Guide to the Selection and Use of ELECTRO-PLATED and Related Finishes

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GUIDE TO THE SELECTION AND USE OF ELECTROPLATED AND RELATED FINISHES

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Foreword

F. A. Lowenheim had nearly completed the final revision of *Guide to the Selection and Use of Electroplated and Related Finishes* at the time of his death in August 1980. Final review was undertaken by his colleagues, and the manuscript was prepared for the printer by the ASTM Editorial Staff. This manual is sponsored by ASTM Committee B-8 on Metallic and Inorganic Coatings.

Related ASTM Publications

Annual Book of ASTM Standards, Part 9, Metallic and Inorganic Coatings; Metal Powders; Sintered P/M Structural Parts, 01-009082-05

Unified Numbering System for Metals and Alloys and Cross Index of Chemically Similar Specifications, DS 56A (1977), 05-056001-01

Metallography—A Practical Tool for Correlating the Structure and Properties of Materials, STP 557 (1974), 04-557000-28

Ferroalloys and Other Additives to Liquid Iron and Steel, STP 739 (1981), 04-739000-01

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A Note of Appreciation to Reviewers

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ASTM Committee on Publications

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Chapter 1—Scope and Purpose

This guide aims to aid the designer, engineer, and others responsible for specifying finishes in the selection of appropriate electroplated and related coatings. It is not a manual of electroplating practice for the metal finisher, who will know how to apply the specified coating, but rather a guide to the available coatings and their methods of application.

The following definitions from ASTM Definitions of Terms Relating to Electroplating (B 374), slightly modified for editorial purposes, outline the scope of this guide.

Electroplating is the electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the basis metal. *Electrodeposition,* in turn, is the process of depositing a substance upon an electrode by electrolysis, which is the production of chemical changes by the passage of current through an electrolyte. An *electrolyte* is a conducting medium in which the flow of current is accompanied by movement of matter. Finally, an *electrode* (explained further below) is a conductor through which current enters or leaves an electrolytic cell, at which there is a change from conduction by electrons to conduction by charged particles of matter, or vice versa.

A few additional definitions from the same source will further define the scope of this guide. *Anodizing* is an electrolytic oxidation process in which the surface of a metal, when anodic (in an electrolyte[1]), is converted to a coating having desirable protective, decorative, or functional properties. (The process is usually applied to aluminum and its alloys; less often to magnesium, titanium, zinc, and a few other metals.[1])

A *conversion coating* is a coating produced by chemical or electrochemical treatment of a metallic surface that gives a superficial layer containing a compound of the metal; for example, chromate coatings on zinc and cadmium, oxide coating on steel. An *immersion plate* is a metallic deposit produced by a displacement reaction in which one metal displaces another from solution. *Autocatalytic plating* (popularly called *electroless* plating) is deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited.

To translate these formal definitions into more familiar terms: The process of electroplating consists in placing the articles to be plated (the "work") as cathodes in electrical contact with the negative pole of a source of direct cur-

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[1] The material in parentheses is not part of the definition.

rent, usually a rectifier, in an electrolytic solution (the "bath"), which is almost always a water solution of a compound of the metal being deposited. The circuit is completed by counter-electrodes (the anodes) hung at an appropriate distance from the work in the same bath. The electroplating setup therefore consists essentially of a tank containing the plating bath; means for hanging the work in the bath (racks) and connecting them to the negative terminal of a rectifier or generator; means for hanging anodes opposite to the work; the external circuit of bus bars or other conductors for conveying the current to the tank; and appropriate instrumentation, including ammeter, voltmeter, thermometer, etc. Much auxiliary apparatus may be needed, including heating or cooling coils, filters, and the like, to constitute a practical setup.

At the surface of the work the passage of the electrical current converts (reduces, in chemical terms) the metal from the dissolved compound in the solution to a metallic coating on the work.

Large numbers of small parts (for example, nuts and bolts) may be put into a barrel made of nonconducting material and containing electrical contacts through which the parts are in electrical contact with the power supply. The barrel is continuously rotated and thus continuously brings new parts to the surface of the load where they receive the electroplate.

Anodes are usually, but not always, made of the metal being deposited on the work. Under the influence of the electroplating current they dissolve in the bath and replace the metal deposited on the work.

Autocatalytic plating is accomplished by the use of chemical-reducing agents in the bath which convert the metal compound to the metallic coating. The process dispenses with the need for bus bars, rectifiers, electrical instrumentation, etc., but this economic saving may be more than offset by the higher cost of the chemicals required. Nevertheless, it is a useful and, for some applications, necessary process.

Immersion deposition depends on coating the work by a displacement reaction in which the substrate metal dissolves while the metal compound in the bath is reduced to the metallic state. It is of limited application but convenient where applicable.

Electroplating is not the only method of producing finish coatings on metals. Organic coatings, such as paints and lacquers, are perhaps even more widely used, including the electrodeposition of paint ("electropainting"). Also used are spraying of molten metal, vacuum metalizing, chemical vapor deposition (CVD), ion plating, and porcelain enameling. None of these methods is considered in this guide, except incidentally to compare some of them with electroplating with regard to their advantages and disadvantages. Also excluded is consideration of precoated metal stock such as tin-plate and galvanized steel, either electrolytic or hot-dipped.

The scope and possibilities of electroplating as a finishing method are wide and varied, but there are limitations. The material to be finished must be an electrical conductor or must be capable of being rendered conductive. The finish to be applied must be capable of being electroplated by established methods; not all metals can be electrodeposited, at least not by any commercially proved technique. In general, the article to be plated must be of such a size and configuration that it can be handled in a typical electroplating plant; that is, moved from one tank to another, and fitted into the available tanks. In certain cases some of these limitations may be overcome: special tanks may be built or the localized method known as "brush electroplating" may be employed.

Chapter 2—Purposes of Electroplating

Electroplated coatings are applied to metals for many reasons. The design engineer and others responsible for specifying finishes must know the purpose of the finish in order to specify it intelligently. Not only must the metal to be electroplated be specified, but also its thickness and often other properties specific to the use of the article. For example, gold can be applied as a coating so thin that it serves only to impart its characteristic color, merely for customer appeal, or its thickness can be sufficient to survive many years of use. Since most metals are expensive, and since the cost of an electroplated coating rises with its thickness, it is important to specify sufficient coating to serve the purpose but no more.

Electroplated and related finishes may be classified into three categories, according to their main function. Although these categories overlap, the classification is convenient.

Protective Coatings

When the function of the coating is to protect the basis metal and appearance is of minor importance, the meaning of the word "protection" must be understood. Its usual meaning and the one that will be understood in what follows, unless specifically modified, is protection against environmental corrosion as is undergone by many metals such as steel in seacoast, industrial, or rural environments; in other words, rusting, corrosion, and their equivalents. Other forms of protection, against specific environmental degradation, may be important but should be detailed for each case.

As protective finishes, electroplated coatings compete with organic finishes and porcelain enamels, as well as some others previously mentioned. The choice may sometimes be difficult, but usually other considerations will determine which type of finish to use.

Decorative Coatings

Electroplated finishes may be used to improve the appearance and thus the marketability of an article. This appearance must be maintained for a reasonable time, so in most cases some protective function is also involved. For example, automobile bumpers would probably fulfill their function even if rusty, but the appearance of the car would be unsatisfactory to the consumer; thus the plated finish must protect the basis metal as well as maintain its own luster. There are a few examples of purely decorative finishes, with no protective function, but most so-called decorative finishes might better be called decorative/protective.

Engineering Coatings

Electroplated finishes may be used to modify the chemical or physical properties (other than strictly appearance) of the surface, or to change the dimensions of the article. This is a broad, heterogeneous classification; it includes improvement of bearing properties, solderability, wearability or abrasion resistance, building-up dimensions of worn or mismachined parts, modification of hardness and reflectivity, and much besides. Clearly there is no all-purpose coating for such applications and each case must be considered individually. Coatings in this category are often called "functional", but "engineering" seems preferable since improvement of protection and appearance are also "functions".

Chapter 3—Metallic Finishes Available for Electroplating

Of the 92 elements in the periodic system (excluding the trans-uranium elements) 73 are metals; of these, only about 16 are available as electroplated finishes (the number is somewhat more if alloys are included).

The electroplateable metals may be classified as follows:

(1) Commonly electroplated, from solutions that are well established and present few problems to the qualified electroplater.

(2) Can be electroplated readily, but have found few uses and accordingly have not been thoroughly tested commercially.

(3) Probably can be electroplated but, because of lack of commercial utility and proved processes, will probably call for some preliminary experimentation based on published literature.

(4) Cannot be plated from water (aqueous) solution, but have been applied semicommercially by processes based on molten salt baths or organic solvents.

To the designer or engineer choosing a coating, these classifications translate to:

(1) These metals are widely used, job platers can easily be found to apply them, and there will be few problems in setting up in-house facilities.

(2) Few job platers are prepared to provide the necessary facilities, few supply houses offer technical service, and setting up in-house facilities may present problems.

(3) These are in the research stage and, although "beaker plating" has been reported, few or no commercial installation exists. Small scale or laboratory investigation will have to precede commercialization.

(4) These have been plated on a semicommercial scale, but the processes were proprietary and (it is believed) no longer operating. This group should not be seriously considered for finishing by electroplating unless a research program is thought to be warranted. The only metal commercially plated from organic electrolytes is aluminum, and this only by a very few specialists.

The metals in these groups are:

(1) Major metals, widely plated—copper, chromium, nickel, tin, gold, silver, zinc, cadmium.

(2) Minor metals, easily plated but not widely available from job platers—lead, palladium, rhodium, iron, indium, cobalt, platinum, rhenium. The first three could have been included in Group 1; the distinction is a fine one.

(3) Plateable, but not commercial—aluminum (a special case, since nonaqueous baths must be used; some facilities are available), antimony, bismuth, manganese, iridium, osmium, ruthenium.

(4) Not available (molten salt baths only)—tungsten, zirconium, niobium, tantalum.

Metals not included in any of these categories have been little investigated or results have been essentially negative.

Groups 3 and 4 will not be further discussed.

To this list is added the great number of alloys that can be deposited—some readily available, some rather specialized, and still others the results of experimental research ("beaker plating") and not yet commercialized.

Alloys commercially plated include: brass (copper and zinc, in almost any proportion); bronze (copper and tin, in almost any proportion but especially in the range of 10 to 20 percent tin); copper-cadmium (miscalled "bronze"); tin-zinc, especially in the range of 15 to 25 percent tin; tin-lead (in all proportions, and sometimes with a little copper); various gold alloys with many metals, with the purpose of modifying color or hardness; nickel-iron; nickel-cobalt; copper-tin-zinc; tin-cobalt (plus a small amount of a third metal); and tin-nickel. Not all are readily available from platers "off-the-shelf" but either are or have been commercially plated.

The number of possible alloys is almost unlimited. Several others may be mentioned as having had some serious investigation, but not commercialized to any extent. They are not further considered here, but include cadmium-zinc, nickel-zinc, silver-tin, tungsten-cobalt, tungsten-nickel, molybdenum-cobalt.

In autocatalytic plating of nickel, the deposits are usually nickel alloys, either nickel-phosphorus or nickel-boron. These will be considered in Chapter 10. Nickel-cobalt alloys are also produced by autocatalytic plating.

Fine particles can be incorporated in a metallic deposit during deposition. This can be for the purpose of modifying mechanical properties, particularly at high temperatures. Particles are sometimes added to nickel to induce microscopic porosity in a subsequent chromium layer. Addition of abrasive particles to a nickel deposit yields an abrasive finish.

Chapter 4—Advantages and Disadvantages of Electroplated Coatings

The designer and engineer have many means available for finishing a metal article; whether to choose electroplating or some other method may be determined, if the answer is not obvious on its face, by a consideration of the advantages and disadvantages of each method. Some pros and cons of electroplating are listed below.

Advantages

Electroplating is adaptable. It is usable on articles as small as tiny semiconductor parts and as large as the capacity of the electroplating facilities (for example, paper rolls for printing that are as much as 2 m in diameter and 4 m in length). With proper care, electroplating can be used on the inside of pipe and tubing and on continuous strip and wire.

The choice of coatings is large and composite (or multilayer) coatings are easily produced; copper, followed by nickel, followed by chromium, for example, is one of the most widely used finishes.

There are many shops set up to do the necessary work, in all parts of the country. Most of these shops are affiliated with trade and professional organizations such as the National Association of Metal Finishers (NAMF),[1] the American Electroplaters Society (AES),[2] and others, allowing them to keep abreast of the latest knowledge.

Electroplating is an old technology, continuously improving. Most of the staples of the trade—copper, nickel, etc.—have been used as coatings for many years and there is long background and experience in their use. Except for exotic coatings for very special uses, there is little of an experimental or uncertain nature about the results, provided, of course, that the practitioner follows recognized practices.

Electroplated coatings are, or can be, subject to rigid specifications, promulgated by ASTM as well as other associations and governmental bodies, and increasingly by the internationally recognized standardizing body ISO.

[1] 111 East Wacker Drive, Chicago, Ill. 60601.
[2] 1201 Louisiana Ave., Winter Park, Fla. 32789.

These specifications are based on expert opinion and experience with the coatings and how they perform.

Electroplated coatings, being metallic, do not interfere with electrical connections as do organic coatings and porcelain enamels. In most cases they do not change the characteristics of the basis metal. They are usually relatively thin (from less than a micrometre to approximately 25 to 50 μm) and do not cause significant dimensional change unless such change is specifically required.

Disadvantages

Electroplated coatings are not adaptable to all substrates, although most materials can be electroplated if proper preplating procedures are used.

Electroplates offer a limited choice of colors. Most metals are grey to silvery-white; exceptions are copper, gold, and their alloys. (But anodized coatings, considered in Chapter 10, can be dyed almost any color; a "black chrome" and a "black nickel" are available; and conversion coatings may be obtained in a limited range of colors.)

Large structures, after assembly, are plated with extreme difficulty or not at all—one would hardly attempt to plate a bridge (but see brush electroplating, Chapter 5).

Use of electroplated coatings imposes some restraints upon the design of the product if results are to be satisfactory.

Among the competing means of finishing articles that should be considered before deciding on electroplating may be mentioned metal spraying, vacuum metalizing, organic finishing, and porcelain enameling. Except for organic finishing, none is truly comparable to electroplating in results or application, and the choice will usually be obvious.

Chapter 5—Methods of Application

This chapter will not provide detailed directions for applying the plating metals. That is the province of the plater, not the purchaser or specifier of electroplated coatings. Nevertheless, the purchaser should have some elementary background in the general techniques and possibilities of electroplating, so that he can intelligently specify its results, and so that he will know what can be expected and what is impracticable.

Electroplating is carried out in a solution (almost invariably aqueous; that is, water-based) containing a chemical compound of the metal to be deposited. Direct current, transformed from the utility's alternating current by means of rectifiers or motor generators, is passed through this solution (called the bath by platers) from anodes (the positive electrodes) to the cathodes (the negative electrodes), which consist of the work to be plated as well as the means for positioning this work in the bath. Anodes are usually made of the metal being deposited. Under the flow of the electroplating current they dissolve, maintaining the metal content of the bath by replacing the metal plated out at the cathodes. Sometimes (always, with chromium plating) anodes are "inert"—that is, they do not dissolve in the bath but merely serve to introduce the current—and replenishment is by chemical means.

The cathodes, or work, can be placed in the bath in essentially two ways: they may be hung on racks individually or they may be loaded into a barrel. In rack plating, electrical contact to the part is made by the rack, which is in turn in contact with the cathode bus bar. Contact with the parts is preferably at points not important to the final appearance or performance of the article, since these contact points will receive little or no deposit. Racks may be more or less standard, or may have to be individually designed for the work at hand. If the latter, additional cost may be involved which the purchaser must usually bear.

Barrel electroplating is used with the many articles that are almost impossible to rack individually: screws, nuts, bolts, small electrical connectors and terminals, and the like. Such parts are placed in barrels of various types. The barrel is of a nonconducting material, usually a plastic, and contact with the parts inside is made with metallic danglers, buttons, or other means. Deposition occurs only on the parts that are on the outside of the load. The barrel is rotated in the electroplating bath, which induces the load to shift and to bring all the parts to the outside where they receive the coating. Intrinsically, therefore, barrel electroplating has statistical characteristics, and the coating thickness will vary more part to part than it does in rack electroplating.

The electroplating cycle includes a series of tanks and stations. These may vary according to the nature of the work being handled, the manufacturer of the equipment, the nature of the plating process, and other factors, but those listed below are fairly standard:

1. A racking or loading station where a worker hangs the parts on the racks.
2. Tanks containing cleaners to prepare the work for electroplating.
3. A pickling tank to remove the alkaline residue and residual oxides.
4. One or more electroplating tanks.
5. A final rinse tank, to remove as far as practicable the last traces of electroplating solution so that salts will not dry on the work.
6. Means for drying the work, by heat, compressed air, sawdust, or other.
7. An unracking station, where a worker removes the finished parts from the racks. This may precede instead of follow the drying operation.

Rinsing stations are provided between any or all of these steps.

For barrel electroplating, the steps are about the same except, that in place of racking, the barrel is loaded with the parts, and, instead of unracking, the barrel is emptied. Since barrels are usually heavy, they are generally handled mechanically; racks may be handled manually but most modern shops use mechanical equipment for these also. Racks and barrels may be moved through the electroplating cycle manually or mechanically, with almost any degree of automation including computer control.

Equipment size may range from large tanks holding many thousands of litres to containers hardly larger than laboratory beakers (for plating the precious metals).

The plating shop, in addition to the outlined equipment, must also possess filters, pumps, control means for the solution sent to waste, and other ancillary equipment which does not concern the present discussion.

Some characteristics of most plating solutions must be recognized by the purchaser so that he may specify more intelligently and aid the plater in producing a satisfactory product.

Parts to be plated must be clean. Cleaning is the responsibility of the plater, but the purchaser can help; some types of drawing lubricants and other soils introduced in fabrication are much more difficult to remove than others, and consultation with the plater before fabrication can save considerable money and prevent disagreements. Heavy mill scale and other gross contamination of the surface might well be removed by the manufacturer before delivery to the plater.

Parts submitted to the plater should be metallurgically sound and as free as possible from surface defects, scratches, pits, torn metal, and other faults.

Most plating specifications state that the plater is not responsible for plating defects resulting from these flaws in the substrate, unless special arrangements are made beforehand.

The purchaser should also be aware of some of the limitations of the electroplating process itself. In almost all rack plating some areas of the articles will be nearer to the anodes than others, and with most plating solutions these areas will receive more deposit than those farther from the anodes. Edges and projections will also receive more current (and deposit) than other areas. Blind holes should be avoided in parts to be plated.

The ability of a plating solution to produce deposits more uniform in thickness than would be expected over a shaped cathode is known as the throwing power of the solution, defined as the improvement in deposit distribution over the primary current distribution; the latter is the distribution of current dependent only on the geometry of the plating cell. Plating baths differ widely in this property. Chromium plating baths actually have "negative" throwing power; that is, high-current density areas receive even more deposit than would be expected from the geometry. Most nickel-plating baths have about zero throwing power, while most cyanide baths—copper, silver, cadmium, zinc—have fairly high throwing power, and stannate tin baths have perhaps the highest among the common plating solutions. The practical effect of these considerations is that, depending on the metal being deposited and the bath used, the designer must be willing to accept a fair degree of nonuniformity in the thickness of metal deposited on various areas of the parts. He should specify minimum allowable thickness on the "significant surfaces" of the article; if this entails excess deposit on other areas it will enter into the cost of the plating. The problem can be mitigated by judicious use of various expedients by the plater: conforming or bipolar anodes, and current robbers or shields, which divert some current from prominent areas or permit the deposit to "throw" into angles or recesses. These adjustments entail additional costs, again emphasizing the desirability of cooperation and consultation between the designer and the plater before the part is manufactured. It may often be just as easy and satisfactory to design a part that is easily plated with good uniformity as to design a difficult-to-plate part and face the plating problems later; certainly it will be cheaper.

When barrel plating such items as screws, in order to deposit sufficient plate in the bottom of threads, it will almost surely be necessary to apply excess plate on the tops. This must be allowed for if dimensional tolerances are close.

Since uniformity of deposit thickness over the surface of a part cannot usually be expected, it is important to specify those surfaces considered significant—that is, required for the proper operation or appearance of the part. Significant surfaces may be agreed upon by the manufacturer and the plater; they may be indicated on part drawings, or they may be defined, as in several ASTM specifications, as "those normally visible, directly or by reflection, which are essential to the appearance or serviceability of the article when assembled in normal position, or which can be the source of corrosion products that deface visible surfaces on the assembled article." Sometimes significant surfaces are defined as those that can be touched by a ball 19 mm in diameter; this recognizes the inability of most plating solutions to deposit specified thicknesses in recesses and holes. Regardless of how significant surfaces are defined, they must be agreed upon by the purchaser and the plater beforehand.

The other techniques mentioned in this guide—autocatalytic plating, immersion plating, conversion coatings, and anodizing—are not subject to quite the same limitations on coating thickness in recesses. Either they do not depend on the flow of current or, as with anodizing, the parts first coated become insulating and current is diverted to areas still uncovered. Nevertheless, in all cases fresh solution must have access to the area to be coated; blind holes or other small diameter openings may trap stagnant solution unless precautions are taken.

A third highly specialized method of electroplating is brush electroplating or selective electroplating. The term "selective electroplating" is also used with respect to various other electroplating techniques in which by masking or other approaches the metal is deposited in specific areas on a product. In brush plating, the electroplating solution is applied to the product by a swab that is wrapped around an anode, usually a carbon rod. The part is made cathodic and the current flow from the anode through the swab to the product causes deposition of metal wherever the swab is rubbed on the part.

Brush electroplating is used where it is impracticable or impossible to immerse the product in an electroplating tank: repair of damaged coating, deposition on only part of the product, coating of a part in an assembly, and coating products that are too large to be coated in any other way. The dome of the California capitol in Sacramento was gold plated by brush plating. In 1971 and 1972 the four larger-than-life equestrian statues in the Lincoln Memorial Circle in Washington, D.C. were stripped and replated first with 0.0005 in. of nickel and then with 0.00017 in. of gold by using brush plating.

Equipment and solutions for brush plating range from the sophisticated capable of producing high-quality deposits to simple and inexpensive kits of dubious quality.

An additional characteristic of electrodeposited metallic coatings should be recognized by the design engineer. Although most electrodeposited metals have the same crystal structure as thermally prepared metals, and electrodeposited alloys usually (with some exceptions) compare well with thermally prepared alloys in phase structure, these similarities may not apply to their densities and electrical or thermal conductivity. Most electrodeposited metals are somewhat less dense than massive metal, and their electrical conductivities are correspondingly somewhat lower. These differences are not usually of great magnitude nor are they serious; however, they can be a problem. For example, several methods of measuring the thickness of electrodeposits actually measure mass per unit area, which is translated into thickness by using the handbook value for the density. Usually this assumption—that the handbook value represents the true density of the electrodeposit—introduces an error smaller than other errors of the measurement and is thus of no concern. In a few cases, of which gold is the outstanding example, this difference between the handbook value and the actual density of the electrodeposit is significant and has been the source of considerable controversy. The beta backscatter method, the most widely used method of thickness measurement for gold, actually measures mass per unit area rather than thickness directly. Because of the high cost of gold and the close tolerances to which it is plated, differences in density that might be negligible for most metals can be significant for gold. The problem has been the subject of much study; those interested should consult manufacturers of backscatter instruments or the current literature for details.

Chapter 6—Design for Electroplating

Although some parts, by their nature or function, can be designed in only one way, many more offer alternatives; the same function can be satisfied in several ways. Some designs offer great difficulties to the plater, while others are easily finished satisfactorily. It has already been mentioned that edges and projections will normally receive more deposit than other areas; thus if a certain thickness is specified, as it usually is, excess deposit must be applied to some areas in order to meet the specification. This entails longer plating times and consumption of more plating metal; from the purchaser's standpoint these translate into extra cost. Alternatively, the plater may be forced to use conforming or bipolar anodes, or thieves, shields, or other expedients. This also increases his costs, which he will pass along to the purchaser.

To some extent, these considerations may be modified by the nature of the deposit. Some plating solutions have higher throwing power than others; that is, they are not quite so subject to the same limitations on design. For example, stannate tin and most alkaline cyanide baths "throw" well into recesses and deposit less excess plate on projection. Acid baths such as nickel possess this property to a lesser extent and here design considerations are more important. In chromium plating the bath actually has "negative" throwing power, which exaggerates the difficulties. But whatever the deposit is to be, it is unwise to rely too much on the throwing power of the bath, for in no case is this property unlimited (except for autocatalytic plating) and, to a greater or lesser degree, the design of the part has a major effect on the uniformity of the deposit and hence on the cost of plating it to specification. Where dimensional tolerances are important, the excess plate on some areas may be unacceptable.

ASTM Practice for Design of Articles to be Electroplated on Racks with Nickel (B 507) offers excellent guidance to the designer. This standard refers chiefly to nickel plating and thus may have to be modified to some extent for other deposits, but its principles are universal.

Detailed guidance is offered in the booklet "MFSA Quality Metal Finishing Guide: Zinc and Cadmium Plating" from which the following few paragraphs are quoted:[1]

> The program to improve and control the quality of a metal product should start at the desk of the designer. A most important term used when specifying metal finishes is

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[1] Metal Finishing Suppliers Association, 1025 East Maple Rd., Birmingham, Mich. 48011.

"significant surface" because on many products the same standard of quality is not required at all points on the surface. Significant surfaces preferably should be agreed upon between purchaser and manufacturer (plater) and should be indicated on drawings. Furthermore points at which the measurements are to be made should be identified.

Design for barrel processing. Avoid blind holes, recesses and joint crevices which can retain tumbling compounds and metal debris. Avoid intricate surface patterns which will be blurred by barrel finishing. Parts must be sturdy enough to withstand the multiple impacts of barrel rotation. Small flat parts which tend to nest together should be provided with ridges or dimples to prevent this. Design for good entry and drainage of solutions during rotation by using simple shapes. Significant surfaces must be exterior for barrel work in order to undergo proper mechanical preparation and cleaning or to receive their share of metal deposit. They should be convex, if possible, rather than recessed.

There are design considerations other than the above for parts which are to be mounted on racks for processing in cleaning and electroplating tanks. Among them are the following. Products that would occupy a volume in processing tanks large in proportion to surface area should be designed to be plated in sections for assembly after coating. Consult the plating department (or out-plater) to make certain that parts can be held securely on a plating rack with good electrical contact without masking any significant surface. Many difficult racking problems can be solved by design modification. Provide for good drainage of cleaning and other processing solutions from racked parts. Certain shapes tend to trap solutions which then cause contamination by carryover, possible corrosion of the part and waste of materials. Carryover also aggravates the problem of waste disposal. In design avoid rolled edges, blind holes and spot-welded joints. Provide drain holes in recessed area. Avoid shapes which can trap air on entry into a processing tank if this air can prevent access of solutions to areas requiring treatment. Wherever air can be trapped, hydrogen or oxygen may also accumulate during cleaning and plating.

In summary: Avoid concave or perfectly flat significant surfaces; convex or crowned areas receive more uniform coating. Edges should be rounded. Reentrant angles or corners should be filleted with a generous radius; make such radii as large as possible. Blind holes must usually be exempted from minimum thickness requirements. Protruding fins, knobs, and ridges tend to rob current from surrounding areas, hence should be avoided or reduced in height. Assist the plater by clearly marking significant surfaces in part drawings. Avoid the use of a variety of basis metals in any one part to be plated. The contact of dissimilar metals may interfere by galvanic action with covering power or with the adhesion of the deposit.

Chapter 7—Factors to be Considered in Choosing an Electroplated Coating

Assuming that electroplating has been chosen as the preferred method, the choice of the particular coating must next be made. This will be determined by many factors, principally:

1. *Nature of the Substrate*—in particular, its composition, size, and configuration.

2. *Purpose of the Finish*—previously considered in Chapter 2.

3. *Cost Performance*—the cheapest metal commonly electroplated is zinc, the most expensive, rhodium; all other commonly plated metals fall between these extremes. One would normally choose the cheapest metal that will do the job. It should be mentioned that, although the total cost of a plating job is not determined solely by metal cost, since overhead and other factors enter the equation, metal cost remains an important variable.

4. *Probable Service Conditions*—including expected service life. As a general, though not invariable, rule, electroplated coatings will serve their purposes for times approximately proportional to their thicknesses. Because of cost, one normally chooses the thinnest coating that will serve.

5. *Availability of Producers*—unless it is desired to set up in-house facilities.

Chapter 8—Criteria of Choice

The choice of a coating depends on the purpose for which it is applied.

Protection from Corrosion

The word "corrosion" alone, without specifying what the corrosive environment is to be, is not sufficient to define the use. Normally, protective coatings are thought of as those that protect from ordinary atmospheric deterioration, such as takes place when uncoated steel or other metal is exposed to ordinary atmospheres. For most such cases, zinc is the coating of choice. Zinc protects steel and other ferrous alloys from attack by the usual atmospheric corrodents better than any other plateable metal, it is the cheapest metal that can be applied to most substrates, and it is widely available from most suppliers of plating services (job platers). As normally applied, zinc is rather dull in appearance; it can be plated brightly, or brightened chemically after plating, but this bright appearance does not long survive in service.

Zinc protects steel and many other metals by a mechanism known as sacrificial protection. Whenever two different metals are in contact and exposed to a corrosive environment, the more chemically active of the two metals tends to corrode and in doing so generates an electric current that opposes the corrosion of the less active metal. When the more active metal is a coating on a less active metal substrate, wherever the substrate is exposed (pores, scratches, cut edges, and the like) the surrounding coating corrodes and protects the exposed substrate. Such coatings are called sacrificial or anodic coatings.

If, on the other hand, a coating is less active than the substrate, the same process will cause accelerated corrosion of the substrate wherever it is exposed. Such coatings must, therefore, be reasonably free from defects. This usually means that they must be substantially thicker than sacrificial coatings.

The manner in which a zinc coating is applied is relatively unimportant with respect to its corrosion resistance. Electroplating is only one of several coating methods, but it is the most popular (hot-dip galvanizing is not considered here; mechanical plating is considered below). Precoated galvanized strip is available and, because of the sacrificial protection already mentioned, cut edges that expose the substrate are of little moment.

Under conditions of high atmospheric salinity, roughly approximated by the widely used salt spray test [ASTM Method of Salt Spray (Fog) Testing (B

117)],[1] zinc coatings produce unsightly white corrosion products (frequently called white rust) long before the red rust of the underlying steel forms. This is sometimes of no concern, but if important, a post-plating treatment known as chromating can be done. These chromate treatments (conversion coatings) are widely used, and are of several types, considered later. They may be iridescent, pale blue, yellow, brown, olive drab, or nearly black; they delay the formation of "white rust" for considerable periods, though it is somewhat questionable whether they similarly prolong the time to actual rusting. They are also useful in avoiding fingerstaining of plated parts during the manufacturing process.

Zinc is relatively nontoxic and can be applied from several types of solutions; there are many suppliers of materials and proprietary processes; it is one of the most popular electroplated coatings. Widely recognized and used specifications apply to zinc coatings on steel, for example, ASTM Specification for Electrodeposited Coatings of Zinc on Iron and Steel (B 633).

Zinc may be "mechanically" deposited on small parts by a process widely known as "Peen Plating"; ASTM Specification for Mechanically Deposited Coatings of Cadmium and Zinc on Ferrous Metals (B 454) applies to this technique.

The only other commonly applied electroplated coating comparable to zinc for protection of the substrate is cadmium. Cadmium should be preferred to zinc only in certain well-defined situations: (*1*) when the coating must be solderable; (*2*) when the exposure will be principally to a seacoast type of atmosphere; (*3*) when the somewhat more pleasing appearance of cadmium is wanted; and (*4*) when the "white rust" of zinc, which is voluminous, would interfere with the function of moving parts. Cadmium is also applied to threaded fasteners to provide lubricity.

Cadmium, like zinc, may be chromate-treated for further corrosion-protective qualities.

Set against these advantages, cadmium suffers several drawbacks that limit its applications to the situations previously mentioned. Cadmium, unlike zinc, is extremely toxic. Its vapors are also dangerous; this must be considered when soldering to cadmium-coated surfaces, even though the boiling point of the metal is not approached. Because of the toxicity of cadmium, its use in electroplating has been banned in some governmental jurisdictions owing to the effluent problem. Much consideration is being given to finding alternatives to cadmium plating in applications where its use has been considered routine.

Cadmium-coated surfaces must never be used in contact with foods or beverages. (It is unwise to use zinc for contact with foods, too, but the danger is not nearly so great; much larger quantities must be ingested before damage is done.)

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[1] Though not entirely reliable, at least for electroplated coatings.

Cadmium is much more expensive than zinc; the ratio varies with market conditions. It has been, off and on, in short supply, and "black markets" have appeared from time to time. Cadmium is not mined for itself, but is always a by-product of zinc mining and production. Therefore its supply depends on the supply of and demand for the much more available zinc. At times the demand for cadmium for nuclear reactors has required practically the entire supply; and further development of the nickel-cadmium battery, as well as possible future demand for cadmium for solar cells, could create additional demand for a relatively inflexible supply.

Although many job platers are still available to supply cadmium-plating services, their number is tending to decrease, as stringent regulations render more difficult the removal of the metal from plant effluent. Similarly, both zinc and cadmium have traditionally been plated from cyanide-based solutions; cyanide also poses a disposal problem, which has been largely solved though at some cost. But while cyanide-free zinc-plating baths are now available and are being installed by platers, no truly commercial cyanide-free cadmium-plating process has (1980) been offered to the trade.[2]

Cadmium plating is covered by ASTM Specification for Electrodeposited Coatings of Cadmium on Steel (A 165), Federal specifications, and others. Cadmium, like zinc, can be "mechanically" plated.

Zinc, and to a lesser extent cadmium, are the metals of general choice where protection of ferrous metals is the principal object of the coating. Under rather less usual circumstances, some other metals may be considered.

Lead, and lead alloys containing 5 to 10 percent tin, are protective to steel, especially in industrial atmospheres, where the principal contaminants include sulfur dioxide and other sulfur-containing gases. The protection offered by lead does not depend on the same mechanism as for zinc and cadmium. Lead is initially corroded, but the corrosion pits are quickly filled and the lead surface covered by the very insoluble corrosion product (lead sulfate) which then protects the material from further attack for some time. Lead is fairly cheap (by weight, but because of its high density not so much by thickness), easily deposited on many metals, and quite satisfactory for the limited number of its uses. It is not attractive and bright deposits are not available. Deposits of lead and low-tin lead alloys are covered by ASTM Specification for Electrodeposited Coatings of Lead and Lead-Tin Alloys on Steel and Ferrous Alloys (B 200).

Tin is not generally used as a protective coating because its electrode potential is more noble (that is, it is less chemically active) than those of many metals on which it is deposited; thus the sacrificial mechanism discussed under zinc does not operate, and through any pores it is the substrate rather than the coating that corrodes. Nevertheless, because of the relatively low

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[2] This and similar statements in this guide are not meant to disparage claims put forward by various supply houses that advertise newly developed or improved processes.

toxicity of tin and most of its inorganic compounds, tin is the coating of choice when contact with foods and some pharmaceutical preparations is involved. Although by far the most significant use of tin in this connection is in the manufacture of tinplate by the steel mills (now universally electroplated rather than hot-dipped), and thus is outside the scope of this guide, some tin plating is carried on by job and "captive" shops for food-handling materials such as diary equipment, meat choppers, and similar items.[3] To be truly protective in such cases, the tin deposit must be of sufficient thickness to be essentially nonporous. As normally plated, tin is dull, but bright plating baths are available, and deposits can be brightened by a post-plating treatment known as flow-melting. See ASTM Specification for Electrodeposited Coatings of Tin (B 545).

Decorative Coatings

There are few instances where improvement of appearance is the *only* reason for applying an electroplated coating; some protection of the substrate is usually also desired, even if that is a secondary consideration. The most common decorative coating is "chrome"—a misnomer for chromium but well entrenched in usage. The final chromium plate, which lends the article its distinctive color, is usually, though not always, applied over undercoats of copper and nickel or nickel alone. On some materials such as brass (plumbing fixtures, for example) and stainless steel automotive trim (mainly for color but also affording some additional corrosion resistance) the chromium is often applied without undercoats. There is no difference in principle between copper/nickel/chromium (or nickel/chromium) plating for purely decorative effect and the same coatings meant to offer considerable protection as well (see the following section). For decorative appeal alone, in relatively noncorrosive exposures (indoors, dry atmosphere), generally the coatings are merely much thinner (and therefore cheaper) than when, as in the case of exterior automotive brightwork, the coatings are intended to withstand corrosive conditions. Furthermore, as will appear, the types of nickel and chromium intended for corrosive conditions may be of special character.

For mild indoor exposure, relatively thin bright nickel (undercoated with copper if desired) followed by very thin conventional chromium deposits usually suffices. The thickness of nickel may be determined by the characteristics of the nickel-plating bath. Many proprietary bright nickel baths require a minimum thickness before full brightness is attained, and this thickness suffices for the purpose; it may be about 2.5 μm. A thin topcoat of chromium (not usually specified as to thickness) is applied for tarnish protection and appearance. Copper is used as an undercoat if the substrate metal is not

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[3] Other uses of tin (for example, for solderability in electronics equipment) are not discussed in this section.

readily plateable directly with nickel, or if some buffing is required before nickel plating, copper being easier to buff than steel. Such coatings may not be subject to specification, although ASTM Specification for Electrodeposited Coatings of Copper Plus Nickel Plus Chromium and Nickel Plus Chromium (B 456) does have a class for "indoor, mild" or "S-1" conditions. These include many types of home appliances and handbag frames, toys, and similar items not expected to withstand severe handling in corrosive atmospheres.

Nickel-iron alloy electrodeposits have been promoted as a means of cost saving; about 35 percent of the nickel can be replaced by the much less expensive iron with apparently equivalent results as regards appearance. These proprietary processes and the resultant deposits have not been subject to specification by ASTM, but if appearance is the only criterion they appear to be satisfactory. There also are reports of successful use in corrosive environments. The user needs to keep in mind that the experience with these coatings is as yet somewhat limited. He may wish, therefore, to perform additional testing to satisfy himself of their suitability for his application.

Many other finishes are available for decorative purposes; depending on the color desired, bronze (copper-tin) or brass (copper-zinc) may be used. High-zinc (70 percent) brass is about as white as nickel and may substitute for it in some applications. Brass and bronze are used for both purely decorative and functional applications. In the decorative field their colors are the determining factors. The copper-tin alloy bronze may, depending on plating conditions and composition of the alloy, duplicate the color of gold; it is so used for trophies and similar relatively inexpensive items. In such applications the tin content is about 15 percent and the remainder copper, and the coating is only thick enough to impart the necessary color. Brass is plated on lower cost metals such as steel entirely for color; brass-plated steel costs much less than solid brass.

Both bronze and brass, when used in this fashion, must be further protected by clear lacquers to prevent the tarnish typical of copper and its alloys.

Silver, as is well known, is widely used for plating flatware and hollowware; it is hard to decide whether this function should be classified as decorative or protective. Federal specifications regulate the thickness of silver required in order that an item be classified and sold as silver-plated, and further specify several grades such as triple-plate.

Gold is used as a decorative coating, from a mere coloring flash a few millionths of an inch thick to substantial thicknesses, depending on both the intended use and the price to be charged. Gold is very expensive and the cost of plating varies almost linearly with the thickness applied; unlike most metals, metal cost is more important than overhead.

Rhodium, even more expensive than gold, is used on some of the finer grades of costume jewelry as a nontarnishing and brilliant coating. It has a bright silver-like appearance that is very attractive.

Almost any metal can be used for special decorative effects. Even lead, dull in appearance, may find application for antique types of finishes.

Decorative/Protective Coatings

This category overlaps the preceding category; again the main example is nickel/chromium or copper/nickel/chromium. As stated previously, there are some differences in detail in the system depending on whether the coating is intended for appearance alone or is also expected to withstand aggressive atmospheres. In the latter case, the use of so-called duplex and triplex nickels and special forms of chromium known as microdiscontinuous add to the corrosion resistance of the composite. While for purely decorative applications thin bright nickel followed by a flash of chromium suffices, if this decorative appearance is expected to endure through outdoor winters and the attack of de-icing salt and the like, as on automotive brightwork, the nickel must be considerably thicker, preferably applied in two or three layers, and the chromium preferably microporous or microcracked. These requirements are spelled out in ASTM B 456. Tests for expected service life are considered in a later section. It may be well to warn the user that all accelerated tests, even though mentioned in specifications, are at best approximations to actual service, and the user should by all means supplement these tests with knowledge gained from his own experience.

There has been considerable controversy concerning the role of copper undercoats for nickel/chromium deposits; till recently ASTM B 456 permitted the use of copper but required the same thickness of nickel regardless of whether copper was present. The latest revision of this specification, however, permits somewhat thinner nickel deposits if the copper is of the ductile bright acid leveling type.

Because of the high price of nickel, some plating supply companies have been promoting a nickel-iron alloy coating, containing up to about 35 percent iron (see the previous section). It can be plated bright, and overplated with chromium in the usual way. These coatings do not have the years of testing and service experience that unalloyed nickel coatings have. For this reason they cannot yet be unqualifiedly recommended for severe service.

Also on the market are several types of tin-cobalt alloys claimed to be superior to chromium in some ways and to resemble it in appearance; the throwing power is better and barrel plating is less of a problem. The promoters of these coatings do not claim corrosion resistance equivalent to that of chromium.

No standard specifications are at present available for either nickel-iron or tin-cobalt, and since all are proprietary their merits or demerits cannot be discussed here. The designer should be aware of their existence; they may serve in some applications, which must be considered individually.

Few other widely used coatings are available for the combined functions of decoration—that is, appearance—and protection. Bronze (copper-tin) has been claimed to be superior as an undercoating for the nickel/chromium system, but it is not widely used for this purpose. Tin-nickel alloy has a color somewhat warmer than that of chromium, and properly deposited over a copper or bronze undercoat (on steel) it has been shown to have excellent corrosion resistant properties. Its color may be attractive in applications where chromium is considered too garish, and an ASTM Specification for Electrodeposited Coatings of Tin-Nickel Alloy (B 605) is available. The coating is somewhat brittle and should not be used on objects expected to withstand much flexing or deformation after plating.

Engineering Applications

Electroplating is not always done for reasons of appearance or protection of the substrate; there are many specialized applications that, for want of a better term, may be classified as "engineering". Such uses of electroplating are intended to afford specific properties to the surface, appropriate to the application. Not all of them can be mentioned here, since they are so numerous and in some cases applicable only to a single end use. Some of the principal properties are outlined below.

Solderability

Copper and brass, especially the former, are widely used in all types of communications equipment. Copper has the highest electrical conductivity of any metal except silver, which is far more expensive and also suffers from some specific disadvantages ("migration") which rule it out in many applications in microcircuitry. Copper is easily solderable when the surface is fresh, but on standing it soon acquires a tarnish film that renders it difficult to solder without the use of strong fluxes, which, because of the corrosive nature of their residues, are forbidden in many applications. To render the surface easily wet by soft solders and to ensure the maintenance of this solderability over reasonable periods of storage time, copper wires, leads, terminals, and the like (both miniature and standard size) are usually plated with tin or with tin-lead alloys (solder itself) containing at least 50 percent tin. ASTM issues specifications for both tin (B 545) and high-tin lead alloys [B 579, Electrodeposited Coatings of Tin-Lead Alloy (Solder Plate)]; the thicknesses of the coatings are related to expected service life under a variety of conditions.

Tin may also be plated on copper by immersion (see below); both open and proprietary processes are available. There is some disagreement whether such thin coatings really serve the purpose, although some users are apparently satisfied with the results.

Gold (ASTM B 488, Electrodeposited Coatings of Gold for Engineering

Uses) may also be used to improve solderability. It is, of course, much more expensive than tin or tin-lead alloys, and is usually specified only when some additional property besides solderability is required. Gold forms brittle alloys with tin, and the integrity of soldered joints must be assured when using this coating. Tests for solderability, though not entirely standardized, are included in the ASTM standards cited above. A simple dip test is provided by ASTM Test for Solderability of Metallic Coated Products (B 678).

Hardness and Wear Resistance

Many steels have high hardnesses in themselves, but when it is desired to impart properties of hardness and wear resistance to the surface of ordinary steel, or sometimes to other metals, some electroplated coatings serve the purpose admirably. Perhaps the most widely used is so-called "hard" chromium. This term is a misnomer, since the chromium is no harder than conventional chromium deposits used for decorative and protective purposes, but it is usually applied in thicknesses much greater than would be considered for the latter. Since chromium plating rates are relatively slow, hard chromium plating generally takes much more time—hours or even days—compared with the few minutes normally consumed for decorative deposits. The properties of hard chromium deposits have been well investigated from the standpoints of both their hardness and their resistance to various types of wear. ASTM Specification for Electrodeposited Engineering Chromium Coatings on Ferrous Substrates (B 650) covers "hard" chromium on steel.

Hard chromium is used on many types of equipment: bores of gun barrels, oil-well drilling rigs, dies for plastics and rubber, hydraulic pistons, various machine parts, to mention a few. Most plating shops equipped to do hard chromium plating specialize in this technique and usually do little or nothing else. While the principles of hard chromium plating do not differ from those of electroplating in general, a considerable amount of art and experience is involved, and the purchaser should consult with the supplier for recommendations regarding his particular application.

Although hard chromium plating may be expensive, it is often a cheaper and more effective way of obtaining the desired results than alternative means.

For some applications, when the extreme hardness of chromium is not required, heavy nickel deposits may be considered. Depending on the bath used and the plating conditions, nickel deposits can have many different properties: highly stressed or almost unstressed, bright or dull, tensile strengths varying from about 385 to 620 MPa. Its corrosion resistance is in general good, but of course the particular agents with which it will come in contact will determine whether it is appropriate.

Hardness and wear resistance often, but not necessarily, go together; not all hard deposits are resistant to wear. While the measurement of hardness is relatively straightforward, even for thin electrodeposits, the exact measurement of wear resistance is subject to some debate and no test is universally recognized. Sample parts should probably be tested under conditions simulating use before making final commitments.

Chromium has a very low coefficient of friction against most materials and is applicable to parts such as cutting shears. Chromium may also be deposited in a form known as "porous" (not to be confused with microporous), which by virtue of channels in the deposit holds oil films well; it has been used for diesel cylinder linings and the like.

"Electroless" nickel-phosphorus alloys (considered later) have been suggested in the literature as a substitute for, or an improvement over, hard chromium on certain moving parts such as camshafts. At present this application must be considered somewhat experimental, although the evidence appears fairly convincing.

Electrical Contact Resistance

In the communications and computer industries, gold is the preferred coating material for combinations of wear resistance and low contact resistance as well as good electrical conductivity. Unlike silver, gold does not tarnish in the atmosphere and, though its electrical conductivity is not so high as that of silver, the absence of tarnish films provides better electrical contacts. The thickness of gold required for various applications is detailed in ASTM B 488. Because of the cost of gold, many users specify so-called spot plating; that is, the gold is plated only on those areas of the item where it is needed. Many techniques have been devised for attaining this end.

The high cost of gold has stimulated research into substitute materials, and some such replacements appear to have promise, although none has received official recognition in the form of ASTM specifications. Palladium (ASTM B 679, Electrodeposited Coatings of Palladium for Engineering Use) is cheaper than gold on a weight basis, and since it is much less dense the cost advantage is multiplied. It has been successfully used as a substitute for gold in some computer applications. Its disadvantages at present are that few platers are equipped to provide this coating and, in contrast to the many years of experience in gold plating, practical palladium plating is a relatively recent addition to the plater's arsenal. Ruthenium electroplating is being used to a small degree and may grow in importance as more is known about it.

Although even more expensive than gold, rhodium has engineering uses for electrical contacts, especially where severe wear conditions are encountered. The coating is used also for its excellent light reflectance; thickness requirements are specified in ASTM B 634, Electrodeposited Coatings of Rhodium for Engineering Use.

Autocatalytic ("electroless") nickel-boron deposits are said to be equivalent to gold for some applications involving contact resistance; at this writing

(1981) these claims have been somewhat promotional and the user must satisfy himself as to the suitability of the coating for this use.

In the electrical industry there is a tendency to substitute aluminum for copper in bus bars, heavy wire, and similar conductors. This application is of course of an entirely different nature from what has been discussed above, where most parts are miniature. Although the conductivity of aluminum (weight basis) is comparable to that of copper, problems may arise in connecting two or more aluminum conductors because of the high resistance of the natural oxide film on aluminum and its alloys. This problem has been met by tin plating or silver plating the aluminum at points of contact. Bolted aluminum bus bars show much less voltage loss and consequent heating at the bolted connection when they have been tin plated than when left bare. The improvement may be caused by two factors: (*1*) the softness of tin allows better physical contact under the pressure of the bolt, and (*2*) tin does not acquire heavy oxide films on atmospheric exposure. Although tin is a relatively poor electrical conductor, the plating is so thin that this factor is insignificant.

Rubber Adhesion to Steel

Brass (copper-zinc) has been the standard coating for steel wire for adhesion to rubber, as in automotive tires. No alternatives have been proposed.

Miscellaneous

Many other surface properties besides those mentioned may be modified by choice of the correct electroplated finish. Steel-backed bearings have long been plated with tin, tin-lead alloys, and ternary tin-lead-copper alloys (where copper is a minor constituent). Indium and lead also find use in bearing applications.

Silver is the preferred coating for the interior of radar wave-guides; the important property in this use is electrical conductivity.

Reflectors of large searchlights may be plated with rhodium for high and durable reflectivity; although not so reflective as silver, rhodium does not tarnish in the atmosphere as silver does (see ASTM B 634).

Chapter 9—Nature of the Basis Metal (Substrate)

The material to be plated upon may or may not influence the choice of coating. Most basis metals can, by proper treatment, be electroplated with almost any plateable metal, but there are some cautions and exceptions.

Mild Steel

Low-carbon steel will accept almost any plateable metal with only conventional preplating treatments. The plater may wish to follow ASTM Practice for Preparation of Low-Carbon Steel for Electroplating (B 183).

Alloy, High-Strength, and High-Carbon Steels

The pretreatments required for plating on high-alloy steels, and the plating sequence itself, may cause hydrogen embrittlement. This can usually be reversed by suitable post-treatment, including baking out the hydrogen, procedures for which are detailed in appropriate ASTM standards on metallic coatings. ASTM F 519, Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals, provides means for evaluating the overall finishing process for limiting or avoiding hydrogen embrittlement and means for the routine monitoring of the processes. The user should be aware of the problem and include in his order the requirement and testing for embrittlement relief when necessary. High-alloy steels are often difficult to plate upon, and adhesion of the coating may be a problem. ASTM publishes practices for preparation of and electroplating on stainless steel (B 254), high-carbon steels (B 242), iron castings (B 320), and nickel and its alloys (B 558 and B 343).

Copper and Brass

These will accept all plateable metals. Recommendations are offered in ASTM B 281 for electroplating on copper and copper base alloys. When plating on brass a "barrier" layer of copper or nickel is advisable or even necessary when the top coat is to be tin or tin-lead alloy, or any other deposit into which the zinc constituent of the brass may diffuse. In fact, when tin or tin-lead coatings are applied to brass for solderability, the barrier layer is mandatory if specifications of ASTM (B 545, B 579) and other specifying bodies are to be followed.

Aluminum, Magnesium, and Beryllium

Because any metal plateable on these metals will be cathodic to the basis metal, corrosion of the latter may be a problem unless proper pretreatments are employed and the electroplate is substantially free of pores. Normally, these metals should be electroplated only for compelling reasons. Some pretreatments for aluminum have been shown to be superior to the conventional zincate process as regards corrosion resistance, and the user may wish to specify one of these; since they are proprietary further discussion is not appropriate here. The historically standard zincate process is covered by ASTM Practice B 253. (This document is in process of revision; future editions will include some of the patented and proprietary processes that have shown advantages over or are equal to the zincate.)

Zinc Alloy Die Castings

Like aluminum, though to a lesser extent, zinc is anodic to the metals that can be deposited on it. Blistering and even peeling of the deposits are ever-present dangers that can be avoided only by scrupulous attention to proper practice. ASTM B 252, Practice for Preparation of Zinc Alloy Die Castings for Electroplating, offers guidance to the plater. Zinc die castings are universally copper-plated as a first step. Following this initial copper plate, other deposits are applied by standard techniques. The usual sequence is the familiar nickel/chromium finish.

Nonconductors

By proper treatment, any nonconducting solid can be electroplated. These nonconductors fall into two distinct classes. The first contains items such as leather, wood, and art objects of various types that require pretreatment by some sort of semi-mechanical means (lacquering with metallic paints, rubbing with graphite, or similar methods) to make the surface conductive. True adhesion of the electroplate is not obtained, and complete encapsulation of the substrate is required. The art is old and still used in some applications, for example, bronzing of baby shoes for sentimental reasons.

The other class of nonconductor, on which true adhesion (though not comparable to that obtained on metals) is obtained between the substrate and the electroplate, consists of a class of plastics that by suitable pretreatment can be made conductive by autocatalytic ("electroless") plating, after which almost any metal can be used as a final coating. Not all plastics are amenable to such treatments, though the number is growing as research and development in the field progress. Approximately 90 percent of the volume of plating on plastics is on ABS (acrylonitrile-butadiene-styrene). Also plated are (*1*) "alloys" of ABS with polycarbonate and with polysulfone, and (*2*) polysulfone, polypropylene, mineral-filled nylon, polyphenylene oxide, polycarbonate, polyester, polytetrafluoroethylene, and nylon.

The manufacturer of the plastic part has almost as great a responsibility for success in plating on plastics as does the plater: proper die design and feeding rate, use of suitable die-release agents, and other factors influence the final result. The manufacturer and designer should by all means consult with the finisher for best results; they should not simply present the finisher with a batch of plastic parts with the admonition to plate them. At its best, the adhesion between the plastic and the metallic electroplate does not approach the values obtainable in plating on metals like steel, but when done correctly it is sufficient for many applications.

"Unusual" Metals

Finally, there is a class of "unusual" metals which, though usually plateable, require individual preplating cycles. ASTM Practices are available for plating on titanium (B 481), tungsten (B 482), magnesium (B 480), and lead (B 319). Other standards are in various stages of action within the appropriate ASTM Committee, B-8 on Metallic and Inorganic Coatings. The occasion for plating on most of these metals is confined to fairly special situations; most job shops are not equipped to handle these materials and specialists should be consulted. Many other metals have been electroplated upon, and methods and results reported in the literature; tantalum and uranium are two examples. No "standard" procedures have emerged and these processes must be regarded as experimental.

Limitations

Regardless of the substrate, certain limitations apply to all basis metals if satisfactory results are to be obtained in the electroplating process. These requirements are usually detailed in the individual ASTM specifications for specific electrodeposits. Typical is section 6.1.2 of B 456:

> Defects in the surface of the basis metal, such as scratches, porosity, nonconducting inclusions, roll and die marks, cold shuts, and cracks, may adversely affect the appearance and the performance of coatings applied thereto despite the observance of the best plating practices. Accordingly, the plater's responsibility for defects in the coatings resulting from such conditions shall be waived.
>
> NOTE—In order to minimize problems of this type, the specifications covering the

basis materials or the item to be electroplated should contain appropriate limitations on such basis metal conditions.

In other words, the electroplater should not be expected to hide, nor be held responsible for, basis metal defects such as tears, slivers, nodules, undue roughness, and other such defects mentioned above, in the materials he is called upon to finish, unless the contract calls for additional surface treatment for which the purchaser must expect to pay.

Chapter 10—Related Finishes

Anodizing and Chromating of Aluminum

Although aluminum and its alloys can be coated by electroplating to yield satisfactory finishes such as nickel/chromium or tin, much more widely practiced is the anodizing of this metal. In anodizing, the natural oxide film always present on aluminum and its alloys is replaced by a synthetic oxide, which can be more corrosion resistant, can enhance the decorative appearance, and can be colored by both organic and inorganic dyes and pigments. Surface properties such as hardness, wear resistance, emissivity, and others can be altered by suitable anodizing and chemical treatments.

In anodizing, the aluminum part is made anodic in a chemical solution; this is the opposite of electroplating, where the parts to be plated are cathodes in the electroplating bath. The action of the solution and the electric current forms an aluminum oxide on the surface of the aluminum article; this oxide is essentially nonconducting, so that as the process progresses and the coating increases in thickness, higher and higher voltages must be imposed to enable the current to flow; or at constant voltage the current begins at a high value and gradually decreases. Both methods are used.

Anodizing coatings are highly porous on a submicroscopic scale; it is through these pores that the anodizing current passes. The anodizing process usually includes a final operation ("sealing") in which the pores are closed. There are several ways in which sealing is done. A common one is immersion of the freshly anodized work in near-boiling, high-purity water. The oxide coating reacts with the water to form a bulkier hydrated oxide that tends to plug the pores.

Anodizing solutions are usually of sulfuric acid, but chromic, phosphoric, and oxalic acids and other electrolytes are also used. There are many proprietary treatments available for anodizing aluminum. They may involve coloring other than by dyes or the production of very hard and wear-resistant surfaces.

ASTM specifications cover a number of practices and tests for the properties of anodized coatings on aluminum. ASTM Specification for Anodic Oxide Coatings on Aluminum (B 580) covers most types of anodic coatings except the nonporous barrier layer anodic coatings used for electrical capacitors. Table 1 of that specification enumerates minimum film thicknesses for various types of service; it is reprinted here as Table 10-1.

TABLE 10-1—*Anodic coatings descriptions.*

Type	Coating (Industry) Description	Minimum Film Thickness, μm
A	Engineering Hard Coat	50
B	Architectural Class I	18
C	Architectural Class II	10
D	Automotive—Exterior	8
E	Interior—Moderate Abrasion	5.0
F	Interior—Limited Abrasion	3
G	Chromic Acid	1

Another common method for treating aluminum and its alloys is the (non-electrolytic) chromate conversion coating. To quote from ASTM Recommended Practice for Chromate Treatments on Aluminum (B 449):

> ... color and color uniformity will vary somewhat between one alloy and another and from a polished surface to an etched surface. Iridescence and variations in color intensity from one area of the surface to another are normal and should not be considered objectionable.
>
> Coatings are usually applied by immersion or spray; however, application by brush or swab is also used, chiefly for touchup. Roll coating is also used for continuous strip processing.
>
> Chromate conversion coatings are used on aluminum to retard and prevent corrosion, as a base for paint, and as a protective surface coating having lower electrical contact resistance than anodized coatings. They can also be used to change the emissivity and absorption properties of the metal, or may be dyed for identification purposes.
>
> The coatings produced by this method will generally provide protection in proportion to film thickness. They provide a high degree of protection against marine and humid environments. When coatings are dried at room temperature, hexavalent chromium compounds, loosely bonded in the film structure, are slowly soluble on exposure to aqueous media and will heal minor abraded or scratched areas.
>
> The hexavalent chromium compounds in chromate conversion films become insoluble in aqueous media when heated above 71°C (160°F), eliminating the self-healing characteristic and gradually reducing the protective value of the film as the temperature and time at temperature increase. It has been found that corrosion protection is reduced to a greater degree in heavy coatings than in thin coatings. The paint base properties of the coatings are not adversely affected by the short elevated drying times normally used in production.

For both anodizing and chromate conversion coatings on aluminum, the same cautions are applicable that have already been mentioned for electroplated coatings: defects in the basis metal will result in inferior final product, and the finisher should not be held responsible if the material sent to him for finishing is in poor condition to begin with.

Generally, anodizing or chromating are always the preferred treatments for aluminum articles, and electroplating is reserved for cases that require the special properties or appearance not available by these treatments.

Autocatalytic ("Electroless") Plating

Although more frequently called "electroless" plating, the term "autocatalytic" is now considered preferable. Autocatalytic plating is similar to electroplating in several ways, in that aqueous solutions are used in which the articles to be coated are immersed. No current, however, is employed; instead the reduction of metal compounds to metal takes place by the action of a chemical reducing agent in the solution. Because all practical chemical reducing agents are more expensive than an electric current as a source of the necessary energy, autocatalytic plating is intrinsically more expensive than electroplating, and should be considered only when electroplating is not suitable for the job.

Autocatalytic deposits of nickel or copper must be employed as a first step in plating on the plateable plastics mentioned previously; direct electroplating is not possible.

Autocatalytic plating has essentially perfect "throwing power" (see Chapter 6); in plating complicated shapes, where electroplating might not cover deep recesses or the inside of tubing or pipe, autocatalytic plating may provide a satisfactory solution to the problem.

The uses of autocatalytic nickel-phosphorus and nickel-boron alloys as substitutes for hard chromium and gold, respectively, have already been mentioned.

Autocatalytic plating of copper is widely used in the printed-circuit industry.

Many shops are equipped for autocatalytic plating, and there is a large and growing literature. Formulas are widely published, and many proprietary processes are available.

Only a few metals can at present be deposited by the autocatalytic method; the principal ones are nickel (actually usually alloys of nickel with phosphorus or boron) and copper. Autocatalytic processes are also available for tin, cobalt, gold, and some of the platinum metals, but these are much less commonly used.

Autocatalytic nickel deposits are in fact alloys; the second constituent depends on the reducing agent used. The commonest is sodium hypophosphite, yielding deposits containing phosphorus in amounts varying from about 5 to 15 percent. Heat treatment at 400°C substantially increases the hardness of the coating.

When borohydrides or amine boranes are used as the reductants, the deposits contain boron, though usually in lesser amounts than the phosphorus content of the nickel-phosphorus alloys. Hydrazine can be used to yield essentially pure nickel deposits, but the process is seldom used commercially.

The properties of the nickel-phosphorus alloys have been extensively investigated; the plater can, by proper control of the solution and operating conditions, provide almost any desired phosphorus content within the range mentioned.

ASTM Practice for Autocatalytic Nickel Deposition on Metals for Engineering Use (B 656) offers detailed guidance for plater and user for carrying out the process and selecting appropriate thicknesses of the deposit in its various applications. As the title indicates, the standard refers only to deposition on metals (plastics are not covered) and a note explains that only nickel-phosphorus alloys are considered.

Immersion Coatings

In immersion plating—also called galvanic deposition or cementation—the deposition of the coating metal takes place by an electrolytic reaction between the substrate metal and the metal ion in solution, without the employment of an outside source of electric current. The substrate metal acts as the reducing agent (the energy source), its ions passing into solution while the ions of the electrolyte are reduced to metal. The most familiar example is the freshman chemistry experiment of dipping a steel knife blade into a solution of copper sulfate, yielding a deposit of copper on the steel. This particular reaction is of no practical use, because the copper deposit is powdery and nonadherent, but a few immersion-coating processes are of some commercial importance.

Parenthetically, it may be mentioned that the popularity of "electroless" plating has caused some confusion in the nomenclature and literature. Many authors have referred to immersion coatings as "electroless" apparently under the impression that any process not requiring electricity must be electroless. Reference to "electroless tin" deposits, for example, are fairly common, but at present most are immersion coatings.

Immersion processes have obvious advantages: the solutions used are usually simple, no electrical equipment is necessary, and the solutions themselves require neither the careful control nor the expensive reducing agents of autocatalytic electrolytes. The principal limitation, however, is important. Once the basis metal is covered with the immersion coating, action stops or slows down to the rate at which metal atoms or ions can diffuse through the coating layer. Immersion processes are therefore limited to much thinner deposits than those obtainable by either electrolytic (electroplating) or autocatalytic means. In practice, immersion methods are confined to tin and gold, the former being the more important.

Tin is immersion-coated on three substrates: copper and its alloys, steel, and aluminum. Either open formulas or proprietary methods may be used.

Tin on copper is used for its color (for example, to distinguish between the two wires in electrical fittings), to coat the inside of copper pipe to avoid "green stain" in the water, and to improve or preserve the solderability of the copper. In the last-named application there is considerable disagreement whether the coatings are thick enough to be of much utility, but several manufacturers do use these methods.

Tin, or more usually tin-copper alloys, is used to coat steel wire, both for coloring (paper clips, bobby-pins, etc.) and as a lubricant for subsequent drawing operations. This process is known as liquor finishing.

Tin is immersion coated on aluminum alloy automotive pistons to reduce or eliminate scoring of the cylinder walls during the running-in period; it replaces the natural aluminum oxide surface, which is very abrasive. The process is not applicable to all aluminum alloys; it is used mainly on the alloys employed for pistons, which contain significant amounts of copper or silicon.

The so-called "gold wash" is used to impart a gold color to base metals and alloys. This process has been little studied; it is one of the more "arts and crafts" aspects of electroplating. No specifications appear to be available. The gold coating is very thin and is used for appearance only. Such articles may not, by law, be labeled gold electroplate.

Mechanical Plating

In this method, one aspect of which has been trade-marked "Peen Plating", the coating metal, usually zinc, cadmium, or a tin/cadmium mixture, is in the form of a fine powder. The powder, water, various reagents, impacting media, and the work are loaded into a closed, horizontal barrel which is then rotated for an appropriate time. The action of the media used forces the coating metal onto the substrate by mechanical action. The coatings must be soft metals like zinc and cadmium, which can be compacted in this way. Because of the nature of the process, it is adaptable mainly to small parts. The method has advantages over electroplating in some applications: the risk of hydrogen embrittlement from the coating process is virtually eliminated; the coverage in recesses may be superior, although coverage on sharp edges and corners is inferior; and few if any pollution problems are created, such as cause trouble with electroplating solutions.

Chapter 11—Properties of Coating Metals

This chapter offers a short summary of the principal properties of the more commonly employed coating metals. For more details, reference to William Safranek, *The Properties of Electrodeposited Metals and Alloys*, Elsevier, New York, 1974, is recommended. This book offers detailed data on the properties, principally physical and mechanical, of these metals as they are influenced by the type of bath used and the plating conditions.

Copper

Copper is a relatively "noble" metal, that is, not easily oxidized or not easily going into solution to form ions. It is not as noble as silver, gold, and the platinum metals, but much more so than most other common metals. It does, however, easily form tarnish films in sulfur-containing gases, and it oxidizes superficially, sufficiently so that all but fresh surfaces require aggressive fluxes for easy solderability.

Some physical properties of copper are summarized in Table 11-1.

At room temperature copper reacts with oxygen to form a superficial oxide; at red heat copper (II) oxide CuO is formed; at higher temperatures the result is copper (I) oxide Cu_2O. Halogens (chlorine, bromine, etc.) attack

TABLE 11-1—*Selected properties of copper.*

Melting point, °C	1083
Boiling point, °C	2582
Density, g/cm^3, 20°C (also g/m^2 for 1 μm deposit)	8.94
Crystal structure	face-centered cubic
Electrical resistivity $\mu\Omega \cdot$ cm, 20°C	1.673
Electrical conductivity, %IACS[a]	101.8
Brinell hardness	
Annealed[b]	43
Hard-rolled	103
Tensile strength	
Annealed, MPa[b]	220 to 255
Drawn, MPa	380 to 420

[a] International Annealed Copper Standard.

[b] For massive metal. Values for electrodeposited copper vary depending on bath and plating conditions; see Safranek, *op. cit.*

copper; it is not attacked by dilute nonoxidizing acids such as hydrochloric in the absence of air. It dissolves readily in nitric acid and, when air is present, in sulfuric acid. With air present it dissolves in ammonia and cyanide solutions.

Copper and its salts are relatively nontoxic, although EPA regulations limit discharge into watercourses. In large doses copper compounds can be lethal.

Copper is easily electroplated on almost any substrate. Being relatively soft, it is easily buffed and polished, so that it is often easier and cheaper to use a copper coating on steel for subsequent buffing than to buff the steel. For this reason copper is widely used as an undercoat for further deposits.

Copper may be deposited from a variety of solutions; it may be plated either dull or, with proper additives and solutions, fully bright. Bright ductile copper deposits are often preferred as the undercoat for further plating on plastics, after the initial autocatalytic deposit.

Except for its use in printed circuits and other communications and electronic equipment, copper is seldom used as a final finish. When it is desired, for its color, as a decorative finish, it is almost always protected by clear lacquers to prevent or retard tarnishing.

Copper is almost universally used as the first coat on zinc die castings and widely used on aluminum and its alloys. For these purposes the cyanide bath must be used, at least at present. On steel a cyanide strike is used before transferring the work to more rapidly acting acidic solutions such as the sulfate and fluoborate.

Copper alloys with zinc and with tin are also fairly widely used. Copper-zinc alloys (brass), as has been mentioned, are the preferred coating for rubber adhesion to steel. The color of brass is also valuable for its decorative qualities. Brass has also been used as an undercoat for nickel/chromium on some automotive parts; this is a "white" brass, containing about 50 percent zinc versus the usual 30 percent. Although used with apparent satisfaction by one automobile manufacturer, the practice has not taken hold. White brass may also substitute for nickel on some types of home appliances, tubular furniture, and the like.

Copper-tin (bronze) has decorative applications, since it can be plated to resemble gold. It is harder than copper and therefore somewhat more resistant to cut-throughs on buffing, without sacrificing the easy buffability of copper. Under nickel/chromium it offers somewhat more corrosion protection than copper. It has been used as the final finish on TV chassis and builders' hardware.

Nickel

Nickel comes nearest to being the "all-purpose" metal of the electroplating trade. It is the main ingredient of the widely used copper/nickel/chromium decorative-protective system, and the serviceability of the composite is to a great extent determined by the thickness and type of nickel used. It is also the most commonly electroplated metal in terms of total tonnage, if one excepts the tin used in producing electrolytic tinplate, which is a specialty of steel companies and not usually considered part of the plating business.

There are many reasons for the wide use of nickel: (*1*) a long history of research and development; (*2*) its great theoretical interest, particularly in the mode of action of the many brighteners and other additives, which has prompted a large amount of academic research; and (*3*) the highly competitive position of the supply houses that offer nickel-plating processes, which prompts much industrial research aimed at better solutions and additives. Nickel can be plated from a wide variety of solutions, using many types of additives or none at all, yielding deposits with a correspondingly wide range of physical and mechanical properties. Nickel can be plated dull, semibright, or fully bright; highly stressed or with little residual stress; essentially pure or containing small amounts of residues (principally sulfur and carbon) from the additives used; having little corrosion resistance or much.

This is not to say that there are no difficulties in nickel plating, but these are the concern of the plater, not the purchaser. The latter can specify almost any property required, to any reasonable thickness, within of course the possible properties of the metal itself.

Some properties of nickel are summarized in Table 11-2.

The metal is ferromagnetic at ordinary temperatures. Above its Curie point it becomes paramagnetic. Nickel is moderately hard and strong, tough, and ductile. It will retain a high polish.

Dry or moist air does not attack nickel at ordinary temperatures. At red heat it reacts with steam. Nickel tarnishes in urban atmospheres; therefore it is generally over-plated with chromium for decorative applications. Cold nonoxidizing acids such as hydrochloric attack nickel slowly. Dilute nitric acid dissolves nickel rapidly but stronger solutions passivate it (render it unreactive). Most alkaline and neutral salt solutions and most organic compounds have little effect. Its resistance to caustic alkalis, even molten, makes it useful in the chemical industry.

TABLE 11-2—*Selected properties of nickel.*

Melting point, °C	1453
Boiling point, °C	2730
Density, g/cm^3, 20°C (or g/m^2 for 1 μm deposit)	8.92
Curie point, °C	353
Electrical resistivity, $\mu\Omega \cdot$ cm, 20°C	6.84
Tensile strength, annealed, MPa[a]	317

[a] For massive metal; see Safranek, *op. cit.*, for electrodeposited nickel.

Finely divided nickel (powder) on the other hand is pyrophoric (catches fire spontaneously in air) and is a powerful and widely used catalyst.

Nickel and its salts are relatively nontoxic,[1] except that some susceptible individuals may develop so-called "nickel itch" on contact. An exception is nickel carbonyl [$Ni(CO)_4$], which is highly toxic but not likely to be encountered in the finishing trade.

Although nickel is relatively easily buffed, buffing of dull deposits is seldom done now, since the advent of proprietary bright and semibright processes has practically eliminated the need for mechanical finishing to achieve decorative effects.

The types of nickel plate may be briefly summarized, with an indication of their general utility. Although the list is not complete, it may indicate the wide applicability of the metal.

Dull nickel, usually fairly thick, is used for engineering purposes, for building up worn and mismachined parts. Properties such as hardness, tensile strength, and ductility can be controlled by choice of operating conditions and bath, of which many are available: "Watts," high chloride, sulfamate, and fluoborate, with some variations within these broad classes. It is also useful in electroforming, which is not within the scope of this guide. Occasionally, dull Watts nickel is subsequently buffed for chromium plating, but this practice, as previously mentioned, is now quite unusual, though the results in corrosion protection are excellent.

Semibright and leveling nickel is a low- or non-sulfur-containing nickel deposit which, though not fully bright, is brighter than one produced from a bath without additives, and has the further advantage of leveling; that is, the final deposit is smoother than the substrate. Seldom used alone, it is the preferred undercoat for the fully bright nickel used in nickel/chromium deposits for decorative/protective applications. Its value is shown by the fact that when this "duplex" (two-layer) nickel is used, less is required for a given service condition than when only bright nickel is employed.

Bright nickel is fully bright as it comes from the bath, ready to receive the final chromium plate. Almost all processes are proprietary, and competing claims are made for various properties such as chromium receptivity, corrosion resistance, brightness at minimum thicknesses, and ease of control. The deposits invariably contain sulfur from the additives used, and are more chemically active (less corrosion resistant) than either semibright or dull nickel. This increased activity, however, aids in the corrosion resistance of the composite nickel/chromium plate. When a pore or crack develops, or is incorporated, in the chromium layer, the bright nickel, being anodic both to the chromium and to the underlying semibright nickel, corrodes preferen-

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[1] In 1977 nickel dust and nickel compounds, including those used in electroplating, were implicated in causing cancer of the lung and nasal passages.

tially (is sacrificial); thus corrsion spreads laterally and takes much longer to reach the underlying steel or other substrate. This illustrates a general view about corrosion; namely, it is usually not the total amount of metal corroded that matters so much as whether it corrodes all in one place (forming pits and pores) or generally over the piece. The latter is usually much more favorable to the service life of the article.

Bright nickel processes fall into several classes. Some are formulated to "build brightness" so that the finished article will appear bright with a minimum of nickel plate; this is favorable for inexpensive and purely decorative articles. Other processes build brightness more slowly, but this is no disadvantage if the coating is being plated to a specification that calls for sufficient nickel, that is, is meant for relatively severe service. Other baths are specially formulated to be tolerant of specific impurities such as zinc, which will enter the bath when the basis metal is a zinc die casting.

Composite nickel deposits also include a "triplex" nickel, similar to a duplex system, but with a third high-sulfur layer to improve corrosion behavior.

Nickel deposits may be caused to entrain minute particles of inorganic nonconductive material (for example, barium sulfate or alumina). Such deposits are used for two purposes: (*1*) to give a satin appearance to the plate, and (*2*) to act as a base for "microporous" chromium (see next section).

Chromium

After nickel, chromium is the most important metal used by platers. It is almost universally plated from one of several variations of the chromic acid bath, wherein all of the deposited metal is added by the use of chemicals (chromium trioxide [CrO_3], commonly called chromic acid); insoluble anodes (usually of lead or lead alloys) are used. A trivalent bath has been introduced to the trade and is in commercial use. Several operating advantages are claimed for it; at present the bath has been in use for too short a time for either commercial success or performance characteristics of the deposit to be disinterestedly judged. So far as the user, as distinct from the plater, is concerned the principal caveat is that the color of the deposit does not exactly match that of "conventional" chromium plate. Recently improvements in color have been reported.

Some properties of chromium are listed in Table 11-3.

The mechanical properties of chromium are very sensitive to impurities, especially carbon, sulfur, and oxygen, which in small amounts can destroy its ductility. The metal is not sufficiently ductile to be worked at room temperature.

Chromium is white, hard, lustrous, and brittle. Although electrochemically "active" it is fairly corrosion resistant because it becomes passive or nonreactive in many environments.

TABLE 11-3—*Selected properties of chromium.*

Melting point, °C	1875
Boiling point, °C	2199
Density, g/m^3, 20°C (or g/m^2 for 1 μm deposit)	7.19
Crystal structure	body-centered cubic
Electrical resistivity, $\mu\Omega \cdot$ cm, 20°C	12.9
Electrical conductivity, %IACS[a]	14
Tensile strength, MPa, 500°C[b]	275

[a] International Annealed Copper Standard.

[b] Very variable; values to 550 MPa have been reported for electrodeposited coatings; see Safranek, *op. cit.*

Chromium reacts with the halogens. Aqueous halogen acids (hydrochloric acid etc.) and sulfuric acid dissolve it; concentrated nitric acid and aqua regia do not affect chromium.

Most oxidizing acids (concentrated nitric, perchloric, etc.) form a thin oxide layer on chromium which passivates it and renders it very corrosion resistant. In neutral solutions, dissolved oxygen has a similar effect, but in acid solutions the oxidizing potential must be stronger and the halogen acids must be absent for passivity to persist.

At high temperatures (600 to 700°C) chromium is attacked by many chemicals, including alkali hydroxides and sulfides. In air it is hardly attacked at room temperature but forms oxides when heated.

In decorative and protective/decorative coatings based on nickel or copper/nickel, chromium is the almost universal topcoat. The chromium is very thin, varying from 0.1 to 0.8 μm, but it has the important function of preventing the nickel from tarnishing. Without it, the nickel would soon acquire a greenish or yellowish stain, which, while not detracting from its corrosion protection, is unsightly.

From the electroplating standpoint, chromium is an unusual metal, and special considerations must be borne in mind when applying and specifying it. As has been pointed out, the bath has very poor "throwing power"[2] and articles to be plated in it must be of relatively simple design (see Chapter 6), without deeply recessed or internal angles, unless the purchaser is willing to pay for the special anode setups required to permit these remote areas to be covered with the deposit. Plating efficiency is quite low, so that for all but the very thin deposits used in decorative work extended plating times are required. Because of these long times, control of such variables as electroplating current and bath temperature and composition become more critical than when the work is in the bath for only a few minutes; the purchaser

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[2] This statement refers to baths based on hexavalent chromium (chromic acid). Its relevance to the new trivalent systems is not known with certainty.

should recognize the need for the additional cost entailed. Hard chromium plating requires considerable expertise. Plating shops specializing in hard chromium plating should be consulted; the average shop offering decorative plating is usually not equipped to do this work.

At least three types of decorative chromium deposits are recognized: conventional, microcracked, and microporous. All are relatively thin.

Conventional chromium is electroplated from either the openly published chromic acid baths or from proprietary solutions (which differ in only minor respects). This chromium plate tends to crack in a random pattern, and no control is exercised over the number or density of these cracks. They are not detrimental and usually are not visible. Chromium plated on bright nickel should also be bright, without need for any mechanical treatment. The principal function of conventional chromium deposits is tarnish prevention.

Microcracked chromium is produced by use of specially formulated solutions and operating conditions, from which the chromium deposit is made to crack in a regular pattern. There should be a least 300 cracks per linear centimetre when examined by standard tests. This cracking has a definite purpose. Since chromium tends to be passive, through any cracks in the chromium layer the underlying nickel is active and corrodes. When this corrosion is spread over multitudes of cracks, instead of being concentrated at a few, penetration of the corrodent to the substrate is greatly retarded and the article will retain its bright appearance much longer, without the bleeding out of rust spots from the underlying steel. Thus its function is similar to, and additive to, that of the duplex nickel undercoat. ASTM B 456 sets out the requirements for this type of chromium.

Microporous chromium has the same function as microcracked chromium, but the porosity is obtained in a different way; the underlying nickel is plated with a thin layer of nickel containing nonconducting inclusions. Chromium does not plate over these nonconducting areas, and the resulting plate is "microporous". The effect in service is the same, and so far as ASTM specifications are concerned, both types of chromium, if plated according to specification, can be expected to have equivalent service life.

Microcracking may also be obtained by use of a thin layer of highly stressed nickel immediately beneath the chromium. The chromium plate causes the stressed nickel to crack, which induces cracks in the chromium.

From the purchaser's standpoint, the method of inducing microcracking or microporosity should probably be of no concern; he can accept whichever his supplier is prepared to provide, so long as the results meet specification.

Both microcracked and microporous chromium are included in the term "microdiscontinuous".

Other types of this versatile metal can be obtained for special applications. So-called "crack-free" chromium is available by a proprietary process; it can be electroplated dull or bright. Not much used on automotive brightwork and similar parts because it does not necessarily remain crackfree under the bombardment of road dust etc., it is nevertheless useful and very corrosion resistant for applications not involving this type of service.

"Porous" (not microporous) chromium has channels, either from the plating bath itself or mechanically induced, which serve to retain oil films.

In summary, when purchasing chromium plating the purchaser should specify in accordance with ASTM B 456 if he requires any but ephemeral service; this specification includes requirements for various types of service, from mild to very severe. When purchasing hard or industrial chromium plating for engineering purposes, the best procedure is to discuss the application frankly and in detail with the plater, because each application is essentially different. Special racks or even specially built tanks may be involved. One caution must be inserted: it does little good to plate "hard" chromium on top of very soft metals such as copper unless the plating is very thick. Chromium deposits applied on ferrous parts for engineering application are covered in ASTM B 650.

Zinc and Cadmium

Although zinc and cadmium are in the same group (IIb) of the periodic system, their properties have little in common except electronegativity and valence.

Zinc is bluish white when freshly fractured. When pure, it is about as hard as copper. Commercial zinc is too brittle to be cold-rolled at room temperature, but at 100 to 150°C its ductility improves. High-purity zinc is ductile at room temperature.

Dry air does not attack zinc appreciably at room temperature, but the rate of attack increases rapidly above 225°C. Moist air attacks zinc at room temperature, and when carbon dioxide or sulfur dioxide is present the rate of attack increases. Heated in air, zinc burns with a blue flame. Zinc dust can inflame spontaneously in moist air and must be considered a fire hazard.

Normal atmospheric corrosion produces a hydrated basic carbonate of indefinite composition. The purer the metal the lower the rate of attack. This is also true of its reaction with the halogens and mineral acids, which rapidly attack ordinary zinc.

Cadmium is not nearly so electronegative (anodic) as zinc, but is sufficiently so to form a sacrificial coating on iron and steel. Cadmium dissolves in most mineral acids but, unlike zinc, does not react with alkalis.

Some properties of zinc and cadmium are listed in Table 11-4.

Zinc

Zinc electroplating is never used for its physical or mechanical properties, which are therefore of little interest to the electroplater. Except for manganese, which has no plating uses, zinc is the most active metal that can be

TABLE 11-4—*Selected properties of zinc and cadmium*

	Zinc	Cadmium
Melting point, °C	419.5	321
Boiling point, °C	907.0	767
Density, g/cm^3, 25°C	7.133	8.65
Crystal structure	hexagonal close-packed	
Electrical resistivity, $\mu\Omega \cdot$ cm, 20°C	5.92	6.83
Hardness, Knoop		
400-g load, rolled	55	30 to 50[a]
Annealed	47	...
Tensile strength		
Rolled sheet, MPa	4.43	...
Annealed sheet, MPa	1.86	...
Electrodeposited, MPa	48 to 110	70

[a] Electrodeposited.

plated from aqueous solution; this deposition is possible only because hydrogen has a high overvoltage on most substrates and on zinc. If it were not for this, only hydrogen would be produced at the cathode; zinc could not be deposited at all. The practical effect of this is that on a few substrates, notably cast iron, zinc plating is difficult. In the case of iron this is owing to the graphite inclusion; hydrogen overvoltage is extremely low on graphite. The situation can be overcome by using a thin underplate ("flash") of tin or cadmium, then applying the zinc deposit.

Zinc is used overwhelmingly for corrosion protection and to some extent for decorative purposes as a secondary function. It is usually, though not always, post-treated with chromate conversion coatings for better life and appearance.

The years of service that can be expected of zinc-plated articles is roughly proportional to the thickness of the zinc coating, and affected little (or not at all, according to some workers) by the method of application. Most galvanized steel is made by the hot-dip process, though some and increasing amounts of electrolytic galvanized sheet is made. Mechanical or "Peen" plating is also used, especially on small parts. The metal can also be sprayed. "Sherardizing" is another method of application.

Zinc may be plated from several types of solution, ranging from the conventional cyanide to low-cyanide and noncyanide alkaline baths to neutral and acid baths; some yield bright plates, others dull ones that can be brightened by chromate coatings. It has not been conclusively shown that one bath yields better results than another, though some claims for one or another process have appeared. ASTM Committee B-8 is conducting comparative corrosion tests of zinc deposits from several kinds of baths. Because of pollution control regulations the tendency is away from cyanide-containing solutions. From the purchaser's standpoint, the type of bath used should in most cases be a matter of indifference. The principal factor is the thickness and soundness of the zinc plate; see ASTM Specification for Electrodeposited Coatings of Zinc on Iron and Steel (B 633).

A zinc coating is not easily soldered, though it can be spot-welded. It is readily barrel-plated and lends itself well to continuous strip, wire, and conduit plating.

Cadmium

Cadmium is somewhat similar to zinc in physical properties; it is soft, weak, and never used for its physical properties. Its use is decreasing for several reasons: high toxicity (unlike zinc, which is only mildly toxic), high price, and occasional scarcities. It is superior to zinc, thickness for thickness, in corrosion protection in purely marine (salt) atmospheres; zinc is at least as good, and may be superior, in industrial atmospheres. Cadmium has another advantage over zinc in being solderable. The present tendency is to substitute zinc where possible; occasionally the tin-zinc alloy (80Sn-20Zn) is an acceptable substitute.

Cadmium is almost universally plated from a cyanide bath. A warning for both zinc and cadmium plating, but especially the latter, is hydrogen embrittlement of high-strength steels, which is always a danger in plating such steels but is especially characteristic of cadmium plating. A so-called "Ti-Cad" (titanium-cadmium) deposit (patented) is said to avoid this embrittlement effect; the user should satisfy himself as to the validity of these claims, since a good deal of controversy has been engendered by the development. It seems almost certain that the deposit cannot contain any metallic titanium, though it does seem to contain titanium in some form. Several publications are available on hydrogen embrittlement, with special attention to cadmium. For example, see *Hydrogen Embrittlement Testing, ASTM STP 543,* 1974, and W. Beck, E. J. Jankowsky, and P. Fischer, "Hydrogen Stress Cracking of High-Strength Steels," Naval Air Development Center NADC-MA-7140, Warminster, Pennsylvania, 1971, and the references cited therein.

Tin

Tin is a soft, ductile metal having little strength. Its ductility is of importance in electroplating of bearings (usually with tin-lead alloy rather than pure tin), and articles plated with it can be deformed without danger of cracking the deposit. Its principal uses are in food-handling equipment (including, of course, the "tin can") and electrical equipment, for its solderability.

Some properties of tin are listed in Table 11-5.

Tin is easily cold-worked by rolling, extrusion, and spinning. It is silvery-white, but as-cast may have a yellowish tinge owing to a thin film of oxides. Highly polished tin has good light reflectivity.

TABLE 11-5—*Selected properties of tin.*

Melting point, °C	231.9
Boiling point, °C	2270
Density, g/cm^3	
α (gray)	5.77
β (white, ordinary)	7.29
Transition temperature, α β °C	13.2[a]
Resistivity, $\mu\Omega \cdot$ cm, 20°C, β-form	11.5
Electrical conductivity, %IACS[b]	15
Tensile strength, cast, 15°C, MPa	14
Brinell hardness, 10 kg, 20°C	3.9
Crystal structure	
α (gray)	cubic
β (white)	body-centered tetragonal

[a] Authorities disagree; figures as high as 18°C have been reported.
[b] International Annealed Copper Standard.

Tin reacts with both acids and bases, but usually oxygen or an oxidizing agent must be present if the reaction is to proceed rapidly. Distilled water has no effect, and tin vessels and pipes have been the preferred medium for storing and transporting it; tin pipes are also used for dispensing beer.

The tin-iron galvanic couple is the basis of the can industry. Although normally cathodic to iron, in the oxygen-free environment inside the can the potentials reverse and the tin is sacrificial.

Most gases do not react with tin; exceptions are moist sulfur dioxide, the halogens, and oxygen at high temperatures. Hot sulfuric acid and cold dilute nitric acid dissolve tin. Concentrated nitric acid reacts to form an insoluble "metastannic acid". Several other less common acids also dissolve tin.

Dilute ammonia and alkali carbonates have little effect; strong alkalis react readily. Oxidizing salt solutions dissolve tin; the reaction with ferric chloride is used in the printed circuit industry as an etchant.

Tin and its inorganic compounds are relatively nontoxic; this property makes the tin can industry possible. Many organo-tin compounds are highly toxic, but they are not likely to be encountered in the finishing trade.

Tin is easily plated from a wide variety of solutions. The conventional alkaline stannate solutions, and the stannous sulfate and fluoborate acid baths, yield dull deposits. Baths yielding bright deposits have been developed, based on the sulfate bath.

Dull deposits can be brightened by a heating process known variously as flow-brightening, reflowing, and fusing. In this technique, the tin coating is heated above its melting point of 232°C and quickly quenched. The temperature required is low enough so that articles are seldom adversely affected, though, of course, it cannot be used on printed-circuit boards and similar substrates.

There is considerable disagreement as to the virtues of a bright tin electroplate. Since tin is seldom used decoratively, it would seem that brightness is of little importance. Nevertheless, the bright acid solutions are in wide use. Flow-brightening, on the other hand, can be of benefit beyond the brightening effect; the melting process tends to smooth out the plate and cover any pores or discontinuities. There is little convincing evidence that, so far as performance goes, the type of bath used and whether the tin is bright or dull make much difference; see ASTM B 545.

Tin is subject to two types of degradation of which the user should be aware, even though their perils are often exaggerated. "Tin pest" is an allotropic modification of tin, the so-called alpha- or gray tin. It is essentially nonmetallic (in fact is a semiconductor) and possesses none of the favorable properties for which tin is used. The transformation of beta- or ordinary tin to the alpha or gray form can take place at temperatures as high as about 15°C (there is some doubt as to the equilibrium transformation temperature), but at these temperatures the transformation is so slow as to be of no concern. When, however, tin (including tin deposits) is held at very low temperatures for extended periods (for example, an extremely cold winter in an unheated warehouse) the transformation may, not necessarily will, take place. Once started, the transformation spreads fairly rapidly, hence the name "tin pest" or "tin disease". This transformation is normally of no concern; when the purchaser has cause to worry about it, it may be inhibited or prevented by codepositing with the tin a small amount (0.1 to 0.5 percent) of bismuth or perhaps antimony or lead. A proprietary process for depositing the bismuth alloy is available.

The second warning about the use of tin has to do with "tin whiskers". Tin is by no means the only metal coating that grows "whiskers"; in fact many metals under appropriate conditions develop these growths. They are, however, of particular interest for tin, because of the wide use of tin plate on miniature electronic equipment. Thin filaments of tin can grow from the coating and reach lengths up to a few millimetres. In these components, this amounts to a conductive path that can cause short-circuiting and failure. High voltage quickly burns off the whiskers, but the low voltages that are characteristic of much electronic equipment cannot do this. Considerable research has been reported, both on the occurrence of whiskers and on the means of avoiding them. Heat treatment after plating, and codeposition of small amounts of lead, are among the remedies suggested. Again, the danger should not be exaggerated; many cases of so-called tin whiskers have been shown to be merely lint or other adventitious excrescences.

Lead

Lead is a soft, ductile metal with little strength; its physical and mechanical properties are of little interest to its use as a coating material. Some properties of lead are listed in Table 11-6.

Under a load lead will flow, even at room temperature. This property

TABLE 11-6—*Selected properties of lead.*

Melting point, °C	327.43
Boiling point, °C	1740
Density, g/cm^3	11.34
Crystal structure	face-centered cubic
Electrical resistivity, $\mu\Omega \cdot$ cm, 20°C	20.65
Brinell hardness, cast	4.2
Tensile strength, MPa	14

renders it easy to fabricate by rolling and extrusion. Lead can be stiffened by alloy additions and is readily welded and extruded. In combination with other low-melting metals it is used for fusible alloys in sprinkler systems and electrical fuses. It is the heaviest common metal and is impermeable to most types of radiation.

Lead tarnishes readily in moist air but not in perfectly dry air or in air-free water. Molten, it oxidizes in air. It dissolves readily in dilute nitric acid, less rapidly in the concentrated acid. Dilute hydrochloric and sulfuric acids have little effect owing to the formation of insoluble films of lead chloride and lead sulfate. Lead resists sulfuric acid at all concentrations up to about 200°C; above that temperature it is attacked and at 260°C it dissolves.

Many organic acids attack lead in the presence of air. At high temperatures it is attacked by sulfur dioxide. Hydrofluoric acid attacks it at first exposure, but a film of lead fluoride inhibits further reaction.

All soluble compounds are toxic and the fumes or dust of the metal are hazardous. The hazard is enhanced because the effects are cumulative.

Lead electroplating is not very common; it is used on parts for storage batteries and some chemical equipment for its resistance to sulfuric acid. Much more common is the plating of lead-tin alloys of various compositions: low (5 to 10 percent) tin, for bearings, lining of gasoline tanks, and roofing (terne plate), more commonly hot-dipped than electroplated; and higher (50+ percent) tin, for solderability. This "solder plate" is useful in plating printed-circuit boards and other communications equipment requiring easy solderability; since it has the same composition as the solder used, no change in the composition of the solder pot takes place. Bright solder plating, from proprietary baths, is available. Like bright tin, the advantage of the bright over the usual mat plate is principally cosmetic, since neither coating is used decoratively and components are in general not visible to the ultimate consumer.

Silver

The decorative uses of silver are well known. Although silver is a noble metal, it tarnishes readily in sulfur-containing atmospheres; otherwise it is fairly unreactive.

Some properties of silver are listed in Table 11-7.

TABLE 11-7—*Selected properties of silver.*

Melting point, °C	960.8
Boiling point, °C	2212
Electrical resistivity, $\mu\Omega \cdot$cm, 20°C	1.59
Electrical conductivity, %IACS[a]	
Pure	108.4
Ordinary 999 fine	104
Crystal structure	face-centered cubic
Density, g/cm^3, 20°C	10.941

[a] International Annealed Copper Standard.

Silver is a brilliantly white metal, much prized for tableware and ornamental pieces. Pure silver has higher electrical and thermal conductivities than any other metal, and the lowest contact resistance, although the last may deteriorate owing to tarnish films.

Silver is inert to many reagents. Its reaction with sulfur-containing gases to produce tarnish is well known. Its principal reaction is with nitric acid, at all concentrations. At elevated temperatures silver reacts with all the halogens; it is dissolved by cyanide solutions in the presence of air. Most of the reactions of silver with a long list of other reagents are slow.

The purity of silver is quoted in parts per thousand or "fineness" rather than percent; commercial silver is "999 fine" or 99.9 percent pure. Sterling silver is 92.5 percent pure.

Soluble silver salts are poisonous, but the metal presents little if any hazard.

For items such as flatware and hollowware, silver plate comes in many thicknesses, depending on trade designations (for flatware) such as hotel plate and triple plate; the thicknesses (strictly speaking, the mass of silver per stated number of items) are subject to Federal regulations. The use of silver for flatware is decreasing somewhat, but silver plate is used widely on other items such as trays, hollowware, and candlesticks.

The engineering uses of silver are becoming more important. Its high conductivity makes it the preferred coating for the interior of wave-guides for radar and other advanced technology components. In printed circuits it must be used with caution, if at all, because of its tendency to "migrate"—that is, to creep across insulation and cause electrical shorts.

Although many attempts have been made to protect silver against tarnishing, none has had outstanding success. When justified, a thin overplate of gold may serve. See ASTM Specification for Electrodeposited Coatings of Silver for Engineering Use (B 700).

Gold

Owing to its high, and extremely variable, price, gold is used as a coating metal only when nothing else will do, unless the aim is purely decorative. For most metals, the cost of plating will be determined more by the plater's labor and overhead than by actual metal price. This is not true of gold (and the other precious metals); the cost of plating will, of course, include the usual overheads, but the cost of metal deposited will be a major factor. The capital investment in gold-plating solutions is high, more than one hundred dollars a litre. This leads to fairly obvious conclusions: (*1*) specify gold plating only when no cheaper substitute is available to do a comparable job, (*2*) specify only such a thickness as will satisfy the performance requirements, and (*3*) if possible, use the gold plate only on functional areas. Even with these reservations, the uses of gold plating are many; especially in the communications industry, for parts that must perform without failure for many years, there is no completely satisfactory substitute.

Some properties of gold are listed in Table 11-8.

Gold is extremely noble and does not react with oxygen, sulfur, selenium, nitrogen, or carbon at any temperature.

The halogens, when dry, react slowly if at all, except for bromine. In the presence of moisture, bromine reacts rapidly, chlorine and iodine somewhat more slowly.

Gold resists most acids unless oxidizing agents are present. The most active solvent is aqua regia (nitric acid 1 part, hydrochloric acid 3 parts). The only single acid that dissolves gold in the absence of oxidizing agents is selenic at about 225°C.

Gold is not attacked by alkalis, but cyanide solutions dissolve it in the presence of oxygen. Mercury readily amalgamates with gold; contact with mercury and mercury salts should be avoided since it may cause cracking. Gold dissolves in molten tin, an important factor in soldering to gold-plated parts, since the resulting gold-containing solder may be brittle.

For decorative purposes the uses of gold electroplating are well known and need not be discussed in detail. Although tin-bronze plating can simulate gold in color, it cannot equal it in tarnish resistance. By judicious alloying, gold electroplating can be produced in many colors and shades.

In the trade, the purity of gold is expressed in karats. A karat is $\frac{1}{24}$ part of pure gold in an alloy; therefore 24K gold is pure, 18K is $\frac{18}{24}$ or 75 percent gold, etc. 24K gold is so soft that it is seldom used for decorative applications;

TABLE 11-8—*Selected properties of gold.*

Melting point, °C	1063[a]
Boiling point, °C	2809
Crystal structure	face-centered cubic
Density, g/cm^3, 25°C	19.302
Electrical resistivity, $\mu\Omega \cdot$ cm, 20°C	2.06
Tensile strength, annealed, MPa	124
Hardness, Vickers	25

[a] Calibration point on the thermometric scale.

18K is more common. (However, relatively pure gold electrodeposits can be produced that are significantly harder.) The alloying metal(s) may be copper, silver, nickel, cobalt, tin, and others. The United States and other countries have strict rules concerning the labeling and description of gold coatings on consumer goods.

Although gold may be electroplated from solutions whose formulas are in the open literature, most platers use one or more of the many proprietary processes on the market. The supply houses in this field are fiercely competitive and formulations are promoted offering almost any combination of color, purity, and physical properties desired. In the decorative field—jewelry, watch cases, and the like—the manufacturer should specify the thickness required and the purity and color, the last-named preferably by offering samples for matching. He may then represent the article as, for example, "10% 18K gold plated," which means that 10 percent of the weight of the article is gold, of 18K purity. Governmental regulations concerning decorative gold coatings and their nomenclature are complex and not necessarily logical.

Today, more gold is used industrially than decoratively. It owes its use to a unique combination of properties: tarnish resistance, good conductivity, low contact resistance, good solderability, and high emissivity and other light- and heat-absorbing or reflecting properties.

ASTM B 488 specifies many types and thicknesses of gold for these applications. In terminals that must undergo millions of makes-and-breaks without intermittency or failure, gold is unsurpassed as a surface coating. Because of the high price of the metal, many means have been developed for putting the gold only where needed; for example, just on the tip of the terminal connector rather than the whole piece. For most of these applications, the gold should be fairly pure, 99 percent or better, and the alloying metal used mainly for hardening.

Gold coatings are usually as thin as practicable for the application, often a micrometre or less. Determining the thickness can be a problem. Most users use the beta backscatter method. With proper precautions this technique is reliable, but manufacturer's directions should be scrupulously followed, since there are, without these precautions, many chances for error. The purchaser must know the thickness and the density of the gold plate not only to be sure it meets his performance requirements, but also to satisfy himself that the plater has delivered the amount of gold he is charging for.

The remaining plateable metals are rarely used and will be considered in lesser detail.

The Platinum Metals

Of the six platinum metals, the only two that have had significant uses in plating are palladium and rhodium. Brochures on the metals and a booklet outlining the electroplating applications are available.[3] A useful summary of the corrosion resistance of the metals to various reagents is provided by R. F. Vines in *Corrosion Resistance of Metals and Alloys,* 2nd ed., F. L. LaQue and H. R. Copson, Eds., Reinhold, New York, 1963.

Palladium is the least noble of the group. It is very permeable to hydrogen, a property that has been made use of in several types of diffusion apparatus. In some applications it may substitute for gold, but these uses, though being actively studied, are not yet well established, and the user should assure himself by appropriate tests that the substitution is justified. The advantage of palladium is its much lower cost, by both mass and volume; metals are purchased by mass but used by the volume. Engineering coatings of palladium are covered in ASTM B 679.

The other platinum metal in fairly wide use is *rhodium.* It is the most expensive metal commonly plated, and in general only very thin coatings are used, principally for reflectance and tarnish prevention. Thick deposits tend to crack. It is electroplated almost entirely from proprietary solutions. ASTM B 634 offers guidance to thicknesses of rhodium appropriate to various applications.

The other four platinum metals—*iridium, osmium, ruthenium,* and *platinum* itself—are little used as coatings. Platinum plating is fairly well established; the other three are strictly experimental, but there is increasing interest in ruthenium.

Some properties of the platinum metals are listed in Table 11-9.

Iron

Although electroplated iron is somewhat more corrosion resistant than ordinary iron or steel, perhaps because it is purer, it is difficult to plate consis-

TABLE 11-9—*Selected properties of the platinum metals.*

	Ru	Rh	Pd	Os	Ir	Pt
Melting point, °C	2310	1960	1552	3045	2443	1769
Boiling point, °C	4100	3700	2900	5000	4500	3800
Density, g/cm^3	12.45	12.41	12.02	22.5	22.65	21.45
Electrical resistivity, $\mu\Omega \cdot$ cm						
0°C	6.6	4.33	9.93	8.8	4.71	9.85
20°C	7.2	4.5	about 10.4	9.5	6.11	10.6
Tensile strength, annealed, MPa	540	755	165	...	1100	137
Vickers hardness, annealed	220	120	38	400	500	39
Crystal structure	hcp[a]	fcc[b]	fcc	hcp	fcc	fcc

[a] hcp = hexagonal close-packed.
[b] fcc = face-centered cubic.

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[3] From INCO, One New York Plaza, New York, N.Y. 10004.

tently and has few applications. It is occasionally used for its physical and mechanical properties. Because it does not easily alloy with solder, copper soldering iron tips are sometimes plated with iron. Iron is used by the Bureau of Printing and Engraving for printing plates. The alloy of iron with nickel is mentioned later.

Indium

Indium is expensive. It is easily deposited, but aside from a few applications in the computer and allied fields, and as a constituent of bearings, it has few uses.

Rhenium

Rhenium is extremely rare. It has been used for some aerospace applications, and an alloy with silver has a low coefficient of friction at high temperatures, but on the whole it is of little importance in electroplating.

Cobalt

Cobalt is so much like nickel, and so much more expensive, that it has seen few uses in general plating. The metal and some of its alloys with iron, nickel, and phosphorus have interesting magnetic properties, which has led to some applications in memory devices. Other methods than electroplating, however, are generally used to produce these devices.

Alloys

The tin-lead alloys and the various gold alloys have already been mentioned, as have brass (copper-zinc) and bronze (copper-tin). Much research has been published on alloy plating, but little of it has led to commercialization. The following alloys have also had some commercial applications.

Nickel-Iron

This deposit may be of interest when it is desired to economize on the use of expensive nickel. Alloys containing up to about 40 percent iron are commercially plated and decoratively appear to be equivalent to bright nickel. Their corrosion behavior has not been fully investigated, and the alloys should not be considered equivalent to nickel in ASTM B 456 without prior testing.

Nickel-Cobalt

This alloy has some interesting magnetic properties for special applications in the computer and allied fields. Although it was used for a time as a substitute for pure nickel when the latter was in short supply, cobalt is more expensive than nickel and unless the latter once again becomes scarce there is little reason for the substitution.

Tin-Zinc

An alloy containing about 20 percent zinc and the remainder tin has been extensively investigated and has enjoyed limited use as a solderable coating. It is a possible substitute for cadmium in some applications.

Tin-Nickel

This alloy, an intermetallic compound (SnNi) containing 65 percent tin and 35 percent nickel, is the subject of ASTM B 605. Tin-nickel is very corrosion resistant, provided that when the substrate is steel, a copper or bronze flash is used as an undercoat. It is resistant to many chemicals and may be useful as an etch resist in printed circuits and related items. Its color is somewhat warmer than that of chromium, nearer to that of stainless steel; it has some uses as a decorative coating on interior household appliances. Although not fully bright as plated, tin-nickel is only somewhat hazy and easily brightened mechanically, or if thin enough, over a bright substrate, the brightness persists. Like all intermetallic compounds, it is somewhat brittle, and cannot stand much deformation after plating. Tin-nickel has been used as a gold substitute in some applications. It is solderable, though not so easily as tin or tin-lead.

Tin-Cobalt

This alloy (with a small amount of a third constituent) has been promoted as a substitute for chromium as a topcoat over bright nickel for decorative purposes. It may be useful for parts being barrel plated; barrel plating of chromium poses problems owing to the current interruptions to individual parts. Tin-cobalt appears to have better throwing power than chromium and so may be valuable for plating complicated shapes. In appearance it bears a fair resemblance to chromium. At present, however, tin-cobalt should not be regarded as the equivalent of chromium for protective applications—certainly not for hard chromium—and should not be substituted for chromium in ASTM specifications.

Chapter 12—Tests for Compliance

It is assumed that the plater will have performed his own testing to assure himself that his work will be acceptable to the purchaser. However, the purchaser will also wish to perform at least some of these tests. Such matters as who is to pay for tests, what proportion of the parts may be "out of spec" for a lot to remain acceptable, for umpire tests in case of disagreement, and for the period of time allowed the purchaser to notify the plater of rejection of a lot, are matters that should be written into the contract. Many tests are destructive, so that agreement must also be reached on what proportion of the parts may be tested to destruction; this must also be part of the original contract.

It is usually not possible to test every piece in a lot; therefore sampling plans must be agreed in advance also. ASTM B 602, Method of Attribute Sampling of Electrodeposited Metallic Coatings and Related Finishes, and ASTM B 697, Guidelines for Selection of Sampling Plans for Inspection of Electrodeposited Metallic Coatings and Related Finishes on Products, offer guidance, but many other plans are available. Some of these are mentioned in B 602 and B 697. With critical items that can be tested nondestructively, it may be necessary to test each part. More often, however, some statistical sampling plan will be more practical.

Thickness of the deposit, either minimum or average, is the most commonly specified property of electroplated coatings, and many tests are available. Several are described in ASTM Practice for Measuring Thickness of Electrodeposited and Related Coatings (B 659). Thickness tests may be classified as destructive, semidestructive, or nondestructive. As the names imply, the first destroys the part; the second destroys the coating but not the part, which may be replated; and the third leaves the part intact. All three types are useful; the third may be preferred if applicable.

The most common destructive test is microscopical examination of a cross section. Directions may be found in ASTM Method for Measurement of Metal and Oxide Coating Thicknesses by Microscopical Examination of a Cross Section (B 487). This procedure, once considered a referee method, has been called into question, as reports of cooperative tests indicate that, although one laboratory can achieve good replication, agreement among laboratories is often unsatisfactory. The results appear to depend to some extent on operator idiosyncrasy. The method also requires expert technicians, is time-consuming, and is, of course, completely destructive. Although it maintains a place among the thickness testing procedures, it is no longer the method of choice.

Among other destructive methods may be mentioned several chemical techniques, not subject to ASTM specification but rather obvious in execution. These methods yield average rather than local thicknesses. In one, the whole part, or a number of small parts, is dissolved in an appropriate chemical reagent and the resulting solution is analyzed for the coating metal. The handbook value for the density of the coating metal is used to calculate the average thickness of the coating over the total area dissolved. The method is especially useful for small parts such as nuts, bolts, and terminals. The coating metal can not be the same as one of the constituents of the basis metal—for example, a zinc coating on brass—or dissolution of the basis metal will yield incorrect measurements.

A similar, but sometimes only semidestructive method, is the weigh-strip-weigh technique. If a reagent that dissolves the coating without attacking the basis metal is available, the part may be weighed, stripped in the reagent, and reweighed. Alternatively, the stripping solution may be analyzed for the coating metal; this method is commonly used for determining the weight of tin on electrolytic tinplate.

One of the most useful semidestructive techniques is the coulometric, described in ASTM Method for Measurement of Thickness of Metallic Coatings by the Coulometric Method (B 504). The technique is usually considered to be among the more accurate ones available; commercial instruments are available, calibrated directly in thickness. The coating is stripped from only a very small area, and if such an area can be found that is not significant to the appearance or function of the part (and whose coating thickness is still representative) the method can even be deemed nondestructive. In any case, the part itself is not damaged and can be stripped and replated.

Among other semidestructive tests for local thickness may be mentioned the Dropping Test (ASTM B 555), applicable to zinc, cadmium, copper, and tin coatings; and the Spot Test for Thin Chromium Coatings (ASTM B 556). These tests are of limited precision and applicability, but are easy to perform and require little apparatus—an advantage in cases where major outlays for instrumentation are not justified.

Finally, in the semidestructive category, is ASTM Method for Measurement of Thickness of Transparent or Opaque Coatings by Double-Beam Interference Microscope Technique (B 588). This test is precise but requires considerable instrumentation. It is especially applicable to anodized coatings on aluminum, and for heavier coatings of this type it may be nondestructive.

There are several methods by which the thickness of a coating can be measured nondestructively. None is universally applicable and some are applicable to a limited group of finish-substrate combinations. Except in special cases, they are limited to measuring single coatings.

A widely used method is covered by ASTM B 567, Measurement of Coating Thickness by the Beta Backscatter Method. A small radioactive source of beta particles (electrons) is brought near the coated product. Some of the electrons are reflected by the product and are detected and counted by a Geiger counter. The proportion of electrons that is reflected is determined by the atomic numbers of the product. With a coated product both the coating and the substrate reflect electrons, and the amount will be determined by the quantity of coating present and the atomic numbers of the coating and substrate. These atomic numbers must be sufficiently different for the method to distinguish between them. Generally, the difference must be at least five units. Thus gold coatings (atomic number 79) on nickel (atomic number 28) can be measured because the difference is 51 units; conversely, nickel coatings on copper (atomic number 29) cannot be measured, because the difference is only one unit. The equipment for beta backscatter is moderately expensive, easy to operate, and available from several sources.

A generally applicable method of measuring metallic coatings utilizes X-ray fluorescence (ASTM B 568, Measurement of Coating Thickness by X-ray Spectrometry). The coated product is irradiated with X-rays and the intensity of the radiation stimulated in the coating is measured. The intensity of the stimulated radiation is determined by the amount of coating present. The instrumentation is expensive and requires a skilled technician.

Nonconductive coatings on nonmagnetic, conductive substrates can be measured by inducing electrical eddy currents into the substrate and measuring their intensity. A nonconductive coating, by separating the probe from the substrate, attenuates the current to an extent that is determined by the thickness of the coating. This method is covered by ASTM B 244, Measurement of Thickness of Anodic Coatings on Aluminum and of Other Nonconductive Coatings on Nonmagnetic Basic Metals with Eddy-Current Instruments. The equipment is moderately expensive, simple to operate, and available from several sources.

Two nondestructive methods work by measuring the magnetic properties of the coating or the substrate. The application of the two methods is apparent from their ASTM titles: B 499, Measurement of Coating Thicknesses by the Magnetic Method: Nonmagnetic Coatings on Magnetic Basis Metals; and B 530, Measurement of Coating Thicknesses by the Magnetic Method: Electrodeposited Nickel Coatings on Magnetic and Nonmagnetic Substrates. The instruments range from inexpensive to moderately expensive. They are easy to operate and are available from several sources.

A final nondestructive method covered by ASTM has a specific usage: B 681, Measurement of Thickness of Anodic Coatings on Aluminum and of Other Transparent Coatings on Opaque Surfaces Using the Light-Section Microscope. A thin beam of light is directed at 45 deg onto the surface. The reflected light contains an interference pattern as the portion of the beam that was reflected directly from the coating surface interacts with the portion that penetrated the coating and was reflected by the substrate. The spacing of the interference pattern is a function of the thickness of the coating. The equipment is moderately expensive and requires some degree of skill in use.

Adhesion of the deposit to the product is essential if the deposit is to perform its function. For this reason an adhesion requirement is always, or should always be, part of a plating specification. The standard preparatory and electroplating processes in a large majority of electroplating applications will yield deposits that have "perfect" adhesion to the substrates. By "perfect" is meant that the strength of the bond between the deposit and the substrate is at least as great as the ultimate tensile strength of the weaker of the metals, deposit and substrate. With perfect adhesion, no matter how an electroplated product is stressed, if it fractures the break will occur either in the substrate or the deposit or across both but there will be no separation of the deposit from the substrate. An exception may be a baking test in which the coated product is raised to some moderately elevated temperature, cooled, and examined. This test depends on differences in thermal expansion or in the evolution of gases or vapors to break the bond between an inadequately adherent deposit and the substrate. However, at the test temperature metallurgical and chemical reactions may occur between the substrate and deposit and improve or degrade adhesion.

There is no quantitative method for measuring the adhesion of a deposit on a product. The tests that are used are of the go-no-go type and, with the possible exception of the bake test, are destructive. ASTM B 571 describes the most commonly used tests and gives guidance in selecting one. The fact that the tests are qualitative only is intellectually unsatisfying but adequate practically because of the aforementioned fact that perfect adhesion is the norm. The test needs only detect deviation from a readily attainable condition.

There are deposit-substrate combinations where perfect adhesion is not the norm and possibly is unattainable. These involve unusual substrate metals such as tungsten, molybdenum, titanium, and uranium. In these cases, special adhesion tests are used which may simulate service conditions. The electroplater and the designer need to work together to devise a suitable test and adhesion criterion.

There are quantitative adhesion tests that require special test specimens. They are of value in developing processes and trouble-shooting process problems, but are not applicable to testing products. More about these tests may be found in the literature.

Appearance of the deposit is commonly controlled by the specification of the electroplated coating. The importance of appearance in decorative coatings is obvious. The attractiveness of a coating is highly subjective and thus difficult to define quantitatively. The best practice is for the electroplater and the buyer to agree upon what is to be supplied and to select standard specimens that represent acceptable appearance.

Appearance is also important to protective and engineering coatings because it can indicate the quality of the coating. Therefore appearance is controlled in the specifications for these coatings. Some defects are obvious, such as blisters, peeling, and roughness. Others, minor variation in color and luster, are more subtle, but can be recognized by an experienced inspector. ASTM standards always contain appearance requirements.

Corrosion resistance for the deposit usually is defined in terms of performance in an accelerated corrosion test. Coated products are exposed for stated periods, usually a few hours to a few days, to an artificial corrosive environment such as a spray of a water solution of common salt, copper chloride, and acetic acid (CASS Test, ASTM B 368). In another, a slurry of clay and salts is applied to a coated item which is then exposed to high humidity (Corrodkote Test, ASTM B 380). Other spray tests use salt water (ASTM B 117), salt water plus acetic acid (ASTM B 287), and synthetic sea water (ASTM G 43).

Although corrosion tests are used to determine whether a coating will perform as intended in a corrosive environment, the tests cannot be used to predict the service life of the coating (because corrosive environments are so variable in nature) nor can the tests be used to compare performances of different kinds of coatings. The value of the corrosion tests is that from experience it is known how a particular coating should perform in an accelerated test and that if a tested coating performs as expected it should also perform as expected in service.

Closely related and often overlapping the corrosion tests in purpose are tests for *porosity*. All practical electroplated coatings contain microscopic pores that expose the substrate to the environment and that can be sites for undesirable corrosion and tarnishing. Porosity can be reduced by proper preparative processes and electroplating practices. Total elimination of pores usually can only be obtained by increasing the thickness of the coating. Porosity tests treat the coated product with a chemical that does not affect the coating but reacts with the substrate to form readily visible corrosion products. Evaluation consists of counting the number of pores revealed by the test and referring to a maximum allowable number.

Gold coatings are tested for porosity by exposure to nitric acid vapor or to moist sulfur dioxide (ASTM B 583). The salt spray test (ASTM B 117) is used as a porosity test of coatings that are unaffected by the salt solution; for example, lead and lead tin alloy coatings on steel (ASTM B 200). Several ASTM specifications contain porosity tests and requirements. ASTM Committee B-8 is preparing test methods for the more commonly used porosity tests.

Depending on specific applications it may be necessary to measure electrical and thermal conductivity, reflectivity, temperature resistance, and other properties needed for specific applications. Standard tests often are not available for these less commonly controlled characteristics. The designer and electroplater may have to design tests that are appropriate to the application.

Other tests that are used to a lesser extent than those hitherto described concern the *ductility* of the coating (ASTM B 489 and B 490), which can be important if the coated product is flexed in service; *hardness* (ASTM B 578), where wear resistance is important; and *solderability* (ASTM B 678), for coated products that are soldered to other products during assembly operation. *Composition* is determined in alloy coatings (lead and lead/tin, ASTM B 200; tin/lead, ASTM B 579; and tin/nickel, ASTM B 605), and *purity* is important in gold plating (ASTM B 488) and nickel plating (ASTM B 456 and B 604).

Conclusion

Metallic coatings offer a wide range of properties which provide the designer with a versatility well beyond that of single substances. The effective utilization of these coatings, however, is absolutely dependent on some understanding of their properties, the coating processes, the pertinent specifications, and the methods of evaluation. The intent of this manual has been to provide the prospective user of coatings with the insight needed to work with the suppliers of coatings so that together effective products of reasonable cost can be produced.