Second Edition

NICKEL AND CHROMIUM PLATING

J. K. Dennis and T. E. Such

Butterworths

Nickel and chromium plating

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Nickel and chromium plating

Preface to the first edition

This book is written for scientists, technologists and students who may have diverse backgrounds but who wish to acquire a knowledge of the fundamentals on which the important industrial processes of nickel and chromium plating are based. Its scope includes descriptions of the methods of deposition and the properties of the coatings of these metals obtained from aqueous solutions (with or without electric current) and either applied individually or superimposed. (The latter is the case for most of the 'chrome' plating that is carried out today.) The emphasis is placed on the modern techniques employed for the deposition of these metals, whether it is for decoration, corrosion protection or engineering applications. However, obsolete processes are briefly described in the first chapter, which it is felt makes an essential and interesting introduction to current practice.

We hope that scientists who are already working in this field will find our review of this modern technology to be of assistance to them, whether they are in fundamental or applied research, or employed in the industry. It must be pointed out that the book is intended to provide information of a standard that is also suitable for undergraduates reading for degrees in industrial metallurgy or chemistry and graduates taking specialized M.Sc. courses in corrosion and protection; it is not meant to serve as a practical handbook to give shop-floor guidance on how to prepare and operate production plating baths. It will also be of assistance to students studying for qualifications awarded by bodies such as the Institute of Metal Finishing, Institution of Corrosion Technology, Royal Institute of Chemistry and Institution of Metallurgists. We have therefore included chemical, electrochemical and metallurgical theory where such knowledge is essential to the full understanding of the processes described. The most significant features of the organic compounds added to produce bright nickel plate are summarized in Appendix 1, so that the effect of these addition agents can be understood more easily by the reader, who otherwise could be confused by the proprietary nature of these processes and the large number of patents in existence. Those involved in production plating should derive considerable help from the detailed descriptions and critical comparisons of alternative plating processes now available and of the control techniques that can be used for the solutions and the coatings they produce. The analytical appendix should assist those plating in either 1 litre beakers or 1000 gal vats. In view of the arrival of SI units, these have been used wherever possible, but have been slightly adapted where it seemed desirable.

Our main reason for writing this book was to fill a gap that we felt existed in metal-finishing literature. We considered that there was no up-to-date English text dealing with both nickel and chromium plating, except from the operational approach. This might well encourage newcomers to the field to consider it to be more an art than a science. The subject matter of this book has been included in some previous publications, but it has usually been treated in a limited manner based mainly on the particular scientific discipline in which the author was trained. Metal deposition does not fit neatly into the sphere of any pure science, for it is concerned both with the properties of the electrolyte solution (chemistry) and of the metal deposit (metallurgy) and, of course, the process of obtaining one from the other (electrochemistry). We considered that our experience could be combined to enable us to write a text suitable not only for those first encountering this technology but also for those experienced in the field, by reviewing, as far as possible, all of the most important information published in widely scattered papers, including very recent ones. Some unpublished work and many new optical and electron photomicrographs are also included.

We hope that we have achieved our aim of providing our readers with the opportunity of obtaining in one book detailed scientific information on nickel and chromium plating, previously available only in scattered and unconnected texts.

We are most grateful to those colleagues who aided us by supplying information, assisting with photographic work or taking part in helpful discussions. We also wish to thank all those organizations who supplied or allowed us to reproduce illustrations and graphs. Reference to their original source is given in the captions or accompanying text. However, we are particularly grateful to the following for their permission to include a number of figures that were originally published by them:

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J.K.D.
T.E.S.

Preface to the second edition

A most far-reaching change to the nickel and chromium electroplating industry has occurred since 1972. This is the vast decrease in the usage of bright nickel plus chromium electrodeposits for decorative purposes on vehicles and many other consumer-durables. However, this is partly compensated by the increasing use of nickel plate for all kinds of engineering applications.

Therefore, we have not merely updated the first edition but have also placed additional emphasis on certain methods that have achieved more industrial use in the 14 years since the first edition was published. This is particularly the case for autocatalytic (electroless) nickel deposition and for nickel plating onto aluminium and other difficult substrates and to a lesser extent to plating onto plastics and high-speed plating. Each of these is now the subject of a separate chapter. Also, since the first edition was published, the deposition of various nickel alloys has expanded greatly, both for decorative and functional applications, and so a new chapter on this topic was felt to be essential. Other topics, such as composite coatings and tampon (brush) plating, are now included, for although only forming a very small proportion of the total quantity of the nickel plated annually, they are usually employed for very demanding applications, for which other techniques may not be suitable.

The inclusion of this extra material has obviously lengthened the book. It would have been even longer, if some material from the first edition had not been deleted. The former Chapter 2 and the Appendices have, therefore, been eliminated. The majority of Chapter 2 was concerned with the electrochemistry of electrodeposition from aqueous electrolyte solutions, and this information is available in many other textbooks. The subject matter of Appendix 1 can be obtained and updated by anyone who wishes to study published Patents, while analytical methods of Appendix 2 are contained in books and papers dealing with this subject. The properties of the metals listed in Appendix 3 are given in many standard reference works.

We hope that those new to the plating industry will find this book to be of assistance and that those experienced in the industry will find its revised version enables them to keep up-to-date with the latest developments in this specialized technology.

Finally, we wish to thank all those who have helped us by supplying information or critically perusing parts of the manuscript.

J.K.D.
T.E.S.

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Contents

Chapter 1

Introduction and historical review

Electrodeposited metals can often be employed as an ideal means of providing a thin surface coating which has some property (or properties) superior to that of the substrate. It may, for example, be possible to employ a cheaper or stronger substrate than could otherwise be used and yet achieve good corrosion resistance by applying a suitable electrodeposited coating.

Electrodeposited nickel is typical of metals which can be included in the above category. It is often applied for decorative and protective purposes to cheap mild-steel pressings and to die-cast zinc or aluminium alloy components. Die-casting is an economical means of mass-producing exact dimensional replicates of the original, but the alloys used are not suitable for service in a corrosive atmosphere without some form of protective coating. About 90% of the estimated 60 000 t of nickel consumed during 1980 in the electroplating industry of the non-communist countries was used in the form of thin, corrosion resistant and often also decorative coatings on cheaply produced or strong substrates. Most nickel coatings of this type are subsequently chromium plated to form the familiar composite nickel plus chromium system.

While nickel coatings may be applied solely for corrosion resistance where their inherent dullness is of no importance, the majority have to provide both decorative and protective functions. If a final bright appearance is required, dull deposits have to be polished to a high lustre before chromium plating and, since this polishing operation is so expensive, the major part of nickel plated for decorative applications is now deposited in a fully-bright condition. Such coatings are obtained from solutions which contain organic chemicals in addition to the inorganic constituents. Not only can these additions modify the structure of the nickel deposit so that polishing is unnecessary, but many also have scratch-filling (the so-called 'levelling') properties which also eliminate or reduce the amount of polishing of the basis metal which is required. Variants of these solutions give bright, levelling deposits and form the vast majority of nickel baths now in industrial use.

However, it is not intended to minimize the importance of the remaining uses of nickel electrodeposition. Indeed, they are of great economic importance. Often a comparatively thin nickel coating of which the weight and cost expressed as anode metal are quite small, may be used to repair a most expensive component which would otherwise have to be scrapped. Large engineering components which have involved much costly machining and heat-treatment, and have been damaged, worn or over-machined, perhaps only on small portions of their surface, can be salvaged by building up these specific portions with nickel to restore their original dimensions. If a large nickel thickness is necessary, this reclamation involves the deposition of more nickel than required, followed by machining to size. Obviously, the economics of these operations must be compared with those of fabricating an entirely new component.

The benefits conferred on the surface by thick or 'heavy' nickel plate are not only better corrosion protection, but also the greater abrasion resistance obtainable from certain types of nickel coatings. These advantages are now utilized on many new as well as reclaimed parts; this will be discussed in Chapter 4. The superior wear-resistant properties of these nickel electrodeposits are often further enhanced by the deposition of fairly thick chromium coatings. This is the 'hard' chromium plate of the engineer.

Electroforming is the fabrication of articles entirely by electrodeposition. Nickel is a popular metal for this purpose since it can be plated in a ductile and low stressed form which has moderate hardness. Electroforms which have higher hardness and strength, both at ambient and elevated temperatures, can be produced from special solutions from which are deposited nickels whose structure is modified either by inorganic or organic chemicals present in the electroplating bath or by containing other metals as alloying ingredients. Sometimes the thick skin of the electroform is backed by even thicker copper plate, which although softer than nickel, can be deposited at a faster rate than can most types of nickel. Alternative and even faster means of applying a backing material to the electroformed nickel shell are by casting a low melting point alloy into it or by flame-spraying of a suitable alloy having a higher melting-point. The 'working' surface of the electroform may be chromium plated after removal from the mandrel.

The functional uses of nickel whether as electroplated coatings or electroformed artifacts are growing steadily, as the advantages of this metal in its naturally electrodeposited form or as modified by various techniques become evident to design and production engineers. As mentioned on page 67, this versatility enables electroformed dies to be used for casting of metals and glass, in addition to moulding of plastics. The use of nickel for electroforming mesh is also a growth industry, for this mesh according to its hole dimensions and shapes can be used for a wide variety of applications.

It has been stated that between 1972 and 1976, the European market for electroformed nickel doubled in size and has continued to achieve further substantial growth since then. This increase has partly compensated for the decreased use of nickel electroplate in its traditional form as a bright coating. This decrease is partly due to the decline in world industrial output only too evident at the time of writing but was occurring before the current trade recession commenced. The number and size of bright finished components on individual cars and domestic durables had been deliberately reduced as a policy. This policy was partly influenced by a wish to change to black or coloured finishes, partly due to new safety requirements for cars but also a result of attempts to lower the costs of finishing. The combination of these factors has produced a serious decrease in the use of nickel electroplate for decorative coatings. Therefore, in spite of the increased use of electrodeposited nickel for functional purposes, the total world usage of this metal for electroplating has remained static during the last decade.

It will be noted that for most decorative/corrosion protective purposes, many engineering uses and sometimes when electroformed, electrodeposited nickel is given a top coat of chromium. For this reason, it is impossible to dissociate chromium electrodeposition from that of nickel. Therefore, although the main purpose of this text is to discuss the deposition of nickel, the technology of chromium plating will be discussed wherever it is relevant.

The chief emphasis will be on electrodeposition of nickel, but Chapter 11 will describe the autocatalytic plating of chemically reduced nickel (electroless nickel), as this is a valuable and increasingly used technique for applying uniform coatings to articles of complex shape, where the inherent limitations of the electrolytic process form an impossible barrier to obtaining a uniform coating of nickel over the whole surface. The properties of the nickel alloys deposited are often also advantageous.

Although the science of electroplating is a comparatively young one, being only 180 years old, nickel was first deposited 150 years ago and chromium some 20 years later. However, the great advances in its technology have been achieved only in the last 70 years. Both these and the early pioneering work form a fascinating historical introduction to the present processes used in industry.

History of nickel plating

The electrodeposition of nickel was first described in 1837. G. Bird[1] electrolysed solutions of nickel chloride or sulphate for some hours and so obtained a crust of metallic nickel on a platinum electrode. In 1840, the first patent for commercial nickel plating was granted to J. Shore[2] of England who specified a solution of nickel nitrate. Soon afterwards a number of investigators published the results of their experiments. A. Smee of England (1841), Ruolz of France (1843) and Bottger of Germany (1843) were the first of these. Ruolz used nickel chloride or nitrate but Bottger's was the first publication to mention an electrolyte solution based on 'acid ammonium sulphate'; this bath, with variations, was the one mainly used in commerce for the next 70 years. However, G. Gore (1855) seems to have been the first to publish[3] details of the neutral nickel ammonium sulphate bath (nickel ammonium sulphate is colloquially known as *double nickel salts*). Becquerel also published the process in 1862, using a concentration of 70–80 g/l, although it is possible he used an excess of ammonia. Therefore, undue credit has perhaps been given to Dr. I. Adams of the U.S.A. for developing this process, although he did apparently use it in the laboratory at Harvard University in 1858–1860[4]. However, he certainly appears to have been the first to commercialize it by plating gas burner tips in 1866[5].

In 1868, W. H. Remington of Boston also commenced the deposition of nickel on a commercial scale using a nickel ammonium chloride solution but ran into difficulties, probably due to the use of an excess of ammonia in the bath. He was the first to describe[6] the use of electrolytic nickel anodes and the use of insoluble baskets (in this case made of platinum) to contain nickel cubes, although these were impure, containing 5% copper and nearly 1% iron.

Meanwhile, Dr. Adams was endeavouring to perfect his own technique which resulted in his master patent for nickel ammonium sulphate baths being published in 1869[7]. This, together with his business ability, gave his company a virtual monopoly of commercial nickel plating for the next 17 years.

This patent's principal claim was that 'the nickel solution should be free from the presence of potash, soda, alumina, lime or nitric acid, or from any acid or alkaline reaction'. Methods of preparing this solution were detailed. His competitors claimed that in essence this only implied that pure nickel ammonium sulphate should be used, but Adams's reference to the necessity for neutrality is a vital and possibly a novel feature. This type of bath has certainly always been associated with Adams and it is from the time of its introduction by him, that nickel plating first became a commercially feasible operation. Because of this and Adams' energetic publicity, it rapidly became utilized throughout the then industrial world.

In the autumn of 1869, Adams visited Europe to sell his process there. A small experimental bath was soon set up in Liverpool and one of about 2000 litres was set up a little later (December) in Paris by A. Gaiffe. A bath of the same size was installed in Birmingham by the spring of 1870. This may have been at the works of Bouse and Muncher, for in 1873 they were reported to be using the Adams solution imported from the USA, with cast nickel anodes containing 6–10% iron. Up to 15 hours' plating time was necessary to obtain a good coating. In 1873 Adams patented a plating process based on nickel sulphate[8]. In 1878 Weston patented[9] the addition of boric acid, while in 1879 Powell patented the addition of citric or benzoic acids as additives.

About 1880, nickel plating salts were being made in Vienna by Pfanhauser and in Birmingham by Canning. In the latter's first handbook, published in 1889, the preparation of a neutral plating bath from 100 g/l double nickel salts is described. In their catalogue, published concurrently with the handbook, single nickel salts (nickel sulphate) were also listed.

In their 1891 catalogue, Canning were able to announce that their salts and anodes were free from copper and iron. During the 1890s the use of boric acid as a buffer and chlorides as anode corrodants became more popular, but far from universal. Although in 1900 Canning listed double and single nickel salts, boric acid, citric acid and sodium chloride as being available for nickel plating, they still preferred the neutral nickel ammonium sulphate solution, this to be used at room temperature and at low current densities, a plating time of 4–5 h being required. In contemporary publications Langbein and Pfanhauser mentioned the use of boric acid and chloride in only some of their formulations. However, in 1906 Bancroft spoke out strongly in favour of the necessity of chloride ions in the nickel bath to ensure satisfactory anode corrosion. Foerster in 1897 and 1905 had already described the use of nickel sulphate or chloride in hot solutions at high current densities.

In 1910, Canning offered a proprietary mixture which contained nickel sulphate, sodium chloride and boric acid and was to be maintained 'slightly acid'. This was to be used at a concentration of 237 g/l at a temperature of not less than 16°C and could be worked at a current density twice that of a double nickel salts solution, but a voltmeter and ammeter were said to be essential and so were anodes of 99% purity. This bath, although its composition was not revealed, was in all essentials similar to the Watts bath, formulated in 1916 by Professor O.P. Watts of the University of Wisconsin. He published[10] the formula for a bath which has stood the test of time and even now is used with little modification for a large percentage of commercial electroplating operations. He recommended the following solution to be used hot at much higher current densities than then employed:

Nickel sulphate, $NiSO_4 \cdot 7H_2O$	240 g/l
Nickel chloride, $NiCl_2 \cdot 6H_2O$	20 g/l
Boric acid, H_3BO_3	20 g/l

This solution and its modifications have been endowed with the name of the man who first thoroughly described its benefits over the double nickel salt process. While Professor Watts strongly recommended that this bath be used hot, he did not mention agitation. Therefore, although the Watts bath with variations, which usually contain increased concentrations of one, two or all three of its constituents, was gradually adopted over the course of years as the almost universal basis of industrial plating processes – whether dull or bright, there have been, until recently, differences in the US and UK practice of agitation. By the end of the 1920s British platers were starting to adopt air agitation, which did not achieve popularity in the USA until thirty years later.

In 1931, the similarities and differences between the best US and UK practice can be seen by comparing two contemporary papers, in which the English author[11] praised the use of air agitation, with the concomitant necessity for filtration, while the American[12] feared the troubles that agitation might cause. However, in 1931 a large proportion of the nickel baths in Europe and USA were still operated at room temperature with no agitation.

It will be noticed that values for acidity on the pH scale are given in Table 1.1 which gives typical operating conditions. The use of pH measurements for controlling nickel baths was first suggested in 1921 and by the end of that decade was common industrial practice.

Both the UK and USA were using the Watts nickel bath and it is from this type of bath that bright nickel deposits are now obtained. However, it appears that the first commercial bright nickel plate was obtained from a double nickel salt solution, probably containing small amounts of cadmium as a brightener. Certainly in their 1910 catalogue, Canning described a nickel plating process named *Velete*, which was said to give a 'brilliant bright deposit in 5 to 10 min without further polishing and for any period up to 30 min gives the brightest and whitest deposit obtainable'. This may well have been the same type of solution described[13] as being used at

Elkingtons in Birmingham in 1912. It was soon found that small additions of zinc salts had the same brightening effect. Other investigators showed that glucose, glycerine, gum traganath or gum arabic also helped to produce a bright nickel deposit. These deposits were only fully bright when very thin and their wider application was limited by their great brittleness. Aromatic sulphonates were to prove far superior brighteners in both these aspects. Lutz and Westbrook were the first to take out a patent[14] for these compounds. However, not until Schlötter[15] marketed his process in 1934 did bright nickel become a commercial reality for mass production of all classes of plated goods. His bath and variants were quickly adopted in the industrial world. Another bright nickel process was put forward[16] in 1936 and this was based on the deposition of a cobalt-nickel alloy. This proved a serious competitor to the organic type process although its greater cost has gradually resulted in its almost total elimination; one point in its favour is that it has reasonably good ductility.

The ousting of the cobalt-nickel alloy bath has resulted in the present domination of the market by organic brighteners. These have been greatly improved by investigations which have resulted in the achievement of many of the properties of the ideal bright nickel process as first postulated by Eckelmann[17] in 1934. These developments are discussed in Chapter 5.

TABLE 1.1. Operating conditions formerly used for nickel plating

Country	*Temperature*	*Current density*	pH
UK	32–35°C	2–2.5 A/dm^2	5.6–5.8
USA	50–55°C	3–4 A/dm^2	5.2–5.5

Suffice it here to say that the first truly levelling solution was introduced in 1945, but this gave only a semi-bright plate which needed polishing. A little later, levelling and fully bright processes were developed and these are now used for most commercial nickel plating. Semibright levelling deposits still have an important use in that they constitute the major part of double-layer nickel coatings and so confer improved corrosion resistance onto these. Bright levelling processes may have almost reached their limit as regards brightening and levelling properties and the tendency now is for investigation of new processes to give these desired properties without the deleterious effects of brittleness, stress and darkness, the latter being particularly troublesome in low current density areas. All these faults are accentuated if the organic compounds decompose during electrolysis, as will be discussed later.

Many other electrolyte solutions apart from the Watts bath have been mentioned in the literature as having been investigated in laboratories. However, apart from electroplating baths based on nickel sulphamate and, to a much lesser extent, nickel fluoborate, they appear to offer no major advantages even for specialized applications. Hence, they do not appear likely to supplant the Watts solution, although this has now been in use for over 70 years. The Watts solution has formed the basis for those baths used for electroplating of nickel-iron alloys, which were reintroduced in the