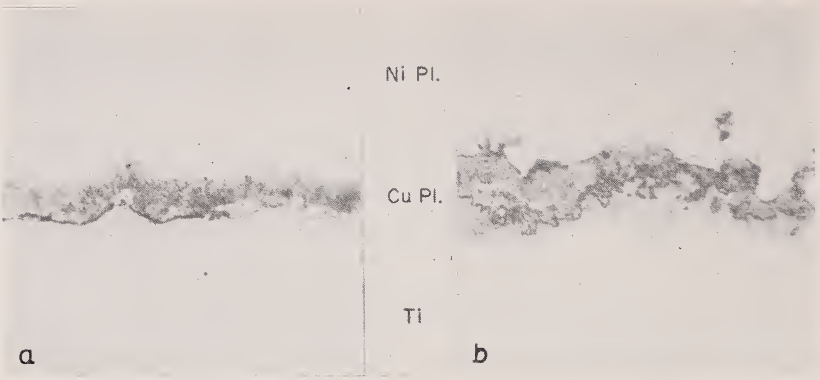

FIGURE 8.1. *Microstructure of copper-plated titanium*

The photomicrographs show the difference in structure of bond between nonadherent and adherent plate. Note in the nonadherent bond the presence of an intermediate layer (probably oxide) between the copper-zinc and the titanium and the absence of this layer in the adherent bond. (a) Nonadherent bond between plate and titanium base. 10% $(NH_4)_2S_2O_8$. ×500. (b) Adherent bond between plate and titanium base. 10% $(NH_4)_2S_2O_8$. ×500.

2 by 1/16 in., and adherence was tested by clamping half the specimen in a vise and beating back the exposed part until either the metal failed or the plate parted from the base metal. In those cases where the adherence was considered excellent, the specimens required bending through an angle of 180°, at which point the metal failed (see fig. 8.1).

A serious drawback to the nonaqueous bath described above was the inconsistency of adherence. Completely adherent plates could not always be produced. Apparently, either the conditions of plating were extremely critical or the bath suffered some form of deterioration. In either case, this factor was detrimental. Other solvents were tried. None of these gave any improvement over the acetic acid, but ethylene glycol seemed to be as good. Because ethylene glycol had other advantages over acetic acid, it was decided to concentrate on it as a solvent rather than acetic acid.

At present, experiments are being performed to determine optimum hydrogen fluoride and water concentrations. Baths are also being allowed to age to determine the effect of time on the inconsistency factor.

Silver Plating of Waveguides

This project is sponsored by Squier Signal Corps Laboratory. Its objective is the determination of optimum conditions for silver plating brass waveguides and the adaptation of these conditions to commercial plating practice. In a previous project it was found that the new periodic-reverse plating technique seemed to offer some advantages over ordinary plating.

Waveguides are rectangular tubes used to "pipe" electromagnetic waves of the order of 1-cm wavelength. They are made in various sizes and lengths, which are determined by the frequency range for which they are to be used. The sizes range from 0.100 by 0.050 in. to 7.7 by 3.85 in. inside dimensions. Waveguides are made of coin silver for the very small sizes, of silver-plated brass for the intermediate sizes, and of aluminum or silver-plated stainless steel for the large sizes. It is quite important that the inner surfaces of waveguides have high electrical conductivity and smooth surfaces.

The plating problem then is to deposit a high-conductivity metal, silver, as uniform and smooth as possible. Early experiments were concerned with attempts at forming thick immersion plates on brass surfaces, but the maximum thickness that could be obtained was only 0.1 mil, and even then the smoothness was not good. It was apparent that plating would have to be effected by using an internal anode. Several straight-length waveguides 1 by ½ by 36 in. were plated, using a stainless steel wire anode centered by spacers. The plating solution was pumped through the waveguides, which were totally immersed in cylindrical tanks. The plating thickness varied about 33 percent peripherally and about 55 percent from end to end. These were the best results obtainable with ordinary techniques. These variations in thickness, although admittedly large, were considered an improvement over the uniformity of thickness found in plated waveguides bought on the open market.

It was felt that uniformity of thickness and smoothness could be considerably improved by special plating techniques. Accordingly, the research program is now directed toward an investigation of the PR plating process as a possible answer to the problem. Early experiments showed that under certain conditions of plating, PR gave a conductivity in the silver plate of about 99 percent IACS, whereas the best value obtained by d-c plating was 94 percent IACS. The improved conductivity is a result of a denser plate in the PR specimen, 9.84 g/cm^3 as compared with 9.18 g/cm^3 for the d-c specimen. This conclusion is based on a series of specimens in which it was found that conductivity was a direct function of the density. However, these experiments do not indicate the best obtainable results because the baths were not filtered as well as they should have been.

Several rather interesting experiments were carried out during the course of the research. In one experiment, a series of silver-plated specimens were exposed to 200 hours of salt spray. It was found that specimens having a silver thickness in excess of 0.7 mil were relatively pore free and showed no penetration of the silver. Those plated with less than 0.7 mil of silver were porous and showed green brass-corrosion products at the pores. Electropolished silver-plated brass seemed to withstand the salt spray better than buffed silver. This was due possibly to the inclusion of buffing compound in the surface. On very heavily silver-plated brass, the base-metal finish and/or rhodium or palladium flashes did not appreciably improve the corrosion resistance.

Another experiment of a rather qualitative nature revealed the large amount of porosity in very thin deposits of silver. It was found that in films of the order of 0.2 to 0.4 mil the density dropped to around 5 g/cm^3 and the conductivity to about 50 percent IACS. It is felt that PR plating under optimum conditions may be beneficial in the problem of thin-film porosity.

Present work is directed along a rather fundamental study of optimum PR plating characteristics to obtain highest conductivity and finish of silver plate.

Deposition of Magnetic Nickel-Cobalt Alloy

Armour Research Foundation is presently doing considerable research work on magnetic recording. In one phase of one of the programs it became necessary to electrodeposit a nickel-cobalt alloy having certain magnetic properties. The properties important to magnetic recording that are easily tested are the coercive force, H_c and the residual magnetism, B_r.

H_c is related to the performance of the recording medium at high frequencies, and B_r is related to the performance at low frequencies. The particular values required of these variables are strongly dependent on the use to which the recorder will be put. To determine the feasibility of controlling these properties by varying the plating conditions, an experimental bath was set up to plate brass-rod specimens 0.094 in. in diameter by 12 in. in length. The selection of this specimen size was based on the requirements of the 60-cycle Hysteresis Loop Tester, in which H_c and B_r were determined.

The composition of the bath was such as to contain 50 g/liter each of nickel and cobalt ions and sufficient boric acid to buffer the bath at pH of 4. The variables tested were superimposed alternating on direct current, current density, and bath temperature. The superimposed a-c on d-c plating was conducted by using a 4.0-v lead storage battery as the d-c source and a series-connected secondary of a 115/11.5-v transformer as the a-c source. The a-c voltage was controlled by a variac on the primary of the transformer. Figure 8.2 shows the results of a series of experiments. Note that a-c voltage has no effect on H_c and B_r until the peak voltage equals the d-c voltage. At a-c voltages in excess of 4.0-v peak (2.8-v rms) H_c increases and B_r decreases. This is the point beyond which the voltage is reversed and causes some dissolution of the deposit. H_c attains a maximum value of 300 oersteds at 8.5-v peak (6.0-v rms) and decreases at higher a-c voltages. B_r decreases when the peak voltage exceeds 4.0 v, and at 8.5 v the B_r curve has its greatest slope.

It was found that favorable magnetic properties could be obtained by using no alternating current. The effect of d-c current density on

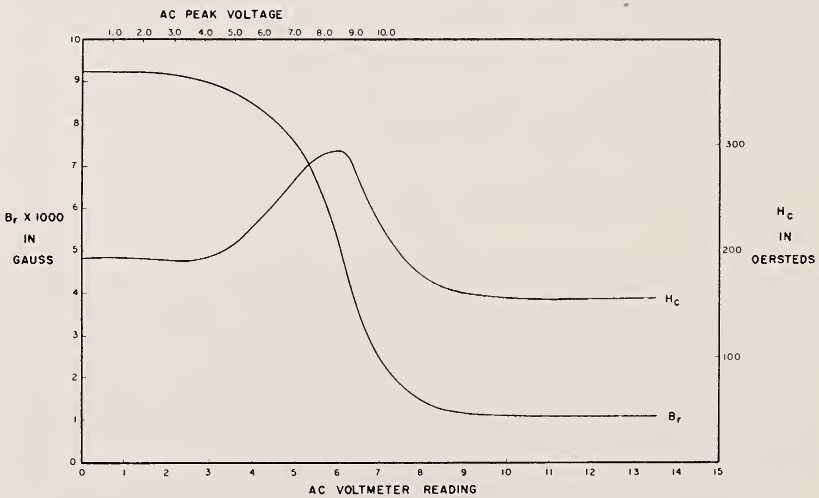

FIGURE 8.2. *Effect of a-c voltage on H_c and B_y in plating, using superimposed alternating on direct current.*

Direct-current source voltage 4.0 v; temperature 70° C; d-c current density 100 amp/ft².

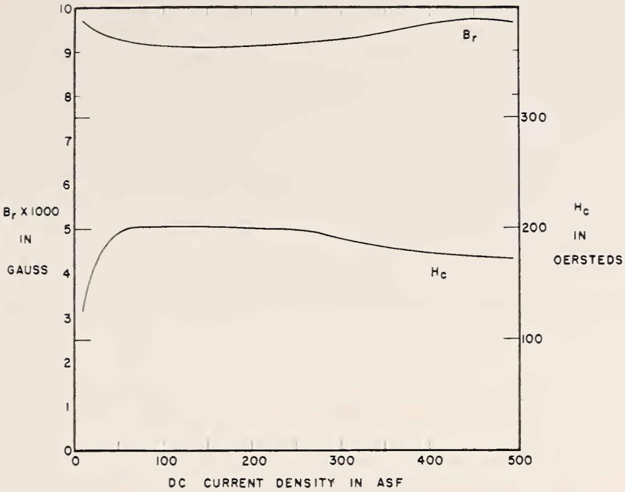

FIGURE 8.3. *Effect of current density on H_c and B_y, using no alternating-current.* Temperature 70° C.

the magnetic properties was studied, and the results are shown in figure 8.3. No significant effect was noted between 75 and 275 amp/ft^2. Above and below this range, H_c decreased and B_r increased. Finally, the effect of bath temperature was studied. It was found that deposits plated between 60° and 90° C showed little difference in magnetic properties. Below this range B_r dropped to rather low values, and H_c was somewhat erratic.

It was concluded from the rather preliminary study outlined that magnetic properties could be controlled by adjusting the a-c voltage superimposed on direct current, and that with no alternating current, the d-c current density had little effect on magnetic properties in the range studied. Finally, it was concluded that the temperature of the bath above 60° C had little effect on the magnetic properties. Many other studies would be required for a complete understanding of the characteristics of the bath. Most important of these are the effects of pH, nickel, and cobalt content, alternate immersion, and a-c to d-c voltage ratios at various d-c voltages.

Discussion

MR. I. W. MARCOVITCH, U. S. Gauge Co., Sellersville, Pa. In doing your work on the silverplating of waveguides, did you try various addition agents and brighteners in the silver solution to see what effect they would have on the smoothness of the deposit? And if so, would you care to report on it?

MR. W. H. COLNER. We found definite improvement in brightness over no addition agent at all. We have not studied the relative brightness between PR and addition agents. I understand that the PR process did not involve any organic agents.

MR. MARCOVITCH. What addition agents did you try?

MR. COLNER. Carbon disulfide.

DR. A. BRENNER, National Bureau of Standards, Washington 25, D. C. I am very much interested in the work on adherent coatings on titanium because our work has followed in an almost parallel path. We had a project to find out how to get adhesion of coatings to titanium, and we found that no matter what aqueous solution we used we obtained no adhesion and very soon gave that up and came to the decision that nonaqueous solutions would have to be the answer.

We did some work with zinc but in a little different manner. We produced the zinc coating on titanium as an alloy by subjecting the titanium to vapor phase deposition of the zinc and then plated over that, but we were not satisfied with that process. I think the best results were achieved by some people at Fort Belvoir who used the evaporation method of producing a precoating of titanium followed by copper. The results were extremely good.

9. Electrodeposition Research of Westinghouse Electric Corporation

By George W. Jernstedt [1]

In 1946 it was decided to form an electroplating development group and provide adequate facilities for this work. This conclusion was reached because it was felt that electroplating in the past had been more of an art than a science, and that it was an opportune time for Westinghouse to put forth an effort in this field employing the development of periodic reverse current (PR) as a nucleus. The 12-story Engineering Building houses the electroplating laboratories on the sixth floor.

The first year was spent in setting up a laboratory and providing equipment to develop electroplating processes in the most efficient manner possible. Our laboratory took approximately 1 year to build, at a relatively low cost, considering the excellent equipment and facilities we secured. The total cost was $59,000 for all initial laboratory construction, services, benches, and ventilating system. A grand total of $91,000 was expended, including all specialized equipment. These costs were comparable to other laboratory construction in the Pittsburgh area.

Our laboratory is basically a complete installation for the development and application of electroplating processes. No wires or pipes are visible, and, at the same time, they are accessible for service. All the materials employed in the laboratory construction were selected because of their low-maintenance factor and durability to corrosive atmospheres. The entire laboratory is air-conditioned and "precipitron" air-cleaned. There is no recirculation of the air, and 10,000 ft^3 of fresh air are treated every minute. All the windows and doors are sealed to prevent dirt from entering. The glass on the benchtops is tempered Carrara glass and has proved to be very serviceable. We have standardized our equipment and procedures as much as possible in order to facilitate our research programs. It was felt that if sufficient effort were put forth into procedures involved, the men would enjoy their work and would do a better job.

To supplement the plating facilities for research work in small tanks, a pilot line was constructed. The main pilot line consists of 100-gallon tanks. All the plating tanks are equipped with diaphragms, continuous filtration, and air agitation. Deionized water is supplied to some of the solutions through electronic liquid-level control. A panel board at the end of the pilot line has a clock mechanism that will turn on the tank heaters during the night so that the solutions are up to temperature in the morning. There are six different current sources supplying over 3,500 amp to the entire laboratory. A new pilot line of smaller-sized tanks is under

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[1] Engineering Manager, Special Products Development Division, Westinghouse Manufacturing Co.' Pittsburgh, Pa.

construction. It was necessary to provide an intermediate size between the 4- and 100-gallon tanks. Fifty-gallon tanks were selected. An effort is being made to conceal the wiring and piping so that the unit can be easily maintained and readily available for work.

In addition to the plating facilities, an adequate library is maintained. Because patents are so important to this type of work, we work closely with the Patent Department. We have in our laboratory files all of the important electroplating patents. This file consists of over 3,000 patents, and in addition, as patents are issued in this field, they are received within 2 days in our laboratory. Because patents are one of the technical phases of the electroplating field, it was thought to be essential that our men be exposed to this patent education.

After a literature search, one of the first steps in investigating new electroplating processes is preliminary testing in a Hull cell. We have spent much time in research and development of the actual construction of a Hull cell. Since we plate on the order of 10,000 panels each year, we have standardized the panel itself. The panels are obtained with a protected polished side and with a commercial finish on the other side. The standard Hull cell was improved by installing an immersion heater in the base, which is controlled with a variable transformer. In addition, we experimented with air agitation and found a design that made possible air agitation as the panel is being plated. We are at present completing a design that utilizes the air to pump the solution over a diaphragm in front of the anode. The timers, ammeters, voltmeters, and other controls were built into the reagent shelf. This requires a minimum of exposed wiring.

After the panels are plated, they are rinsed, dried and stored in sealed cellophane envelopes. A file of over 20,000 panels is kept up-to-date with related information in a record book. It takes only a few minutes to secure any panel in the file for the purpose of comparison.

We have used oak furniture throughout the laboratory for several reasons. Wooden furniture is less expensive than the metal furniture, and in addition, is more serviceable where chemical processes are involved.

After the work in the Hull-cell stage is completed in the research program, the process, if it shows promise, is moved to our 4-gallon tanks. After the work is completed in the research program, a similar 4-gallon unit is employed for our application phase of the program. All the services required for the 18 plating stations, including current, temperature controls, ventilation, drainage, and utilities are built into the reagent shelf. Filtration, agitation, diaphragming, pumping—all are investigated in the 4-gallon-tank stage of any development program. The construction of our 4-gallon-tank line features flexibility and durability. The anode and cathode rods are coated to prevent poor contacts. Circular spring contacts are provided at the ends of the electrode rods to minimize the chance of high resistance. Each solution is continuously filtered through rubber-lined filters and Hastalloy-C filter pumps. This equipment can be used for any of the common plating solutions, including the all-chloride nickel solution.

Air agitation has been investigated in many of our plating processes. Surprising as it may seem, it was determined that air agitation could be used in a hot cyanide copper plating solution without materially affecting the carbonate build-up. One of the research programs on PR plating was an investigation of leveling. A standard bumper section with its characteristic line graininess had a surface roughness between 12 and 15 rms microinches. After PR copper plating, the surface roughness was reduced to approximately 1 to 2 microinches. This ability of PR plating to level was secured through an intense research program in which the effect on leveling of each constituent and each variable in the plating process was investigated.

After copper plating the bumper section it was nickel plated by means of a new PR process, which can produce a full-bright deposit without any organic addition agents. A research program on periodic reverse current for nickel disclosed that bright nickel without organic addition agents could be produced if the current is reversed for 1/120th of a second every 6/120th of a second. Over PR-leveled copper the PR nickel exhibits as much brightness as any of the organic addition-agent processes. A 500-amp PR converter is used to produce this nickel PR cycle. It is comparable in size to conventional generators or rectifiers. It has a specially designed commutator with brushes to pick off the desired portions of the cycle. Our first machine, used for development work in this range of PR cycles, was a small motor-driven cam arrangement. The cams could be varied to produce the cycle desired and the motor speed varied the frequency of the cycle. After our cycles were approximately established, a variable-speed rotating commutator was designed, and research work proceeded on a somewhat larger scale. At present we have built one 5,000-amp PR converter.

Standard buffing and grinding equipment is located in the heavy equipment room. In order to facilitate our research program, considerable salt-spray corrosion testing was done in our early work. Although we recognize that a salt spray does not duplicate outdoor environment, we have employed this tool to evaluate variables in a plating system.

Our research has indicated that leveled PR copper can reduce corrosion in scratch lines on polished steel parts. Experimental panels indicate that as the thickness of leveled PR copper is increased, the corrosion resistance improves. With our research program, we were able to develop a copper deposit that can produce results comparable to those produced by buffing. The corrosion resistance of zinc-base die castings is improved by plating with PR copper, since no buffing is required, and therefore the zinc surface is not disturbed.

Some commercial use has been made of our research program in the last few years. For the last 2 years we have been producing electric iron covers plated with PR copper and chromium directly over the copper. This was not done as a defense expedient; we were using this process before the nickel shortage.

One of our interesting research programs has been the evaluation of the physical properties of deposits. One device used is a bulge tester modeled after one described by Harold Read at Pennsylvania State College. This device supplies oil under pressure against a foil of the stripped deposit. As the pressure is applied, a microscope is focused on the bulge in the foil until it ruptures. The ductility of the deposit is determined in this manner. The mechanism is made flexible by having four different pressure ranges.

Fundamental research in the laboratory may be grouped into three parts, although the work is interrelated, and the results along one line of study are useful in another. One phase of the work is the study of the structure of organic and inorganic compounds that produce bright electrodeposits. It is now apparent that quite often there is one key chemical relationship common to most organic brightening addition agents for each plating solution. In another phase of the program, a method is being investigated which we hope will indicate quantitatively the value of an addition agent in electroplating processes as a brightener or surface-leveling agent. The method involves the displacement of the cathode-potential versus current-density curve as a function of the addition agent. Our latest research program is a study in the field of zinc plating to determine the type of solution and current that will produce bright, stain-free zinc deposits.

Discussion

Mr. W. H. Colner, Armour Research Foundation, Chicago, Ill. Do you find any bad effects from using rubber-lined filters in your strong alkaline cyanide copper solution?

Mr. G. W. Jernstedt. Needless to say, we have run into difficulty on occasion, and you can pick it up very quickly where you use heavy air agitation. However, the rubber that we have in those commercial filter units is excellent, and commercially it is not nearly as much of a problem because we use continuous filtration over activated carbon and—and this is very important—continuous electrolytic purification. You can do it batch-wise. You can get into some difficulty, but you can get out of it readily.

Mr. L. Weeg, National Lock Co., Rockford, Ill. Would you, George, elaborate on your concept of stain-free zinc?

Mr. Jernstedt. I believe that we all recognize that dull zinc is certainly more susceptible to staining than bright zinc. That is one part of it. The second part is that there are certain types of zinc plates that do resist staining. We have seen evidence of it with certain organic addition agents. That is, you can handle it or ship it, and it will look fairly bright when the customer gets hold of it. It isn't that we have in mind that this zinc is going to be fundamentally different. We are attempting to produce that type of brightness that will resist handling stains without organic addition agents.

Mr. C. J. Wernlund, DuPont Co., Niagara Falls, N. Y. How does the PR bright nickel stand in brittleness to the other bright nickels?

Mr. Jernstedt. Our preliminary work has indicated that we have bright nickel with the greatest ductility we have ever seen in any deposit. Still, again, I want to say it is our preliminary work, and some tests were made by Dr. Reed at Penn State, and I believe he verified some of those findings. We have not produced this uniformly. We are still exploring the field.

Dr. W. Blum, National Bureau of Standards, Washington 25, D. C. I would like to ask, George, whether this new type of generator is or can be readily adapted to the longer cycles, such as the 10- or 12-second cycles.

Mr. Jernstedt. No, it cannot.

Question. What is the effect of PR on the micro-throwing power both on cyanide copper and your bright nickel?

Mr. Jernstedt. I would say it would not be too long before commercially we will be able to level what we call 75 percent. In other words, take a surface from 15 microinch down to 2 microinch, something in that order, and do it commercially. We are just starting.

On nickel it is a different matter. You will notice in the movie I was very careful to say "On leveled PR copper, the nickel exhibits full brightness." With the nickel process we can detect leveling, but that is all. It is not negative. If anything, it is positive, but it certainly is not anything more than 5 or 10 percent. It exhibits no leveling in the order of bright-nickel processes by organic addition agents.

Question. You say there are no organic addition agents; what inorganic addition agents are there?

Mr. Jernstedt. None.

Mr. I. W. Marcovitch, U. S. Gauge Co., Sellersville, Pa. George, with reference to the diaphragms that you were using. I noticed that you stressed diaphragming in practically all the plating baths that you operated. Are they the standard materials listed in the literature or have you worked out your own?

Mr. Jernstedt. We have done a great deal of work on diaphragming. At the present time we are developing a new diaphragm material. We have just sent out our first samples to a couple of production plants. It is a washed canvas impregnated with a high-temperature vinylite, and our preliminary tests indicate that it is superior, for example, to Dynel.

Question. George, what have you done in the field of acid copper plating?

Mr. Jernstedt. We have a new acid copper process that we are just beginning to market. Frankly, I do not care very much for acid copper. It has its applications, and the process we have demonstrated we think is as good as any on the market. Maybe it has some advantages, but it contains an organic addition agent. It produces leveling of the same order that we produce in a cyanide copper bath, but close control composition of the solution is important. If out of balance, you get unusually brittle, and perhaps off-color deposits. Carbon treatments then become essential.

Question. Is PR used?

Mr. Jernstedt. No, it is not used. It can be used to secure certain advantages, but on normal deposits of the order of half a thousandth to a thousandth, I would not recommend PR. We can detect the improvement, but I do not think it has commercial benefit.

Question. How about a compromise in the organic addition agents? Can you use organic additions with the PR, for example, with the nickel or copper?

Mr. Jernstedt. Yes, you can. We had anticipated marketing a process, but the nickel shortage came along, and we could not do it. The process is this: using this PR converter and one-twentieth of the usual concentration of any organic addition agent, you get the same degree of brightening that you would get with the usual concentration of organic addition agent without PR. However, we have decided that if we are going to market anything in nickel plating, we are going to do it without any organic addition agents. At the moment the thing that holds us up the most is just the source of current. In other words, you cannot use a conventional generator or rectifier or any modification thereof. Just try to reverse the current for 120th of a second.

Mr. F. Passal, United Chromium, Inc., Detroit, Mich. In your investigation of the PR cyanide copper-plating bath, have you made any study of the accumulation of organic materials, say, the hydrolysis of cyanides or polymerization products or other possible reactions? I know the bath has been alluded to in some instances as being free of organic addition agents, but I would consider cyanide as essentially organic in its future.

Mr. Jernstedt. I have always taken it as being understood that we would accept the cyanide as a major constituent and not being an organic compound that would decompose into harmful ingredients. Of course, the cyanide decomposes. I believe mainly electrolytically. We have not done as much work as the people at DuPont. All I would say is that there is no detrimental decomposition. I do not believe there is any polymerization.

10. Brass Plating

By K. G. Compton [1] and R. A. Ehrhardt [1]

The electrodeposition of brass for decorative purposes has been practiced for many years, and numerous papers have been written on the subject. Since, for this purpose, appearance is of prime importance, the baths are usually controlled by observation of the color of the deposit. Brass plating for rubber adhesion, on the other hand, cannot be controlled by color because the color of the deposit is not necessarily related to the composition of the deposit, which is the important factor in rubber bonding. The composition of deposit required for rubber adhesion depends on numerous factors in the vulcanization process but generally falls between 65 to 75 percent of Cu. Because the items to be bonded are sometimes complex, the composition throwing power of the solution is of great importance. The purpose of these studies was to develop brass-plating solutions producing deposits containing between 65 and 75 percent of Cu, with a minimum variation of composition with current density.

In order to deposit brass of constant composition at varying current densities the shape of the cathode potential-current density curves and the cathode efficiency must be controlled in a very definite manner, and, in the case of alloys in the range in which we are interested, must be nearly identical because half of the current used to deposit metal will deposit copper and half zinc when the composition is 66 percent copper. This implies that the degree of ionization, ionization rate, and diffusion rate of both metals and hydrogen must all be balanced over a wide range of current densities. This does not seem to be possible at low current densities, and consequently low polarization, and our experiments show considerable variation in this area. Most solutions used for brass plating are used at low current densities and low metal concentrations and are subject to variation of composition with current density and probably would not be capable of plating at higher current densities due to their low metal content. Uniform deposits can be obtained over a wide range of current densities if sufficient metal is present and the current density is high enough.

Consequently, the solutions studied were all higher in metal content and other constituents than those normally employed.

The zinc content of the deposit can be increased by increasing the zinc content of the bath, which also may, by dissociation and common ion effect, decrease the ionization of copper, but it was felt that the zinc content should be increased by raising the pH because this would not appreciably alter the behavior of the copper. In a sense, this is similar to the use of pH to control the tin in a copper-tin bath where the copper is complexed with cyanide and the tin with caustic. In the brass solution the zinc is also complexed by the cyanide, but it was felt that at higher pH this effect would be minimized. The addition of cyanide in high pH baths does not suppress the deposition of zinc

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[1] Bell Telephone Laboratories, Summit, N. J.

as much as that of copper, so that increasing the cyanide would also increase the zinc content of the deposit.

The following variables were studied; pH, temperature, free cyanide, metal content, and metal ratio. As we were interested in uniformity of composition, most experiments were conducted at relatively high current densities, free cyanide, and pH. Addition of alkali and sodium cyanide decrease the copper content of the deposit. Increasing the copper content of the solution increases the copper content. Increasing the temperature also increases the copper content without adversely affecting the constancy of composition with variation of current density. This permits the deposition of uniform deposits of various compositions by the proper selection of operating temperatures.

The deposits are uniform in composition at current densities between 25 and 125 amp/ft^2, and although agitation decreases the copper content at low current densities, higher current densities can be used and uniform deposits over a wide range of current densities secured.

All the deposits obtained in these experiments were sound metallic deposits of good appearance, although the lower current density deposits were more matte. At the high-copper contents the deposits were coppery, but in the desired range (65 to 75 percent) they were quite uniform yellow deposits, and very little difference in color could be detected, using a Hunter Color Difference Meter. At the lower copper contents the deposits varied from pink to light gray or lavender. Hull cell test panels gave a uniform color except on the back where the current density is extremely low.

The cathode-current efficiencies were naturally not high, being between 25 and 50 percent, but this is amply compensated by the high current densities employed. A coating 0.0002 in. thick could be applied in three to six minutes, and all of the coatings tested were in this range, which is relatively thick for brass plating. As it is not difficult to produce these relatively thick deposits, and it is known that the composition of thin deposits is variable, particularly when deposited on different base metals, it is easier to control the deposit composition by plating test samples at different temperatures on steel panels, from which they can readily be stripped and analyzed. Then, having obtained the proper temperature to produce the deisred composition, the brass is deposited on the desired base metal, which is sometimes a copper alloy, on which the analysis of the deposit is impractical.

The baths developed in this study should be ideal for production brass plating for rubber adhesion because the high concentration of all components make them less susceptible to variation. The uniformity of composition with current density makes them ideal for plating on complex shapes. The control of composition by varying the temperature gives them a great degree of flexibility where different compositions are required and minimizes analytical work where it is desired to maintain any composition. The good, uniform color of the deposits over a wider range of operating conditions and the ease of obtaining thicker deposits, which would eliminate a common criticism of brass plating, make these baths ideal for decorative brass plating.

Discussion

Mr. S. Heiman, Philadelphia Rust Proof Co., Philadelphia, Pa. What about the ammonia content? Did you just let it fall where it may?

Mr. R. A. Ehrhardt. No, the ammonia does not stay in there, particularly in a hot solution. It does not seem to build up because the solution is operated hot and is high in free caustic soda. We don't have any particular concern with it. I have never been able to detect any odor of ammonia.

Mr. Heiman. I see you use both the free-cyanide method and the titratable cyanide. That means you are rather neutral on the subject. On which did you rely more heavily in your control work?

Mr. Ehrhardt. Well, we kept the free cyanide constant, that is, we tried to. I will look that up and let you know.

11. Electroplating in the Sleeve-Bearing Industry

By R. A. Schaefer [1]

Introduction

The chances are very good that you arrived at this symposium with power provided by an internal-combustion engine equipped with precision-plated overlay bearings, the overlay being thinner than the protective plating on the bumper of your automobile. In general, thin functional overlays for these and similar applications are comparable in thickness to decorative plating, except that the former must be considerably more uniform. The decorative field has the ever-present problems of brightness, luster, color, buffability, etc., while the field of functional plating of overlays is concerned with alloy composition, metal distribution, smoothness, wear, and fatigue resistance. The progress in this direction for the past decade or so has been very satisfactory, for today it is not uncommon to find the overlay of lead-tin-copper, lead-tin, or lead-indium intact on the copper-lead or silver intermediate liners of bearings that have completed over 500,000 miles in a heavy diesel or aircraft engine and over 100,000 miles in a truck or passenger-car engine.

Trimetal Bearing Construction

Because it is impossible to correlate mechanical performance of bearing materials with their physical and chemical properties on more than a qualitative basis, development work in this field is slow and largely empirical. However, Mougey [1][2] has indicated empirically the physical properties of materials that must be achieved reasonably well for successful application in practice. The present high-duty bearing is of a trimetal construction consisting [2] of a steel back, copper-lead or silver bearing liner and lead-tin or lead-indium overlay. These materials represent, respectively, the fundamental property of high, intermediate, and low modulus of elasticity, combined as a sandwich construction of different materials. When a constituent of the overlay tends to diffuse into the intermediate, a plated diffusion barrier is interposed, as will be discussed later. This type of construction is illustrated by figure 11.1.

Electroplated Overlays

The tin and lead base babbitts have the most desirable properties for running surfaces in lubricated sleeve-bearing applications. Generally speaking, tin alloys are preferred to lead because of greater resistance to erosion and corrosion. However, as the engines and accessory equipment have increased in horsepower output and efficiency, demands have been made on the various parts of the engine, including bearings. Therefore, the development of high-duty engines demanded a higher-duty bearing, and the babbitts would not operate satisfactorily, especially from an endurance viewpoint.

Each of us is familiar with the evolution of ferrous metallurgy when

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[1] Director of Research, Cleveland Graphite & Bronze Co., Cleveland, Ohio.

[2] Figures in brackets indicate the literature references on p. 64.

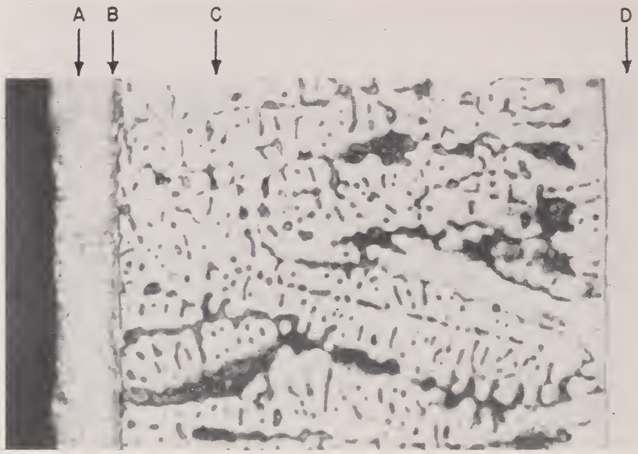

FIGURE 11.1. *Trimetal construction with plated diffusion barrier,* ×250.

A, Plated Pb-Sn-Cu overlay; B, plated diffusion barrier; C, intermediate layer cast-copper lead; D, steel.

physical chemistry was applied to the early cast irons, pure iron, and the low-carbon steels, with the result that a multitude of special-purpose steels were developed. These steels modified the original iron or cast iron with numerous minor alloying constituents combined with specific heat treatments, so that today, one has several hundred steels to choose from—each of which has its physical and mechanical properties well cataloged.

However, the development of higher-duty bearings did not proceed in a metallurgical manner, but rather from a mechanical-engineering standpoint. The metallurgical investigations of tin and lead alloys in the past two decades have failed to find means for increasing their mechanical properties in thicknesses above ten-thousandths, so that higher loads could be carried. However, by reducing the thickness of the babbitt liner, an improvement in life was obtained, especially when the thickness was less than ten-thousandths [3]. The fatigue properties of the babbitts are remarkably improved by reduction of thickness when they are well bonded to stronger materials, especially a steel back. These extremely thin layers of the order of one-thousandth of an inch directly on steel do not give sufficient safety factor in bearings for practical use because of such unknown factors as clearance, dirt in the oil, misalinement, and temperature. However, such a thin babbitt layer, combined with a thick intermediate layer of bearing material that has higher physical properties, although it may have an inferior running surface, offers a practical compromise.

Statistical analyses of babbitt-bearing failures over a period of years reveal that the fatigue cracks start at the surface and proceed toward the bond line to the vicinity of one-thousandth of an inch. They then turn at right angles, and run somewhat parallel to the bond line until they cross other cracks coming from the surface. This, then allows the little pieces of fatigued metal to fall out, as illustrated by figure 11.2.

It has been observed from the researches of Bowden [4] and his associates that with light sliding loads there is a marked deviation from Amontons' laws of friction when strong or hard materials

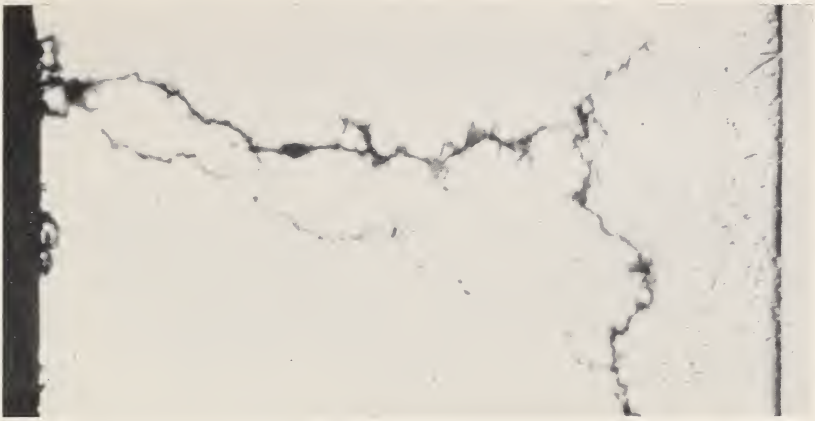

FIGURE 11.2. *Fatigue cracks in a babbitt bearing,* ×225.

are coated with a thin layer of a soft metal. As you will recall, the classic laws of friction state that the friction between two surfaces is independent of the area of their surface of contact and proportional to the force pressing them together when the area of intimate contact increases with the applied load. However, the soft overlays modify the proportionality factor of area with a marked reduction in friction, and the law is no longer valid.

Further, Bowden and Tabor [5] found that the thickness of this overlay and the physical properties of the base metal influenced the frictional behavior of the system with the minimum friction usually occurring at approximately one-half of a ten-thousandth of an inch in thickness for the overlay.

By virtue of the sandwich construction, the thin, uniform overlays have high fatigue resistance and low frictional resistance. Electroplating has been adopted by the industry because it is the most economical commercial process for applying thin, uniform layers of metals or alloys with an accuracy greater than can be obtained by casting and machining.

The lead-tin overlays are being replaced in favor of lead-tin-copper ternary overlays because of somewhat greater wear resistance. The copper plates with lead and tin largely by diffusion, and acts, we believe, somewhat as an addition agent. This factor has allowed us to operate with smaller concentrations of organic addition agents, which we feel is strongly desirable. In general, minimum wear is experienced with those plated alloys whose deposition requires a minimum concentration of organic addition agent. Over a period of years, we have been able to increase the wear resistance of a given overlay by over threefold by the proper selection and concentration of addition agents. The ternary plate of tin (8 to 10%), copper (2 to 3%), and balance lead has been previously disclosed [6].

Another problem has been solved recently by the introduction of a thin barrier layer [7] of iron, nickel, or cobalt to minimize diffusion of the low-melting alloys, especially tin, into the higher-melting metals, such as the copper-leads. The loss of tin into the intermediate layers is undesirable because the lead then erodes and corrodes away at a very rapid rate. The effectiveness of plated barrier layers of various

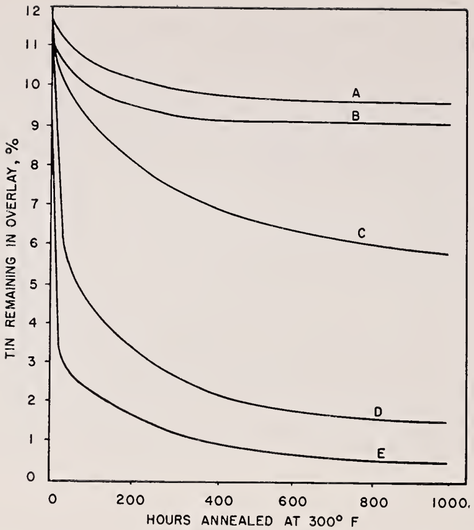

FIGURE 11.3. *Percentage of tin remaining in lead-tin-copper overlay (0.001 in. thick) after diffusion through various thicknesses of barrier layer into cast copper-lead.*

A, 0.0002-in. barrier-layer thickness; B, 0.0001 in.; C, 0.00005 in.; D, 0.00002 in.; E, none.

thicknesses in reducing diffusion of tin from a lead-tin-copper overlay into a cast on copper-lead (25% lead) is shown in figure 11.3.

Intermediate Bearing Liners

The four common processes of casting, plating, cladding, and powder metallurgy and their combinations are all used for sleeve-bearing manufacture, the choice depending on the particular bearing material. Today, the most common intermediate bearing-liner material is copper-lead with other minor alloying constituents such as tin, antimony, and silver. Silver as an intermediate layer is limited primarily to the aircraft industry because of its cost. Recently, there has been some experimental production of aluminum, alloyed with minor constituents such as tin, cadmium, copper, and silicon. The particular process or material used appears to be dominated by the factors of economics and the over-all level of performance. Materials generally used for intermediates can be conveniently graded qualitatively as follows:

Material	Over-all fatigue performance	Usual fabricating process
Silver	1	Plating.
Copper-lead (25% lead)	2	Casting or powder metallurgy.
Copper-lead (40% lead)	3	Do.
Aluminum-tin (6% tin)	2	Casting and cladding.
Aluminum-cadmium (2%)	2	Do.

The performance and behavior of these materials has been adequately described in the literature by numerous individual researches and summarized in a recent publication [8], and will not be repeated here. The thickness of these intermediate bearing materials will usually vary from ten to thirty thousandths of an inch.

Future Trends

The development of electroplated overlays at the present time is only in its infancy. No doubt there will be a number of new types of overlays with specific properties that will out-perform present materials. The rate of progress is slow because of the complex nature of alloy plating and the lack of basic data. In the past 6 years we have plated over 50 alloys of lead and tin for bearing evaluation and several of them look extremely interesting. The problem of addition agents and their tremendous effect on wear and fatigue resistance is very important, but progress along this line is necessarily slow. The prime objective is to develop plated alloys having specific properties superior to those made by other processes.

The intermediate liners are of sufficient thickness that plating will probably not be considered in the near future. As a general rule, when thicknesses beyond five-thousandths of an inch are involved, electroplating is uneconomical, unless the special metallurgy and/or mechanical properties obtained overbalance the increased cost factor. This, for example, is true in the case of a silver intermediate layer.

The uniformity of metal distribution is a very basic factor in this field. Electroplating and electroforming will be advanced every time additional basic information on the current and resulting metal-distribution relationship becomes available. The solutions of these problems are difficult and time consuming. This, coupled with expensive tooling and masking, requires large volumes to achieve an economical cost for the product. In general, shields and anodes can be empirically worked out either alone or in combination to distribute the current and the resulting metal uniformly, regardless of the complexity of the cathode. However, the large development and operating costs necessary to accomplish uniform metal distribution by such means can only be justified by high, sustained production. This type of problem can be conveniently illustrated on complex cathodes in figures 11.4 and 11.5.

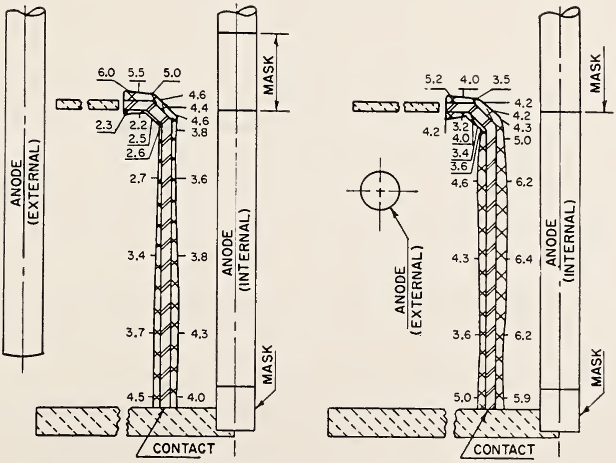

Figure 11.4. *Effect of varying anode and insulating-shield positions on metal distribution (full size).*

Plate distribution in mils. Pb-Sn (10%) at 20 amp/ft².

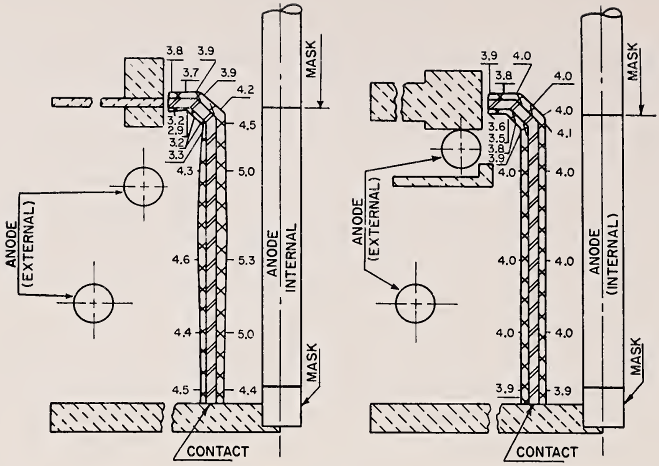

FIGURE 11.5. *Effect of varying anode and insulating-shield positions on metal distribution (full size).*

Plate distribution in mils. Pb-Sn (10%) at 20 amp/ft^2.

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[5] F. P. Bowden and D. Tabor, Commonwealth of Australia, Council for Scientific and Industrial Research Bulletin No. 155, p. 15 (1942).
[6] R. A. Schaefer, Iron Age **159,** 60 (1947).
[7] H. W. Luetkemeyer and R. A. Schaefer, U. S. Patent 2,459,172.
[8] R. W. Dayton and others, Sleeve bearing materials, Am. Soc. for Metals, Cleveland, Ohio (1949).

Discussion

DR. D. G. FOULKE, American Electroplaters' Society, Jenkintown, Pa. Ralph, you mentioned the use of iron, nickel, and cobalt as barrier layers. Has there been any trend toward iron particularly, or has nickel and cobalt been used principally?

DR. R. A. SCHAEFER. We use nickel at the moment and are going to use iron because we cannot get nickel. But we prefer nickel simply because we know how to plate it. The iron bath offers additional problems.

MR. L. M. MORSE, Chrysler Corp., Detroit, Mich. Ralph, you mentioned the nickel barrier layer. You run across some bearings that will wipe through the overlay. What does the nickel do to the scoring journal?

DR. SCHAEFER. Virtually nothing if it is thin enough.

Question. I could not help but remember some of the work on plating the inside of tubing, where the amount of agitation or rate of flow of solution through the unit had a very great effect upon the distribution of metal. Did you observe this effect in your bearings, and if so, how close a control of velocity did you have to maintain in order to get those unusually close thicknesses?

Dr. Schaefer. The answer is a compromise. The more uniform I want the plate, the less I agitate it. If we plate for blue jobs, we do very little agitation beyond cathode-rod agitation. If we can have half a thousandth variation, which is normally good machine practice, then you can use conventional agitation. If you can stand 100-percent variation in the plate, you can do almost anything. You can't vary it that much usually. The more uniform plate you want, the less you agitate. For absolute uniformity, we don't agitate at all.

Mr. J. G. Poor, Van der Horst Corp., Olean, N. Y. I would like to ask Dr. Schaefer in what medium he carries out these corrosion tests.

Dr. Schaefer. SAE–30 oil, noninhibited, if you can buy that on the market. It is quite a job. As soon as you buy inhibited oil, anything can happen. These rates can reverse. You get no corrosion or you get many times more. But there are certain companies that will make uninhibited oils. Actually, what we did was to buy some astronomical quantity of this oil about 10 years ago.

Mr. S. Heiman, Philadelphia Rust Proof Co., Philadelphia, Pa. Would you care to elaborate on the lead-addition system?

Dr. Schaefer. Resorcinol and gelatin has been published, or resorcinol and glue. There are some others that I would not care to disclose, but those have been traditional.

12. Research at Enthone, Inc. on Metal Finishing

By Walter R. Meyer [1]

Introduction

The fundamental and practical research conducted at Enthone, Inc., must, of necessity, cover the entire scope of electroplating. However, this research can be subdivided into eight classifications, as follows: 1, Conversion coatings; 2, blackening and coloring of metals; 3, chemical displacement coatings; 4, oxide coatings on metals; 5, selective dissolution of metals; 6, study of detergents, cleaning processes; pickling inhibitors, or methods pertaining to preparation of metals for electroplating; 7, stripping of organic coatings; and 8, study of electroplating solutions.

In an effort to understand the theoretical principles involved in many of the practical processes that have been developed or are being studied, sponsored research work is conducted outside of the Enthone laboratories on fundamental problems. In general, universities are used for this work. The research is directed by a professor or department head at the university concerned, and the actual work is conducted by instructors, research associates, or full-time fellows. Monthly meetings are held to discuss the status of the problems, and frequently, general research conferences are held. Some of the fundamental problems that have been considered include extensive studies of chelating compounds, polarographic studies on oxidation or reduction, the change in electrode potentials with complex ion formation, thermodynamic studies of reactions involving oxidation or reduction, and the influence of various chemicals on reaction rate. It is unfortunate that the results of these studies cannot be published, but commercial laboratories must of necessity keep this information secret to gain a commercial advantage to pay for the research. The work done at the Enthone laboratory concerns itself largely with the application of these fundamental studies, with the formation of practical solutions, and with the testing of products that have been developed.

Conversion Coatings

Enthone's study of conversion coatings has been limited to chromate coatings on aluminum, zinc, and cadmium, and phosphate coatings on steel, zinc, and aluminum. New processes for producing chromate coatings have been developed that involve the use of low concentrations of chemicals, of the order of 10 g/liter. The amount of metal lost in chromate processing, as well as the influence of drying conditions on the corrosion resistance of the coating, has been extensively investigated. It has been shown, for example, that the salt-spray life of chromate coatings on zinc and cadmium is seriously reduced by drying

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[1] President and Research Director, Enthone, Inc., New Haven, Conn.

at temperatures of 150° F or higher. In regard to phosphate coatings, the work has concerned itself with finding new activators that allow phosphating to be performed at room temperature with the production of adherent dense zinc phosphate coatings. A process for producing iron phosphate coatings on steel was recently offered to the public. Extensive tests on salt-spray resistance and adhesion, comparing iron and zinc phosphate coatings, are under way.

Blackening and Coloring of Metals

Materials for producing black and colored finishes on metals have represented important products sold by Enthone. Because of this, continuous work is in progress to develop better methods for blackening. During the past year, there was extensive cooperation with various branches of the Armed Services in the obtaining of the proper conditions of operation to secure highest wear resistance and adhesion of coatings. In this study falling sand and abrasor methods were used for determining wear. In general, treating times of the order of 15 to 20 minutes produced maximum wear resistance for alkaline oxidizing-type solutions.

Baths for producing sulfide-type coatings on steel and stainless steel have been investigated for several years, with reluctance to market them because of the poor corrosion resistance imparted these metals by sulfide finishes. This is particularly true of sulfide finishes on steel, where accelerated corrosion occurs from the presence of sulfide finishes of all types investigated. Work is still being conducted on blackening of stainless steel, but to date the method involving immersion in fused dichromates is considered to be the best. A method for blackening cadmium plate has been developed in recent months to produce molybdate-type coatings.

Chemical Displacement Coatings

This subject warrants extensive investigation. Research was conducted on altering the solution potentials of metals by means of various materials that tended to form complex ions. The reason for deposition of tin on copper in cyanide solutions containing tin was determined. Immersion coatings of iron, zinc, and other metals on aluminum are under investigation. Successful immersion deposits of antimony and lead have been obtained on copper and brass.

Oxide Coatings on Metals

In addition to the oxide coatings that are normally black, such as those on copper and steel, processes for production of oxide coatings on other metals would be valuable. Research has been conducted for several years on direct oxidation of aluminum in solutions whereby electric current would not be required. It has been possible to produce oxide coatings in chemical solutions that withstand voltages as high as 90 volts before breakdown, but, unfortunately, at the present time these coatings contain some pores that prevent the formation of an over-all uniform coating.

Oxide coatings have been formed on aluminum by chemical means that are suitable for adsorbing dyes and which can be used undyed for mild-corrosion protection. When treated with dichromate solutions, these coatings protect aluminum from 24 to 100 hours in salt spray, depending upon the alloy treated. They do not compare with anodized coatings in regard to electrical or wear resistance. Beautiful dyed finishes can be obtained on aluminum by the use of a process recently developed.

Selective Dissolution of Metals

This has been the study of very extensive research because of the importance of stripping defective coatings from metals without attacking base metals. Products have been placed on the market for selective dissolution of nickel, copper, silver, zinc, cadmium, and tin from steel as well as nickel, zinc, and cadmium from copper base alloys. Work is continuing on this general problem.

Study of Detergents, Cleaning Processes, Pickling Inhibitors, or Methods Pertaining to Preparing of Metals for Electroplating

This is a classification that is very broad. New detergent materials are being investigated constantly for oil and grease removal. Studies of basic alkali formulation are being conducted because pH and alkali ratios are very important for the proper formulation of cleaners, particularly those that must be operated at high current densities. Studies on quaternary-type pickling additives have been made, and products have been placed on the market.

Within the past few weeks work has been completed on a new method for rust and scale removal from steel that is alkaline in nature and operates at room temperature. The process shows considerable promise for rapid pickling of metals formerly difficult to pickle. Cast and malleable iron, high-carbon steels, and ordinary steels can be rapidly pickled or derusted with this new alkaline solution. The elimination of acids from the pickling cycle reduces tendency for corrosion of surrounding equipment and danger from accelerated rusting due to trapping of acid in the pores of the metal. It has been possible to derust metals in alkaline solutions so that they can be plated thereafter without using an acid dip. It has also been possible to simultaneously clean, derust, and plate in one operation.

Stripping of Organic Coatings

The stripping of organic coatings from various base metals has been one of the major problems of research and development at Enthone. Due to the fact that the formulation of organic finishes is changing constantly, it requires continuous work to develop materials that will sucessfully strip them. In most cases the results have been effective, but there have been certain finishes that have defied all efforts to strip them.

Study of Electroplating Solutions

This study has concerned itself largely with solutions that do not contain cyanides. Work has been conducted for several years on nickel sulfamate solutions with considerable promise. This type of plating solution enables very rapid deposition of metal at high current densities at relatively low temperatures, which is important to the electrotyping and electroforming industry. About 5,000 gallons of solutions have been in use for 1 year with very successful results.

Discussion

Mr. I. W. Marcovitch, U. S. Gauge Co., Sellersville, Pa. You say you have not found a coating for black coloring of aluminum at elevated temperatures? Other than elevated temperatures and other than anodizing, have you found anything that will give you a suitable immersion coating at room temperature up to 150 or 200 deg.?

Dr. W. R. Meyer. No.

Mr. Marcovitch. There is one further question on alkaline descaling of steel. Have you tried it on the scale from heat treating? What effects do you get?

Dr. Meyer. With the scales that are magnetic the results are not too good. We had some spring-bumper stock that had a very strongly conductive scale. The current is discharged from the top of the scale, thus preventing its removal. We take off the ordinary scale, but we don't claim we can take off the magnetic scales—I wish we could.

Mr. L. Weeg, National Lock Co., Rockford, Ill. Can the derusting process be used for small parts, which would be handled in bulk?

Dr. Meyer. We believe so. We know that it works as low as 1 amp/ft^2, and it is used cold. I would say "Yes" to that. We have done it in baskets.

Mr. L. Gilbert, Rock Island Arsenal, Rock Island, Ill. Is there sufficient polarization in the derusting process to remove rust from the inside of a container like a gasoline tank or something of that sort?

Dr. Meyer. The process can be used for derusting tanks providing a carbon anode can be inserted.

Question. Something from the human-interest standpoint on this derusting. We had a counterpart of that in the early 20's, when John T. Pratt, Jr., who was trustee of the Metropolitan Museum of Art, went to Dr. Fink with some ancient bronzes that were unidentifiable, just a mass of corrosion, you might say, and he restored those by cathodic reduction in alkali. From another point of interest, John T. Pratt's introduction to Dr. Fink led to his giving him financial backing to put into the development of chromium plating that led to the Chromium Corporation of today.

Mr. H. Bengston, 608 Foraker Ave., Sidney, Ohio. With respect to heat-resistant coatings on aluminum for any who might be interested, it is possible to pigment anodic oxide coatings on aluminum with cobalt oxide, which is resistant to heating to the extent that you can melt the aluminum out of the coating, but it does take time to produce such a coating.

13. Corrosion Resistance of Copper, Nickel, and Chromium-Plated Zinc, Aluminum, and Magnesium-Base Die Castings*

By M. R. Caldwell,[1] L. B. Sperry,[1] L. M. Morse,[2] and H. K. DeLong [3]

Because of increased use of aluminum and magnesium die castings in the fabrication of parts in the automobile industry, it was felt that specifications for the decorative plating of such parts would be needed. In April 1949 the authors, with the late Carl Heussner, prepared a program of exposure testing as a means of obtaining the basis for such specifications. Panels were prepared, using the best known methods of plating on each of the alloys. Various thicknesses of copper, nickel, and chromium were applied on panels of die-cast zinc-, aluminum-, and magnesium-base alloys.

Schedule of tests

Number of panels prepared and thicknesses of copper and nickel.

Alloy	Cu, 0.0002 in. Ni, 0.0003 in.	Cu, 0.0003 in. Ni, 0.0005 in.	Cu, 0.0005 in. Ni, 0.00075 in.	Cu, 0.0005 in. Ni, 0.0015 in.
Zinc:				
Zamak No. 3	36	36	36	36
Aluminum:				
Alcoa 85	48	192	48	60
Alcoa 380		48		
Alcoa 218	48	64		
Magnesium:				
Dow Metal R		48	240	48

Work was conducted jointly by the Doehler-Jarvis Corporation, Dow Chemical Co., and Chrysler Corporation. The zinc panels were die cast by Doehler-Jarvis Corporation and plated by them, using an accepted commercial method. The aluminum panels were cast by the Doehler-Jarvis Corporation and plated by the Chrysler Corporation Engineering Electroplating Laboratory, using a double-zinc-immersion pretreatment. The magnesium panels were die cast by the Dow Chemical Co. and plated by Chrysler Engineering Electroplating Laboratory, using an adaptation of the pyrophosphate-zinc immersion method published by H. K. DeLong. There were about 36 panels in each lot. The panels were exposed in groups of five in the following locations: Detroit (mild industrial), Coraopolis, Pa. (heavy industrial), Miami Beach (tropical sea coast, 100 yd from the ocean), and Grand Rapids, Mich. (rural site). The panels were exposed in the standard way at an angle of either 45° or 30° with the horizontal, facing south. Some of the panels were scribed across the face with an "×" penetrating to the basis metal. In addition, five panels were salt-sprayed, and a number of extras were available for substitution,

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*This is a condensed version of a paper by the same authors published in Plating **39,** 142 (1952).

[1] Doehler-Jarvis Corporation, Grand Rapids, Mich.

[2] Chrysler Corporation, Detroit, Mich.

[3] Magnesium Laboratory, Dow Chemical Co., Midland, Mich.

adhesion, and thickness tests, etc. All the salt-spray panels were scribed.

An unusual rating system was used for rating exposure test panels. In a previous cooperative program with die castings, the ASTM method of rating had been used, but it was found that for the authors' purposes, this rating method was subject to two criticisms: (1) The numerical rating is based entirely on the proportion of the area showing defects, and the type of defect is only taken into consideration in the shorthand notations. The average person reading the report of an exposure test tends to place too much weight on the numerical values and disregard the shorthand notes. This can result in erroneous conclusions. (2) The system of shorthand notations is not adaptable to averaging, so that it is difficult to apply statistical methods in the study of results.

Accordingly, a system of rating was developed which in some ways appears to be an improvement and which serves the purpose of the automotive user particularly. Defects were classified and a set of numerical ratings were made on each panel for each class of defects. For example, there were three main defects recognized: (1) Corrosion and staining of the plating itself; (2) Corrosion of the base metal; (3) Blistering.

The various types of defects were weighted arbitrarily according to the authors' idea of their relative importance. Blistering was considered to be the most serious. Corrosion of the base metal was given only half the importance of blistering and staining of the plating only one-fourth. The following formula was then used to combine the ratings and arrive at a weighted average:

$$T=10\{10-[(10-B)+(10-R)\tfrac{1}{2}+(10-S)\tfrac{1}{4}]\},$$

where

B=The blister rating from 0 to 10 based on comparison charts similar to the ASTM photograph comparisons,
R=The base-metal corrosion rating,
S=The surface pitting and stain-spotting rating.

It is possible, using this formula, to arrive at negative ratings, but the corrosion protection was arbitrarily considered worthless when a rating of 0 was reached. A 100 rating is perfect. Inspections and ratings of the panels were made at periods of 9, 13, 26, 39, and 52 weeks. At the end of 52 weeks the panels were cleaned and rated again because there was a great deal of staining, which made rating difficult. Some of the panels having 0.002 in. of total plate were placed out for further exposure. A brief summary of the exposure results follows, dealing only with the ratings at the end of 1 year. Although three bright nickels and a Watts nickel were used, the results discussed in this report refer to only one bright nickel and the Watts nickel.

Aluminum. In Detroit all aluminum-base panels failed with the exception of those with 0.002 in. total plate. Likewise, all aluminum panels reached a 0 rating in Pittsburgh, with the exception of the 0.002 in. total plate. In Miami the aluminum panels failed according to their plate thickness. Those with 0.0005 in. total plate reached 0 rating. Those with 0.0007 in. fell to an average rating of 30; those with 0.00125 in. to an average rating of 45, and those with 0.002 in. fell to an average rating of 75. In Grand Rapids the aluminum panels with 0.002 in. plate had a rating of 97 after 1 year. Since in exterior applications all environments must be considered, it was concluded that a minimum plate thickness of 0.002 in. is necessary on aluminum die-cast alloys.

MAGNESIUM. In Detroit the magnesium panels with 0.0008-in. thickness fell to a rating of 8. Those with 0.00125 in. averaged 36, and those with 0.002 in. had a rating average of 91. In Pittsburgh, results were similar, and 0.002 in. resulted in a rating of 84. In Miami the magnesium panels with 0.002 in. had a rating of 90. That was better than that of aluminum panels. In Grand Rapids the rating was 94.

ZINC. The zinc panels were included primarily to serve as a basis for comparison because there is considerable outdoor exposure data on zinc panels, and it was believed that the thickness of plate necessary to produce a satisfactory corrosion-resistant finish has already been established. At the end of 1 year the ratings on the zinc panels with 0.002 in. total plate were somewhat less than the ratings on the magnesium and slightly better than those with aluminum. However, zinc panels with the lower plate thicknesses stood up much better than aluminum and magnesium panels carrying the equivalent lower thicknesses.

In the last analysis, it was concluded that 0.00125 in. total plate on zinc die castings will provide a finish nearly equivalent to that provided by 0.002 in. on the light-metal alloys. An additional 0.00075 in. nickel on the zinc produced only slight improvement.

The panels were again rated after cleaning and the values in Detroit and Pittsburgh were considerably raised, because of the removal of the dark stain and the white corrosion. However, even after the cleaning, the alloy 218, which contains 8 percent of magnesium, was totally unsatisfactory with 0.00125 in. total plate. This is the alloy that gave the most difficulty in obtaining a smooth, pore-free plate.

In any exposure program one must look very carefully at the methods used in the preparation of panels. Also, the condition of the base metal, on which the plating is done, must be considered. In the particular case of this program, the authors observed that the aluminum-base and magnesium-base die castings were not comparable in surface density with the zinc-base die castings. It was suggested that the art of die casting of the lighter metals has not reached the state of refinement that has been reached with zinc die casting. The panels were quite irregular in appearance after etching and apparently contained oxide layers, which resulted in weak surface structure. Special plating procedures were accordingly devised in order to reduce the attack on the base metal to an absolute minimum. A number of panels from each group were checked by high-temperature baking and sawing, and the adhesion obtained after plating was considered satisfactory. The authors consider the quality of the castings to have had significant effect on the ultimate corrosion life.

Discussion

MR. L. WEEG, National Lock Co., Rockford, Ill. We have started to use statistical methods of analysis in the study of plating. It is a little removed from the subject of the last couple of days, but nevertheless it is of interest to us. In just a preliminary undertaking that has been underway for only a short time we have obtained 3,000 measurements that have to be plotted and analyzed by the statistical method, and there are many, many yet to be made. However, one advantage in this tool is the fact that we can undertake this study from our regular production operations, and it does save us there the amount of money and the effort and time that would be necessary if we were to set up our investigation under laboratory control conditions. You are right, there are very, very many measurements to be made.

Mr. E. R. Bowerman, Sylvania Electric Products, Bayside, N. Y. I would just like to comment that the number of measurements, of course, depends on how much information you want, what you consider to be a change, and things like this. We like to approach the problem not from the standpoint of taking our measurements and then analyzing them, but to analyze them continuously as we obtain them to see whether or not we should continue to make the measurements.

14. Plating Research at Sylvania Electric Products

By E. R. Bowerman [1]

Abstract

Plating investigations at Sylvania's Central Engineering Laboratories are showing a trend away from consultation on plant problems toward the development of new materials and processes. Currently under study are methods for cleaning and plating fine wires and a zinc-tin alloy plating bath. The fine-wire plating equipment presents special problems in current supply to the wire and stretching of the wire due to the small cross section, which are not important for the larger sizes. The alloy-plating system is being studied, using a statistically designed system of experiments that has proved to be very effective in disclosing interrelations between the several experimental variables, such as composition, temperature, and current density.

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[1] Sylvania Electric Co., Bayside, N. Y.

15. Determination of Impurities in Electroplating Baths

By Earl J. Serfass [1]

Introduction

Although the effect of minute traces of certain types of impurities in electroplating baths has been well established, very little quantitative information is available on this subject, primarily because of the lack of simple and specific analytical procedures for the determination of these impurities. The AES Research Committee, realizing the importance of precise and simple analytical procedures for the determination of trace constituents in electrodeposition baths instituted a research project at Lehigh University under the writer's direction 5 years ago. It is the purpose of this report to present an extended summary of the approach which was used to tackle the problem as well as to present the results which have been achieved in the way of publication in this field.

History of AES Project 2

In 1945 the Research Committee of the American Electroplaters' Society instituted a project at Princeton University for the purpose of developing methods of analysis for trace constituents in nickel-plating baths. This project was under the supervision of G. Frederick Smith, at the University of Illinois, who consulted frequently with Dr. Duke, who in turn carried out some experimental work at Princeton University. When Dr. Duke left Princeton University, the writer was contacted at Lehigh University in connection with this project. Since 1946 we have been working at Lehigh on the development of simple colorimetric and spectrophotometric procedures for the determination of trace constituents in electrodeposition baths. Eight research assistants have been at one time or another associated with the writer in the development of these methods.

In 1951 the Ohio River Valley Water Sanitation Commission, in conjunction with the AES, enlarged the research project at Lehigh in order to include the development of analytical methods for use in the study of metal-finishing wastes. Simultaneously with the addition of ORSANCO personnel to the AES project, the research committee of the AES directed us to study the literature available and to recommend to the Society specific analytical methods for the major constituents in common plating baths. At present, our work involves development of analytical procedures for (1) microconstituents in the plating baths, (2) macroconstituents in plating solutions, and (3) microconstituents in plating waste solutions.

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[1] Lehigh University, Bethlehem, Pa.

Purpose of AES Project 2

The ultimate goal of AES Project 2 and the ORSANCO project is to present to the electroplating industry as a whole a rather complete set of approved and tested procedures for the analytical determination of various constituents in chemical supplies, processing solutions, and the waste materials commonly found in the metal-finishing industry. Our initial purpose in carrying out this work was twofold, in that we were to attempt to provide analytical methods for use in plating shops as well as analytical methods of a precision type that could be used in research laboratories. Simultaneously with the development of simple and precise methods, our purpose was to supply AES Project 5 and Project 10 dealing with the determination of the effects of impurities on electroplating and the study of plating-waste disposal, respectively, with suitable methods in order to carry out their research project.

Results Obtained to Date

At present we have published a total of 20 tested and approved analytical procedures for the determination of trace constituents in electrodeposition baths. Five analytical procedures have been developed, tested, and approved, and await publication in the official journal of the AES, *Plating*. Experimental work has been completed on the study of five other trace constituents. A complete tabulation of the titles of the analytical procedures, along with their limits of detection sensitivity and their publication dates, are given in tables 15.1 to 15.6, inclusive.

Testing Program

Prior to the publication of any of the analytical methods listed in tables 15.1 to 15.6, an industrial testing program was instituted. This testing program involved submitting for analysis, samples of plating solutions containing small quantities of impurities to a number of industrial and research laboratories. Along with these samples were submitted recommended routine procedures for the determination of trace constituents as developed under the AES Project 2.

As a result of the investigations of the industrial and research laboratories, criticisms of the methods proposed, as well as numerical results for the concentrations of the trace constituents, were submitted to the project director. Correlation of this information permitted the research directing subcommittee, project director, and the editor of *Plating* to revise the initially submitted manuscript. As a result of this rather unique testing program, it is felt that the analytical methods as published in *Plating* are comparatively free of errors and should yield simple yet precise procedures for the average technician to follow.

TABLE 15.1. *Nickel-plating baths*

Subject	Limits	Issue of *Monthly Review*
	ppm	
Introduction	--------	August 1946.
Colorimetric principles	--------	October 1946.
Determination of lead	0 to 50	October 1946.
Determination of iron	0 to 100	November 1946.
Determination of manganese	0 to 100	March 1947.
Determination of copper	0 to 20	April 1947.

Table 15.2. *Nickel plating baths*

Subject	Limits	Issue of *Plating*
	ppm	
Determination of chromium	0 to 50	March 1949.
Determination of zinc	0 to 20	August 1949.
Determination of calcium	0 to 1000	October 1949.
Determination of silver	0 to 100	December 1949.

Table 15.3. *Nickel-plating baths*

Subject	Limits	Issue of *Plating*
	ppm	
Determination of Silica (G)	0 to 1000	February 1948.
Determination of sodium and potassium.	0 to 100	March 1948.
Determination of cadmium	0 to 70	May 1948.
Determination of aluminum	0 to 100	October 1948.
Determination of ammonia	0 to 200	February 1949.

Table 15.4. *Copper-plating baths*

Subject	Limits	Issue of *Plating*
	ppm	
Determination of chloride	0 to 300	January 1950.
Determination of lead	0 to 50	February 1950.
Determination of chromium	0 to 50	April 1950.
Determination of nickel	0 to 200	May 1950.

Table 15.5. *Zinc-cyanide-plating baths*

Subject	Limits	Issue of *Plating*
	ppm	
Determination of lead	0 to 50	May 1951.
Determination of cobalt	0 to 100	Awaiting publication.
Determination of chromium	0 to 100	Do.
Determination of copper	0 to 100	Do.
Determination of iron	0 to 100	Do.

Table 15.6. *Anions*

Subject	Limits	Issue of *Plating*
Determination of cyanide and cyanate.	<1 ppm	Awaiting publication.

Approach to the Problem

In the development of analytical procedures for trace constituents in plating baths and plating wastes we were presented with the possibility of developing the procedures using any one or a combination of the following general techniques: (a) Gravimetric procedures, (b) volumetric procedures, (c) polarographic procedures, (d) potentiometric techniques, (e) emission spectroscopy, and (f) spectrophotometric absorption or colorimetric techniques. As a result of the survey of the training of the personnel and the equipment available in the laboratories of the average plating establishment, it was decided to attempt to carry out the development of all of the methods, if possible, using spectrophotometric absorption or colorimetric techniques. Other factors involved in the selection of colorimetric techniques for the determination of trace constituents were speed of determination, cost of equipment, simplicity of operations involved, and precision. The advantages offered by colorimetric techniques prompted the research directing subcommittee to instruct the project director to carry out all research toward the development of trace constituents along these lines.

Quantitative determination of any trace constituent involves both the separation and estimation of the element or group in question from the complex sample. Five methods of separation may be used for isolation of the test constituents from the sample prior to the development of a color: (1) precipitation and filtration, (2) distillation and rectification, (3) oxidation and reduction, (4) extraction, and (5) absorption. In general, extraction techniques involving the addition of an organic analytical reagent in a solvent are particularly valuable for the separation of trace contaminates in complex samples. Whenever convenient, extraction techniques have been used in the development of our analytical procedures.

The use of organic analytical reagents for the development of colored complexes is a well-established procedure for the colorimetric determination of trace constituents in complex samples. Several examples of procedures that we have developed illustrate the principles of separation and quantitative estimation already outlined.

The determination of manganese, as shown in outline form in (I), involves the oxidation of the manganese in the sample to permanganate and the subsequent determination of the concentration of permanganate by the intensity of the color produced. This determination does not involve a separation of the manganese from the major interfering substances in the sample. Furthermore, the natural color of the permanganate itself is used for the estimation of the manganese content of the sample. Proper selection of the wavelength of light used to irradiate the samples tends to minimize interferences from other colored interferences that may be present in the sample.

(I). Determination of Manganese

Sample
|
$HNO_3 + HClO_4$
|
$H_3PO_4 + NaIO_4$
|
Purple permanganate color developed
|
Compare.

Similar to the determination of manganese in nickel-plating baths, the determination of chromium is an example of the type of determination in which no separation of the test substance is carried out, see (II). In this determination, however, a specific organic reagent, diphenyl-carbazide, is used to intensify the color in the sample due to its chromium content by virtue of the formation of a highly colored chromium diphenyl-carbazide complex. Interference from other elements in the sample is minimized by virtue of the fact that diphenylcarbazide is a specific reagent for producing color in the presence of chromium.

(II). DETERMINATION OF HEXAVALENT CHROMIUM

Sample, 0.5 ml
↓
$HNO_3 + H_2SO_4$ to adjust
Acidity to approximately 0.2N
↓
Add diphenyl carbazide (forms red-violet complex)
↓
Measure transmittancy with colorimeter at 540 mμ.

The determination of lead in nickel-plating baths as shown in (III) involves the separation of the lead as a colored lead dithizonate from the major interfering portion of the sample by means of a solvent extraction. Interference from other elements is prevented by preliminary complexing of the interfering ions with tartrate and cyanide.

(III). DETERMINATION OF LEAD

Sample
↓
$Na_2C_4H_4O_6, NH_4OH, KCN$
↓
Adjust pH
↓
Extract with dithizone
↓
Add alkaline KCN
↓
Lead dithizonate, red color
↓
Compare.

Another example of the determination of a trace constituent by means of a specific organic reagent followed by extraction is the determination of iron in nickel-plating baths as shown in (IV). In this procedure the iron is separated from the sample by means of extraction with a solvent in the presence of cupferron. Inasmuch as the iron cupferride color is not particularly intense, another specific, organic analytical reagent, orthophenanthroline, is used to redevelop an intense iron orthophenanthroline blood-red color.

(IV). DETERMINATION OF IRON

Sample
|
Cupferron + amyl acetate
|——Discard aqueous layer
Fe cupferride in solvent
|
HNO_3
|
Discard solvent | $Fe(NO_3)_3$ formed
|
$NH_2OH \cdot HCl$, orthophenanthroline
|
NaAc
—
Red iron complex
|
Compare

Macroconstituents of Plating Baths

As mentioned above, another phase of AES Project 2 involved the investigation of standard methods for the determination of the major constituents in plating baths. In this program we investigated the available methods for major constituents with a view toward simplifying them and improving their precision. Table II lists a number of analytical determinations that we have investigated and revised for nickel- and copper-plating baths. In the course of this work it was evident that a number of commercially available methods were unsatisfactory for one reason or another. A few of these methods were completely revised in order to rectify this situation, and several entirely new methods for the determination of macroconstituents were devised. For example, a new and improved method for the determination of boric acid in Watts nickel-plating baths was developed, in which the boric acid may be determined by direct titration by using the common indicator, phenolphthalein, for endpoint detection. An outline of this relatively new procedure is shown in (V).

TABLE 15.7. *Macromethods*

NICKEL BATHS	
I. Introduction.	III. Cobalt.
II. Nickel.	IV. Chloride.
a. Volumetric.	V. Sulfate.
b. Colorimetric.	VI. Boric acid.
COPPER BATHS	
I. Introduction.	V. Copper.
II. Sulfuric acid.	a. Iodometric.
III. Carbonate.	b. Specific Gravity.
IV. Hydroxide.	c. Electrolytic.
	VI. Cyanide.

TABLE 15.8. *Ohio River Water Sanitation Commission water effluents*

Subject	Limits	Report Issued
	ppm	
Determination of lead	0 to 50	July 15, 1951.
Determination of cyanide	0 to 50	August 15, 1951.
Determination of manganese	0 to 50	September 15, 1951.
Determination of iron	0 to 50	October 15, 1951.
Determination of copper	0 to 50	November 15, 1951.

All analyses in the presence of 100 to 5,000 ppm of each of 24 elements.

(V). MACRODETERMINATION OF BORIC ACID

↓

Sample of nickel bath

↓

Saturated potassium ferrocyanide and bromcresol purple indicator

↓

Titrate with sodium hydroxide for mineral acid

↓

Mannitol slurry and phenolphthalein indicator

↓

Titrate with sodium hydroxide for boric acid content

Analysis of Plating Wastes

The research project sponsored by the Ohio River Valley Water Sanitation Commission under the writer's direction at Lehigh University has been cooperating with the AES in the revision and testing of the trace analytical methods previously published for plating baths. It has been the purpose of this project to revise and extend the previously developed colorimetric procedures to apply them to the analysis of minute quantities of cations and anions in metal-finishing wastes.

At the date of this writing five completed methods have been developed and tested and have been submitted to the Commission for approval. Table 15.8 contains a list of the reports submitted to date.

Future Course of the Work

During the course of the next few months the work of AES Project 2 will be devoted to the development of analytical procedures for the determination of trace constituents in cadmium-plating baths. In addition to this experimental work, it is the hope of the AES Project Directing Subcommittee that a compendium of all the methods developed to date may be compiled and distributed for the general use of industry. Research will continue on the ORSANCO Project for the ultimate purpose of presenting a series of at least 20 recommended routine analytical procedures for the determination of trace constituents in metal-finishing wastes.

16. Effects of Impurities in Plating Solutions

By D. T. Ewing,[1] John K. Werner,[1] and Arthur Brouwer [1]

This report summarizes the recent results of the American Electroplaters' Society Research Project 5. Previous work on this project has been published as a bibliography [1],[2] critical review and abstract [2], methods of operation [3], and the effects and removal of copper in nickel-plating solutions [4]. In addition, several other reports on the effects of copper on the corrosion resistance of electrodeposited nickel have been issued [5, 6, 7].

The primary object of this project is to determine any changes caused by single metallic impurities in the physical properties of electrodeposited nickel from four types of nickel-plating solutions used today. The evaluation of practical methods for the removal of impurities is also included in the investigation.

The physical properties selected for this study are adherence, ductility, throwing power and efficiency, corrosion resistance to salt-spray–fog, hardness, and appearance, Methods for the evaluation of changes in these properties have been intentionally limited to those that save time and avoid the complicated procedures sometimes necessary for precision results. The values for each physical property are expressed as changes necessary to establish a definite trend. These changes are expressed as percentages. All changes are deviations in the physical property of the deposited metal from a solution with an impurity compared with deposits from a solution free of that impurity.

The four types of nickel solutions that were selected for this investigation were prepared in the following manner. For studies on an organic brightener solution the following was selected: 35 oz/gal of nickel sulfate, 8 oz/gal of nickel chloride, 4.5 oz/gal of boric acid, 1 oz/gal of nickel benzenedisulfonate, and 0.14 g/liter of triaminotolyldiphenylmethane. This was operated at 55° C and 40 amp/ft^2. The following was used for an alloy-type solution: 32 oz/gal of nickel sulfate, 6 oz/gal of nickel chloride, 4 oz/gal of boric acid, 6 oz/gal of nickel formate, 2 oz/gal of cobalt sulfate, 0.33 oz/gal of ammonium sulfate, and 0.33 oz/gal of formaldehyde. This solution was operated at 60° C and 40 amp/ft^2. The Watts nickel solution was used at two pH values, 2.2 and 5.2. The solution was formulated as follows: 32 oz/gal of nickel sulfate, 6 oz/gal of nickel chloride, and 4 oz/gal of boric acid, and operated at 50° C and 40 amp/ft^2.

Nickel deposits were formed on steel panels 2 inches wide, extending 4¾ inches below the surface of the solution. The lower 1¼ inch was bent sharply at a right angle and faced the anode. The panels were SAE 1010 cold-rolled tin-can stock of 0.010-inch thickness supplied through the courtesy of Richard Wick and the Bethlehem Steel Corporation. Prior to plating, the panels were degreased in carbon

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[1] Michigan State College, Lansing, Mich.

[2] Figures in brackets indicate the literature references on p. 90.

tetrachloride and electrocleaned as an anode for 2 minutes in a hot solution of 2.8 oz/gal of sodium hydroxide, 2 oz/gal of sodium metasilicate, 2.4 oz/gal of trisodium phosphate, and 0.8 oz/gal of sodium carbonate. The temperature of the solution was 80° C and the current density was 75 amp/ft^2. The panels were then dipped into a strong hydrochloric acid solution, water rinsed, and plated with nickel.

Investigations of the project have dealt with nickel solutions and the effects of and removal of small amounts of copper [4], zinc, iron, chromium, and lead. The experimental work on chromium is nearly completed. This report further summarized the results for zinc and iron. A report in detail of the behavior of these two metals will be published at an early date.

The following is a summary of the effects of zinc in some nickel-plating solutions:

Ductility. Strip deposits of nickel were made from the four solutions. These foils of nickel had a thickness of 0.001 inch and were uniformly creased and straightened until rupture resulted. The number of operations gave comparative ductilities.

The ductility of the deposits from the Watts pH 2.2 and 5.2 solutions decreased as the concentration of zinc increased to 300 mg/liter. The ductility of the deposits from the organic-type solution showed no appreciable change. In the case of the deposits from the nickel-cobalt solutions, no change in ductility of the deposits occurred until a concentration of 300 mg of zinc per liter was reached, when a decrease was noted.

Throwing power. Thickness measurements of deposits on selected portions of the lip of bent cathode were made by the method of Ewing, Rominski, and King [3], and from these data the throwing power was evaluated.

Nickel deposits from a Watts pH 2.2 solution showed a loss in throwing power as the concentration of zinc increased to 300 mg/liter. The Watts pH 5.2 solution showed an increase in throwing power for solutions with 25 to 300 mg of zinc per liter. An increase in throwing power was noted for the nickel-cobalt and the organic-type solutions.

Adhesion. Using the bending test previously described [3] and horizontal positions of bent cathodes, no appreciable change in adherence was noted for the four solutions containing zinc over the range 0 to 300 mg/liter.

Appearance. Deposits from the Watts pH 2.2 solution showed no change in appearance for concentrations of zinc of 100 mg or less per liter. However, a tendency toward brightness was noted when the concentration of zinc was 300 mg/liter. On very low current density areas 10 mg of zinc per liter gave a darkening effect.

The Watts pH 5.2 solution gave deposits with a dark appearance when zinc was present in amounts greater than 10 mg/liter. A general darkening of the surface was noted on very low current density areas.

The nickel-cobalt solution gave deposits of decreasing brightness as the concentration of zinc increased to 300 mg/liter. A general darkening on low-current-density areas was noted, as in the two Watts solutions.

The brightness of the deposits from the organic-type solution increased for concentrations of zinc between 150 to 300 mg/liter. Solutions of greater zinc concentration were not studied.

The methods for evaluating appearance and brightness have been previously described [3].

The Salt-Spray–Fog Corrosion Resistance. Nickel deposits on steel panels were made of three thicknesses—0.0003, 0.0010, and 0.0015 inch from each of the four solutions. The concentrations of zinc in the solutions varied in amounts of 2.5 to 300 mg/liter.

An improvement in salt-fog corrosion resistance was found for each of the four solutions, and the results are summarized in figures 16.1, .2, and .3.

Hardness. The effects on the hardness of nickel deposits from the four types of solutions are summarized in table 16.1. The results are expressed as percentage changes.

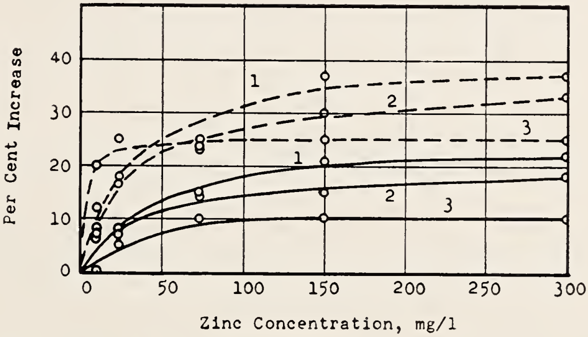

FIGURE 16.1. *Effects of zinc concentration in Watts-type solutions on the salt-spray (fog) corrosion resistance of deposits of varying thickness.*

Curve 1: 0.0010-in. deposits; curve 2: 0.0015-in deposits; curve 3: 0.0003-in. deposits. ———— pH 2.2; — — — — pH 5.2.

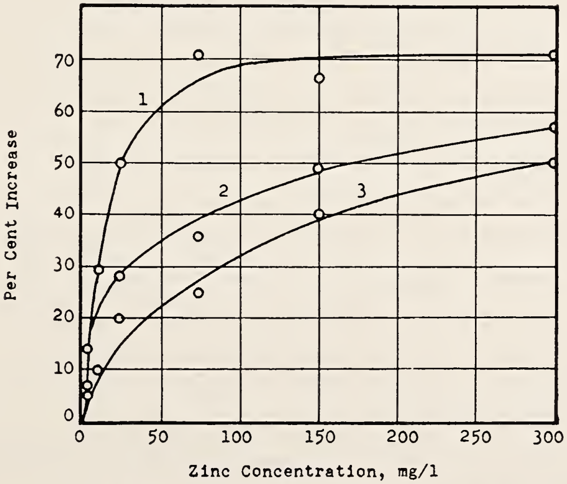

FIGURE 16.2. *Effect of zinc concentration in an organic-type nickel-plating solutions on the salt-spray (fog) corrosion resistance of deposits of varying thickness.*

(Curve 1: 0.0010-in. deposits; curve 2: 0.0015-in. deposits; curve 3: 0.0003-in. deposits).

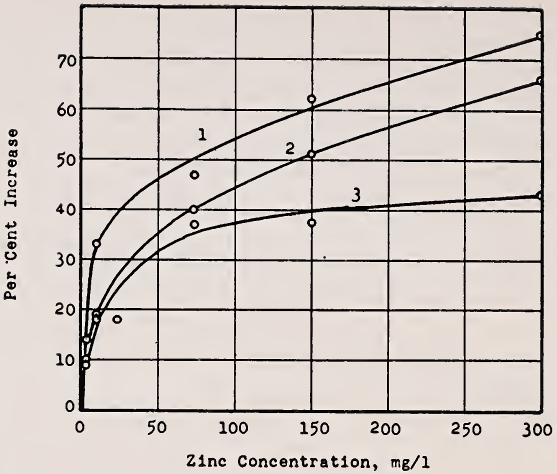

FIGURE 16.3 *Effects of zinc concentration in an alloy-type (nickel-cobalt) plating solution on the salt-spray (fog) corrosion resistance of the deposits of varying thickness.*

Curve 1: 0.0010-in. deposits; curve 2: 0.0015-in. deposits; curve 3: 0.0003-in. deposits.

TABLE 16.1. *Effect of zinc on the hardness of nickel deposits*

Zinc concentration	Watts		Bath-type nickel-cobalt, pH 3.75	Organic pH 3.2
	pH 2.2	pH 5.2		
mg/liter	*% change*	*% change*	*% change*	*% change*
2.5	0	0	0	0
10	+8	0	−3	+19
25	−6	+4	+22	+56
75	+38	+27	−19	+40
150	+41	+21	−4	+21
300	+48	+33	−31	+5

The microhardness tests were made by AES Research Project 9 at the National Bureau of Standards.

The following is a summary of the effects of iron in some nickel-plating solutions.

The methods for the determination of the physical properties for the iron effects are the same as those used for the zinc studies.

Ductility. The nickel-cobalt solution containing added ferrous sulfate to give 200 mg/liter of iron gave deposits of no decrease in ductility. For the other solutions, iron present in amounts of 25 to 50 mg/liter caused a decrease in ductility of the deposits.

Throwing Power. In general, it was observed that iron in the four nickel solutions in concentrations up to 200 mg/liter did not appreciably affect the throwing power.

Adhesion. Ferrous iron in concentrations to 200 mg/liter in the four nickel solutions caused no appreciable change in the adherence of nickel deposits to steel.

Appearance. The deposits from the Watts pH 2.2 solution containing 10 to 200 mg/liter of iron were somewhat whiter than those from the iron-free solution. The same solution at pH 5.2 gave grey deposits that were somewhat brighter. The mirror-bright deposits from the other two solutions did not seem to be changed.

Hardness. The measurements of the hardness of the nickel deposits were made at the National Bureau of Standards by the AES Project 9 group. An Eberbach microhardness apparatus was used. Both surface-hardness and cross-sectional readings were taken, and these were converted to Vickers pyramid numbers. The changes in hardness of the nickel deposits from the four types of solutions are summarized in table 16.2.

Table 16.2. *Effect of iron on the hardness of nickel deposits*

Iron-concentration	Watts		Bath-type nickel-cobalt, pH 3.75	Organic pH 3.2
	pH 2.2	pH 5.2		
mg/liter	*% change*	*% change*	*% change*	*% change*
0	--------	--------	--------	--------
2½	+6	+15	+12	−7
10	+7	+14	+18	+3
25	+26	+16	+23	+1
50	+12	+6	+2	−18
100	+22	+13	+10	−17
200	+18	+26	+10	+10

Salt-Spray–Fog Corrosion Resistance. Nickel deposits on steel panels were prepared from the four different types of nickel solutions, each containing an added amount of ferrous iron. Figures 16.4, .5, .6, and .7 summarize the changes in corrosion resistance.

Removal of Zinc. Two methods for the removal of zinc were investigated, high pH precipitation, using nickel carbonate to raise the pH; and low current density electrolysis under normal operating conditions.

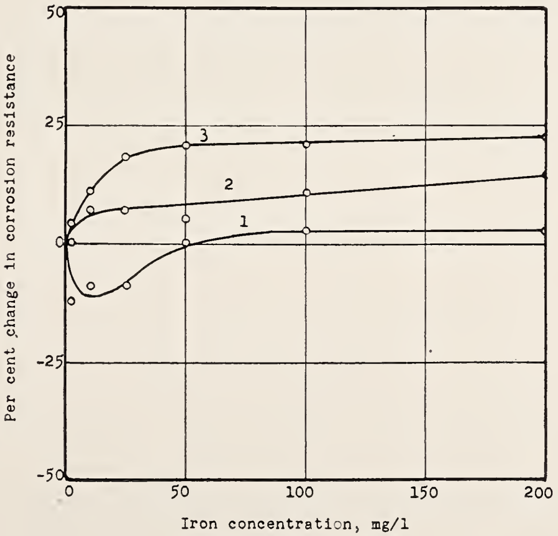

Figure 16.4. *Effect of iron concentration in an alloy-type nickel-plating solution on the salt-spray (fog) corrosion resistance of nickel deposits of varying thickness.*

Curve 1: 0.0003-in. deposits; curve 2: 0.0010-in. deposits; curve 3: 0.0015-in. deposits.

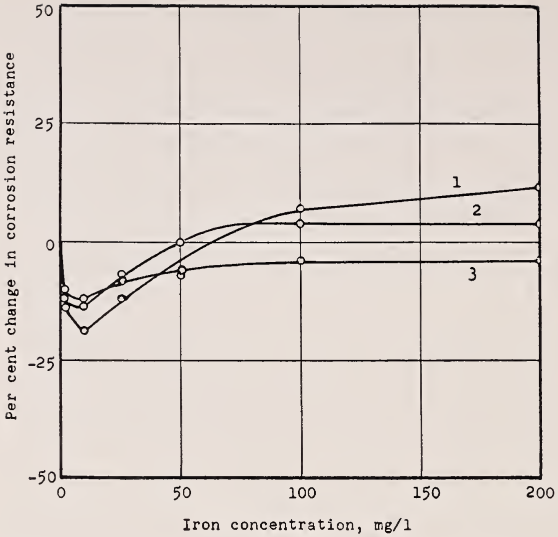

Figure 16.5. *Effect of iron concentration in an organic-type nickel-plating solution on the salt-spray (fog) corrosion resistance of nickel deposits of varying thickness.*

Curve 1: 0.0003-in. deposits; curve 2: 0.0010-in. deposits; curve 3: 0.0015-in. deposits.

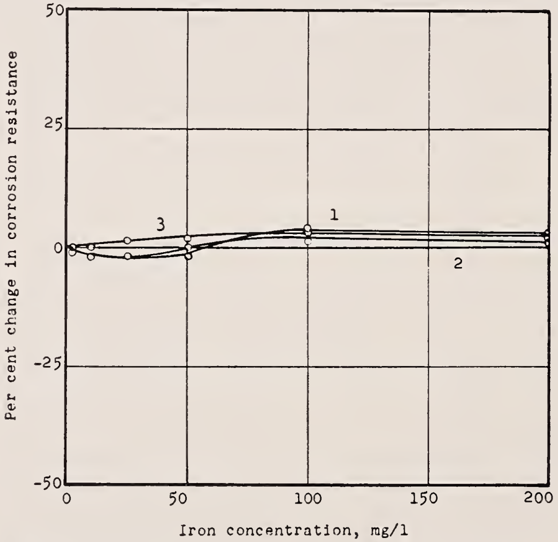

Figure 16.6. *Effect of iron concentration in the Watts-type plating solution,* pH *5.2, on the salt-spray (fog) corrosion resistance of nickel deposits of varying thickness.*

Curve 1: 0.0003-in. deposits; curve 2: 0.0010-in. deposits; curve 3: 0.0015-in. deposits.

It was found that concentrations of zinc below 250 mg/liter are not removed by the high pH precipitation method without appreciable loss of nickel. This method is not recommended for the complete removal of zinc from nickel-plating solutions.

Zinc can be removed by electrolysis to concentrations less than 1

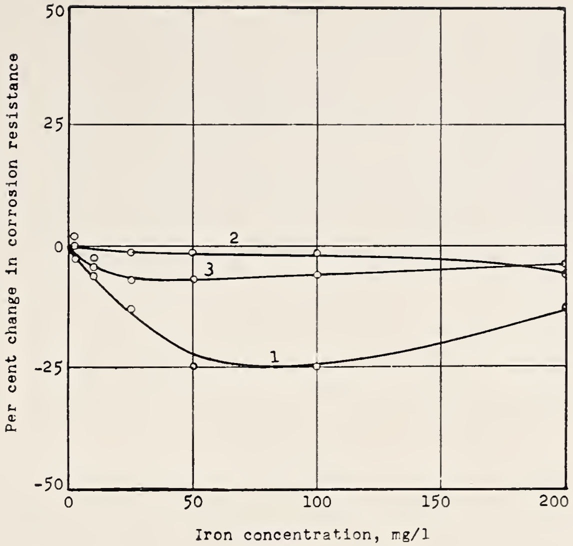

FIGURE 16.7. *Effect of iron concentration in the Watts-type plating solution,* pH *2.2, on salt-spray (fog) corrosion resistance of nickel deposits of varying thickness.*
Curve 1: 0.0003-in. deposits; curve 2: 0.0010-in. deposits; curve 3: 0.0015-in. deposits.

mg/liter. The most economical current-density range was found to be 2 to 4 amp/ft^2. Using higher current densities removes the zinc at a faster rate but increases the ratio of nickel to zinc in the deposit.

Removal of Iron. High pH precipitation and low current density electrolysis under normal operating conditions were investigated as methods for the removal of iron from nickel-plating solutions.

Low current density electrolysis, most efficient on the basis of nickel deposited at 5 to 7 amp/ft^2, was found not very effective unless extended periods of time were allowed. High current density electrolysis at 40 amp/ft^2 was found to reduce the iron much more rapidly and completely but with greater loss of nickel. The general method of electrolysis to remove the iron is ineffective if it is desired to remove iron to a concentration below 50 mg/liter without excessive deposition of nickel.

Iron can be removed from nickel-plating solutions by raising the pH of the solution with nickel carbonate. A concentration of 25 mg/liter or less can be attained with no appreciable loss of nickel. By oxidizing the iron to the trivalent state, a more complete removal is attained at a lower pH value and in a shorter time. Figure 16.8 shows the comparative rates of removal of the iron from the Watts pH 5.2 bath felt to be typical of the solutions investigated.

The behavior of iron in nickel-plating solutions presents a complicated problem. Ferrous iron may be oxidized by the atmosphere. The rate depends on the pH of the solution, temperature, and availability of oxygen. Nickel-plating solutions that operate at the higher pH values contain the iron in part in a colloidal state. We have found, somewhat unexpectedly, that the ferric ion is reduced rapidly by metallic nickel whether the metal is active as an anode or not. An analogous reaction with chromate-ion to give chromium in a lower

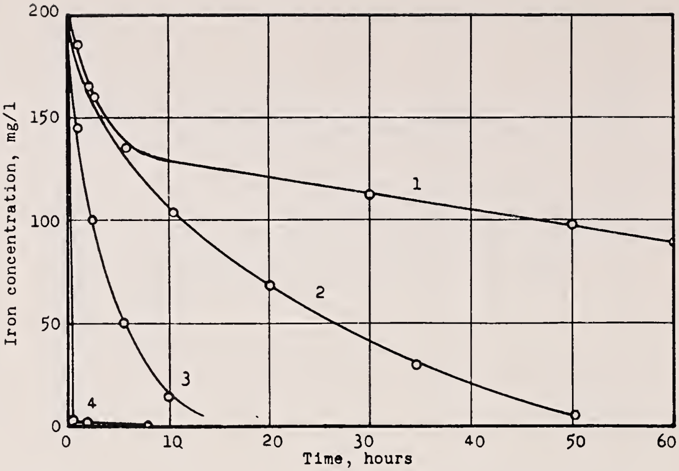

Figure 16.8. *Comparative rates of iron removal, Watts bath,* pH *5.2.*

1, Operating conditions with no current; 2, low current density removal, 5 to 7 amp/ft^2; 3, high current density removal, 40 amp/ft^2; 4, hydrogen-peroxide treatment.

valence state has also been observed. This interesting phenomenon will be discussed in detail in a forthcoming publication.

We thank the Hanson-Van Winkle-Munning Co. for a fellowship grant and a liberal quantity of supplies, which has made the project move more efficiently, and also Mr. B. C. Case for his suggestions and interest in this investigation.

[1] D. T. Ewing and William D. Gordon, Monthly Rev. Am. Electroplaters' Soc. **34**, 180 (1947).
[2] D. T. Ewing and William Gordon, Plating **36**, 58 (1949).
[3] D. T. Ewing, R. J. Rominski, and W. M. King, Plating **36**, 1137 (1949).
[4] D. T. Ewing, R. J. Rominski, and W. M. King, Plating **37**, 1157 (1950).
[5] D. T. Ewing, Proc. Am. Electroplaters' Soc. **33**, 209, (1946).
[6] D. T. Ewing and William D. Gordon, Proc. Am. Electroplaters' Soc. **34**, 213, (1947).
[7] D. T. Ewing, Robert Rominski and William King, Plating **35**, 1122 (1948).

Discussion

Mr. D. Price, Oakite Products Co., New York, N.Y. I would just like to start off with one question. Isn't it true that in the course of your work you have made a good deal of use of the analytical methods developed by Prof. Serfass to determine the amounts, etc.?

Dr. D. T. Ewing. If it were not for Prof. Serfass' work, we could not work as fast as we do. I would say that half the time has been saved by using those methods, and we have used them in all cases.

Dr. W. Blum, National Bureau of Standards, Washington, 25 D. C. If you are working with a fairly high pH nickel solution and any ferric iron is introduced, will it not mostly go into the sludge?

Dr. Ewing. That is correct. I think the pH is around 4.7. This precipitate forms rather slowly at room temperature, and if we allow it to stand maybe 2 days before we filter it, some more will form. We have found that if we heat this solution up to the boiling point for about 3 hours, we get rid of the iron.

Furthermore, trivalent chromium will also come out very fast along with the iron, but the six-valent, no.

Dr. W. R. Meyer, Enthone, Inc. New Haven, Conn. Some years ago at a meeting of the Electrochemical Society at Savannah, Ga., 1937 or 1938, they published a paper on the effects of impurities in copper solutions and tried to correlate these effects and characteristics and that sort of thing, and achieved a moderate degree of success in trying to show something.

But there are many things concerning impurities that are not understandable. One of them is why, for example, does copper have such an effect on a nickel deposit? Copper should fit very nicely into the nickel lattice and form solid solutions throughout the entire range, and should not have profound effects, and still it seems to. One thing I pointed out then, and probably many other people have, is that it may be that we are getting precipitation of basic salts. Instead of copper, it may be copper hydroxide, for example. Copper hydroxide precipitates at a lower pH than nickel hydroxide.

And so in these studies there are two things that could be done that would help us. I don't know whether you did it, Dr. Ewing. One would be actual photomicrographic cross sections of some of these things. You can't do them all. I realize it is a tremendous task. The other would be the potential changes at a cathode as they show for copper and lead. You get a potential that correlates itself with the structure; maybe someone else has another suggestion to throw in to try to understand why these effects are so profound and how we can prove whether it is just metal or other materials that enter into it.

Dr. Ewing. I agree entirely with Dr. Meyer's line of thinking here. We have suspected for some time from our own observations and the behavior of nickel, that there are differences in potentials in different portions, probably because of stress. I don't think there is any question but that a potential will change. We are about to undertake a measurement of the single electrode potential of electrodeposited nickel.

N. F. Murphy, Va. Polytech. Inst., Blacksburg, Va. Doctor Ewing, I do not know whether I misunderstood or not, but when you said that the ferric iron is reduced to ferrous, in the electrolyte, were you talking about electrochemical reduction, and if so, what mechanism did you suggest?

Dr. Ewing. I probably did not clarify. No, I would not say that there is electrolytic reduction going on at the anode.

Question: If I may make a comment, I think it would be well for all of us to remember that it is seldom that a working electrode be anode or cathode. If you view the thing by microscope, some of these things that look as if they cannot happen, may very possibly take place when we consider that the electrodes are not at the same potential over the surface.

17. Porosity in Perspective[1]

By Nathaniel Thon [2]

Porosity of electrodeposits has been inferred from appearance of localized spots on exposure to corrosive agents. The observation that some such spots can occasionally appear at very early stages of the exposure, or be revealed by very short action of a relatively mild, but obligatorily corrosive, so-called "porosity reagent," had implanted the belief in a systematic gross initial porosity, ascertainable by chemical reagents and spot counts and solely or mainly responsible for corrosion of the base metal. Actually, such initial gross defects are either trivially accidental or else the result of the very action of the "reagent". The fact is that under definite conditions of exposure, corrosion attacks at certain points in depth, giving rise to pores and, hence, to spots due to exudation of base-metal corrosion products.

Work of AES Project 6 has shown that long before the appearance of visible gross pores, commonly referred to as first visible failure, there is a growing invisible porosity detectable by permeability to a noncorrosive gas. A simple method and apparatus were devised whereby this gas permeability can be measured and expressed numerically by a permeability constant. The discovery of the increase of gas permeability in metal foils exposed to depth-corrosive conditions, and the development of a quantitative method for its measurements, have resulted in a broadened and more precise definition of porosity in electrodeposits. No longer does this term apply to sporadic gross defects or visible holes produced (and, consequently, "revealed") by corrosive agents, but it includes the fine porosity detectable by gas permeability. With progressing corrosion, the fine pores increase both in number and in dimension. Ultimately, a few pores will have become large and straight enough to be visible as gross holes, and give rise to base-metal corrosion spots. The points of visible failure are only quantitatively, not qualitatively different from the fine pores responsible for gas permeability.

The transition from gradually increasing permeability to visible failure, indicative of their common nature, is supported by numerous observations of parallelism between the rate of increase of the gas permeability and the incidence of first visible failure. The latter occurs at a later stage, the slower the increase of the permeability. The resistance of a given electrodeposit to a given corrosive exposure, from the point of view of continuity of the deposit and protection of the underlying base metal, can therefore be adequately and quantitatively described and characterized by the rate of increase of the gas permeability of an isolated sample of that deposit.

The conclusion that the rate of increase of permeability, at steps preceding appearance of visible failure, is a measure of the protective power of the given deposit in the given exposure is, of course, subject

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[1] Presented by Mr. B. C. Case, Hanson-Van Winkle-Munning Co., Matawan, N. J.

[2] Frick Chemical Laboratory, Princeton University, Princeton, N. J. Project Director, AES Project 6

to further extensive investigation and verification. To test it, it is necessary to have, along with the now existing quantitative measure of increase of gas permeability, an equally quantitative criterion of the degree of corrosion of the base metal through the failing deposit. The customary count of corrosion-product spots over a given area is obviously uninformative, and the specification of a minimum diameter for a corrosion point to qualify for the dignity of a spot, is as arbitrary as it is unhelpful; a "spot" three times as wide as the specified diameter, and actually formed by a merger of several spots exuded from closely adjacent pinpoints, counts as one spot, whereas a multitude of tiny spots, amounting to a sizable sum total of corrosion products, does not count at all, and the thickness of a spot is disregarded. In brief, the conventional spot count stands in no simple relation to and is not a measure of the degree of corrosion of the base. Aspect ratings, based on subjective comparisons with nonrepresentative and dubious scales of appearance, are even less significant, and by no stretch of imagination a match for the quantitative permeability determinations. What, then, is a suitable quantitative measure of the degree of corrosion of the base metal? Clearly, more advanced corrosion, paralleling poorer over-all appearance of the article, corresponds to a greater total amount of corrosion products having exuded through the now gross pores and spread over the surface. The task of finding a quantitative measure of the degree of base-metal corrosion thus boils down to a method of quantitative analysis of the amount of these products.

Such an analytical method, permitting the determination of the corrosion products of iron base metal formed and exuded across a partially failed protective electrodeposit, was worked out and is due for early publication in *Plating*. It should, possibly with minor modifications, be applicable to a variety of corrosive exposures, including intermittent immersions, exposure to gaseous atmospheres, etc. The "degree of corrosion" is expressed numerically in grams of corrosion product per unit surface area. The progress of the visible corrosion of the base metal can be determined and plotted as a function of the length of the exposure, and the rate determined at each stage.

With these two quantitative tools, increase of gas permeability of isolated electrodeposits over early stages of an exposure, and increase of the amount of base-metal corrosion products across an adherent deposit at the stage of visible corrosion, it will henceforth be possible to investigate systematically and extensively the correlations between these two phenomena, and the protective values of electrodeposits in different corrosive exposures in objective quantitative language. This is a vast program, which we can only chart, in the expectation that it will be taken up and carried forward in many other quarters.

One can expect characteristic differences of the shapes of curves of degree of corrosion as a function of time, depending on both the nature of the coating and the corrosive medium. Self-accelerated, constant, or self-decelerated rates can be expected, depending on the nature and effects of the corrosion products.

A complex corrosive medium raises problems of the identity of the specific factors responsible for the greater or lesser rate and degree of depth corrosion. Application of the increase of permeability test can provide ready answers. A striking instance is the recent finding of Project 13—which we welcome as an illustration of the fertility of the gas-permeability method—which showed absence of measurable permeability after prolonged exposure of nickel foils to hydrochloric acid vapor under conditions excluding condensation at the surface.

Another illustration of the potential usefulness of the gas permeability test as a sure guide in the appraisal of the protective worth of a deposit is the successful production, in two different laboratories, of thin electrodeposited nickel foils of very low or practically no permeability. If, as we have postulated and, to some extent, demonstrated, absence or smallness of initial permeability is a guaranty of better resistance to depth corrosion in exposure, exploration of conditions of electrodeposition conducive to lowest possible permeability should point ways to improve the protective value of the deposits. In this connection, I cannot but consider it fortunate that our early work was done with much less perfect thin nickel deposits than those produced lately in other laboratories; but for that, we might have missed the basic phenomenon of the possible (but not necessary) existence of measurable gas permeability in foils appearing macro- and microscopically porefree. We might have missed that very phenomenon which now, in the hands of those who develop and apply our early work, promises to suggest possibilities of practical importance.

From the point of view of depth corrosion, uniform corrosive attack on the surface, resulting in the dissolution and removal of shallow slices of metal, is significant in an indirect way insofar as a throughway pore across the deposit, giving access to corrosion of the base metal, is likely to be formed at an earlier stage, the thinner the deposit has become through surface corrosion. Quantitative determinations of the degree of surface corrosion by the loss of weight, or amount of metal attacked, are classic and need not be gone into. A factor that may be of decisive importance for the incidence of failure is the pattern of the surface corrosion, in the sense of local depth distribution of the surface corrosion. The roughness factor, i. e., the ratio of the true and the apparent (geometric) surface area, will, in general, change with the progress of the surface corrosion. It can remain unchanged only if that corrosion is uniform, attacking raised and depressed parts of the surface to the same degree. If the elevated parts are attacked preferentially, the surface will become smoother, i. e., the roughness factor will decrease. If, however, corrosion attacks, to a preferred degree, recessed parts of the surface, the roughness factor will increase. It is obvious that in the latter case, earlier development of outright depth corrosion will be favored. In view of that connection between the pattern of change of the surface roughness in corrosion, and development of porosity, it appeared of interest to obtain exact information about these changes. The reason that such important information is practically nonexistent lies, simply, in the inadequacy of the usual methods based on surface exploration (brush analyzer, profilometer) which can give no significant figures for the over-all roughness of an area. Once more the need was felt for a reliable quantitative method. The answer is the Brunauer-Emmett-Teller low-temperature adsorption isotherm method. For electrodeposited metal surfaces, adsorption of butane at the temperature of melting diethyl ether was found suitable. Exploratory determinations showed, so far, a consistent increase of the true surface roughness of electrodeposited nickel in exposure, with a tendency to level off at later stages of the corrosion. It can be expected that, on further study, the behavior of the roughness factor will prove to be more complex and diversified. We believe this tool, too, will be adopted and prove useful for obtaining needed information.

From the fundamental point of view, the phenomena of porosity, as defined in this report, raise two outstanding problems. One is, what factors determine the permeability and porosity development of an electrodeposit? Variations in terms of current density, temperature, concentration, addition agents, impurities, base surface, grain size of the deposit, heat treatment, etc., still remain to be investigated systematically: our own work could only touch lightly on these questions, and our conclusions are subject to further confirmation and development. I want to mention only one aspect, which we believe has a direct bearing on the fundamental problem of porosity with which we are dealing. On the theory that porosity is contingent on polycrystallinity and dislocations, there ought to be a relation between it and another manifestation of grain boundaries and dislocations, namely, occlusion of hydrogen, other than and in excess of the normal interstitial solid solubility. This has led us to the study of hydrogen occlusion particularly in electrodeposited nickel, and to the experimental establishment of a marked difference between the energy of fixation of the very firmly held hydrogen occluded in the very process of electrodeposition, and the more loosely held hydrogen which can be incorporated electrolytically into a ready-made deposit. The first layers of electrodeposited nickel, close to the base metal, are markedly richer in hydrogen than farther layers, a fact which accounts for well-known stress phenomena in nickel deposits; the correspondingly higher depth-corrosion resistance of the outward, hydrogen-poorer layer of the deposit, could well be an added factor in the markedly greater protective power of sufficiently thick deposits. Deposits produced on a polished base tend to occlude more hydrogen, and be more easily depth-corrodible, than when produced on a crystalline base.

With no experimental confirmation in sight yet, we predict that single-crystal deposits of nickel should prove to be poor in occluded hydrogen, and be much more resistant to development of porosity than any polycrystalline foils of the same thickness.

A second set of problems concerns the numbers and size distributions of the invisible pores. The effusion character of the permeation of gases was confirmed by the observed very near inverse proportionality between the rate of permeation and the square root of the molecular weight, with hydrogen, nitrogen, carbon dioxide, and (dry) sulfur hexafluoride. An effect of pore size could not be felt in these experiments, as the molecular dimensions are of approximately the same order. Wider variation of the size of the permeating gas molecules, e. g., by the use of vapors of higher organic compounds, appears to be promising. Another approach will be permeability to dissolved molecules. Finally, closer investigation of the systematic variation of the permeability constant with the value of the pressure difference, observed by Project 13, should provide information about the pore-size distribution and the types of flow, particularly in the range of very low overpressures.

18. Correlation of Gas Permeability of Electrodeposits with their Weathering Behavior

By Fielding Ogburn [1] and Asaf Benderly [1]

This project is an outgrowth of American Electroplaters' Society Project 6, which developed a method of measuring the gas permeability of detached electrodeposited foils. The purpose of Project 13 is to determine whether this new tool might be used to predict the performance of adherent electrodeposits in service. To date, the work of Project 13 has been confined to nickel foils produced in a typical Watts nickel bath.

A method of photographing gross porosity has been employed instead of the microscopic survey method used by Project 6. The photographic method involves pressing a film against one side of a foil and exposing the other side of the foil to diffuse light. Under the conditions used, the gross pores appear on the film as black spots of roughly 20 times the true pore diameter. This method, as compared to the microscopic method, appears to be more reliable, more sensitive, and less tedious. It further provides a permanent record of the size and distribution of the pores. A simple modification will yield considerably greater enlargement of the gross pores.

Photographs of the 10- by 15-cm foils proved to be very interesting. The number and size of the pores are closely related to the thickness of the foil. As the foils increase in thickness, the number of photographable pores diminishes and their sizes decrease. At a foil thickness of about 25 microns (0.001 inch) no pores whatever are photographically detectable. These contact photographs provide a means of checking the performance of the plating bath and may prove to be a valuable tool for measuring gross porosity and for investigating the nature of porosity.

Gas-permeability measurements were made for a number of electrodeposited foils on areas free of photographable porosity. The apparatus used was similar to that developed by N. Thon for AES Project 6. Our apparatus permits ready detection of permeabilities as low as 10^{-10} liter/cm^2—min.

Areas with no measurable permeability were readily found on foils as thin as 5 microns (0.0002 inch) and a foil 3.5 microns (0.00014 inch) thick had a permeability of 3×10^{-5}. It is probable that this last value does not represent the minimum permeability obtainable with such thin foils, as only one measurement was made. Although duplicate measurements on the same sample seldom differed by as much as 10 percent, the permeability of different samples from a given 10- by 15-cm (4 by 6 inch) foil varied over a wide range.

It was found that a foil might actually have a few photographable pinholes and still have a low permeability. In some cases the permeability was too low to be measured by this apparatus. On the other hand, some corroded foils that showed no photographable pinholes

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[1] National Bureau of Standards, Washington 25, D. C.

exhibited substantial gas permeability that could readily be measured. This seeming contradiction can probably be explained by the fact that in the latter case a large number of holes were present but were too small to be detected photographically. There also exists the additional possibility of tortuous channels that gas, but not light, can permeate.

The basic equation that describes the permeation of gas through foils in our apparatus is

$$\frac{d\Delta p}{dt}=\frac{2F}{V}k\Delta p,$$

where

Δp is the pressure difference at time t,
F is the foil area,
V is the volume of the apparatus,
k is a "permeability constant."

Measurements show that the permeability constant is actually not constant but rather is a linear function of the average of the front and back pressures on the foil. For each of four foils investigated, the slope of this function was found to be different. In some cases the permeability constant changed as much as 30 percent with a change of 1 mm of average pressure. With a fifth foil, which had been corroded over hydrochloric acid, a clear example of orifice flow was encountered. This type of flow is radically different from that normally obtained and does not yield a constant directly comparable with the normal permeability constant.

The initial gas permeability of pore-free areas of detached foils does not appear to be a practical quantity to correlate with the weathering behavior of panels protected by electrodeposited coatings. This permeability is either virtually zero or is greatly overshadowed by the gross porosity of the surrounding areas of the deposit. Gross porosity, as measured photographically, might be used for evaluating thin deposits; but because pores are not photographable for thicknesses above about 25 microns, the method is not suitable for thick deposits.

The proposed method for thick deposits is to correlate the corrodibility of the foils with weathering behavior. The corrodibility would be measured by the rate of development of permeability to gas or light, or both, when the foils are corroded by rapid chemical means. With this in mind, several methods of accelerating corrosion were tried. Simple exposure of foils over concentrated hydrochloric acid in a desiccator proved to be nonreproducible. This may be due to erratic condensation on the foils or to nonuniformity of the foils themselves. Placing the desiccator in an insulated box greatly reduced condensation, resulting, however, in a very slow rate of corrosion. Corrosion by hot water was also found to be very slow. Further efforts are being made to develop a suitable "corrodibility test" that may be correlated with the behavior of adherent coatings under service conditions.

Discussion

Dr. A. Brenner, National Bureau of Standards, Washington 25, D. C. I think these two researches on porosity to a certain extent do not coincide, and it seems to me to raise a rather basic issue that ought to be settled, and that is whether there are really two types of porosity, an accidental random type and a permeability. It seems to me there is a slight suspicion that the Thon permeability may be accidental porosity that has escaped the detection of the microscope.

I think it is important that this should be settled before one starts theorizing too much about the usefulness of the methods for correlation with outdoor exposure.

That brings up the second proposition. Can any accelerated test such as made here, either with the permeability or the photographic method, have any relation to the results obtained in the field? Certainly one would have to make careful studies to correlate that. It is difficult for me to conceive how corrosion experiments carried on with concentrated hydrochloric acid are likely to lead to results representative of those in the field. For example, if corrosion in the field is due to a particle of soot on the specimen, how can one obtain a similar result with hydrochloric acid? It seems to me these two basic problems should be settled.

Mr. B. Case, Hanson-Van Winkle-Munning Co., Matawan, N. J. I would like to comment not as a reader of Dr. Thon's article, but on Dr. Brenner's first problem. Dr. Thon made a division, an arbitrary division, in permeability. I think it is rather unfortunate that he was forced to do it. At one time, visible pores were conceived to be things that were visible with the naked eye, that you could hold a deposit on steel and look at it, and if you did not see any holes in the steel, you said there were no gross pores; next, stripping it off and looking at it. Thon went from there to looking at the foil over a light, still with the naked eye, and what he could not see he called intrinsic permeability, and what he could see was called accidental porosity. Next, he went to magnifying. He still said everything he could see was gross porosity.

Now, admittedly they can see pores they still can't measure with permeability. You still call what you see gross pores. I don't think this is correct. Somewhere back we ought to change the definition. We are getting to see too well.

Dr. W. Blum, National Bureau of Standards, Washington 25, D. C. Mr. Chairman, we seem to be shooting lots of holes into the theory. This whole problem reminds me of a remark made some years ago by Dr. Conant, President of Harvard. He said, "When anyone published results of research they should be able to answer at least three questions regarding it: first, what is it? What did you learn? Second, how did you find it out? What is your evidence? and third, what of it?" Now, that, in brief, is what we on Project 13 are trying to find out. I want to go on record as commending Dr. Thon for his imagination and his persistence in working out new tools. That is what we need in the whole field of science, new tools. We find ourselves so often up against a stone wall. We say if we could find out where these inclusions are that we know are present in electrodeposits—we have to do that and we know we have to find new tools. I am not going to discuss or attempt to give an interpretation of the theory or anything of the sort, but just to call attention to one possible factor that still needs to be surveyed and studied much more. That is the cause of the localized attack of a coating by any reagent, whether it be the atmosphere or hydrochloric acid, or anything of the sort. We know that the coatings of this type, unlike zinc coatings, do not just go away. They are not attacked uniformly. They are attacked locally, preferentially, by what Dr. Thon calls a depth corrosion. Here is just a speculation. I think more work can and should be done on it.

We know that all electrodeposits have inclusions. A great deal of work has been done on those basic materials. I have the idea, which I am unable to prove, that much of this localized depth corrosion is caused by the presence of these inclusions and the selective attack of the reagent on those inclusions.

Now, in postulating that theory or possibility, if you choose, that is somewhat different from the theory of Dr. Evans, which Dr. Gardam briefly referred to in his talk on Tuesday morning, in which he was thinking of this permeability, etc., as due to voids. I do not say that voids may not exist between crystals, but simply that we do know that there is basic material in practically all electrodeposits, and, therefore, if your particular reagent or environment attacks, that you could easily have selected corrosion, just some more to work on.

Mr. L. Weeg, National Lock Co., Rockford, Ill. Mr. Ogburn, in the early part of your paper you mentioned obtaining various degrees of gross porosity plated from the bath; under what conditions did you get these results, or were the results accidental?

Mr. F. Ogburn. For the most part they were accidental. Originally, we were plating out of a beaker without any filtration, and then more recently we switched to another system using a different tank, continuous filtration, et cetera, and with that change our deposits improved quite a bit. That might be attributed to the filtration or something else. We also found that the cleaning procedure had a bit to do with it. You can take the stainless-steel panel right out of the acid dip, rinse it off, put it in a bath. Occasionally we take it out of the acid dip, rinse it off, and not being quite ready for it, put it into a beaker of distilled water for a little while before plating. We found that that latter panel would have more photographable pores than the first one. That is about all I can say to your question.

Dr. G. E. Gardam, Design and Research Centre, London, England. When the foils were made, on stainless steel, and then torn off or pulled off, was any examination made for metal left on the stainless steel? It seems to me if there is some adhesion, you may leave little flecks behind on the stainless steel and consequently leave little holes in the foil.

Mr. Ogburn. We have not been able to detect anything. Actually, we haven't done a great deal in that direction. If you calculate the volume of the holes in the foil, the corresponding volume of nickel would be less than you could detect with dimethyl glyoxime. The shape of these pores is not what I would expect if they were ripped in or torn in. When we treat the stainless steel so as to decrease the adhesion we get more of these holes, which is the opposite of what you would expect if the pores were due to good adhesion.

In other words, we do not have positive proof that any of these holes are not torn in, but the indications are, from the various things such as I have mentioned, that these holes were already there. I might also mention that if there is any nickel left on the stainless steel, it would have some effect on subsequent deposits, and we haven't been able to detect any such effects.

Dr. A. K. Graham, Graham, Crowley Associates, Jenkintown, Pa. There are many aspects of this problem that certainly we do not know anything about. I want to raise a further question, which I think is pertinent. If we are plating on a base metal that has a microopening, has a pit or a fissure, the deposit over top of that for a substantial thickness will reflect that indentation on the surface of the base metal as the deposit builds up.

Now, when we start plating over openings in a base metal that are of smaller dimensions similar to what we have in a piece of metal made up by powder metallurgy, we find that the ability to plate in the capillaries, or pores, of the powdered metal base is amazingly good when we are plating from an acid electrolyte. Nickel or acid-copper, and even chromium, is excellent. On the other hand, the ability to throw into pores is amazingly poor when we are plating from the so-called high-throwing-power types of plating baths, such as silver, cadmium, zinc, and cyanide copper.

Now that, in itself, is a challenging observation. One might conclude that going from microfissures in a base metal, under which conditions we do not fill those voids readily without building up great depths of deposits and sometimes not then, to these openings of capillary dimensions, that it is easier to fill those capillary dimensions particularly with certain types of plating baths. Now, if we plate nickel that has permeability, we are presumably talking about openings that are of even smaller dimensions than the capillaries that we are referring to in a powdered metal base. If we can fill these easily, and there is some evidence to indicate it, why wouldn't we continue to fill the smaller dimensions we are calling permeability? Why are they there at all? To me, it is a very striking lack of agreement, and I think it confirms what Dr. Blum and others have said as to the justification for doing research to get information to answer questions that we are wholly unable to answer today.

As far as the practical application is concerned, I think that it is very evident that many of our research efforts bear no relation to practice when they are first worked upon, but I can foresee—at least, I am optimistic—about much good coming from such work as this for the plating industry.

19. Properties of Electrodeposited Nickel

By Abner Brenner[1]

Electrodeposits find many varied uses in industry, and yet few of those who produce them realize the extent to which each application is determined by the properties of the electrodeposits. One reason for this is that most electrodeposition is done for purposes of decoration or corrosion protection, which applications effectively utilize few of the properties of the metals. For decoration, mainly surface characteristics of the metal are important, such as reflectivity and perhaps wear resistance. For corrosion protection, mainly the chemical reactivity of the metal is important. The relation of these properties to the application of the deposit was obvious without the need of exact measurement.

Within recent years the applications of electrodeposition to engineering purposes, such as building up worn or undermachined parts, or electroforming, has increased. For these applications a knowledge of the mechanical properties, such as hardness, tensile strength, and ductility, is important. Realizing that data on the properties of electrodeposits would expand their uses, the research committee of the AES set up Project 9 almost 4 years ago to study the properties of electrodeposits. Because nickel was the most widely used electrodeposit, it was studied first. The project was begun with Charles Jennings as research associate and was continued and finished by Victor Zentner.[2]

The AES project was a cooperative one to which many sections of the National Bureau of Standards contributed as well as the Electrodeposition Section. The main objective of this investigation was to obtain data on those mechanical properties of nickel that would be of immediate value in engineering applications of plating. In addition, less complete data on a number of other properties was to be obtained to lay the ground work for new uses of plating in the future. A subsidiary but important part of the project was to correlate between properties of the deposits and the conditions of deposition, for unless these relations were known, the consistent production of a given type of deposit with desired physical properties would be difficult on a commercial scale.

One phase of the subject in which we were particularly interested was the factors that are responsible for the great differences in physical properties of deposits obtained under different conditions, and this subject has been chosen for discussion here. This presentation will involve an examination of the relations between physical properties and the structure and composition of the deposits. To illustrate the correlations, certain data on the properties of dull nickel, or Watts nickel, and bright nickel will be used, because these two types of deposits show the greatest contrast in physical properties, and the relations are somewhat easier to see. Also, the effect of a few variables on the properties of dull-nickel deposits will be discussed.

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[1] National Bureau of Standards, Washington 25, D. C.

[2] Plating **39**, 865 (1952).

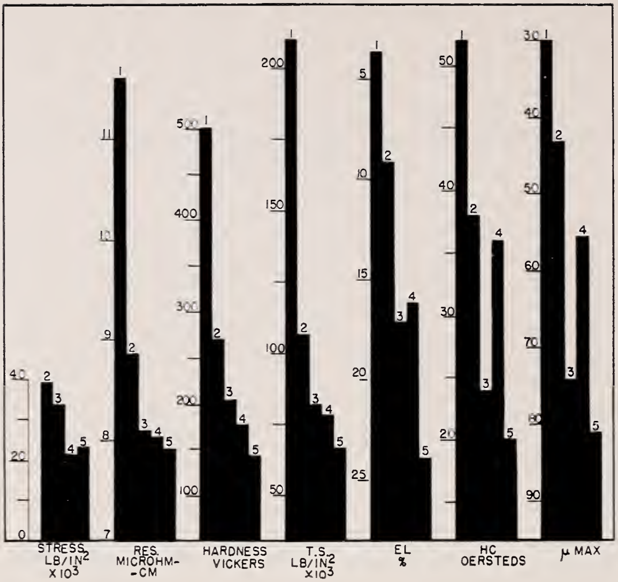

FIGURE 19.1. *Range and trend of physical properties of nickel deposited from five different types of baths.*

Each point is the average of the properties of five or more deposits obtained under various conditions of plating. 1, Bright nickel baths; 2, chloride-type baths; 3, half-chloride, half-sulfate bath; 4, sulfate baths; and 5, Watts-type baths.

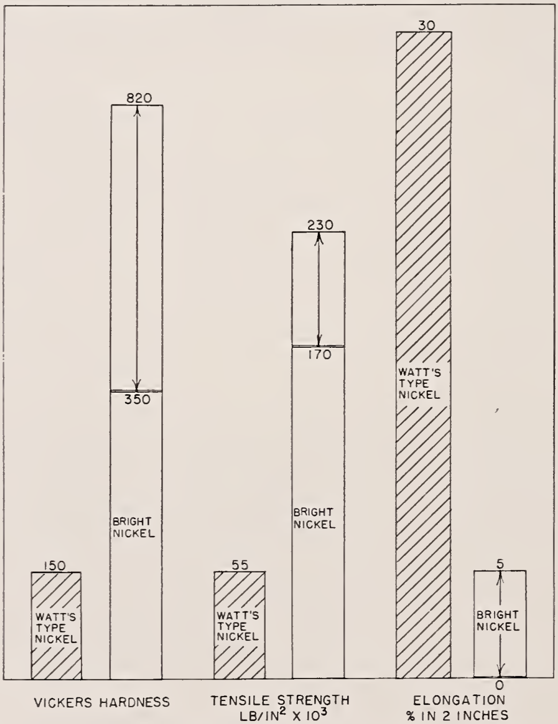

FIGURE 19.2. *Comparison of mechanical properties of deposits from Watts-type and bright-nickel solutions.*

The mechanical properties of commercial metals do not have definite values like the melting point or boiling point of a pure substance, but they depend to a certain extent on the previous history of the metal. Thus the mechanical properties of a specimen of copper may vary according to whether it has been cast or cold-worked by rolling, drawing, or extruding. The properties of electrodeposited metal vary over a far wider range of values than metals produced by ordinary metallurgical methods. In a sense, an electroplater can tailor his metals to suit a given purpose. He can deposit it in a hard or soft, brittle or ductile condition.

In our study of the properties of nickel deposits we found that the most potent factor in producing differences in the character of nickel deposits was the composition of the bath, that is to say, the type of anion used and the presence of special additives. The effect of operating conditions was minor. Figure 19.1 shows that the properties of deposits from the Watts bath and those from the bright-nickel bath represent the extremes in properties. If the composition of the baths were not the most important factor in determining properties of deposits, curves drawn through the tops of the blocks would cross one another. The properties of the chloride deposits are intermediate. A comparison between the mechanical properties of bright and dull nickel (see fig. 19.2) shows that bright nickel is harder and has a higher tensile strength but is much less ductile than Watts nickel.

We will now inquire into the causes for the great differences in the mechanical properties of bright and dull nickel. A partial explanation is found in the differences in the microstructures.

Watts nickel (fig. 19.7) has a coarse, columnar texture, whereas bright nickel (fig. 19.3) has no visible crystal structure, usually only laminations parallel to the basis metal. These structures are consistent with the properties of the deposits, for it is common knowledge in metallurgy that a metal has greater hardness and tensile strength when it is in a fine-grained condition than when it consists of large crystals. The differences in the structures of bright and dull nickel go deeper than the microstructure. Figure 19.4 shows the X-ray diffraction patterns of dull nickel (upper left) and bright nickel (lower right). The pattern of the bright nickel is diffuse, indicating a very small grain size as compared with dull nickel and the presence of stress or distortion in the space lattice.

The fundamental cause of the differences in the structure of bright and dull nickel is probably the presence of larger amounts of impurities in bright nickel. Analyses of the latter show that it contains a total of approximately 0.1 percent of carbon, plus sulfur, whereas dull nickel contains no readily determinable amounts of these elements. The impurities may affect the properties of the deposits in two ways: (a) through their very presence in a fine state of dispersion they result in hardening in a manner analogous to precipitation or age hardening, and (b) the codeposition of the impurities (during the plating process) causes the deposit to be very fine grained. As noted above, this type of structure modifies the properties of a metal.

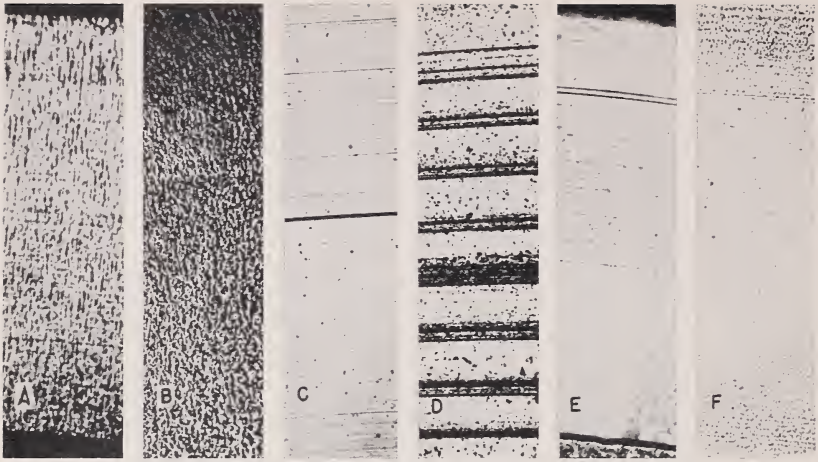

FIGURE 19.3. *Photomicrographs of bright-nickel deposits.*

Cross section, ×250. Etchant: glacial acetic and nitric acid. A, Cobalt-nickel type; B, benzene sulfonic acid and reduced fuchsin brightners; and C, D, E, and F, commercials deposits.

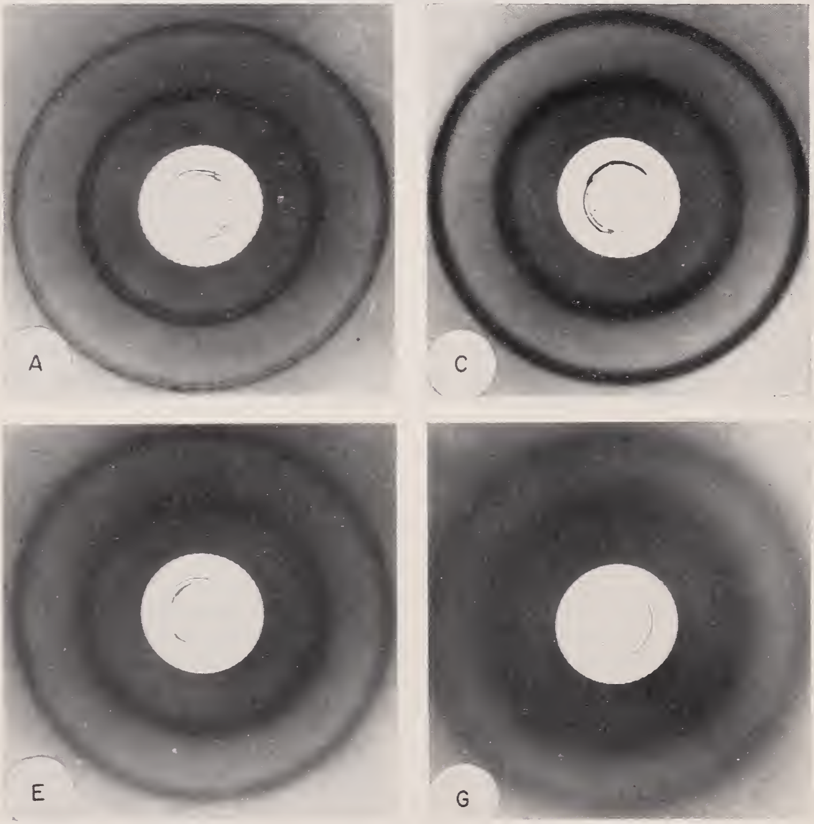

FIGURE 19.4. *Back reflection X-ray patterns of nickel deposits illustrating different degrees of diffuseness and line broadening.*

A, Deposit from Watts bath; C, deposit from chloride bath; E, deposit from acetate-chloride bath; and G, deposit from bright-type bath.

The differences in the structure and purity of bright and dull nickel causes differences in the behavior in the two types of deposits on heat treatment. Most specimens of bright nickel warp on being heated to 1,000° C. Figure 19.5 shows some electroformed tubes that either blistered, warped, or cracked. Dull nickel does not do this. The effect of heat treatment on the microstructures of the deposits is shown in figures 19.6 and .7. Heat-treated dull nickel (fig. 19.7) consists of large grains with clean boundaries. Bright nickel (fig. 19.6) shows numerous black areas, which may be either voids or segregated impurities. The thermal expansivity of bright and dull nickel also shows considerable differences, as shown in figures 19.8 and .9. Dull nickel expands linearly with rise of temperature. On cooling, the heating curve is retraced. Bright nickel undergoes a rapid expansion at temperatures above 500°, probably because of voids formed by gases liberated from the decomposing impurities. On cooling the specimen, the heating curve is not retraced and the specimen is permanently elongated.

The following discussion will deal with nickel deposited from the commoner types of nickel-plating solutions. Several correlations between properties and the structure and composition of the deposits will be considered. However, the relations will not be as evident as when contrasting bright and dull nickel. Figure 19.10 shows the microstructure of nickel deposited from six of the more common plating solutions. Little difference in microstructure exists between deposits from a Watts-type bath (fig. 19.7) a Watts bath containing sodium sulfate (fig. 19.10, A) or a fluoborate bath (fig. 19.10, D). Consistent with the microstructures, the hardness and tensile strength of the deposits are similar. The three deposits C, E, and F, from baths containing, respectively, ammonium sulfate, free ammonia, or acetate, are much finer grained than the above three, and in correlation with their structure have a higher hardness and tensile strength.

One of the most important variables in nickel plating is pH, and it is well known that the hardness and tensile strength of nickel deposits increase with pH (fig. 19.11 and 19.12). We now wish to inquire into the reason for the variation of the mechanical properties of deposits with pH. The changes in the microstructure of deposits produced at various pH's afford a partial explanation. Figure 19.13 shows that nickel deposited at pH ranging from 2 to 5 has a similar coarse texture. If anything, the deposits obtained at a pH of 3 have a coarser texture than those obtained at 2 and 5, and this correlates with the minimum hardness and tensile strength at a pH of 3, as shown in figures 19.11 and 19.12. At a pH of 5.5 and above the microstructure becomes much finer, in correlation with the increase in tensile strength and hardness.

We now wish to inquire into the manner in which changes in pH are able to affect the structure and properties of nickel deposits. It is believed that the basic cause for the change in properties is the codeposition of impurities. Watts nickel does not contain carbon or sulfur as do bright-nickel deposits. The codepostied impurities are basic inclusions adsorbed from the cathode film. The latter is always at a higher pH than the body of the solution. Figure 19.14 shows

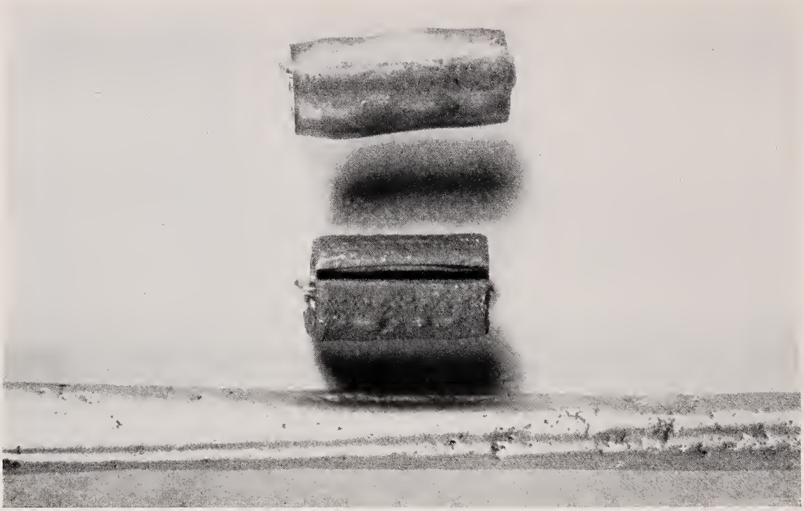

FIGURE 19.5. *Distortion and cracking of bright-nickel deposit resulting from heat treatment.*

Temperature of heat-treatment from top to bottom 600° C (1,112° F), 800° C (1,472°F), and 1,000° C (1,832° F).

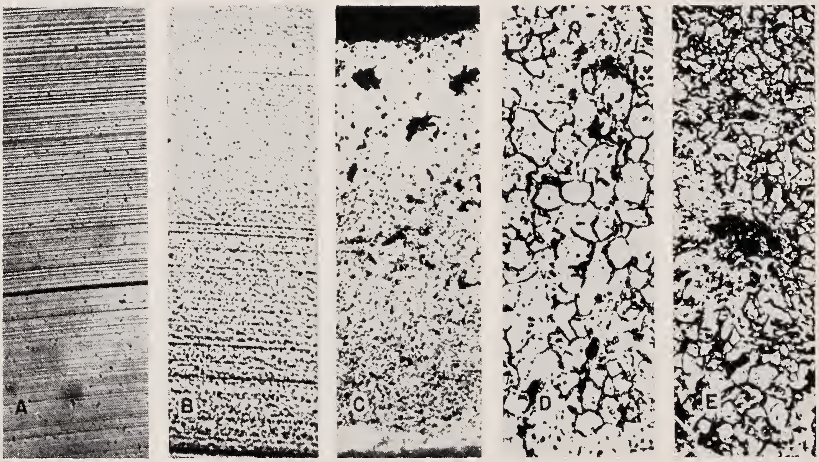

FIGURE 19.6. *Photomicrograph showing the effect of heat treatment on structure of typical bright nickel deposit.*

Cross section, ×250. Etchant: Glacial acetic and nitric acid. A, As deposited; B, heat-treated at 400° C (752° F); C, heat-treated at 600° C (1,112° F); D, heat-treated at 800° C (1,472° F); and E, heat-treated at 1,000° C (1,832° F).

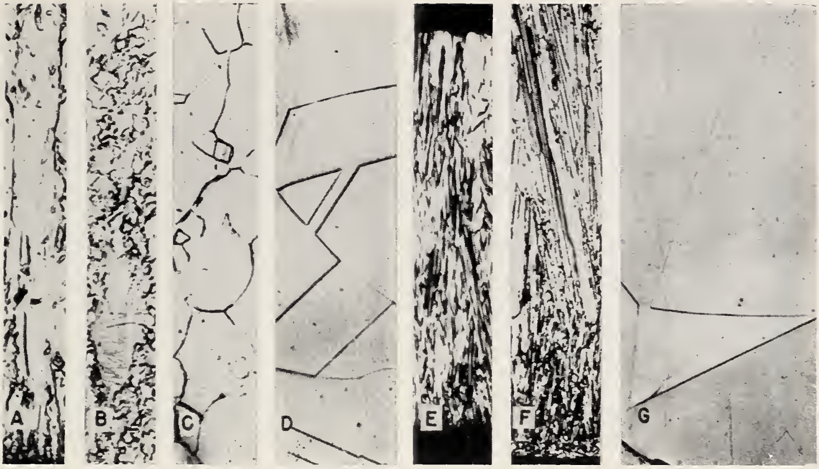

Figure 19.7. *Photomicrograph showing the effect of heat treatment on structure of nickel deposited from the Watts-type bath.*

Cross section, ×250. Etchant: Glacial acetic and nitric acid. Deposits at 30° C (86° F): A, As-deposited; B, heat-treated at 400° C (752° F); C, heat-treated at 800° C (1,472° F); D, heat-treated at 1,000° C (1,832° F). Deposits at 80° C (176° F): E, As deposited; F, heat-treated at 400° C (752° F); G, heat-treated at 1,000° C (1,832° F).

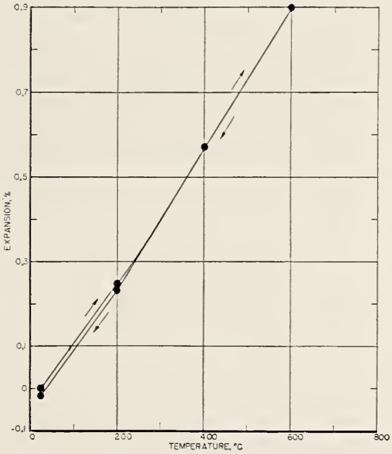

Figure 19.8. *Thermal expansion of nickel deposited from cobalt-free Watts bath.*

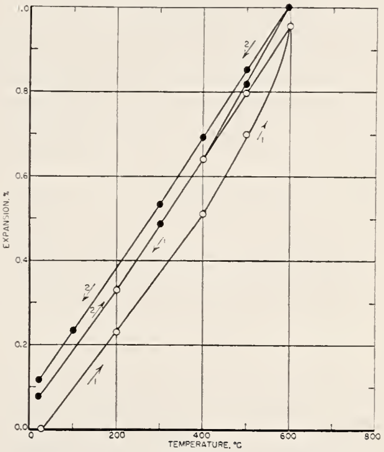

Figure 19.9. *Thermal expansion of a bright-nickel deposit.*

Curve 1, first heating and cooling cycle; and curve 2, second heating and cooling cycle.

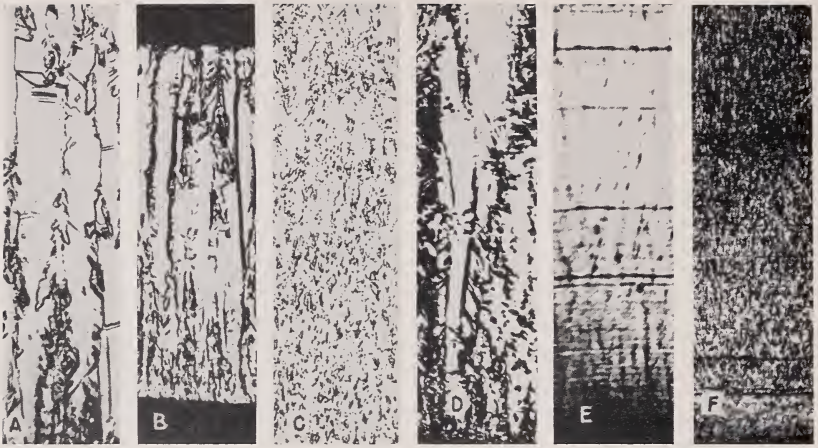

FIGURE 19.10. *Photomicrographs showing nickel deposited from different types of baths at 55° C (131° F) and 5 amp/dm² (46 amp/ft²).*

Cross section, ×250. Etchant: Glacial acetic and nitric acid.

A, Watts bath with sodium sulfate at pH 3.0; B, Watts bath with ammonium salts at pH 3.0; C, bath B at pH 5.0; D, fluoborate bath at pH 3.0; E, ammoniacal bath at pH 8.5; F, acetate-chloride bath at pH 4.5

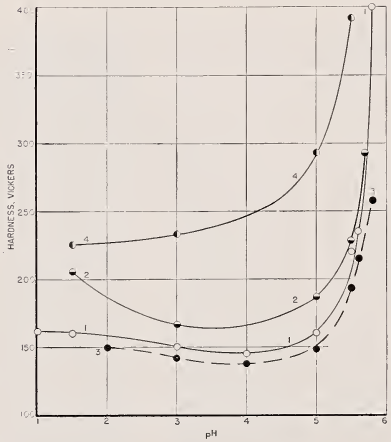

FIGURE 19.11. *Effect of* pH *plating solution on hardness of nickel deposits.*

Curve 1, Watts bath; curve 2, modified Watts baths, containing sodium or ammonium ions; curve 3, composite data from Macnaughton and Hammond (48), Macnaughton, Gardam, and Hammond (60), and Roehl (190); curve 4, chloride-type baths. References refer to bibliography in Plating **39,** 926 (1952).

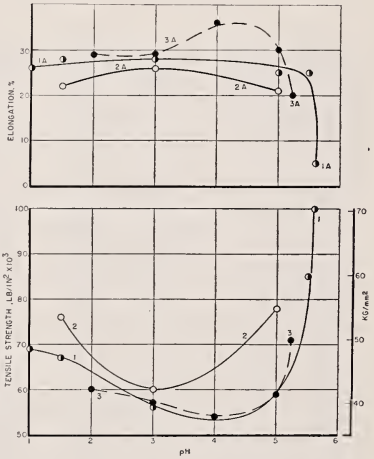

FIGURE 19.12. *Effect of* pH *of plating bath on tensile strength and elongation of nickel deposited at 2 and 5 amp/dm² (18 and 46 amp/ft²).*

Curve 1, Watts bath at 55° C (131° F); curve 2, Watts-type baths at 30° C (86° F) and 55° C 131° F); and curve 3, composite of data from Gardam and Macnaughton (57) and Roehl (180 and 190). References refer to bibliography in Plating **39,** 926 (1952).

Figure 19.13. *Photomicrographs showing the effect of the* pH *of the plating bath on the structure of nickel deposited from the Watts bath at 5 amp/dm² (46 amp/ft²) and 55° C (131° F).*

Cross section, ×250. Etchant: Glacial acetic and nitric acid. A, pH 1.0; B, pH 1.5; C, pH 3.0; D, pH 4.0 E, pH 5.0; F, pH 5.5; G, pH 5.7.

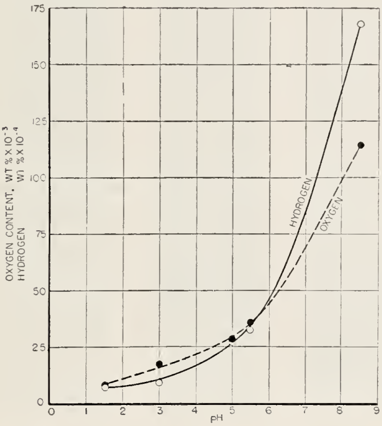

Figure 19.14. *Effect of* pH *of plating bath on oxygen and hydrogen content of nickel deposits.*

Average values for 26 deposits obtained from 10 different solutions at various temperatures and current densities.

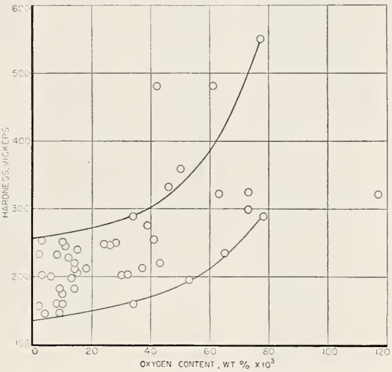

Figure 19.15. *General relation between hardness and oxygen content of nickel deposited from all solutions under various plating conditions.*

that the oxygen content of nickel deposits increases with the pH of the plating bath. The oxide inclusions affect the properties of the deposits probably by a mechanism similar to that described above in the discussion of the carbon and sulfur impurities codeposited with bright nickel. In figure 19.15 the hardness of deposits obtained from a number of different baths, under a variety of conditions, is plotted against oxygen content. Here a trend exists, but it is not as striking as in figure 19.14 because other variables also have an effect on hardness.

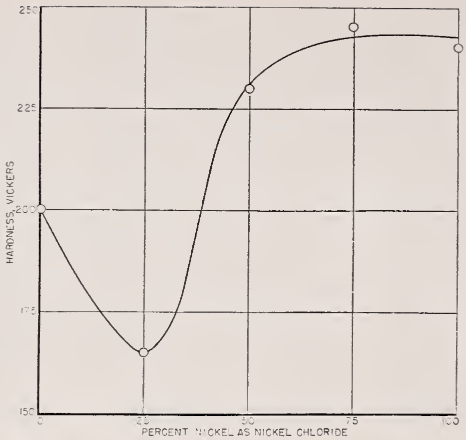

FIGURE 19.16. *Effect of chloride content of plating bath on hardness of nickel deposits.*

Each point represents the average hardness of 5 to 10 deposits each produced under different conditions of plating. Temperature range, 30° to 80° C (86° to 176° F); current-density range, 2 to 5 amp/dm^2 (18 to 46 amp/ft^2); pH range, 1.5 to 5.0.

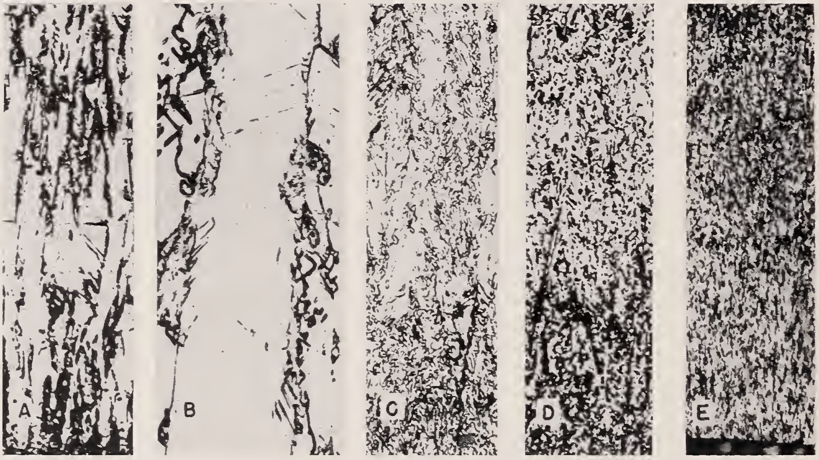

FIGURE 19.17. *Photomicrographs showig the effect of increasing chloride content of the bath on the structure of nickel deposited at 55° C (131° F), 5 amp/dm^2 (46 amp/ft^2), and a* pH *of 3.0.*

Cross section, ×250. Etchant: Glacial acetic and nitric acid. A, All-sulfate bath O; B, bath with 3 parts of nickel as sulfate and 1 part as chloride; C, half-sulfate, half-chloride bath; D, bath, 1 part sulfate, 3 parts chloride; E, all-chloride bath.

The effect of the chloride content of a nickel-plating bath on the hardness of the deposit has been previously studied, but the results reported have been somewhat contradictory. The reason for this may be seen from figure 19.16, which shows that deposits from a bath prepared with 25 percent of the nickel as chloride and 75 percent as sulfate have the lowest hardness. This bath corresponds to the Watts bath. Addition of chloride to a nickel-plating bath may either raise or lower the hardness of the deposit, depending on whether the initial composition of the bath was to the right or left of the minimum point. A good correlation between the hardness and microstructure is shown by the microstructures in figure 19.17, the harder deposits having the microstructures of finer texture. It is believed that the basic cause of the fine structure, as was the case with other deposits previously discussed, is the presence of impurities. Although data on the content of impurities are not complete enough to be conclusive, the deposits from the all-chloride baths contained several hundredths percent of chloride, whereas the soft Watts deposits contained no determinable amount.

These few examples show that a correlation exists between the mechanical properties of nickel deposits and their structure and composition. The manner in which the impurities, which are the primary cause of the fine structure and of the correlating mechanical properties, are codeposited is a matter for conjecture. It is believed that the impurities are adsorbed on the surface of the fresh, active metal rather than introduced into the deposit by electrochemical action. If this hypothesis is correct, it should be capable of demonstration by adsorption experiments, which could be made, for example, with radioactive tracers.

Discussion

Mr. N. F. Murphy, Virginia Polytechnic Institute, Blacksburg, Va. Dr. Brenner, in that curve where you showed the effect of chloride on hardness. You had one point—you plotted only a single point. I assume that represented averages of data?

Dr. A. Brenner: Yes, that is right, averages of a number of deposits.

Mr. Murphy. Now, have you found any correlation between, we will say, a spectroscopic analysis and the hardness curve?

Dr. Brenner. I do not think chlorine can be determined by spectrochemical means. We find that deposits from an all chloride bath contain certain amounts of chloride. In the deposit from the Watts bath, which is the softest, there is no detectable amount.

Question. You stated that there was no sulfur in the deposits from the Watts bath. Is that an absolute statement or relative?

Dr. Brenner. It is relative. We could not find any. Maybe somebody else can with more careful techniques.

Mr. E. J. Roehl, Thomas Steel Co., Warren, Ohio. Was that the sulfate bath for plating on zinc?

Dr. Brenner. It was simply a nickel sulfate with no sodium sulfate or anything else. Boric acid, yes.

Dr. R. J. McKay, International Nickel Co., New York, N. Y. In the curves that showed the relation between hydrogen and oxygen content and physical properties, did I read that correctly, that the weight percent of oxygen was something in the same order as hydrogen?

Dr. Brenner. The scales differed by a factor of 10. In other words, there was roughly that difference in the weight percent of oxygen and hydrogen. You would notice that on the ordinate.

Dr. McKay. So that it would not rule out OH. No, it would not entirely. It is possible that there could be a little free hydrogen in there to change the ratio.

Mr. H. Brandes, Sylvania Electric Products, Bayside, N. Y. I think from about 1931 to 1933 there was a series of papers on the properties of nickel. I remember they used the double sulfate solution and showed the correlation of mechanical properties, microstructure and hardness, and the pH and concentration of salts and current density. In the last of that series there is some speculating as to the mechanism whereby the variables influence the results as they do. As I remember, the pH of the cathode films was one of the determining factors.

In your work where you froze the cathode and machined off, would you tell us about that, how you attempt to tie these things together?

Dr. Brenner. There may be some relation. In only one instance did we attempt that. We had the result that at a low current density from an ordinary Watts bath, we obtained a harder deposit than we obtained at a normal current density of 5 amp/dm^2. We were surprised at that and measured the pH of the cathode film, believing that the low current density might have caused an increase in pH, but it was about the same in both cases.

Mr. Brandes. How carefully was the solution purified?

Dr. Brenner. I would say that all the solutions were very carefully purified by very long electrolysis and other procedures.

Dr. G. E. Gardam, Design and Research Centre, London, England. May I comment on that, sir? In reference to the last speaker, it seems to me that McNaughtan and Hothersall's findings and Dr. Brenner's much more careful one are in agreement. Dr. Brenner is more careful, and he says, "It does not matter but it may well be absorption." He has shown by analysis that the impurities are there so the two things tie up very well.

Dr. Brenner. I think that is quite correct. As a matter of fact, we have plotted some of those curves along with our own to show agreement, and there was only one curve that showed a discrepancy.

20. Disposal of Cyanide Wastes From Plating Operations*

By Barnett F. Dodge,[1] Charles A. Walker,[1] and Walter Zabban [1]

This paper represents a summary of reports on experimental investigations of methods of disposal for electroplating wastes containing cyanides. These investigations are being sponsored by the American Electroplaters' Society for the purpose of providing the electroplating industry with unbiased information on the most economical methods of treating its wastes to avoid pollution of surface and ground waters and deleterious effects on sewer lines and sewage-disposal plants.

Plating wastes containing cyanides were selected for the first phase of this research program because (a) they are used in numerous plating procedures, (b) they are highly toxic, (c) methods of disposal, as reported in the literature, have not been completely investigated, and (d) independent reports on certain disposal methods are frequently conflicting.

The actual research on methods of disposal for electroplating wastes containing cyanides was preceded by an extensive laboratory program [1] [2] for the purpose of selecting methods of analysis for cyanides and cyanates that would be adequate and reliable for the concentration ranges to be investigated. The analytical investigations were undertaken in cooperation with Research Project 2 at Lehigh University. This research project is engaged mainly in developing or adapting methods of analysis for constituents in plating baths.

In the above analytical research program, staff members of both Projects 2 and 10 tested and modified known methods of analysis to be used for the determination of cyanides and cyanates in the presence of such constituents as are found in waste solutions or effluents from electroplating operations. On the basis of these investigations, some micro- and macro-methods of analysis were chosen as being the most reliable of the methods investigated.

The following methods of disposal of cyanides and metal constituents of cyanide plating solutions have been investigated to date:

(1) The oxidation of cyanides and cyanates by treatment with chlorine or chlorine compounds (sodium hypochlorite, calcium hyprochlorite).

(2) The oxidation of cyanides by treatment with ozone.

(3) The oxidation of cyanides by treatment with oxidizing agents other than those given in (1) and (2).

(4) The conversion of cyanates to ammonia by acid hydrolysis.

(5) The removal of cyanides from plating solutions by batchwise acidification and aeration.

(6) The application of ion exchange to the problem of removing cyanides and metallo-cyanide complexes from rinse waters, followed

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*Presented by Dr. Donald Foulke, American Electroplaters' Society, Jenkinstown, Pa.

[1] Department of Chemical Engineering, Yale University, New Haven, Conn.

[2] Figures in brackets indicate the literature references on p. 121.

by recovery of the cyanides in a more concentrated form which might be reused in plating.

(7) The removal of cyanides by forming insoluble complexes with some metallic ions.

(8) The removal of cyanide by continuous acidification and continuous stripping with air in a packed tower (currently being investigated).

The removal of cyanides and the recovery of the metals by electrolytic oxidation will constitute the next topic for research. It is believed that this method of disposal of cyanides, together with the above-mentioned methods, will complete the phase of research concerned with cyanide solutions.

All the above methods will be compared from an engineering point of view to assist the electroplater in the selection of a method of disposal that will be best suited to his needs.

The next research topic will be concerned with the removal of the hexavalent chromium ion from chrome plating and anodizing bath waste solutions.

Before beginning a discussion of the above-mentioned methods, it should be added that they are directed toward the removal of toxic substances to obtain a final concentration that is considered to be nontoxic. There is lack of agreement as to what these values should be. The allowable concentrations and distances from the point of discharge in a public waterway where such concentrations should be observed seem to vary from State to State.

It would be difficult to give reliable figures on threshold toxic concentrations because the latter vary with different types of aquatic living organisms and are affected by temperature, pH, dissolved oxygen content, and the presence of other ions. We will consider here that the maximum allowable concentrations are about 0.1 ppm for cyanide and about 0.1 to 0.2 ppm for copper and zinc.

1. *Treatment of Cyanide Wastes with Chlorine and Hypochlorites* [2]. Cyanides in aqueous solutions may be oxidized by hypochlorites in two stages, first to cyanates, then to carbon dioxide, nitrogen, and some nitrites and nitrates. The removal of cyanide is complete (less than 0.1 ppm of total CN in the treated solution). By hypochlorite is meant a material such as chlorine, sodium hypochlorite, or calcium hypochlorite, which will make available the hypochlorite ion in an aqueous solution.

The oxidation of cyanides to cyanates is usually very rapid (less than 5 minutes), whereas that of cyanates is very slow at basic pH values (see fig. 20.1), requiring sometimes several hours for completion and very rapid (less than 5 minutes) at somewhat acidic pH values (6.5 to 6.8).

The reagent requirements are 2.73 lb of available chlorine per pound of total CN for the first stage of the oxidation and 7.3 to 7.6 lb/lb of total CN for complete oxidation beyond the cyanate stage. If oxidizable metals are present, a larger amount of hypochlorite reagent must be used. An additional 0.51 lb of available chlorine is used per pound of monovalent copper, and an additional 2.2 lb of available chlorine is used per pound of nickel. These and other metals present in plating baths are precipitated by the hypochlorite treatment in the form of oxides, hydroxides, carbonates, or chlorides.

The pH of the solution being treated should be kept above 10.0 for the first stage of the oxidation, that of cyanide to cyanate, to avoid

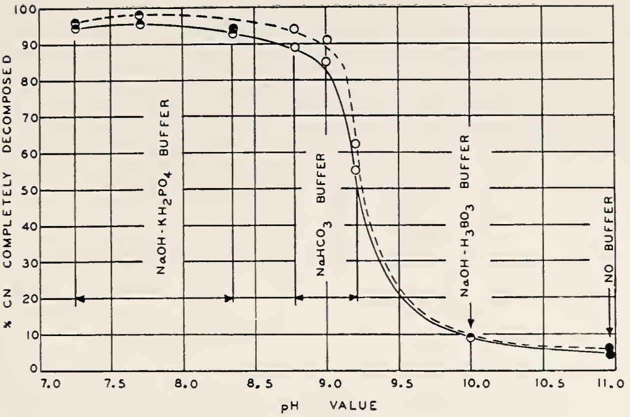

FIGURE 20.1. *Effect of* pH *on the rate of oxidation of cyanides in aqueous solutions, 100 ppm of total* CN, *to carbon dioxide and nitrogen.*

Ratio of reagent to reactant: 8.2 lb available CL_2 per pound of CN. Temperature, 28° C; ○, $NaHCO_3$ buffer; ●, no buffer used; ◒, KH_2PO_4-NaOH buffer. Time: ———— ½ hour; — — — — 1 hour.

volatilizing toxic quantities of cyanogen chloride. If chlorine is used, an alkali metal hydroxide or lime must be added to maintain the pH value above 10.0. These reagents do not have to be used with sodium hypochlorite. The presence of nickel slows down even the first stage of the oxidation and requires the use of a relatively large excess of reagent (20%) to speed up the reaction instead of the usual small excess (less than 1%).

Ferro- or ferri-cyanides are not oxidized appreciably by hypochlorites.

The laboratory investigations and some work with 75-gallon batches have indicated the importance of providing adequate agitation during treatment of cyanide wastes with hypochlorites or chlorine. Unless sufficient agitation is provided, there will be a tendency for the metallic cyanides to precipitate without reacting with the hypochlorite ion and to go back later in solution. This condition is likely to be dangerous because tests (after the oxidation) on the bulk of the liquid will show the presence of excess available chlorine and lead to the conclusion that the oxidation of cyanide to cyanate is complete.

It is believed that the presence of excess available chlorine should be used more as an indication that the "free" cyanide has been oxidized rather than the "total" cyanide.

2. *The Removal of Cyanides by Batch Ozonation* [3]. Ozone is a gas with an oxidizing potential second only to that of fluorine. The rapid recent strides in the manufacture of ozonators have made it possible to produce ozone in "tonnage quantities," thus reducing its cost to a level where it may compete from an economic point of view with some of the most common commercial oxidizing agents. Ozone may be manufactured from either air or oxygen in a dilute mixture containing about 1 to 2 percent of ozone. Because of its instability, it must be manufactured wherever it is used. Ozonators with varying capacities are commercially available.

The oxidation of the free and complex cyanide ions by ozone results in the formation of cyanates and insoluble metal oxides or hydroxides. This reaction is very rapid if catalyzed by such ions as copper and manganese. The oxidation beyond the cyanate stage is so slow that a great percentage of the ozone may leave the solution unreacted.

The pH does not seem to have a detectable effect on the first stage of the oxidation within the pH range of 7 to 12.5. The ozone requirements varied in these investigations between 0.60 and 0.87 mole of ozone per mole of cyanide (CN) for the oxidation of cyanide to cyanate, indicating that this reaction may be of an intermediate type between that which uses one atom of oxygen and that which uses the whole ozone molecule.

3. *Treatment of Cyanides with Other Oxidizing Agents.* Other oxidizing agents, such as permanganates and peroxides, have been used by different investigators [4] without satisfactory results. Some attention was given by the authors to the possible use of the hexavalent chromium ion to oxidize cyanides. Hexavalent chromium could be obtained from chrome plating and anodizing bath waste solutions.

A method using such an oxidizing agent would be inexpensive because it would treat the chromium waste as well, the hexavalent chromium being reduced to trivalent chromium, which is relatively nontoxic and can be removed by precipitation as the hydroxide.

It has been found, however, that hexavalent chromium does not oxidize cyanide over a pH range of 3 to 10 between 20° and 60° C. It is believed that this is a case where the rate of oxidation is extremely slow because this reaction would be expected to take place on the basis of the oxidation potential of the hexavalent chromium ion.

4. *The Conversion of Cyanates to Ammonia by Acid Hydrolysis* [2]. The removal of cyanates by oxidation, as shown above, may suffer from the disadvantage of slow reaction or, in the cases where the reaction can be accelerated by proper control of the pH, the reagent requirements may be considerably higher than those for the oxidation of cyanide to cyanate only.

Although cyanates are supposed to be about one-thousandth as toxic as cyanides, the attention of some recent antipollution regulations has been directed toward the removal of such compounds from waste products prior to their disposal into public waterways. A simpler and probably more economical method of treatment for cyanates in aqueous solutions is acidification with either mineral acids or acid reagents, such as sodium bisulfate. Cyanates are rapidly hydrolyzed by acids into ammonia. The ratio of reagents necessary for completion of the reaction is stoichiometric (½ mole of H_2SO_4 or 1 mole of $NaHSO_4$ per mole of cyanate), unless the solution is very dilute (less than 200 ppm of CNO), and in this case more than the stoichiometric amount of acid reagent must be added to lower the pH value of the solution to about 3. The time of reaction is about 15 to 30 minutes at room temperature and may be decreased by raising the temperature of the solution being treated.

5. *Stripping of Hydrogen Cyanide by Batch Acidification and Aeration* [5]. The batch-volatilization method of disposal may be effected in two ways: (1) by impounding cyanide waste solutions in large shallow ponds, and (2) by acidifying the waste solution to a pH value at which most of the cyanide (CN) is present as hydrogen cyanide, and accelerating the evolution of the latter by aerating the solution or passing steam through it. Method (1) has been practiced for many years but might not be used in the future because of many obvious disadvantages. Method (2) might be acceptable, provided that the escaping cyanide-rich air is properly diluted to con-

tain nontoxic concentrations of HCN or is continuously absorbed in a caustic solution. Other factors, such as the size of the electroplating establishment, may have considerable bearing on the adoption of such a method.

A correlation was developed to include the effect of the following main variables in the batch aeration of acidified cyanide solutions: Temperature, time, and the rate of aeration.

The correlation is

$$\log_{10}\frac{C_0}{C}=k\theta,$$

where

$$k=(1.77\times10^{-3}Q+0.04)\left[1+\frac{0.113}{Q^{0.19}}(t-78)\right]$$

C_0=initial concentration of hydrogen cyanide in ppm
C=final concentration of hydrogen cyanide in ppm
θ=time, in hours
Q=air flow in cubic feet per cubic foot of solution per hour
t=temperature in °F.

This equation was verified in measurements, using laboratory-size equipment for the ranges of Q between 50 and 1,400 and of temperature between 78° and 144° F. Calculated values for residual cyanides were found to be in fair agreement with those obtained experimentally with 75-gallon batches of solutions (see fig. 20.2).

6. *Treatment of Cyanides by Ion Exchange* [6]. The removal of cyanide from rinse waters by ion exchange is probably economically feasible only if the simple and metallo-complex cyanide ions, which are adsorbed by exchange on the ion-exchange resin, can be recovered in a reasonably concentrated form and reused in a plating bath.

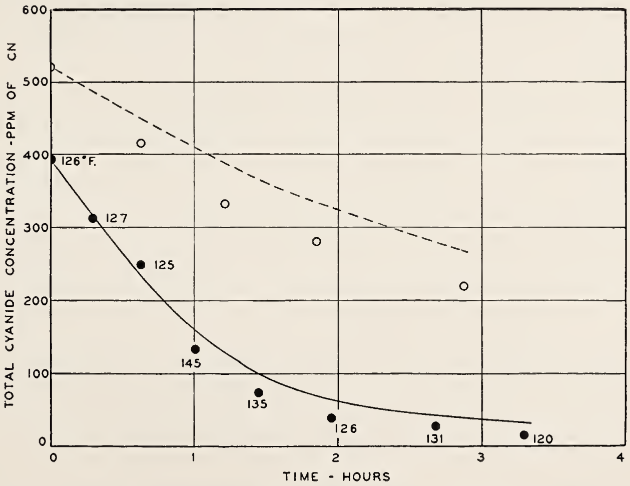

FIGURE 20.2. *Batch acidification and aeration of dilute cyanide zinc-plating solutions.*

Curves are based on calculated values. Points are experimental values. ○, Temperature, 78° F; volume of solution, 4.3 ft³. Q=34.8 ft³/ft³-hr. $2<\text{pH}<3$. ●, Average temperature, 130° F; volume of solution, 6 ft³; Q=25 ft³/ft³-hr. $2<\text{pH}<3$.

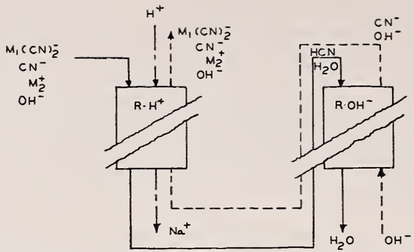

FIGURE 20.3. *Treatment of a metallic cyanide solution with a cation and an anion exchange resin placed in series.*

————, Exhaustion cycle; — — — —, regeneration cycle; —— — ——, regeneration cycle; M, metallic cation.

The limited number of investigations on the removal of cyanide by ion exchange, which have appeared in the literature only recently, seem to give the impression that the use of ion exchange in the treatment of dilute cyanide solutions does not give encouraging results. However, it should be noted that the resins used by the investigators have been definitely inferior to some of the newer resins that have been developed recently and are available in commercial quantities.

The general ion-exchange scheme selected by the authors on the basis of experimental investigations is one consisting of a strongly acid cation exchange resin (hydrogen type) placed in series with a strongly basic anion exchange resin (hydroxyl type) (see fig. 20.3). In the cation exchanger the sodium or potassium ion in the solution is replaced by the hydrogen ion from the resin. The hydrogen ion unites with the free cyanide ion forming the hydrogen cyanide molecule. This exchange of ions is accompanied by a lowering of the pH to about 3. At this pH value the metallo-cyanide complex is at first decomposed into metal cyanide and hydrogen cyanide, then the metal cyanide is decomposed into metal ion and hydrogen cyanide. The metal ion is then adsorbed on the resin by exchanging with the hydrogen ion.

The effluent from the cation exchanger consists of a dilute hydrocyanic acid solution. By passing through the anion exchanger, the HCN is split into H ion and CN^- ion. The latter replaces the hydroxyl ion on the resin and is therefore adsorbed. The H^+ ion in the solution is neutralized by the displaced OH^- ion so that the resulting effluent is practically demineralized water with a neutral pH.

The cyanide and metal ions can be regenerated in such concentrations (5,000 to 30,000 ppm) that they can be reused in plating baths.

The regeneration is usually done by passing a sodium or potassium hydroxide solution (4 to 10% by weight) through the anion and then the cation exchanger. The latter must be regenerated again with either a hydrochloric or sulfuric acid solution (4 to 10% by weight) to change the resin to the hydrogen form so that it may be reused.

7. *Removal of Cyanides by Complexing.*—Among the possible complexing methods that result in the formation of very insoluble double metallo-cyanide complexes, the treatment of cyanide solutions with ferrous sulfate to form an insoluble ferrocyanide complex was been used over a period of years on a commercial scale in few installations in this country and more widely in Great Britain, but it seems to have been superseded by the oxidation method involving the use of hypochlorites.

This particular phase of research was conducted by Brace [7] under an AES Research Fellowship. A sodium cyanide solution was used for most of the investigations. The main variables investigated were ratio of reagents, cyanide concentration, temperature, pH, and time of reaction. Solutions containing 100 to 10,000 ppm of total CN were treated.

It was found that if it was desired to remove only the "free" cyanide content of the solution, i. e., the toxic form of cyanide, an iron/cyanide molar ratio of 0.25 could reduce the "free" cyanide content of sodium cyanide solutions from 100 to 1,000 ppm of CN to 0.5 to 1.0 ppm, whereas an iron/cyanide molar ratio of 1.0 was needed to reduce the total cyanide content to 3 to 10 ppm of CN. A higher ratio of iron to cyanide such as 2.0 did not seem to have any more effect on the residual total cyanide content than a ratio of 1.0.

The reproducibility of these results was poor perhaps because of the colloidal nature of the insoluble product, hence the inability to separate by filtration either all or the same amount of the solids from the supernatant liquid.

The final conclusion was that the above method did not remove the total cyanide "completely" and that a considerable amount of sludge formed as a result of the reaction. This sludge would have to be impounded, and unless it were dewatered and kept dry, it might decompose under the effect of light liberating toxic quantities of cyanides, as reported in the literature [8].

Acknowledgment is due to Henry B. Smith, R. Wallace & Sons, Mfg. Co., F. J. Holt, E. I. du Pont de Nemours & Co., D. Milne and L. A. Danse, General Motors Corp., M. A. Orr, International Silver Co., and C. F. Gurnham, Department of Chemical Engineering, Tufts College, who, as members of the Project Committee, gave valuable assistance to this project.

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[1] B. F. Dodge, R. B. Freeman, E. J. Serfass, and W. Zabban, Quantitative determination of cyanides and cyanates in plating solutions and effluents from electroplating operations, Plating **39,** 267-73 (1952).

[2] B. F. Dodge and W. Zabban, Plating **38,** 561–566, 571–586 (1951).

[3] C. A. Walker and W. Zabban, Batch ozonation of cyanides (to be published in *Plating*).

[4] B. F. Dodge and D. C. Reams, Plating **36,** 463–469, 512, 571–577, 664, 723–732 (1949).

[5] B. F. Dodge and W. Zabban, Batch volatilization of cyanides, Plating **39,** 1133–39; 1235–44 (1952).

[6] C. A. Walker and W. Zabban, Treatment of cyanides by ion exchange (to be published in *Plating*).

[7] D. G. Brace, Treatment of cyanides with ferrous sulfate and alkalies (AES Monthly Reports, unpublished).

[8] G. E. Burdick and M. Lipschuetz, Trans. Am. Fish Soc. **78,** 192–202 (1948); Water pollution abstracts **23,** No. 12, Abstract No. 1526 (Dec. 1950) (Gt. Brit.)

Discussion

Dr. G. E. Gardam, Design and Research Centre, London, England. May I ask a question? Are you not in the difficulty that when you wash back you have the same problem of getting rid of the cyanide? What do you propose to do about it?

Dr. D. G. Foulke, American Electroplaters' Society, Jenkintown, Pa. I have felt all along that that was a problem. Actually, I am not on that committee. I don't know how far it has gone nor how far it has been discussed.

Dr. L. Gilbert, Rock Island Arsenal, Rock Island, Ill. In answer to Dr. Gardam's question about what to do about the return wash water from the exchange units, there are a number in existence today that are being used to reclaim precious metals. In addition, we have found that cyanide may be recovered in usable form and flushed directly into the tank to replace drag-out losses. It is a good method for handling wastes from small units where it is not economically feasible to set up a large disposal plant. The lowest cost disposal plant of which I know at the present time, on the oxidation plan costs in the neighborhood of $40,000. Obviously, the small job-shop plater cannot afford that, whereas with the simple exchange unit he can recover the metals without too much difficulty, as well as the cyanide.

21. Current and Metal Distribution in Electrodeposition[1]

By John Kronsbein [2]

This paper is based mainly on certain phases of the American Electroplaters' Society Research Project 11 that are not scheduled for publication in *Plating*. The project committee felt that some of the theoretical aspects are not suitable for immediate presentation to electroplaters because the experimental results require further confirmation before they can be accepted. Nevertheless, they appear interesting and challenging.

A search of the literature revealed that many arrangements of anodes and cathodes in electrolytic cells have been studied by mathematicians and physicists in connection with electric-potential distribution, ignoring polarization, and the results are available for the study of current and metal distribution by suitable mathematical transformations. Until Charles Kasper of the National Bureau of Standards considered the problem, electroplaters in general ignored these mathematical presentations. In addition to his general studies, Kasper [3] has worked out one new case in detail when polarization effects are included, one having been previously published.

Theoretically, there are eight possible arrangements of one anode and one cathode, so that the current distribution on the cathode is uniform, but only six of these have practical utility. It is not known whether cases exist where cathode-current distribution, ignoring polarization, may be made uniform over the entire surface by using an array of a finite or infinite number of anodes in a finite or infinite tank. No attempts to prove or disprove this have been made by mathematicians or physicists. It is not difficult, however, to construct cases where no arrangement of anodes will produce complete uniformity of current density; the case of a sharp angle-shaped cathode with one or more anodes in a finite or infinitely long tank being an example. Similar remarks apply to cases where polarization effects enter, as long as these are limited to the so-called linear polarization, i. e., polarization proportional to current density as used by Kasper.

A new theoretical case was developed during the present investigation where the angle-shaped cathode with finite shank length is plated in an arrangement approaching an infinitely large tank and an infinitely distant anode. The formula for current distribution on the cathode was explicitly derived. In the corner of the angle, the current density tapers to zero, even if polarization is taken into account, and on the outside corner, as well as on the ends of the shanks, it is infinite.

An interesting relation concerning deposited-metal distribution was evolved.[4] This states that if q is the fraction of 360 degrees repre-

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[1] Presented by Dr. R. A. Schaeffer, Cleveland Graphite and Bronze Co., Cleveland, Ohio.
[2] Evansville College, Evansville, Ind., and Chicago University, Chicago, Ill.
[3] C. Kasper, Trans. Electrochem. Soc. 78, 131, 147 (1940).
[4] J. Kronsbein, to be published in *Plating*.

sented by the outside angle of such a cathode, so that $2\pi(1-q)$ is the inside angle in radians and $2\pi q$ the outside angle in radians, then the fraction of total deposit on the outside is

$$D_0=1-[1/\pi]\cos^{-1}(2q-1),$$

and the fraction of total deposit on the inside is

$$D_i=[1/\pi]\cos^{-1}(2q-1)=0.3183\ \cos^{-1}(2q-1).$$

Table 21.1 shows comparison between experimental results and theory, as represented by the above relationship in the case of an acid copper-sulfate bath.

TABLE 21.1. *Percentage of deposit on the outside of an angle specimen*

Angle aperture	Measured outside deposit		Theoretical outside deposit
	Inside-corner radius 0.008 in.	Inside-corner radius 0.060 in.	
	%	%	%
135 degrees	60.8	62.1	
	58.0	56.8	
	57.4	58.2	
Average	58.7	59.0	58.1
90 degrees	70.0	66.2	
	68.9	68.6	
	68.3	63.7	
Average	69.1	66.1	66.7
45 degrees	76.5	75.2	
	78.5	79.0	
	80.5	81.0	
Average	78.5	78.4	88.4

These theoretical equations were developed for a perfectly sharp corner, both inside and outside, and because the actual specimens had small, irregular fillets, some departure is to be expected.

The experimental work of Project 11 to date has been limited to angle-shaped cathodes with various corner fillets. Two different cathode assemblies have been experimentally evaluated. The first arrangement consisted of a single angle-shaped cathode, insulated on the top and bottom, with the metal deposited over the entire surface and with a tank and anode assembly approaching infinite distance with respect to the cathode. The second arrangement employed the uniform-current-density cell[5] modified to accommodate an angle-shaped cathode, so that it was entirely surrounded, including its edges, with an insulator. Because this cathode assembly gives uniform metal distribution on a flat plane in a conventional plating setup, any metal-distribution variation on the angle-shaped specimens, therefore, is directly related to cathode geometry. Only the inside of the angle was plated and studied in this cell. The theoretical aspects of the angle-shaped cathode is not altered by these insulators. Because the experimental results obtained from this second arrangement are the most consistent, they are scheduled for early publication as part of Project 11, and, therefore, will not be discussed here. It may be

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[5] J. B. Mohler and R. A. Schaefer, Monthly Rev. Am. Electroplaters' Soc. **34**, 1361 (1947).

mentioned, however, that the measurements support the theoretical results obtained, i. e., that as a first approximation, current density at a fillet is related to the radius of the latter by the equation: current density is proportional to $R/12$, where R is the radius. A second approximation would be hyperbolic, with 1/12 representing the slope of the asymptotes. The low value of this slope was somewhat surprising, because it implies that only a small increase in deposit thickness in a corner will result from increasing the fillet radius, providing the original fillet is small.

The experimental results verified theory, even though some polarization was present in the actual solutions used. It was thought that this effect would be much larger than was actually found to be the case.

Figures 21.1 and 21.2 show the effect of fillet radius for Watts nickel baths with 5.2 and 2.3 pH, respectively, at different current densities. The temperature was 122° F. It will be observed that polarization effects increase with increasing current density. The curves seem to converge to one point with increasing fillet radius. This is to be expected because ultimately the fillet will tend to reach the edge of the angle. Because these graphs are for a single-angle cathode in the tank, with no insulation along the edges, polarization will be reduced at the edges. The theoretical current density at the edges is infinite,

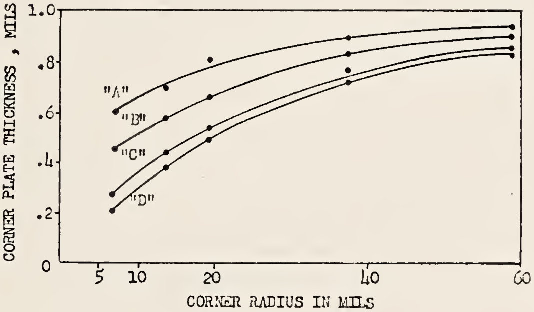

FIGURE 21.1. *Thickness of nickel deposited on a corner.*
pH of bath 5.2. A, 10 amp/ft²; B, 20 amp/ft²; C, 40 amp/ft²; D, 60 amp/ft².

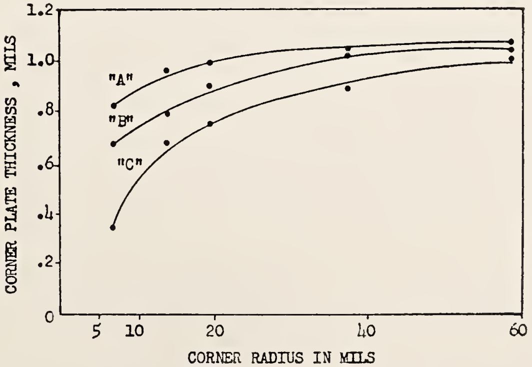

FIGURE 21.2. *Thickness of nickel deposited on a corner.*
pH of bath 2.3. A, 10 amp/ft²; B, 20 amp/ft²; C, 40 amp/ft².

both when there is polarization and when there is not, but the rate of increase is less under polarizing conditions.

Some preliminary work with radioactive tracer copper, Cu^{64}, was done to determine deposited-metal distribution. It was found to be an extremely sensitive method. This work was reported at the AES convention in Boston, 1950.[6] It is suggested that the autoradiographic method, especially using stripfilm, will prove very useful for future studies.

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[6] J. Kronsbein, Proc. Am. Electroplaters' Soc. **37,** 279 (1950).

22. A New Degreasing Evaluation Test: The Atomizer Test[1]

By H. B. Linford [2]

Project 12, Cleaning and Preparation of Metals for Electroplating, sponsored by the American Electroplaters' Society, was established at Columbia University beginning in the fall of 1949. It was decided at the outset to concentrate on one phase of this problem, namely, degreasing. However, it was obvious from the literature that the entire field needed a critical survey with definite recommendations as to proper testing procedure.

So far, considerations of inorganic films, including oxide films, have not been emphasized, and it can be stated that they have been ignored except where the presence of oxide would affect either the soiling of the panel or the operation of the degreasing-evaluation test under consideration. At the outset, it was decided that mild matte-surface steel would be a satisfactory material to use in this study, and, therefore, all results reported to date have been on that basis material.

Reproducible cleaning and soiling procedures could not be developed with rectangular panels drilled near the top to allow inert hooks to be employed for handling, as previous investigators have done, because of nonuniform drainage from the surface. Therefore, a new sample design was evolved consisting of a central rectangular portion 2 in. wide, 3 in. long, with a tongue ½ in. wide and approximately 3 in. long at the top, and a triangular section at the bottom. The triangular section effectively eliminates the ridge or roll of fluid that normally forms at the bottom of a rectangular plate. The tongue was left in order to enable the operator to handle the specimen without contamination. Contamination from handling could be still further reduced by introducing an S bend in the tongue, thereby making it impossible for any condensates gathering on the brass clips used to support the specimen to flow down over the test-panel surface. All results are reported on the central 2- by 3-in. rectangular area. These panels were all cut with a precision shear, which leaves edges free of burrs. All cleaning and rinsing was carried out in containers suitably designed for overflow in order that the surface of the liquid might be skimmed free of oils or greases. Because this project is primarily concerned with degreasing evaluation, no extensive study of cleaner formulation has been made, and for the purposes of this research, the following cleaner was arbitrarily chosen as a representative alkaline degreasing bath:

Sodium orthosilicate (Na_4SiO_4)	85% by weight.
Sodium carbonate (Na_2CO_3)	10% by weight.
Wetting agent (Nacconol-NR)	5% by weight.

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[1] This report based on the following publications:
H. B. Linford and E. B. Saubestre, Plating **37**, 1265–1269 (1950); **38**, 60–65, 254 (1951); **38**, 158–166 (1951); **38**, 367–375 (1951); **38**, 713–717 (1951); **38**, 847–855 (1951); **38**, 1157–1161 (1951). Also, unpublished progress reports.

[2] Columbia University, New York, N. Y.

The solution was used in a concentration of 6 oz/gal (45 g/liter). The procedure followed in cleaning and soiling the specimens is illustrated in table 22.1.

In the course of the study of the currently used degreasing evaluation tests, it became obvious that the wettability type of test should be the simplest. Therefore, considerable attention was given to the study of existing tests. In the course of this study, it was observed that areas that appeared to be clean by the water-break test would appear soiled if the sample is allowed to dry and then be sprayed with water. It should be recalled that the spray-pattern test, as developed by S. Spring, is based on the water-break test, in which the panel is allowed to drain for a given period of time. The areas from which the water film has broken receive a coating of water droplets. If, however, the panel is dried completely and then sprayed, it was shown that, if the sample is clean, a continuous film would form. However, if the sample is contaminated, the surface would be covered with a series of droplets. The details of the test, as developed, are as follows.

The equipment consisted of an ordinary atomizer.[3] The bulb was removed and the atomizer connected to the compressed-air line. The air enters a 5-gallon carboy, half-filled with distilled water, and goes thence to a tube filled with glass wool and an empty 2½-liter bottle, which acts as a surge vessel. Between the surge vessel and the atomizer, a glass tee is installed to allow a mercury manometer to be connected into the line. The solution used may be distilled water. However, it has been found that for the purposes of recording results it is desirable to add a dye.[4]

Table 22.1. *Soiling and cleaning procedure*

Process	Operation	Temperature	Time
		° *C*	*Min.*
(a) Precleaning	Waste cleaner	100	18[a].
	Water rinse	Room	5[a].
(b) Pickling	20%-acid dip	do	2.
	Water rinse	do	2.
(c) Solvent Treatment	Alcohol dip	do	2.
	Benzene dip	do	2.
(d) Soiling	Oil dip	do	5.
	Drainage in air	do	20.
(e) Cleaning	Alkaline cleaner	Variable	Variable.[a]
	Water rinse	Room	5.[a]
(f) Preparation for testing	1%-acid dip	do	1.
	Water rinse	do	2.[a]

[a] Overflow was employed. The time includes both the process and overflow time.

After the cleaning and rinse, the panels are hung in a vertical position in air at room temperature and allowed to dry completely in the central 2- by 3-in. portion of the panel. This normally requires 3 to 5 minutes. It is not necessary to wait for the water to evaporate from the lower triangular portion of the panel. Because, in general, oils do not spread on the water-wetted surface, and the elapsed time after drying is, in general, very short, only minor difficulties arise from the spreading of the oils during this portion of the test. The spraying is done at a pressure of 18 ±3 inches of mercury, at a distance of 2 feet. The total time for the spraying is approximately 30 to 45 seconds. If the spraying time is too short, the contrast between dirty and clean area

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[3] De Vilbiss No. 251 bulb atomizer of 15-ml capacity.
[4] 0.1% Niagara sky blue 6B conc. dye (National Aniline and Dye).

is vague. If the spraying time is excessive, water droplets build up and flow down the panel surface. This obscures the pattern. A little experience will indicate the desired time. As soon as the spraying has been completed, the panels are dried by a heat lamp placed about a foot away from the panels. This "freezes" the pattern for permanent recording, staining with a blue dye wherever there are water globules present. Where the uniform thin film forms, the dye is too diluted to leave much stain behind upon drying. The oil will spread during this operation as soon as the water globules have been evaporated, but this in no way affects the dye pattern.

The recording of the results is best done by first taking a pencil and outlining either the clean areas or the soiled areas, depending upon which is predominant, and, then, by means of a pantograph with a 2× magnification, record these areas on paper for a permanent record. The fundamental difference between the atomizer test and the water-break test is that the atomizer test depends upon the advancing contact angle of the water droplet, whereas the water-break test depends upon the receding contact angle of the water film. It has been clearly demonstrated in the literature that such a hysteresis exists. Any person observing water droplets rolling down a window pane will recall that the droplet does not maintain a symmetrical form, but that the advancing angle is considerably greater than the receding angle. From this consideration, it becomes obvious that the atomizer test should be superior. There is another phenomenon that occurs with the water-break test that also deserves mention, namely, the bridging effect. A small isolated droplet of oil on the surface of an otherwise clean metal will often, when flooded with water, not show any water-break due to the bridging effect in which the film remains continuous over this droplet. However, in the atomizer test, such a droplet would retard the advance of spreading of a water droplet, and would, therefore, show up as a soiled area.

The various degreasing evaluation procedures available are tabulated in table 22.2. In our sequential testing, the atomizer test is compared with the fluorescent-dye test, spray-pattern, ferricyanide and copper dip. It must be borne in mind that the spray-pattern test is simply a quantitative interpretation of the water-break test, and that the gravimetric test does not fit into the same pattern as these because it does not in any way give us a measure of the percentage of the clean area. So far in this project we have not investigated the

TABLE 22.2. *Degreasing evaluation tests*

Type	Name	References
Wettability	Water-break	Harris; Mankowich; Mantell; Nielsen; Spring, Forman and Peale.
	Spray-pattern	Spring, Forman, and Peale.
	Atomizer	Linford and Saubestre.
Tracer	Fluorescent dye	Morgan and Lankler.
	Radioactive	Harris and Kamp.
Chemical	Copper replacement	Hogaboom; Mankowich; Mantell; Tartakovskaya.
	Potassium ferricyanide paper	Brenner; Hothersall, and Hammond; Later; MacNaughton; Mantell; Strausser; Thon and Addison; Walker.
Miscellaneous	Gravimetric	Federal Specifications; Greulich; Mankowich.
	Residue-pattern	Mankowich.

radioactive-tracer technique, feeling that at the present time the cost of the test is such that the average plating shop could not afford to install it.

Table 22.3 gives an indication of the cleaning index as measured by these various tests on samples prepared in an identical manner. The relative sensitivity of these tests has been estimated from results obtained on samples cleaned as described above. However, in order to obtain more quantitative information, the method recommended by Devoe was employed. It must be borne in mind that oil residues remaining after alkaline cleaning are in the form of discrete droplets, whereas the Devoe method results in a nearly uniform distribution of the contaminant over the surface and, as would be expected, changes relative sensitivities somewhat. This method consists of evaporating solvents containing known amounts of oil on a given surface area. By progressively increasing the quantity of oil deposited on the surface, it is then possible to determine the minimum concentration, in terms of grams per square centimeter, that can be detected. The results of this study are given in table 22.4.

Table 22.3. *Sensitivity of degreasing evaluation tests*

Soil Cleaning conditions	Lard oil 70°C, 3 min	Lard oil 70°C, 10 min	Mineral oil 40°C, 3 min
Test	Cleaning index [a]		
Atomizer	9.5	23.1	41.0
Fluorescent dye	51.7	85.2	83.9
Spray-pattern	84.3	94.4	95.6
Ferricyanide	85.6	96.6	98.4
Copper dip	88.7	98.3	98.3

[a] Equals percentage of surface that appears to be clean.

Table 22.4. *Test sensitivity*

Test	Lard oil	Mineral oil
	g/cm ^{2}	*g/cm* ^{2}
Atomizer	6.5×10^{-8}	3.0×10^{-7}
Water-break	6.5×10^{-7}	9.0×10^{-6}
Fluorescent dye	2.5×10^{-5}	4.0×10^{-5}
Copper dip	3.0×10^{-5}	----------
Ferricyanide	3.0×10^{-5}	1.0×10^{-4}

As would be expected, the sensitivity is a function of the polish. Samples with an rms value of 33 (matte) were compared with polished samples[5] having an average or rms value of 0.66. The polished samples showed a sensitivity, for the most part, between two and three times greater than the matte surfaces for both lard and mineral oils.

Discussion

Mr. G. B. Hogoboom, Consultant, New Britain, Conn. I would like to ask whether the removal of the soil is not more dependent upon the composition of the cleaner. Is it possible to use the same cleaner for lard oil and for mineral oil? And unless you have a cleaner that is adaptable to each one, the comparison has little value.

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[5] These samples prepared through the courtesy of E. T. Candee, Lea Manufacturing Co., Waterbury, Conn.

Dr. H. B. Linford. Mr. Hogoboom, in answer to your question, we have meticulously avoided the problem of trying to determine which is the best cleaner. The comparison is made on residual quantities of lard oil and mineral oil on metal surfaces, and we were comparing as to which test can detect those residual quantities more sensitively.

Dr. L. M. Morse, Chrysler Corp., Detroit, Mich. I may have missed this in reading the article, but after the soiling of the panel, then the cleaning and then the acid dip, you dried it before you applied the atomizer test, is that right?

Dr. Linford. That is right.

Dr. Morse. How do you prevent rusting of the panel at that point?

Dr. Linford. You don't have to wait until the panel is dry. The last rinse of water will be at the base, and you can start the atomizer test going.

Dr. Morse. You feel it does not affect the wettability?

Dr. Linford. No.

Mr. Hogoboom, Consultant, New Britain, Conn. I would like to ask about the oxide film. Let us take nickel, for example. Of course, it is a different character of metal. Dry nickel, and you cannot plate it again. Keep it wet, and you can. Dry steel, and you may get an invisible oxide film. That has been brought out by Evans in his work. The mere fact that on a dry surface you cannot get precipitation of copper indicates that an oxide film is present.

Dr. Morse, Chyrsler Corp., Detroit, Mich. It seems to me that we are getting two things mixed, one the activation of the surface and the other the removal of oil from the surface. Dr. Linford is talking about the removal of oil.

Dr. Linford, Columbia University, New York, N. Y. That is correct.

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